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Metal Carbonyl Complexes with Ligands of Biological Origin

A.A.Ioganson

The methods of synthesis, structure, and physicochemical and chemical properties of transition metal carbonyl derivatives containing biological ligands, namely porphyrins, nucleic bases and nucleosides, aminoacids, and peptides, are examined. The possibility of using metal carbonyl complexes with biological ligands in various branches of chemistry is discussed. The bibliography includes 124 references

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INTRODUCTION

The rapid growth of interest in recent years in the chemistry of transition metal complexes with ligands of biological origin is due to the extremely important role which metal ions play in a wide variety of biological processes.[1-6] The multifunctionality of metal ions in biological systems is undoubtedly associated with the wide variety of the chemical and stereochemical characteristics of the complexes formed by metals with protein molecules. The problem of the elucidation of the nature of the metal–protein interaction has therefore assumed special importance. Model compounds which are usually inorganic coordination compounds containing ligands of the acido-type in addition to biological ligands, namely porphyrins, amides, aminoacids, low-molecular-weight peptides, etc., are usually employed for the solution of this complicated problem. However, these complexes do not as a rule contain atoms or groups changes in the characteristics of which would permit fairly reliable inferences to be drawn about the steric and electronic features of the molecules investigated. Furthermore, the interaction of metal ions with biomolecules in an aqueous medium, usually employed for the synthesis in an investigation of inorganic complexes, is hardly an adequate model for the real interactions within the bulky protein molecules, which possess appreciably hydrophobic properties.

Numerous organometallic complexes of transition metals of various bioligands have been obtained in recent years. One can apparently speak of the establishment at the present time of a new branch of science—*bioorganometallic chemistry*, which is concerned with the study of transition metal complexes which contain, apart from the bioligands, at least one organic group linked to the metal atom via a metal carbon bond. Vitamin B_{12} is a representative of this class of compounds discovered in nature.

In contrast to inorganic coordination compounds, organometallic complexes are as a rule volatile and soluble in organic solvents. This makes possible a wide-scale use of methods such as mass spectrometry, NMR involving different nuclei, various types of vibrational spectroscopy, etc., for their investigation. Metal carbonyl complexes constitute a large class of such compounds. The presence in these substances of carbonyl groups linked to the metal atom, which are very sensitive to changes in the electronic and stereochemical characteristics of the metal atom and its ligand environment, and have highly characteristic infrared and Raman spectroscopic properties, makes it possible to establish in many instances the character of the metal–ligand bonds and the disposition of the ligands around the central metal atom.

Thus organometallic compounds of transition metals with ligands of biological origin have many important advantages over traditional inorganic compounds. It therefore appears likely to be useful to employ them as model systems for the investigation of the interaction between metal atoms and the active centres of protein molecules. It is noteworthy that the reactions with carbon monoxide, leading to the formation of metal carbonyl complexes, have already found extensive applications in the study of the properties of natural metal–porphyrin systems and their synthetic models.

The study of organometallic complexes with bioligands proved useful for the modelling of various catalytic processes *in vivo* with participation of metalloenzymes, for example, the fixation of nitrogen, the oxidation of alkanes, etc. Derivatives of metal carbonyls can also be used to introduce transition metals into protein molecules as labels, to impart new transport properties to biomolecules, and, in particular, to increase their solubility in organic solvents and fats, and as intermediates in the synthesis of proteins and other biologically active compounds. Furthermore, it appears useful to use metal carbonyl derivatives for the synthesis and study of biologically active complexes of those transition metals whose content in the biosphere increases as a result of anthropogenic factors.

This review deals with the results of studies in recent years on the synthesis and chemical and physicochemical properties of derivatives of metal carbonyls with certain most important biological nitrogen-containing ligands: porphyrins, nucleic bases and nucleosides, aminoacids, and peptides. So far as the present author is aware, no reviews devoted to this branch of chemistry have been published hitherto with the exception of the paper by Tsutsui,[7] which considers mainly the results of the author's studies of metal carbonyl porphyrin complexes. The present author thought it desirable to include in this review certain data on non-carbonyl organometallic aminoacid and peptide complexes of

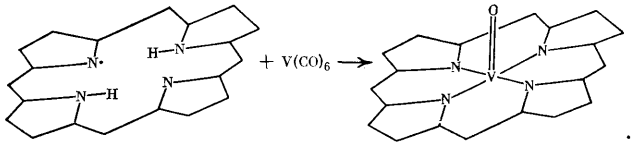
transition metals whose methods of synthesis and properties are close to those for the analogous metal carbonyl compounds.

II. PORPHYRIN DERIVATIVES OF METAL CARBONYL COMPOUNDS

Two discoveries at the beginning of the 1950's served as a direct stimulus for the investigation of metal carbonyl porphyrin complexes. The organometallic nature of one of the most important natural biologic reactive compounds, the vitamin B_{12} coenzyme, was established. In this compound the cobalt atom, coordinated to a corrin macroring which largely resembles the porphyrin macroring, is linked via a σ-bond to an alkyl carbon atom.[8,9] In addition, it has been elucidated that the cause of the deactivation of haemoglobin by carbon monoxide is the formation of a stable iron-porphyrin carbonyl complex the stretching vibration frequency of the C≡O bond of which in the infrared spectrum [ν(CO) = 1970 cm^{-1}] is close to the analogous frequencies of other derivatives of iron carbonyl.[10]

The study of the reactions of metal carbonyls with various porphyrins, initiated in the middle of the 1960's,[11,12] not only made it possible to synthesise a number of new metalloporphyrin complexes but also led to the establishment of certain hitherto unknown characteristics of the behaviour of porphyrin macrorings.

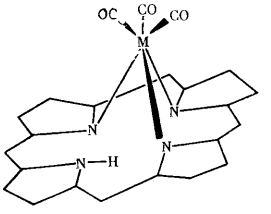
When vanadium hexacarbonyl reacts with H_2MP† in an inert atmosphere in decane at 170 °C, all the carbonyl groups are split off, the metal atom is oxidised, and the vanadyl complex (MP)V = 0 is formed:[13,14]



An analogous complex has been obtained[15] by the interaction of H_2AEP with (η^5-C_5H_5)V(CO)$_4$. The nature of the oxidant both in the reactions quoted above and in other processes involving a change in the oxidation state of the metal atom has not been elucidated. The most probable source of oxygen is apparently CO, which can disproportionate at high temperatures in the presence of transition metals.

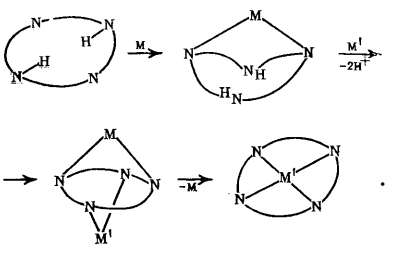
Heating of chromium hexacarbonyl and H_2MP in decane at 170 °C leads to the formation of chromium(II) porphyrinate (MP)Cr and complexes of the same composition have been obtained by heating H_2PP with nickel and cobalt carbonyls.[12,14] However, when H_2TPP interacts with Mo(CO)$_6$ in decalin, more extensive oxidation of the metal atom takes place and the oxomolybdenum complex (TPP)MoO(OH) is formed.[16]

A series of unusual complexes have been obtained in the reactions of porphyrins with Group VII metal carbonyls. Depending on the reactant ratio, mono- or bi-metallic complexes are formed on heating H_2MP or H_2TPP and $M_2(CO)_{10}$ (M = Tc or Re) in decane or decalin.[17–22] In the presence of a deficiency of the carbonyl, the monometallic compounds (HL)M(CO)$_3$(I), where L = MP and M = Tc or Re or L = TPP and M = Re, have been obtained. The infrared spectra of the complexes (I) contain two (three for Tc derivatives) ν(CO) bands at 2010–2025 and 1875–1900 cm^{-1}, which are characteristic of complexes of the type XM(CO)$_3$L$'_2$ (X = Hal, Alk, or Ar and L$'$ = Py or amine) and a ν(NH) band at 3350–3380 cm^{-1}. At room temperature the ^{1}H NMR spectra show the signal of one proton linked to the pyrrole nitrogen atom in the range δ = −4.0–−5.0 p.p.m., as well as the signals of the non-equivalent methylidyne and β-pyrrole hydrogen atoms. With increase of temperature, the signals of the methylidyne and β-pyrrole hydrogen atoms merge in the ^{1}H NMR spectra, indicating a dynamic behaviour of the metal tricarbonyl groups in relation to the porphyrin macroring. The free energy of activation for this process, involving the complex (HMP)Tc(CO)$_3$, is $\Delta G^{\neq}$ = 19.3 ± 2 kcal mol^{-1}.[23] On the basis of spectroscopic data, it has been suggested that the metal atom in complex (I) is not located in the plane of the porphyrin ring and is linked to only three pyrrole nitrogen atoms.



(I) M = Tc, Re

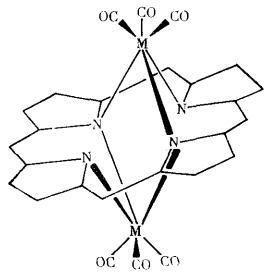
The effect of copper(II) acetate on (HMP)Re(CO)$_3$ at room temperature leads to the substitution of the rhenium tricarbonyl group and the formation of copper porphyrinate.[22] It has been reported[24] that unstable bimetallic complexes are formed in the analogous reactions with Ag^+, Hg^{2+}, and Pb^{2+} salts. These data agree well with the mechanism proposed previously[25] for the insertion of metal ions in porphyrin rings. It has been suggested that one of the metal atoms is initially coordinated to several nitrogen atoms of the macroring, which results in a breakdown of the coplanarity of the latter, after which the attack by the second metal atom from the opposite side of the macroring leads to the formation of an unstable bimetallic complex, which is rapidly converted into a stable metalloporphyrin:



†The following notation has been adopted for porphyrins in the present study: H_2MP = dimethyl ether of *meso*-porphyrin IX, H_2AEP = aetioporphyrin, H_2TPP = tetraphenyl-*meso*-porphin, H_2PrTPP = tetrakis(*p*-isopropylphenyl)-*meso*-porphin, H_2PP = dimethyl ether of protoporphyrin IX, H_2HeP = dimethyl ether of haematoporphyrin X, H_2OEP = octaethylporphyrin, MeHOEP = *N*-methyloctaethyl-porphyrin, and EtHOEP = *N*-ethyloctaethylporphyrin. To simplify the representation, the double bonds and substituents in the porphyrin macrorings have been omitted in the reaction schemes and structural formulae.

Treatment of porphyrins with an excess of Group VII metal carbonyls results in the formation of the bimetallic complexes $L[M(CO_3)]_2$ (II), where L = MP or TPP and M = Tc or Re, whose infrared spectra are analogous to those of compounds (I) in the $\nu(CO)$ region.[17-24] The reaction proceeds via the intermediate formation of monometallic complexes (I), which are capable of combining with yet another metal tricarbonyl group. Thus treatment of the monorhenium complex $(HMP)Re(CO)_3$ with technetium carbonyl yielded the mixed bimetallic complex $(MP)[Tc(CO)_3][Re.(CO)_3]$.[21,22,26] The bimetallic compounds (II) are probably thermodynamically more stable than (I). It has been found[21] that $(HMP)Tc(CO)_3$ disproportionates irreversibly in boiling decalin with formation of $(MP)[Tc(CO)_3]_2$ and the free porphyrin.

The structure of two bimetallic compounds $(TPP)[M(CO)_3]_2$ (M = Tc or Re) has been established by X-ray diffraction.[21,26,27]



(II) M = Tc, Re

The metal tricarbonyl groups are located on both sides of the planar porphyrin macroring and each metal atom, separated from the plane of the porphyrin by ~1.40 Å, is linked to only three nitrogen atoms. Thus in these compounds the porphyrin behaves as a hexadentate ligand. The metal–nitrogen distances are non-equivalent: one of them (2.15 Å for M = Re and 2.142 Å for M = Tc) corresponds to the M–N σ-bond and the other two, whose lengths are ~2.40 Å, are apparently the M ← N donor–acceptor bonds. The distances between the metal atoms (3.127 Å for M = Re and 3.101 Å for M = Tc) are close to the metal–metal bond lengths in the dinuclear decacarbonyls $M_2(CO)_{10}$, but calculation of the number of electrons shows that there should be no direct metal–metal covalent bonding in complexes (II).

The oxidation-reduction properties of the tetraphenylporphyrin complexes (I) and (II) for M = Re have been investigated by polarographic methods.[28-31] In solutions in CH_2Cl_2 or dimethylformamide the complexes undergo two-electron oxidation and reduction in stages at a platinum electrode with formation of chemically stable products in each stage. The polarographic waves for the complexes are analogous to the waves for reversible oxidation-reduction processes involving the free porphyrin:

$$H_2L^{2+} \xleftarrow{-e^-} H_2L^{+} \xleftarrow{-e^-} H_2L \xrightarrow{+e^-} H_2L \xrightarrow{+e^-} H_2L^{2-}.$$

However, the potentials are displaced towards more positive values for the cathodic processes and more negative values for the anodic processes. The ease of reduction decreases in the sequence

$$(TPP)[Re(CO)_3]_2 > (HTPP)Re(CO)_3 > H_2TPP,$$

which indicates the involvement of the rhenium tricarbonyl groups in the delocalisation of the charge of the porphyrin ring. The electrochemical oxidation of complex (I) is irreversible and leads to the formation of a bimetallic product, probably with a structure similar to that of compounds (II).

The reaction of $(TPP)[Re(CO)_3]_2$ with $SbCl_5$ at −70 °C in CH_2Cl_2 led to the isolation of three thermally unstable ionic complexes which are sensitive to moisture: $\{(TPP)[Re.(CO)_3][Re(CO)_3Cl]\}^+[SbCl_6]^-$ (III), $\{(TPP)[Re(CO)_3.Cl]_2\}^{2+}2[SbCl_6]^-$ (IV), and $\{(TPP)[Re(CO)_3]_2\}^+[SbCl_6]^-$ (V). In inert solvents all these compounds decompose with regeneration of the initial compound (II). It has been suggested that compounds (III) and (IV) possess Re–Cl bonds. The structure of the cation in the complex (V), elucidated as a result of X-ray diffraction analysis, proved to be very similar to that of the uncharged complex (II), but the distance between the rhenium atoms, which is 2.95 Å, enabled the authors[32] to conclude that an Re–Re bond passing through the aperture in the porphyrin macroring, is present in this compound. Such structures of the pseudorotaxane type had not been known previously.

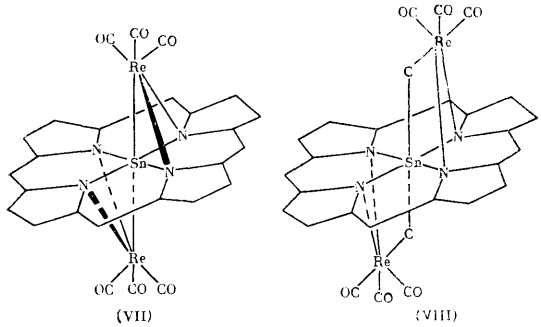
Prolonged heating of complexes (II, L = MP, M = Tc or Re) leads to the formation of insoluble products containing metal carbonyl groups with $\nu(CO)$ = 2044 and 1925 cm^{-1}. The structure of these compounds is unknown, but it has been suggested that they are polymers formed as a result of the coordination of the metal atoms to the ester groups linked to the porphyrin ring.[18]

On refluxing H_2OEP with $ClRe(CO)_5$, $BrRe(CO)_5$, or $[BrRe(CO)_4]_2$ in decalin, dark red crystalline ionic compounds $[H_3OEP]^+[Re_2(CO)_6X_3]^-$ (VI) (X = Cl or Br) were obtained together with the bimetallic complex of type (II). Solutions of these complexes in CH_2Cl_2, tetrahydrofuran, or methyl acetate are stable, but in alcohols, acetone, or in water they rapidly decompose with liberation of the free porphyrin. Prolonged heating of compound (VI) in aprotic solvents leads to the formation of the monorhenium complex (I). It has been established by X-ray diffraction of compound (VI, X = Cl) that the latter has no direct bond between the porphyrin macroring and the rhenium atoms. It is noteworthy that, on heating $ClRe(CO)_5$ and H_2TPP in decalin, complexes of type (VI) are not formed and only $[H_4TPP]^{2+}.2Cl^-$ has been isolated as a result of the reaction.[33,34]

Several unusual compounds have been obtained as a result of the reactions of $Re_2(CO)_{10}$ with tetraphenylporphyrin derivatives of non-transition metals. On heating $Re_2(CO)_{10}$ and $(TPP)SnCl_2$ in decalin at 180 °C, a dark-green crystalline complex $(TPP)Sn[Re(CO)_3]_2$ (VII) is formed and a symmetrical structure with an Re–Sn–Re bond chain has been proposed for it.[35] Compounds of analogous composition have also been obtained on interaction of rhenium carbonyl with zinc, magnesium, and calcium porphyrinates, although it is unlikely that the ions of these metals can form σ-bonds with the rhenium atoms.

A comparatively slight decrease of the temperature of the reaction between $Re_2(CO)_{10}$ and $(TPP)SnCl_2$ (decalin, 160–165 °C) led to the formation of another, red complex $(TPP).Sn[CRe(CO)_3]_2$ (VIII) whose structure has been established by X-ray diffraction.[36] Two carbide C atoms, each of which is linked to the tin atom located at the centre of the porphyrin macroring and to the $Re(CO)_3$ group, were found in this compound. The Sn–C bond length is close to that of a

single bond, while the short C–Re distances (1.75 Å) led to the conclusion[36] that the bond between these atoms has the character of a triple bond.

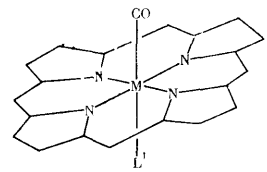


(VII) (VIII)

The C–Sn–C linear fragment is perpendicular to the plane passing through the four nitrogen atoms and the tin atom; the Sn–C–Re angle is 138.5°. Formally the rhenium atoms in complexes (VII) and (VIII) are electronically and coordination unsaturated since only three CO groups are linked to each of them, apart from the Sn or C atoms. However, the infrared spectra of these complexes show identical ν(CO) frequencies of 2000, 1995 and 1920 cm^{-1}, which are close to the analogous frequencies in the spectra of compounds of the type $XRe(CO)_3L_2$, where L is a neutral nitrogen-containing ligand. It is therefore logical to suppose that the Re atoms in the complexes (VII) and (VIII) undergo electronic and coordination saturation as a result of interaction with the pyrrole nitrogen atoms and (or) the π-electron system of the porphyrin ring, despite the fact that the rhenium atoms in complex (VIII) are separated from the plane of the ring by more than 3.5 Å.

The reactions of the iron carbonyls $Fe(CO)_5$ and $Fe_3(CO)_{12}$ with H_2MP and H_2PP proceed with elimination of all the CO groups and the formation of non-carbonyl iron (III) complexes.[12,14] Nevertheless the chemistry of iron-porphyrin carbonyl complexes has been studied in fair detail,[2] since there are many parallelisms in the behaviour of CO and O_2 in relation to natural systems such as haemoglobin, myoglobin, etc. By virtue of the ease of monitoring by means of infrared spectroscopy, the greater strength of the Fe–CO bond compared with Fe–O_2, and the absence of side processes, the reactions of both natural haems and their synthetic models with CO are widely used to elucidate the steric and electronic characteristics of these molecules. It has been established[37,38] that deuteriohaem and (TPP)Fe combine in succession with two CO molecules in inert solvents, but one of them is readily substituted on treatment with nucleophiles such as histidine, pyridine, etc. It has been established by X-ray diffraction that the Fe–C–O fragment in (TPP)Fe(CO)Py is linear and is arranged at right angles to the plane of the macroring,[39] while in the carbonylated natural haems the Fe–C–O angle is 135–145°.[40,41]

The ruthenium-porphyrin carbonyl complex, to which the formula (TPP)Ru(CO)Cl had been attributed initially,[42] has been obtained by treating an ethanol solution of $RuCl_3$ with CO and H_2TPP. Subsequent investigations[43,44] showed that this compound, which is also formed when H_2TPP is refluxed with $[Ru(CO)_3Cl_2]_2$ or $Ru_3(CO)_{12}$ in organic acids or benzene, contains no chlorine atoms and its composition is in fact (TPP)RuCO (IX). Coordination-unsaturated complexes of type (IX) have also been obtained from H_2MP, H_2AEP, and H_2PrTPP. These are brick-red crystalline compounds, stable in air, whose infrared spectra contain one ν(CO) band at ~1940 cm^{-1}. In solutions complexes (IX) combine with one molecule of the electron-donating solvents to form unstable 1:1 adducts from which the compounds LRu(CO)L' (X), where L = MP, AEP, or PrTPP have been obtained on treatment with the nucleophiles L' = pyridine, 2-methylpyridine, and 4-t-butylpyridine. It has been established by ^1H NMR[44–48] that compounds (X) (L = PrTPP) are capable of undergoing readily the intermolecular exchange of the ligand L' for the free nuclecphile present in solutions. For L' = 3,5- and 4,5-dimethylpyridazine, an intramolecular interchange of the two positions of the coordinated L' was observed,[48] its rate being 20–85 times greater than the rate of the intermolecular exchange.



(X) M = Ru
(XI) M = Os

Reactions involving the substitution of the CO groups in complexes (IX) and (X) by other ligands have been hardly investigated. It has been established[49] that, when a solution of (MP)RuCO in benzene is treated with NO at room temperature, the dinitrosyl complex $(MP)Ru(NO)_2$ is formed in a quantitative yield. When an attempt was made to brominate (OEP)Ru(CO)Py in the presence of an excess of KCN, the ionic complex $K^+[(OEP)Ru(CN)_2]^-$ was obtained.[50] Irradiation of (AEP)Ru(CO)Py solutions in pyridine or benzene with visible or ultraviolet light led to the formation of the dimer $[(AEP)RuPy]_2$, which the authors believe to contain the metal–metal double bond.[51]

Two communications concerning the X-ray diffraction analysis of the product of the reaction $Ru_3(CO)_{12}$ with H_2TPP have been published. The first of these,[52] in which the compound is described as a dicarbonyl complex (TPP).$Ru(CO)_2$ with non-linear Ru–C–O groups (with an Ru–C–O angle of 153.3°) and very long Ru–C distances (2.04 Å), is probably wrong. In the second communication,[53] the structure (X), where L' = EtOH, was attributed to the same complex recrystallised beforehand from a $CHCl_3$ – EtOH mixture. According to the former data,[52] the ruthenium atom is at the centre of the porphyrin macroring, the distance between the Ru atom and the oxygen atom of the coordinated ethanol molecule is 2.21 Å, the Ru–C bond length is 1.77 Å, and the Ru–C–O angle is 180°.

Similar parameters of the Ru–CO fragment have been observed also for the crystal structure of the complex (TPP)Ru(CO)Py,[53,54] but in this compound the Ru atom is displaced from the plane of the porphyrin macroring by 0.079 Å in the direction of the CO group.

At pH close to 7 the complex (MP)RuCO forms a 1:1 adduct with apomyoglobin. The study of the ultraviolet and visible spectra of this adduct led to the hypothesis that the distal histidine of apomyoglobin interacts with the Ru–CO group, deflecting the carbonyl group from the axis perpendicular to the plane of the porphyrin ring.[55] An analogous effect has been observed in the ruthenium carbonyl complex of the natural myoglobin.[56]

A brick-red dicarbonyl complex $(OEP)Ru(CO)_2$ has been obtained in a quantitative yield by treating benzene solutions of (OEP)Ru(CO)THF) or (OEP)Ru(CO)(EtOH) with CO. Analogous compounds have been obtained from H_2TPP and its derivatives containing the isopropyl or trifluoromethyl groups in the *para*-positions in the benzene rings. All

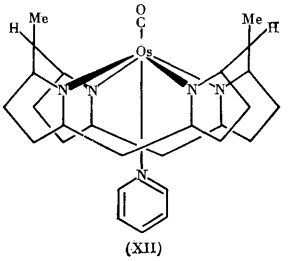
these compounds readily split off one CO molecule on storage or treatment with nucleophiles, for example, t-butylpyridine. As was to be expected, the ν(CO) band in the infrared spectra of the dicarbonyl complexes is at a much higher frequency (~1990 cm^{-1}) than in the spectra of compounds (IX) and (X) (~1940 cm^{-1}).[57]

The compounds (OEP)Ru(CO)(SR), where R = Et, CMe_3, or $CH_2CH_2CO_2Me$, which are possible models of the product of the addition of the CO group to the reduced cytochrome P 450, have been obtained by the reaction of (OEP)RuCO with mercaptide anions. The observed decrease of the ν(CO) frequency in the infrared spectra by 30 cm^{-1} and the upfield shift of the signals in the ^1H NMR spectra compared with complexes (IX) permit the conclusion that there is charge transfer from the negatively charged thiolate group to the Ru atom and (or) the porphyrin macroring.[58]

The osmium monocarbonyl complexes (XI) are much more stable than their iron and ruthenium analogues. They are formed when OsO_4 and H_2OEP are heated above 200 °C in the monomethyl ether of diethylene glycol with subsequent addition of nucleophiles L' [59] or on treatment of (OEP)OsPy with CO.[60] The complexes (OEP)Os(CO)L'(L' = MeOH, EtOH, THF, Py, PPh_3, or $AsPh_3$) are red or violet crystalline substances, stable in air, and comparatively stable in solutions. The ν(CO) frequencies in their infrared spectra increase from 1897 cm^{-1} for L' = THF to 1926 cm^{-1} for L' = PPh_3, which indicates a decrease of the strength of the M–CO bond with increasing π-acceptor capacity of the substituent L'. When compound (XI, L' = Py) is treated with the stronger π-acceptor $P(OMe)_3$, both pyridine and CO are substituted and (OEP)Os$[P(OMe)_3]_2$ is formed.

Comparison of the ν(CO) frequencies of the carbonyl pyridine complexes of metals of the iron triad (OEP)M(CO)Py, namely 1902 cm^{-1} for M = Os, 1932 cm^{-1} for M = Ru, and 1970 cm^{-1} for M = Fe, demonstrate unambiguously an increase of the capacity of the metal atom for the reverse transfer of electron density to the CO group in the sequence Fe < Ru < Os. These data agree well with the increase of the thermal stability of the complexes in the same sequence.

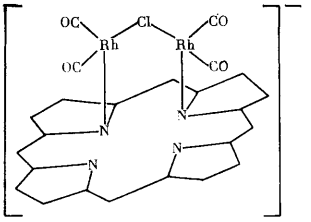
The electrochemical oxidation of the complex (XI, L' = Py) leads to the formation of the cation $[(OEP)Os(CO)Py]^+$ in which the presence of the Os^{3+} species has been postulated.[61] The reduction of this compound with sodioanthracene in THF does not entail a change in the oxidation state of the metal atom: after the addition of MeI to the reduced solution, the complex (XII), containing, according to X-ray diffraction data, a non-planar tetrapyrrole ligand (the angle of inflection along the axis passing through the sp^3-hybridised C atoms is 142°), was isolated. The Os atom lies 0.18 Å above the plane of the four pyrrole nitrogen atoms. The decrease of the ν(CO) frequency to 1963 cm^{-1} in the infrared spectrum of compound (XII) is probably associated with the decrease of the reverse electron donation by the metal atom to the orbital of the non-conjugated dimethylporphyrin ligand.[62]



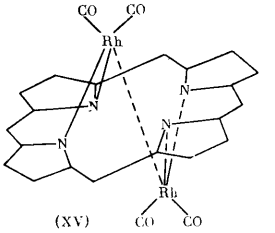
(XII)

The structure of the porphyrin complexes of rhodium depends greatly both on the reaction conditions and on the nature of the porphyrin. The reaction of $[Rh(CO)_2Cl]_2$ and H_2TPP in boiling benzene yielded the monocarbonyl complex (TPP)Rh(CO)Cl (XIII) and the σ-phenyl compound (TPP)Rh(Ph)Cl;[42,63] only a non-carbonyl product is formed in acetic acid.[64] The complex (XIII) is also obtained on treatment of (TPP)RhCl with CO under mild conditions (25 °C, 1 atm).[65]

In benzene at 20 °C H_2OEP reacts with $[Rh(CO)_2Cl]_2$ to form a dark-green product, to which the formula $H^+[(OEP).Rh_2(CO)_4Cl]^-$ (XIV) [ν(CO): 2045, 2035, 1983, and 1950 cm^{-1}] was attributed on the basis of spectroscopic data.[66] Complex (XIV) is comparatively unstable and is readily oxidised in air, being converted into the red (OEP).RhCl.$2H_2O$. In CH_2Cl_2 compound (XIV) splits off HCl and forms the neutral bimetallic product (OEP)$[Rh(CO)_2]_2$ (XV).[67,68] X-Ray diffraction analysis of compound (XV) showed that it contains two $Rh(CO)_2$ groups each of which is linked to two nitrogen atoms located on different sides of the macroring; the short metal–metal distance (3.094 Å) suggests the occurrence of interaction between the metal atoms via the aperture in the macroring.[69]

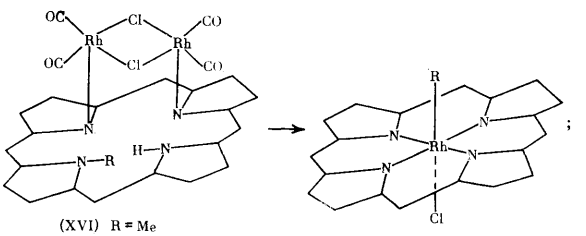


(XIV)



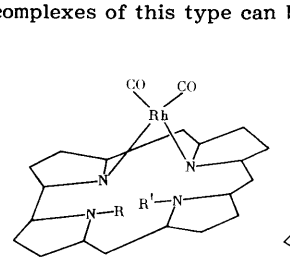
(XV)

Treatment of MeHOEP with $[Rh(CO)_2Cl]_2$ in benzene results in the formation of the dark-violet (MeHOEP) $[Rh(CO)_2Cl]_2$ (XVI) [ν(CO): 2075, 2050, 2010, and 1980 cm^{-1}].[70] Slight heating of compound (XVI) in $CHCl_3$ or its chromatography on a Al_2O_3 column entail a profound rearrangement of the molecule accompanied by the migration of the alkyl group to the Rh atom and the formation of the non-carbonyl complex $(OEP)Rh(CH_3)Cl$. The analogous reaction of rhodium carbonyl chloride with EtHOEP immediately results in the formation of (OEP)Rh(Et)Cl.

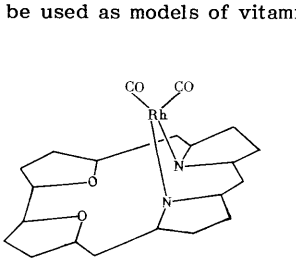


(XVI) R = Me

The reactions of $[Rh(CO)_2Cl]_2$ with corrole and dioxacorrole yielded the neutral monometallic complexes (XVII) and (XVIII) in which the macrorings play the role of bidentate four-electron ligands. It has been suggested that complexes of this type can be used as models of vitamin B_{12}.[71]



(XVII) R = Me, R' = H; R = H, R' = Me



(XVIII)

The stable monocarbonyl complexes LIr(CO)Cl have been obtained by the reactions of H_2L (L = MP or HeP) with π-olefin derivatives of iridium in alcoholic solutions or with $[Ir(CO)_3Cl]_2$ in acetic acid.[68,72] The CO group [ν(CO) ≅ 2060 cm^{-1}] is retained when these compounds are acted upon by pyridine, acids, and dilute solutions of alkalis; the dissociation of the Ir–CO bond, accompanied by a change in the oxidation state of the Ir atom, occurs only after prolonged heating of the complexes or on treatment with $NaBH_4$ or concentrated solutions of alkalis.

The bimetallic complex (OEP)$[Ir(CO)_3]_2$ (XIX) has been obtained by the reaction of $[Ir(CO)_3Cl]_2$ with H_2OEP in benzene. Its structure is probably analogous to that of the rhenium complex (II). The bis(chlorotricarbonyliridium) complex (MeHOEP)$[Ir(CO)_3Cl]_2$ (XX), whose structure is apparently close to that of compound (XIV), is formed from MeHOEP under the same conditions. When compound (XIX) is refluxed in $CHCl_3$, the monocarbonyl complex (OEP)Ir.(CO)Cl is obtained, while compound (XX) is converted into the σ-methyl derivative (OEP)$Ir(CH_3)Cl$.[73]

Thus the study of the metal–porphyrin carbonyl complexes revealed many previously unknown characteristic features of porphyrin macrorings:

1) A high capacity for coordination, which makes it possible to obtain stable bi- and tri-metal complexes in which the porphyrin functions as a hexa- and octa-dentate ligand.

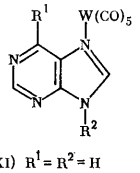
2) Stereochemical non-rigidity and the ability of the substituents at the pyrrole nitrogen atoms both to migrate between the pyrrole rings and to be transferred to the metal atom.

3) The ability of the π-electron system of the porphyrin not only to interact actively with the *d* orbitals of the metal atom at the centre of the macroring but also to form bonds with metal atoms located at a considerable distance from the plane of the porphyrin.

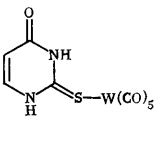
III. COMPLEXES OF METAL CARBONYLS WITH NUCLEIC BASES AND NUCLEOSIDES

Nucleic bases and nucleosides HL react with derivatives of metal carbonyls to form stable complexes in which they are usually linked to the metal atom via N → M donor–acceptor bonds.[74,75]

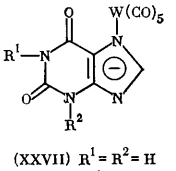
When $W(CO)_5$(THF) was acted upon by HL, neutral pentacarbonyl complexes $(OC)_5W(HL)$ (XXI–XXIV) were obtained. Reactions of this type also take place with the anions of nucleic bases. The charged complexes $[(OC)_5WL]^-$, isolated in the form of salts with the Na^+ or Ph_4As^+ cations [compounds (XXV)–(XXIX)], are formed in such cases. On the basis of spectroscopic data (Table 1), it has been established that adenine and adenosine are coordinated to the metal atom via a nitrogen atom in the five-membered heterocycle and not via the amino-group. An analogous coordination has been suggested for purine, theophylline and xanthine derivatives, while in the thiouracil complexes (XXIV) and (XXIX) the base is linked to the metal atom via an S–W bond.[74]



(XXI) $R^1 = R^2 = H$
(XXII) $R^1 = NH_2$, $R^2 = H$
(XXIII) $R^1 = NH_2$, R^2 = ribose



(XXIV)



(XXVII) $R^1 = R^2 = H$
(XXVIII) $R^1 = R^2 = Me$

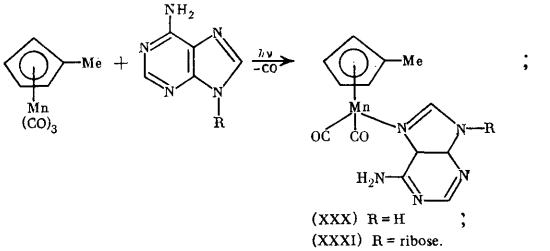
Analysis of the infrared spectra of complexes (XXI)–(XXIII) in the region of ν(CO) vibrations shows that, in terms of their donor–acceptor properties, the nucleic bases are close to nitrogen-containing Lewis bases such as pyridine.[76] There is virtually no difference between the type *E* frequencies of the neutral complexes (XXI) and (XXII), on the one hand, and the ionic complexes (XXV) and (XXVIII), on the other, which unambiguously demonstrates the delocalisation of the negative charge over the organic part of the complex anion. At the same time the slightly lower ν(CO) frequencies of type A_1 in the infrared spectra of the ionic complexes indicate a partial transfer of electron density from the herterocycle to the d_π orbitals of the tungsten atom.

Table 1. Parameters of the infrared spectra [in $CHCL_3$, ν(cm^{-1})] of complexes of tungsten carbonyl with nucleic bases and nucleosides.[74,75]

Compound	Base LH	C≡O			C=O	NH_2
		$A_1^{(1)}$	*E*	$A_1^{(2)}$		
Neutral compounds $(CO)_5W(LH)$						
(XXI)	purine	2073	1930	1895	—	—
(XXII)	adenine	2072	1925	1890	—	3445, 3410
(XXIII)	adenosine	2075	1933	1890	—	3420
(XXIV)	2-thiouracil	2075	1940	1800	1680	—
Ionic complexes $Na^+[(CO)_5WL]^-$						
(XXV)	purine	2064	1932	1884	—	—
(XXVI)	adenine	2060	1925	1880	—	3450, 3380
(XXVII)	theophylline*	2065	1925	1880	1638	—
(XXVIII)	xanthine*	2066	1932	1883	1690	—
(XXIX)	2-thiouracil*	2065	1922	1870	1661	—

*in ethanol.

The ethylenediamine complex of molybdenum *cis*-$Mo(CO)_4$(en) reacts with adenine, guanine, and theophylline salts at 110 °C with substitution of one CO group and the formation of the ionic complexes $K^+[Mo(CO)_3(en)L]^-$. The CO group is also substituted in the photochemical reactions of $(\eta^5\text{-}MeC_5H_4)Mn(CO)_3$ with adenine and adenosine:[74]

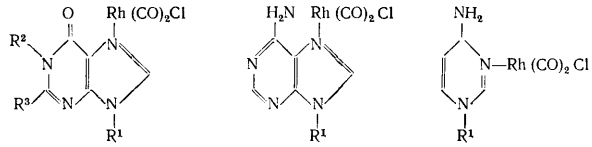


(XXX) R = H ;
(XXXI) R = ribose.

The higher ν(CO) frequencies in the infrared spectrum of the nucleoside complex (XXXI) (1910 and 1832 cm^{-1}) compared with the nucleic base complex (XXX) (1895 and 1825 cm^{-1}) indicate the electron-accepting character of the ribose fragment. An analogous conclusion can be reached from the comparison of the ν(CO) frequencies of the tungsten complexes (XXIII)–(XXII) (see Table 1).

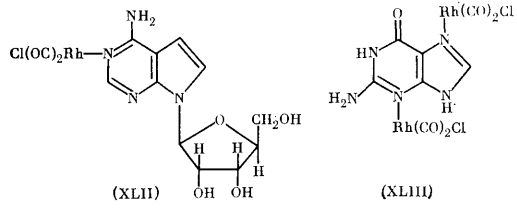
The dinuclear rhodium carbonyl chloride $[Rh(CO)_2Cl]_2$ reacts with nucleic bases with the opening of the chloride bridges and the formation of the monometallic complexes

$(OC)_2RhCl(HL)$ (XXXII)–(XLI), of which the infrared spectroscopic parameters are given in Table 2.[75]



(XXXII)–(XXXVII) (XXXVIII) (XXXIX)–(XLI)

Complex (XLII) with $\nu(CO)$ = 2075 and 2000 cm^{-1} has been obtained by the reaction of $[Rh(CO)_2Cl]_2$ with 7-desaza-adenosine (tubercidine). The reaction with guanine leads to the formation of the bimetallic complex having $\nu(CO)$ = 2103, 2080, 2040, 2012, and 2000 cm^{-1}, for which the structure (XLIII), having two independent $Rh(CO)_2Cl$ groups linked to the imidazole and pyrimidine nitrogen atoms, has been proposed.[75]



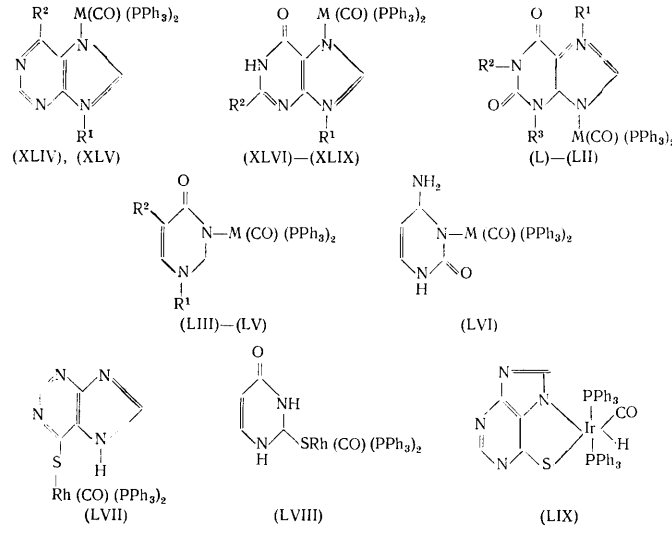
(XLII) (XLIII)

Table 2. Parameters of the infrared spectra (in ethanol) of complexes of the type $ClRh(CO)_2(LH)$.[75]

Compound	Base				$\nu(CO)$, cm^{-1}
	LH	R^1	R^2	R^3	
(XXXII)	hypoxanthine	H	H	H	2083, 2010
(XXXIII)	9-methylguanine*	Me	H	NH_2	2065, 1985
(XXXIV)	inosine	ribose	H	H	2085, 2015
(XXXV)	guanosine	ribose	H	NH_2	2084, 2013
(XXXVI)	1-methylguanosine*	ribose	Me	NH_2	2065, 1983
(XXXVII)	2',3'-*O*-isopropylidene-guanosine**	2', 3'-*O*-isopropylideneribose	H	NH_2	2088, 2016
(XXXVIII)	adenosine	ribose	—	—	2074, 2017
(XXXIX)	cytosine	H	—	—	2082, 2010
	methylcytosine	Me	—	—	2083, 2010
	cytidine	ribose	—	—	2084, 2010

*in DMSO.
**in $CHCl_3$.

In the reactions with $ClM(CO)(PPh_3)_2$ (M = Rh or Ir), the anions of nucleic bases and nucleosides L^- behave as one electron ligands, substituting the chlorine atom and forming the neutral complexes $M(CO)(PPh_3)_2L$ (XLIV)–(LVI), whose properties are listed in Table 3.[74] In contrast to the rhodium complexes, the iridium compounds are more reactive and form adducts with oxygen both in solutions and in the crystalline state.



(XLIV), (XLV) (XLVI)–(XLIX) (L)–(LII)

(LIII)–(LV) (LVI)

(LVII) (LVIII) (LIX)

Table 3. Parameters of the infrared spectra (in $CHCl_3$) of compounds of the type $M(Co)(PPh_3)_2L$.[74]

Compound	Base				$\nu(CO)$, cm^{-1}	
	LH	R^1	R^2	R^3	M = Rh	M = Ir
(XLIV)	purine	H	H	—	1992	1980
(XLV)	adenine	H	NH_2	—	1990	1978
(XLVI)	hypoxanthine	H	H	—	—	1975
(XLVII)	inosine	ribose	H	—	1985	1974
(XLVIII)	guanine	H	NH_2	—	1976	1962
(XLIX)	guanosine	ribose	NH_2	—	1985	1974
(L)	xanthine	H	H	H	1989	1977
(LI)	theophylline	H	Me	Me	1987	1975
(LII)	theobromine	Me	H	Me	1973	—
(LIII)	uracil	H	H	—	1985	1971
(LIV)	uridine	ribose	H	—	1975	1965
(LV)	thymine	H	Me	—	1983	1967
(LVI)	cytosine	—	—	—	1981	1967

The complexes $Rh(CO)(PPh_3)_2L$ (LVII) [$\nu(CO)$ = 1986 cm^{-1}] and (LVIII) [$\nu(CO)$ = 1983 cm^{-1}], in which the anions of nucleic bases add to the metal atom via the sulphur atom, have been obtained by treating $ClRh(CO)(PPh_3)_2$ with potassium 6-mercaptopurinate and 2-thiouracil respectively. The metal hydride complex $HIr(CO)(PPh_3)_2L$ (LIX) with $\nu(CO)$ = 2047 cm^{-1} and $\nu(IrH)$ = 2155 cm^{-1}, in which the dianion of 6-mercaptopurine is apparently a two-electron chelate ligand, has been obtained by the reaction of potassium 6-mercaptopurinate with Vaska's complex $ClIr(CO).(PPh_3)_2$. In a neutral medium two 6-mercaptopurine molecules add to Vaska's complex and $HIr(CO)(PPh_3)_2L_2$ (LX) [$\nu(CO)$ = 2055 cm^{-1}, $\nu(IrH)$ = 2180 cm^{-1}], from which one molecule of the nucleic base is split off on treatment with KOH, the complex being converted into compound (LIX). The reaction of $ClIr(CO)(PPh_3)_2$ with 2-thiouracil yielded the complex (LXI), the infrared spectrum of which contains two $\nu(CO)$ bands at 2055 and 2034 cm^{-1}.[74] Judging from the high $\nu(CO)$ frequencies, this compound is also a hydride, i.e. $HIr(CO)(PPh_3)_2$, and the presence of two $\nu(CO)$ bands in the infrared spectra is probably associated with the formation of various isomers of compound (LXI) in the course of the reaction.

In conclusion of this Section, one may note that, despite the fact that the data available at present are limited, the use of metal carbonyl complexes has proved useful in securing

additional information about the active centres of purine and pyrimidine bases involved and about the electronic donor–acceptor properties of the monomeric fragments of nucleic acids.

IV. METAL CARBONYL COMPLEXES WITH AMINOACID AND PEPTIDE LIGANDS

Metal complexes of aminoacids and peptides have served for more than 100 years as models of the products of the reactions of metals with proteins and as models of biological systems in which the properties of proteins have been modified by the addition of metal atoms to them.[2,77,78] The synthesis and study of the properties of organometallic compounds containing aminoacid and peptide ligands opens up new possibilities for the determination of the mechanism of the interaction of protein systems with transition metal atoms.[79,80]

Three types of metal carbonyl derivatives incorporating aminoacids and peptide fragments are known at the present time:

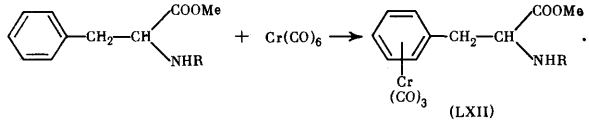
1) π-Complexes based on aminoacids and peptides.

2) Compounds formed as a result of the condensation of aminoacids with the ligand at the metal atom.

3) Metal carbonyl complexes formed as a result of the coordination of the metal atom to the functional groups of aminoacids and peptides.

1. π-Complexes Based on Aminoacids and Peptides

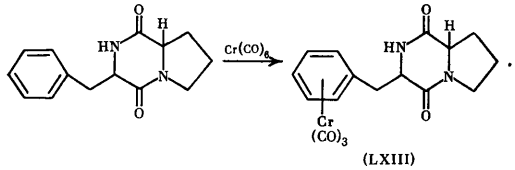
Aminoacids and peptides whose side chains incorporate an organometallic fragment belong to compounds of this class. It has been established recently[81] that derivatives of aromatic aminoacids with protected carboxy- and amino-groups readily react with chromium hexacarbonyl in ethereal or water-tetrahydrofuran media, forming the corresponding η^6-arene-chromium tricarbonyl complexes:



(LXII)

Derivatives of phenylalanine (LXII) are thermally unstable: R = CHO, m.p. 90 °C; R = CMeO, m.p. 99 °C; R = C(t-Bu)O, m.p. 130 °C. The analogous reactions with tryptophan and tyrosine derivatives lead to the formation of less stable compounds.

Stable π-complexes (LXIII) have been obtained by the reactions of $Cr(CO)_6$ with diastereoisomeric cyclic peptides whose composition includes a phenylalaninate fragment, no racemisation of the peptides being observed in the course of the reactions.



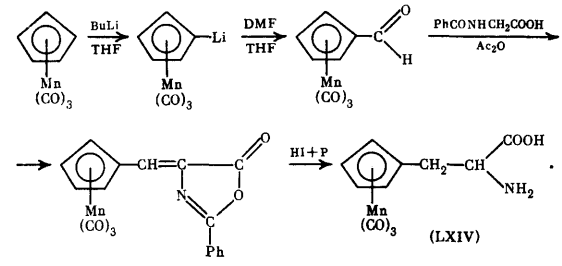
(LXIII)

LL, $[\alpha]_D$ -73.6° LL, $[\alpha]_D$ -90.4°, m.p. 228°

LD, $[\alpha]_D$ +51.2° LD, $[\alpha]_D$ +57.6°, m.p. 218°

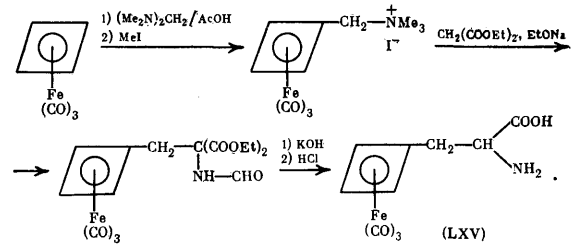
The formation reactions of the π-arene derivatives of metal carbonyls can probably serve as a good test of the presence of aromatic rings in various natural products.

Organometallic aminoacids can be obtained also directly from the corresponding π-complexes of transition metals. Thus cymantrenylalanine (LXIV) has been synthesised from η^5-cyclopentadienylmanganese tricarbonyl in 60% yield (m.p. 230 °C):[82]



(LXIV)

Another method has been used[82] to obtain (η^4-cyclobutadienylalanine)iron tricarbonyl (LXV) in 30% yield (m.p. 220 °C, with decomposition):

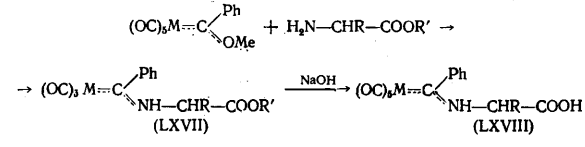


(LXV)

The properties of metal carbonyl aminoacids are apparently close to those of the usual aromatic aminoacids. It had been established earlier that the non-carbonyl analogue of these compounds, namely ferrocenylalanine (η^5-C_5H_5)Fe[η^5-C_5H_4.$CH_2CH(NH_2)COOH$] (LXVI), which has been synthesised by a method[83] close to that used for the synthesis of compound (LXV), behaves in many reactions in the same way as phenylalanine. It enters into metabolic hydroxylation reactions and reactions involving coupling to glucuronic acid[84,85] and it can participate in peptide synthesis reactions.[86] Compound (LXVI) has been inserted in natural peptides such as encephalin and bradykinin.[82,87] The arene complexes of transition metal carbonyls are similar in many respects to ferrocene derivatives, but, by virtue of the presence of the M–CO groups in the molecules, it is much easier to follow the behaviour of these compounds in various processes. It therefore appears useful to employ metal carbonyl aminoacids as labels in protein molecules.

2. Compounds Formed as a Result of the Condensation of Aminoacids with the Ligand at the Metal Atom

Among compounds of this type, the carbene derivatives of Group VI metal pentacarbonyls, obtained by Fischer and Weiss[88–90] as a result of the condensation of aminoacid esters with phenyl(methoxy)carbene-chromium and tungsten pentacarbonyls have been most thoroughly investigated:



(LXVII) (LXVIII)

The complexes are formed readily at 20 °C in ether. Compounds (LXVII) and (LXIII) are readily fusible crystalline or oily substances, stable in air, and readily soluble in

polar organic solvents (Table 4). The ester groups in compounds (LXVII) are readily hydrolysed on treatment with alkalis and the acids (LXVIII) formed can participate in peptide synthesis reactions. A series of consecutive reactions involving the condensation of compound (LXVIII) with aminoacid esters in the presence of *N*-hydroxysuccinimide and dicyclohexylcarbodiimide yielded di-, tri-, and tetrapeptide complexes, which decompose on treatment with CF_3COOH at room temperature with liberation of the free peptide:

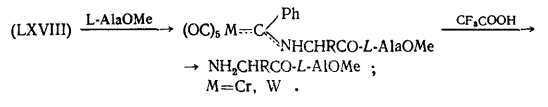
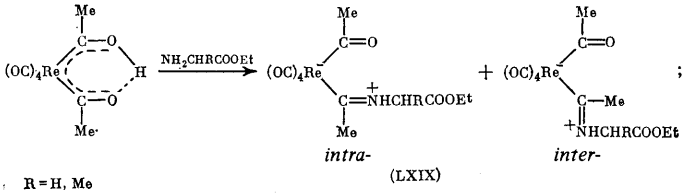


Table 4. Aminoacid – and peptide – carbene complexes of Group VI metals of the type $(OC)_5M[C(Ph)(NHCHRCOX)]$.[80–90]

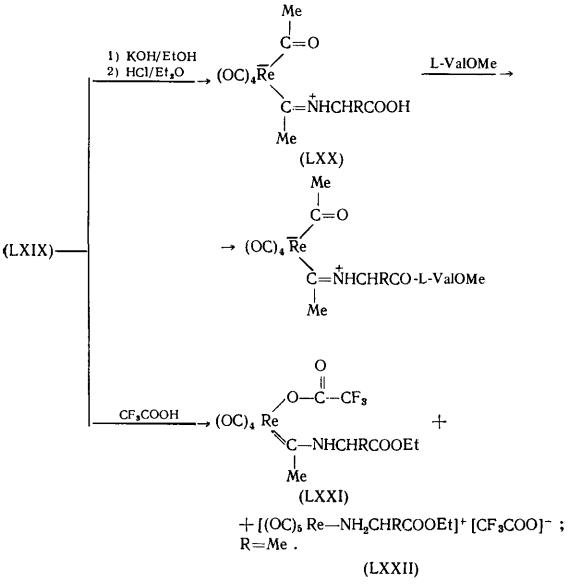
NHCHRCOX	Yield, %	M.p., °C	$[\alpha]_{589}^{20}$, °
	M = Cr		
GlyOH	79	106—109	—
GlyOMe	66	55—72*	—
ClyOEt	97	—	—
L-AlaOH	87	77—82	+16
L-AlaOMe	87	87—88*	+13
L-ValOMe	70	75—78	—94
L-MetOMe	92	70—74	—77
L-SerOMe	76	135—145*	—35
L-PheOMe	87	—	—
L-ProOMe	78	86—89	—63
L-Glu(OMe)2	94	113—115	—95
Gly-GlyOH	98	120*	—
Gly-GlyOMe	67	105—106	—
L-Ala-L-AlaOMe	79	93—104*	—15
L-Leu-L-LeuOMe	82	143—145*	—98
L-Ala-L-Ala-L-AlaOMe	82	120*	—50
L-Ala-L-Ala-L-Ala-L-ProOMe	63	82—86	—48
Gly-L-Ala-L-Pro-GlyOMe	79	103—108*	—50
	M = W		
GlyOH	86	113—115*	—
GlyOMe	63	70—73	—
L-LeuOMe	77	86—108*	—52
Gly-L-ValOMe	75	139—145*	—22

*With decomposition.

The organorhenium analogue of acetylacetone, namely tetracarbonyl rhena-acetylacetone, reacts with aminoacid esters in CH_2Cl_2 to form the isomers of the corresponding dipolar complexes (LXIX):



The crystal structure of the *inter*-isomer (LXIX, R = H) is illustrated in Fig. 1. Hydrolysis of compound (LXIX) leads to the formation of the corresponding acids (LXX), which are capable of participating in subsequent condensation reactions with aminoacid esters. Complexes (LXIX) and (LXX) are much more stable than the related chromium and tungsten complexes (LXVII) and (LXVIII). When compound (LXIX) is acted upon by CF_3COOH, the neutral carbene complex (LXXI) and the ionic complex (LXXII), in which an ethyl alaninate molecule is coordinated to the metal atom via the amino-group, are formed:[91]



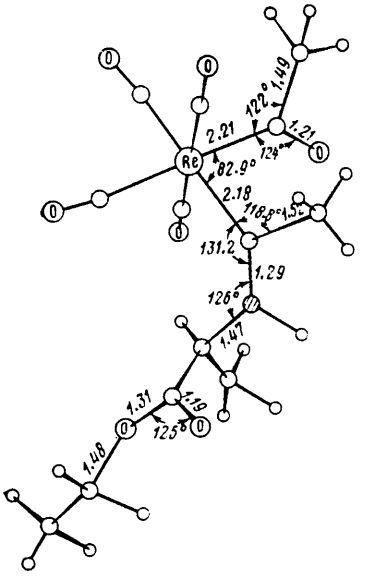
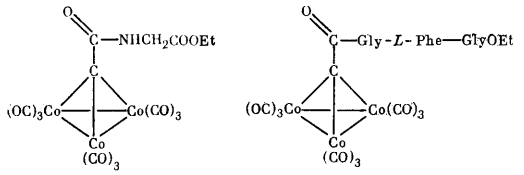


Figure 1. The structure of *inter*, *cis*-$(OC)_4Re[C(O)Me]$. $.[C(Me)(L\text{-}AlaOEt)]$.[91]

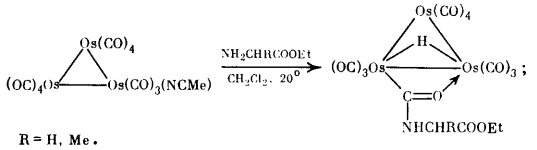
Instances of the addition of aminoacids and peptides to transition metal cluster compounds containing an active carbon atom are known. When the ionic complex $[(CO)_9.Co_3CCO] + [PF_6]^-$ was allowed to react with ethyl glycinate in CH_2Cl_2, the neutral carbamide derivative (LXXIII), melting at 117 °C, was obtained. The tripeptide complex

(LXXIV) has been synthesised by an analogous reaction.[92]



(LXXIII) (LXXIV)

The chiral carbamide complexes (LXXV) have been obtained by the reaction of $Os_3(CO)_{11}(NCMe)$ with glycine and alanine esters.[93]



R = H, Me.

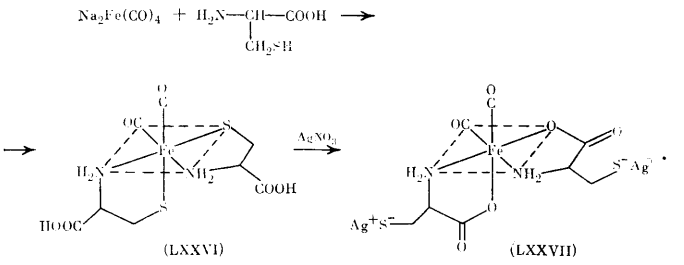
(LXXV)

With the aid of aminoacid esters deuteriated at the nitrogen atom, it has been established that the hydride bridge in compound (LXXV) is formed as a result of hydrogen transfer from the amino-group.

3. Metal Carbonyl Complexes Formed as a Result of the Coordination of the Metal Atom to Functional Groups in Aminoacids and Peptides

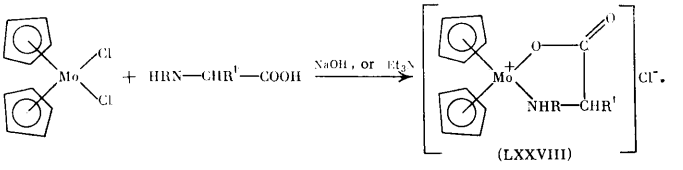
Complexes in which the aminoacid fragments are directly linked via their functional groups to the metal atom constitute the most thoroughly investigated class of organometallic aminoacid derivatives. In these compounds the aminoacids can behave as either monodentate one-electron (for coordination to the carboxyl oxygen) or two-electron (for coordination to the amino-group substituents) or as three-electron chelate or bridging ligands. The functional groups of aminoacids are coordinated to metal atoms comparatively readily and the problem of the synthesis of organometallic aminoacid complexes reduces mainly to the problem of the solvent in which both the aminoacids and the initial organometallic compounds are equally readily soluble.

The first aminoacid metal carbonyl complex, namely dicysteinatoiron dicarbonyl, was synthesised as early as 1933,[94] but its structure was not established until the end of the 1960's after detailed spectroscopic investigations.[95,96] The red crystalline product (LXXVI), obtained by the reaction of cysteine with $Na_2Fe(CO)_4$, contains chelating aminoacid ligands coordinated to the iron atom via the amino-group and the sulphur atom. The presence in the infrared spectrum of compound (LXXVI) of bands at 1717 and 1690 cm^{-1} indicates the presence of free COOH groups in this complex. Treatment of solutions of compound (LXXVI) with silver salts leads to a rearrangement of the chelating ligands and the cysteinate groups in the resulting green complex (LXXVII) are linked to the iron atom via the nitrogen and oxygen atoms: $\nu(COO)$ = 1608 and 1417 cm^{-1}. The increase of the stretching vibration frequencies of the CO groups at the iron atom after the change in the coordination of the aminoacid ligand, i.e. $\nu(CO)$ = 2030 and 1978 cm^{-1} for compound (LXXVI) and 2050 and 1990 cm^{-1} for compound (LXXVII), unambigously demonstrates the more pronounced electron-accepting character of the carboxylate group compared with the sulphide group:



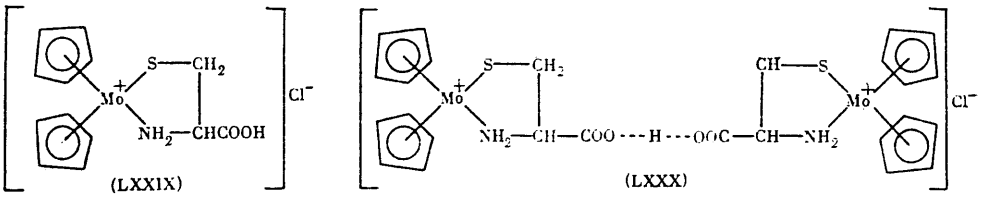
(LXXVI) (LXXVII)

The organometallic aminoacid complexes of molybdenum were first synthesised from dicyclopentadienylmolybdenum dichloride:[97]



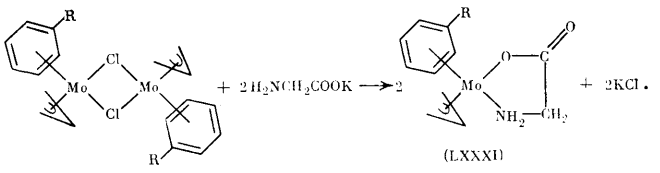
(LXXVIII)

where HRNCHR'CO = Gly, L-Ala, L-Phe, L-Val, L-Leu, L-Ile, L-Pro, L-Met, L-Ser, CH_3NHCH_2CO, or $CH_3NHCH_2.CH_2CO$. The complexes (LXXVIII) are crystalline substances stable in air and resistant to the action of strong acids. The study of the ^1H NMR spectra of these compounds showed that the hydrogen atoms at the α-carbon atoms readily exchange with D_2O in weakly alkaline solutions. When Cp_2MoCl_2 is treated with cysteine, two products are formed: the monomer (LXXIX) and the dimer (LXXX), in which the cysteinate ligands are coordinated to the molybdenum atom via the sulphide and amino-groups. The reaction of Cp_2MoCl_2 with cystine is accompanied by the dissociation of the S–S bonds and leads to the formation of compound (LXXIX).



(LXXIX) (LXXX)

The red crystalline glycinate complexes (LXXXI, R = H or Me) have been obtained by treating bis(η^6-benzene-η^3-allylmolybdenum chloride with potassium glycinate:[98]



(LXXXI)

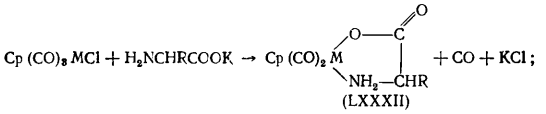
In contrast to the dicyclopentadienyl compounds (LXXVIII), the complexes (LXXXI) are decomposed by acids with liberation of propene.

Table 5. Aminoacid chelate complexes of molybdenum and tungsten.[99–101]

Compound	M.p., °C	ν(CO)	ν(COO)	ν(NH$_2$)	ν(OH)
Cp(CO)$_2$Mo(GlyO)	240	1965, 1864	1610	3224, 3110	—
Cp(CO)$_2$Mo(SerO)	210	1965, 1865	1630	3180	—
Cp(CO)$_2$Mo(*N,N*-Me$_2$GlyO)	205	1967, 1870	1660	—	—
Cp(CO)$_2$Mo(L-AlaO)	230	1964, 1865	1610	3220, 3110	—
Cp(CO)$_2$Mo(L-2-MeAlaO)	225	1963, 1865	1608	3223, 3132	—
Cp(CO)$_2$Mo(L-ValO)	235	1962, 1865	1630	3225, 3110	—
Cp(CO)$_2$Mo(L-SerO)	250	1965, 1865	1625	3270, 3140	3400
Cp(CO)$_2$Mo(L-TryO)	250	1965, 1865	1625	3280, 3220, 3105	3500
Cp(CO)$_2$MO(D-TryO)	250	1965, 1865	1625	3280, 3220, 3105	5300
Cp(CO)$_2$Mo(L-HisO)	190	1967, 1870	1615	3220, 3203	—
Cp(CO)$_2$Mo(L-PheO)	205	1965, 1865	1635	3220, 3105	—
Cp(CO)$_2$Mo(L-N-PhCH$_2$PheO)	175	1967, 1870	1632	3090	—
Cp(CO)$_2$Mo(L-ProO)	210	1963, 1865	1613	3145	—
Cp(CO)$_2$Mo(D-ProO)	210	1963, 1865	1613	3245	—
Cp(CO)$_2$Mo(L-LysO)	230	1965, 1865	1630	3220	—
Cp(CO)$_2$Mo(L-GluO)	150	1964, 1864	1630	3220, 3105	—
Cp(CO)$_2$Mo(L-S-MeCysO)	165	1967, 1867	1636	—	—
Cp(CO)$_2$Mo(L-CysO)Li	146	1947, 1850	1600	—	—
Cp(CO)$_2$Mo(L-CysOMe)	55*	1955, 1852	—	—	—
Ind(CO)$_2$Mo(L-AlaO)**	—	1965, 1870	1617	3210, 3110	—
Cp(CO)$_2$W(SerO)	209	1948, 1844	1640	3190, 3120	—
Cp(CO)$_2$W(L-AlaO)	240	1945, 1840	1620	3220, 3110	—
(MeC$_5$H$_4$)(CO)$_2$W(L-AlaO)	210	1942, 1840	1637	3220, 3133	—

*With decomposition.
**Ind = η^5-indenyl.

An analogous approach has been used to synthesise η^5-cyclopentadienyl-molybdenum and -tungsten dicarbonyl complexes with chelating aminoacid ligands:[99,100]

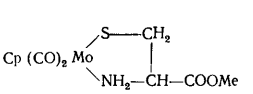


(LXXXII)

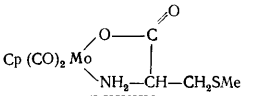
M=Mo, W

The complexes (LXXXII) (Table 5) are comparatively stable crystalline substances soluble in polar organic solvents. Since the metal atom in these compounds is chiral, the complexes exist in the form of two stereoisomers, which can be separated chromatographically. The structure of one of these complexes, established by X-ray diffraction, is illustrated in Fig. 2.

Cysteine and its methyl ester react with Cp(CO)$_3$MoCl to form the complexes (LXXXIII) with a chelate N,S-ring, but the analogous reaction with *S*-methylcysteine leads to the formation of compound (LXXXIV) with the ligand coordinated via the N and O atoms.[100,101]



(LXXXIII)



(LXXXIV)

As for the iron cysteinate complexes (LXXVI) and (LXXVII), the infrared spectra of the molybdenum derivatives show a significant increase of the ν(CO) frequencies on passing from complexes with N,S-coordination of the ligand to the N,O-isomers: 1947 and 1850 cm^{-1} for compounds (LXXXIII) and 1967 and 1867 cm^{-1} for compounds (LXXXIV) respectively. Thus the type of coordination of the cysteinate fragment to the metal atom can be readily established on the basis of the infrared spectra of the carbonyl complexes in the ν(CO) region.

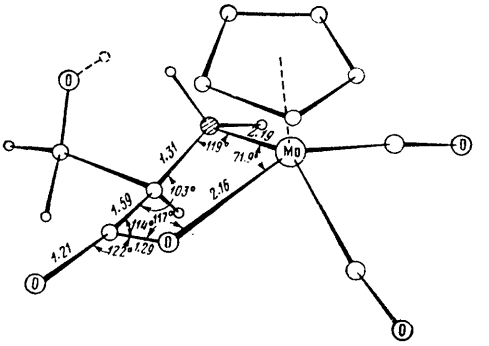
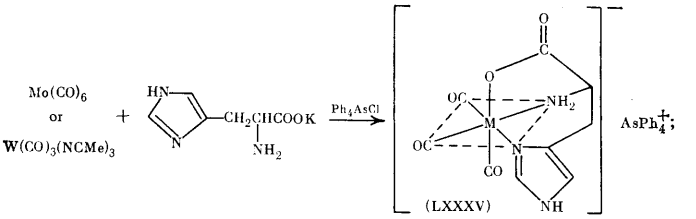


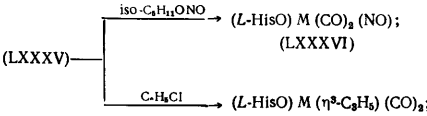
Figure 2. The structure of η^5-cyclopentadienyldicarbonyl-(L-serinato)molybdenum Cp(CO)$_2$Mo(L-SerO).[100]

The reactions of Mo(CO)$_6$ or W(CO)$_3$(NCMe)$_3$ with potassium histidinate in alcoholic solutions lead to the formation of the ionic tricarbonyl complexes (LXXXV) in which the histidinate anion behaves as a five-electron tridentate ligand. By treating them with isopentyl nitrite or allyl bromide, it is possible to obtain the neutral dicarbonyl histidinate compounds (LXXXVI) and (LXXXVII) respectively:[102]



(LXXXV)

M = Mo, ν(CO) 1895, 1763, 1730 cm^{-1}; M = W, ν(CO) 1877, 1737 cm^{-1}.



(LXXXVI), M=Mo, ν (CO) 2014, 1913 cm^{-1}; (LXXXVII), M=Mo, ν (CO) 1937, 1846 cm^{-1}; M=W, ν (CO) 1927, 1837 cm^{-1}.

The tungsten pentacarbonyl complexes with aminoacid ligands linked to the metal atom only by the amino-group are relatively unstable. They can be obtained[103] by irradiating tungsten hexacarbonyl and aminoacid esters with ultraviolet light in non-polar solvents, for example:

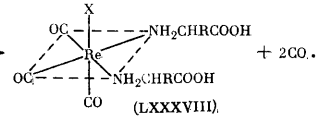
$$W(CO)_6 + NH_2CHRCOOMe \xrightarrow[C_6H_6]{h\nu} (OC)_5W(NH_2CHRCOOMe) + CO;$$

R=CH_2CHMe_2, ν (CO) 2072, 1925 and 1893 cm^{-1}; ν (COO) 1738 cm^{-1}.

The dipeptide pentacarbonyl complex $(OC)_5W$-Gly-GlyOH, which decomposes on heating above 80 °C, has been obtained by the photochemical reaction between $W(CO)_6$ and glycylglycine.[103] In polar solvents, aminoacid compounds of the type $(OC)_5WL$ readily split off a ligand molecule.

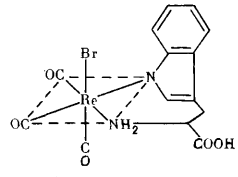
The reactions of aminoacids and their derivatives with rhenium carbonyl complexes have been studied in detail. When rhenium pentacarbonyl halides and α-aminoacids are refluxed in dioxan, stable bisaminoacid complexes (LXXXVIII) with a facial disposition of the non-carbonyl ligands at the metal atom are formed:[104–107]

$$XRe(CO)_5 + 2NH_2CHRCOOH \longrightarrow \text{(LXXXVIII)} + 2CO.$$



where $NH_2CHRCOOH$ = GlyOH, DL-AlaOH, DL-LeuOH, DL-ValOH, DL-β-Ph-α-AlaOH, or DL-β-2-thienyl-α-alanine. Compounds of the same type have been obtained with certain β-aminoacids: β-AlaOH, DL-β-Ph-β-AlaOH, and DL-β-2-thienyl-β-alanine.[104–107] The analogous manganese compounds are formed in the reactions of manganese carbonyl halides with GlyOH and AlaOH.[108] The study of the kinetics of the formation of the complexes (LXXXVIII) showed that the reaction proceeds preferentially via a dissociation mechanism and its rate is determined by the rate of dissociation of CO.

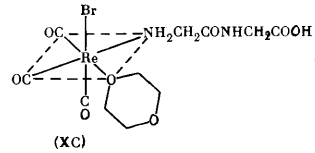
The monoaminoacid complex (LXXXIX), in which a tryptophan molecule is coordinated to the rhenium atom via both the amino-group and the indolyl nitrogen atom, has been obtained by the reaction of $BrRe(CO)_5$ with tryptophan.[106]



(LXXXIX)

The reactions of $BrRe(CO)_5$ with cysteine and threonine led to the formation of complexes of type (LXXXVIII), in which these potentially tridentate aminoacids are coordinated to the metal atom only via the amino-groups.[109] In the reaction of $BrRe(CO)_5$ with glycylglycine in boiling dioxan, two CO molecules are also evolved, but the resulting complex (XC) incorporates only one dipeptide molecule coordinated via the amino-group, while the other vacant site is occupied by a solvent molecule:[110,111]

$$BrRe(CO)_5 + NH_2CH_2CONHCH_2COOH \xrightarrow[-2CO]{\text{dioxan}} \text{(XC)}.$$

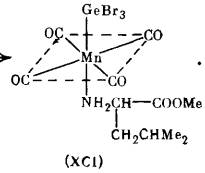


The additional interaction between the peptide CONH group and the rhenium atom apparently plays a decisive role in stabilising complex (XC). The impossibility of the addition of a second glyglycine ligand to the metal atom can hardly be due to steric hindrance, because the more bulky β-indolylacetic acid gives rise to a disubstituted product of type (LXXXVIII) in an analogous reaction with $BrRe(CO)_5$.[107] The approach of a second dipeptide molecule to the rhenium atom in complex (XC) is apparently hindered by purely electrostatic factors.

The complexes (LXXXVIII)–(XC) are yellow oily or solid amorphous substances, which are resistant to the action of oxygen and water. At the same time they are hygroscopic and readily form solvates on reaction with both water and polar organic solvents such as dioxan, alcohols, acetone, etc. Aqueous solutions of the complexes give an acid response and can be titrated with alkalis. The infrared spectra of compounds (LXXXVIII)–(XC) in polar organic solvents show the absorption band due to the free COOH group in the range 1700–1730 cm^{-1} and three intense ν(CO) bands near 2030, 1910, and 1890 cm^{-1}, indicating a facial configuration of the CO groups linked to the rhenium atom.

The introduction of a strong π-acceptor substituent at the metal atom weakens the M–CO bond in the *trans*-position relative to the substituent and promotes the substitution of the carbonyl group by n-donor ligands. Thus, treatment of $Br_3GeMn(CO)_5$ by the methyl ester of leucine yielded the relatively unstable bimetallic complex (XCI) with the *trans*-configuration of the non-carbonyl ligands, the infrared spectrum of which contains ν(CO) bands, at 2082 and 2002 cm^{-1}, which are characteristic of the local D_{4h} symmetry of the $M(CO)_4$ group:[112]

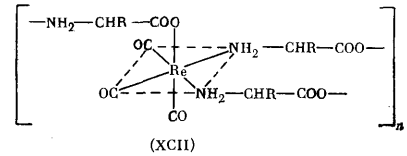
$$Br_3GeMn(CO)_5 + NH_2CH(CH_2CHMe_2)COOMe \longrightarrow \text{(XCI)}.$$



However, when the stannyl derivatives of rhenium carbonyl, namely $X_3SnRe(CO)_5$ (X = Cl or Br), are treated with aminoacid esters, the Sn–Re bond is ruptured and the disubstituted carbonyl halide complexes of type (LXXXVIII) are formed.[113] The reaction probably proceeds in such cases via the intermediate ionic complexes $[(OC)_5ReNH_2CHRCOOR']^+ . [SnX_3]^-$, resembling the complex (LXIX) examined above. A stable aminoacid compound with an Sn–Re bond has been obtained by the reaction of $SnCl_2$ with the bis(ethyl leucinate) derivative of rhenium carbonyl chloride:[113]

$$fac\text{-}ClRe(CO)_3[NH_2CH(CH_2CHMe_2)COOEt]_2 + SnCl_2 \rightarrow$$
$$\rightarrow fac\text{-}Cl_3SnRe(CO)_3[NH_2CH(CH_2CHMe_2)COOEt]_2.$$

In the interaction of salts of α-aminoacids with rhenium pentacarbonyl bromide or on treatment of solutions of the complexes (LXXXVIII) with KOH, the bromine atom is substituted and the polymeric compounds (XCII) are formed, in which the aminocarboxylate fragments function as bridges between the metal atoms:[104,114]

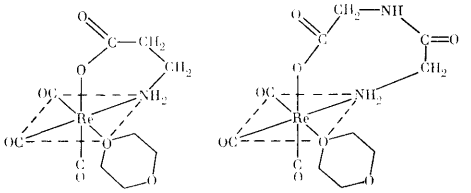


(XCII)

These are solid amorphous substances, which soften at 70–120 °C and are readily soluble in THF, $CHCl_3$, acetone, and alcohols. The cryoscopic determination of the molecular weight of the DL-α-phenylalaninate derivative, carried out in dioxan, showed that the number of units *n* in the polymer

molecule is close to four. The infrared spectra of the complexes (XCII) are analogous to those of compounds (LXXX-VIII), but, instead of the band due to the COOH group, they exhibit in the region of 1730 cm^{-1} bands associated with the vibrations of a bound COO group near 1650 and 1400 cm^{-1}.

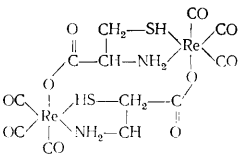
The reaction of $BrRe(CO)_5$ with salts of β-alanine and glycylglycine lead to the formation of the crystalline chelate complexes (XCIII) and (XCIV) respectively, which are sparingly soluble in organic solvents.[104,105,110,111]



(XCIII) (XCIV)

The complex (XCIII) is formed in polymers also on direct interaction between $BrRe(CO)_5$ and β-alanine in boiling dioxan. On the other hand, the reaction between $BrRe(CO)_5$ and salts of β-aminoacids containing an aromatic substituent (the phenyl or 2-thienyl group) at the β-carbon atom lead only to polymeric products of type (XCII).

Treatment of $BrRe(CO)_5$ with potassium DL-cysteinate yielded[109] a pale brick-red amorphous product (XCV), readily soluble in polar organic solvents. Solutions of this compound cannot be titrated with either alkalis or acids and the complex is inert with respect to nucleophiles. Determination of its molecular weight (by cryoscopy in dioxan) showed that it is a dimer. On the basis of these data as well as the analysis of the infrared spectra, it was suggested that all the functional groups of the aminoacid ligand in compound (XCV) are linked to the metal atom.

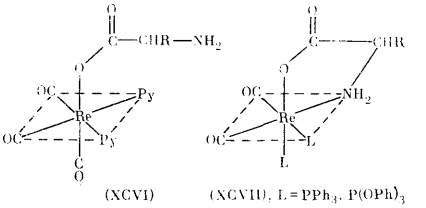


(XCV)

The analogous reaction of $BrRe(CO)_5$ with the potassium salt of DL-threonine gave rise to the colourless tetramer $\{(OC)_3ReNH_2CH[CH(Me)OH]COO\}_4$, whose solutions give an alkaline response. Probably not all the amino-groups in this compound are linked to the metal atoms.

The Re–N bonds in the aminoacid derivatives of rhenium carbonyl are comparatively weak and are readily ruptured in the presence of stronger Lewis bases L = Py, PPh_3, or $P(OR)_3$. Treatment of compounds of type (LXXXVIII) with L leads to the liberation of the free aminoacids and the formation of the complexes $BrRe(CO)_3L_2$, whose structure depends both on the nature of L and on the characteristics of the aminoacid ligands.[104,107,115] The reactions with pyridine in all cases give rise to *cis*-$BrRe(CO)_3(Py)_2$, while the reactions with $P(OPh)_3$ give rise to *trans*-$BrRe(CO)_3.[P(OPh)_3]_2$. The pathway followed in the reactions between compounds (LXXXVIII) and PPh_3 depends on the steric characteristics of the aminoacid ligands. When the complexes (LXXXVIII) with small aminoacid ligands such as glycine or β-alanine are acted upon by PPh_3, the product is *cis*-$BrRe(CO)_3(PPh_3)_2$, while the reactions with the complexes containing more bulky aminoacids, such as, for example, valine or leucine lead to *trans*-$BrRe(CO)_3(PPh_3)_2$. In the intermediate cases (α-alanine, β-phenyl-β-alanine, threonine) a mixture of the *cis*- and *trans*-isomers of $BrRe(CO)_3(PPh_3)_2$ was obtained. The sensitivity of the reactions of compounds (LXXXVIII) and PPh_3 to the steric effects of the aminoacid ligands is very great: the replacement of the phenyl group in β-phenyl-α-alanine by the 2-thienyl group alters the geometry of the substitution product. These results lead to the possibility of using aminoacid derivatives of metal carbonyls for the specific synthesis of complexes with a given structure.

The structure of the complexes formed when the polymeric compounds (XCII) are treated with nucleophiles also depends on the nature of L.[114,115] Pyridine ruptures the Re–N bond and the resulting mononuclear products (XCVI) contain an aminocarboxylate fragment coordinated to the metal atom only via the oxygen atom.

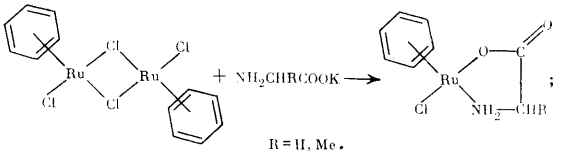


(XCVI) (XCVII), L = PPh_3, $P(OPh)_3$

The complexes (XCVI) are colourless crystalline substances melting above 200 °C and readily soluble in polar organic solvents and water. The aqueous solutions have an alkaline response and can be titrated with HCl. The infrared spectra are seen to contain three intense ν(CO) bands in the range 1900–2030 cm^{-1} and ν(COO) bands at 1645 and 1390 cm^{-1}. It was not possible to convert compounds (XCVI) into chelate complexes even by prolonged refluxing in dioxan.

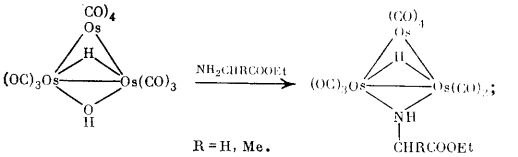
On the other hand, the reactions of compounds (XCII) with PPh_3 and $P(OPh)_3$, i.e. with nucleophiles exhibiting an appreciable π-acceptor capacity, lead to the formation of the chelate dicarbonyl complexes (XCVII)–crystalline products which are soluble in polar and organic solvents but are insoluble in water. Complexes of type (XCVII) with six-membered chelate rings have been obtained from compounds (XCII) having β-aminoacid ligands and also on treating $BrRe(CO)_3(NH_2CH_2CH_2COOH)_2$ with $P(OPh)_3$. The infrared spectra of all the complexes (XCVII) each show two ν(CO) bands at 1940 and 1860 cm^{-1} for L = PPh_3 or 1965 and 1880 cm^{-1} for L = $P(OPh)_3$ and ν(COO) bands at 1640 and 1400 cm^{-1}.[114]

The aminoacid derivatives of Group VIII metals have been less thoroughly investigated. The preparation of η^6-benzeneruthenium complexes with chelating glycinate and alaninate ligands has been reported:[116]



R = H, Me.

When $HOs_3(OH)(CO)_{10}$ is treated with the ethyl esters of glycine and α-alanine, compounds with an unusual imide bridge group are formed:[93,117]



R = H, Me.

A series of mononuclear crystalline dicarbonyl complexes with the chelating aminocarboxylate ligands $(OC)_2$RhNHRCHR'COO (XCVIII), where NHRCHR'COOH = GlyOH, L-AlaOH, β-AlaOH, DL- and L-LeuOH, L-HisOH, L-TyrOH, SerOH, DL- and L-PheOH, and p-$HOC_6H_4NHCH_2COOH$, have been obtained[118–120] by the reactions of aminoacids with the dinuclear rhodium carbonyl chloride $[Rh(CO)_2Cl]_2$ in benzene. It has been observed that these compounds readily react with tetracyanoethylene to form 1:1 adducts. The nucleophiles L, which consist of amines, 2,2'-bipyridyl, and o-phenanthroline, substitute both CO groups in the complexes (XCVIII), while treatment of the latter with L = PPh_3 or $AsPh_3$ in benzene or acetone entails the substitution of only one CO group and the formation of the monocarbonyl compounds L(CO)RhNHRCHR'COO (XCIX). The complexes (XCIX) can also be obtained by treating a mixture of $RhCl_3 . xH_2O$ and PPh_3 in benzene with aminoacids in an atmosphere of CO. The reactions of compounds (XCVIII) with PPh_3 in chloroform leads to the elimination of the aminoacid ligands and the formation of $[Rh(CO)(PPh_3)Cl]_2$ and an analogous result is obtained when gaseous HCl or HBr are passed over the solid complexes (XCIX). On the other hand, when gaseous chlorine is bubbled through a suspension of $(Ph_3P)(CO)$RhNH$_2$CHR'COO (R = H or Me) the bond between the aminoacid ligand and the metal is retained and an ionic complex is formed to which the composition $[Ph_3P)(CO).RhNH_2CR'ClCOO]^{2+}.2Cl^-$ has been attributed.[120]

The data examined in this review show that aminoacids and their derivatives can form complexes having a wide variety of structures with transition metals in low oxidation states under comparatively similar conditions. By virtue of their ambident nature, the aminoacid fragments can function as terminal ligands coordinated to the metal atom via the N or O atoms, can participate in the formation of metallocycles, and finally can serve as bridges between two metal atoms. Arene π-complexes can be obtained from aromatic aminoacids. In all these reactions the metal atoms show a tendency to retain their 16- or 18-electron valence shell, which greatly facilitates the determination by spectroscopic methods of the structures of the complexes formed.

Derivatives of rhenium carbonyl, which exhibit an enhanced stability and contain numerous CO groups, some of which are retained under the conditions of the substitution reaction and which have a fixed octahedral configuration of the ligands around the metal atom, are especially convenient as model compounds for the study of the reactions of protein molecules with transition metal compounds. With the aid of these compounds, it has been possible to discover the importance of the steric features of the aminoacid ligands and their influence on the chemical properties of aminoacid complexes.

The formation of comparatively stable metal carbonyl aminoacid complexes and the possibility of a subsequent ready dissociation of the metal–nitrogen bonds on treatment with nucleophiles suggest the likely usefulness of the employment of the metal carbonyl groups for the protection of the amino-groups in the synthesis of peptides and in other reactions of biological compounds containing aminoacid fragments.

The possibilities inherent in the application of organometallic compounds in biochemistry are by no means exhausted by the examples quoted in this review. Reports have been published recently concerning the synthesis of metal carbonyl complexes with biological ligands such as vitamins,[121] monosaccharides,[122] steroids,[123] etc. Certain natural products, which are difficult to obtain otherwise, have been synthesised successfully with the aid of metal carbonyls, for example, one of the insect pheromones whose molecule includes the vinylallene group.[124]

There is no doubt that further development of bioorganometallic chemistry will make a significant contribution to our understanding of the role of metals in biological processes. Furthermore, studies in this field should provide a basis for a search for a new type of catalyst and for the development of fundamentally new technological processes, the conditions in which will be similar to those in reactions occurring in living organisms in the presence of metalloenzymes.

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Institute of Chemistry and
Chemical Engineering,
Siberian Division of the USSR
Academy of Sciences,
Krasnoyarsk