

## Common and less-common coordination modes of the typical chelating and heteroaromatic ligands

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### Abstract

Data on the different modes of bonding the metals to the most widely spread chelating [ $\beta$ -diketones, *o*-oxyazomethines, *o*-oxy(mercapto) derivatives of azoles and azines] and heteroaromatic ligands are generalized and systematized. It is shown that, besides the common  $\beta$ -diketonates, aldiminates, phenolates and mercaptophenolates structures, these complex compounds exhibit less-common modes of coordination. Five- and six-membered heterocycles form  $\sigma$ - as well as  $\pi$ -complexes. © 1998 Elsevier Science S.A.

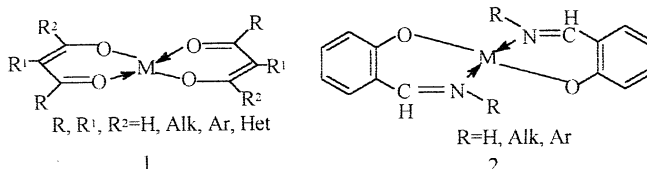
**Keywords:** Coordination mode; Competitive coordination; Diketones; Azomethines; Mercaptoazoles; Mercaptoazines; Heteroaromatic ligands

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## 1. Introduction

In modern coordination chemistry, many different inorganic and organic compounds are used as ligands (e.g. refs. [1–4]). In spite of the tremendous variety of these ligand systems, typical structures are defined as a basis for the study of their coordination chemistry. Thus, in the second volume of the most complete seven-volume edition of *Comprehensive Coordination Chemistry* [1], the following ligands are considered: aliphatic, aromatic and heteroaromatic amines, mixed nitrogen-containing compounds (including N, E-containing derivatives where E is O, S and Se, in particular, the triatomic heteroanions or pseudohalides, amides and imides, nitriles, oximes, cyanides, aminoacids and peptides), ligands with oxygen donor atoms (water, oxides and hydroxy-anions) and chalcogens (sulfides, dithiolenes, sulfoxides, organoselenides and organotellurides). Among the chelating compounds, the classical ligands include  $\beta$ -diketones and their thio analogues, Schiff bases (azomethines), hydroxy- and mercapto-derivatives of the nitrogen-containing heterocycles, porphyrines, and other macrocyclic ligands.

In the review publications mentioned above, the typical ligands are usually regarded to form complexes with a single mode of localization of the coordinative bond.<sup>1</sup> For example, complexes of  $\beta$ -diketones and Schiff bases (*o*-oxyazomethines) are represented as metal-chelates (**1** and **2**), respectively.



However, such an approach gives an incomplete account of the coordination functionalities of these compounds and does not take into consideration the less-common bonding modes of ligands to metals which are relatively common for a majority of these typical ligands.

The effect of the less-common coordination is most illustrative for the tautomeric (prototropic) chelating organic compounds and heteroaromatic ligands which dominate discussion in the present review. The discussion is based predominantly on X-ray structural data.

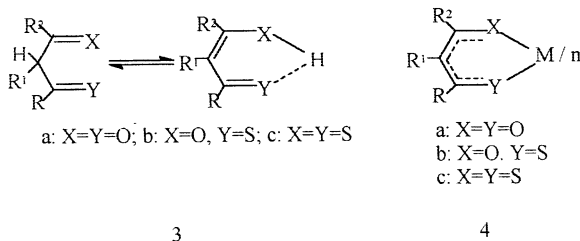
## 2. Different coordination modes of the chelating ligand systems

### 2.1. Complexes of $\beta$ -diketones and their analogues

It is known that  $\beta$ -diketones (**3a**) (e.g. refs. [1,7–21]), their monothioderivatives (**3b**) [22–25] and the dithio analogues (**3c**) [25,26] (LH) are sources for the synthesis

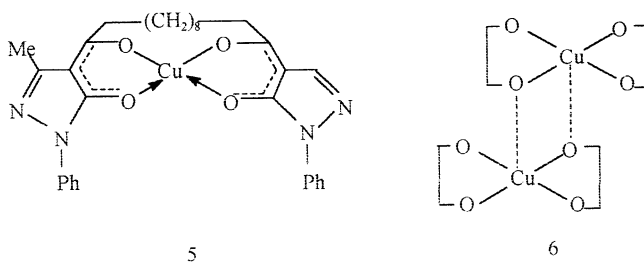
<sup>1</sup>The absence in ref. [1] of the separate consideration of  $\pi$ -donors is due to the fact that complexes with these ligands are referred to as organometallic compounds and considered in separate publications [5,6].

of intramolecular complex compounds of the type (**4**) where the anion ( $L^-$ ) functions as the bidentate  $\eta^2-O,O'$ ,  $\eta^2-O,S$  or  $\eta^2-S,S'$  coordinated ligand.



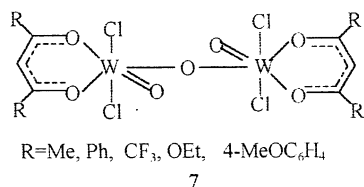
$\beta$ -Diketonates (**4a**) represented [7–21] by a broad series of complexes of composition  $ML_n$  (where M are metals of practically all groups of the periodic system) are prepared mainly by the reaction of (**3a**) with metal salts, or by the interaction of the  $\beta$ -diketonates of alkali metals and metal salts. The intramolecular complexes (**4a**) may also be prepared by a direct method from the zero-valent metals using electrochemical [27–32], gas-phase [31–33] or liquid-phase [27,31,32,34] synthesis. Substantial interest is attracted to the fluorinated  $\beta$ -diketonates [35], due to the enhanced acidity of the ligands. This allows us to synthesize the intramolecular complexes (**4a**) not only from the salts but also from the metal hydroxides. For example, the bismuth metal chelates [36].

The structure of the intramolecular complex (**4a**) has been proven by X-ray structural analysis in numerous studies summarized in the reviews [7,13,14,20,37]. Among recent publications, reports [38–44] devoted to copper  $\beta$ -diketonates are remarkable. Thus, in ref. [44], a copper(II) complex with a  $\beta$ -diketone derivative containing the pyrazole fragment (**5**) is associated via the oxygen atoms (**6**). This intramolecular complex (**5**) is a dimer [44], and its framework can be illustrated as (**6**) with  $Cu \cdots O$  distances being 2.546 and 2.463 Å.



On the other hand, in the complex with 2-triethoxy-2,6,6-trimethylheptane-3,5-dione (**4a**) ( $R=R^2=C_3H_6OCH_3$ ,  $M=Cu$ ) association takes place via the  $Cu-O$  bond, including the oxygen atom of the methoxy group [40].

Dimeric structures of the  $\mu$ -oxotrifluoroacetylacetone complexes of tungsten(VI) are formed via the oxygen bridge (**7**) [45,46].

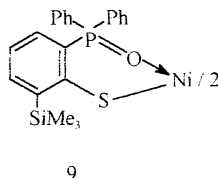
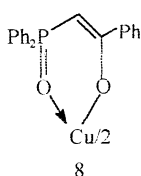


The mixed-ligand complexes  $[\text{Gd}(\text{dpm})_2\text{piv} \cdot \text{H}_2\text{O}]_2$  are also dimeric [47]. There is a comparatively small number of monomeric  $\beta$ -diketonate complexes. Therefore the dipivaloylmethanate of yttrium  $[\text{Y}(\text{dpm})_3]$  [48] and the mixed-ligand complexes  $\text{M}(\text{dpm})_3 \cdot \text{Hpiv}$ , where  $\text{M} = \text{Ho}, \text{Eu}, \text{Yb}$  [49], are of interest.

The *X*, *Y*-chelate coordination was proven by X-ray structural analysis for complexes of the type (**4b**) synthesized from monothio- $\beta$ -diketones (**3b**) [22–25]. Their structure is remarkable since for the  $d^8$  metals (divalent nickel, platinum, and palladium) the *cis*-planar coordination predominates.

The dithio- $\beta$ -diketone anions in the intramolecular complexes (**4c**) are characterized by composition  $\text{ML}_2$  and coordination unit  $\text{MS}_4$  [25,26]. The number of such complexes is considerably less than the number of chelates (**4a** and **4b**), and structural studies are practically absent [7,25].

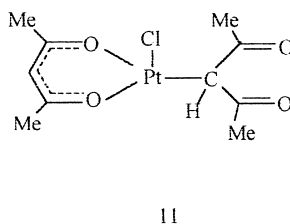
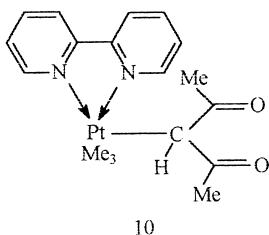
Similar chelate units are typical of the intramolecular complexes of the phosphorus analogues of  $\beta$ -diketones (**8**) [50–52] and their thio analogues, e.g. (**9**) [53].



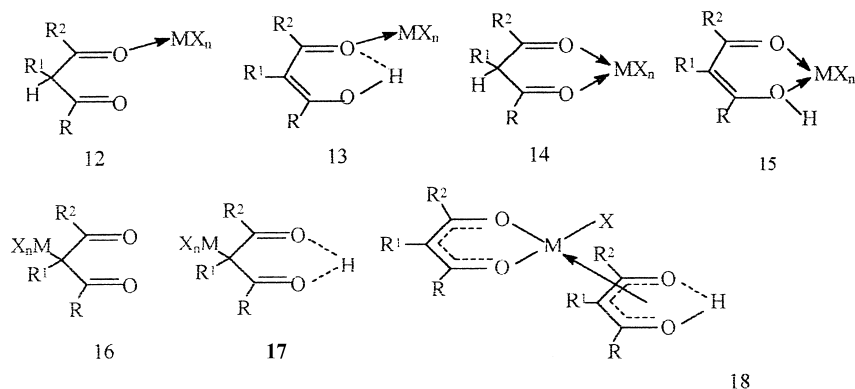
Structural analysis of these chelates confirms the  $\text{M}-\text{OC}$  and  $\text{M} \leftarrow \text{O}=\text{P}$  donor–acceptor bonds [53].

$\beta$ -Diketones may form complex compounds that are coordinated in a less-common fashion, specifically metal bonding not only via O but also via C donor sites [2,7–12,54].

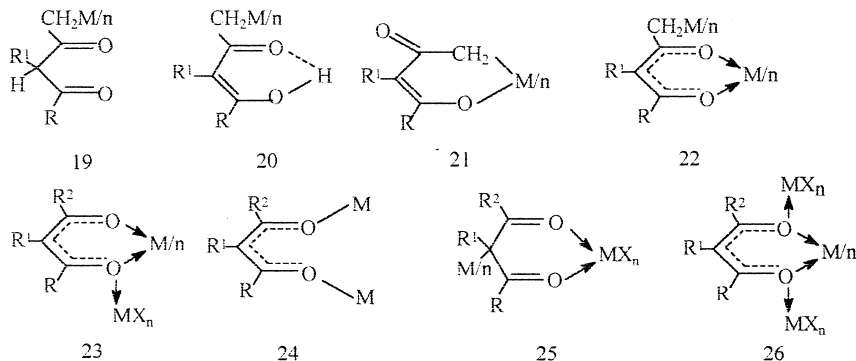
In the early 1960s, in a series of papers devoted to the  $\beta$ -diketone complexes of trimethylplatinum (reviewed in refs. [2,7,13]), bonding to platinum via the methylene carbon atom (**10**) was demonstrated. Two coordination modes are realized — via the carbon atom as in (**10**), and via O and C donor sites simultaneously (**11**).



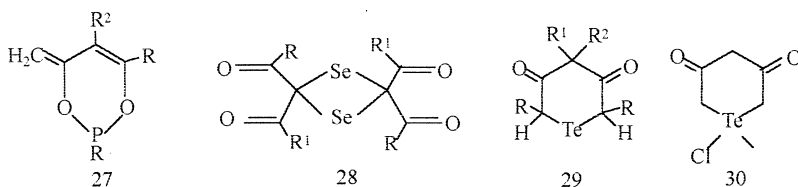
These and more recent studies revealed that  $\beta$ -diketones (**3a**) can form not only chelates (**4a**) but seven other types of coordination mode via the oxygen atoms<sup>2</sup> [in a mono- (**12**, **13**) and bidentate (**14**, **15**) fashion], carbon atoms (**16**, **17**),  $\pi$ -quasiaromatic system (**18**), and simultaneously via the O and C donor sites.



The most complete scheme of the less-common coordination modes of the 1,3-dicarbonyl compounds is given in reviews [2,9,10,54,55] and includes, besides (**4a**, **12–18**), the monoanionic  $\beta$ -diketonates where a hydrogen atom of the exocyclic methyl group is replaced by a metal (**19**, **20**), the dianionic complexes (**21**), as well as di- (**22–25**) and trinuclear (**26**) complexes.

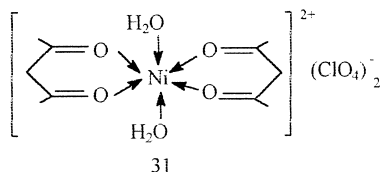


Dianionic complexes of  $\beta$ -diketones with phosphorus (**27**), selenium (**28**), or tellurium (**29**) as the central atoms are known.

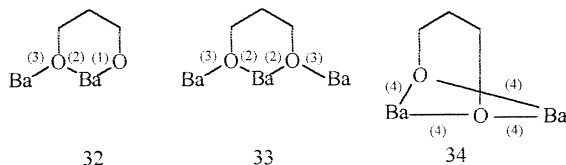


<sup>2</sup>In (**12–29**), R, R<sup>2</sup>=Alk, Ar; R<sup>1</sup>=H, Alk, Ar; MX<sub>n</sub> represents a wide variety of transition metal salts.

The less-common O coordination (**12–14**) was proven by X-ray structural analysis for a series of complex compounds. Structure (**12**) is realized, for instance, in the complexes  $[\text{Cu}(\text{aa})_2(\text{en})_2 \cdot 2\text{H}_2\text{O}]$  and  $[\text{Cu}(\text{hfaa})(\text{MeNHCH}_2\text{CH}_2\text{NHMe})]$ ; (**13**) is characteristic for the compound  $[\text{Re}(\text{Hba})(\text{CO})_3\text{Cl}]$  and  $[\text{Mn}(\text{Haa})\text{Br}_2]$ , while (**14**) was established for the chelates  $[\text{Ni}(\text{Haa})_2\text{Br}_2]$  and  $[\text{Ni}(\text{Haa})_2(\text{H}_2\text{O})_2(\text{ClO}_4)_2]$ . For the latter complex, X-ray analysis defined all the protons showing the existence of the  $\text{CH}_2$  group in the chelate and, hence, the fixed diketononic form of the ligand in (**31**) as a result of complex formation [2, 54–56].

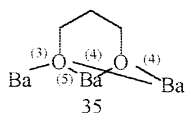


Structure (**23**) was discovered in a series of barium complexes with the tridentate chelate-bridged ions of dipivaloylmethane (**32**) [57,58]. In such a situation, one oxygen atom is monodentate, another is bidentate, as illustrated in (**32**). In order to differentiate among the various functions of the donor oxygen atoms, the authors of ref. [58] suggested the concept of the chelate (**1**), chelate-bridging (**2**), and bridging (**3**) Ba–O bonds. The *bis*-chelate bridging bonding is labeled as (**4**). This notation is shown in (**32–34**).

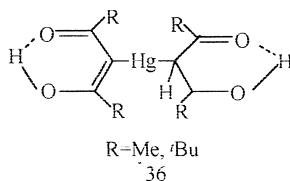


The chelate-double-bridging coordination of the tetradentate dipivaloylmethane ion, similar to (**26**), is also observed in the barium complexes (**33**) [58]. Compounds with a previously unknown coordination mode for  $\beta$ -diketones may be obtained with the tetradentate anion of dipivaloylmethane, namely (**34**) [59–62]. This is observed in the complexes  $[\text{Ba}_2(\text{dpm})_4(\text{NH}_3)_4]$  [59],  $[\text{Ba}(\text{dpm})_2\text{Et}_2\text{O}]$  [60],  $[\text{Ba}_4(\text{dpm})_8]$  [61], and  $[\text{Ba}_2(\text{dpm})_4\text{bpy}_2]$  [62].

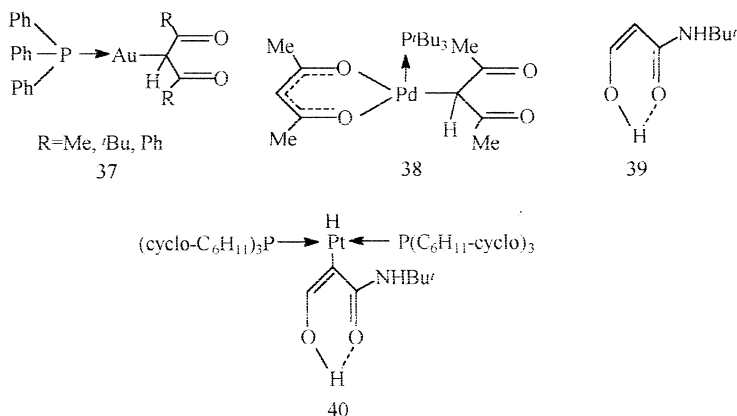
An example is known of the *bis*-chelate bridging structure in the complex  $\text{Ba}_5(\text{dpm})_9(\text{piv})$ , where the dipivaloylmethanate anion is a pentadentate species and forms a previously unknown [7,8,54,55] framework (**35**) [61]. In the tetranuclear complex  $\text{Ba}_4(\text{dpm})_8$ , the dipivaloylmethanate fragment plays the role of both the tridentate (**23**) and the usual chelating bidentate (**4**) ligand [57].



The C coordinated  $\beta$ -diketone complexes represented by a series of structures (**10**, **11**, **16–20**, **28–30**) are of considerable interest and discussed in reviews [2, 7, 9, 54, 55]. Among the basic studies in this field, publications [63–68] should be noted. An original synthesis of the C-metal substituted  $\beta$ -diketone attracts special attention. Thus, complexes (**36**) were prepared [68] by interaction of  $\beta$ -diketones with bis(hexamethyldisilylamino)mercury in ether.



A structure of the type (**16**) where there is an M–C bond and the ligand is in its keto-form, has recently been proven by X-ray structural analysis for complexes of triphenylgold(I) with the  $\beta$ -diketonates — diacetylmethane (**37**) ( $R = \text{Me}$ ) [69], dipivaloylmethane (**37**) ( $R = t\text{-Bu}$ ) [70], and dibenzoylmethane (**37**) ( $R = \text{Ph}$ ) [71]. In the complex compound (**38**) the usual chelate coordination of the type (**4a**) is paralleled by the M–C bonding of the diketone form of the ligand [72]. However, according to X-ray structural data for the complex of the C-amino substituted  $\beta$ -diketone —  $\text{Pt}(\text{H})\text{L}[\text{P}(\text{C}_6\text{H}_{11}\text{-cyclo})_3]$ , where L is (**39**), the enolic form of the ligand in (**40**) is fixed [73].



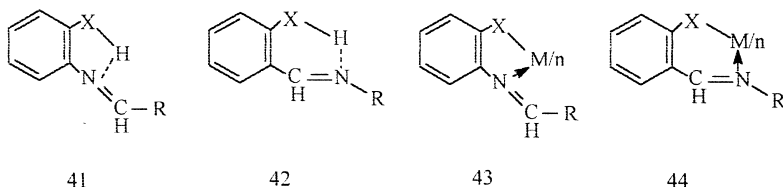
For complex compounds prepared from monothio- (**3b**) and dithiodiketones (**3c**), the less-common structures similar to (**12–30**) are, to our knowledge, not described.

In the molecular complex of uranyl nitrate with  $\beta$ -ketophosphone,  $[\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{CO})\text{Ph}]_2\text{UO}_2(\text{NO}_3)_2$ , the phosphorus analogue of the  $\beta$ -diketones is a monodentate ligand, and coordination of the uranium atom is via the oxygen atom of the  $\text{P}=\text{O}$  group. The same coordination mode is observed in the complex  $\text{UO}_2(\text{ClO}_4)_2(\text{HL})$  [74]. However, in  $\text{UO}_2\text{L}_2(\text{HL})_2$  the mixed-ligand coordination

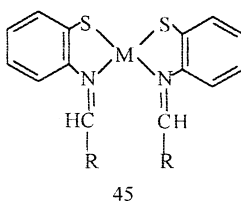
mode prevails [L is a bidentate anion similar to (**4a**)], whereas the neutral molecule HL is bound to uranium via the oxygen atom of the P=O group.

## 2.2. Coordination compounds of *o*-oxyazomethines and related ligands

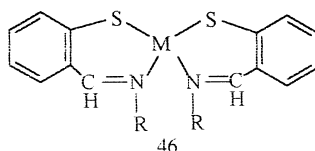
It is widely accepted [4,75–85] that *o*-oxyazomethines (**41** and **42**) and their N, S, Se-containing analogues form chelates with the five- (**43**) or six- (**44**) membered metallocycles. Here X=NTs, O, S, Se; R=Ar, Het;  $n=2, 3$ .



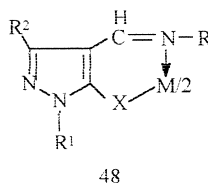
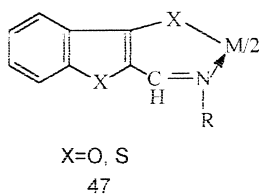
The coordination mode based on the five-membered H-cycle (**42**, LH) was proposed in the early papers [86–91] and further proven by X-ray structural analysis [4,92–99]. In complexes of the *o*-aminophenol derivatives (**41**) (X=O; R=Ar, Het), tetrahedral,  $\text{ML}_2$  [99], bipyramidal,  $\text{ML}_2\text{L}^1$  ( $\text{L}^1=\text{CH}_3\text{CN}$  [97]) and octahedral  $\text{ML}_2\text{L}^1\cup\text{L}^1$  ( $\text{L}^1\cup\text{L}^1=\text{bpy}$  [95,96], *o*-phen [98]) structures are known. Simultaneously, for the similar chelates of  $d^8$  metals prepared from the mercapto derivatives (**41**), the *cis*-planar configuration (**45**) [4,92,93] is discussed in reviews [4,80,100,101].



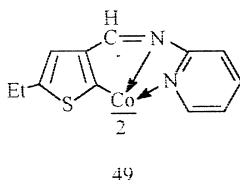
The formation of six-membered metallocycles (**44**) has been proven by numerous X-ray studies [1,4,75–85]. Chelates of this type are most widely spread among the 3d metals, cobalt [102], nickel [4,100,103–106], copper [4,107,108] and zinc [4,109–111]. If X=O, NTs, the *trans*-planar or tetrahedral polyhedra are formed [1,4,75–85], while with X=S, Se the *cis*-planar structures (**46**) are typical [4,100,101].



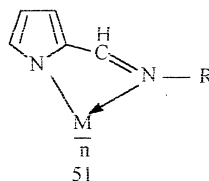
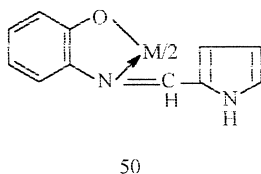
Annellation of the benzofuran (**47**) ( $X=O$ ) or pyrazole (**48**) rings to metallocycles leads to tetrahedral structures irrespective of the nature of the heteroatom  $X$  [4,84,85]. Palladium complexes are exceptions to this rule. They are characterized by the *trans*-planar configuration (**48**) ( $X=S$ ,  $M=Pd$ ,  $R=cyclohexyl$ ) [112,113]. However, for the benzothiophene derivatives (**47**) ( $X=S$ ) as for (**44**) ( $X=S$ ,  $M=Ni$ ), the *cis*-planar configuration is formed [4,84,85].



The influence of the coordinatively active substituents in the amine framework ( $R$ ) on the structure of the metal-chelates (**44**) was discussed for complexes of the ligand types (**41** and **42**). The  $\alpha$ -pyridyl framework may not or may participate in coordination: (**44**) ( $R=\alpha$ -py,  $X=O$  [4,84,85,104,111,114–118]), (**48**) ( $R=\alpha$ -py,  $X=S$  [4,84,85,104,111]) or (**49**) [119].

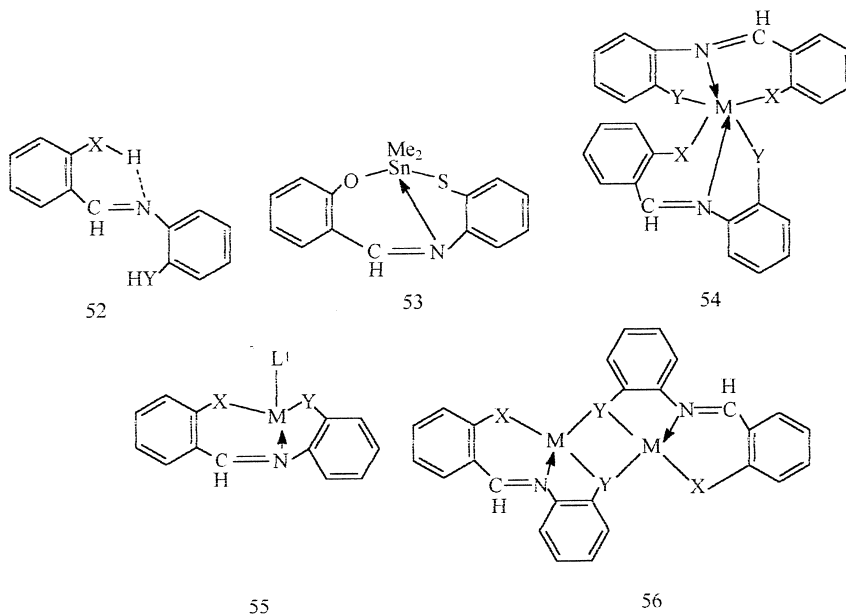


X-ray structural analysis revealed that the pyrrolic fragment does not take part in coordination in the metal-chelates (**50**) [95–98]. However, the coordinative activity of this heterocycle was established in numerous complexes of 2-pyrrole aldimines (**51**) [79,120–125].

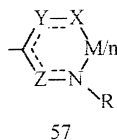


For the tridentate azomethine ligands (**52**), all the coordination frameworks take part in metal bonding, forming four types of complexes, monomeric (**53**) [126], (**54**) [127–130] and (**55**) [75,131–139] and dimeric (**56**) [75,135,136,139–143]. In

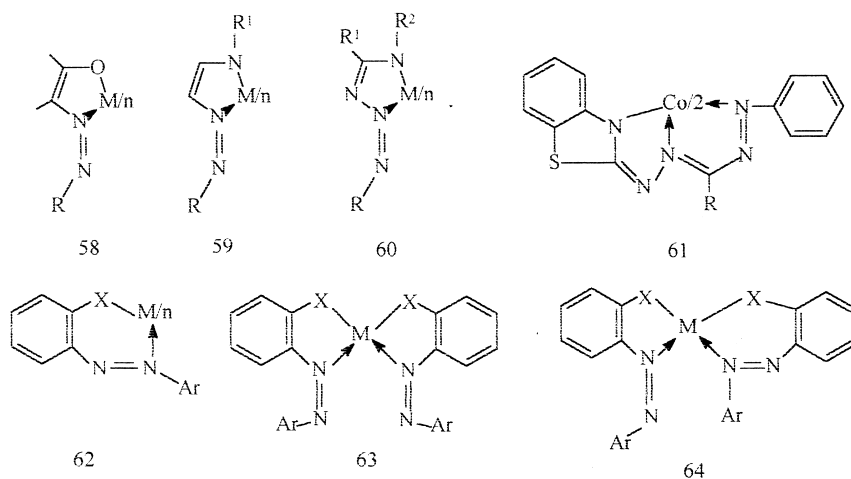
(**52–56**),  $X=Y=NTs$ , O, S, Se;  $L^1=py$  [75,132,134,135,139], bpy [133], *o*-phen [136], DMSO [137], 1-methyl-2-aminobenzimidazole [138,139].



The six-membered metallocycles are typical for chelates (**57**) prepared from ligands related to the azomethines, namely  $\beta$ -aminovinylketones (**57a**) ( $X=O$ ,  $Y=Z=CR$ ) [4,75,76],  $\beta$ -aminovinylthiones (**57b**) ( $X=S$ ,  $Y=Z=CR$ ) [4,144,145],  $\beta$ -aminovinylimines (**57c**) ( $X=NR$ ,  $Y=Z=CR$ ) [84,85,146–148], hydrazones of the  $\alpha$ -dicarbonyl compounds (**57d**) ( $X=O$ ,  $Y=N$ ,  $Z=CR$ ) [149,150], hydrazone imines (**57e**) ( $X=NR$ ,  $Y=CR$ ,  $Z=N$ ) [151–153] and formazanes (**57f**) ( $X=NR$ ,  $Y=Z=N$ ) [84,85,147,154–156].



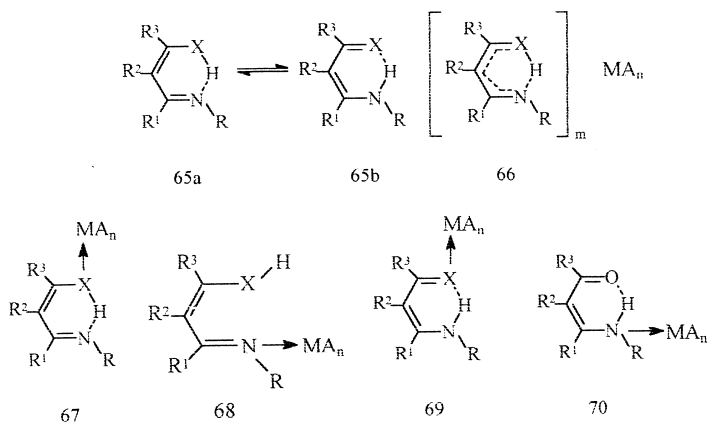
For the hydrazones of the  $\alpha$ -dicarbonyl compounds (**57d**), hydrazone imines (**57e**) and formazanes (**57f**), chelates with five-membered coordination units are proposed (**58–60**, respectively, where  $R=H$ , Alk, Ar, Het). However, such a structure was proven by X-ray analysis only for the complex compounds of hetarylformazanes, e.g. (**61**) [156]. A similar situation is characteristic of the complexes of the azo-compounds (**62–64**) ( $X=NTs$ , O, S) related to the chelates (**41** and **44**).



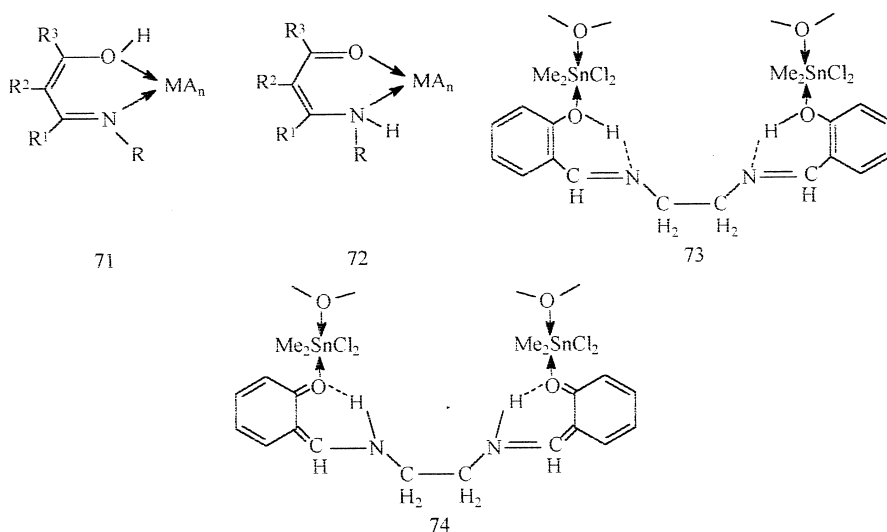
Structure **(62)** ( $X=O$ ,  $n=2$ ) is the most typical of the chelates of the *o*-oxyazocompounds [84,85,157–159]. As far as **(62)** ( $X=O$ ) is concerned, it is similar to the structure of the *o*-oxyazomethine complexes **(44)**. The chelates of divalent nickel and copper are *trans*-planar, while the cobalt and zinc complexes are tetrahedral [84,85,152,157–159]. There are two five-membered metallocycles in the *cis*-planar nickel complex of the *o*-mercapto azo compound **(63)** ( $X=S$ ,  $Ar=Ph$ ,  $M=Ni$ ) [80,159–161], while the five- and six-membered coordination units are characteristic of the similar palladium chelate **(64)** ( $X=S$ ,  $M=Pd$ ) [80,159,162] and the tetrahedrally distorted copper complex of the *o*-mono-*N*-tosylamino derivative **(64)** ( $X=NTs$ ,  $M=Cu$ ,  $Ar=C_6H_4CH_3-p$ ) [152,163]. Such a situation is customary for the series of chelates of the azomethine and related ligands.

However, it is less known that these typical chelating ligands may behave as monodentate ligands and form molecular complexes (adducts) with a fully intact ligand. Thus, the possibility of forming molecular complexes of general formula **(65)** is assigned to *o*-oxyazomethines, and this complex formation mode occurs together with chelate formation **(44)** [4,75–85]. Taking into account tautomerism (**65a**  $\rightleftharpoons$  **65b**) and the existence in molecules **(65)** of an intramolecular hydrogen bond [4,82,83], the complexes **(66)** are characterized by several kinds of structures, when the azomethine ligand plays the role of a monodentate species **(66–70)** ( $R, R^1, R^2, R^3=H, Alk, Ar, Het$ ) [4,164].

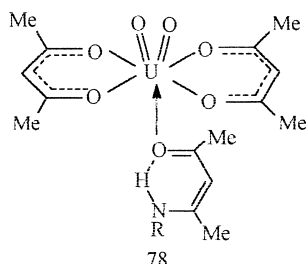
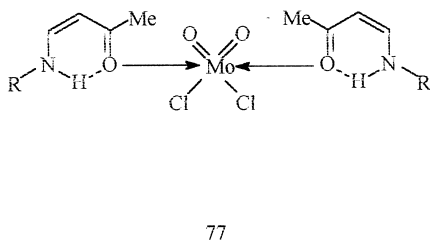
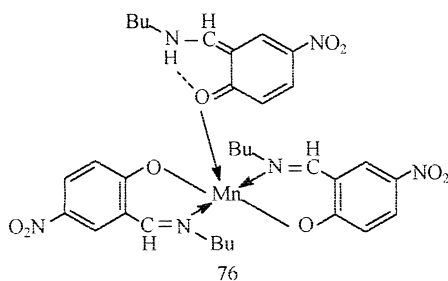
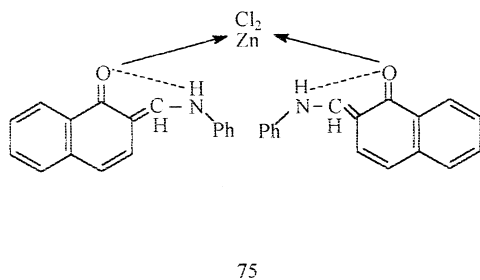
Chelate structures **(71, 72)** are not excluded. They differ from **(42)** not only by composition but by the fact that the ligands are coordinated in a molecular fashion [4,164]. However, only the coordination mode with a metal–oxygen bond **(67 or 69)** is proven for adducts **(66)**. In a preliminary study [165] it was shown by X-ray analysis that in the polymeric complex of bis(salicylidene)ethylenediamine with dimethyltin(IV) dichloride of composition 1:1, the structure can be illustrated as **(73)** similar to **(68)**. These studies were carried out with a low level of accuracy of localization of a proton. This practically excluded the choice between structures **(67**



and **69**), i.e. preference of the enol (**73**) or quinonoid (**74**) tautomeric species of the ligand.

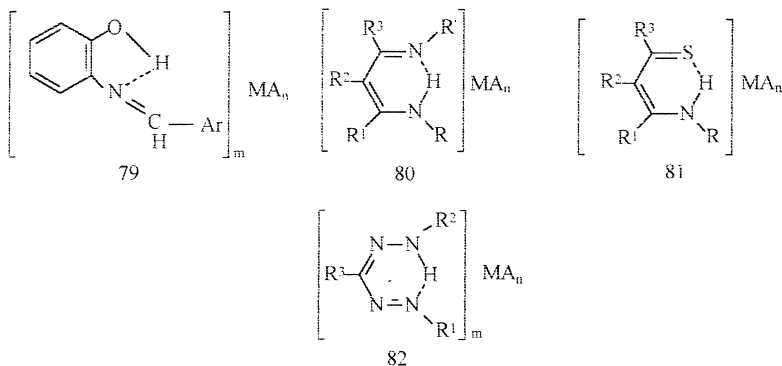


In subsequent, more accurate, structural studies it was shown that molecular complexes of *o*-oxyazomethines [164] and  $\beta$ -aminovinylketones [166–168] contain the quinonoid (ketonic) tautomers of the O coordinated ligands, i.e. only one structure (**69**) is valid. This tautomeric species of the ligand is coordinated in the 2-oxy-1-naphthalideneaniline complex with zinc dichloride (**75**) [166], in the manganese chelate adduct with 4-nitrosalicylideneaniline (**76**) [169], molecular complexes of N-phenyl- [167] and N-heptyl- [168] acetone imines with molybdenum dioxydichloride (**77**), and  $\beta$ -aminopropenone with uranyl acetylacetonate (**78**) [9].



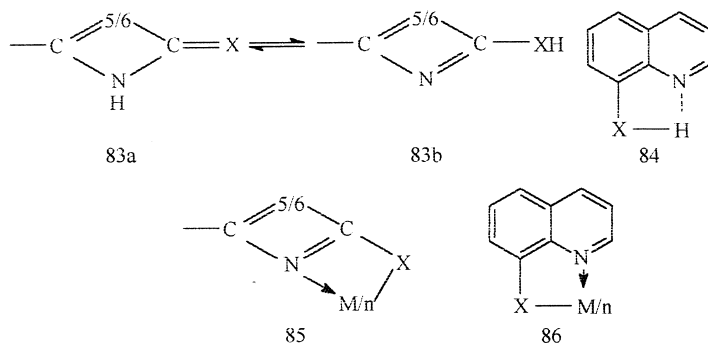
The situation remains unchanged for the O coordinated salicylaldimines in the zwitter-ionic form [170]. Proof for coordination via the oxygen atoms in *o*-oxyazomethines follows from synthesis of the molecular adducts from chelates [171–175], the O coordination proven by X-ray analysis [176].

In the reviews [4,164] molecular complexes with a less-common coordination were prepared involving aryald-*o*-aminophenoles (**79**),  $\beta$ -aminovinylimines (**80**),  $\beta$ -aminothiones (**81**) and formazanes (**82**). However, the information on their structure is based mainly on IR spectroscopy, and is equivocal.



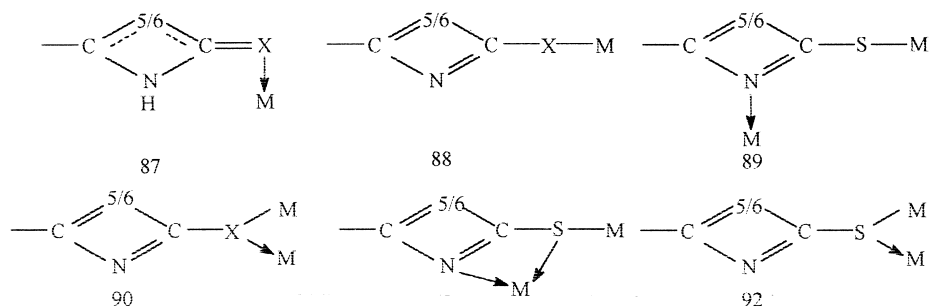
### 2.3. Metal complexes of *o*-oxy(mercapto) derivatives of nitrogen heterocycles

The *o*-oxy(chalcogen) derivatives of the nitrogen heterocycles of types (**83** and **84**) form chelates in which four- (**85**) and five- (**86**) membered metallocycles are formed [177–179].

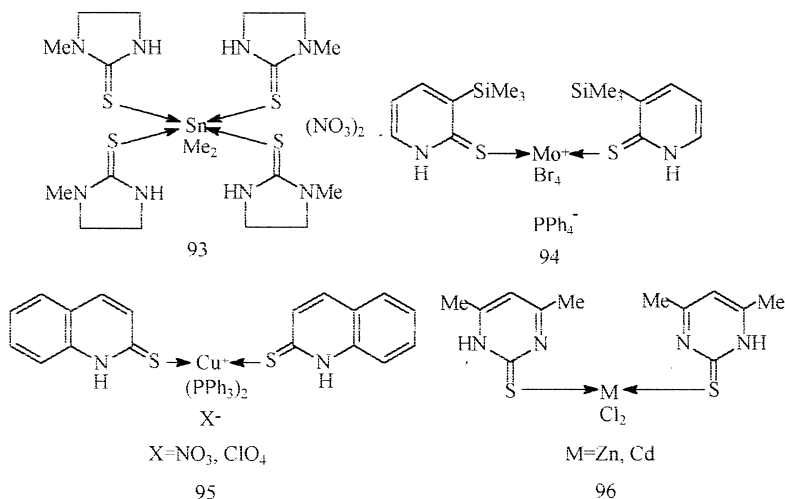


Chelates (**85**) are broadly represented in the series of 2-mercaptoazoles [177,178,180–182] and the related azines [177–179,182–195]. They are usually prepared by the direct interaction of ligands (**83**) with metal salts [181–183,188,190] and by electrosynthesis when zero-valent metals are applied [30–32,184,189,192,195]. Among complexes where  $\eta^2\text{-N,S}$ -chelate coordination takes place (**85**) ( $\text{X}=\text{S}$ ), there are cobalt [188] and cadmium [191] complexes of 3-trimethylsilyl-2-pyridine thione and the zinc chelate of 4,6-dimethyl-2-pyridine thiol [193], recently characterized by X-ray analysis. The same coordination mode (**85**) is observed upon metal bonding in the N-base adducts (en, py, bpy, phen) with the nickel complexes of 2-mercapto derivatives of benzothiazole [184], pyridine [185] and pyrimidine [184]; cobalt [188,194], zinc [192] and cadmium [189] chelates of 4,6-dimethyl and 3-trimethylsilyl substituted azines specified above, and also the ethylenediamine adduct with the 2,4-dithiouracil cobalt complex [190].

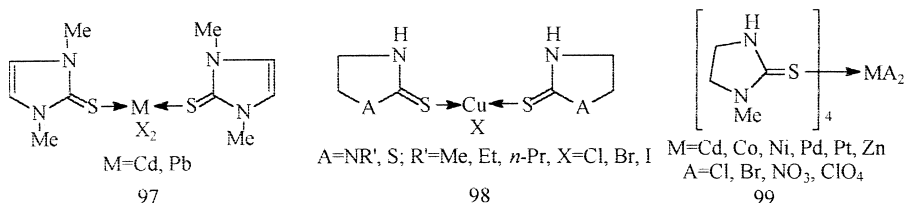
The presence in ligands (**83**) of the N, X-donor sites and the prototropic tautomerism ( $\text{83a} \rightleftharpoons \text{83b}$ ) means an opportunity for the various coordination modes with these ligands. This aspect is considered in detail elsewhere [31,32,177,179,185–189,196–199]. The coordination modes can be reduced to types (**87–92**). Complexes containing the  $\eta^1:\eta^1:\mu$  mode (**89**) are described in refs. [200–208], while the  $\eta^1:\eta^2:\mu$  mode (**91**) is analyzed in publications [209–211]. Various research groups have described the simultaneous realization of these two coordination modes [206,212–218].



Structures (87) where compound (83) ( $X=S$ ) is a monodentate thione (83a) ligand (LH) are represented by a whole series of complexes of composition  $(LH)_m(MA_n)$  considered in refs. [180,186,219–221]. Structural characterization is given for complexes prepared from 1-methyl-2(3H)-imidazolinthione (93) [219], 3-trimethylsilylpyridine-2-thione (94) [186], quinoline-2-thione (95) [220] and 4,6-dimethylpyrimidine-2-thione (96) [221].

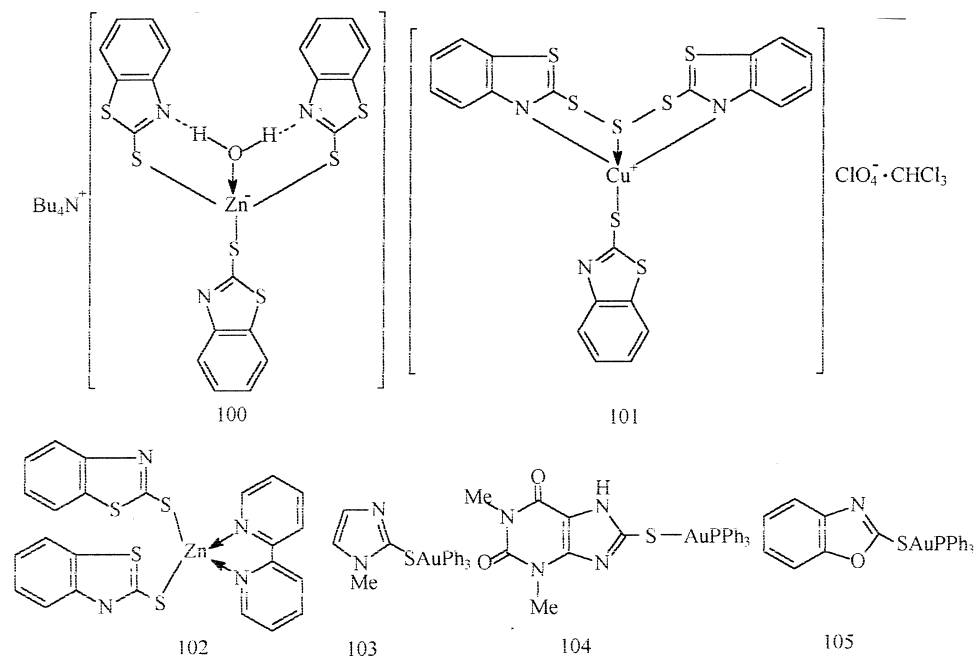


The  $C=S \rightarrow M$  coordination (87) is of course observed in metal complexes with the fixed thione species of the ligands — 1,3-dimethyl-2(3H)-imidazolethione (97) [222], N-alkylimidazolin-2-thione (98) ( $A=NR'$ ) [223] and thiazolidin-2-thione (98) ( $A=S$ ) [223]. X-ray data are reported for the S coordination of imidazolin-2-thiones, and their N-methyl- and N-ethyl-substituted derivatives of the types (98) ( $A=NR$ ,  $R=Me, Et$ ) and (99) are discussed in review [177].



Few complex compounds of type (88) are structurally characterized. They are interesting from the point of view that in contrast to (85), the thione form of the ligand does not lead to chelate structures. Thus, monodentate S coordination is observed in the anion  $\{n\text{-Bu}_4\text{N}^+[\text{ZnL}_3](\text{H}_2\text{O})\}$  (100) [177], and in the cationic complex compound of a rather peculiar trisulfide derivative of benzothiazole (101) [177]. The monodentate bonding of a ligand, according to X-ray structural data, occurs in the zinc adduct of 2-mercaptobenzothiazole with *o*-phenanthroline (102) [31,32]. The  $\eta^1\text{-S}$ -monodentate coordination mode (88) is observed in complexes

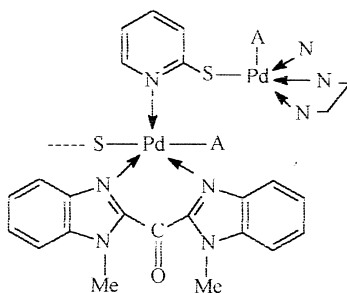
of triphenylphosphine gold with 2-mercapto-1-methylimidazole (**103**) [224], 8-mercaptotheophiline (**104**) [225] and 2-mercaptobenzoxazole (**105**) [226].



In complexes of the nitrogen-containing heterocycles the less-common structures with the bridging  $\mu^2$ -N,S,M bonds of the types (**89**) (e.g. refs. [197, 198, 200, 201, 212, 227–235]) are quite typical. Thus, the coordination (**89**) is observed in complexes of the 2-mercapto derivative of 1-methylimidazole [233], pyrimidine and its 4-methyl substituted compound [233] and quinoline [231] with palladium chloride, and 1-methylimidazolidine-2(3H) with copper(I) salts [201].

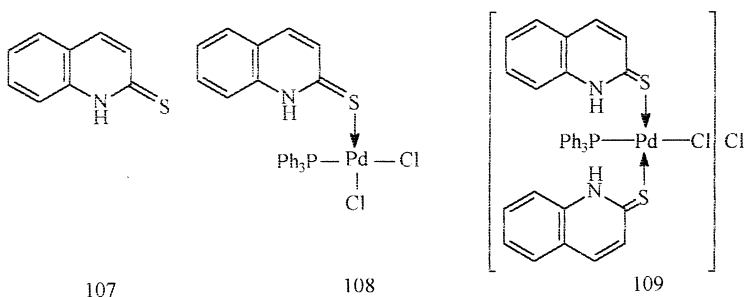
The bridging  $\mu^2$ -N,S coordination (**89**) is observed in the binuclear palladium adducts of pyridine, pyrimidine and 1-methylbenzimidazole with bis(1-methylbenzimidazolyl-2)ketone, e.g. (**106**) [197]. All these complexes have the cation  $[\text{PdL}_2\text{L}'_2]^{2+}$ , where palladium is bonded to the sulfur atom and three nitrogen atoms of the pyridine type, participating in the heterorings of the thiol and ketone fragments. The Pd...Pd distances are within the range 2.886–2.970 Å. The bis(benzimidazole)ketonic fragment behaves as a bidentate N,N-donor ligand; the carbonyl group does not participate in coordination.

In refs. [230, 233], influence of the complex-formation conditions on the structure of the complexes was thoroughly studied. Thus [230], the same reactants, (**107**) and  $[(\text{Me}_3\text{P})(\text{Cl})\text{Pd}(\mu\text{-Cl})_2]$ , lead to different products as a function of the solvent, temperature and pH. Two products (**108**, **109**) are of the type (**87**). They are the molecular mono-S coordinated adducts with the thione tautomeric form of the ligand. In the binuclear complex (**110**), the 2-mercaptoquinoline ligand is in the thiol form and there are simultaneously Pd–S bond (type **88**) and the bridging



106

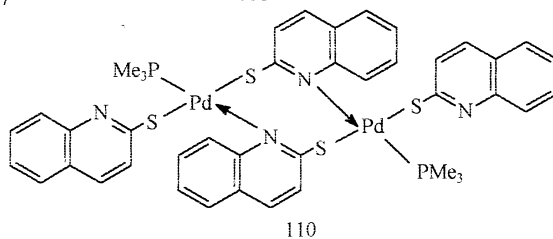
$\mu$ -N,S- $\eta^2$ -bonding mode of the ligand (type **89**). The same coordination mode is realized in the dimeric palladium complexes of 2-mercaptopyrimidine (**111**), which are unstable in solution and decompose in deuterotoluene generating the monomer (**112**) containing the  $\eta^2$ -N,S coordinated chelate structure of the type (**85**) [233]. Complexes (**111**–**113**) are in equilibrium, and the possibility of the intermediate  $\eta^1$ -S-monodentate species (**113**) (type **88**) is not unrealistic [233].



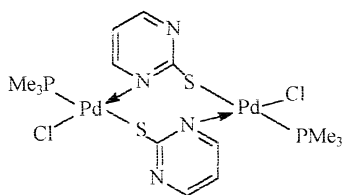
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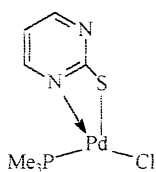
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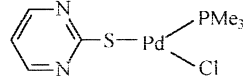
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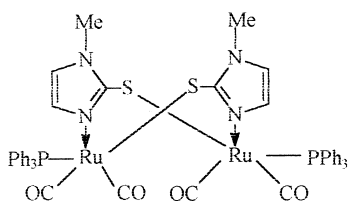


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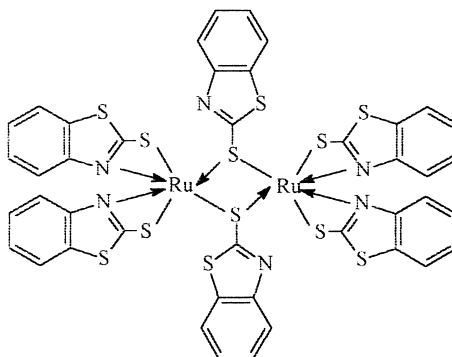


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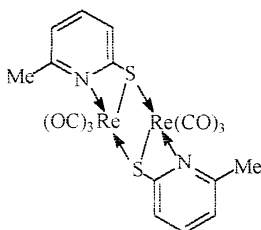
The bridging  $\mu$ -N,S- $\eta^2$  coordination (**90**) is observed in the hexanuclear complex of cadmium with 4,6-dimethylpyrimidine-2-thione (LH) of composition  $(\text{CdL}_2)_6$ , having a rather peculiar cyclic (calixarene) structure that includes six types of cadmium atoms united by the sulfide bridges [198]. The same coordination mode is assigned to the dimeric ruthenium carbonyl complex (**114**) prepared by interaction of the trinuclear cluster  $[\text{Ru}_3(\text{CO})_6(\text{PPh}_3)_3]$  with 1-methyl-2-mercaptoimidazole in its fixed thiol form [219,234]. The coordination (**90**) together with the chelate bonding (**85**) is characteristic of dimeric ruthenium complexes with benzothiazole (**115**) [177] and rhenium carbonyl with 2-mercapto-6-methylpyridine (**116**) [228].



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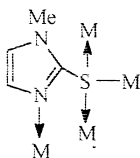


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116

In the 12-nuclear cluster  $[\text{Cu}_{10}\text{Cu}_2^{\text{II}}(\text{C}_4\text{H}_5\text{N}_2\text{S})_{12}(\text{MeCN})_4]$ , where  $\text{C}_4\text{H}_5\text{N}_2\text{S}$  is 1-methyl-2-mercaptoimidazole, the thiol sulfur may coordinate simultaneously to three copper atoms [227]. In this case, there is a coordination mode (**117**) that has not so far been considered.

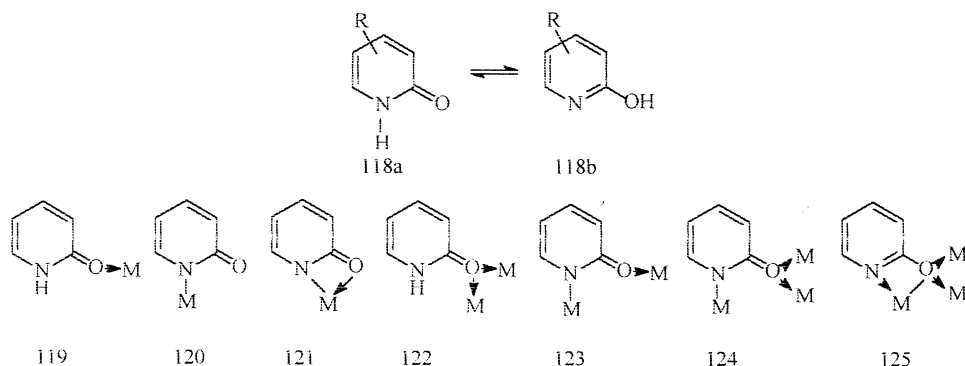


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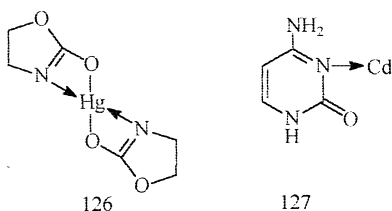
The imidazole derivative behaves as a tetradentate bridging ligand.

The coordination chemistry of the oxygen-containing analogues of (**83**) ( $\text{X}=\text{O}$ ),

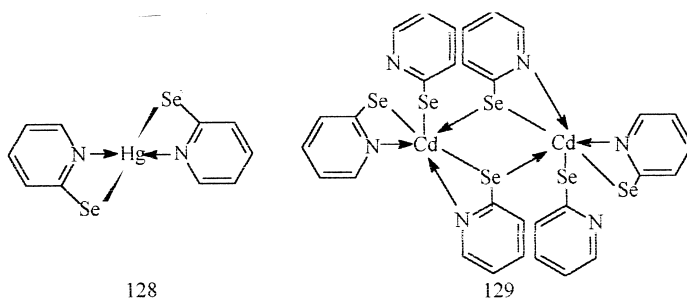
basically of pyridinone (**118**), is considered in review [179] and will not be discussed. The authors of ref. [179] analyzed the mono- (**119–121**), di- (**122, 123**) and tri- (**124, 125**) nuclear bonding of metals with ligand (**118**) and account for tautomerism ( $118a \rightleftharpoons 118b$ ). Special attention is paid to the bridging function of ligands (**118**) in complexes with multiple metal–metal bonds [179]. This aspect is mentioned in monograph [235].



Among complexes with the oxygen analogues of (**83**) ( $X=O$ ), the chelate structures (**85**) are typical. Such a metallocyclic structure is observed, for example, in mercury complexes of 1,3-oxazolidine-2-one (**126**) [236]. There exists X-ray structural information on the less-common monodentate O coordination of a ligand in the copper perchlorate complex with 2-pyridone, having structure (**88**) ( $X=O$ ) [237]. When substituents containing additional donor sites are introduced to the 2-oxo derivatives of azines, the basic coordinating fragment may be omitted. Thus, in the cadmium complexes of 4-amino-1,4-pyrimidine-2-one (cytosine, LH),  $[CdCl_2L_2(H_2O)_2]$  and  $\{[CdL_3Cl][CdLCl_3]\}H_2O$ , the metal is bonded to the pyridine type N atom; structure (**127**) was proven by X-ray structural analysis [238].

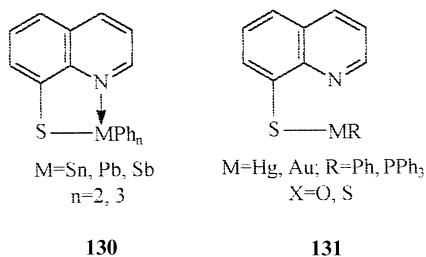


Complexes of the selenium-containing analogues of (**83**) ( $X=Se$ ) are scarce. Thus [239], the mercury complex of 2-pyridine selenol (**128**) has a structural type (**85**) ( $X=Se$ ,  $M=Hg$ ), while in the cadmium dimer (**129**) prepared on the basis of the same ligand, the chelate and bridging functions are simultaneous as in (**89**). This follows from X-ray structural analysis.



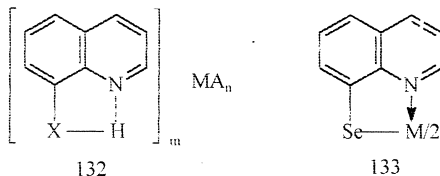
The coordination chemistry of 8-oxy- (**84**, X=O) [178,240,241] and 8-mercapto- (**84**, X=S) [178,242–246] quinolines is represented by X-ray proven chelate structures (**86**) (X=O, S). Review [178] contains data on the structure of bis(thiooxynates) of cobalt, nickel, zinc and cadmium. Recently, molecular and crystal structures of 8-mercaptoquinolines of indium [240,243], cobalt [240], nickel [242], palladium [244], rhodium [241,245], ruthenium [241], osmium [241], and iridium [246] have been described. The potassium complex of 8-oxyquinoline (LH) of composition  $\text{KL}(\text{LH})_2$  is of interest. The ligand is coordinated not only in a chelate but in a molecular monodentate fashion. The synthesis and rigorous proof of structure of two mixed-valent vanadium complexes with 8-mercaptoquinoline (LH) are noted [247].

The organometallic derivatives of oxine [248–253] and thioxine [249,254–256] are of special interest. Analysis of the data [178,249–256] shows that the coordination mode of ligands (**85**) in complexes of mercury [248,250,252], gold [251,254–256], tin [249], lead [249] and antimony [253] is as yet unsolved. According to the proposal [249,253], in complexes (**130**), the standard chelate structure (**86**) typical of ligands (**84**) is realized. In complexes (**130**) both sulfur [249] and nitrogen atoms bond, leading to the trigonal bipyramidal configurations (compare with ref. [178]). However, in complexes of 8-hydroxy- and 8-mercaptoquinolines with phenyl mercury and triphenylphosphine gold (**131**), a less-common coordinative interaction is assumed, where there might be only one covalent X–M bond and the  $\text{N}\cdots\text{M}$  interaction is very weak [250–252,254–256].



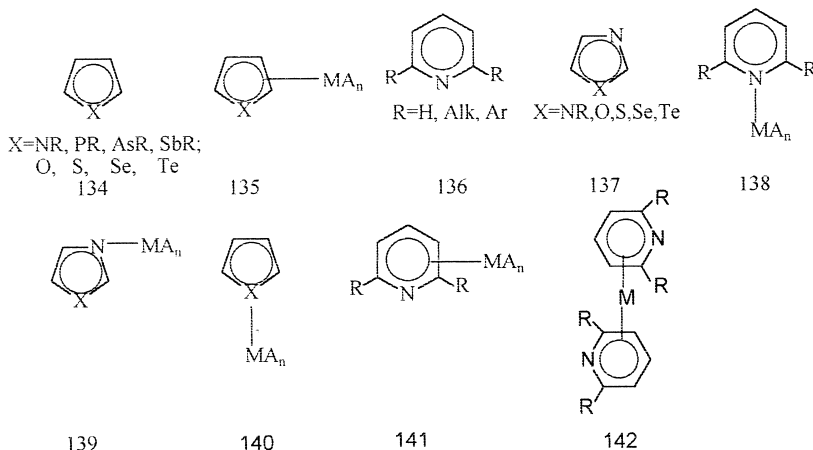
It is likely that metal–ligand coordination will be less common in molecular adducts of 8-oxy- and 8-mercaptoquinoline with Lewis acids (**132**) [4,84,85,164]. Their structures are unknown. Possibly by analogy with the molecular complexes

of *o*-oxyazomethines [4,164], the coordinative bond may be localized at the donor site X in the adducts (**132**). There is no clarity on the structure of the complex compounds of 8-hydroselenoquinoline (**84**) (X=Se), although the chelates (**133**) have been known for a relatively long time [257–260]. Tellurium derivatives of the type (**83** and **84**) (X=Te) [261,262] have not been described to our knowledge [263–265].



### 3. Coordination variations of the five- and six-membered hetrocycles

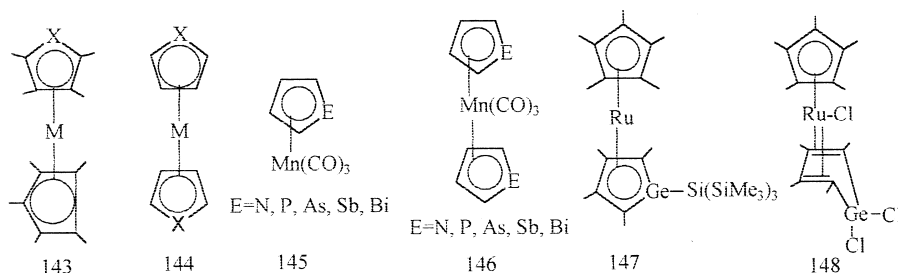
The  $\pi$ -excessive [266] five-membered heterocycles (**134**), excluding pyrrole (X=NR), form mainly  $\pi$ -( $\eta^5$ )-metallocomplexes (**135**) [5,6,267–270], whereas the  $\pi$ -deficient heteroaromatic systems, in particular azines (**136**) and azoles (**137**), tend to form  $\sigma$ -( $\eta^1$ ) coordinated compounds (**138**) [175,271–273] and (**139**, **140**) [175,272,274–278]. However, this standard situation is violated in many cases and is followed by the formation of  $\sigma$ -( $\eta^1$ ) complexes for ligands (**134**) [269,270,279–281] and  $\pi$ -( $\eta^6$ ) coordinated derivatives (**141**, **142**) for ligands (**136**) [5,31,32,175,268].



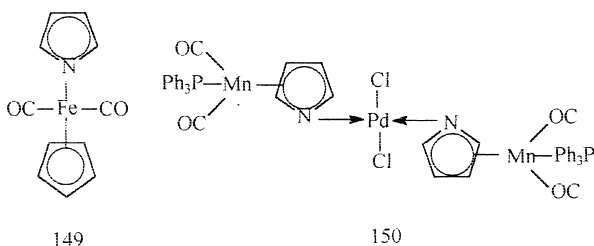
#### 3.1. Metal bonding in complexes of the fundamental five-membered heterocycles and their analogues

Reviews [267–269] as well as publications [5,6,175] contain a large number of examples describing the  $\pi$ -( $\eta^5$ ) complexes (**135**) for pyrrole (X=NR), phosphole

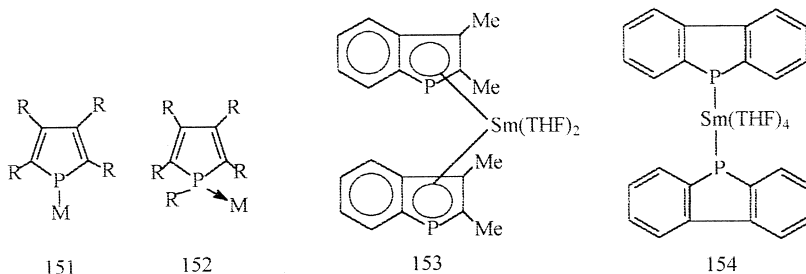
(X=P), arsole (X=As), stibole (X=Sb), thiophene (X=S), selenophene (X=Se) and tellurophene (X=Te). As Lewis acids  $MA_n$ , the metal–carbonyl frameworks, especially  $Mn(CO)_3$  and  $Cr(CO)_3$ , are most frequently used, e.g. phosphacymantrene [281]. The other group of the  $\eta^5$  coordinated systems are the sandwich structures (**143** and **144**). However, one should not look at  $\eta^5$  complexes of the five-membered fundamental monoheterocycles as routine coordination chemistry. Among numerous recent publications, the successful synthesis of the tricarbonylchromium ( $\eta^5$ -tetramethylpyrrole) [282], the complete series (**145**, **146**) [283,284], and especially the first  $\eta^5$ -germole complex (**147**) [285] but not the traditional  $\eta^4$ -species (**148**) [286] are obviously remarkable.



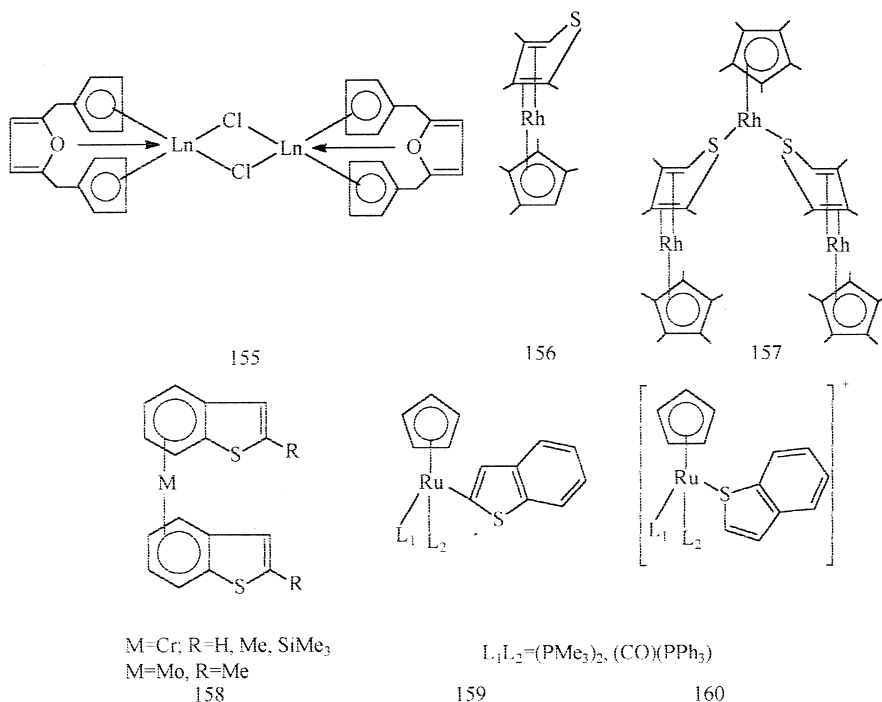
The  $\sigma$ -( $\eta^1$ ) coordinated structures (**140**) are represented principally by complexes of pyrrole (X=N), phosphole (X=P, PR) and thiophene (X=S). Among the N coordinated complexes of pyrrole and its derivatives, there are not only the M–N substituted derivatives, e.g. refs. [4, 79, 120], but complex compounds containing the organometallic framework (**149**) [287] and (**150**) [269].



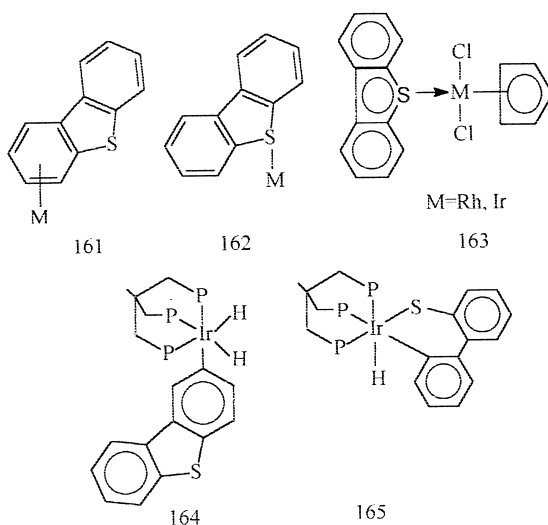
The P coordinated complexes of phosphole are represented by the two structural types (**151** and **152**) [269,270,288], (**151**) being more common than (**152**) [269,270]. The  $Mn(CO)_5$  complexes with  $\eta^1$  coordination are known for a complete series of heteroatoms (E=N, P, As, Sb, Bi) [283,289,290]. A number of the complexes (**152**, heteroatom is arsenic; R=Me, Ph, *t*-Bu; M=Cr, W) with the  $\eta^1$  coordination mode of the arsole ring was prepared [291]. Two remarkable organosamarium(II) compounds reveal an unusual coordination capacity of the benzophospholyl ligand as the  $\eta^5$  coordinated species (**153**) (a rather rare opportunity!), whereas dibenzophosphole tends to form the  $\eta^1$  derivative (**154**) [292].



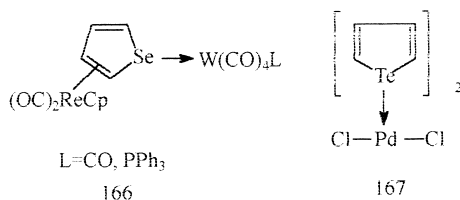
The problem of the oxygen atom as the possible donor site for furan is still open. Recently, an example of the O–M coordination (**155**) appeared [293]. In the absence of X-ray data, the structure (**155**) was elucidated on the basis of IR and  $^1\text{H}$  NMR spectra, and hence is ambiguous. Complexes of thiophene where the coordinate bond is localized on the sulfur atom are numerous [269,279]. Some examples of the  $\eta^1$  coordination for the thiophene complexes are given in refs. [294–296]. The typically  $\eta^4$  coordinated complex of rhodium (**156**) slowly decomposes into (**157**) with a mixed  $\eta^1:\eta^4$  coordination mode [297]. The ligand 2-benzo[b]thiophene serves classically as the  $\eta^6$  donor (**158**) [298]. However, complexes (**159**) are well known [299], and they can be converted into (**160**) upon protonation, both (**159** and **160**) being the less-common coordination modes.



For dibenzothiophene, the classical coordination mode appears to be  $\eta^6$  (**161**), whereas  $\text{Cp}^*\text{Rh}(\text{PMe}_3)$  is able to form the  $\eta^1$  coordinated intermediate (**162**) [300]. Moreover,  $\text{Cp}(\text{CO})_2\text{Re}(\eta^1\text{-DBT})$  [301–303] is a structurally proven species. The sulfur atom of DBT appears to have sufficiently strong coordinating power as indicated by the cleavage of the chloro-bridging ligands in  $[\text{Cp}^*\text{MCl}_2]_2$  ( $\text{M}=\text{Rh}, \text{Ir}$ ) to give  $\text{Cp}^*\text{MCl}_2(\text{DBT})$  (**163**) [304]. The C–H and C–C bonds of DBT can be activated by means of  $[(\text{triphos})\text{IrH}_2(\text{C}_2\text{H}_5)]$  leading to the other unusually coordinated species (**164**, **165**) [305,306].

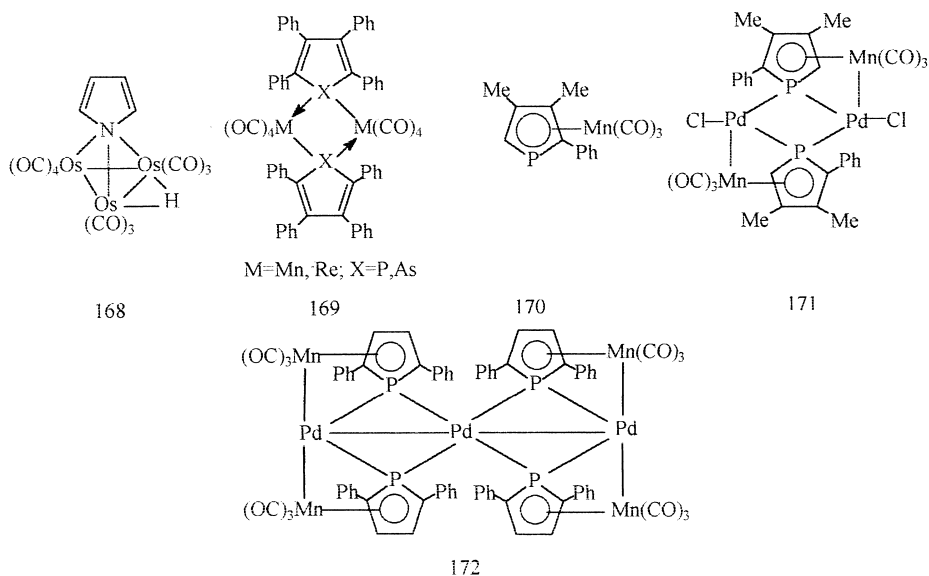


The selenium atom of selenophene takes part in coordination in (**166**) [307]. The  $\eta^1\text{-Te}$  complexes are exemplified by the palladium dichloride compound (**167**) [263,308]; Te heterocycles may also undergo ring-opening [309].

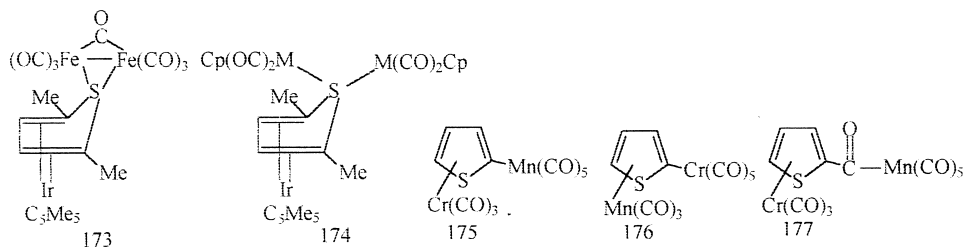


Sometimes the heteroatom of the ligands (**134**) plays the role of a bidentate or even tridentate donor site [269,270]. Such a less-common coordination is observed in the pyrrole cluster (**168**) [269]. The  $\eta^2$  coordination via phosphorus or arsenic in the series of phospholes is described for the manganese and rhenium dimers (**169**) [310]. Recently upon reaction of 2-phenyl-3,4-dimethylphoshacymantrene (**170**) with the complex of palladium dichloride and benzonitrile in methylene chloride, the

binuclear palladium cluster with  $\eta^2$  coordinated phosphole (**171**) was prepared [281]. The coordination of phosphorus in the trinuclear cluster (**172**) prepared from reaction of 2,5-diphenylphosphole with  $\text{Pd}(\text{DBA})_2$  is similar. The arsole analogues of (**154**) are also known [310].

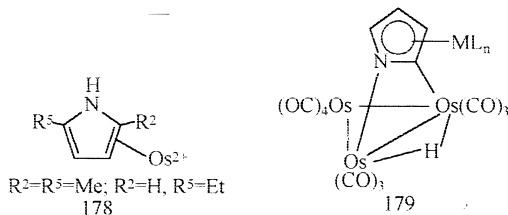


The  $\eta^2$  coordination of the X atom (**134**) occurs in the thiophene complexes ( $X = \text{S}$ ), whose heteroring simultaneously takes part in  $\eta^4$  coordination [311–313] with the iridium pentamethylcyclopentadienyl substituent (**173**) [314] and (**174**) [315], where there is a mixed coordination mode, common among complexes of the ligands (**135**) [269,270]. Another case of the mixed coordination known for thiophene includes the species of the type (**175–177**) [316].

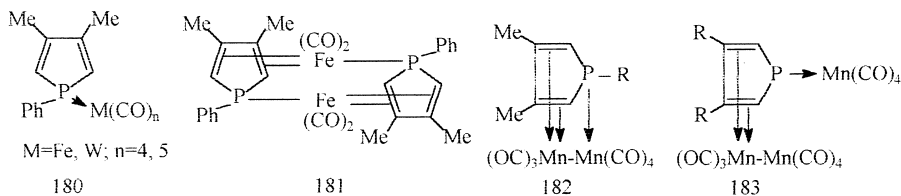


Pyrrole is known to undergo electrophilic attack preferentially at the  $\alpha$ -position of the ring. The unusual  $\eta^2$  coordinated pyrrole complexes (**178**) engage both C(2) and C(3) positions of the ring [317–319]. Azaferrocene or tricarbonyl manganese ( $\eta^5$ -pyrrolyl) as the classically coordinated species are able to react with the cluster

$[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$  to afford the orthometallated products (**179**) [320]. However, the most remarkable representative of the mixed coordination is the polymeric complex of iron with pyrrole where the heterocycle is coordinated via the  $\sigma$ -( $\eta^1$ ) (**140**) and  $\pi$ -( $\eta^5$ ) (**135**) types [269,321].



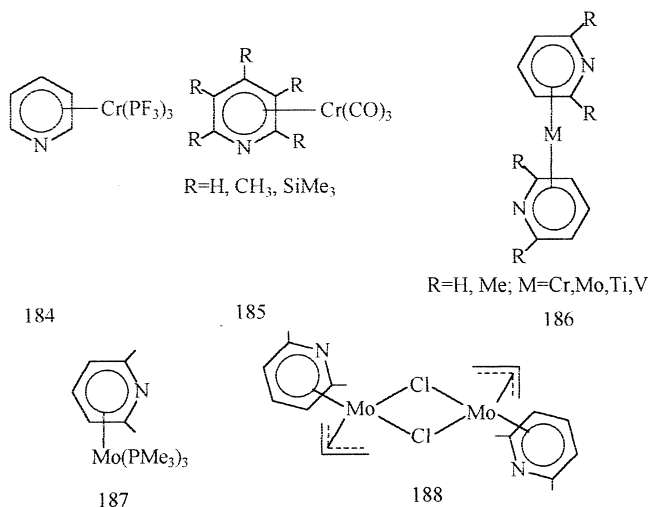
Similar complexes are described in ref. [322], among them (**180** and **181**). The binuclear (**182**) [269,323] and trinuclear (**183**) [269,324,325] complexes of manganese contain the metal–metal bond and the  $\sigma$ -( $\eta^1$ ) and  $\pi$ -( $\eta^4$ ) coordinated ligands. In (**182**, **183**), R = H, Me, Ph [323], *t*-Bu [324,325]. Other examples of different coordination modes in complexes of the fundamental five-membered heterocycles (**134**) are discussed in the reviews [269,270].



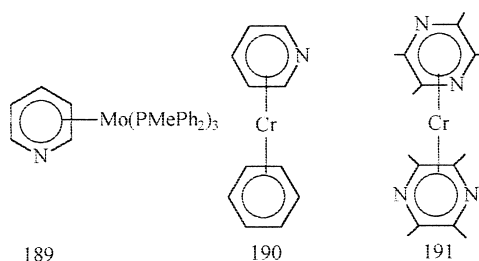
### 3.2. Bonding modes of metals in azines

The standard coordination mode for pyridine (**138**) and other six-membered nitrogen-containing heterocycles (azines) is via the nitrogen heteroatom [271–273,326–336].

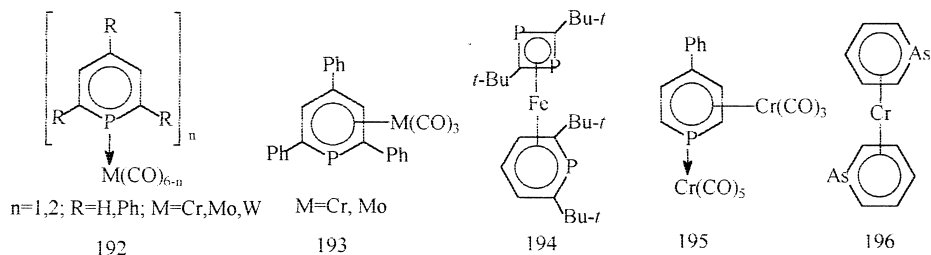
This coordination mode (**138**) was considered as the only one until the middle 1970s, a view supported by unsuccessful attempts to prepare  $\pi$ -( $\eta^6$ ) coordinated pyridine complexes [268,337,338]. In 1975–1976 in three independent studies, unusual  $\pi$ -( $\eta^6$ ) coordinated complexes of pyridine were prepared, (**184**) [339,340], (**185**) [341–343] and (**186**) [344,345]. Complexes  $[\text{M}(2,6\text{-lutidine})_2]$  (M = Ti, V, Cr, Mo) (**186**) were prepared using metal vapor techniques [346]. Further interaction of  $[\text{Mo}(2,6\text{-lutidine})_2]$  with  $\text{Me}_3\text{P}$  gives (**187**), with allyl chloride (**188**) [347]. Later the complexes (**185**) [348] and (**186**) [349] with the unsubstituted pyridine (R = H) were prepared. The starting agents in the synthetic routes for both complexes were the trimethylsilyl substituted derivatives of pyridine. At the final stage the silicon-containing groups were eliminated.



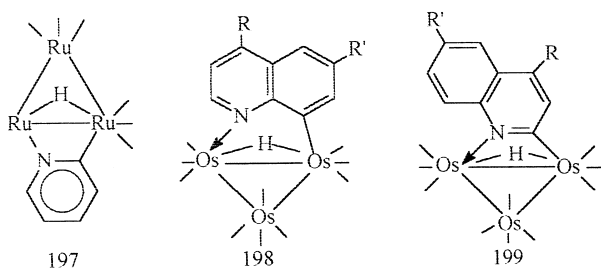
Complexes similar to **(184)** were prepared with molybdenum **(189)** [350]. By means of co-condensation of three components, pyridine, benzene and zero-valent chromium in the gaseous phase, the mixed ligand complex **(190)** was prepared [349]. The metal vapor phase synthesis played a decisive role in the preparation of the basic types **(184, 186, 190)** of the  $\pi$ -( $\eta^6$ ) coordinated complexes of pyridine. Co-condensation of tetramethylpyrazine with vanadium atoms at  $-196^\circ\text{C}$  gave the first  $\eta^6$ -pyrazine complex  $[\text{V}(\eta^6\text{-Me}_4\text{pyrazine})_2]$  **(191)**, confirmed by X-ray analysis [347].



Complexes of the phosphorus analogue of pyridine, phosphabenzene are less represented [351,352]. Both  $\sigma$ -( $\eta^1$ ) and  $\pi$ -( $\eta^6$ ) complexes of phosphabenzene are known [351,352]. The  $\sigma$ -( $\eta^1$ ) coordination is observed in complexes of phosphabenzene with Group VI metal carbonyls **(192)** [353,354]. The  $\pi$ -( $\eta^6$ ) coordination is observed in complex **(193)**, which was known earlier than the analogous pyridine complexes [355]. The molybdenum complex similar to **(193)** is also known [356]. The mixed-ligand sandwich complex **(194)** [357] and compound **(195)** [351,352] are also of interest. In the latter complex there is a mixed  $\sigma$ ,  $\pi$  coordination of 4-phenylphosphabenzene. The chromium complex of arsabenzene contains the  $\eta^6$  coordinated ligand **(196)** [358,359].

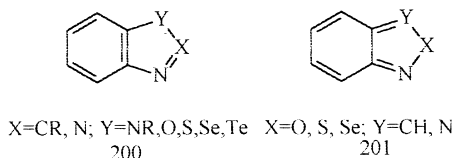


Complexes of the boron analogue of pyridine,  $C_5H_5BR^-$  ( $R=Me, Ph$ ),  $Co(\eta^6-C_5H_5BR)_2$  and  $Co(\eta^5-C_5H_5)(\eta^6-C_5H_5BR)$  or  $Fe(\eta^6-C_5H_5BCMe_3)_2$  are known and have been continuously studied since the early 1970s [360–364]. The cyclometallated derivatives of pyridines (**197**) [365,366] and quinolines (**198**, **199**) [367] are worth mentioning.



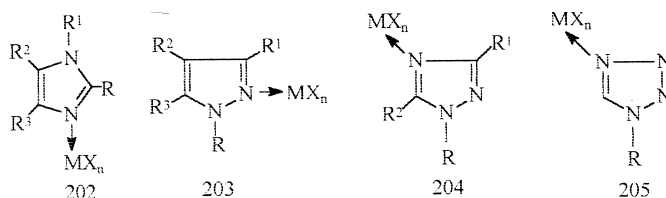
### 3.3. Coordination modes of azoles

The azoles (**137**) and their benzo analogues, e.g. (**200**, **201**), are typically  $\eta^1-(N_{py})^3$  monodentate ligands and form the complexes (**139**) [272,274–277].

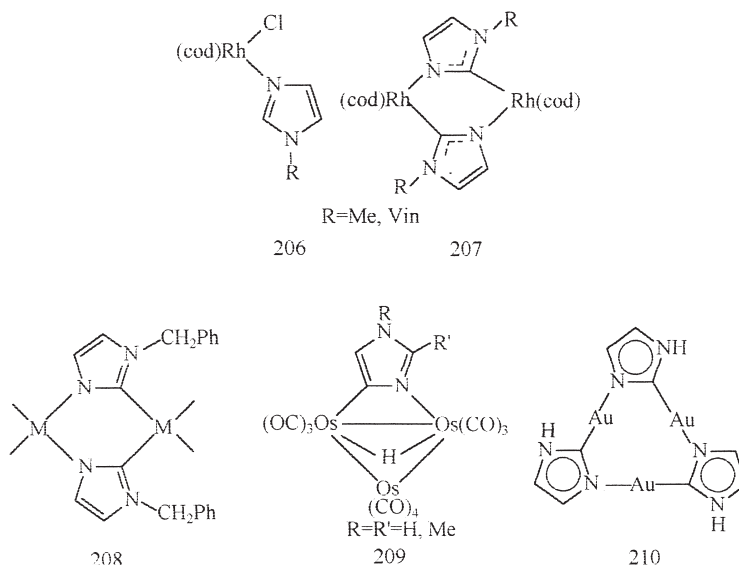


The  $\eta^1(N_{py})$  metal bonding is observed in complexes of imidazole and its derivatives (**202**) [275,368–372]. Among the complexes of imidazole (L), there is the unexpected monomeric complex of composition  $CuAc_2L_2$  [371] and the complexes  $ZnS_6L_2$  and  $ZnSe_4L_2$  [370], where  $L=1$ -methylimidazole. There are numerous illustrations of azole complexes with the  $\eta^1-(N_{py})$  coordination, e.g. the complex compounds of pyrazole (**203**) [272,274,278,373,374], 1,2,4-triazole (**204**) [375] and tetrazole (**205**) [376]. However, azole may be bridging,  $M-N-X-N-M$  ( $X$  is nothing, or  $CH, N$ ) [234,274,277,278,377–380].

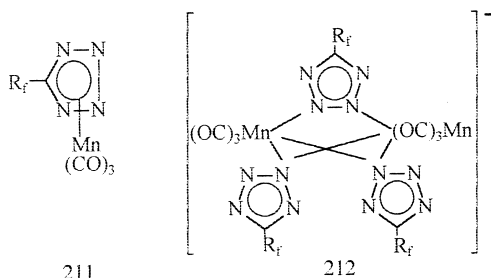
<sup>3</sup> $N_{py}$  is the nitrogen atom of pyridine type.



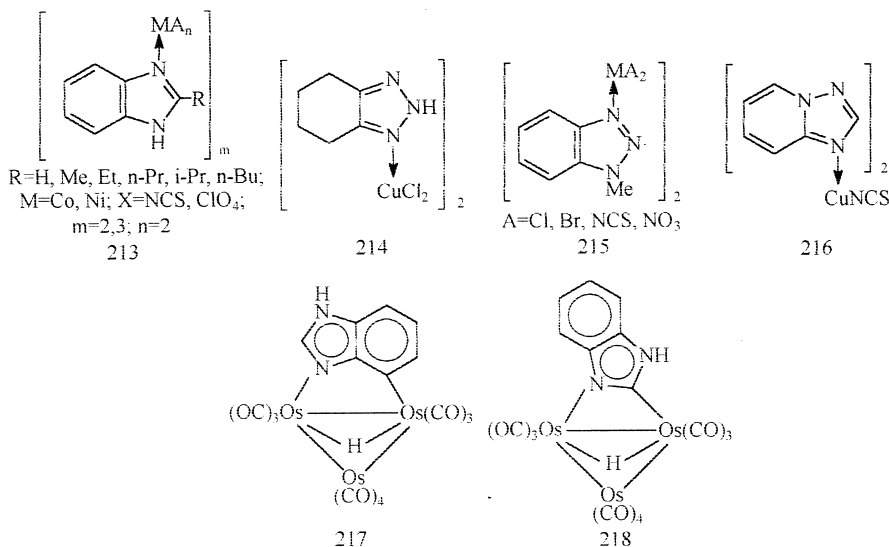
The first orthometallation of the 2-position of the imidazole ring was achieved by reaction of methyllithium with (**206**). As a result, the binuclear complexes (**207**) were produced [381]. Complexes [M<sub>2</sub>(μ-Cl)<sub>2</sub>L<sub>2</sub>] (M = Rh, Ir; L<sub>2</sub> = cod, nbd) react with N-benzyl-2-imidazolate to yield (**208**) as shown by X-ray analysis [382]. Interaction of [Os<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub>] with a variety of imidazoles leads to the products (**209**) [383,384]. Orthometallated derivatives of gold (e.g. **210**) are also known [385–387].



However, the breakthrough to less-common coordination in the azole series was publication [388]. The authors note that tetrazoles are isoelectronic with cyclopentadienes and similar to them in acidity and ring symmetry. 5-(Perfluoroalkyl) tetrazoles containing F<sub>2</sub>NCF<sub>2</sub> and CF<sub>3</sub>(R<sub>F</sub>) substituents enhance the ability of the ring to η<sup>5</sup> coordination. According to IR spectroscopy, the product of interaction of (5-perfluoroalkyl) tetrazolates of sodium with BrMn(CO)<sub>5</sub> has structure (**211**), while upon removal of solvent complexes (**212**) are formed with μ-2,3-η<sup>2</sup> coordination (X-ray analysis) [388]. No X-ray analysis of (**211**) is available.

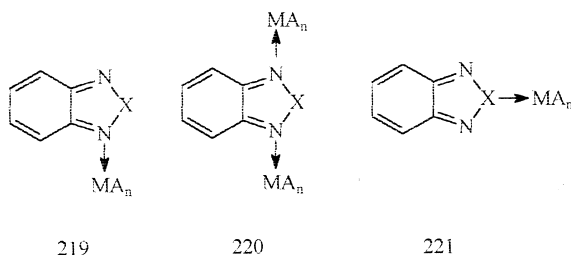


Complexes of benzo analogues of azoles (**200** and **201**) are represented by the N coordinated compounds as observed, for example, for the 2-substituted derivatives of benzimidazole (**213**) [389], tetrahydroindazole (**214**) [390] and 1-methylbenzotriazole (**215**) [391]. The  $\eta^1$ -(N) coordination in complexes (**214**) [390] and (**215**) ( $X = \text{NO}_3$ ) [391] was confirmed by X-ray structural analysis. The copper complex (**216**) has a coordination mode similar to (**214**) [392]. An alternative coordination mode for benzimidazole is exemplified by the cyclometallated derivatives of osmium (**217**, **218**) [383].

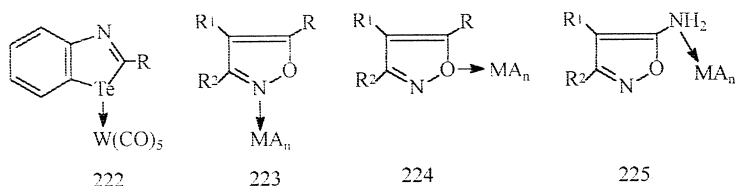


The N, S (Se)-containing azoles and benzoazoles form the N coordinated complexes (**139**) ( $X = \text{S}, \text{Se}$ ) [275,393–395], (**200**) ( $X = \text{CH}, Y = \text{S}, \text{Se}$ ) [275], (**201**) ( $X = \text{S}, \text{Se}; Y = \text{N}$ ) [275,396–406]. The problem of coordination mode (**219**, **220** or **221**) in complexes of benzo-2,1,3-thiadiazole and its selenium analogue has been discussed [396–406]. The authors of refs. [396–403] note that ligands (**201**) ( $X = \text{S}, \text{Se}$ )

coordinate only via nitrogen atoms (**219**), while in refs. [404–406] the localization of the coordinative bond via the chalcogen atom (**221**) was not excluded. X-ray data [400–402] indicate coordination exclusively via the nitrogen atom.



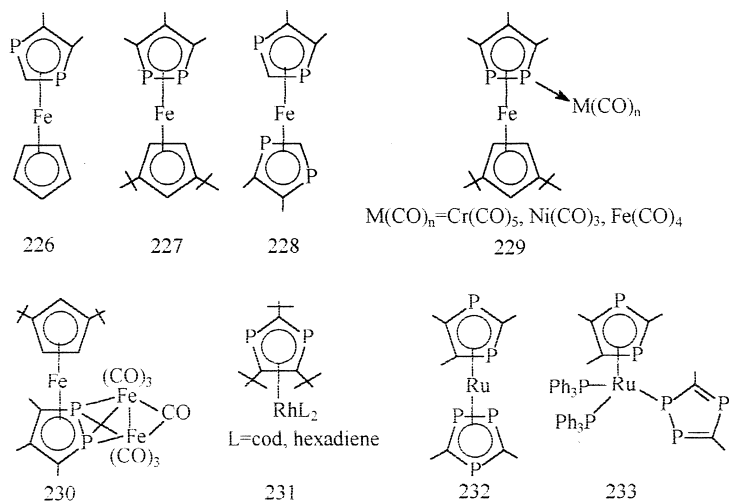
The less-common coordination of the azole ligands via the X heteroatom was proven by X-ray structural analysis for the complex of benzotellurazole with tungsten pentacarbonyl (**222**) [407]. There are several possible coordination modes of oxazole and its derivatives (**223–225**). However, only one (**223**) was confirmed by X-ray structural analysis [408].<sup>4</sup>



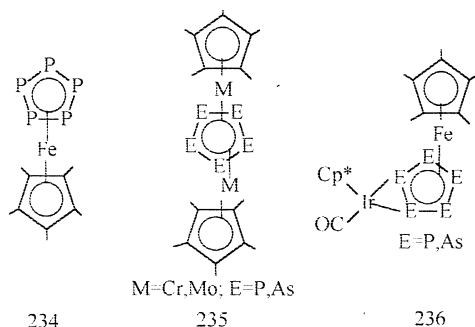
The  $\pi$ -( $\eta^5$ ) coordination mode becomes predominant for the phosphorus and boron analogues of azoles. We do not cover this aspect of coordination chemistry [270,412] fully, but present the most illustrative examples.

Diphospha- (**226**, **227**) and tetraphosphapherrocene (**228**) are known [413,414]. For the diphosphorus derivative (**227**), there exists an indication of the  $\eta^1$ : $\eta^5$  (**229**) and mixed P coordinated (**230**) derivatives [415]. For rhodium, the  $\eta^5$  species was observed (**231**) [416]. A series of papers is devoted to organometallic complexes containing both di- and triphosphorus five-membered heterocycles as well as complexes containing these ligands separately [417–422]. In this respect, the formation of such complexes, e.g. (**232**), proceeds via the intermediate formation of the  $\eta^1$  coordinated complex (**233**) [423].

<sup>4</sup>The electronic structure of the azoles and azines has been studied by quantum-chemical methods, e.g. refs. [268,409]. However, conclusions on the preferential localization of the coordinative bond in the ambidentate azole systems based on the electronic distribution in the non-coordinated ligands could lead to ambiguous results. In this sense, the quantum-chemical calculations that compare the stability and geometry of the azole complexes in the different coordination situations [410,411] are of interest.

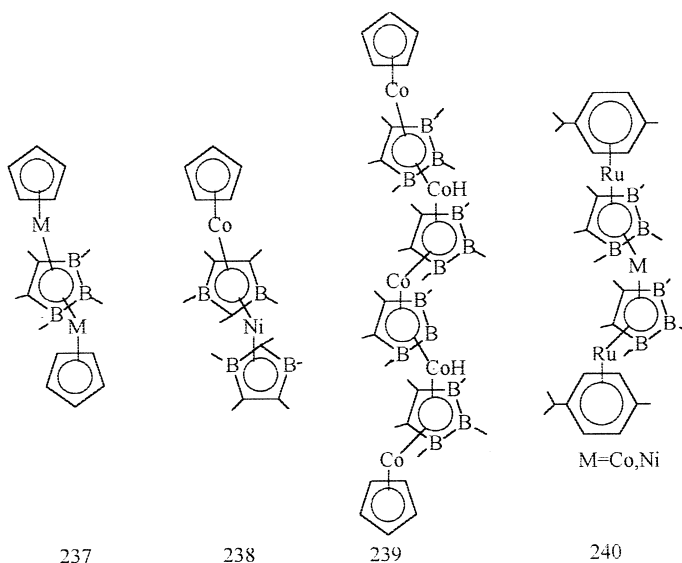


The  $P_5$  and  $As_5$  ligands are of enormous interest due to the variety of their coordination modes. The  $\eta^5$  is the common one [424,425], but other coordination modes are observed. The  $\eta^5$  coordinated six-electron donor ligands of this type occur both in sandwiches (**234**) [426–428] and triple-decker complexes such as (**235**) [429–434]. A remarkable  $\eta^2$  side-on coordination has recently been structurally proven (**236**) [435].

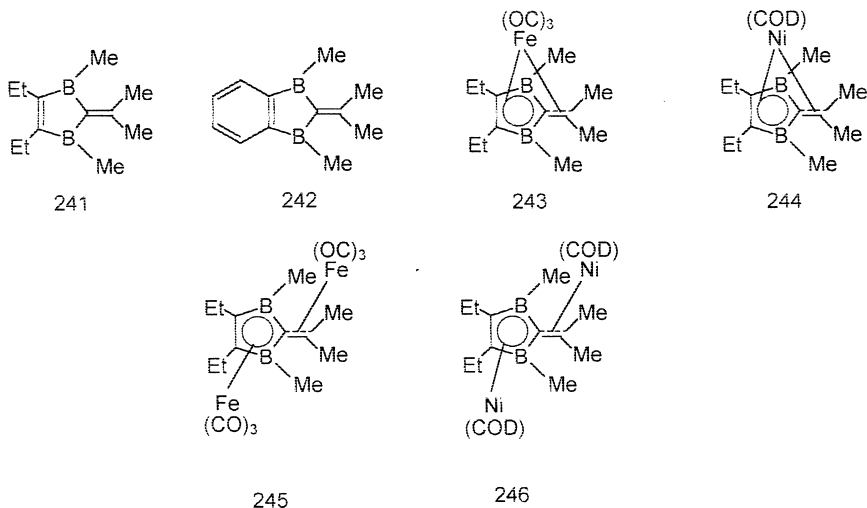


Whole families of multidecker sandwiches bridged by the planar carborane,  $C_2B_3$  (**237**) [436–440] or diborole,  $C_3B_2$  (**238**) [441–447] rings were prepared. Recently the first crystallographically established hexadecker molecular sandwich (**239**) was described [448], and a series of the new complexes (**240**) was initiated [449].

The diborafulvenes (**241**) and their benzo analogues (**242**) are coordinated in a different manner to that described above [450–455]. Thus, the  $\eta^5$  coordinated mononuclear compounds of ligands (**243** and **244**) containing the  $Fe(CO)_3$  [450,451] and  $Ni-COD$  [455] frameworks, respectively, have been described. The unified  $\pi$ -electronic system of ligands participates in coordination with iron and nickel. In

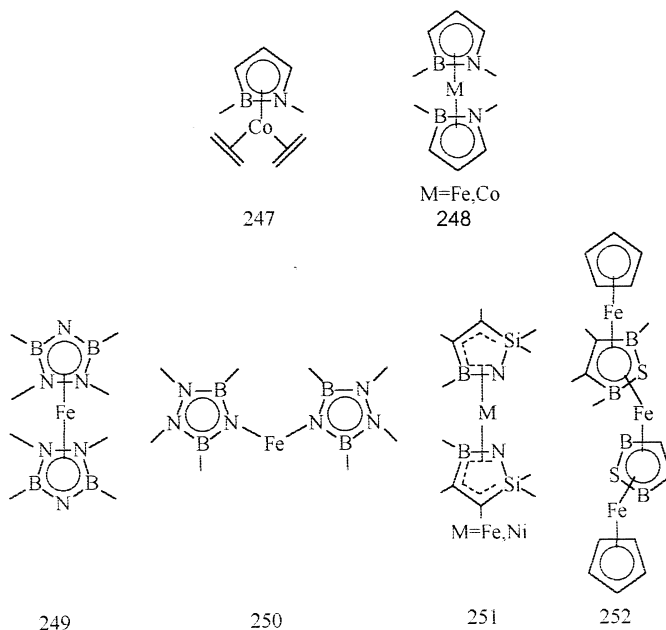


the binuclear complex compounds metals bond separately to the  $\pi$ -system of a boron-containing ring and the  $\pi$ -system of the exocyclic ethylene framework, for instance in **(245)** [452] and **(246)** [455].



The 1,2-azaborolylcobalt moiety is isoelectronic with cyclopentadienylcobalt, and a wide range of complexes based on the parent derivative **(247)** has been observed [456,457]. Earlier sandwiches **(248)** were prepared [458,459]. The structural problem for the cycles containing two boron and three nitrogen atoms (**249** or **250**) was not resolved [460] due to the lack of X-ray data. The partially  $\pi$ -delocalized boron-,

nitrogen-, silicon-containing rings form sandwiches (**251**) [461]. Finally, the thiadiborolene ligand forms a number of remarkable multidecker species, especially tetra-decker (**252**), a trigonal bipyramid with the mutual *trans*-disposition of the sulfur atoms [462,463].



#### 4. Conclusion

The most probable and least common coordination modes of typical and common ligands are considered in this review. This is the part of the general problem of the competitive coordination embracing the study and interpretation of the different modes of metal-bonding by ambidentate ligands [175,464]. Such ligands involve not only those considered, but much simpler compounds such as nitrogen [465,466], oxygen [467,468], carbon monoxide [469,470] and carbon dioxide [471–473], the analogous sulfur derivatives [474,475] and other heteroatomic molecules [473,475]. The ambidentate anions —  $\text{CN}^-$  [475–477] and especially  $\text{NCX}^-$  ( $\text{X}=\text{O}, \text{S}, \text{Se}$ ) [475,478–480] are among ligands reacting in a competitive way. However, the comparative evaluation of such ligands from the viewpoint of common or less-common coordination modes is a difficult task. Thus, the number of directly prepared complexes with a given coordination mode is considerably less for the simple inorganic ambidentate than for the chelating or heteroaromatic ligands. The directed regioselective synthesis of the complexes of the ligands considered above, especially azomethines, is important, and comprises one of the urgent tasks of modern coordination chemistry.

## Abbreviations

|                   |                                                     |
|-------------------|-----------------------------------------------------|
| aa                | acetylacetonate                                     |
| Alk               | alkyl                                               |
| Ar                | aryl                                                |
| bpy               | 2,2'-bipyridyl                                      |
| Bu <sup>t</sup>   | t-butyl                                             |
| cod               | 1,5-cyclo-octadiene                                 |
| cp                | cyclopentadienyl                                    |
| cp*               | pentamethylcyclopentadienyl                         |
| DBA               | dibenzylideneacetone                                |
| DBT               | dibenzothiophene                                    |
| dpm               | dipivaloylmethanate                                 |
| en                | ethylenediamine                                     |
| Et                | ethyl                                               |
| Et <sub>2</sub> O | diethyl ether                                       |
| Haa               | acetylacetone                                       |
| Hba               | benzoylacetone                                      |
| Het               | hetaryl                                             |
| hfaa              | hexafluoroacetylacetonate                           |
| Hpiv              | pivalic acid                                        |
| Me                | methyl                                              |
| <i>o</i> -phen    | <i>o</i> -phenanthroline                            |
| Ph                | phenyl                                              |
| piv               | pivalate                                            |
| triphos           | MeC(CH <sub>2</sub> PPh <sub>2</sub> ) <sub>3</sub> |
| Ts                | tosyl                                               |
| Vin               | vinyl                                               |

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