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REVIEW: METAL COMPLEXES AS LIGANDS

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Ligand properties of coordination and organometallic compounds are examined on the basis of acid–base interactions of metal-containing bases and Lewis acids. Such interactions lead to homo- or heteronuclear di- and polynuclear complexes. Special attention is given to coordinatively-unsaturated molecules of classic Werner complexes, *o*-hydroxyazomethine chelates, metal carbonyls and their derivatives, ferrocenes with donor fragments, and coordinated heteroaromatic compounds.

Keywords: Bimetallic; Coordination complexes; Lewis base; Lewis acid; Polynuclear

INTRODUCTION

Reactivity of complex compounds is an important direction of modern coordination chemistry [1–8]. During the last 15 years, a lot of experimental work and generalizations of obtained data on the reactions of coordinated ligands have been carried out, in particular amines [3], the nitro group [3,9], nitriles [3,10–12], isonitriles [12], nitrosyl [13], thiourea [14], halides, pseudo-halides [15], and dialkylsulfoxide [3] ligands.

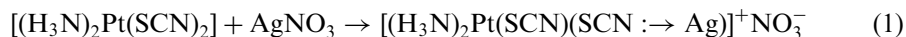
Considerable attention is given to the acid and base properties of complex compounds [2]. It is emphasized that “transition metal complexes reveal basic properties in relation to not only protons, but also to Lewis acids” [2]. The present review is dedicated to the state of the art of this problem.

Coordination and Organometallic Compounds as Ligands

The principles of formation of multi-nuclear (super-complex) coordination compounds, widely represented in Werner’s work [16], were formulated, in particular by Grinberg [17]. One of the most important aspects is the acid–base interaction, reactions of

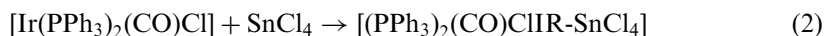
*Corresponding author. E-mail: bkhariss@ccr.dsi.uanl.mx

complex compounds with metal salts or other Lewis acids [17]. An example of such an interaction is transformation (1) [2,17]:

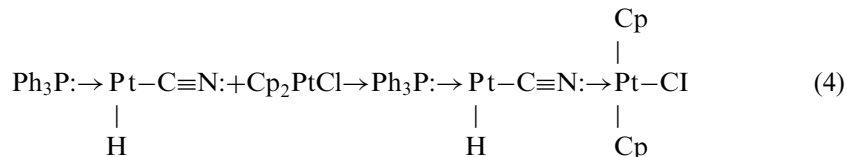
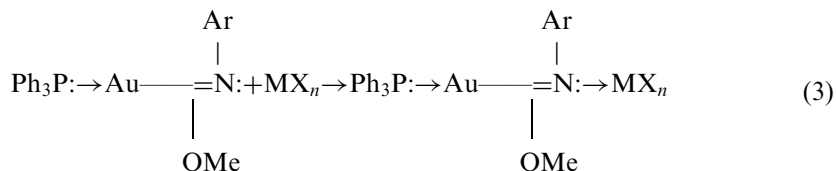


where the coordinatively-unsaturated platinum complex acts as a base and silver nitrate, as a Lewis acid. The acid-base reaction yields a dinuclear silver-platinum adduct.

These ideas were developed by Kukushkin, who discussed [2] the basicity of transition metal complexes and examined a series of acid-base reactions, where iridium atom plays the role of base, *e.g.*, (2):



The uncoordinated nitrogen atoms of the azomethinic C=N (rxn 3) and nitrile C≡N (rxn 4) groups possess donor properties [18]:

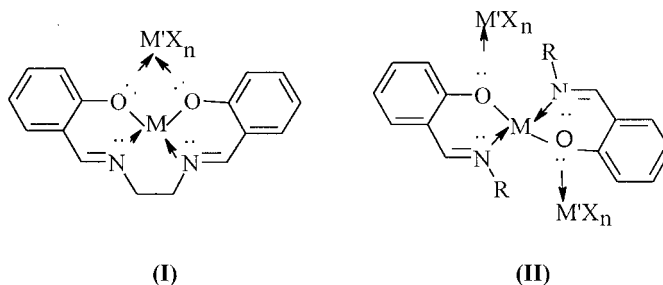


Cp – cyclopentadienyl

It was recently demonstrated [19] that a mixed-valence complex containing bridging nitrogen atom can be derived from a rhenium nitrido complex (rxn 5):



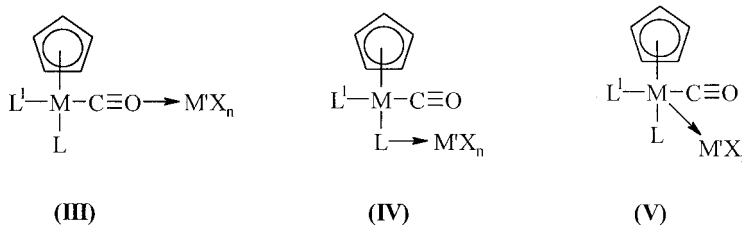
Metal chelates with *o*-hydroxyazomethines and their analogues react with metal halides to yield di- (I) and trinuclear (II) structures [20–22]:



Numerous similar coordination compounds have been obtained; the results of these studies are generalized in reviews [22,23] and a monograph [18].

Considerable opportunities for preparing homo- and heteronuclear complexes opened up after the complex compounds containing extra chelating group became used as ligands. In this respect, the use of hydrazone [24,25] and phthalocyanine [26,27] complexes is noteworthy. For example, the mononuclear complexes with 2,6-diformyl-4-methylphenol bis(hydrazone) derivatives react with metal halides to give a number of homo- and heteronuclear compounds exhibiting, in the case of paramagnetic ions, pronounced antiferromagnetism [24,25]. Phthalocyanine complexes containing crown-ether substituents on the benzene fragments are also used [26,27].

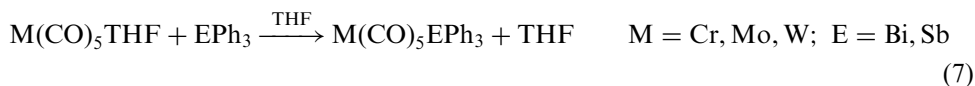
Organometallic compounds, primarily metal carbonyls [18,28–35] and ferrocene derivatives [36–46] have long been used as ligands. Metal carbonyl complexes are of interest as ambidentate ligand systems, in which several modes of localization, rxn III–V, can be realized for the coordination bond [18,28,29]:



The $\text{M} \rightarrow \text{M}'$ coordination (V), where M behaves as a d -base, is widespread in complexes containing metal carbonyl ligands [28,29]. For example, the interaction between anionic iron carbonyl complex and cyclopentadienylaluminium chloride dimer results in a dinuclear compound containing an Fe–Al bond (rxn 6) [30]:



Group VI metal carbonyl complexes with tetrahydrofuran (rxn 7) and Group V triphenyl derivatives were used to synthesize dinuclear complexes containing the M–E bond [31], proved by x-ray single crystal diffraction $\text{M} = \text{Mo}$, $\text{E} = \text{Bi}\{r(\text{Mo-Bi}) = 2.832(1) \text{ \AA}\}$ and $\text{M} = \text{W}$, $\text{E} = \text{Bi}\{r(\text{W-Bi}) = 2.829(1) \text{ \AA}\}$ [31].

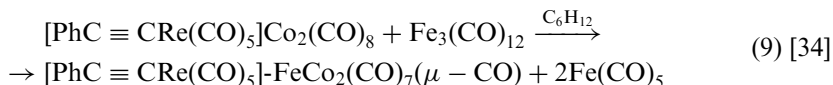


Metal–metal bonds are formed in a complexes of the type $\text{R}_m[\{\text{M}(\text{CO})_5\}_n\text{M}'\text{X}_p]$ where $\text{R} = \text{Nbu}_4, \text{PPh}_4$; $\text{M} = \text{Cr, Mo, W}$; $\text{M}' = \text{Sn, Pb}$; $\text{X} = \text{Cl, Br}$; $m = 1-2$; $n = 2, 3$; $p = 3-4$ [32]. In the case of the trinuclear complexes ($n = 2$), M acts as a bridging fragment.

In the above-mentioned adduct formation reactions involving metal carbonyl bases, complex compounds [33] and multinuclear iron carbonyl [34] play the role of acceptors (A). In this respect, the following recently described reactions (rxn 8,9) are noteworthy:

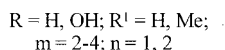
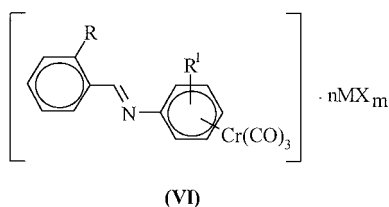


where $A = [Wl_2(CO)\{PhP(CH_2)_2PPh(CH_2)_2PPh_2-P,P'\}\eta^2(RC=CR')]$; $M = Cr, Mo, W$; $R, R' = Me, Ph$; $m = 3-5$; $n = 1-3$.



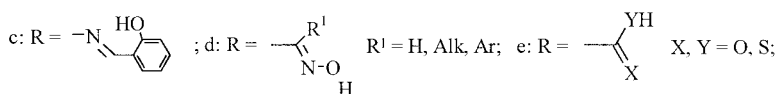
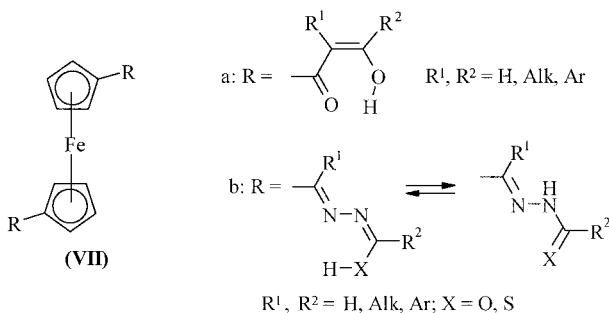
The presence of the Co-Fe bonds [2.499(2), 2.559(2) Å] and Re-Fe [2.982(2) Å] was proved by x-ray single crystal diffraction [34].

The reaction of azomethines containing the η^2 -arene-Cr(CO)₃ group with soft (HgCl₂) and hard (BF₃, AlBr₃, SnCl₄) Lewis acids yields adducts (rxn VI) [35].



The IR spectral data suggest that soft mercury chloride is coordinated to the chromium atom, while the indicated hard acids are bound to the N or O ($R=OH$) donor centers [35]. This conclusion requires x-ray diffraction proof since, in the presence of $C \equiv O$ fragment, coordination is also possible to the oxygen atom of carbonyl group [18,29].

Ferrocenes, VII, are distinguished by a wide variety of chelating group (R): β -diketones [36] (rxn VIIa), semicarbazones and thiosemicarbazones [36] (rxn VIIb), azomethines and their analogues [36-38] (rxn VIIc), oximes VIIId, carboxylic, thiocarboxylic (rxn VIIe), and amino acids (rxn VIIf) [36].

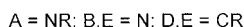
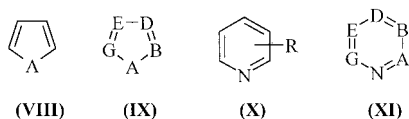


The ferrocene derivatives containing N-donor substituents are coordinatively active. Among such fragments are bis(benzoethyne)pyridine [39], aminopyridine [40], and pyridinepyrazole [41] and pyrazolylborate [42]. Ferrocenediphenylphosphine [43,44] and ferrocenedialkylphosphines [45] acts as P-donors. The tri- and tetranuclear ruthenium and osmium ferrocenylacetylene clusters have also been reported [46].

Complexes Containing Five- and Six-Membered Heterocycles

Recently, there has been growing interest in using coordinated heterocycles as ligands [47–51]. Similar to the above-mentioned complexes containing free donor atoms, the coordinatively unsaturated heteroaromatic complexes react with Lewis acids (mostly with metal salts and carbonyls) to give di- and oligonuclear structures. In most cases, Group VA and VIA elements and the nonsaturated bonds serve as donor centers.

The metal-containing heteroaromatic ligands [52–54] divided into the fundamental five-membered heterocycles containing one heteroatom VIII: A=NR (pyrrole), PR (phosphole), AsR (arsole), O (furan), S (thiophene), Se (selenophene); five-membered heterocycles containing two and more heteroatoms, IX: (A = NR, O, S, Se, Te; B, D, E, G = CR, N, P – azoles; A = PR, AsR; B, D, E, G = P, As – di- and oligophospholes, phosphoarsoles); and six-membered heterocycles containing one (for pyridine or its derivative (X)), two, and more nitrogen atoms (XI): (A, B, D, E, G = CR, N-azines).

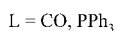
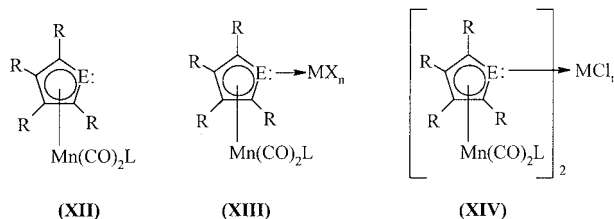


Among the other coordinated heterocyclic fragments, N,N-bis(azole) and N,N-bis(azine) systems, N,P-diphenylphosphinopyridine, and boron-containing donor derivatives (borazoles, borazines) are noteworthy.

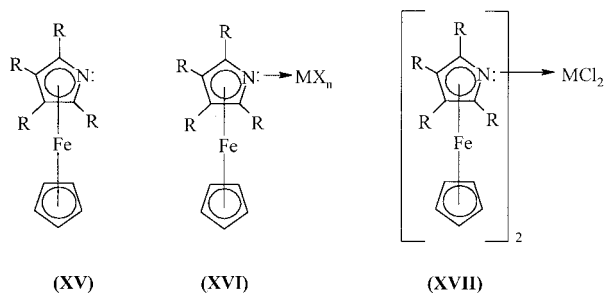
Five-Membered Heterocycles with One Heteroatom

Ligands with N,P-Donor Centers

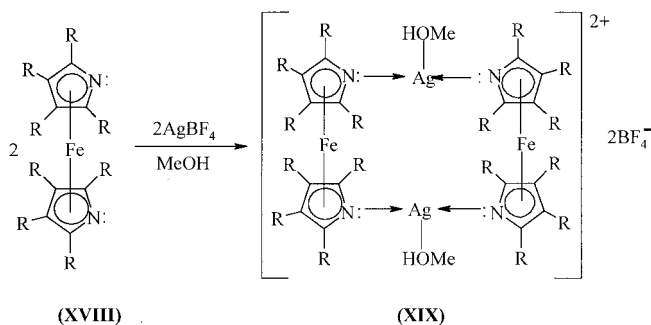
Reactions with azacymantrene XII (E = N, R = H, L = CO) and its derivatives (e.g., XII: L = PPh₃) with metal carbonyls and chlorides yield dinuclear XIII (E = N, MX_n = M(CO)₅, M = Cr, Mo, W; M(CO)₂Cp, M = Mn, Re) [55–57] and trinuclear XIV (E = N; M = Ti, Pd, Pt, Hg, Sn; n = 2, 4) [58] structures.



Similar transformations are typical of azaferrocene (rxn XV) ($R=H$), resulting in complex compounds (rxn XVI) ($R=H$; $M=Cr$; $X=CO$; $n=5$) [57,59] and (rxn XVII) ($M=Pd$, Pt) [58]. The adducts of 2,3,4,5-tetramethylazaferrocene (rxn XV: $R=Me$) and $MX_n=BH_3$ (rxn XVI: $R=Me$; $M=B$; $X=H$; $n=3$) have been reported [60].

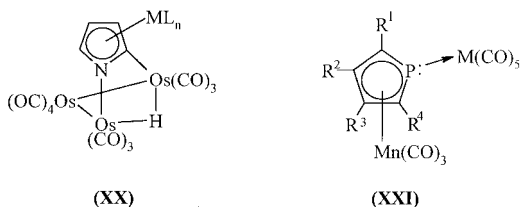


Octamethyl-1,1'-diazazaferrocene XVIII behaves as a bidentate N,N' -base [47] and with $AgBF_4$ in methanol forms a tetranuclear cyclic product XIX, whose structure was proved by x-ray diffraction [47,61].



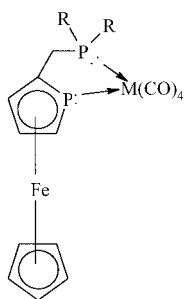
XVIII reacts similarly to two donor N-atoms with BH_3 , BF_3 , and $HgCl_2$ [62], however, structures of these adducts are not proved [62].

Not only N-, but also C-atoms can act as donor centers in azacyclopentadiene XII ($R=H$; $E=N$; $L=CO$) and azaferrocene XV ($R=H$). Formation of a tetranuclear osmium carbonyl adduct XX as a result of the interaction of the azacenes with the acetonitrile complex of triosmium decacarbonyl provides an example [63].



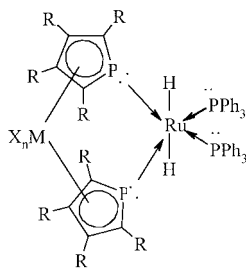
The phosphacyclopentadiene, as well as its R-derivatives, behaves as a P-donor and, reacting with metal carbonyls, forms binuclear complexes, for instance XXI ($R=H$) [64]. A tetranuclear dimanganesedipalladium chloride complex is formed as a result

of the interaction of 2-phenyl-3,4-dimethylphosphacymantrene (XII: E = P; R¹ = H, R² = Ph, R³ = R⁴ = Me; L = CO) with [PdCl₂(PhCN)₂] in CH₂Cl₂ (25°C, 4 h) [65]. The reaction of the same ligand with [Pd(DBA)₂], where DBA is dibenzylideneacetone, in the same conditions yields a tetramanganesetrichloride complex of phosphacymantrene. Complex structures of these compounds, as well as of similar clusters, are proved by x-ray diffraction [65]. The phosphanyl-substituted derivatives of phosphaferrrocene act as P,P'-chelating ligands and form metal-cyclic structures, for instance XXII [66]. Its structure (R = Ph; M = Mo) was shown x-ray diffraction [66].



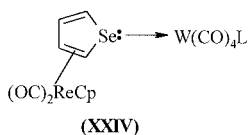
(XXII)

A series of diheteronuclear complexes was obtained from metal bisphospholy chlorides (tetrahydroborates) [67]. These compounds are bidentate P-donor chelating ligands and form metallocyclic structures. The chelates XXIII are typical examples of such compounds [67].

(XXIII) : R = H, Me; M = Zr, Yb, U; X = Cl, BH₄

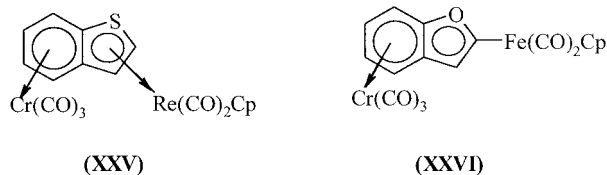
Ligands with $\eta^5(\pi)$ S, Se-Donor Centers

Among the coordinated five-member heterocycles with endocyclic Groups VIA elements, reactions with Lewis acids are mainly described for organometallic derivatives of thiophene and selenophene [48,50,51]. As a result of such a synthesis, the complex XXIV is reported [50,51]:



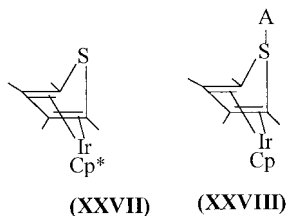
(XXIV)

η^6 -Ar-Coordinated benzothiophene acts as a η^5 -heteroaromatic π -base and reacts with $\text{ReCp}(\text{CO})_2(\text{THF})$ forming a binuclear η^5, η^6, π -complex XXV [68].



The C-Fe-derivative of benzofuran contains a η^6 - π -Ar-donor fragment and leads to π -complexes of chromium tricarbonyl XXVI [68]. However, the coordination modes above are assigned from synthetic and IR-spectral data and need further confirmation.

The η^4 -coordinated thiosphene complexes of iridium cyclopentadienyl XXVII were studied in detail [66–71]:



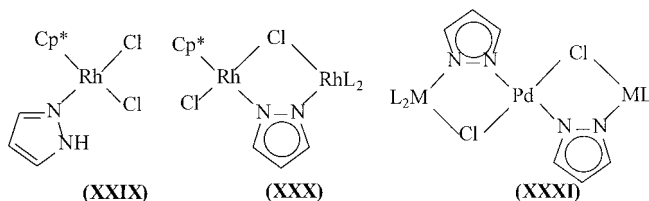
Their interaction with boron hydride and metal carbonyls yields di- and trinuclear compounds of XXVIII type ($A = \text{BH}_3, \text{Fe}(\text{CO})_4, \text{Fe}_2(\text{CO})_7, \text{Cp}_2\text{M}_2(\text{CO})_4$, where $M = \text{Mo}, \text{W}$) [69]. The adduct XXVIII with $A = \text{Fe}(\text{CO})_4$ is formed also by the interaction of XXVII and $\text{Fe}_3(\text{CO})_{12}$ [70]. Reactions of XXVII with $\text{Co}_2(\text{CO})_8, \text{Co}_4(\text{CO})_{12}$ and $[(\eta^6\text{-C}_6\text{H}_3\text{Me}_3)\text{Co}_4(\text{CO})_9]$ yield XXVIII ($A = \text{Co}(\text{CO})\text{-}\mu\text{-(CO)}_2\text{-Co}_3(\text{CO})_8$) as one reaction product [71].

Five-Membered Heterocycles with Two and More Heteroatoms

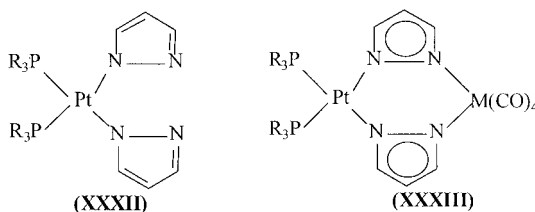
Azoles

Among the azole complexes, the metal-containing pyrazole (IX: $A = \text{NR}, B = \text{N}; D, E, G = \text{CR}; R = \text{H}, \text{Alk}, \text{Ar}$), imidazole (IX: $A = \text{NR}, D = \text{N}; B, E, G = \text{CR}$), 1,2,4-triazole (IX: $A = \text{NR}, B, G = \text{N}, D, E = \text{CR}$), and thiazole (IX: $A = \text{S}; D = \text{N}; B, E, G = \text{CR}$) derivatives are mostly used as ligands. Rhodium complexes containing terminal pyrazole ligands (Hpz) can be further coordinated. If the reactions are carried out in presence of even weak bases, the non-coordinated nitrogen atom of pyrrole produces a wide range of bridging pyrazole complexes. For example, the pyrazole complex XXIX reacts with $(\text{acac})\text{Rh}(\text{CO})_2$ forming products with a bridging pyrazole ligand XXX [72]. $[\text{IrCl}(\text{Hpz})(\text{cod})]$ interacts with $[\text{Ir}(\text{acac})(\text{cod})]$ forming $[\text{Ir}_2(\mu\text{-pz})(\mu\text{-Cl})(\text{cod})_2]$, where acac is acetylacetonate and cod is 1,5-cyclooctadiene [73]. Another example is the interaction of $[\text{PdCl}_2(\text{Hpz})_2]$ with $[\text{M}(\text{acac})(\text{diolefine})]$

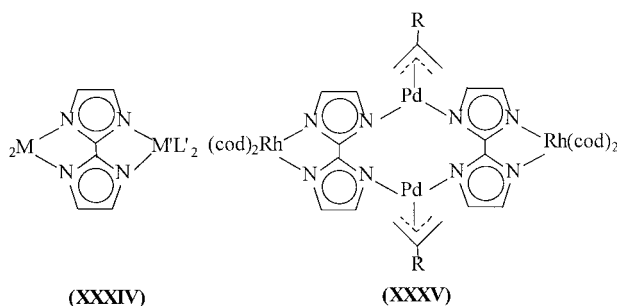
(M = Rh, Ir), leading to XXXI [74]. Analogous transformations have been reported [75–81].



Numerous reactions have been reported where deprotonation of the coordinated pyrazole and its derivatives XXXII occurred [82]. In such processes, the transition from the terminal XXXII to the bridging XXXIII (M = Cr, Mo, W) pyrazolate ligand takes place [83]. In a series of cases bridge formation occurred after transformation of complex with the terminal pyrazole by protonation [49,84].

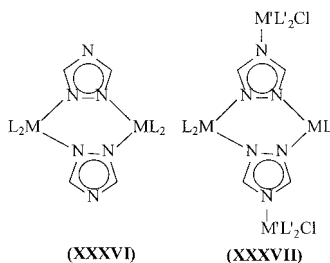


The bis-imidazole (H_2biim) complexes are frequently used metal-containing imidazole ligands [85–92]. Thus, reactions of $L_2M(H_2biim)$, where L_2 is cyclooctadiene (cod), $(CO)_2$; M = Rh, Ir, with $[M'(cod)(OMe)]_2$ or $[M'(cod)(acac)]$ yield complexes of the type XXXIV ($L_2 = L'_2 = cod$; $L, L' = CO$, M = M' = Rh, Ir; M = Rh, M' = Ir; $L_2 = L' = CO$) [85].



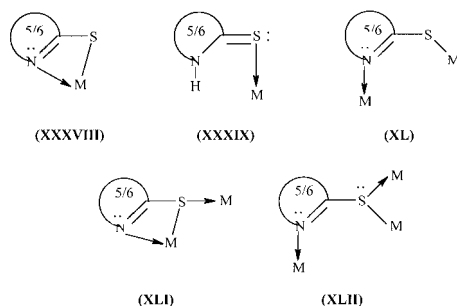
Later, the structure $Rh_2(CO)_4(biim)$ was reconsidered in favor of $Rh_4(CO)_8(biim)$ [86,87]. Similar complexes, containing palladium and gold have been studied in detail [88–92]. The tetranuclear structures XXXV were synthesized by interaction of two molecules of the complex $[Rh(Hbiim)(cod)]$ with $[Pd(\eta^3-2R-C_3H_4(acac))]$ [93].

The bridging complexes of 1,2,4-triazole XXXVI contain non-coordinated nitrogen atoms:



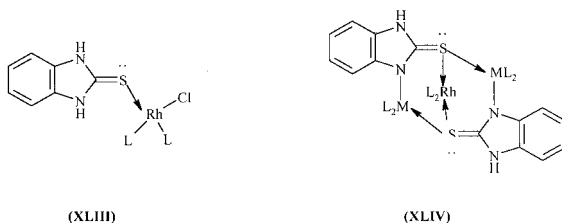
These complexes react with $[M'(\mu\text{-Cl})(\text{cod})]_2$ ($M = \text{Rh}, \text{Ir}$) or $[\text{Rh}(\mu\text{-Cl})(\text{CO})_2]_2$ forming a series of products XXXVII, in which $M = M' = \text{Rh}$, $L_2 = L'_2 = \text{cod}, (\text{CO})_2$; $M = \text{Rh}$, $M' = \text{Ir}$, $L_2 = L'_2 = \text{cod}$; $M = \text{Pd}$, $M' = \text{Rh}$, $L_2 = \eta^3\text{-C}_3\text{H}_5$, $\eta^3\text{-C}_4\text{H}_7$, $L'_2 = (\text{CO})_2$ [94].

The complexes of 2-mercapto(thione) derivatives of nitrogen-containing five- and six-membered heterocycles, form a series of mono-(XXXVIII, XXXIX), di (XL, XLI), and trinuclear (XLII) structures [50,51,95].

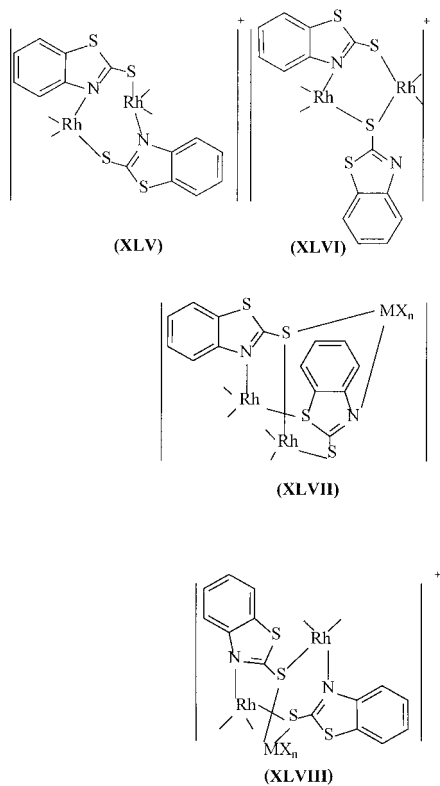


For the mononuclear complexes XXXVIII–XL, the S or N atoms remain coordinatively non-saturated. This leads to the formation of numerous di-(XLI) and trinuclear (XLII) structures, generalized in reviews [51,95]. Only some examples of such compounds are presented here.

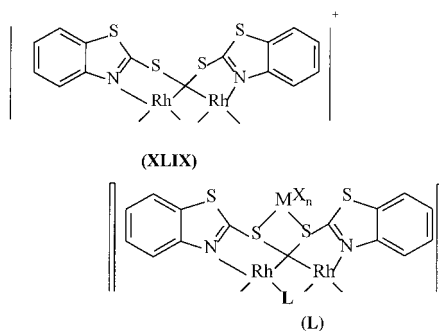
In the complexes with diene (L) rhodium and iridium derivatives, 2-mercaptobenzimidazole is present in the thione tautomeric form XLII ($M = \text{Rh}, \text{Ir}$) [96]. When this complex reacts with $[\text{Rh}(\text{acac})(\text{cod})]$ in the presence of silver tetrafluoroborate, deprotonation of one NH group yields a trinuclear complex XLIV [96].



Binuclear cyclic complexes XLV and XLVI are used as ligands, forming trinuclear structures XLVII and XLVIII by interaction with MX_n [97].

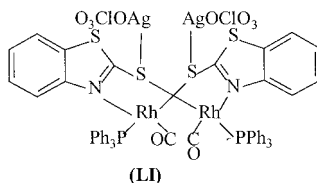


Binuclear XLIX also possesses ligand properties forming trinuclear S,S-coordinated structures L [98]. $[Rh_2L_2(Me_2CO)_2]$ (L) [98] or $AgClO_4$ [99] acts as Lewis acid in the complexes.

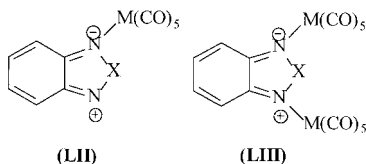


Reactions of $[\{Ir(\mu-C_7H_4NS_2)(cod)\}_2]$ and $[\{Pd(\mu-C_7H_5NS_2)(\eta^3-C_3H_5)\}]$ with $[ML_2(Me_2CO)_2]^+$ result in homotrimeric angle complexes $[M_3(\mu-C_7H_4NS_2)_2(L_2)_3]^-$. For precursors $[\{Rh(\mu-C_7H_4NS_2)(CO)(PPh_3)\}_2]$ and $[\{M'(\mu-C_7H_4NS_2)(cod)\}_2]$ ($M = Rh, Ir$), this synthetic method produced heterotrimeric structures $[(Ph_3P)_2(OC)_2Rh_2(\mu_3-C_7H_4NS_2)_2ML_2]^+$ [$ML_2 = Ir(cod)$ or $Pd(allyl)$],

$[(cod)_2M_2'(\mu_3-C_7H_4NS_2)AgX]^{n+}$ ($n=0$, $X = ClO_4$, Cl , NO_3 or BF_4 ; $n=1$, $X = PPh_3$, py) and $[(cod)_2M_2'(\mu_3-C_7H_4NS_2)_2M''Cl]$ ($M'' = Cu$ or Ag), for instance LI [100].

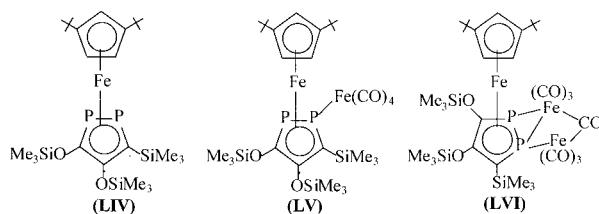


$M(CO)_5$ -derivatives of type LII ($M = Cr, Mo, W$) of oxa-, thia-, and selenodiazoles ($X = O, S, Se$) function as ligands leading, for example, to a binuclear compound LIII [101].

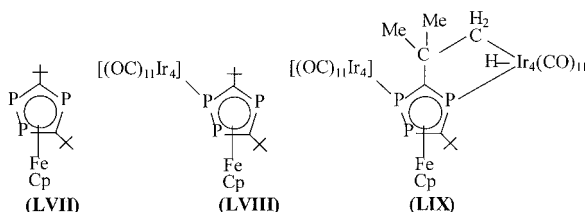


Di- and Oligophosphorus-Containing Heterocycles

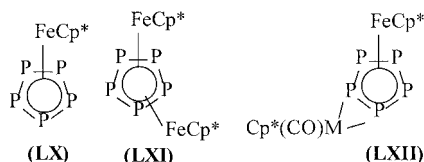
This group of metal-containing heteroaromatic ligands is represented by π -complexes of five-membered heterocycles, containing two and more endocyclic phosphorus atoms. (IX: $A = PR$; $B = P$; $D, E, G = CR$; $A = PR$; $B, D = P, E, G = CR$; $A = PR$; $B = D = E = G = P$). In π -complex-ligands further binding of metals takes place to σ -P-donor centers and yields π, σ -coordination compounds. Thus, on the basis of diphosphoferrocene derivative LIV, the di-(LV) and trinuclear (LVI) complexes are prepared [102,103].



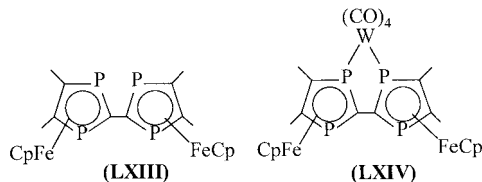
The reaction of LVII with $Nbu_4[(Ir_4(CO)_{11})Br]$ takes place specifically [104]. In the first stage, the P-coordinated compound LVIII is formed. In excess of the noted iridium reagent, activation of one C–H bond occurs yielding the product LIX [104].



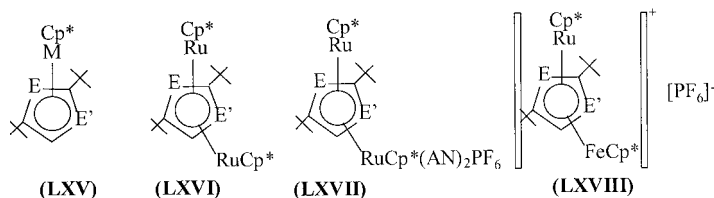
The complete phosphorus analogue of pentazole (IX: A = PR; B = D = E = G = P) is an interesting ligand [105]. For example, the pentamethylcyclopentadienyl iron sandwich LX can serve not only as a source triple decker systems of the type LXI, but also as unique $\mu\text{-}\eta^5\text{:}\eta^2\text{-cyclo-P}_5\text{-coordinated}$ derivative LXII (M = Rh, Ir) [106]. Other similar reactions have been reported [107]. For this series of compounds, the so-called "docking" reactions are known [108]. Thus, the interaction of $[(\eta^5\text{-Cp}^*)\text{M}(\eta^5\text{-E}_5)]$ (E = P, As; M = Fe, Ru) with $[\text{M}'(\text{CO})_3(\text{AN})_3]$ (M' = Cr, Mo; AN is acetonitrile) yield a neutral triple decker complex $[(\eta^5\text{-Cp}^*)\text{M}(\mu\text{-}\eta^{5:5}\text{-E}_5)\text{M}'(\text{CO})_3]$, having 30 valence electrons.



Phosphorus analogues of biimidazole (structures XXXIV–XXXVIII) as ligands were reported. Thus, the tetraphosphafulvalene, where both heteronuclei are η^5 -coordinated with FeCp-groups (LXIII), is capable for further binding with metals, yielding chelate triple decker complex LXIV [109].



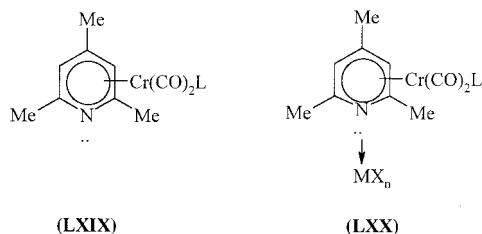
Some heterocycle complexes, containing equal or different (P, As) atoms have been reported. Sandwich complexes, LXV, are a source of triple decker structures; reaction with $\text{Cp}^*\text{Ru}(\text{AN})_3\text{PF}_6$ (E = E' = P, As; E = As, E' = P; E = P, E' = As) results in compounds LXVI and LXVII. Heating LXVII produces the cationic three-decker compound LXVIII [110].



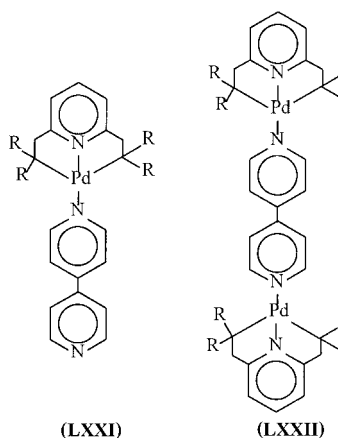
In contrast to the complexes LIV–LXIV above, the complex compounds LXVI–LXVIII are representatives of triple decker structures, in which the π,π -coordination bonds are realized.

Six-Member Heterocycles and Their Derivatives (X, XI)

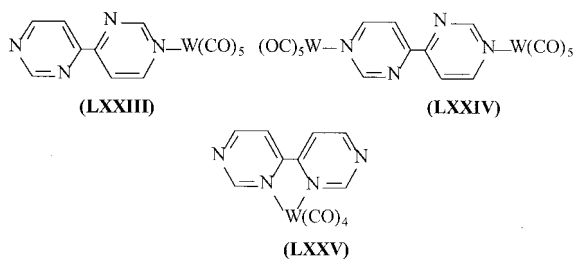
The heterocycle nitrogen in adducts of η^6 -coordinated chromiumtricarbonyl 2,4,6-collidine LXIX ($L = CO$) and its triphenylphosphine derivative ($L = PPh_3$) coordinated to metal LXX [111,112].



Bipyridyl complexes, in which one nitrogen atom does not take part in coordination, are often used as ligands. An example of such metal-containing ligands is a N-coordinatively unsaturated complex LXXI ($R = CO_2Et$), forming a binuclear compound LXXII [113].

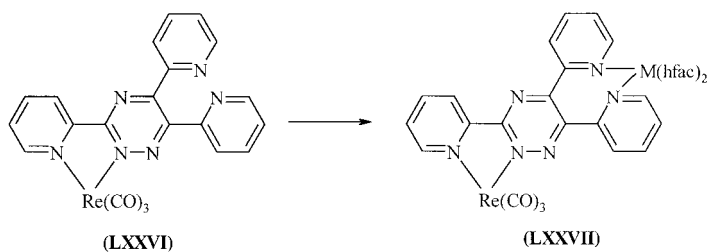


Use of non-coordinated donor centers of diazines, for instance in LXXIII, is widespread. Bridging two metal carbonyl groups, for example as in LXXIV, as well as chelating one metals LXXV, are observed [114].

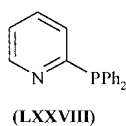


A mononuclear complex $[ReCl(CO)_3(tpt)]$ ($tpt = 3,5,6$ -tri(2-pyridyl)-1,2,4-triazine) LXXVI is a bidentate N,N-donor metal-containing ligand. It reacts with $[M(hfac)_2]$

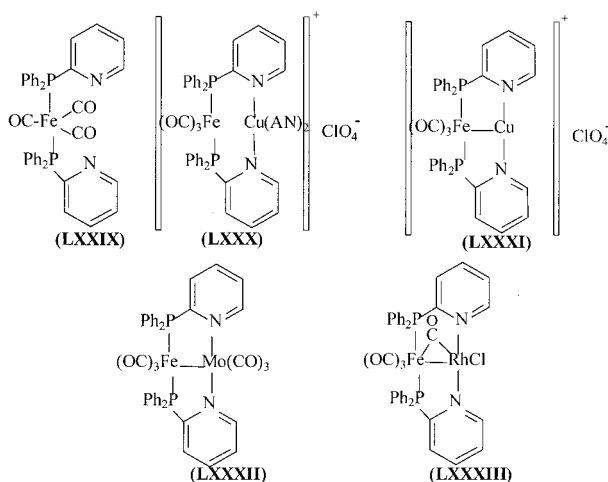
($M = \text{Mn, Fe, Co, Ni, Zn}$; hfac is hexafluoroacetylacetonate) yielding heterobimetallic compounds LXXVII [115].



Among the azine derivatives, 2-diphenylphosphinopyridine (dppy) LXXVIII is of particular interest as a hard-soft ambidentate ligand system [116].



As expected from the principle of hard and soft acids and bases [18,29,117], reactions with soft metal carbonyls yields P-coordinated complexes (*e.g.*, LXXIX), in which the pyridine nitrogen atoms remains uncoordinated [116].

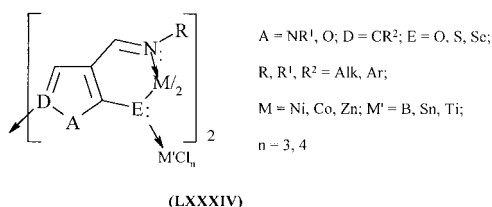


In this respect, reactions of LXXIX with metal salts and carbonyls yield binuclear complexes LXXX-LXXXIII [116]. Complexes without a metal-metal bond are reported, for instance LXXX [118,119], formed from reaction of LXXIX with $[\text{Cu}(\text{AN})_4]\text{ClO}_4$. Numerous structures LXXXI-LXXXIII are known, in which a heteronuclear metal-metal bond is detected [120-125]. Such compounds are examined for binuclear perchloro copper complexes of 2-diphenylphosphino-6-(pyrazolil-1)pyridine with azide and thiocyanate bridges [126].

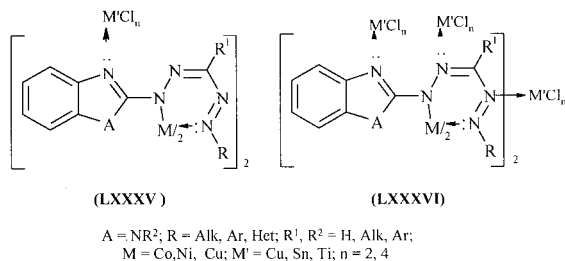
The interaction of $[\text{Pt}(\text{dppy})_2(\text{PhC}\equiv\text{C})_2]$ with $[\text{M}(\text{AN})_4]$ ($\text{M}=\text{Cu}, \text{Ag}$) belongs to the same group of transformations [126,127], yielding $[\text{Pt}(\text{dppy})_2(\text{PhC}\equiv\text{C})_2\{\text{M}(\text{AN})_x\}_2]^{2+}$ ($\text{M}=\text{Cu}$, $x=1,2$; $\text{M}=\text{Ag}$, $x=1$). The grouping $\text{M}\cdots\text{Pt}\cdots\text{M}$ is kept with two bridging 2-diphenylphosphinopyridine and $\mu\text{-}\eta^2\text{-PhC}\equiv\text{C}$ ligands. Two phosphorus atoms are coordinated to the platinum central atom and two pyridine nitrogen atoms are connected to the M-atoms (copper or silver).

Chelates of Heterocyclic Compounds as Ligands

Trinuclear complexes, LXXXIV, are isolated on the basis of chelates of five-membered heterocycles [18 and ref. therein].



By analogy with I and II, the structure LXXXIV is the most probable coordination mode, however metal coordination to the nitrogen atom of the pyrazole ring is also possible at $\text{D}=\text{N}$. Another example of using heterocyclic chelates as ligands is the formation of structures LXXXV and LXXXVI as a result of reaction of hetarylformazane complexes with Lewis acids ($\text{M}'\text{Cl}_n$) [128].

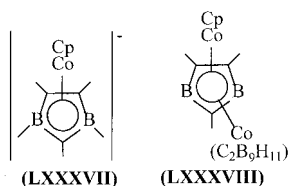


Composition of the formed complexes depends on the nature of the Lewis acid: at $\text{M}'=\text{Cu}$ the quantity of acceptors is determined by number of heterorings (which can take part as substituents R and R^1); in the case of Sn and Ti the composition depends on the number of nitrogen donor atoms of heterocyclic and formazane fragments. The proposed structures require additional x-ray diffraction study.

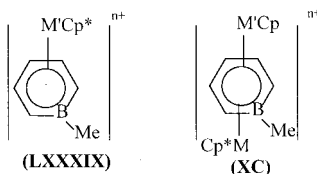
Boron-Containing Heterocycles

The five-membered heteroaromatic ligands containing two or three endocyclic boron atoms form various sandwiches and multi-decker structures [51,129]. Complexes of these ligands allow numerous examples of construction of compounds with differing numbers of heteroaromatic fragments. An example is provided by the reaction of

three components *nido*-6-Me-5,6,9-C₃B₇H₉⁻ (η^5 -Cp)Co(η^5 -MeEt₄C₃B₂)⁻ and FeCl₂-THF, yielding the triple-decker compound (η^5 -Cp)Co(μ - η^5 -MeEt₄C₃B₂) Fe(η^5 -5-2,3,5-C₃B₇H₉) [129]. The completion of triple decker LXXXVIII from sandwich LXXXVII proceeds in a similar manner [130–132]. Quadruple-deckers are constructed following the same principle [133]. A number of papers are devoted to the construction of multiple-decker complexes containing C₃B₂-heteroaromatic ligands [134–137].

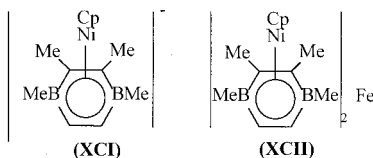


Among the complexes containing six-membered heterocycles with boron atoms π -complexes LXXXIX are noteworthy because they readily convert into triple-decker structures XC (M = Fe; M' = Fe, Ru, n = 1; M = Rh, Ir, n = 1) [138].



The transformations take place [138] by the interaction of mononuclear ligand LXXXIX with complex cations [CpM'(MeCB)₂]²⁺ or [CpM'(MeNO₂)₂]²⁺.

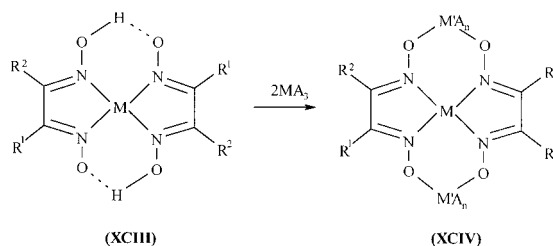
The complexes containing six-membered heterocycles with the two boron atoms, similar to the other boron-containing heterocycles, are capable of coordinating to additional metal-containing centers through the π -system [139–145]. For example, the anionic complex XCI reacts with FeCl₂ with visible light forming XCII [145].



Metal-Containing Proton-Donating Ligands

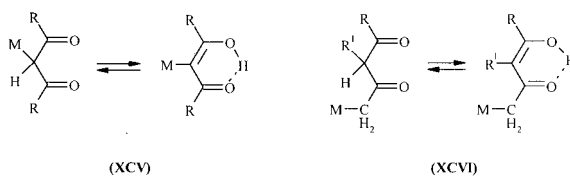
This type of ligand system is of considerable interest because they exhibit properties of H-acids and provide the possibility of using free coordinatively-active OH and NH groups of the complexes in reactions with Lewis acids. Metal oximes are prominent examples of such ligands. A proton of their OH group is replaced in reactions with Lewis acids [146–151]. This transformation was first observed in reactions of nickel dimethylglyoximate (XCIII: R¹ = R² = me) with boron and aluminum halides yielding

the trinuclear complexes XCIV ($R^1 = R^2 = \text{Me}$; $M = \text{Ni}$; $M' = \text{B, Al}$; $A = \text{F, Cl}$, $n = 2$) [152,153].

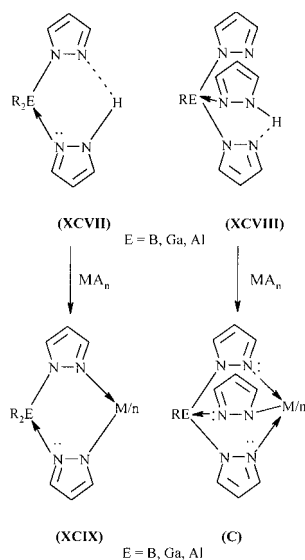


More recently, this transformation was extended to mono- and diglyoximates with different substitutes R^1 and R^2 , different complexing metals ($M = \text{Co, Fe, Ni, Pt, Pd, Cu}$), and different Lewis acids ($BX_3, AlX_3, SnX_4, GeX_4$) – XCIV ($n = 2,3$) [146–151]. The structure of the resulting complexes were proved by x-ray diffraction [154].

The C-metal derivatives of β -diketones XCV and XCVI are promising metal-containing proton-donating ligands bearing the OH group [50,155,156]. However, complexes are not yet known.

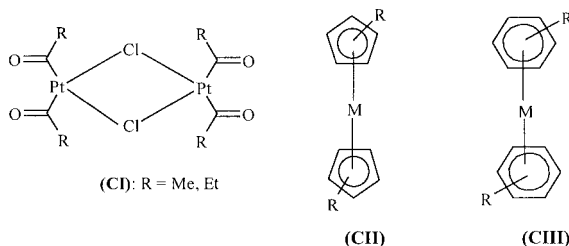


A variety of di- and tripyrazole organoelement ligands, e.g., XCVII and XCVIII, contain the NH fragment [51,157–161], and react with metal salts to give di- and multinuclear complexes of the XCIX and C types [51,157–161].



CONCLUSIONS

The data presented in this review, as also those published in reviews [23,28,29,36,47, 117,146–151,155–164] and a monograph [18], are evidence that complexes and organometallic compounds can be used as ligands in a wide range of processes. Although many of the structures reported in the literature are proved x-ray single crystal diffraction, their physico-chemical properties call for further study.



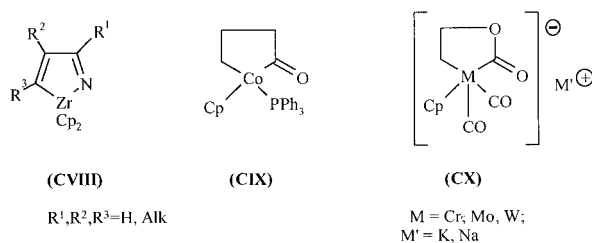
R = -C≡N, -HC=N-OH, -HC=NR, -N=CHR, among others.

Among the perspective metal-containing ligands, such as XCV and XCVI, it is necessary to note recently described platinum β -diketonates CI [165], containing two chelate-forming fragments.

Additionally to the ferrocene derivatives described above, η^5 -cyclopentadienyl and chromium η^6 arene derivatives with coordinatively-active fragments [166] are also interesting, as well as metallocyclic compounds of the types CIV–CVII [167–169].

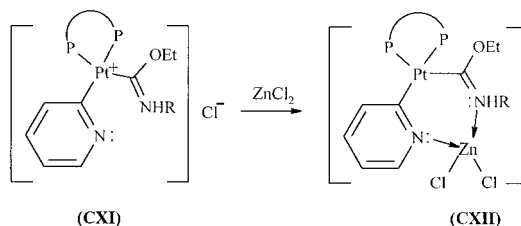


In this respect, the systems with uncoordinated endocyclic nitrogen atoms CVIII [168] or exocyclic carbonyl oxygens CIX [168] and CX [169] are of interest.



There are comparatively little data on ligand properties of azine C-metalloderivatives. So, a possibility of using C-Pt-substituted pyridine CXI in reactions with Lewis

acids, for example ZnCl_2 (CXII) [170] is of interest.



The prospect of using the coordination and organometallic ligands is primarily associated with the directed syntheses of the homo- and heteronuclear compounds [171] opening the way to synthesis of substances with controlled physicochemical, especially magnetic and optical, properties.

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