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Organometallic complexes of heterocycles
II. Complexes of pyrazoles

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Contents

Abstract

Metal carbonyl and dienyl complexes of pyrazoles are generalized. Material is arranged in accordance with transition metal groups of the Periodic Table. Behavior of pyrazoles as monodentate ligands with coordination via the pyridinic nitrogen atom, *endo*- or *exo*-bidentate bridging ligands in the form of the pyrazolate anion is systemized within each section. Several organometallic derivatives of rare earth elements are also included. The bibliography includes 196 references.

Keywords: Pyrazole complexes; Organometallic complexes

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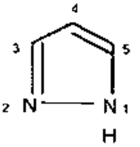
List of abbreviations

Acac	acetylacetonate
APzH	aminopyrazole
Ar	arene
Bipy	2,2′-bipyridine
Bu	butyl
Cod	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cp′	pentamethylcyclopentadienyl
Cy	cyclohexyl
Dpe	bis(diphenylphosphino)ethane
Dppen	*cis*-1,2-bis(diphenylphosphino)ethylene
Dppm	bis(diphenylphosphino)methane
Dppp	1,3-bis(diphenylphosphino)propane
En	ethylenediamine
ESR	electron spin resonance
Et	ethyl
Hal	halogen
Ln	lanthanoid
Me	methyl
Mes	mesityl
Nbd	norbornadiene
Ph	phenyl
Pr	propyl
Py	pyridine
PzH	pyrazole
Pz	pyrazolate
3,5-dmPzH	3,5-dimethylpyrazole
3,5-dmPz	3,5-dimethylpyrazolate
THF	tetrahydrofuran
Tfb	tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene
3,4,5-tmPz	3,4,5-trimethylpyrazolate
UV	ultraviolet

1. Introduction

This review is the second in the series on organometallic complexes of heterocycles. The first [1] was devoted to the five-membered monoheterocycles. Logically, the next step would be to review the coordination chemistry of azoles towards metal carbonyls, cyclopentadienyls and other metal-carbon compounds. However the bulk of the existing material is so vast that we had to subdivide it into further parts and start with the organometallic complexes of pyrazoles, rather popular ligands [2–14]. We concentrate our attention on pyrazole and its simple derivatives. Development of this field of organometallic chemistry started in the early seventies and during about 25 years essential progress has been achieved.

According to numerous estimates [15–23], pyrazole (**1**) is a substantially aromatic ligand, being close to π-neutral, although it is classified as a π-excessive compound [24]. The free radical of 1-pyrazolyl may exist as the σ- or π-radical. In the first case (**2**), an unpaired electron occupies an orbital of the σ-type formed as a result of combination of two nitrogen non-bonding σ-orbitals. In the π-radical (**3**), an unpaired electron occupies an orbital embracing all five ring atoms.



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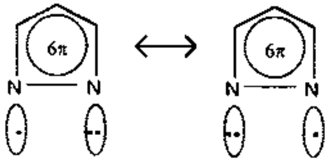

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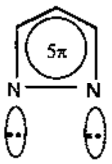

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Non-empirical quantum-chemical calculations [25,26] predict two low-lying π-doublet states having symmetry B_1 and A_2, representing most probably two minima with vibrational interconversion. A doublet of σ-type is characterized by B_2 symmetry and has a greater energy. However the energy difference suggests that pyrazolyl may exist as a metastable σ-radical if it is generated in the excited $^2B_2$ state.

In accordance with theoretical estimates, pyrazoles are σ-donor ligands and are able to behave in different ways: as monodentate ligands with coordination via the pyridinic nitrogen atom; bidentate or polydentate ligands if substituents containing additional donor sites are attached to the pyrazole nucleus; *endo*- or *exo*-bidentate bridging ligands in the form of the pyrazolato anion. In the latter case, the reaction course as a rule requires deprotonation of the pyrazole ligand to form the pyrazolate anion. This process is facilitated by application of an alkali or a base (typically, triethylamine) or by means of interaction of pyrazole with n-butyllithium, pyrazole with an alkali metal in THF, or pyrazole with an alkali metal hydride in THF.

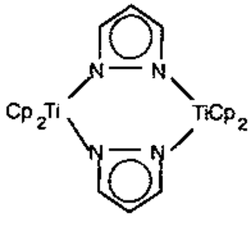
We are not going to consider each coordination mode separately but prefer to move along the groups of the transition elements starting with titanium complexes.

2. Organometallic complexes of pyrazoles

2.1. *Derivatives of titanium, chromium, molybdenum, tungsten, manganese and rhenium*

The data for the pyrazole complexes of titanium, chromium and manganese groups are scarce and considered under one subheading. To our knowledge, organometallic compounds of the other Group IVA-VIA metals with pyrazoles are not yet available.

Bis(cyclopentadienyl)titanium monochloride reacts with sodium pyrazolate to give (**4**). X-ray analysis reveals a structure with two coplanar pyrazolate groups [27,28] being the 1,2-η^2-linkage between two titanium atoms. The Ti_2N_4 framework has a chair conformation (a unique case of this type of chelate, as will be seen later), where the titanium(III) centers are above and below the plane of the heterocyclic anionic ligands. This dimer shows only a weak magnetic exchange interaction that could be revealed only by the ESR method. The reason for this phenomenon is ascribed to the disposition of the titanium(III) ions relative to the pyrazolates [28].



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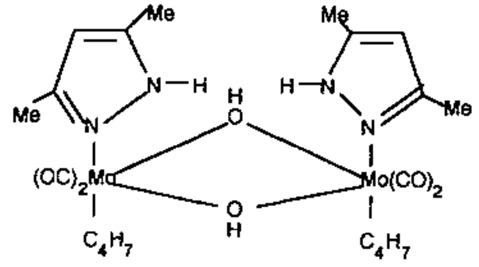

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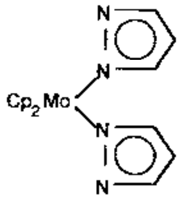
Chromium hexacarbonyl and pyrazole or 3,5-dimethylpyrazole form $(\mathrm{PzH})\mathrm{Cr}(\mathrm{CO})_5$ or $(3,5\text{-dmPzH})\mathrm{Cr}(\mathrm{CO})_5$ irrespective of the ratio of the reactants. In similar circumstances, tungsten hexacarbonyl forms both $(\mathrm{PzH})\mathrm{W}(\mathrm{CO})_5$ or $(3,5\text{-dmPzH})\mathrm{W}(\mathrm{CO})_5$ and, in addition, the more exhaustively substituted $(\mathrm{PzH})_2\mathrm{W}(\mathrm{CO})_4$ or $(3,5\text{-dmPzH})_2\mathrm{W}(\mathrm{CO})_4$ [29–33].

Molybdenum and tungsten hexacarbonyls are able to form anionic complexes in $(\mathrm{AsPh_4})_2[(\mathrm{OC})_4\mathrm{M}(\mu\text{-Pz})_2\mathrm{M}(\mathrm{CO})_4]$ upon reaction with sodium pyrazolate [34]. The cationic complexes $[(\eta^5\text{-Cp})_2\mathrm{M}(\mu\text{-Pz})_2\mathrm{M}(\eta^5\text{-Cp})_2]^{n+}$ ($n=2,3$) are known as well [35].

X-ray analysis of the solvate of (**5**) with one molecule of benzene [36] shows that the molecule is a dimer with a $\mathrm{Mo}(\mu\text{-OH})_2\mathrm{Mo}$ unit and contains two distorted octahedra. The pyrazolyl ligands are in the axial positions and form NH···O intramolecular bent hydrogen bonds with the bridging hydroxyls.

Reactions of the metallocene derivatives of molybdenum with pyrazole lead to the mononuclear complexes of the type (**6**). The structure (X-ray analysis) shows the impossibility of application of (**6**) as a ligand for the preparation of binuclear complexes due to geometric constraints [37,38]. In acetone an unusual complex is formed (**7**). As shown by X-ray analysis [37], the molybdenum atom is coordinated via two η^5-Cp ligands and a bidentate ligand being the product of the reaction of pyrazole and acetone.



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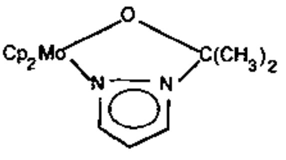

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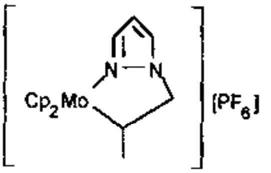
Reaction of 1-allylpyrazole with $[\mathrm{Mo}(\eta^5\text{-Cp})2\mathrm{HI}]$ gives mixtures of metallocyclic isomers (**8**, **9**) resulting from coordination of the nitrogen atom to molybdenum followed by internal cyclometallation [39].



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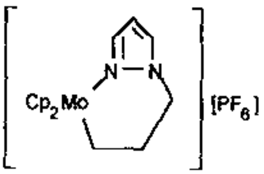

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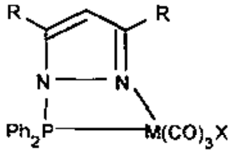
In complexes containing one *N*-substituted diphenylphosphino group per pyrazole ring (**10**) there exists a four-membered PN_2M metallocycle as confirmed by X-ray analysis of the rhenium derivative of pyrazole [40]. Molybdenum(0) and tungsten(0) complexes are more subject to the opening of a cycle than manganese(I) and rhenium(I) analogs.



R=H,Me; M=Mn, X=Cl; M=Re,X=Br;
M=Mo,W; X=CO

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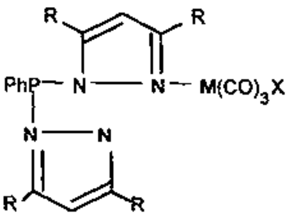

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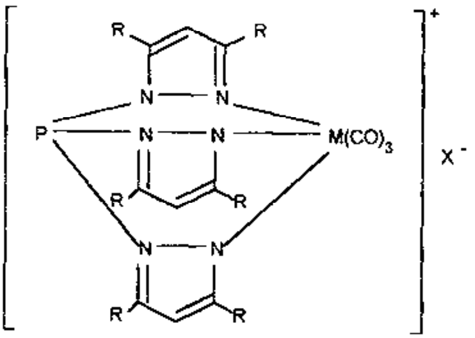
In complexes where there is one phenylphosphino unit per two pyrazole rings (**11**, the meaning of R, M and X is the same as in **10**) the phosphorus atom is not coordinated via the metal. The reduced basicity of phosphorus is due to the electron acceptor effect of the pyrazolyl groups. The facial structures of (**10**) are more favorable than the meridional structures containing *trans* carbonyls (X-ray analysis of the rhenium and tungsten derivatives of pyrazole).

The proposed tris-chelate structures (**12**) of the complexes containing one phosphorus atom per three pyrazole rings do not exclude the possibility of bis-chelate structures containing the covalently bonded halogen rapidly exchanging with one pyrazole group.



R=H,Me; M=Mn,X=Cl; M=Re, X=Br; M=Mo,W, no X

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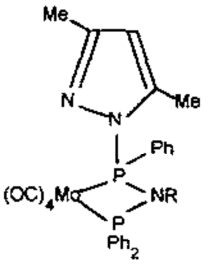

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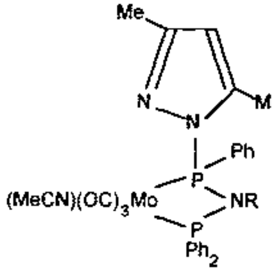
The complexes studied (**10**–**12**) are characterized by a regular octahedral configuration around the central atom, and three carbonyl groups have the facial disposition.



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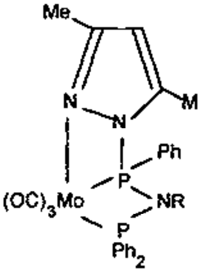

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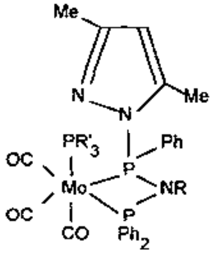
The piperidine complex *cis*-[$Mo(CO)_4(NHC_5H_{10})_2$] undergoes displacement of the coordinated amine by the pyrazolyl-containing diphosphazane ligand yielding the mononuclear *cis*-molybdenum tetracarbonyl derivative (**13**) [41]. The product of the reaction of *fac*-[$Mo(CO)_3(MeCN)3$] with the same ligand has structure (**14**) as shown by X-ray analysis. The coordination unit represents a slightly distorted octahedron. Complex (**14**) appears to be unstable in hot acetonitrile and redistributes to the stable tetracarbonyl species (**13**). In contrast, in hot heptane (**15**) is produced along with (**13**), the latter still being the major product. Complex (**14**) reacts with triphenylphosphine or triphenylphosphite. During the first stage a *fac*-isomer (**16**) is produced, which rearranges intramolecularly to the *mer*-isomer (**17**).

Bis(3,5-dimethylpyrazol-1-yl)cyclotriphosphazene containing phenyl substituents at the phosphorus atoms (R) reacts with molybdenum and tungsten hexacarbonyls to give (**18a**,**b**) [42]. If R = $N(Me)(CH_2)_2O$, (**18c**,**d**) are produced having better solubility in organic solvents. The structures of (**18a**,**d**) represent an example of distorted trigonal antiprismatic coordination around the metal atom (molybdenum or tungsten) and show the novel tridentate *NNN*-feature of the ligands.



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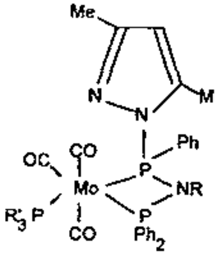

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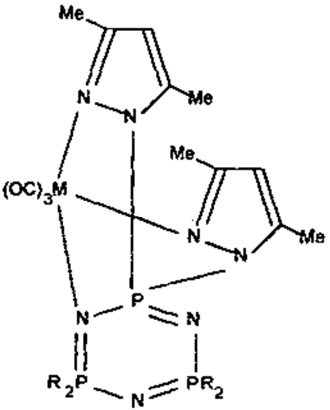
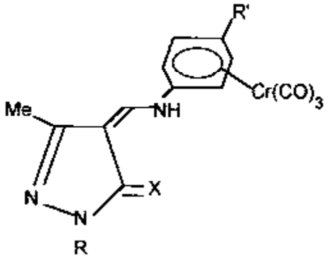


a: R=Ph, M=Mo; b: R=Ph, M=Mo
c: R=N(Me)(CH$_2$)$_2$O, M=Mo
d: R=N(Me)(CH$_2$)$_2$O, M=W

18

Condensation of [(η^6-$PhNH_2$)$Cr(CO)_3$] or [(η^6-Me-*p*-$C_6H_4NH_2$)$Cr(CO)_3$] and the corresponding pyrazole-containing aldehydes yields compounds (**19**) [43–45]. They have an amino-ethylene structure with a strong intramolecular hydrogen bond. They can be used as ligands and indeed their further reaction with zinc(II), cadmium(II), mercury(II) or nickel(II) acetates yields the metal-chelates (**20**). The nickel(II) chelates have magnetic moments within 3.0–3.6 BM both in the solid state and in solution thus exhibiting the expected behavior for a d^8 ion in a tetrahedral field. The nickel atom in (**20**, X = S, R = H) possesses a slightly *cis*-distorted pseudo-tetrahedral configuration as shown by the X-ray data. The ligand is in its delocalized iminothiolate form.

Cis-bis(pyrazolyl)platinum(II) phosphine complexes react with chromium hexacarbonyl upon UV irradiation and form the heterobinuclear species (**21**) [46]. Similarly, molybdenum and tungsten analogs and 3,5-dimethylpyrazolyl derivatives have been prepared. For R = Et (**21**), X-ray analysis shows a non-planar boat conformation for the central six-membered PtN_4Cr ring.



R=Ph, *iso*-Pr; R'=H,Me; X=S,Se

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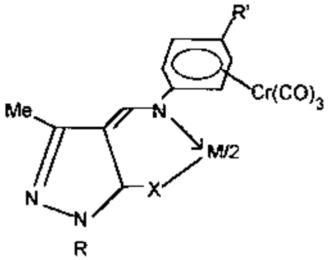

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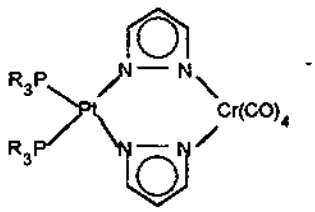
The nucleophilic substitution reaction of the carbonyl group in dimanganese decacarbonyl by pyrazole leads to [$Mn_2(CO)_9(PzH)$] [47]. If a pyrazolate ion is used the reaction mixture perhaps contains [$Mn_2(CO)_9(Pz)$]$^-$, the sodium ion being the counterion. Chromatography of the mixture on alumina protonates the pyrazolate ion again into a neutral molecule, where the pyrazole molecule is likely to occupy the equatorial position. The nucleophilic substitution is accompanied by a redox process affording two types of compounds, [$Mn(PzH)_4(solv)$]$^{2+}$[$Mn(CO)_5$]$^-_2$ (solv = EtOH, THF) and the tetraethylammonium salt of the binuclear anion, (NEt_4)[$Mn_2(CO)_6(\mu$-$Pz)_3$], the bridged tris-μ-pyrazolato derivative. The solvated salts are the paramagnetic d^5 complexes of divalent manganese (ESR). The proposed structure for these ions (**22**) takes into account the possible proton transfer from cation to anion. [(3,5-dmPz)$Re(CO)_3Cl$] is known [48].

[$Br(Mn(CO)_5$] reacts with the pyrazolate anion to yield the charged complex (**23**) [49]. Here two metals are bridged by three pyrazolate ligands [50].

1-Phenylpyrazole upon reaction with [$MeMn(CO)_5$] yields (**24**) [51]. This product is cyclometallated and contains a five-membered ring.

1-(Diphenylphosphinosulfide)-3,5-dimethylpyrazole, 1-diethylphosphinopyrazole and 1-diphenylphosphino-3,5-dimethylpyrazole react with [$M(CO)_5X$] and [$M(CO)_4X_2$] (M = Mn, Re; X = Cl, Br) to form products where coordination is fulfilled only via the phosphorus atom in [(1-$Ph_2PPz)Re(CO)_4Br$], or via two donor sites in the chelate fashion (**25**,**26**) [52]. For (**25**, M = Mn), X-ray analysis confirms the existence of the four-membered chelate ring [53].



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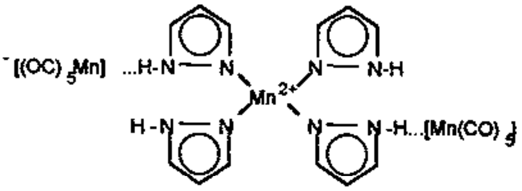

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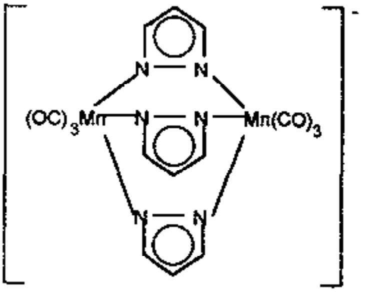

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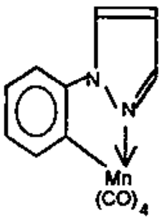

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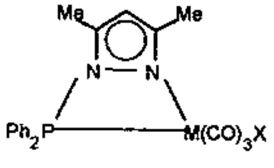

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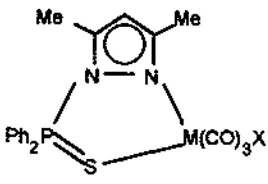

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2.2. *Derivatives of iron, ruthenium and osmium*

There are some common features in the organometallic derivatives of iron, ruthenium and osmium with pyrazoles. All form metal-metal bonds in the carbonyl complexes. Ruthenium and osmium complexes are often metallated. However since there are many peculiar examples especially for the iron and ruthenium compounds and since the ruthenium chemistry is developed rather systematically, organometallic derivatives of each of these metals will be considered separately.

Iron pentacarbonyl and 3,5-dimethylpyrazole yield [(3,5-$dmPzH)_2Fe(CO)_3$] [54]. However, pyrazole as the parent ligand in the same reaction gives the polymeric [$Fe(Pz_2)]_n$ [55].

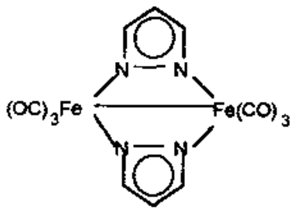
Reactions of [$Fe_2(CO)_9$] and [$Fe_3(CO)_{12}$] with pyrazole and 3,5-dimethylpyrazole (L) give [$LFe(CO)_4$], the σ-complexes having trigonal bipyramidal structures with axially located heterocycle [56]. This sort of transformation occurs in

THF. In ether [$Fe_3(CO)_{12}$] and pyrazole or 3,5-dimethylpyrazole form [$Fe(CO)_3(\mu$-Pz)]$_2$ or [$Fe(CO)_3(\mu$-3,5-dmPz)]$_2$, where each pyrazolyl ligand is bridging and coordinated to two iron atoms. The product contains the iron-iron bond [57]. [$Fe(CO)_4I_2$] reacts with sodium pyrazolates to give the same products.

The pyrazolate anion is a one-electron reductant for [$Fe(CO)_5$], [$Fe_2(CO)_9$], [$Fe_3(CO)_{12}$] and [(η^3-C_3H_5)$Fe(CO)_3I$] [58]. It reduces iron(II) in [(η^5-Cp) $Fe(CO)_2X$] (X= Hal) forming [(η^5-Cp)$(CO)_2$Fe]2 [59]. It is able to reduce iron(III) compounds and ferrocenium cations [(η^5-Cp_2)Fe^+] to [(η^5-Cp_2)Fe]. Subsequently the hydrogen atom in the ferricinium cation or ferrocene is substituted by the heterocyclic radical. The reaction occurs by the free-radical mechanism and the neutral pyrazolyl ferrocene is formed [60,61].

Reaction of [(η^5-Cp)$Fe(CO)_2$(THF)]$^+$ with 3,5-dimethylpyrazole gives a mononuclear complex [(η^5-Cp)$Fe(CO)_2$(dmPzH)]$^+$ [62]. [(η^5-Cp)$Fe(CO)_2$Pz] is known as well [63].

Reaction between [(η^3-C_3H_5)$Fe(CO)_3I$] and potassium tris(pyrazolyl)borate is followed by cleavage of the boron-pyrazolyl bond [64]. A mixture of products is formed. Complex (**27**) contains the iron-iron bond ensuring that each iron atom attains an inert gas configuration and the diamagnetism of the product is accounted for. Structure (**28**) is likely for the second product of the reaction. The best evidence for such a proposal is that *N*-allylpyrazole and [$Fe_2(CO)_9$] react to give an identical product. The latter is obtainable upon photolytic reaction of allylpyrazole with [$Fe(CO)_5$] [65] or sodium pyrazolate with [(η^3-allyl)$Fe(CO)_3I$] [66]. Bis(3,5-dimethylpyrazolyl) borate in similar conditions yields the complex having structure (**28**) [64].



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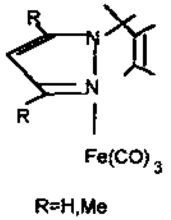

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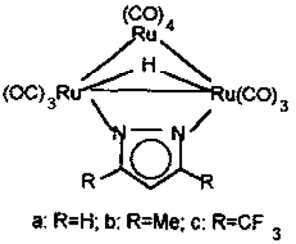
Reaction between [$Ru_3(CO)_{12}$] and pyrazole gives (**29a**) [67]. This compound is formed as a result of the oxidative addition of the pyrazole ligand to the cluster followed by elimination of the CO groups. In a similar way, complexes (**29b,c**) are made. X-ray analysis of (**29c**) shows that the pyrazolate group is symmetric in these complexes.



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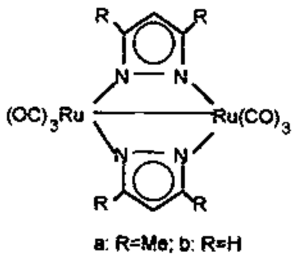
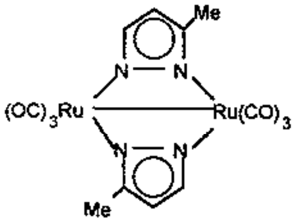
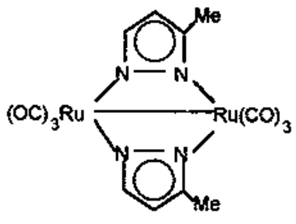


30

Treatment of $RuCl_3 \cdot nH_2O$ by carbon monoxide in refluxing 2-methoxyethanol and subsequent reduction with pyrazoles gives (**30a,b**) and (**31a,b**) [68]. Isomers (**31a,b**) are formed in the ratio 1 : 1. An attempt of the direct reaction of $[Ru_3(CO)_{12}]$ with pyrazoles leads to (**30a**) (X-ray analysis) only in the case of 3,5-dimethylpyrazole, the product being isolated from the mixture of $[Ru_3(CO)_{12}]$ and $[Ru_3(\mu\text{-}3,5\text{-dmPz})(\mu\text{-}H)(CO)_{10}]$. Each ruthenium atom is in an octahedral environment. The Ru_2N_4 framework has the boat conformation.

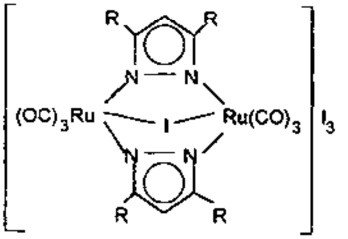


31a



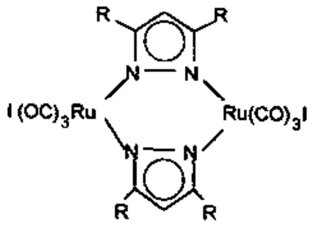
31b

The same products (**30**, **31**) can be trapped as the ruthenium(I) intermediates by zinc reduction of $RuCl_3$ with CO is fulfilled in the presence of the pyrazoles [69]. This time the authors managed the direct reaction of $[Ru_3(CO)_{12}]$ with pyrazole and 3-methylpyrazole. However they did not separate the mixtures of $[Ru_3(CO)_{12}]$, $[Ru_4H_4(CO)_{12}]$, $[Ru(\mu\text{-}H)(\mu\text{-}Pz)(CO)_{10}]$ and $[Ru_2(\mu\text{-}Pz)_2(CO)_6]$. Treatment of (**30**) with iodine leads to (**32a,b**). When the $Ru{:}I_2$ ratio is 2 : 1, the reaction proceeds further to the neutral complex $[Ru_2I_2(\mu\text{-}Pz)_2(CO)_6]$ (**33a,b**). Complex (**32a**) is characterized by octahedral coordination around the ruthenium atoms (X-ray analysis). Compound (**32a**) containing the I_3^- ion oxidatively adds to *trans*-$[IrCl(CO)(PPh_3)_2]$ to yield $[IrI_2Cl(CO)(PPh_3)_2]$ and the neutral species (**33a**).



a: R=Me; b R=H

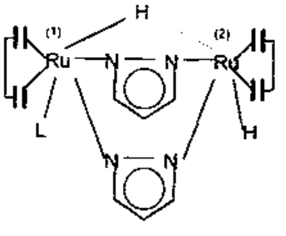
32



a: R=Me, b:R=H

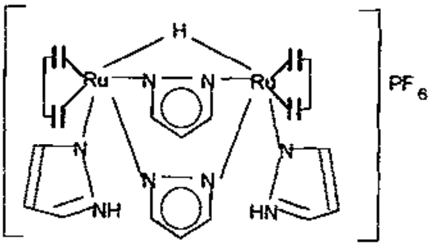
33

$[RuH(\eta^4\text{-}Cod)(NH_2NMe_2)_3]PF_6$ reacts with pyrazole and triethylamine to yield (**34a**) [70]. X-ray analysis indicates a substantial bonding interaction of the type Ru(1)-H···Ru(2) (**34a**). It is described as a two-electron, three-center bond, or a framework with semi-bridging hydride ligand. The metal-metal interaction is minor. Compound (**34a**) interacts with trimethylphosphine to yield the product of substitution of the pyrazole ligand by the phosphine molecule (**34b**). In (**34b**) the bridging character of the hydride ligand is more probable. The starting hydrazine complex reacts with pyrazole to give $[RuH(\eta^4\text{-Cod})(PzH)(NH_2NMe_2)_2]\ PF_6$. More exhaustive substitution [71] leads to (**35**) with a symmetric bridging hydride ligand (X-ray analysis). On standing (**34a**) in chloroform, product (**36**) is formed. X-ray analysis shows that in (**36**) the hydride ligand is unsymmetric and is nearer to the Ru(2) atom.



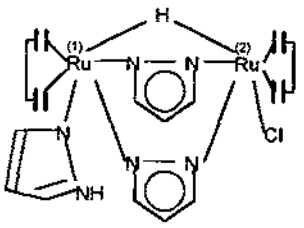
a: L = H, b: L=Me₃P

34



35

$[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and pyrazole yield the products $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)(\mu\text{-}Pz)_2Ru(\eta_6\text{-}C_6H_6)]Cl$ and $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)_2(\mu\text{-}Pz)Ru(\eta^6\text{-}C_6H_6)]Cl$ [72]. Their structures follow from X-ray analysis. 4-Methylpyrazolato-bridged complexes are prepared similarly. The chlorine-bridged products readily undergo Cl-/OH- exchange giving rise to $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OH)(\mu\text{-}Pz)_2Ru(\eta^6\text{-}C_6H_6)]Cl$ and $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}OH)_2(\mu\text{-}Pz)Ru(\eta^6\text{-}C_6H_6)]Cl$. The latter two complexes may be synthesized from $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ and pyrazole in refluxing water–methanol.



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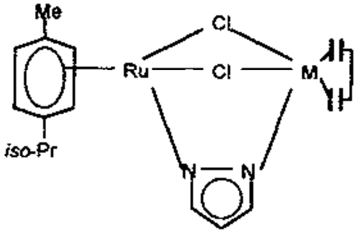
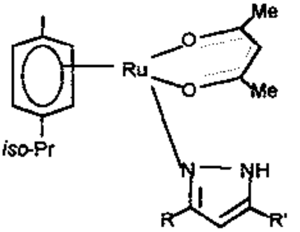


37

The dimeric $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ and pyrazole yield $[(\eta^6\text{-}p\text{-cymene})\ RuCl_2(PzH)]$ [73]. The products react with $[M(Acac)(\eta^4\text{-Tfb})]$ (M = Rh, Ir) and form (**37**). The pyrazolate group in these complexes is in the *exo*-bidentate form (X-ray analysis, M = Rh). The η^6-arene cycle and the other three ligands form the three-legged piano stool conformation around the ruthenium atom. The coordination unit around the rhodium atom is in the form of a distorted square pyramid.

Pyrazole, 3-methylpyrazole and 3,5-dimethylpyrazole can displace the chlorine in $[(\eta^6\text{-}p\text{-cymene})RuCl(Acac)]$ upon reaction with this complex in the presence of potassium hydroxide [74] forming (**38**). If $[(\eta^6\text{-}p\text{-cymene})RuCl(Acac)]$ reacts with silver tetrafluoroborate and pyrazoles, complexes (**39**) are formed. In the case of pyrazole, the intermediate cationic complex $[Ru(\eta^6\text{-}p\text{-cymene})(Acac)(PzH)]Cl$ can be isolated. The cationic complexes, e.g., $[Ru(\eta^6\text{-}p\text{-cymene})Cl(PzH)_2]BF_4$ are prepared from $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\mu\text{-}Cl)]_2$ and excess diazole and sodium tetrafluoroborate. All the chloride ligands in [Ru(η^6-*p*-cymene)Cl(μ-Cl)]$_2$ are removed by addition of silver tetrafluoroborate in a polar solvent. Addition of pyrazole and methanolic potassium hydroxide to the product affords (**40**). It is possible to deprotonate (**40**) further by a second equivalent of potassium hydroxide. The result is [Ru (η^6-*p*-cymene)(Pz)$_2$(PzH)]. In (**40**), according to X-ray analysis, the ruthenium atom has a distorted octahedral coordination. The N-H bond of one of the pyrazole rings participates in the intramolecular hydrogen bond with the pyrazolate ring. Another N-H group is involved in the intermolecular hydrogen bond with the counterion.



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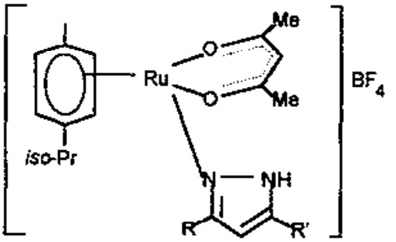
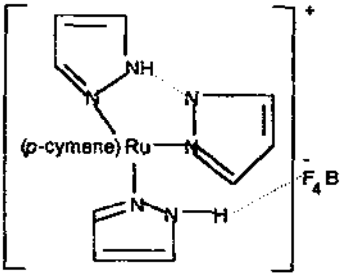


39

The tri-μ-hydroxo complexes [Ru$_2$(η^6-Ar)$_2$(μ-OH)$_3$] react with pyrazole and form the binuclear complexes (**41**, Ar = *p*-MeC$_6$H$_4$CHMe$_2$, C$_6$H$_6$) as tetraphenylborate salts. The structure of the *p*-cymene derivative is shown by the X-ray data. The conformation about the ruthenium(II) atoms is the three-legged piano stool [75]. Pyrazole reacts with [Ru$_2$(η^6-Ar)$_2$(μ-OMe)$_3$]BF$_4$ to yield [Ru2(η^6-Ar)$_2$(μ-Pz) (μ-OMe)$_2$]BF$_4$. A further report on [Ir(*p*-cymene)$_2$Ru$_2$(μ-L)(μ-OH)$_2$]A and [(*p*-cymene)$_2$Ru$_2$(μ-L)$_2$(μ-OH)]A (L = a bridge of the pyrazolic type; A = BPh$_4$, BF$_4$, PF$_6$) has to be mentioned [76].

Complexes [Ru(CO)ClH(PR$_3$)$_3$] (R = Ph, *p*-MeC$_6$H$_4$) react with 1-hydroxymethyl-3,5-dimethylpyrazole to afford [Ru(CO)ClH(3,5-dmPzH)(PR$_3$)$_2$] [77]. The reaction involves substitution of the CH$_2$OH group at the pyrazolic nitrogen atom by hydrogen. Such a reaction course for the triphenylphosphine complex is supported by X-ray data for (**42**).



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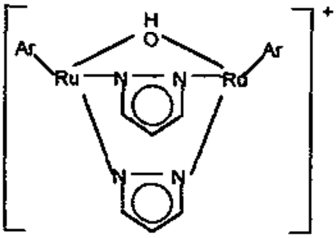
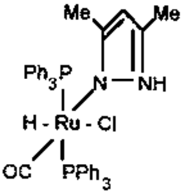


41

The parent analog of (**42**), [RuH(Cl)(CO)(PzH)(PPh$_3$)$_2$], reacts with pyrazole in the presence of methanolic potassium hydroxide to yield the neutral complex (**43**) [78–80]. Protonation of (**43**) with perchloric acid leads to crystallization of the perchlorate salt (**44**). Species (**43**) also reacts with [M(μ-OMe)(η^4-Tfb)$_2$], this being the method of preparation of the heterobinuclear compounds (**45a**, M = Rh, Ir). The diolefin is easily displaced by carbon monoxide (**45b**, M = Rh, Ir). Compounds [H(CO)(PPh$_3$)$_2$Ru(μ-Pz)$_2$Ir(η^4-Tfb)] effectively catalyze hydrogenation of cyclohexene [81,82], different reactions of hydrogen transfer [83,84].



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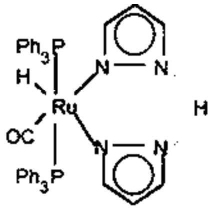
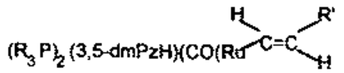


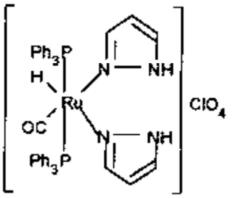
43

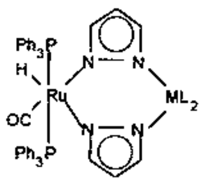
Reactions of [Ru(CO)ClH(3,5-dmPzH){P(p-MeC$_6$H$_4$)$_3$}$_2$] with acetylenes depend substantially on the nature of the solvent. In methylene chloride, reaction with phenylacetylene leads to [Ru(CO)Cl(H$_a$C=CH$_b$Ph)(3,5-dmPzH){P(η^6-p-MeC$_6$H$_4$)$_3$}$_2$] [86]. Reactions of [Ru(CO)Cl(H$_a$C=CH$_b$Ph)(3,5-dmPzH)(PR$_3$)$_2$] (R = Ph, p-tolyl) with monosubstituted acetylenes R′C≡CH (R′ = n-Pr, Bu^t, Ph, CO$_2$Me) in methylene chloride afford simple insertion products of one alkyne molecule to the Ru-H bond,



$$(R_3P)_2(3,5\text{-dmPzH})(CO(Ru)\text{–}C(H){=}C(R')H$$

The alkenyl groups contain two *trans* hydrogen atoms, which agrees with the *cis* insertion of an alkyne. For R = Ph and R′ = Bu^t, X-ray analysis shows that the alkenyl and pyrazolyl ligands have a mutually *trans* disposition, so that insertion is followed by *cis-trans* isomerization. The ruthenium atom is in a distorted octahedral environment. In the complexes with R = R′ = Ph and R = p-tolyl, R′ = Ph, a *cis* disposition of the alkenyl and pyrazolyl ligands is observed. *Trans* disposition is observed in the complexes with R = Ph, R′ = CO$_2$Me and R = p-tolyl, R′ = CO$_2$Me.

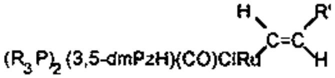




a: L$_2$=Tfb; b: L$_2$=(CO)$_2$

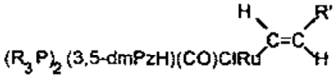
44 **45**

In methylene chloride/ethanol or ethanol under the same conditions an unusual complex (**46**) is formed. X-ray analysis shows formation of a metallocycle containing one nitrogen atom of 3,5-dimethylpyrazole, one phenylalkenyl framework and one oxygen atom of the ether type of ethanol [86]. Compounds



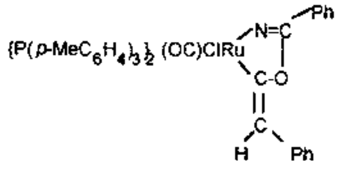
$(R_3P)_2(3{,}5\text{-dmPzH})(CO)ClRu{-}C(H){=}C(R')H$

($R = Ph$, Bu^t; $R = R' = Ph$) produce the alkynyl complexes $[Ru(CO)Cl(C{\equiv}CR')(3{,}5\text{-dmPzH})(PPh_3)_2]$, while



$(R_3P)_2(3{,}5\text{-dmPzH})(CO)ClRu{-}C(H){=}C(R')H$

($R = p$-tolyl, $R' = Ph$) and phenylacetylene form the metallocycle.



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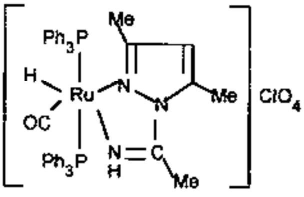
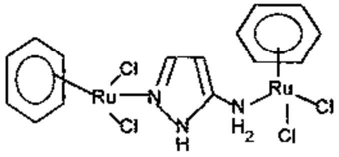


47

Reaction of $[Ru(CO)(H)(NCMe)_2(PPh_3)_2]ClO_4$ with 1-hydroxymethyl-3,5-dimethylpyrazole leads to (**47**), as shown by X-ray analysis [87]. The ruthenium atom has a distorted octahedral coordination. Initially one acetonitrile molecule is substituted by a ligand. The CH_2OH group is split giving $CO + H_2$ and a N-H bond of the pyrazolic type is formed. Finally, insertion of the N-H bond into the $C{\equiv}N$ bond of the coordinated acetonitrile takes place.

Ruthenium species such as $[RuCl_2(CO)_2(\text{solvent})_2]$ undergo cyclometallation reactions with 1-phenylpyrazole to yield $[Ru(\mu\text{-}Cl)(1\text{-}PhPz)(CO)_2]_2$ [88]. The product is dinuclear, cycloruthenated due to the phenyl substituent and contains *cis* coordinated terminal carbonyl and chlorine bridges. It reacts with thallium acetylacetonate to form the mononuclear ruthenium(II) complex $[Ru(Acac)(1\text{-}PhPz)(CO)_2]$. Cleavage of the chloride bridges is also caused by triphenylphosphine, the product being $[RuCl(1\text{-}PhPz)(CO)_2(PPh_3)]_2$. The same type of reaction occurs with 4-methylpyridine leading to $[RuCl(1\text{-}PhPz)(CO)_2(4\text{-}MePy)]$. The cyloruthenated structure is preserved in the monomeric complexes. The latter reveals a *cis* conformation of the dicarbonyl unit.

Complex $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ reacts with 3-aminopyrazole (1:2) without the base to yield $[(\eta^6\text{-}C_6H_6)Cl_2Ru(\mu\text{-}3\text{-}APzH)RuCl_2(\eta^6\text{-}C_6H_6)]$, where the donor sites are the pyridinic atom of the pyrazole ring and the nitrogen atom of the amino group [89]. If the molar ratio used in the reaction is 1:1 complexes (**48**) and (**49**) are obtained. In both of them coordination via the amino nitrogen atoms is realized. Two pyrazolate and two chlorine bridges are formed in (**49**). The structures of (**48**) and (**49**) follow from X-ray analysis.



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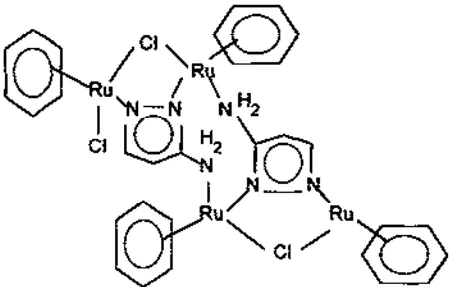
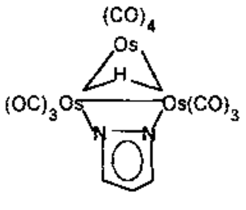


49

Pyrazole and $[Os_3(CO)_{10}(NCMe)_2]$ form two isomeric cluster complexes (**50, 51**) [90,91], corresponding to metallation of both basic nitrogen atoms (the major product having the symmetrical structure **50**) and C,N-metallation (51).



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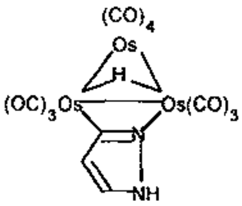
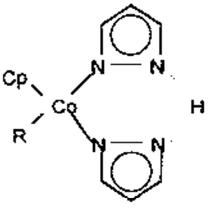


51

2.3. *Derivatives of cobalt, rhodium and iridium*

There are only a few examples of the organometallic derivatives of cobalt. However, the chemistry of rhodium and iridium with respect to pyrazoles has been developed intensively, due mainly to the studies of the Spanish (L.A. Oro and colleagues) and Canadian (S.R. Stobart and colleagues) groups. Owing to progress in this field, pyrazole coordination chemistry has become popular, in particular in view of the versitility of this ligand and its derivatives. Therefore, after a brief account of the cobalt pyrazole compounds, we will proceed to a more systematic review of rhodium and iridium chemistry starting with the dienic and carbonyl rhodium(I) and iridium(I) derivatives, proceeding further to their oxidative addition reactions and then to the numerous cyclopentadienyl derivatives of these two metals.

Pyrazole is able to substitute carbon monoxide in $[(\eta^5\text{-Cp})CoI_2CO]$ to yield $[(\eta^5\text{-Cp})CoI_2(PzH)]$ [92].



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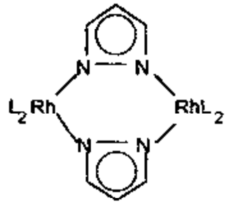


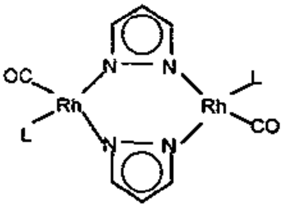
a: L_2=$(CO)_2$; b: L_2=Cod

53

Complexes $[(\eta^5\text{-Cp})CoR(CO)I]$ ($R=CF_3$, C_2F_5, $(CF_3)_2CF$) remove the pyrazolyl ring from the tetrakis(pyrazolyl)borate anion to yield (**52**) [93], diamagnetic and monomeric complexes with hydrogen-bridged pyrazolyl groups.

2.3.1. Derivatives of rhodium(I) and iridium(I) containing ethylene, diene hydrocarbons and carbonyl groups

Reaction of the 3,5-dimethylpyrazolate ion with $[Rh(CO)_2Cl]_2$ gives (**53a**), and $[Rh(\eta^4\text{-Cod})Cl]$ affords (**53b**) [50]. The same neutral complex (**53b**) may be prepared by reaction of $[Rh(\eta^4\text{-Cod})(Bipy)]^+$ or $[Rh(\eta^4\text{-Cod})(PPh_3)_2]^+$ with sodium pyrazolate [94]. Reaction between $[RhCl(\eta^4\text{-diolefin})]_2$ (diolefin = Cod, Nbd, Tfb) and sodium pyrazolate affords a broader range of products of the type (**53b**). $[Rh(\mu\text{-Pz})(C_2H_4)_2]_2$ is obtained in a similar way but in the presence of sodium hydroxide. Bubbling carbon monoxide through $[Rh(\mu\text{-Pz})(\eta^4\text{-diolefin})]_2$ gives non-isolable $[Rh(\mu\text{-Pz})(CO)_2]_2$ (**53a**), and with a phosphorus-donor ligand $[Rh(\mu\text{-Pz})(CO)L]_2$ is formed ($L=P(OPh)_3$, $P(p\text{-ClC}_6H_4)_3$, PPh_3, $P(p\text{-MeC}_6H_4)_3$, $P(p\text{-MeOC}_6H_4)_3$) (**54**). For the triphenylphosphine complex, the *trans* structure (**54**) is shown by X-ray analysis. Each rhodium atom is in a square-planar environment.



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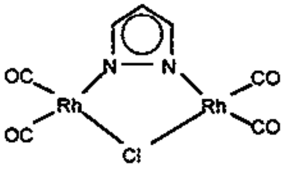
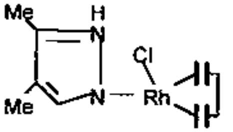


55

However, reaction of $[Rh(\mu\text{-Cl})(CO)_2]_2$ with sodium pyrazolate leads to (**55**) according to the X-ray data [95]. The Rh_2N_2Cl cycle has the conformation of an envelope. The rhodium atom has distorted square-planar coordination. The molecules in the crystalline lattice form one-dimensional stacking units with alternating rhodium atoms in the binuclear units, intermolecularly interacting in a zig-zag chain.

The molecular structure of (**56**) [96] involves a square-planar arrangement around the rhodium atom [97]. The plane of the heterocycle is almost orthogonal to the coordination plane of the central atom. The dicarbonyl analog of (**56**) is completely different (**57**) [98]. The molecular packing in the crystals of (**57**) consists of stacks of square-planar frameworks along one axis [97].



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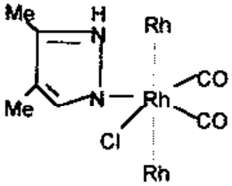
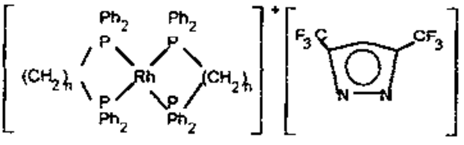


57

Reaction of $[Rh(CO)_2Cl]_2$ with 3,5-bis(trifluoromethyl)pyrazole or 3,5-dimethylpyrazole in a basic medium leads to analogs of (**53a**) which have 3,5-CF_3 and

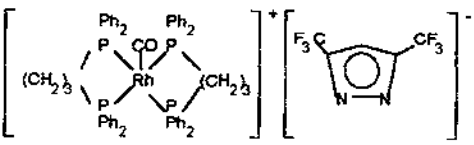
3,5-Me substituents [99]. Reaction with triphenylphosphine does not destroy this cycle but causes substitution of two carbon monoxide ligands and formation of analogs of (**54**). However, reaction of $[Rh(CO)_2(\mu\text{-}3,5\text{-}(CF_3)_2Pz)]_2$ with $Ph_2P(CH_2)_nPPh_3$ forms (**58a**) with $n=2$, (**59**) and (**58b**) with $n=3$. In these complexes an inorganic cycle disappears, and pyrazolyl leaves the first coordination sphere of the rhodium atom. The different nucleophilicities of 3,5-dimethyl- and 3,5-trifluoromethyl-pyrazoles is shown by their reactions with *trans*-$[Rh(CO)Cl(Ph_3P)_2]$. The dimethyl derivative gives the dinuclear species similar to (**54**). The less nucleophilic fluorine derivative gives (**60**), where the pyrazole ligand is monodentate. The fluoro compound similar to (**53a**) may be obtained even in the absence of an alkali. 3,5-Dimethylpyrazole under these conditions forms a four-coordinate volatile 1:1 adduct (**61**). Thus, the 3,5-bis(trifluoromethyl) pyrazolate may function as a monodentate (**60**) or *exo*-bidentate (**53,54**) ligand or serve as a counter anion (**58, 59**).

The rhodium(I) and iridium(I) pyrazolyl-bridged d^8 complexes discussed in this section consist of two bonded square-planar groups comprising C_{2v} symmetry. Compounds $[M_2(\mu\text{-Pz})_2L_4]$ (M = Rh(I), Ir(I); L_4 = (diene)$_2$, $(CO)_4$, $(CO)_2(PR_3)_2$ are characterized by fluorescence and phosphorescence from the singlet and triplet dσpσ excited states.



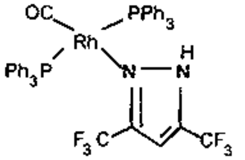
n=2 (a), 3 (b)

58



59

Compound $[Ir(\eta^4\text{-Cod})Cl]_2$ reacts with pyrazole derivatives in the presence of triethylamine to form $[Ir(\eta^4\text{-Cod})(\mu\text{-Pz})]_2$. Bubbling of carbon monoxide yields the complexes $[Ir(CO)_2(\mu\text{-Pz})]_2$ [100]. The electronic absorption and emission spectra of these A-frame complexes display dipole-allowed transitions to emissive singlet and triplet excited states which are stabilized by strong metal-metal bonding. In addition there is a second singlet/triplet pair of excited states which have negligible metal-metal interaction but a substantial metal-to-ligand charge transfer character.



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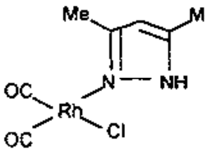


61

The pyrazolyl-bridged iridium dimers are reactive and in this sense may be useful in catalysis, photochemistry and redox chemistry. Their geometric arrangement is such that a six-membered Ir_2N_4 ring (the structure being similar to **53**) is in the boat conformation, metals being disposed at the bow and stern positions (X-ray data [101]). The pyrazolyl bridges draw the metals closer to each other, and the interaction between the filled iridium $d_{z}{}^{2}$ levels increases. These non-bonding interactions lead to comparatively small metal-metal distances and substantial destabilization of the anti-bonding combination corresponding to interaction of the filled orbitals. The Fenske-Hall quantum-chemical calculations [102] show that the d_{xy} orbital of each iridium atom accepts the σ-electron density from the two *cis* disposed carbonyl ligands and two nitrogen atoms of the pyrazolate ligands. The d_x^2-y^2 orbital is stabilized due to the π-back bonding effect directed towards the carbonyls. d_z^2 orbitals interact leading to metal-metal interaction and the destabilization effect due to repulsion of the filled orbitals becomes pronounced. Upon passing from the pyrazolate to the 3-methyl and 3,5-dimethylpyrazolate complexes this kind of interaction increases [103,104], and in some reactions the more sterically crowded pyrazolate complexes appear to be much more reactive that the parent complex containing unsubstituted pyrazolate bridges (e.g., catalytic activity in hydrogenation reactions). Calculations show that this effect follows from the electronic influence of the methyl substitution. However [105], the steric factor changes the predicted trends, sometimes drastically. For instance, the oxidative addition of methyl iodide to 3-methyl and 3,5-dimethylpyrazolate complexes of iridium(I), which is considered in detail later, is much slower than for the parent complex.

Another illustration of the steric effect of the substituents at the pyrazolate ring is shown by X-ray structural determinations for $[M(\eta^4\text{-Cod})(\mu\text{-Pz})]_2$ (M = Rh, Ir), $[Ir(\eta^4\text{-Cod})(\mu\text{-3,5-CF}_3Pz)]_2$ and $[Ir(\eta^4\text{-Cod})(\mu\text{-3-Me-5-CF}_3Pz)]$ [106]. The bis(trifluoromethyl)derivative is remarkably inert due to the crowding effect of the CF_3 groups.

$[Ir(\eta^4\text{-Cod})(\mu\text{-Cl})]_2$ reacts with pyrazoles by Cl-displacement to give $[Ir(\eta^4\text{-Cod})(\mu\text{-L})]_2$, where L represents a wide range of pyrazolates (the unsubstituted derivative, 3-methyl-, 3-trifluoromethyl-5-methyl-, 3-heptafluoro-propyl-5-t-butyl-, 3-trifluoromethyl-5-phenyl-, 3-phenyl-5-methyl- and 3,4,5-tri-methyl-substituted bridging ligands) [107]. For the latter two pyrazolato complexes, the structures follow from X-ray analyses.

The complexes $[M(CO)_2(\mu\text{-L})]_2$ (M = Rh, Ir; L = 3,5-dimethylpyrazolyl, 3,5-diphenylpyrazolyl) react with tertiary phosphines, arsines or phosphites (L′) to give *trans*-$[M(CO)L'(\mu\text{-L})]_2$ [108].

Reactions of *trans*-$[RhCl(CS)(PR_3)_2]$ (R = Ph, Cy) with sodium pyrazolate lead to $[Rh(Pz)(CS)(PR_3)_2]$ [109]. When R = Cy the product is stable. When R = Ph the product is isolated at −50°C, but on warming easily loses one mole of triphenylphosphine and forms $[Rh(\mu\text{-Pz})(CS)(PPh_3)]_2$. Addition of perchloric acid to the latter gives $[Rh(CS)(PzH)(PPh_3)_2]ClO_4$. For $[Rh(3,5\text{-dmPz})(CS)(PPh_3)_2]$ X-ray analysis shows that rhodium is in an approximately square-planar environment, CS and PPh_3 ligands being in the *trans* orientation.

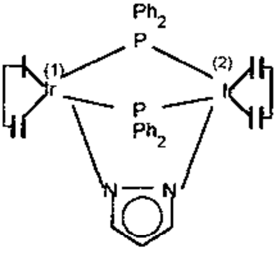
Reaction of $[Rh(CS)(PR_3)_2(Me_2CO)_x]ClO_4$ with pyrazoles (R = Ph, L = PzH, 3,5-dmPzH, 3-mPzH; R = Cy, L = PzH, 3,5-dmPzH) gives $[Rh(CS)(LH)(PR_3)_2]$ ClO_4 [110]. Reaction of these cationic complexes with sodium hydroxide leads to the binuclear complexes $[Rh(\mu\text{-L})(CS)(PPh3)]_2$. The structure of the 3,5-dimethylpyrazolyl derivative is shown by X-ray analysis (it is similar to **54**). Coordination around each rhodium atom is approximately square-planar. The central cycle Rh_2N_4 has the boat conformation. The two pyrazolate rings are nearly perpendicular to each other. $[Rh(\mu\text{-}Pz)(CS)(PPh_3)]_2$ reacts with perchloric acid in the presence of triphenylphosphine forming $[Rh(CS)(PzH)(PPh_3)_2]ClO_4$.

$[Rh\{P(OPh)_3\}_2(Me_2CO)_x]ClO_4$ or $[Rh(Cod)\{P(OPh)_3\}_2]ClO_4$ react with pyrazole and sodium hydroxide to give $[Rh(\mu\text{-}Pz)\{P(OPh)_3\}_2]_2$ [111]. $[RhCl(\eta^4\text{-}Cod)P(OPh)_3]_2$ and pyrazole/sodium hydroxide yield $[Rh(\mu\text{-}Pz)(\eta^4\text{-}Cod)(P(OPh_3)]_2$. The acetone solutions of $[Rh(\mu\text{-}Pz)\{P(OPh_3)_2\}]_2$, $[Rh(\mu\text{-}Pz)(CO)\ P(OPh_3)]_2$ and $[Rh(\mu\text{-}Me_xPz)(\eta^4\text{-}Cod)]_2$ ($x = 2, 1, 0$) catalyze hydroformylation of 1-heptene. Addition of triphenylphosphine to $[Rh(\mu\text{-}Me_xPz)(\eta^4\text{-}Cod)]_2$ causes a decrease in isomerization activity and an increase of activity and selectivity of the major process. $[Rh(\mu\text{-}Me_xPz)(CO)(PPh_3)]_2$ are also the hydroformylation catalysts [112].

Reaction between *trans*-$[Ir(PPh_3)_2(CO)Cl]$ and pyrazolate anion gives rise to the iridium analogs of (**54**, $L = PPh_3$) characterized by X-ray analysis [113,114]. As noted before, each pair of terminal ligands (CO or PPh_3) occupies the mutual *trans* position across the iridium-iridium axis resulting in a disymmetric structure.

For $[Ir(\mu\text{-}3,5\text{-}dmPz)(CO)(PPh_2\{O(CH_2)_2R\})]_2$, the non-bonded diiridium framework is an electron donor, while the acceptor groups are represented in the R substituent of the terminal phosphine ligand. If R is a poor electron acceptor (H, NEt_3), the molecules luminesce from both singlet (^1B) and triplet (^3B) $d\sigma^*p\sigma$ excited states [115,116]. The electronically excited iridium dimers are potential reductants. However if R is the N-bonded pyridine or 4-phenylpyridine, luminescence from both excited states is substantially quenched.

The diiridium(I) dimer, $[Ir(\eta^4\text{-}Cod)(\mu\text{-}Pz)]_2$ on interaction with diphenylphosphine yields a rather unusual product (**62**) [117], as follows from X-ray analysis. Transformation of Cod to $1\text{-}\sigma\text{-}4,5\text{-}\eta\text{-}C_8H_{13}$ takes place, so that formation of (**62**) is likely to proceed via a hydrido-iridium intermediate. It is also highly probable that the iridium(1) atom is in a lower oxidation state than iridium(2), as evidenced by the disposition of the bridging PPh_2 group, so that the proposed formulation of the complex is $[Ir^I(\eta^4\text{-}Cod)(\mu\text{-}Pz)(\mu\text{-}PPh_2)_2Ir^{III}(\eta^3\text{-}C_8H_{13})]$.



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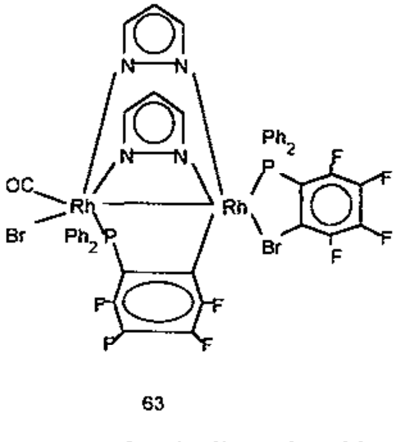


63

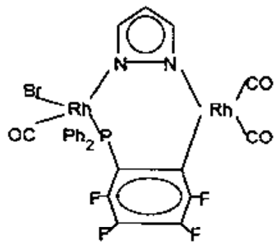
Another example of the unusual reaction course for rhodium-phosphine complexes and pyrazoles arises when diphenyl(*o*-bromotetrafluorophenyl) phosphine is applied as a phosphorus ligand (L) [118,119]. Interaction of $[Rh(Acac)(CO)_2]$ and pyrazole ligands (pyrazole, 3- and 4-methylpyrazoles) leads to a familiar product of the type

(**54**) [110,111]. 3,5-Dimethylpyrazole does not enter into such a reaction. The same compounds are made from $[Rh(\mu\text{-}Pz)(CO)_2]_2$ and phosphine. However, 3,5-dimethylpyrazole again has peculiar properties. The disubstituted compound $[Rh(\mu\text{-}3,5\text{-}dmPz)(CO)L_2]$ is synthesized from [Rh(Acac)(CO)L] with sodium 3,5-dimethylpyrazolate. Thermal reaction of $[Rh(\mu\text{-}Pz)(CO)L]_2$ gives (**63**), implying *ortho*-metallation according to the oxidative addition of the C-Br bond of the phosphine. If the substituted pyrazolate ligands are applied, reaction becomes more selective. The same *ortho*-metallated species is formed from 3-methylpyrazolate analog. 3,5-Dimethylpyrazolate derivative is prepared in an indirect way. Initially $[Rh(\mu\text{-}3,5\text{-}dmPz)(CO)_2]_2$ and phosphine give $[Rh(3,5\text{-}dmPz)_2(CO)_3(L)]$. Thermal reaction produces (**64**). Further reaction of (**64**) with phosphine yields (**63**). This reaction occurs via a two-electron-two-electron oxidative addition. The 3,5-dimethylpyrazolate derivative of (**63**) has two reversible oxidation waves corresponding to the two subsequent one-electron oxidations into Rh(I)-Rh(II) and Rh(II)-Rh(II) cationic complexes. The structure of the pyrazolato- and 3,5-dimethylpyrazolato derivatives of (**63**) is shown by X-ray analysis, indicating that each rhodium atom is octahedrally coordinated.

Trans-$(Ph_3P)_2Ir(CO)(Pz)$ is known and contains a monodentate pyrazolate ligand, as shown by X-ray analysis [120].

Interaction of *trans*-$\{RhCl(CO)(\mu\text{-}Dppm)]_2$ with pyrazolate ligands readily yields the so-called A-frame complexes (**65a-c**) [121]. Complexes (**65b,c**) react with silver perchlorate to yield the perchlorate salts (**65e,f**). Alternatively, these complexes may be prepared by addition of the pyrazolate ligand to $[Rh(CO)(Me_2CO)(\mu\text{-}Dppm)]_2(ClO_4)_2$. Complexes (**65d,g**) may also be prepared by this route. The tetraphenylborate complexes (**65h-j**) are synthesized by addition of sodium tetraphenylborate to the corresponding perchlorate salts. X-ray analysis of (**65f**) shows that each rhodium atom has a square-planar coordination unit.

Addition of *n*-butyllithium to the pyrazole derivatives produces pyrazolate anions. When these interact with $[Rh_2(\mu\text{-}EE')_2(CO)_2(\mu\text{-}Cl)]PF_6$, complexes (**66**) result [122]. Upon addition of one equivalent of t-butylisocyanide to the carbonyl complexes, one carbonyl group is substituted by the Bu^tNC ligand. With two equivalents, both carbon monoxide ligands are replaced. X-ray data exist for $E = E' = As$, $L = L' = CO$, $R^1 = Me$, $R^2 = H$.



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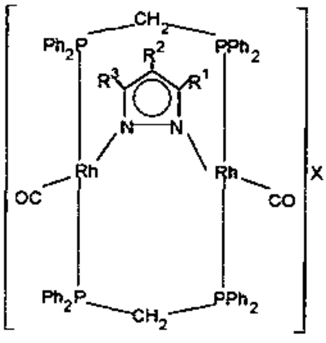
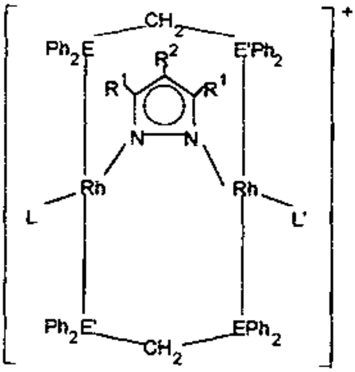


65

	R^1	R^2	R^3	X
a	H	H	H	Cl
b	Me	Cl	H	Cl
c	Me	H	Me	Cl
d	H	H	H	ClO_4
e	Me	H	H	ClO_4
f	Me	H	Me	ClO_4
g	H	Br	H	ClO_4
h	H	H	H	BPh_4
i	Me	H	Me	BPh_4
j	H	Br	H	BPh_4

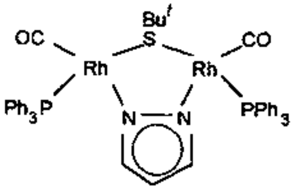
Complexes (**66**) are characterized by two oxidation waves. Each oxidation process is one-electron transfer [123]. The first oxidation process represents conversion of the parent Rh_2^{2+} species to a Rh_2^{3+} form. The second stage involves the conversion $Rh_2^{3+} \rightarrow Rh_2^{4+}$. It appears impossible to isolate the Rh_2^{4+} product. The paramagnetic mixed-valence complexes Rh(I)-Rh(II) can be isolated. According to the ESR data, the unpaired electron spin is delocalized over the two rhodium atoms. In this case the molecular cation appears to be doubly charged [124].

The product of reaction of [Rh(Acac)(η^4-Cod)] and [RhCl(PzH)(η^4-Cod)] is [Rh_2(μ-Pz)(μ-Cl)(η^4-Cod$)_2$]. It reacts with $KSBu^t$ to give the mixed-bridged dirhodium complex [Rh_2(μ-Pz)(μ-SBu^t)(η^4-Cod$)_2$] [125]. Bubbling of carbon monoxide results in substitution of the Cod ligands and formation of [Rh_2(μ-Pz) (μ-SBu^t)$(CO)_4$]. Further addition of triphenylphosphine, trimethylphosphite or triphenylphosphite (L) yields *cis*-[Rh_2(μ-Pz)(μ-SBu^t)$(CO)_2L_2$]. The proposed *cis* arrangement is confirmed by X-ray analysis of (**67**). The two metal atoms are characterized by distorted square-planar coordination. The ring Rh_2N_2S adopts a distorted envelope conformation, flapping at the sulfur atom.



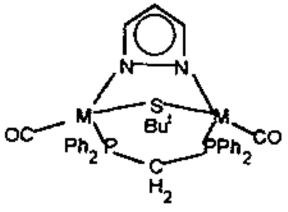
E = E' = P; E = P, E' = As; E = E' =As;
L=CO, L'=t-BuNC; L=L'=t-BuNC; R^1=R^2=H,Me;

66



67

Addition of Dppm to (**67**) yields (**68**). The iridium complexes with one pyrazolato and 3,5-dimethylpyrazolato bridges are similarly prepared [126].



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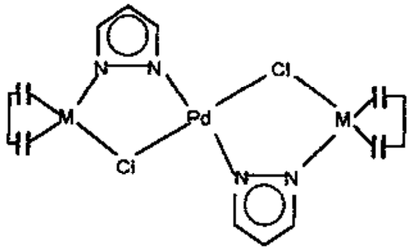
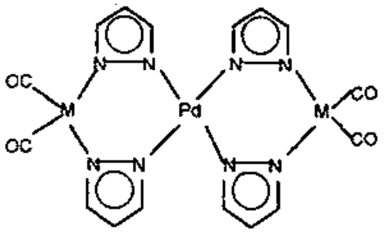


69

Complex [$PdCl_2(PzH)_2$] reacts with [M(Acac)(η^4-diolefin)] (M = Rh, diolefin = Cod, Tfb; M = Ir, diolefin = Cod) to produce (**69**), the trinuclear complex with a *trans* arrangement [127]. Bubbling of carbon monoxide through (**69**, M = Rh) yields the tetracarbonyl derivative with the *cis* dicarbonyl disposition. Addition of potassium pyrazolate to (**69**) affords [(η^4-diolefin)M(μ-Pz)$_2$Pd(μ-Pz)$_2$M(η^4-diolefin)]. Both Cod-complexes undergo diolefin substitution to give (**70**). X-Ray analysis of the rhodium complex shows that all three metals are in the square-planar coordination mode. The complex (**70**, M = Rh) reacts with triphenylphosphine to form [(Ph$_3$P)(OC)Rh(μ-Pz)$_2$Pd(μ-Pz)$_2$Rh(CO)(PPh$_3$)], the six-membered cyclic core showing high stability.

Reaction of (**69**) (M = Rh, diolefin = Cod) with KSBu^t forms the mixed-bridged trinuclear complex [Pd{Rh(μ-Pz)(μ-SBu^t)(η^4-Cod)}$_2$] [128]. Bubbling of carbon monoxide gives a *cis* dicarbonyl complex (**71**). All three metals form a linear chain. Each metal is characterized by square-planar coordination (X-ray analysis). Reaction of (**71**) with triphenylphosphine or trimethylphosphite (L) affords [Pd{Rh(μ-Pz)(μ-SBu^t)(CO)L}$_2$].



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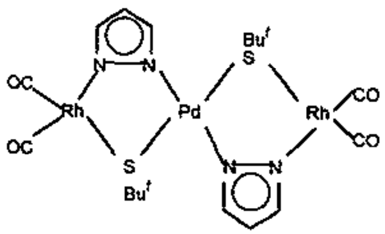
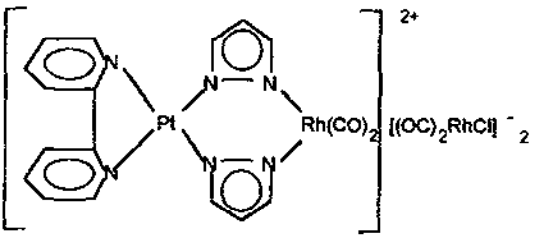


71

[Rh(CO)$_2$Cl]$_2$ reacts with [(Bipy)PtPz$_2$] leading to an ionic adduct of composition 2:1 (**72**) [129].

Reaction of [Ph$_3$PAuL] (L = 3,5-dmPzH, 4-NO$_2$PzH) with [Rh(CO)$_2$Cl]$_2$ fails to produce a heteronuclear complex but affords a binuclear rhodium(I) compound [(OC)$_2$Rh(μ-Pz)$_2$] [130].



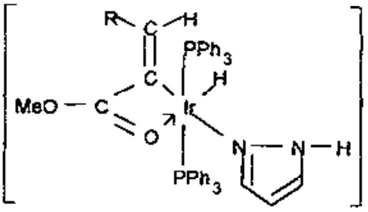
72

A more detailed study [131] showed that reaction of [RhL$_2$(Me$_2$CO)$_x$]ClO$_4$ (L = Cod, (CO)$_2$, (CO)(PPh$_3$)) with [AuPzPPh$_3$] leads to [RhL$_2$(μ-Pz)]$_2$ and [Ph$_3$PAu(μ-Pz)AuPPh$_3$]ClO$_4$. Reaction of [Rh(η^4-Cod)(Ph$_3$P)(Me$_2$CO)]ClO$_4$ with [AuPzPPh$_3$] gives [Rh(η^4-Cod)(μ-Pz)]$_2$ and [AuClPPh$_3$]. [PtPz$_2$(Dpe)], however, plays the role of a bidentate ligand leading to a heterobinuclear platinum-rhodium complex. This happens upon interaction of [Rh(η^4-Cod)(Me$_2$CO)$_x$]ClO$_4$ with [PtPz$_2$(Dpe)] when [(η^4-Cod)Rh(μ-Pz)$_2$Pt(Dpe)]ClO$_4$ is formed. Bubbling of carbon monoxide leads to [(OC)$_2$Rh (μ-Pz)$_2$Pt(Dpe)]ClO$_4$. Addition of triphenylphosphine or triphenylphosphite (L) to the product gives [(CO)LRh(μ-Pz)$_2$Pt(Dpe)]ClO$_4$.

Nevertheless, the heterobimetallic complexes of rhodium(I) with gold(I) exist and are prepared upon reaction of $[Rh(CS)(PR_3)_2(Me_2CO)_x]ClO_4$ with $[AuPz(PR_3)]$ (R = Ph, Cy) [109]. The products have the composition $[(PR_3)_2(CS)Rh(\mu\text{-}Pz)Au(PPh_3)]ClO_4$.

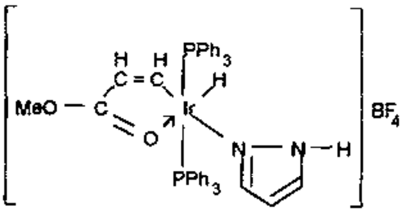
Before we proceed to oxidative addition reactions leading to the higher valent rhodium and iridium derivatives we describe a recent study on a series of iridium(III) compounds based on the starting complex $[IrH_2(Me_2CO)(PzH)(PPh_3)_2]BF_4$ [132,133]. This parent complex is obtained as a result of a ready and selective substitution reaction of acetone in $[IrH_2(Me_2CO)_2(PPh_3)_2]BF_4$ with pyrazole.

The remaining acetone ligand in this product can be displaced by alkynes. Thus, reaction with $HC{\equiv}CCO_2Me$ gives rise to a mixture of two isomers (**73a**, **74**). The structure of the hydride-vinyl derivative (**73a**) is shown by X-ray analysis and corresponds to a distorted octahedral coordination around the iridium atom. Reaction with acetylenedicarboxylic dimethyl ester gives (**73b**).



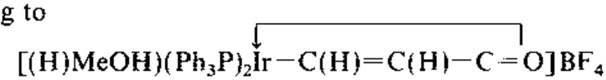
a: R=H; b: R=CO$_2$Me

73



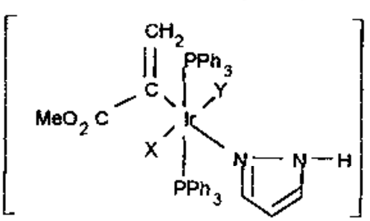
74

For complex (**73a**) the reactivity trends have been studied in depth [132]. With $[Rh(\mu\text{-}OMe)(\eta^4\text{-}Cod)]_2$, the acidic NH proton of (**73a**) enters into a redistribution reaction leading to



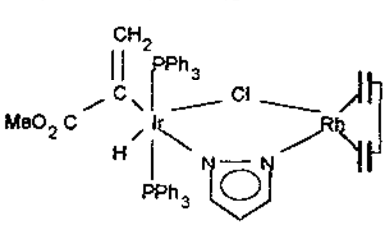
$$[(H)MeOH)(Ph_3P)_2Ir{-}C(H){=}C(H){-}C{=}O]BF_4$$

and $[Rh(\mu\text{-}Pz)(\eta^4\text{-}Cod)]_2$. In the course of this reaction the vinyl ligand isomerizes, and transformation of the four-membered ring containing an exocylic C=C bond is transformed into a five-membered ring with an endocyclic C=C bond takes place. The methanol ligand is easily displaced by trimethyl phosphite and carbon monoxide. The second reaction type studied is displacement of the weakly coordinated C=O group in (**73a**) from the iridium atom by Lewis bases, trimethyl phosphite and chloride ion in sodium chloride (**75a,b**). (**75b**) is the classical reagent for preparation of the heterobinuclear complex (**76**) using $[Rh(\mu\text{-}OMe)(\eta^4\text{-}Cod)]_2$.



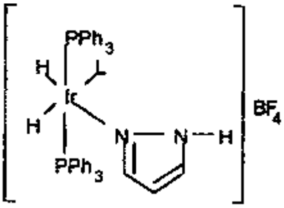
a: X=P(OMe)$_3$, Y=H; b: X=H, Y=Cl

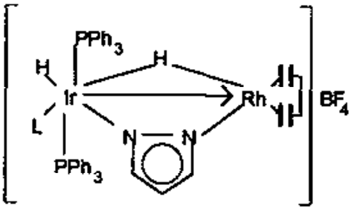
75



76

The acetone molecule in the parent complex is easily replaced by carbon monoxide, trimethylphosphite or acetonitrile leading to (**77**) [133]. The chain of transformations can be continued, since the products (**77**) contain an acidic NH proton able to react with $[Rh(\mu\text{-}OMe)(\eta^4\text{-diolefin})_2]$ (diolefin = Cod, Tfb) to form the heterobinuclear complexes (**78**) where a dative Ir→Rh bond is possible because the rhodium atom is coordinatively unsaturated.

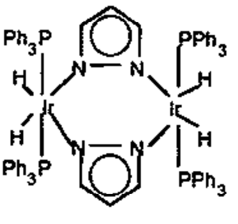




L = CO, P(OMe)$_3$, MeCN

77 78

The starting acetone complex reacts with potassium hydroxide to form (**79**). The pyrazolate bridge in this complex is readily split by tetrafluoroboric acid leading to a mononuclear five-coordinate species (**80**).



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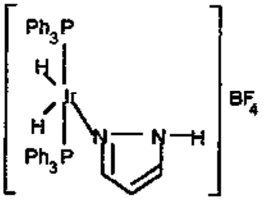


80

Pyrazole displaces the acetone molecule in the starting complex to yield $[IrH_2(PzH)_2(PPh_3)_2]BF_4$ with *cis* disposition of the pyrazoles. A proton in one of the pyrazole ligands can be eliminated using potassium hydroxide giving rise to the pyrazole-pyrazolate species with the bridging proton common for two heterocyclic nuclei, $[IrH_2(Pz)(PzH)(PPh_3)_2]$. The latter reacts with $[M(\mu\text{-}OMe)(\eta^4\text{-diolefin})_2]$ (M = Rh, diolefin = Cod, Tfb; M = Ir, diolefin = Tfb) to form analogs of (**78**), where L = H. The hydrogen-bridged complex reacts with hydrochloric acid to give $[IrH_2Cl(PzH)(PPh_3)_2]$ which contains an intramolecular N-H···Cl hydrogen bond. This is the source of the chloro-bridged dinuclear compounds $[H_2(PPh_3)_2Ir(\mu\text{-}Cl)(\mu\text{-}Pz)M(\eta^4\text{-diolefin})]$ (M = Rh, Ir; diolefin = Cod, Tfb). However, the N-H···Cl bonded complex is used to prepare $[IrH_2(\mu\text{-}OCOMe)(PzH)]$ as a result of reaction with silver acetate. The product contains an intramolecular N-H···O hydrogen bond and reacts with $[M(\mu\text{-}OMe)(\eta^4\text{-diolefin})_2]$ to form $[H_2(PPh_3)_2Ir(\mu\text{-}\eta^2\text{-}O_2CMe)(\mu\text{-}Pz)M(\eta^4\text{-diolefin})]$.

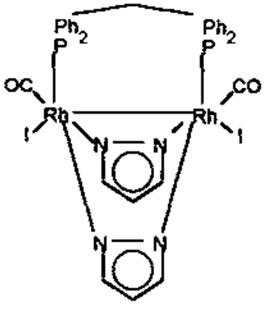
2.3.2. *Oxidative-addition reactions of rhodium(I) and iridium(I) carbonyls and dienyls*

$[Rh(\mu\text{-}Pz)(CO)_2]_2$ oxidatively adds molecular iodine to yield $[Rh(\mu\text{-}Pz)I_2(CO)_2]_2$ [134]. The process occurs through intermediate formulation of $[Rh(\mu\text{-}Pz)I(CO)_2]_2$.

It is regarded as a two-center oxidative addition with competing metal-metal bond formation. Upon transformation from the monohalogen- to the dihalogen-containing complex, a dinuclear rhodium(III) complex is finally formed and the rhodium-rhodium bond breaks. The monoiodo compound reacts with bis(diphenylphosphino)methane giving rise to the displacement of carbon monoxide and formation of (**81**) (X-ray analysis). The binuclear complex is triply bridged by two pyrazolate and one diphosphorus ligands. Each rhodium atom is octahedrally coordinated.

Two one-electron oxidation processes for the methylene chloride solutions of $[Ir(\eta^4\text{-Cod})(\mu\text{-Pz})]_2$ lead first to $[Ir(\eta^4\text{-Cod})(\mu\text{-Pz})]_2^+$ and then to the $Ir^{II}Ir^{II}$ compound [135]. This process is chemically reversible because of the fast addition of solvent molecules or supporting ions to the ends of the doubly oxidized binuclear unit $[Ir(\mu\text{-Pz})(Cod)]_2X_2$. In acetonitrile only the product of monooxidation is formed. In excess benzyltriethylammonium chloride (supporting electrolyte), a binuclear iridium(II) compound is obtained: $[Ir(\mu\text{-Pz})(\eta^4\text{-Cod})Cl]_2$.

$[Ir(CO)_2(\mu\text{-Pz})]_2$ oxidatively adds methylene iodide to yield (**82**) [136]. The diiridium adduct readily undergoes thermal oxidative isomerization to the diiridium methylene complex (**83**). Kinetic data for the process of formation of (**82**) indicate a concerted pathway through a high-energy transition state for the substrate approach above and below the iridium···iridium axis due to the steric effects of the bulky μ-pyrazolate frameworks [137].



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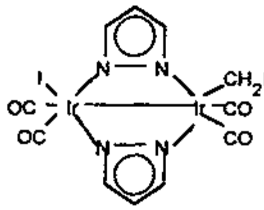

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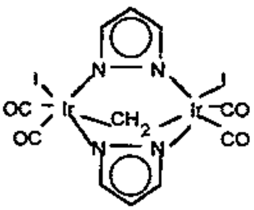
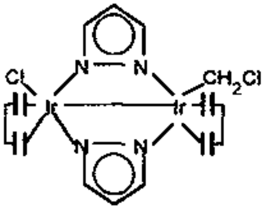


83

Solutions of $[Ir(\mu\text{-Pz})(\eta^4\text{-Cod})]_2$ in methylene chloride or dichloroethane are stable enough in the absence of light. However, under visible radiation there are substantial spectral changes indicating the formation of the products of photoreduction, (**84**) for methylene chloride and (**85**) for dichloroethane [104,138].

The tetracarbonyl dimer $[Ir(CO)_2(\mu\text{-Pz})]_2$ reacts with $CHRI_2$ (R = H, Me) to yield a mixture of products [139]. In particular, for methylene iodide the main products are $[Ir_2(CO)_4(\mu\text{-Pz})_2I(CH_2I)]$, $[Ir_2(CO)_4(\mu\text{-Pz})_2(\mu\text{-CH}_2)I_2]$ and $[Ir(CO)_2(\mu\text{-Pz})I]_2$. The latter is the major product for oxidative addition of $CHMeI_2$ and 1,2-$C_2H_4I_2$. Oxidative addition of 1,3-$C_3H_6I_2$ gives exclusively $[Ir_2(CO)_4(\mu\text{-Pz})_2I(CH_2CH_2CH_2I)]$.



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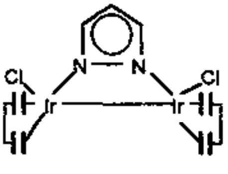
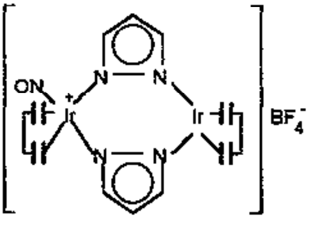


85

Reaction of $[Ir(\eta^4\text{-Cod})(\mu\text{-Pz})]_2$ with nitrosyl tetrafluoroborate yields (**86**), the cationic diiridium nitrosyl complex (X-ray analysis) [140]. The 4-methyl-pyrazolato complex reveals the same type of behavior, while 3,5-dimethylpyrazolato derivatives give a different kind of product. Oxidation of $[Ir(\eta^4\text{-Cod})(\mu\text{-3,5-dmPz})]_2$ with nitrosyl hexafluoroborate or hexafluorophosphate leads to (**87**). According to ESR data, one-electron oxidation to the radical-cation species follows the elimination of NO. The d^8d^7 complex is formed, where the electron spin is delocalized over both iridium centers. Bubbling of hydrogen chloride through (**86**) affords (**88**), characterized as the tetrafluoroborate salt of the nitrosyl-bridged diiridium(III) cation [141]. The cationic complex (**86**) interacts with iodine to yield the analog of (**88**). The structure of (**87**) implies formation of a d^8d^6 species or oxidation only at one iridium center from Ir(I) to Ir(III). However, the two-center oxidation of $[Ir(cod)(\mu\text{-Pz})]_2$ by iodine leads to the oxidative addition products containing the iridium-iridium bond where the d^7d^7 diiridium(II) configuration is achieved. The complex (**88**) is also regular with two non-bonded iridium(III) centers.

The other illustration of oxidative addition to iridium(I) complexes is the interaction of $[Ir(\eta^4\text{-Cod})(\mu\text{-Pz})]_2$ with alkynes, $RC{\equiv}CR'$ ($R=R'=CF_3$, CO_2Me; $R=H$, $R'=CO_2Me$) [142]. In the addition products (**89**) both iridium centers are formally d^7 or Ir(II). In the case with $R=H$, CO_2Me; $R'=CO_2Me$, X-ray analysis implies that the adjacent iridium(II) centers are spin-paired owing to iridium-iridium bond formation.



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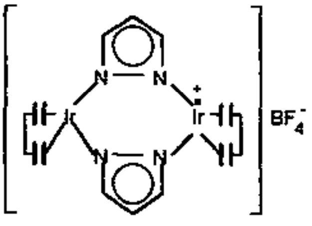
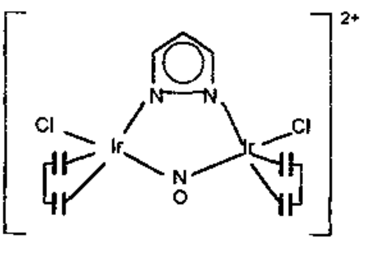


87

The product of the reaction of $[Ir(\eta^4\text{-Cod})Cl]_2$ with pyrazole in triethylamine, $[Ir(\eta^4\text{-Cod})(\mu\text{-Pz})]_2$, contains the bridging framework in a boat conformation. The iridium-iridium distance is unususally short, although the 16-electron metal centers are non-bonded. Addition of hexafluorobut-2-yne or o-chloranil to the products gives complexes of the type (**89**) ($R'=CF_3$ for the acetylenic derivative) [143]. The additional 1,2-dimetallosubstituted ethylenic bridge provides a cap for the pyrazolyl-bridged boat conformation. The result is a tricyclic core and iridium-iridium bonding. By contrast, molecular bromine and chlorine or methyl iodide form oxidative addition products without the metal-metal bond but with a slightly contracted Ir···Ir distance (e.g., **90**). Reaction of (**90**) with methylmagnesium bromide leads to [Ir(η^4-Cod)(Me)(μ-Pz)]$_2$.



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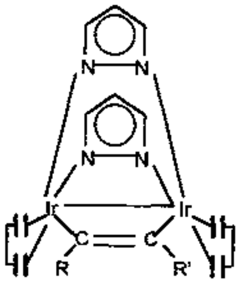
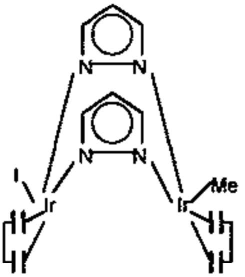


89

The phosphine-, phosphite- and arsine-substituted complexes *trans*-[M(CO)(μ-3,5-dmPz)L]$_2$ (M = Rh, Ir; L = PhMe$_2$P, Ph$_2$MeP, (PhO)$_3$P, PhMe$_2$As) react with iodine or 1,2-diodoethane to give the binuclear metal(II) compounds, [M(Cod)LI(μ-3,5-dmPz)]$_2$ [108]. The structure of (**91**) is shown by X-ray analysis and contains a nearly linear I-Ir-Ir-I chain as well as an Ir-Ir bond. Reactions of [M(CO)L(μ-Pz)$_2$](M = Rh, Pz = 3,5-dmPz, L = Ph$_3$P; pz = 3,5-Ph$_2$Pz, L = Ph$_2$MeP, PhMe$_2$As) with 1,2-diiodomethane proceed differently. The products do not contain terminally bonded carbonyl groups. Thus, X-ray analysis of (**92**) shows a loss of the carbonyl group and the existence of a bridging carbonyl. This species contains 16 electrons. It is five-coordinate, formally Rh(III), where the central metal is approximately in a square-pyramidal coordination.



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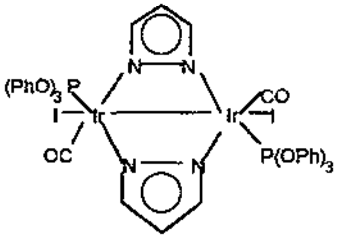
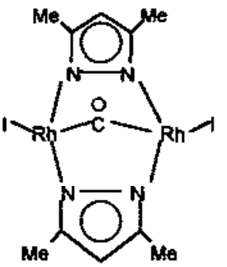


91

Oxidation of [Ir(CO)(μ-Pz)(PPh$_3$)]$_2$ by X$_2$ (X = H, Br, I) affords the diamagnetic iridium(II) complexes [Ir(CO)(μ-Pz)(PPh$_3$)X]$_2$ with an iridium-iridium bond. The corresponding reaction with chlorine in addition involves substitution in position 4 of each pyrazolyl ring with formation of (**89**) (X-ray analysis) [113,114]. Reaction of [Ir(CO)(μ-Pz)(PPh$_3$)]$_2$ with methyl iodide gives a 1:1 asymmetric addition product [(PPh$_3$)(CO)Ir(Me)(μ-Pz)$_2$Ir(I) (CO)(PPh$_3$)]. Interaction with 2-methylbutyliodide proceeds similarly.



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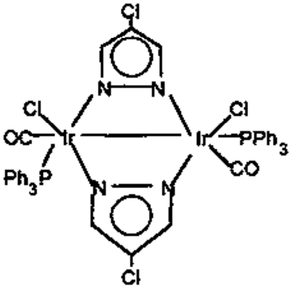
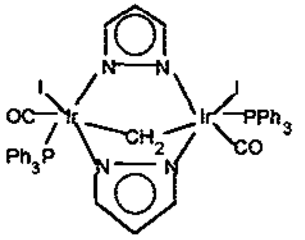
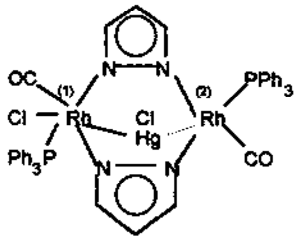


93

Methylene iodide adds to the diiridium(I) complex $[Ir(CO)(PPh_3)(\mu\text{-}Pz)]_2$ to yield a metal-metal adduct of composition $[Ir_2(CO)_2(PPh_3)_2(\mu\text{-}Pz)_2(CH_2I)(I)]$, which undergoes thermal oxidative isomerization to the diiridium methylene species (**94**). According to X-ray analysis the iridium atoms are not bonded and iodine atoms occupy the apical sites [136].



94



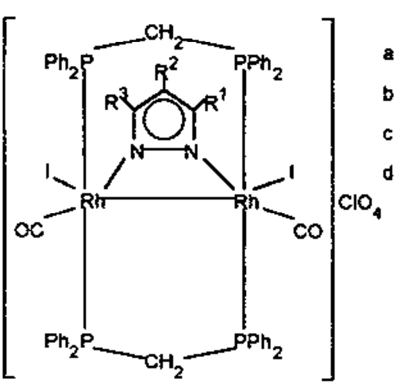
95

The diiridium complex $[Ir(CO)(PPh_3)(\mu\text{-}Pz)]_2$ forms a diiridacyclobutene adduct of the type (**89**) with $MeO_2CC{\equiv}CCO_2Me$, while the same reaction with $F_3CC{\equiv}CCF_3$ leads to alkyne polymerization owing to dissociation of triphenylphosphine [142].

Addition of mercury(II) chloride to $[Rh(\mu\text{-}Pz)(CO)(PPh_3)]_2$ gives (**95**), as confirmed by X-ray analysis [144]. Oxidative addition of $HgCl_2$ to Rh(I) and simultaneous Lewis acid-base bonding between the HgCl fragment and Rh(2) takes place. As a result, an asymmetrical bridge Rh-Hg←Rh is formed. The Rh(1) atom is characterized by an approximate octahedral coordination, while the Rh(2) atom has a square-pyramidal geometry, the apical position being occupied by the mercury atom.

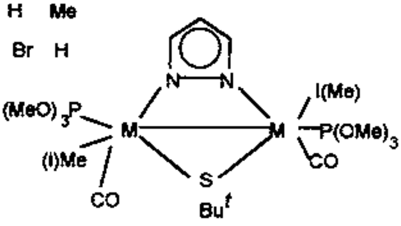
Oxidation of the perchlorate complexes (**65d-g**) by molecular iodine leads to 1:1 adducts (**96a-d**) [121]. X-ray analysis of (**96c**) confirms the existence of the rhodium-rhodium bond. Each rhodium atom is octahedrally coordinated.

Addition of iodine to (**66**) proceeds similarly [122]. However, addition of bromine is accompanied by bromination of 3,5-dimethylpyrazolyl and pyrazolyl ligands at position 4 which is blocked in 4-methylpyrazolyl. The product of electrochemical reduction of (**96**, $R^1=R^3=Me$, $R^2=Br$) is (**65**, $R^1=R^3=Me$, $R^2=Br$, $X=ClO_4$). The terminal positions near the rhodium atoms are obviously occupied by the bromine but not iodine atoms. Chlorination proceeds similarly to bromination.

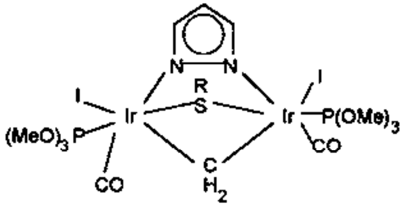


	R^1	R^2	R^3
a	H	H	H
b	Me	H	H
c	Me	H	Me
d	H	Br	H

96


97

Methyl iodide oxidatively adds to $[M_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ (M = Rh, Ir) to give (**97**) [145], this being a typical case of a one-electron oxidative addition at each metal center followed by the competing formation of a metal-metal bond. Addition of diiodomethane to the iridium compound finally yields (**98**) through the stage of normal oxidative addition of iodine to one iridium center and the CH_2I group to another. In (**98**) both iridium atoms are characterized by a distorted octahedral coordination (X-ray analysis). In turn, reaction of $[Ir_2(\mu\text{-dmPz})(\mu\text{-SBu}^t)(CO)_2\{P(OMe)_3\}_2]$ with methylene iodide gives $[Ir_2(\mu\text{-dmPz})(\mu\text{-SBu}^t)(CH_2I)I(CO)_2\{P(OMe)_3\}_2]$, where the two phosphorus ligands are disposed *trans* to the other groups.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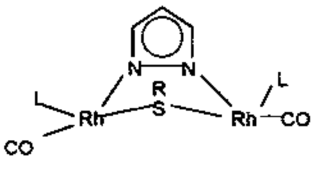
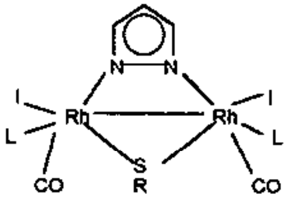
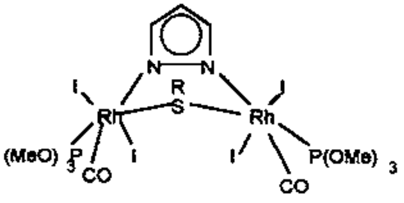

L=CO, P(OMe)$_3$

99

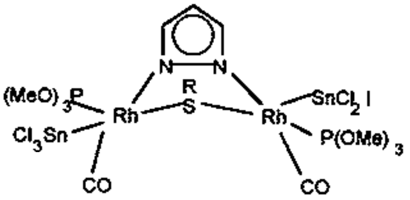
Co-condensation of the two mononuclear complexes $[RhCl(PzH)(\mu^4\text{-Cod})]$ and $[Rh(Acac)(\mu^4\text{-Cod})]$ together with KSPh gives rise to $[Rh_2(\mu\text{-Pz})(\mu\text{-SPh})(\mu^4\text{-Cod})_2]$ [146]. Bubbling carbon monoxide through the product in the presence of triphenylphosphine gives $[Rh_2(\mu\text{-Pz})(\mu\text{-SPh})(CO)_2(PPh_3)_2]$ which has a *cis* configuration. The latter undergoes oxidative addition with iodine or mercury(II) chloride.


L=CO, P(OMe)$_3$

100


101

Complex (**99**), ($R = Bu^t$, $L = P(OMe)_3$) adds iodine in consecutive steps first giving (**100**) and then (**101**). Tetracarbonyl complex (**99**, $L = CO$) synthesized by bubbling carbon monoxide through $[Rh_2(\mu\text{-}Pz)(\mu\text{-}SBu^t)]$ reacts with iodine yielding (**100**, $L = CO$). The symmetrical diiridium(II) compound (**100**, $L = P(OMe)_3$) reacts with $SnCl_2$ forming (**102**). This reaction involves insertion of $SnCl_2$ into the rhodium-iodine bond and formation of the trihalostannyl derivative. Addition of mercury dichloride to (**99**, $L = P(OMe)_3$) gives (**103**), the result of oxidative addition of $HgCl_2$ to one rhodium center with simultaneous Lewis acid-base bonding between mercury and the other rhodium site. Reaction of (**103**) with iodine gives (104) with two different rhodium(III) centers. The two-electron addition to the rhodium center is followed by the splitting of the mercury-rhodium bond.



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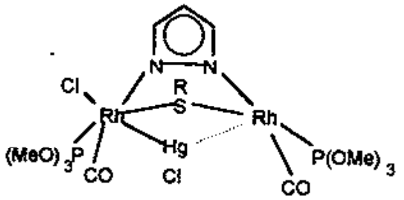
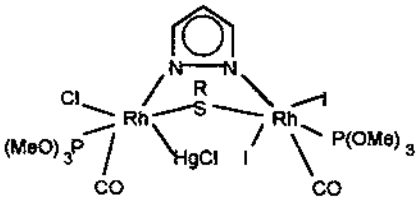


103

Complexes (**68**) react with iodine to form (**105a**) as the typical iridium(II)-iridium(II) symmetrical complexes [126]. The terminal iodide ligands are readily replaceable by means of the silver salts. Thus, (**105a**) upon reaction with silver nitrate produces (**105b**). Complex (**68**, $M = Ir$, $Pz = \mu$-3,5-dmPz) reacts with mercury dichloride to form (**106**), traditionally interpreted as the product of oxidative addition to one iridium atom and simultaneous Lewis acid-base interaction with another. The rhodium μ-pyrazolato derivative is prepared in a similar way. Unexpectedly, the iridium μ-pyrazolato analog in similar conditions produces mercury(I) chloride and forms the dinuclear complex (**107**).

$[IrCl(PzH)(\eta^4\text{-}Cod)]$ reacts with $[Ir(Acac)(\mu^4\text{-}Cod)]$ to yield $[Ir_2(\mu\text{-}Pz)(\mu\text{-}Cl)(\eta^4\text{-}Cod)_2]$. Further reaction with $KSBu^t$ gives $[Ir_2(\mu\text{-}Pz)(\mu\text{-}SBu^t)(\eta^4\text{-}Cod)_2]$, after which bubbling of carbon monoxide and addition of trimethylphosphite produces *cis*-$[Ir_2(\mu\text{-}Pz)(\mu\text{-}SBu^t)(CO_2\{P(OMe)_3\}_2]$ [147]. This product adds molecular iodine in two steps moving from the iridium(I)-iridium(I) complex to iridium(II)-iridium(II) complex with a metal-metal bond and to the iridium(III)-iridium(III) complex in which the metals are non-bonded. The same product reacts with dimethyl acetylene carboxylate to form (**108**) with the symmetrically coordinated *cis* dimetallated olefin. A one-electron oxidative addition to each metal center is followed by iridium-iridium bond formation (X-ray analysis). Coordination around each iridium atom is strongly distorted octahedral. Complex (**108**) undergoes further oxidative addition with iodine or mercury(II) chloride to yield iridium(III)-iridium(III) derivatives (**109**) without the iridium-iridium bond (X-ray analysis for $X = I$). The coordination around each iridium atom this time is a slightly distorted octahedron.



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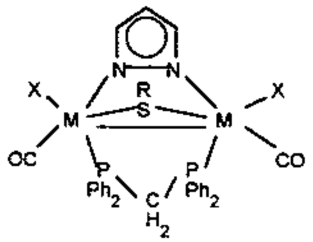
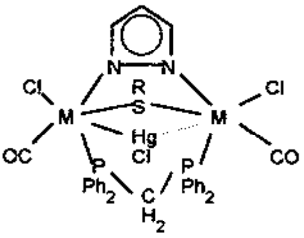


X = I (a), ONO$_2$ (b)

105

Reaction of [(η^6-p-cymene)RuCl(μ-Pz)Rh(CO)$_2$] with iodine in methanol, ethanol, n- and i-propanol containing excess sodium iodide or sodium tetrafluoroborate affords the alkoxycarbonyl complexes [(η^6-p-cymene)Ru(μ-I)$_2$I(μ-Pz)Rh(COOR)I(CO)] (R = Me, Et, n- and i-Pr) [148]. Bromine under the same conditions produces the methoxycarbonyl complex [(η^6-p-cymene)Ru(μ-Br)$_2$(μ-4-BrPz)Rh(Br)(COOMe)(CO)], where bromination usually takes place at position 4 of the heteroring.



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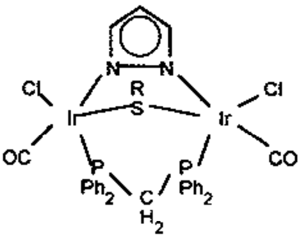
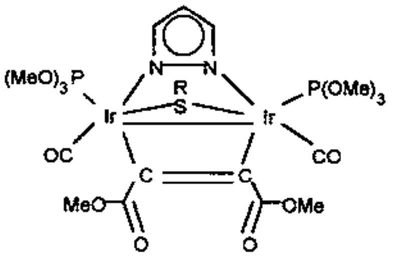


107

Complex (**71**) readily reacts with molecular iodine to give rhodium(III) derivatives [PdRh$_2$(μ-Pz)$_2$(μ-SBu^t)$_2$ I$_2$(CO)$_4$] [128].



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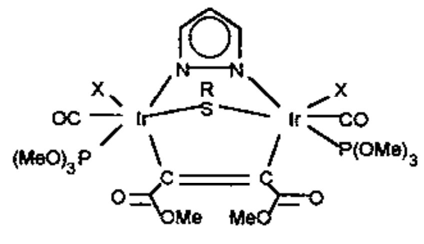
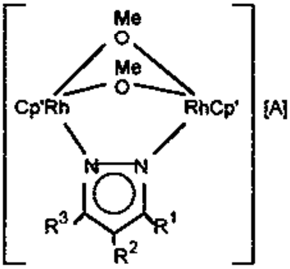


X = Cl, I

109

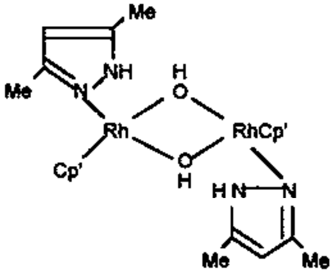
2.3.3. Cyclopentadienyl derivatives of rhodium and iridium

The tri-μ-hydroxo-complex [Rh$_2$(η^5-Cp')$_2$(μ-OH)$_3$]ClO$_4$ reacts with pyrazoles in methanol to give binuclear complexes (**110**) [149], in case of (**110b**) this is shown by X-ray data. An alternative route for the synthesis of (**110b,d,f**) is reaction of the solvated complexes $[Rh(\eta^5\text{-}Cp')(Me_2CO)_3]A_2$ ($A = ClO_4$, BF_4) with pyrazole and triethylamine in acetone followed by methanol. Addition of perchloric acid to (**110c**) affords (**111**) with coordinated neutral pyrazole ligands. This reaction can be reversed by potassium hydroxide in methanol. The structure of the cationic complex (**111**) is fully confirmed by X-ray analysis. $[Rh_2(\eta^5\text{-}Cp')_2(\mu\text{-}OH)_3]ClO_4$ with pyrazoles in acetone forms the μ-hydroxo-complexes (**112a,b**). The existence of two *exo*-bidentate pyrazolate ligands per bridging hydroxo-group is shown by X-ray analysis of (**112a**). In contrast to the triple bridge formation, 3,5-dimethylpyrazole and 3(5)-methyl-5(3)-phenylpyrazole form the double-bridged complexes $[Rh(\eta^5\text{-}Cp')(PzH)(\mu\text{-}OH)]_2(BF_4)_2$.



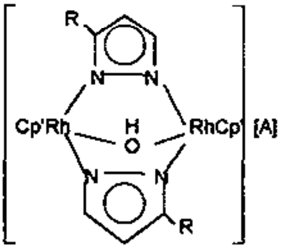
	R1	R2	R3	A
a:	H	H	H	ClO_4
b:	Me	H	H	ClO_4
c:	Me	H	Me	ClO_4
d:	Me	H	Br	ClO_4
e:	H	Br	H	ClO_4
f:	Me	H	H	BF_4

110



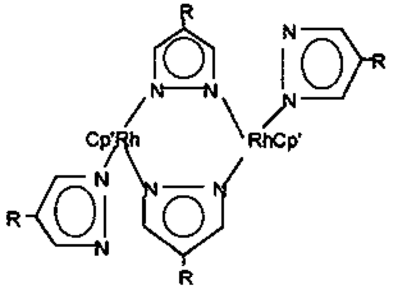
111

Reaction of $[Rh_2(\eta^5\text{-}Cp')_2(\mu\text{-}OH)_3]ClO_4$ with excess pyrazole or 4-bromopyrazole and potassium hydroxide forms the neutral complexes (**113a,b**) [150]. For (**113a**) X-ray analysis shows that each rhodium atom is octahedrally coordinated. Compound (**113b**) and perchloric acid yield (**114**), where the monodentate pyrazolate ligand is protonated. Potassium hydroxide regenerates (**113b**). Cationic complexes of the type (**114**) can alternatively be produced from $[Rh_2(\eta^5\text{-}Cp')_2(\mu\text{-}OH)_3]ClO_4$ and perchloric acid in the presence of excess pyrazole, 4-bromopyrazole, 3-methylpyrazole or 3,5-dimethylpyrazole.



a: R=H, A=ClO_4; b: R=Me, A=ClO_4
c: R=H, A=BF_4

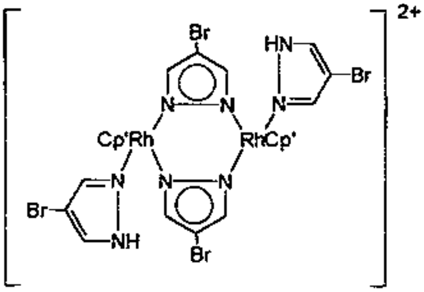
112



a: R = H; b: Br

113

Interaction of $[Rh_2(\eta^5\text{-}Cp')_2(\mu\text{-}OH)_3]BF_4$ with diphenylphosphine in the presence of pyrazole yields a mixture of compounds, among them (**115**) and $[Rh_2(\eta^5\text{-}Cp')_2(\mu\text{-}Pz)(\mu\text{-}PPh_2)_2]BF_4$ and $[Rh_2(\eta^5\text{-}Cp')_2(\mu\text{-}Pz)(\mu\text{-}OH)(\mu\text{-}PPh_2)]BF_4$ [151]. The structure of (**115**) (X-ray analysis). The same reaction in the presence of 3-methyl-, 3,5-dimethyl- or 3(5)-bromo-5(3)-methylpyrazoles affords μ-hydroxo-μ-phosphido compounds, $[Rh_2(\eta^5\text{-}Cp')_2(\mu\text{-}Pz)(\mu\text{-}PPh_2)(\mu\text{-}OH)]\,BF_4$.



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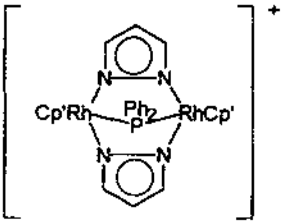
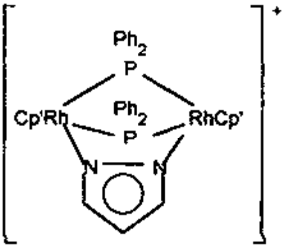
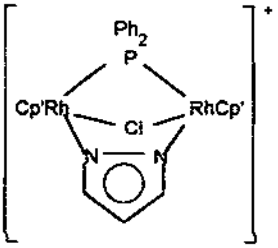


115

In turn, reactions of the di-μ-methoxo complexes (**110**) with diphenylphosphine lead to $[Rh_2(\eta^5\text{-}Cp')_2(\mu\text{-}Pz)(\mu\text{-}PPh_2)(\mu\text{-}OH)]BF_4$ and $[Rh_2\ (\eta^5\text{-}Cp')_2(\mu\text{-}Pz)(\mu\text{-}PPh_2)_2]BF_4$ for pyrazolate, 3-methylpyrazolate and 3(5)-bromo-5(3)-methylpyrazolate ligands [152]. In the latter series of complexes (**116**) X-ray analysis shows that the coordination mode is a pseudo-octahedral three-legged piano stool with no metal–metal interaction. In the chlorinated solvents and upon interaction with hydrochloric acid, the μ-hydroxo-complexes form the mono-μ-chloro derivatives $[Rh_2(\eta^5\text{-}Cp')_2(\mu\text{-}Pz)(\mu\text{-}PPh_2)(\mu\text{-}Cl)]BF_4$. The structure of the pyrazole derivative (**117**) is similar to that of (**116**). Reaction of $[Rh_2(\eta^5\text{-}Cp')_2(\mu\text{-}OH)_3]BF_4$ with pyrazole and diphenylphosphine yields $[Rh_2(\eta^5\text{-}Cp')_2(\mu\text{-}Pz)(\mu\text{-}PPh_2)(\mu\text{-}H)]BF_4$ containing a metal–metal bond.

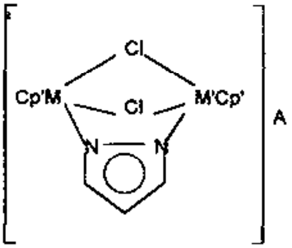


116



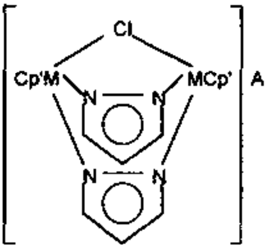
117

Reaction of $[Rh_2(\eta^5\text{-}Cp')_2(\mu\text{-}Pz)(\mu\text{-}OMe)_2]ClO_4$ with hydrogen chloride is the route for the preparation of the triple-bridged complex (**118a**) [153] through the isolable complex (**119a**). Further reaction of (**118a**) with hydrogen chloride yields (**120a**) and (**121**). Complexes (**118b,c**) are the result of reaction of the mononuclear neutral species (**120a,b**) with the acetylacetonate complexes $[Rh(\eta^5\text{-}Cp')(\mu\text{-}Acac)]_2(BF_4)_2$ or $[Ir(\eta^5\text{-}Cp')(Acac)(MeOH)]BF_4$. Interaction of the acetylacetonato-rhodium or -iridium complex and the corresponding chloride complex of the other metal leads to the heterobimetallic complex (**118d**). The triple-bridged complexes (**122b,c**) are prepared by reaction of $[Ir(\eta^5\text{-}Cp')(Me_2CO)_3](BF_4)_2$ with pyrazoles and potassium hydroxides or triethylamine. Reaction of [Ir(η^5-Cp')(MeOH)$_3$](ClO$_4$)$_2$ with pyrazoles and potassium hydroxide yields (**123**). However [Ir(η^5-Cp')(Me$_2$CO)$_3$](BF$_4$)$_2$ and 3,5-dimethylpyrazole with triethylamine produce the di-μ-hydroxo complex [Ir(η^5-Cp')(3,5-dmPzH)(μ-OH)$_2$](BF$_4$)$_2$. In turn, [Ir$_2$(η^5-Cp')$_2$(μ-OH)$_3$]BF$_4$·H$_2$O and pyrazole give [Ir$_2$(η^5-Cp')$_2$(μ-Pz)$_2$(μ-OH)]BF$_4$, which is inert towards substitution by carbon monoxide and t-butyl-isocyanide. The di-μ-hydridorhodium analog, in contrast, reacts with these ligands to give [Rh$_2$(η^5-Cp')(μ-Pz)L$_2$]BF$_4$ (L=Bu^{t}NC, CO). Both isonitrile ligands are terminal. In the dicarbonyl, however, there is one bridging and one terminal carbonyl. A dynamic carbonyl exchange takes place.



a: M=M'=Rh, A=ClO$_4$; b: A=BF$_4$;
c: M=M'=Ir, A=BF$_4$;
d: M=Rh, M'=Ir, A=BF$_4$

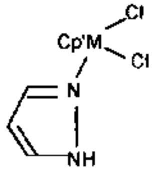
118



a: M=Rh, A=ClO$_4$; b: M=Rh, A=BF$_4$;
c: M=Ir, A=BF$_4$; d: M=Ir, A=BPh$_4$

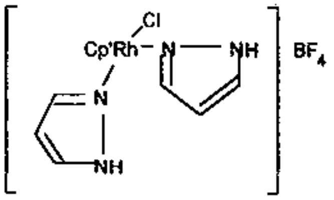
119

The complex [Rh(η^5-Cp')Cl(μ-Pz)]$_2$ is characterized by a chair conformation of the core pyrazolyl-bridged unit. This complex upon reaction with silver tetrafluoroborate yields [Rh$_2$(η^5-Cp')$_2$(μ-Pz)$_2$(μ-Cl)]BF$_4$, where the cation core is in the boat conformation [154]. Reduction of the latter by Zn/Cu yields [Rh (η^5-Cp')(μ-Pz)]$_2$. The Cp-analog is prepared from [Rh(η^5-Cp)Cl(μ-Pz)]$_2$ and posseses a deeply folded boat conformation (X-ray analysis).



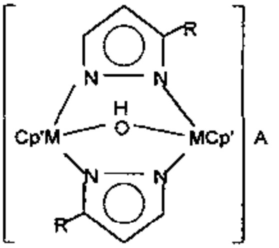
a: M=Rh; b: M=Ir

120



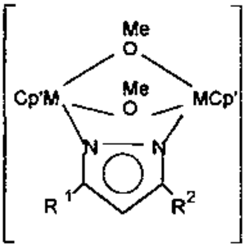
121

The dinuclear complex (**124**) is the product of the interaction of [Rh(η^5-Cp')Cl$_2$(PzH)] and [Rh(Acac)(η^4-Tfb)] and is characterized by the ionic dissociation of one of the chloride ligands [155]. According to X-ray analysis, rhodium(III) is in the pseudo-octahedral, while rhodium(I) in the square-planar environment. X-ray analysis also indicates a twist conformation of the chelate ring which has C_2 symmetry. Carbon monoxide completely substitutes the dienic ligand. [Rh(η^5-Cp')(Acac)Cl] and [Rh(η^4-L)(PzH)$_2$]ClO$_4$ (L=Tfb, Cod) in the presence of potassium hydroxide yield the neutral complexes [(η^5-Cp')ClRh(μ-Pz)$_2$RhL]. 3,5-Dimethylpyrazole behaves differently in these circumstances. The products are $[Rh(\eta^4\text{-}L)(\mu\text{-}3,5\text{-}dmPz)]_2$ and $[Rh(\mu^5\text{-}Cp')$ $(Acac)(3,5\text{-}dmPzH)]ClO_4$. $[Rh(\eta^5\text{-}Cp')(Acac)(Pz)]$ and $[Rh(\eta^4\text{-}Tfb)(PzH)_2]ClO_4$ together with potassium hydroxide form $[(\eta^5\text{-}Cp')(Pz)Rh(\eta\text{-}Pz)_2Rh(\eta^4\text{-}Tfb)]$ containing two types of pyrazolate group, terminal and bridging. $[(\eta^5\text{-}Cp')ClRh(\mu\text{-}Pz)_2RhL']$ readily enters the reaction of carbonylation followed by a *cis* dicarbonyl square-planar rhodium(I) complex, where the chlorine atom is coordinated only to the rhodium(III) atom. t-Butylisocyanide or triphenylphosphine partially substitute the carbonyl groups and form $[(\eta^5\text{-}Cp')ClRh(\mu\text{-}Pz)_2Rh(CO)(NCBu^t)]$ and $[(\eta^5\text{-}Cp')ClRh(\mu\text{-}Pz)_2Rh(CO)(PPh_3)]$. Reaction of $[(\eta^5\text{-}Cp')ClRh(\mu\text{-}Pz)_2Rh(\eta^4\text{-}Tfb)]$ with silver perchlorate and the nitrogen-donor ligand, pyridine, acetonitrile or pyrazole (L) yield the cationic complexes $[(\eta^5\text{-}Cp')LRh(\mu\text{-}Pz)_2Rh(\eta^4\text{-}Tfb)]ClO_4$. Carbonylation of the pyridine complex affords $[(\eta^5\text{-}Cp')(Py)Rh(\mu\text{-}Pz)_2Rh(CO)_2]ClO_4$. Finally, $[Rh(\eta^5\text{-}Cp')Cl_2$ $(PzH)]$ and $[Rh(\eta^4\text{-}Tfb)(Me_2CO)_x]$ give rise to the cationic complex $[(\eta^5\text{-}Cp')(PzH)Rh(\mu\text{-}Cl)_2Rh(\eta^4\text{-}Tfb)]ClO_4$, containing two bridging chlorides.



a: M=Rh, A=ClO$_4$,,R=H
b: M=Ir,A=BF$_4$, ,R=H; c: R=Me

122



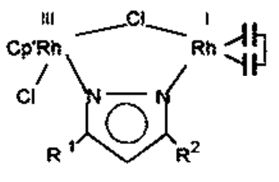
	M	A	R^1	R^2
a:	Rh	ClO$_4$	H	H
b:	Ir	ClO$_4$	H	H
c:	Ir	BF$_4$	H	H
d:	Ir	ClO$_4$	Me	H
e:	Ir	ClO$_4$	Me	Me
f	Ir	BF$_4$	Me	H
g:	Ir	BF$_4$	Me	Me

123

The neutral dinuclear complexes $[(\eta^5\text{-}Cp')ClM(\mu\text{-}Pz)_2M'(\eta^4\text{-}Cod)]$ (M = Rh, M′ = Ir; M = Ir, M′ = Rh; M = M′ = Ir) (**125**) appear to result from reaction of $[M(\eta^5\text{-}Cp')(Acac)Cl]$ (M = Rh, Ir) and $[M'(\eta^4\text{-}Cod)(PzH)_2]BF_4$ in the presence of potassium hydroxide [156,157]. An attempt to obtain the similar ruthenium-containing heteronuclear complex using $[Ru(\eta^6\text{-}p\text{-}cymene)(Acac)Cl]$ and $[Rh$ $(\eta^4\text{-}Cod)(PzH)_2]BF_4$ in the presence of potassium hydroxide leads to a mixture of the major products, $[Ru(\eta^6\text{-}p\text{-}cymene)(Acac)(PzH)]^+$ and $[Rh(\eta^4\text{-}Cod)(\mu\text{-}Pz)]_2$. The desired product $[(\eta^6\text{-}p\text{-}cymene)ClRu(\mu\text{-}Pz)_2Rh(\eta^4\text{-}Cod)]$ is present but in a minor quantity. Two compounds $[(\eta^6\text{-}p\text{-}cymene)ClRu(\mu\text{-}Pz)_2M(\eta^4\text{-}Cod)]$ (M = Rh, Ir) result from interaction of $[Ru(\eta^6\text{-}p\text{-}cymene)$ $Cl(PzH)_2]BF_4$ and $[M(Acac)(\eta^4\text{-}Cod)]$ (M = Rh, Ir) together with potassium hydroxide. Both structures (**126**) satisfy the spectral data. The carbonylation reactions run smoothly and afford $[LClM(\mu\text{-}Pz)_2M'(CO)_2]$ (L = Cp′, M′ = Rh, M′ = Ir; M = Ir, M′ = Rh; L = *p*-cymene, M = Ru, M′ = Rh; M = Ru, M′ = Ir). The ruthenium-iridium (but not the ruthenium-rhodium) complex is a mixture of isomers (**126**) in rapid equilibrium. The chlorine atom in $[Rh(\eta^5\text{-}Cp')Cl(\mu\text{-}Pz)_2Rh(CO)_2]$ is displaced by iodide or azide while reacting with sodium iodide or azide. Complex (**126**) enters into the same type of reaction with sodium bromide and iodide. The products are presented as the left isomer (**126**),

$$[(\eta^6\text{-}p\text{-cymene})\overline{\text{Ru}(\mu\text{-Pz})_2\text{Ir}}\text{X(CO)}_2](\text{X}=\text{Br,I})$$

with a *cis* dicarbonyl disposition.



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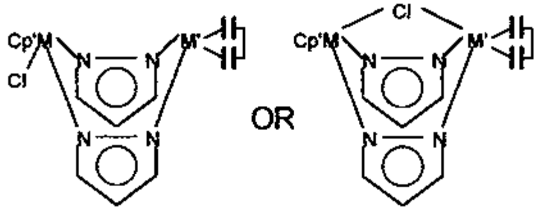
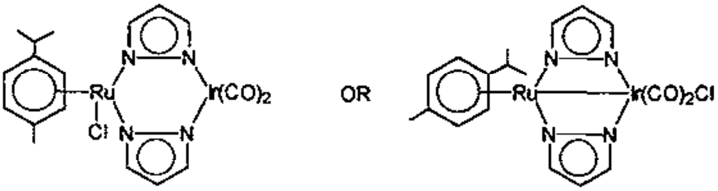


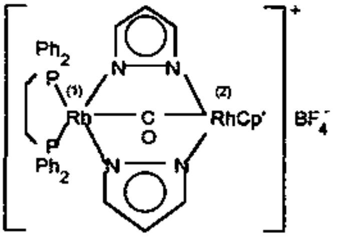
125

$[(\eta^5\text{-Cp}')\text{ClRh}(\mu\text{-Pz})_2\text{Rh(CO)}_2]$, 1,3-bis(diphenylphosphino)propane and sodium tetrafluoroborate react to give (**127**) according to the X-ray structural data [158]. Atom Rh(1) is five-coordinate and has distorted tetragonal pyramidal geometry. Atom Rh(2) is described by a three-legged piano-stool geometry and the bridging carbonyl behaves as a ketonic carbonyl.



126

$[(\eta^5\text{-Cp}')\text{ClIr}(\mu\text{-Pz})\text{Ir(CO)}_2]$ reacts with diphosphines 1,3-bis(diphenylphosphino)propane or *cis*-1,2-bis(diphenylphosphino)ethylene (L-L) and sodium tetraphenylborate to yield $[(\eta^5\text{-Cp})'\text{Ir}(\mu\text{-Pz})_2(\mu\text{-CO})\text{Ir(CO)(L-L)}]\text{BPh}_4$. For the second of the diphosphines, X-ray analysis shows that in (**128**) the coordination about iridium(1) is approximately octahedral and that around iridium(2) is a pseudo-octahedral three-legged piano stool. The iridium(1) atom is formally regarded as a six-coordinate 18-electron site, so that upon formation of (**128**) the oxidation state of this atom changes from +I to +III.



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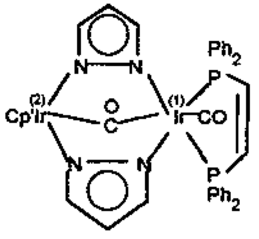
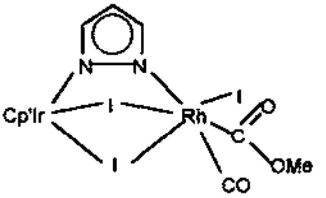


128

The dimeric $[\text{M}(\eta^5\text{-Cp}')\text{Cl}_2]_2$ and pyrazole give $[\text{M}(\eta^5\text{-Cp}')\text{Cl}_2(\text{PzH})]$ (M = Rh, Ir) [73]. The products react with $[\text{M}'(\text{Acac})(\eta^4\text{-Tfb})]$ (M' = Rh, Ir) and form [(η^5-

Cp′)MCl$_2$(μ-Pz)M′(η^4-Tfb)] (M = Ir, M′ = Rh; M = Rh, M′ = Ir). Another mode of preparation of the heterobimetallic Ir^{III}-Rh^I complexes is interaction of [(η^5-Cp′)IrCl(Acac)] and [Rh(η^4-Tfb)(PzH)$_2$] in the presence of potassium hydroxide followed by [(η^5-Cp′)IrCl(μ-Pz)$_2$Rh(η^4-Tfb)]. The pyrazolate group in these complexes is the *exo*-bidentate ligand, while the role of the chlorine atom is not as obvious. As stated before, the corresponding ruthenium-rhodium complex (**37**) contains a triple bridge. Meanwhile, in the isoelectronic [(η^5-Cp′)ClRh(μ-Cl)(μ-Pz)Rh(η^4-Tfb)] there is a double bridge.

The heterovalent Rh^{III}-Rh^I complex [(η^5-Cp′)ClRh(μ-Pz)$_2$Rh(CO)$_2$] reacts with 1,3-bis(diphenylphosphino)propane forming the triple-bridged [(η^5-Cp′)ClRh(μ-Pz)$_2$(μ-CO)Rh(dppp)]$^+$ [159]. *Cis*-1,2-bis(diphenylphosphino) ethylene and sodium tetrafluoroborate under the same conditions form [(η^5-Cp′)Rh(μ-Pz)$_2$(μ-CO)Rh(CO)(Dppen)]BF$_4$. Upon dissolution in acetone, chloroform and methylene chloride, the complex [(η^5-Cp′)Rh(μ-Pz)$_2$(μ-CO)Rh(Dppen)]BF$_4$ is slowly formed. Reactions of the starting complex with monodentate tertiary phosphines, triphenylphosphine and tricyclo-hexylphosphine, in the presence of sodium tetrafluoroborate form the cationic species [(η^5-Cp′)Rh(μ-Pz)$_2$(μ-CO)Rh(CO)L]BF$_4$ (L = PPh$_3$, PCy$_3$) alongside the neutral complexes [(η^5-Cp′)ClRh(μ-Pz)$_2$Rh(CO)L]. Other diphosphines, bis(diphenylphosphino)methane or 1,4-bis(diphenylphosphino) butane or diarsine 1,2-bis(diphenylarsino)ethane (L-L) react with the starting complex and NaBF$_4$ similarly to Dppen forming [(η^5-Cp′)Rh(μ-Pz)$_2$(μ-CO)Rh(L-L)]BF$_4$.



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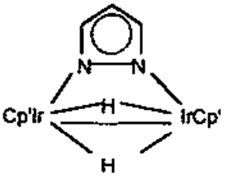
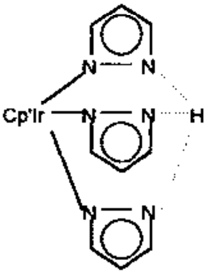


130

Reaction of [(η^5-Cp′)ClM(μ-Pz)$_2$Rh(CO)$_2$] (M = Rh, Ir) with excess iodine in methanol or ethanol and sodium tetrafluoroborate or iodide gives alkoxycarbonyl complexes [(η^5-Cp′)M(μ-Pz)(μ-I)$_2$RhI(CO$_2$R)(CO)] (M = Rh, R = Me, Et; M = Ir, R = Me). X-ray analysis of the iridium complex (**129**) shows pseudo-octahedral coordination of the iridium and rhodium atoms. The triply-hydroxo-bridged [Ir$_2$(η^5-Cp′)(μ-OH)$_3$]OH·nH$_2$O and pyrazole, 3-methylpyrazole or 3,5-dimethylpyrazole



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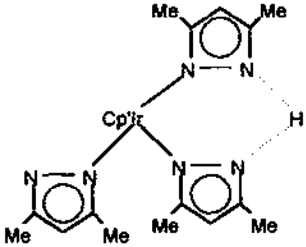
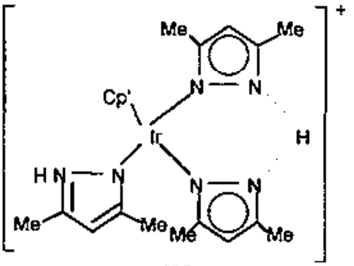


132

form (**130**) [160] (X-ray analysis). The products appear to be inert towards carbon monoxide, t-butylisocyanide or pyrazole under mild reaction conditions.

Reaction of $[Ir(\eta^5\text{-}Cp')Cl_2(\mu\text{-}Cl)_2]$ and pyrazole in the presence of potassium hydroxide leads to complex (**131**) characterized by the dynamic hydrogen bond between three pyrazolic nuclei [161]. 3,5-Dimethylpyrazole in identical conditions produces (**132**) where two pyrazolic nuclei share a proton and one is unprotonated as confirmed by X-ray analysis. Addition of tetrafluoroboric acid to (**132**) yields (133), where the second proton is bonded to the non-chelated ligand. Addition of the third proton causes formation of $[Ir(\eta^5\text{-}Cp')(PzH)_3](BF_4)_2$.



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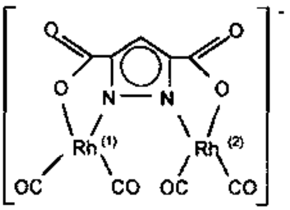
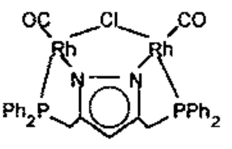


134

Reaction of $[M(\mu\text{-}Cl)(\eta^4\text{-}Cod)]_2$ or $[M(\mu\text{-}OMe)(\eta^4\text{-}Cod)]_2$ (M = Rh, Ir) with pyrazole-3,5-dicarboxylic acid (L) in the presence of different tetraalkyl-ammonium hydroxides, R_4NOH (R = Me, n-Pr, n-Bu) gives $R_4N[M_2(\eta^4\text{-}Cod)_2L]$ [162]. Bubbling of carbon monoxide leads to a ready displacement of the dienic ligand and formation of the $[M_2(CO)_4L]^-$ anions. Structural analysis of one of these anions, $Bu_4N[Rh_2(CO)_4L]$, shows that it exists as layers of anions (**134**) separated by a layer of the tetra-n-butylammonium cation. The intermolecular rhodium-rhodium interactions are substantial, although the chain of metal-metal network is not developed but interrupted. Thus, contrary to expectations, no stacking takes place. Two of the four carbonyl groups are readily displaced by triphenylphosphine resulting in $[Rh(CO)_2L_2(PPh_3)_2]$ with the phosphine ligands *trans* disposed relative to the nitrogen atoms. The iridium analog has not so far been isolated. Upon electrochemical oxidation of $[M_2(CO)_4L]^-$, three cyclic voltammetric waves are interpreted as transformation to a red neutral species, $[M_2(CO)_4L]$, followed by solvation of the latter and formation of the cation $[M_2(CO)_4L]^+$. The red species is considered as a mixed valence Rh(II)-Rh(I) compound, its diamagnetism explained either as a strong spin-spin coupling or a rhodium(II)-rhodium(II) bond between two adjacent molecules. The iridium product of oxidation is $(R_4N)_{0.5}[Ir_2(CO)_4L]$ where both iridium atoms are equivalent, take part in stacking and have the formal oxidation state of 0.5. These complexes possess semi-conducting properties.

The metal transfer method based on the bis(diphenylphosphino)pyrazole complex of nickel(II) allows to afford (**135**) [163]. Reaction of bis(diphenylphosphino)pyrazole and $[M(\eta^4\text{-}diene)_2]BF_4$ (M = Rh, diene = Nbd, Cod; M = Ir, diene = Cod) and then triethylamine yields (**136**). The dienic ligands are readily substituted by carbon monoxide giving (**137**) with the *cis* dicarbonyl disposition. Compound (**137**) with $LiPPh_2$ gives (**138**) with an enhanced electron density on the metal atoms.



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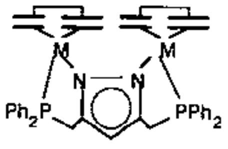
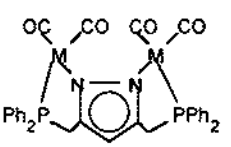


136

Compound (**136**) reacts with acetyl chloride, a reversible oxidative addition on one of the metals taking place [164,165]. The product (**139**) is the rhodium(I)-rhodium(III) complex. Acetyl chloride and methyl iodide react in the same manner with (**138**, M = Rh). For (**139**, RX = MeI) X-ray analysis shows that coordination around rhodium(III) is approximately octahedral, the methyl and iodo ligands being mutually *trans*. The rhodium(I) atom is approximately square planar. Treatment of (**139**, RX = MeCOCl) with additional acetyl chloride gives (**140**, M = Rh, RX = MeCOCl), another reversible oxidative addition step.



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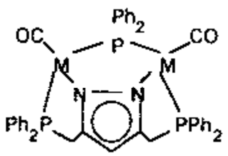
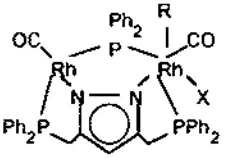
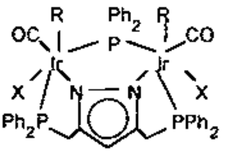


138

2,5-Bis(pyrazol-1′-yl)-1,4-dihydroxybenzene (H_2LL) reacting with di-μ-chloro-dichlorobis(pentamethylcyclopentadienyl)dirhodium(III) or -diiridium(III) forms $[M_2(\eta^5\text{-Cp}')_2Cl_4(H_2LL)]$ (M = Rh, Ir) [166]. The structure of the rhodium complex is shown by X-ray analysis. The rhodium atoms are in a slightly distorted octahedral coordination with a three-legged piano stool environment. There is no rhodium-rhodium bond. Treatment of this complex with two moles of potassium hydroxide leads to (**141a**). The starting ligand (H_2LL) reacts with $[M(\eta^6\text{-Cp}')Cl(Acac)]$ to yield (**141b**) or (**142b**). It is also possible to prepare the heterodinuclear complex by interaction of (**142b**) with $[Rh(\eta^5\text{-Cp}')Cl(Acac)]$.

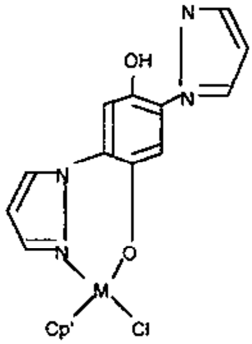


RX=MeCOCl, MeI
139



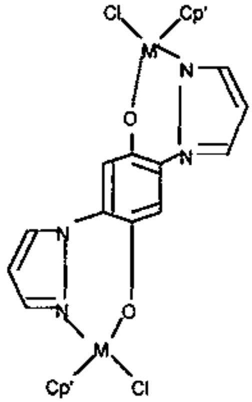
RX=MeCOCl, MeI
140

Finally, we would like to mention a couple of publications on the cyclometallated derivatives of these two metals. 1-Phenylpyrazoles (R = H, Me, **143**) enter into a cyclometallation reaction with rhodium(III) and iridium(III) hydrated halides [167]. The product, $[(1\text{-PhPz})_2MX]_2$ contains the chlorine bridge. The latter is cleaved by phosphines leading to the monomeric complexes $[(1\text{-PhPz})_2MXPR_3]$, and by ethylenediamine yielding $[(1\text{-PhPz})Rh(Eda)]^+$. Reaction of the dimers with $PBu^n{}_3$ affords cyclometallated complexes such as, for example, (**143**).



a:M=Rh;b:M=Ir

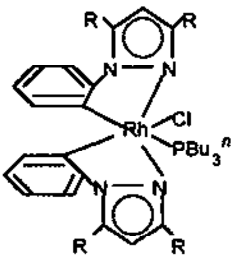
141



a: M=M'=Rh; b: M=M'=Ir; c: M=Rh, M'=Ir

142

$Rh_2Cl_6(PR_3)_4$ cyclometallates 1-phenylpyrazole and 1-phenyl-3,5-dimethyl-pyrazole to give [Rh(1-PhPz)$Cl_2(PR_3)$] [168]. The product reacts with phosphines, the result being the cyclorhodated [Rh(1-PhPz)$Cl_2(PR_3)_2$].



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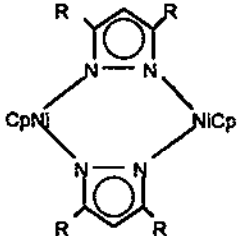


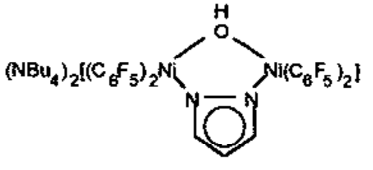
144

2.4. *Derivatives of nickel, palladium and platinum*

Bis(η^5-cyclopentadienyl)nickel and pyrazole readily form a diamagnetic polymeric nickel(II) pyrazolate, approximately (η^5-Cp)[Ni(Pz)]$_{25}$Ni(η^5-Cp) [169]. A similar reaction with 3-methylpyrazole yields (η^5-Cp)[Ni(Pz)]$_9$Ni(η^5-Cp). Reaction between [Ni(η^5-Cp)$_2$] and 3,5-dialkylpyrazoles differs in the sense that the products are dimeric (dimethyl-, di-*iso*-propyl- and di-*tert*-butyl-derivatives). They contain the Ni_2N_4 ring (**144**), characterized by diamagnetism and a low-spin d^8 configuration.

In the crystal structures of [(η^3-C_3H_5)Ni(μ-dmPz)$_2$]Ni, the Ni_2N_4 ring is in the boat conformation [170]. The central nickel atom bonded to four pyrazolyl nitrogen atoms and to an allyl group is square-planar.

Compound $(NBu_4)_2[(C_6F_5)_2Ni(\mu\text{-}OH)_2Ni(C_6F_5)_2]$ reacts with pyrazole in two steps yielding first (**145**) and then (**146**) [171].



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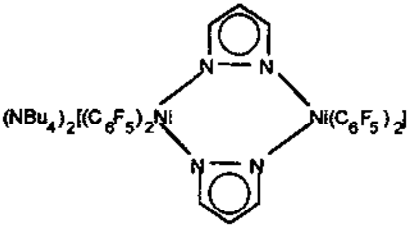
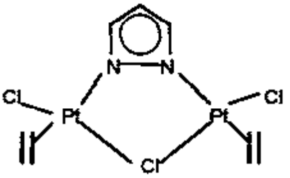


146

Compounds $[Ni(\mu^4\text{-Cod})_2]$ and $[Hg(1\text{-PhPz})_2]$ afford the cyclonickelated $[Ni(1\text{-PhPz})_2]$ [172].

The chloro-bridged binuclear methylpalladium(II) complexes $[PdMe(\mu\text{-Cl})(PR_3)]_2$ ($R_3 = Et_3$, n-Bu_3, Me_2Ph, $MePh_2$, Ph_3) with pyrazole, 3,5-dimethylpyrazole and 3,4,5-trimethylpyrazole in the presence of sodium hydroxide yield the bis(pyrazolato)-bridged $[PdMe(\mu\text{-Pz})(PR_3)]_2$ [173–176]. The platinum analogs (Pz, PMe_2Ph; 3,5-dmPz, PMe_2Ph; 3,4,5-tmPz, PMe_2Ph) are prepared similarly. The Palladium species exists as a single *syn-trans* isomer, while the platinum analogs coexist as *cis* and *trans* isomers.

Reaction of pyrazole with Zeise's anion, $[Pt(C_2H_4)Cl_3]^-$, affords (**147**) as the major product [177]. In addition, a dinuclear *trans,trans*-μ-chloro-1,2-dihapto-pyrazolatodichlorobis(ethylene)diplatinum(II) is obtained. X-ray analysis of the product (**147**) [178] shows that the entire complex exclusive of olefin molecules and namely Pt_2ClN_2 ring are planar. The structure of a neutral adduct of $[Pt(C_2H_4)Cl_3]^-$ and pyrazole (**148**) is planar as well [179]. Such a geometric arrangement is due to an intramolecular hydrogen bond between the ring NH proton of the heterocyclic molecule and the coordinated chlorine atom. Upon deprotonation complex (**148**) forms *trans*-$[PtCl_2(Pz)(C_2H_4)]^-$. The reasonably labile substances are able to generate binuclear complexes, e.g. (**149**) [180].



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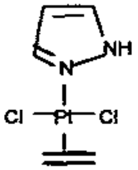
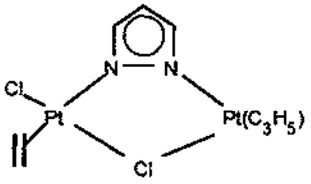


148

Reaction of $[(\eta^3\text{-}CH_2C(R)CH_2)PdCl]$ (R = Ph, Me, H) with pyrazolate or 3,5-dimethylpyrazolate gives (**150**) [50]. Compound (**150**, R = R′ = Me) is in a boat conformation, as shown by X-ray data [181].

Reaction of $[Pd(Acac)(\eta^3\text{-allyl})]$ (allyl = C_3H_5, C_4H_7) with $[PdCl_2(PzH)_2]$ provides the homotrinuclear complexes $[(\eta^3\text{-allyl})Pd(\mu\text{-Cl})(\mu\text{-Pz})Pd(\mu\text{-Cl})(\mu\text{-Pz})Pd(\eta^3\text{-allyl})]$ [127]. Further reaction with the pyrazolate anion yields $[(\eta^3\text{-allyl})Pd(\mu\text{-Pz})_2Pd(\mu\text{-Pz})_2Pd(\eta^3\text{-allyl})]$.



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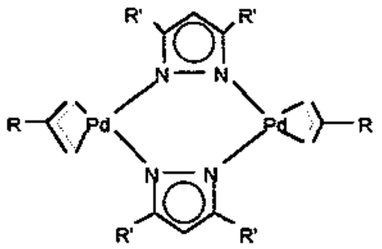
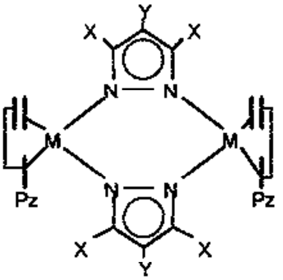


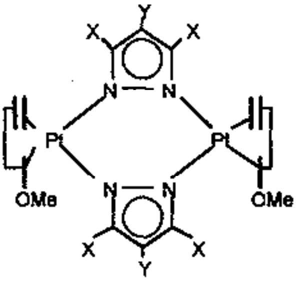
150

Compounds $[(\eta^4\text{-Cod})MCl]$ (M = Pt, Pd) react with excess pyrazole in the presence of sodium hydroxide and form (**151**) or (**152**) [182].



M=Pd, X=Y=H; X=Me, Y=H; X=Me, Y=I
M=Pt, X=Y=H

151

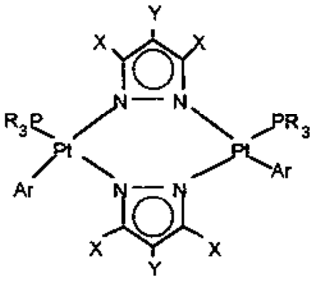


X=Me, Y=Br, I, $N_2C_6H_4Me$

152

Reaction of $[PtAr(\mu\text{-}Cl)(PR_3)]_2$ (Ar = Ph, C_6H_4Me-4, C_4H_3S-2, $R_3 = Bu_3$, Me_2Ph, $MePh_2$) with pyrazole, 3,5-dimethylpyrazole and 3,4,5-trimethylpyrazole yields (**153**) [183]. Different complexes are isolated as *cis* or *trans* conformers, or mixtures of *cis* and *trans* conformers, the latter usually predominating.

Complex $(NBu_4)_2[Pd(C_6Cl_5)_2(\mu\text{-}OH)]_2$ behaves differently with respect to pyrazole and 3-methylpyrazole, on the one hand, and the sterically crowded 3,5-dimethylpyrazole, on the other [184]. In the first case, the complex with the double μ-pyrazolate bridge is formed (**154**), while in the second the product is the μ-hydroxo-complex (**155**). Both products contain the *cis*-$[Pd(C_6Cl_5)_2]$ framework. The starting complex $[(C_6F_5)_2Pd(\mu\text{-}OH)_2Pd(C_6F_5)_2]$ upon reaction with pyrazole, 3-methylpyrazole and 3,5-dimethylpyrazole forms (**156**) [185].



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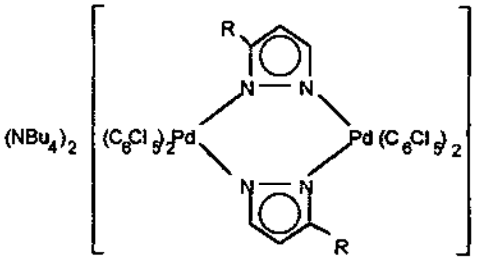
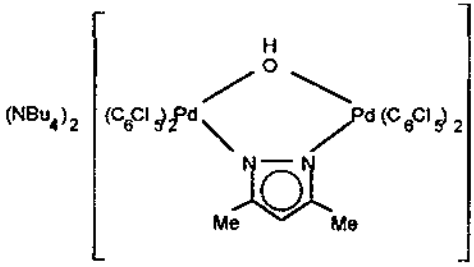


154

Compound $[PtCl(Bu_2{}^tPCMe_2CH_2)]_2$ reacts with pyrazole or 3,5-dimethylpyrazole in the presence of sodium hydroxide to form (**157**) [187]. The chelate ring is not planar in this case, and the *trans* structure of the pyrazolate derivative is shown by X-ray analysis. The four-coordinated platinum atoms are characterized by a distorted square-planar coordination.



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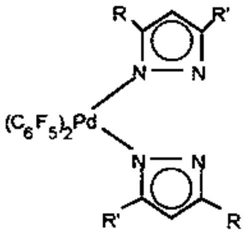
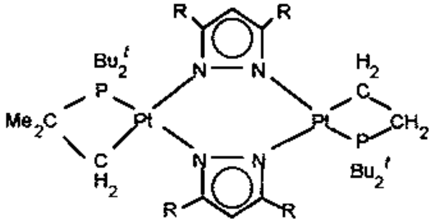


156

Complex (**158**) is made by the metal transfer method starting from the bis(phosphino)-pyrazole complex [163].



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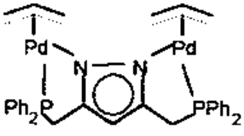
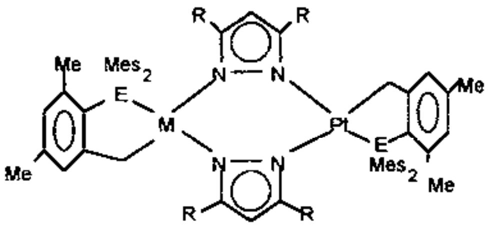


158

The cyclometallated palladium and platinum derivatives of trimesitylphosphine and arsine react with pyrazole and 3,5-dimethylpyrazole to form metal-chelates (**159**) having the *trans* configuration [188].

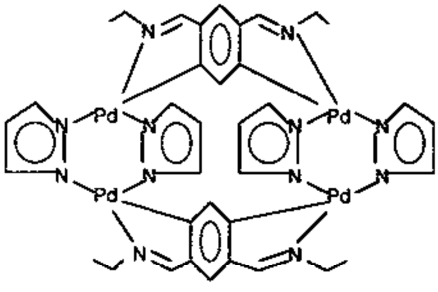


E=P, As; M=Pd, Pt; R=H,Me

159

$[Pd_2L(MeCN)_2(ClO_4)_2]$ (H_2L = *N*,*N*-diethyl-2,6-dialdiminobenzene) and pyrazole form $[Pd_2L(PzH)_4](ClO_4)_2$ [189]. With excess pyrazole and in the presence of triethylamine, perhaps, the tetranuclear complex (**160**) is formed.

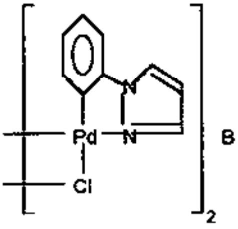
1-Phenylpyrazole upon reaction with $PdCl_4^{2-}$ forms the bis-adduct $(1\text{-}PhPz)_2PdCl_2$ [190] which after prolonged reaction with $PdCl_4^{2-}$ forms (**161**). 3,5-Dimethyl-1-phenylpyrazole reacts similarly.



160

2.5. *Miscellaneous*

There is a scarcity of publications dealing with the organometallic compounds of pyrazoles containing gold, indium and thallium as well as the rare earth metals.



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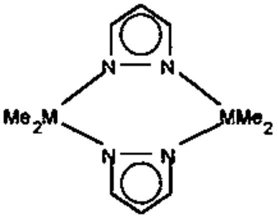


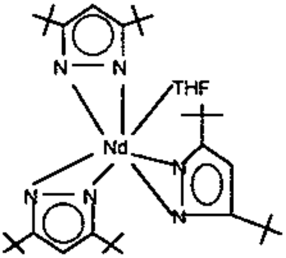
162

Aqueous solutions of methylgold nitrate easily react with pyrazole and 3,5-dimethylpyrazole to form of the pyrazolate complexes (**162**) [191]. However, diphenylpyrazole gives the complex $[Me_2Au(3,5\text{-}Ph_2PzH)_2]^+$, where the ligand is not deprotonated. To obtain the 3,5-diphenylpyrazolate complex, dimethylgold(III) iodide must be reacted with silver diphenylpyrazolate. The same procedure can be used for the derivatives of thallium. A set of compounds $Me_2M(3,5\text{-}R_2Pz)$ (M = Au, R = Ph; M = Tl, R = Me, Ph) is the result of this study.

Reactions of $InAlk_3$ with 3,5-dimethyl- and 3,5-diethylpyrazole or Alk_2InCl with the lithiated pyrazolates afford $[AlkIn_2(\mu\text{-}Pz)]_2$ [192], dimeric in solution and in the gas phase.

Reaction of neodymium metal with $Hg(C_6F_5)_2$ and pyrazole or 3,5-dimethylpyrazole gives $Nd(Pz)_3$ or $[Nd(3,5\text{-}dmPz)_3(THF)]_2$ [193]. X-ray analysis of the latter shows that it has a centrosymmetric dimeric structure. Each neodymium atom is eight-coordinate and characterized by a bicapped trigonal prismatic coordination. The complex contains two terminal chelating pyrazolate ligands, two bridging pyrazolate ligands and two bridging THF ligands.

Interaction of bis(pentafluorophenyl)mercury and 3,5-di(t-butyl)pyrazole with excess lanthanoid metal in THF yields $[\mathrm{Ln}(\mathrm{Bu}^t{}_2\mathrm{Pz})_3(\mathrm{THF})_2]$ (Ln = La, Nd, Gd, Er) [194], a series of mononuclear complexes. Such a formulation is confirmed by X-ray structural determination of the neodymium complex (**163**). The neodymium cation and pyrazolato ligands form ionic, non-directional bonds. Arrangement of ligands around the central ion is intermediate between the trigonal-bipyramidal and square-pyramidal geometries.

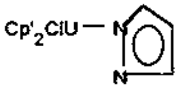


163

164

Tris(cyclopentadienyl)uranium chloride and sodium pyrazolate form (**164**), where the uranium ion is η^5-coordinated by three cyclopentadienyl rings and two nitrogen heteroatoms belonging to the coordinated pyrazolate anion [195]. This is a unique case of the *endo*-bidentate coordination of the pyrazolate ligand in organometallic compounds. This coordination mode can be related to a substantial degree of ionicity of the uranium-nitrogen bond.

$[\mathrm{UCp'}_2\mathrm{Cl}_2]$ and pyrazole form $[\mathrm{UCp'}_2\mathrm{Cl}_2(\mathrm{Pz})]$ [196], as shown by X-ray analysis (**165**). With sodium pyrazolate, $[\mathrm{UCp'}_2\mathrm{Cl}_2]$ forms (**166**) which has a very roughly tetrahedral coordination geometry, if the initial ratio of the reactants is 1:1. If $[\mathrm{UCp'}_2\mathrm{Cl}_2]$ and sodium pyrazolate are taken in the ratio 1:2, complex (**167**) is formed, as shown by X-ray analysis.



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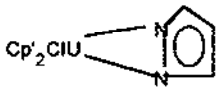
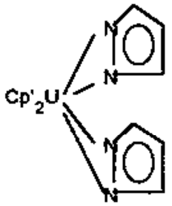


165



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3. Conclusion

The organometallic chemistry of pyrazolic ligands presents a challenge for further studies because of the variety of coordination modes presented by this ligand as well as the model character of typical reactions especially of organoruthenium, -rhodium and -iridium compounds. In our view, study of the oxidative addition reactions of rhodium(I) and iridium(I) complexes provides one with fruitful ideas that may be applied to complexes of these metals containing other ligands. A deeper understanding of the structural features and reactivity of the compounds described above should become possible as a result of serious theoretical calculations. Finally, the range of compounds could be enhanced through new compounds of the early transition metals. No doubt this will enrich organometallic chemistry to a considerable extent.

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