The Role of the Pyrazolate Ligand in Building Polynuclear Transition Metal Systems

GIROLAMO LA MONICA *and* **G. ATTILIO ARDIZZOIA**

Dipartimento di Chimica Inorganica
Metallorganica e Analitica and Centro C.N.R.
Università di Milano
Milano, Italy

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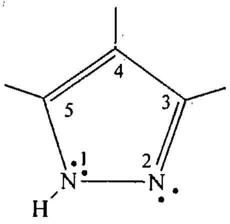
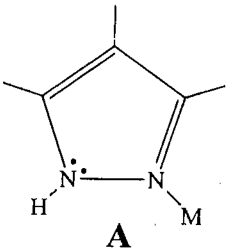
I. INTRODUCTION

The synthesis of multimetallic transition metal complexes where the metals are held at specific distances from each other is an important objective because of their potential role in multimetal-centered catalysis in both biological and industrial reactions (1). Moreover, such systems, through cooperative electronic and/or steric effects between metal centers, might give rise to distinct reactivity patterns for both their stoichiometric and catalytic reactions, which are not available to their monometallic analogues (2). Of the ligands that are able to maintain the metal centers in close proximity, the pyrazolate ion (pz*) appears to be a particularly suitable candidate. Pyrazoles (Hpz*) are weak bases (3, 4) and behave as 2-monohapto ligands.

η^1-Coordination (**A**) for neutral pyrazoles has been extensively described and several X-ray crystal structural studies have been reported (4–9). Factors affecting the maximum number of pyrazole molecules that may coordinate to a metal center have been thoroughly explored (6). The 1-unsubstituted pyrazoles are also weak acids (3, 4). Indeed, they react with alkali metals affording M$^+$(pz*)$^-$ (10), with Grignard reagents (PhMgX) yielding (pz*)MgX (11), or with alkali metal borohydrides to give the corresponding poly(pyrazolyl-1-yl)borates anions (scorpionate ligands) (12).

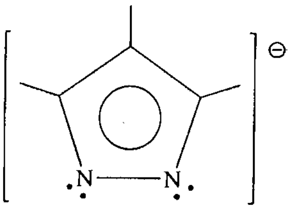
The nucleophilicity of N2 and the acid character of Hpz* may be modified by introducing appropriate substituents in the 3-, 4- or 5-positions of the het-





A

erocyclic ring (3, 4). By far, the pyrazolate anion $(pz^*)^-$ (**B**) is the best studied related species. This species can be easily obtained from Hpz* by deprotonation.



B

The coordination chemistry of Hpz* and pz* has been thoroughly examined by Trofimenko (5, 6) in his notable reviews dealing with the coordination chemistry of pyrazole-derived ligands. The pyrazolate ligand pz* is known to exhibit three coordination modes on binding metal centers (Fig. 1).

It can act as an anionic monodentate (pyrazolate-*N*), exo-bidentate (pyrazolate-*N*,*N*′), or endo-bidentate ligand. In most cases, the pz* ligand coordinates in an exo-bidentate fashion, thus linking two metal centers that may be identical or different. For these complexes, singly bridged $M(\mu\text{-pz}^*)M$ or $M(\mu\text{-pz}^*)M'$, doubly bridged $M(\mu\text{-pz}^*)_2M$ or $M(\mu\text{-pz}^*)_2M'$ and the much less common triply bridged $M(\mu\text{-pz}^*)_3M$ or $M(\mu\text{-pz}^*)_3M'$ and quadruply bridged $M(\mu\text{-pz}^*)_4M$ species were reported.

Heterobridged complexes having an usually puckered five-membered ring, $M(\mu\text{-pz}^*)(\mu\text{-X})M$ or $M(\mu\text{-pz}^*)(\mu\text{-X})M'$ (X = single atom donor ligand), are also known. Much work has been done with metallocycles containing the $M(\mu\text{-pz}^*)_2M$ ring. Various exchange reactions can be carried out on the terminal ligands leaving the central $M(\mu\text{-pz}^*)_2M$ core intact.

Singly bridged complexes are less numerous than doubly bridged ones. Representative examples are the homoleptic species $[M(pz^*)]_n$ [*M* = Cu(I), Ag(I), and Au(I)]. Notably, the number of these binary complexes increased in the last years as well as their X-ray crystal structures (13).

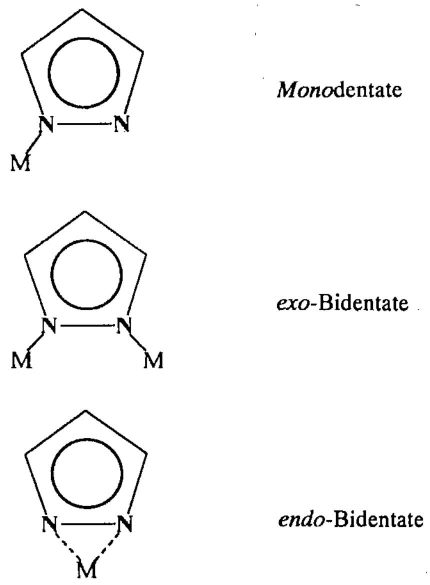


Figure 1. Coordination modes of the pyrazolate anion.

The usefulness of pyrazolate mononuclear complexes containing pz* as a monodentate ligand in the synthesis of dinuclear and trinuclear heterometallic species was demonstrated (14). Apart from a few examples of monodentate behavior, the pz* groups are, generally, such good exo-bidentate donors that when a suitable acceptor is not immediately available, coordination polymers or oligomers formed. Only a few examples of complexes containing the endo-bidentate pyrazolate ligand were also reported.

Research on the coordination chemistry of the pyrazolate ligand has progressed very rapidly as the potentiality of the pz* groups became evident following *two comprehensive reviews on this topic (5, 6). Recent studies recognized* the good catalytic activity, under mild conditions, of some polynuclear heterobridged pyrazolate complexes, thus encouraging the exploration of the unusual and specific features of the pyrazolate ligand.

This chapter covers the years 1985–1995; it is intended to update those of Trofimenko (5, 6), which should be consulted for most earlier references.

II. HOMOLEPTIC PYRAZOLATE COMPLEXES

A. Singly Bridged M(μ-pz*)M Complexes

Binary compounds of the general formula $[M(pz^*)]_n$ are known only for Group 11 (IB) metals [M = Cu(I), Ag(I), or Au(I); pz* acts as a singly bridging ligand]. These few structurally characterized systems were found to possess a variety of stoichiometries, molecular arrangements, and oligomeric or polymeric structures (13). In a few cases, oligomers of different nuclearities were selectively prepared and characterized (13, 15–17).

In 1889, Büchner (18) reported the formation of the insoluble silver(I) pyrazolate $[Ag(pz)]_n$, **1a**, which he simply denoted as a "silver salt". The oligometric or polymeric nature of this species was not clarified until 1994, although it was always referred to as being a polynuclear pyrazolate compound (6). A similar structure was claimed for $[Cu(pz)]_n$, **2**, on the basis of IR evidences (6, 19).

Recently, efforts were made in order to investigate the possibility of solving simple structures in the field of polymeric metallorganic materials, which usually appear as fine powdered samples. For this class of compounds single crystals cannot be grown because of their negligible solubility in common organic solvents (13). Indeed, this is the case for $[Cu(pz)]_n$ and $[Ag(pz)]_n$.

In 1994, the ab initio X-ray crystal stucture determination from powder diffraction data of $[Cu(pz)]_n$ and $[Ag(pz)]_n$ were reported (13). During these studies it was ascertained that copper(I) and silver(I) pyrazolates, depending on the synthetic method used, each appear in two distinct crystalline phases. The α-$[Cu(pz)]_n$, **2a**, and β-$[Cu(pz)]_n$, **2b**, consist of infinite chains of linearly coordinated copper atoms, bridged by exo-bidentate pyrazolate anions (Fig. 2).* The two phases differ mainly in the interchain Cu· · ·Cu contacts, which are 3.34 Å in α-$[Cu(pz)]_n$ and 2.97 Å in β-$[Cu(pz)]_n$.

The α phase was easily obtained by reacting $[Cu(MeCN)_4](BF_4)$ with Hpz in acetone in the presence of triethylamine (13, 18). The complex β-$[Cu(pz)]_n$ was prepared via the high-yield, high-temperature reaction of Cu_2O with molten pyrazole (13). Two crystalline phases were also found for silver(I) pyrazolate (13). The first, $[Ag(pz)]_n$, **1a**, was shown to be isomorphous and isostructural with α-$[Cu(pz)]_n$, (Ag· · ·Ag interchain distances are 3.23 Å). This complex was quantitatively obtained by using the synthetic procedure originally reported by Büchner (18). The second silver(I) pyrazolate phase, $[Ag(pz)]_3$, **1b**, appeared as a truly molecular compound whose topology closely resembles those of other Group 11 (IB) metal trimeric pyrazolates. Complex **1b** was obtained by removing PPh_3 from the dimeric silver(I) pyrazolate complex $[(PPh_3)Ag(pz)]_2$, **38** (21). A detailed study of the IR spectra of **1a**, **1b**, **2a**, and **2b** was performed (13), which is diagnostic for the identification of each phase (Fig. 3).

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*The following figure is a key for atom symbols used in the figures in this chapter.

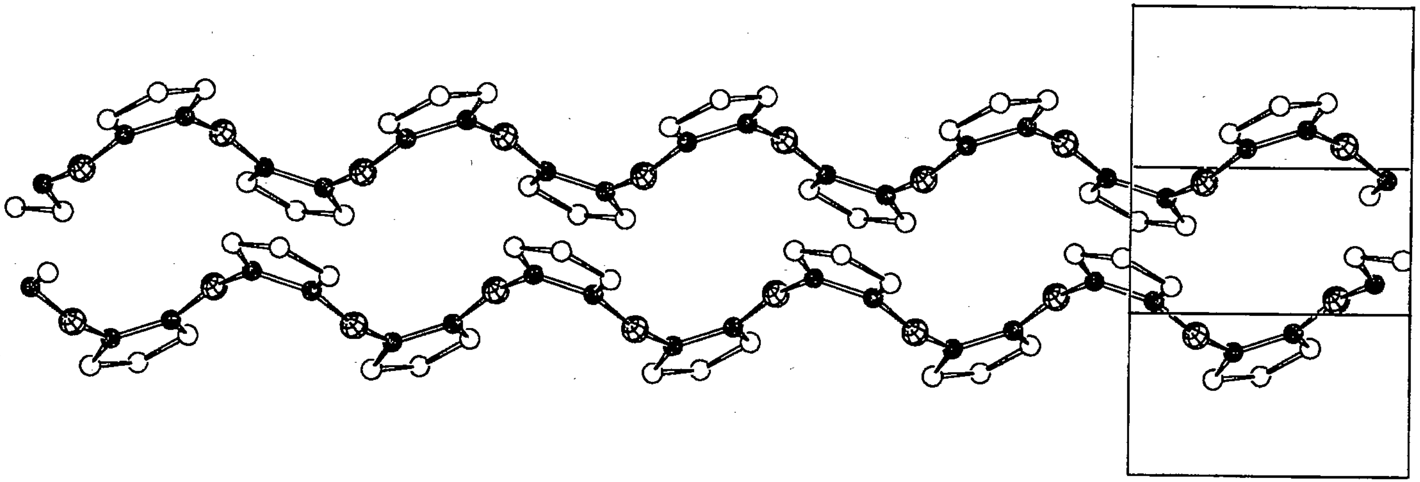


Figure 2. Structure drawing of two adiacent α-$[Cu(pz)]_n$ chains. At the resolution of the draws β-$[Cu(pz)]_n$ chains look similar. [Based on data from (13)]. (All the structure drawings reproduced in this review are obtained by the program SCHAKAL (20), from the data reported in the literature. Throughout the paper, metal, S, O, and N atoms are sketched by cross-hatched, dashed, starred, and dotted circles, respectively. See the footnote on page 155.)

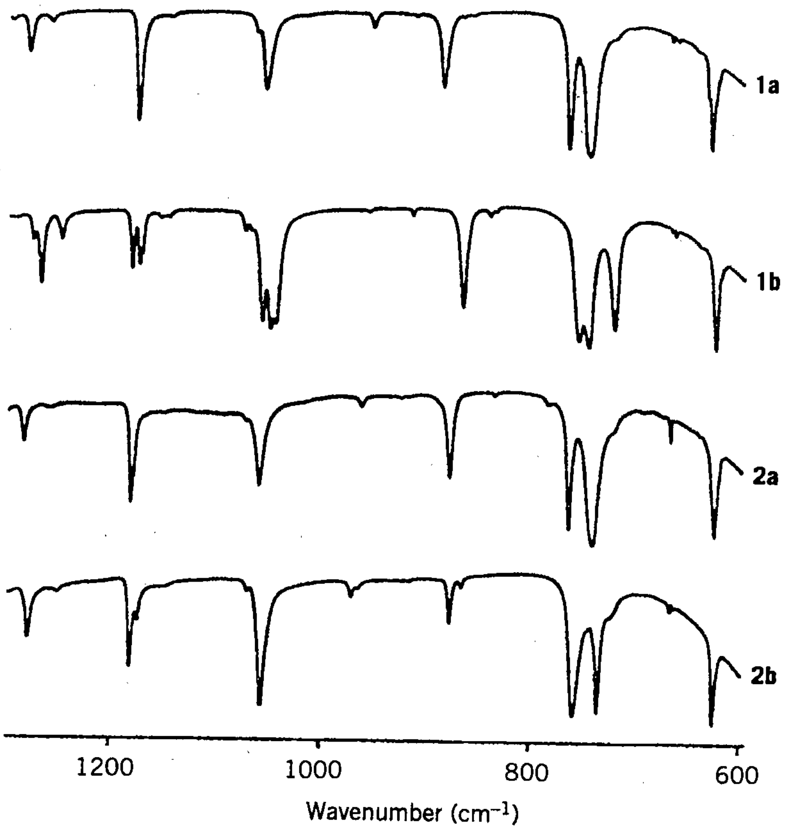


Figure 3. Infrared spectra (Nujol mulls) of [Ag(pz)]$_n$, **1a**, [Ag(pz)]$_3$, **1b**, α-[Cu(pz)]$_n$, **2a** and β-[Cu(pz)]$_n$, **2b**. [Adapted from (13).]

Cyclic trimeric pyrazolate complexes of Group 11 (IB) metals are now somewhat common. In the last few years, several species having such nuclearity were reported. In 1988, Fackler and co-workers (15) reported the synthesis and X-ray crystal structures of [Ag(dppz)]$_3$, **3**, and [Au(dppz)]$_3$, **4**. These structures were obtained by reacting Na(dppz) with AgNO$_3$ and Au(tht)Cl, respectively. In **3**, the three Ag positions do not form an equilateral triangle owing to the significantly different Ag · · · Ag distances [3.305(2), 3.362(2), and 3.486(2) Å)]. Moreover, the nine-membered Ag$_3$N$_6$ ring is not planar. On the contrary, the gold trimer **4** appears as a rigorously planar nine-membered inorganic ring. The intermolecular Au · · · Au distances in **4** are in excess of 2.25 times that of the intramolecular distances.

A low-yield synthesis of [Cu(dppz)]$_3$, **5**, from CuCl and Na(dppz) in the presence of AgNO$_3$ was reported, and its X-ray crystal structure was determined

(16). The structure of **5** consists of a nine-membered $(Cu-N-N)_3$ metallocyclic ring similar to the ones of the isostructural silver(I) and gold(I) compounds (15). Significant deviations from planarity, as found in the silver(I) trimer, are present.

A related copper(I) complex containing exo-bidentate 3,5-dimethylpyrazolate has been known since 1971 (22) and thought to be a polymeric species, that is $[Cu(dmpz)]_n$. The X-ray crystal structure, published in 1990 (23), evidenced the trimeric nature of this copper(I) complex, that is $[Cu(dmpz)]_3$, **6.**

It is now widely accepted that the nuclearity of Group 11(IB) univalent metal binary pyrazolate complexes is strongly affected by the nature of the substituents on the heterocyclic ligand. In some cases, depending on the preparative method, complexes having different nuclearities have been selectively obtained.

The existence of the two quite different phases for silver(I) pyrazolate complexes, that is, $[Ag(pz]_3$, **1a** and $[Ag(pz)]_3$, **1b,** is in this respect indicative. Besides the trimeric complex $[Au(dppz)]_3$, **4,** the hexamer $[Au(dppz)]_6$, **7,** was obtained by reaction of $Au(PPh_3)Cl$ with Na(dppz) in the presence of silver benzoate and was crystallographically characterized (15). Complex **7** contains an 18-membered inorganic ring in the shape of a two-bladed propeller. The geometry of the six gold centers is best described as an edge-sharing bitetrahedron (Fig. 4).

The preparative method reported for the synthesis of α-$[Cu(pz)]_n$, **2a,** was extended to pyrazoles having different substituents in the 3,5-positions (24). In the case of 3,5-diphenylpyrazole, the tetranuclear complex $[Cu(dppz)]_4$, **8,** was obtained (17). In complex **8,** the four copper atoms, which lie at an average nonbonding distance of 3.12 Å, are strictly coplanar, while the four bridging dppz units, each one spanning the ideal Cu · · · Cu edges, stem out from the two sides in an alternate fashion, giving the whole complex an idealized D_2, rather than a fourfold, symmetry. The Cu—N bond distances compare well with those found in $[Cu(dmpz)]_3$, **6,** (23) but are much shorter than in the trimeric species $[Cu(dppz)]_3$ (**5**), which contains the same pyrazolate group (16). Trimeric copper(I) complexes $[Cu\{(p\text{-}ClC_6H_4)_2pz\}]_3$, **9,** and $[Cu\{(pCH_3\text{-}C_6H_4)_2pz\}]_3$, **10,** were obtained by reacting 3,5-di-(*p*-chlorophenyl)pyrazole and 3,5-di-(*p*-tolyl)pyrazole with $[Cu(MeCN)_4](BF_4)$ in the presence of triethylamine (21). While for **9,** an X-ray crystal structure determination definitively confirmed its trinuclear formulation, for **10** the nucleaity was argued on the basis of electron-impact mass spectrometry.

The reaction of molten Htmpz with copper metal shot in air yielded a mixture of the trinuclear copper(I) complex $[Cu(tmpz)]_3$, **11,** and the trinuclear copper(I/II) complex $[Cu(3\text{-}CO_2\text{-}4,5\text{-}Me_2pz)(Htmpz)]_2Cu$ in which the $3\text{-}CO_2\text{-}4,5\text{-}Me_2pz$ ligand, derived from the oxidation of one of the three methyl groups of the tmpz, is present (25). Alternatively, **11** was prepared by reacting cuprous iodide with Htmpz in the presence of triethylamine (26). The structure of **11** is

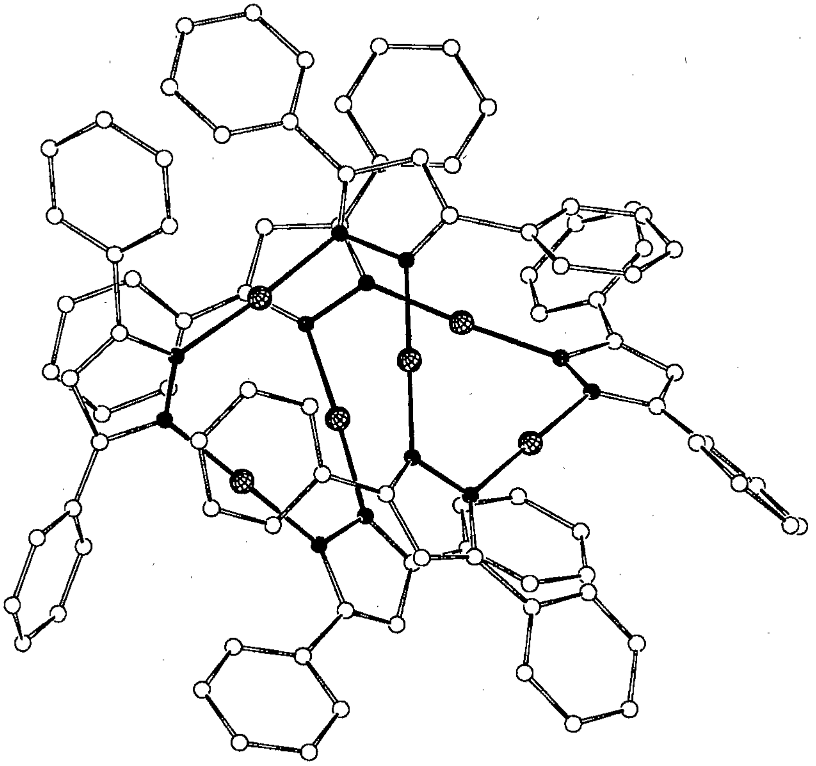


Figure 4. Structure drawing of the hexanuclear gold(I) complex $[Au(dppz)]_6$, 7. [Based on data from (15).]

very similar to that reported for $[Cu(dmpz)]_3$ (23). The latter synthetic method was extended to other pyrazoles of the general formula 4-XdmpzH (X = Cl, Br, or I) from which copper(I) pyrazolates formulated as trimers were prepared (26). This formulation is supported by the fact that they exhibit electron-impact mass spectra in which the most intense peak is that due to the molecular ion expected for the trimer. The isotopic patterns are in excellent agreement with those predicted. The X-ray crystal structure of the copper(I/II) mixed-oxidation state trinuclear species $[Cu(3\text{-}CO_2\text{-}4,5\text{-}Me_2pz)(Htmpz)]_2Cu$ was also reported (25). The $3\text{-}CO_2\text{-}4,5\text{-}Me_2pz$ ligands chelate the central copper(II) atom via the carboxylate oxygen atom and the adjacent ring nitrogen atom. A similar reaction involving 4-BrdmpzH gave the dinuclear copper(II) complex $[Cu(3\text{-}CO_2\text{-}4\text{-}Br\text{-}mpz)(4\text{-}BrdmpzH)_2]_2$ (25).

The reaction of $[Cu(Me_3CN)_4](BF_4)$ with 3,5-dicarbomethoxypyrazole in the presence of triethylamine was reported (27). A copper(I) pyrazolate, [Cu-

(dcmpz)]$_n$, **12,** was obtained. Complex **12** was formulated as an oligomeric complex. Its IR spectrum exhibits only one $\nu(C = O)$ at 1723 cm^{-1}, suggesting the equivalence of the carbonyl groups of the two COOMe substituents in the 3,5-positions of the pyrazole ring. This absorption lies quite at the same frequency as for the dimeric species [Cu(dcmpz)(RNC)]$_2$, **34** (R = cyclohexyl), whose X-ray crystal structure ruled out interactions between the C = O groups and the copper centers (27).

The reaction of (Me)$_2$SAuCl with a pyrazole having bulky substituents in the 3,5-position or with an asymmetrically substituted pyrazole in the presence of a strong base, was described (28). In the case of Hdbpz, a mixture containing two different pyrazolate complexes that were formulated on the basis of NMR data and by electron impact mass spectrometry as trimeric and tetrameric species were obtained (28). By reacting Hdmepz, the formation of a mixture of two oligomers, probably a trimer and a tetramer, was again claimed. The interpretation of the NMR spectra was particularly complicated owing to the concomitant presence of isomers.

The reaction of [Cu(MeCN)$_4$](BF)$_4$) or AgNO$_3$ with 3,5-dimethyl-4-nitropyrazole in the presence of NEt$_3$ was recently studied (21). Two different copper(I) pyrazolate complexes were obtained, depending on the Cu/4-NO$_2$dmpzH/NEt$_3$ molar ratio. Reactions employing a 1 : 1 : 1 molar ratio gave the white [Cu(4-NO$_2$dmpz)]$_3$, **13,** characterized by a powder X-ray structure determination (21). In the presence of excess pyrazole and NEt$_3$, the orange product [Cu$_4$(4-NO$_2$dmpz)$_6$](Et$_3$NH)$_2$, **14,** was isolated. An X-ray crystal structure analysis confirmed its formulation (21). The related trinuclear silver(I) compound, [Ag(4-NO$_2$dmpz)]$_3$ was obtained by using AgNO$_3$. The nuclearity of such species was based on the identity of its IR spectrum with that of **13** (21).

Many structural features observed for Group 11 (IB) pyrazolate complexes can be found in the realm of purely organic pyrazoles, where hydrogen bonding between different molecules is capable of generating, in the solid state, a variety of Hpz* clusters, ranging from dimers up to polymeric chains. This analogy goes even further, as it can be observed that a fairly straight parallelism between pyrazoles (if N—H$\cdots$N links are considered) and Cu(I)-pyrazolates exists: pyrazole and [Cu(pz)]$_n$ (α and β phases) are polymeric (13, 29, 30), 3,5-dimethylpyrazole, 4-nitro-3,5-dimethylpyrazole, [Cu(dmpz)]$_3$, and [Cu(4-NO$_2$-dmpz)]$_3$ are trimers (21, 23, 31, 32); while 3,5-diphenylpyrazole and [Cu(dppz)]$_4$ are tetramers (17, 33, 34) of idealized D_{2d} symmetry. This result might suggest that the static N—Cu—N (with a N$\cdots$N distance of ~ 3.7 Å) and the dynamic (tautomeric) N—H$\cdots$N (with a N$\cdots$N distance of ~ 2.9 Å) bonds, in spite of their different nature and strength, are linear hinges about which the pyrazolate rings are essentially free to rotate. The different steric demands of different substituents in the 3,5-positions of the heterocycle drive the preferred dihedral angle to specific values, thus determining the nuclearity of the oligomers. The analogy of the linear coordination at the H^+ and Cu^+ acidic centers impose local packing of the single molecules but does not determine the supramolecular arrangement in the crystal, so that crystal systems and space groups of the H and Cu derivatives do not match.

B. Doubly Bridged $M(\mu\text{-}pz^*)_2M$ Complexes

Binary pyrazolate complexes containing divalent metals bridged by two pz* groups are known for many transition metals. The increasing interest for this class of complexes stems from the expectation that they may provide useful insights in the field of magnetostructural correlations as well as in multimetal centered catalysis.

Reactions of copper metal shot with molten pyrazole or substituted pyrazoles in the presence of dioxygen were successfully employed by Ehlert et al. (35–37) in the synthesis of binary copper(II) pyrazolates of the general formula $[Cu(pz^*)_2]_n$ (Hpz* = Hpz, 4-ClpzH, 4-BrpzH, or 4-MepzH). The complex $[Cu(pz)_2]_n$, **15**, was obtained in 79% yield as a bright green powder when the reaction mixture was heated at 110°C in the presence of air (35). The polymeric nature of **15** was ascertained by an X-ray crystal structure analysis. The Cu atoms have a D_2 distorted tetrahedral coordination geometry with Cu—N = 1.957(2) Å and N—Cu—N = 94.3(1)–139.5(1)°. In an earlier paper by Vos and Groeneveld (38), reactions of copper(II) salts with Hpz in aqueous base were reported to yield a black material of composition $[Cu(pz)_2]_n$. The latter reactions were checked by Ehlert et al. (35) who attributed the composition $[Cu_2(pz)_3(OH)]_n$ to the black material, rather than $[Cu(pz)_2]_n$.

Magnetic susceptibility studies (4.2–299 K) on **15** revealed very strong antiferromagnetic exchange between copper(II) centers in the extended linear chains (35). A comparison of the low-temperature single-crystal X-ray diffraction study of $[Cu(pz)_2]_n$ with the room temperature study (35) showed that in copper(II) pyrazolate extended-chain polymers interchain distances may be affected by changes in temperature (37). This fact appeared to have little effect on interchain bond lengths and angles, but may significantly alter the dihedral angle between fused Cu—(N—N)$_2$—Cu and N_2C_3 (pyrazole) rings and the dihedral angle between consecutive Cu—(N—N)$_2$—Cu planes.

In addition to the copper/molten ligand method, the syntheses of $[Cu(4\text{-}Xpz)_2]_n$ (X = Cl, **16**, and Br, **17**) on treatment of $Cu(OH)_2$ or Cu_2O with excess 4-XpzH in refluxing xylene were described (36). Two forms of the 4-ClpzH derivative were obtained, one green and one brown. It was apparent from the X-ray powder diffraction pattern that the two forms are structurally distinct. While details of the structure of the brown form still remain unknown, comparison of its solubility and thermal properties with those of the structurally characterized pyrazolate complexes, suggest a polymeric nature for this material also (36).

The crystal structures of $[Cu(4\text{-}Clpz)_2]_n$, **16,** (green form) and $[Cu(4\text{-}CH_3pz)_2]_n$, **18,** confirmed their polymeric nature. In addition, for Complexes **16** and **18,** magnetic susceptibility studies over the temperature range 2–300 K revealed a relatively strong antiferromagnetic coupling (36).

Recently, quite different products were claimed to be formed when $Cu(OH)_2$ reacted with molten 4-XpzH. A brown powder having the empirical formula $[Cu_2(OH)(4\text{-}Xpz)_3(4\text{-}XpzH)_2]$ (X = Cl or Br) was isolated with excess molten pyrazole, while the dinuclear species $[Cu_2(OH)(4\text{-}Xpz)_3]$ (X = H, Me, Cl, and Br) formed when a stoichiometric amount of 4-XpzH was used (39).

On the basis of their IR spectra, complexes $[Cu_2(OH)(4\text{-}Xpz)_3]$ were formulated as containing the copper(II) ions bridged alternatively by a pair of 4-Xpz groups and a combination of 4-Xpz and OH groups to form linear-chain structures. A series of new copper(II) pyrazolate complexes, $[Cu(4\text{-}Xdmpz)_2]_n$ (X = H, **19**; Cl, **20**; Br **21**; Me, **22**) were synthesized and characterized (26). As a group these compounds differ from those previously studied (35, 36) in that they have bulky methyl substituents in the more sterically sensitive 3,5-positions. Compound **19** could be obtained from the metal/molten ligand reaction employed earlier in the preparation of $[Cu(pz)_2]_n$, (**15**), (35); for the other complexes this reaction led to impure products. A successful route to the required copper(II) compounds starting from the corresponding copper(I) derivatives, $[Cu(4\text{-}Xdmpz)]_3$, was developed (26). This method, which gave high yields in all cases, consists in the reaction at high temperature of the trinuclear copper(I) complexes $[Cu(4\text{-}Xdmpz)]_3$ with the pyrazole 4-XdmpzH under a dioxygen atmosphere.

Complexes **19–22** were reported to most likely have structures involving extended chains of copper ions linked by double pyrazolate bridges in analogy with the structures of species $[Cu(4\text{-}Xpz)_2]_n$, where X = H, Me, and Cl (35, 36). However, it is possible that the presence of methyl substituents in the 3,5-positions of the heterocyclic ring, causing steric hindrance, prevents the formation of an infinite polymeric chain.

Pyridine abstraction from $[Cu(dcmpz)_2(py)_2]$, **229,** via azeotropic distillation with benzene, allowed the isolation of the linear trinuclear complex $[Cu_3(dcmpz)_6]$, **23,** whose X-ray crystal structure was determined (40) (Eq. 1).

$$3[Cu(dcmpz)_2(py)_2] \rightleftharpoons [Cu_3(dcmpz)_6] + 6py \qquad (1)$$

In complex **23,** each copper atom is roughly square planar, with apical contacts involving some of the carbonylic oxygen atoms of the dcmpz ligands for the *external* copper(II) centers. The synthesis, characterization, and magnetic properties of a series of Cobalt(II) complexes containing the pyrazolate anion and several of its C-substituted derivatives have been reported (41). These compounds possess the general formula $[Co(pz^*)_2]_n$ (where Hpz* = Hpz, Hmpz, Hdmpz, Htmpz, 4-CldmpzH, and 4-BrdmpzH).

The complex $[Co(pz)_2]_n$ (**24**), was prepared by reacting $CoCl_2$ with Hpz in the presence of aqueous NaOH under anaerobic conditions. The remaining five binary Cobalt(II) (substituted)pyrazolates were synthesized with the metal/molten pyrazole method: Cobalt metal was combined with the appropriate substituted pyrazole and the mixture was heated in a dioxygen atmosphere. In all cases, the cobalt(II) pyrazolates were obtained as purple powders (41). The materials are microcrystalline and, although none could be obtained in a form suitable for single-crystal X-ray diffraction studies, indirect evidences supported polymeric doubly pyrazolate-bridged chain structure with pseudotetrahedral cobalt centers. Magnetic studies at variable temperature revealed anisotropy in the susceptibilities and the presence of significant antiferromagnetic exchange (41).

A limited number of $[M(pz^*)_2]_n$ species (M = Zn, Pt, or Pd) were obtained by removing the neutral coordinated Hpz* ligands from complexes of the general formula $[M(pz^*)_2(Hpz^*)_x]_2$ by thermolytic methods.

Heating $[Zn(dmpz)_2(Hdmpz)]_2$, **31**, at 240°C (see Fig. 5) caused the loss of Hdmpz and the formation of the species $[Zn(dmpz)_2]_n$, **25** (42). Complex **25** is assumed to be polymeric, with an infinite chain structure, by analogy with the known structure of other binary copper(II) pyrazolates (35).

The trimer $[Pt(pz)_2]_3$, **26**, was obtained mixed with the polymeric $[Pt(pz)_2]_n$, **27**, on decomposition of the dimeric complex $[Pt(pz)_2(Hpz)_2]_2$, **244** (43, 44). For **26**, the X-ray crystal structure confirmed that the Pt atoms are each bridged by two pyrazolate ligands in a ring configuration (43). The polymeric nature of complex **27** was only suggested.

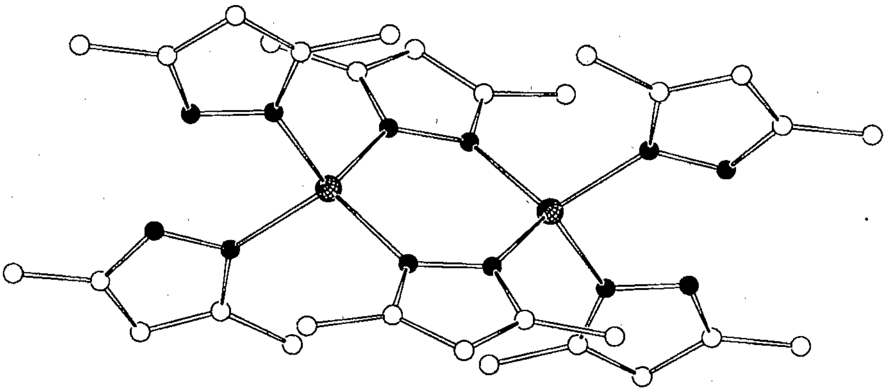


Figure 5. Structure drawing of $[Zn_2(dmpz)_2(Hdmpz)]_2$, **31**. [Based on data from (42).]

TABLE I
List of Structurally Characterized Binary Metal Pyrazolates

Cu	Reference	Ag	Reference	Au	Reference	Pt	Referenc
$[Cu(pz)]_n$	13	$[Ag(pz)]_n$	13	$[Au(dppz)]_3$	15	$[Pt(pz)_2]_3$	43
$[Cu(dmpz)]_3$	23	$[Ag(pz)]_3$	13	$[Au(dppz)]_6$	15		
$[Cu(dppz)]_3$	16	$[Ag(dppz)]_3$	15	$[Au(dfmpz)]_3$	47		
$[Cu(dppz)]_4$	17	$[Ag(dmpz)]_3$	21				
$[Cu\{(p\text{-}ClC_6H_5)_2pz\}]_3$	21						
$[Cu(tmpz)]_3$	26						
$[Cu(4\text{-}NO_2dmpz)]_3$	21						
$[Cu_4(4\text{-}NO_2dmpz)_6]^-$	21						
$[Cu(pz)_2]_n$	35						
$[Cu(dcmpz)_2]_3$	40						
$[Cu(4\text{-}Mepz)_2]_n$	36						
$[Cu(4\text{-}Clpz)_2]_n$	36						
		$[Pd_2Ag_4(dmpz)_8]$	45				

A related thermal reaction, carried out on the palladium(II) complexes $[Pd(pz)_2(Hpz)_2]_2$, **245**, and $[Pd(dmpz)_2(Hdmpz)_2]_2$, **246**, gave $[Pd(pz)_2]_n$, **28**, and $[Pd(dmpz)_2]_3$, **29**, respectively (45). An alternative synthesis of $[Pd(pz)_2]_n$ was already reported (46). It was obtained by reacting $PdCl_2$ with sodium pyrazolate, and was formulated as a polymeric species. For the palladium(II) Complex **29**, a trimeric structure has been suggested in analogy with the platinum(II) derivative **26** (43, 45).

The unique bimetallic homoleptic pyrazolate complex $[Pd_2Ag_4(dmpz)_8]$, **30**, was recently isolated and its X-ray crystal structure was determined (45). The hexanuclear complex **30** was obtained by reacting **246** with $AgNO_3$. Its molecular structure revealed close analogy with the precursor; indeed, Complex **30** can be thought of as derived by the formal substitution of the isolobal H^+ and Ag^+ fragments. The related Pd(II)/Cu(I) bimetallic complex $[Pd_2Cu_4(dmpz)_8]$ was analogously obtained (45), but its formulation was based only on IR evidences. Table I reports the structurally characterized binary metal pyrazolates.

III. COMPLEXES CONTAINING THE $M(\mu\text{-}pz^*)_2M$ CORE AND ADDITIONAL NEUTRAL OR CHARGED LIGANDS

In these complexes, identical or different metal centers are, generally, connected by two pyrazolate ligands coordinated in an exo-bidentate fashion. In most cases, the $M(\mu\text{-}pz^*)_2M$ core exhibits a boat conformation. Doubly bridged pyrazolate complexes are usually dimeric; however, in the last years some homo-(MMM) and heterotrinuclear (MM'M) species containing the metallocycles $M(\mu\text{-}pz^*)_2M(\mu\text{-}pz^*)_2M$ and $M(\mu\text{-}pz^*)_2M'(\mu\text{-}pz^*)_2M$ were reported.

A. Group 12 : Zn

Cleaned zinc metal shot was reported to react with excess Hdmpz in the presence of dioxygen at 90°C affording the dimeric complex $[Zn(dmpz)_2(Hdmpz)]_2$, **31**, in virtually quantitative yields (42). The molecular structure of **31** consists of two zinc atoms bridged by two dmpz groups with each zinc center being end-capped by a monodentate pyrazolate ion and a neutral Hdmpz molecule (Fig. 5). Strong hydrogen bonding occurs between the capped ligands.

The unexpected bis(dmpz) bridged tetrachloride di-zinc(II) anionic complex $[Zn_2(dmpz)_2Cl_4]^=$, was obtained by metal ion induced breakdown of a pyrazole-containing ligand, debd, when reacted with $ZnCl_2$ in methanol. The X-ray crystal structure of $[Zn(debd)Cl]_2[Zn_2(dmpz)_2Cl_4]$ was also determined (48).

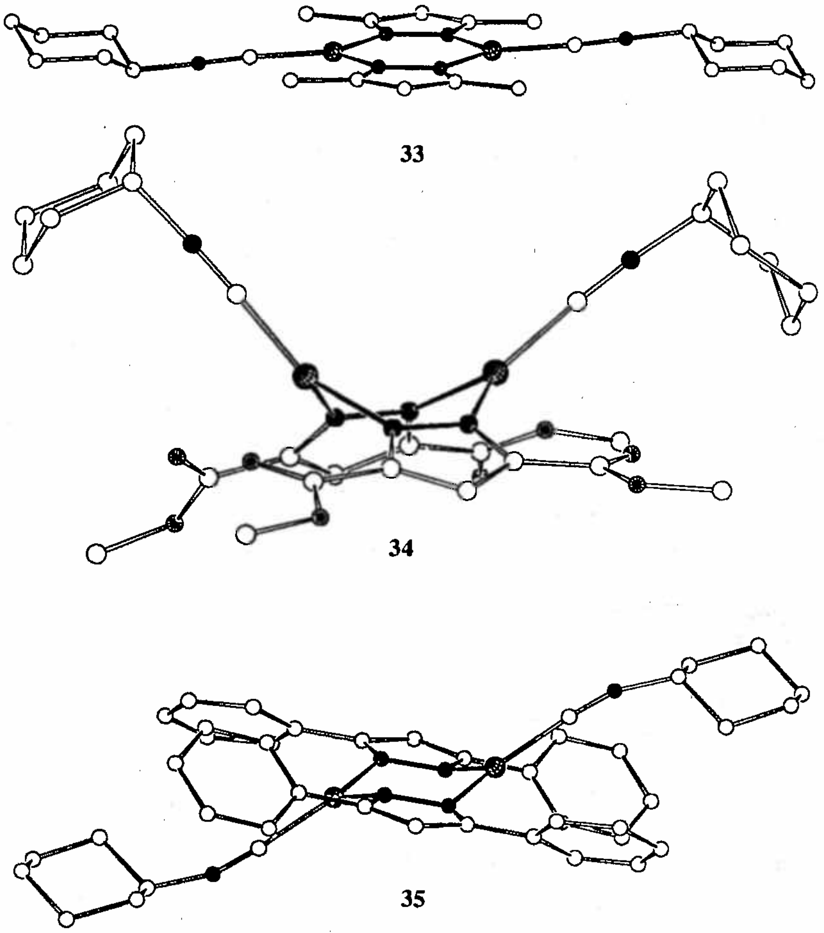
B. Group 11: Cu, Ag, or Au

Dinuclear complexes were obtained by reacting some binary copper(I) and silver(I) homoleptic pyrazolate complexes with neutral ligands. The trimeric $[Cu(dmpz)]_3$ (23) readily reacted with phen or RNC (R = cyclohexyl) to give the doubly bridged species $[(phen)Cu(\mu\text{-}dmpz)_2Cu(phen)]$, **32**, (49) or $[(RNC)Cu(\mu\text{-}dmpz)_2Cu(RNC)]$, **33** (50). The dimeric nature of **32** was argued from its spectroscopic and chemical properties, while **33** was characterized by an X-ray crystal structure analysis (50).

The $Cu(\mu\text{-}dmpz)_2Cu$ core in Complex **33** was found in an uncommon planar conformation. The related compound $[(RNC)Cu(pz)]_2$ was obtained from $[Cu(pz)]_n$ (**2a** or **2b** isomers) (13) on treatment with RNC (50). Dinuclear copper(I)-cyclohexylisocyanide complexes were also obtained by reacting $[Cu(dcmpz)]_n$ (27) or $[Cu(dppz)]_4$ (17) with RNC. The Complex $[(RNC)Cu(dcmpz)]_2$, **34**, is topologically equivalent to the dmpz analogue **33**; however, the pattern of bond distances and angles of the $Cu{-}(N{-}N)_2{-}Cu$ ring, as well as its conformation, is markedly different (27). The X-ray crystal structure of $[(RNC)Cu(dppz)]_2$, **35**, was reported and the results were compared with those of the parent Complexes **33** and **34** (17). Complex **35** possesses a $Cu{-}[N{-}N]_2{-}Cu$ ring in a chairlike conformation, which has only a few precedents (51–53) (Fig. 6).

The reactions of **33** with some heterocumulenes were described (50). The products result from *formal* nucleophilic addition of the dmpz anion to the central carbon of the heterocumulene to give a new bidentate ligand.

Carbon disulfide reacted with **33** in the presence of free RNC affording $[Cu\{dmpz\text{-}CS_2\}(RNC)_2]$, **36**. The $\nu(C{=}S)$ in **36** appeared at 1330 cm^{-1}, suggesting an NS coordination of the dithiocarboxylate anion. This mode of coordination was suggested in 1968 by Trofimenko (54) in the case of metal(II)



33

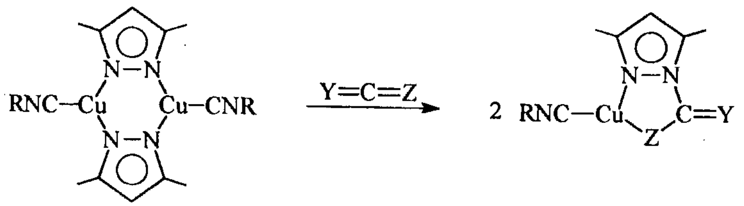
34

35

Figure 6. Structure drawings of [Cu(dmpz)(RNC)]$_2$, **33**, [Cu(dcmpz)(RNC)]$_2$, **34**, and [Cu(dppz)(RNC)]$_2$, **35** (R = cyclohexyl). Note the different conformations of the Cu-[N-N]$_2$-Cu rings. [Based on data from (17, 27, 50).]

pyrazolecarbodithioates. The X-ray crystal structure determination of Complex **36** substantiated such a hypothesis (55).

An unexpected reaction was reported to occur on treatment of [Cu(dcmpz)]$_n$, **12**, with CO in pyridine (27). The dinuclear monocarbonyl complex [Cu$_2$(dcmpz)$_2$(py)$_2$(CO), **37**, was obtained and its X-ray crystal structure was determined. An analogy was drawn between the CO-hemocyanin adduct and the dinuclear carbonyl Complex **37**. The observed stoichiometry of CO bonding



R = cyclohexyl

Y = O, Z = NR
Y = S, Z = NPh
Y = O, Z = S

to hemocyanin has been interpreted in terms of different actual coordination of the copper atoms (56). The formation of the carbonyl complex **37** was attributed to steric effects due to the pyridine ligands, which prevent the bonding of a second molecule of carbon monoxide.

Two $Ag^{(I)}/PPh_3$ pyrazolate complexes, $[(PPh_3)Ag(pz)]_2$, **38**, and $[(PPh_3)_3Ag_2(pz)_2]$, **39**, were isolated by reacting $[Ag(pz)]_n$, **1a**, with PPh_3 (21). The molar ratio PPh_3/Ag plays a determining role in order to isolate the two species in a pure form. The X-ray crystal structure was determined for both complexes (21).

The dinuclear species **38** contains the two silver(I) centers joined by two pz groups, giving rise to a planar $Ag—[N—N]_2—Ag$ ring conformation. Each silver(I) center coordinates a PPh_3 ligand. In Complex **39**, the two metal centers exhibit different coordination numbers (3 and 4, respectively). The geometries of the two silver atoms are planar trigonal and distorted tetrahedral, giving rise to an $Ag—[N—N]_2—Ag$ ring in a distorted boatlike conformation (21).

It was reported that $[Au(dppz)]_3$, **4**, on treatment with aqua regia formed a gold(III) dimeric species formulated as $[Au(4\text{-}Cldppz)]_2Cl_4$ on the basis of analytical data, molecular weight measurements, and spectroscopic properties (57). This reaction was reinvestigated and a crystallographically characterized product was isolated (58). The latter was shown to be a mixed-valence Au^I_2/Au^{III} complex in which the pyrazolate rings have been chlorinated, that is, $[Au_3(Cldppz)_3Cl_2]$, **40**. The molecule consists of three gold atoms bridged by three pyrazolate ligands, forming a $(Au—N—N)_3$ nine-membered planar metallocycle. Two of the metal atoms are two-coordinate linear Au^I centers and the third one is a square planar trans Au^{III} bearing the two chlorine ligands (58). A related mixed-valence Au^I_2/Au^{III} pyrazolate complex, $[Au(dppz)]_3Cl_2$, **41**, surprisingly formed by reacting the monomeric gold(III) species $AuCl_3(py)$ with Na(dppz) (59). This result was interpreted in terms of an unusual stability for the $d^{10}d^{10}d^8$ configuration of the pyrazolate metallocycle. The X-ray crystal structure (59) and an XPS study (58) of the heterovalent gold-pyrazolate trimer **41** was also reported.

C. Group 10: Ni, Pd, or Pt

The considerable nucleophilicity of the OH bridges in the anionic complexes $[\{R_2M(\mu\text{-OH})\}_2](NBu_4)_2$ (M = Ni, Pd, or Pt) is indicated by their reactivity toward weak acids such as pyrazoles, with formation of homodinuclear complexes of the formula $[\{R_2M(\mu\text{-pz}^*)\}_2](NBu_4)_2$ (Scheme 1) (60–66).

The di-μ-pyrazolate complexes reported in Scheme 1 are obtained in methanol using a 1 : 2 molar ratio of reactants. Their formulation was ascertained on the basis of analytical, spectroscopic, and conductance data. Moreover, the same complexes are obtained when the mixed-bridged μ-hydroxo-μ-pyrazolates species (see Section IV.A and Scheme 1) are reacted with Hpz*. This fact suggested the possible intermediate formation of complexes containing both μ-pz* and μ-OH bridges, from which the doubly bridged pyrazolate products are formed (60, 66).

Neutral pyrazolate-bridged dinuclear palladium(II) complexes of the general formula $[Pd_2X_2(\mu\text{-pz}^*)_2(PR_3)]$ (Hpz* = Hpz or Hdmpz; X = Cl, Br, I; PR_3 = PBu_3, PMe_2Ph, or $PMePh_2$) were prepared (67). These complexes were char-

$$\begin{tikzcd}
{[\{R_2M(\mu\text{-OH})\}_2](NBu_4)_2 + 2\,\mathrm{Hpz}^*} \arrow[rr, "-H_2O"] \arrow[dr, "\mathrm{Hpz}^*"', "-H_2O"] & & {[\{R_2M(\mu\text{-pz}^*)\}_2](NBu_4)_2} \\
& {[R_2M(\mu\text{-pz}^*)(\mu\text{-OH})MR_2](NBu_4)_2} \arrow[ur, "\mathrm{Hpz}^*"', "-H_2O"] &
\end{tikzcd}$$

M	R	Hpz*
Ni	C_6F_5	Hpz, Hmpz
Pd	C_6F_5	Hpz, Hmpz, Hdmpz
Pd	C_6Cl_5	Hpz, Hmpz
Pd	$C_6F_3H_2$	Hpz, Hmpz, Hdmpz
Pt	C_6F_5	Hpz, Hmpz, Hdmpz

Scheme 1. Exploiting the nucleophilicity of the OH bridges in the anionic complexes $[\{R_2M(\mu\text{-OH})\}_2](NBu_4)_2$ (M = Ni, Pd, or Pt) is possible to prepare a large number of doubly bridged pyrazolate complexes (see text for references).

acterized by elemental analysis, ^1H and ^{31}P NMR data and, in the case of $[Pd_2Cl_2(\mu\text{-dmpz})_2(PMe_2Ph)_2]$, **42,** by single-crystal X-ray diffraction methods. Attempts to synthesize platinum(II) analogues by using the same method of preparation as for the palladium(II) species, that is, by reaction of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with Hpz* in the presence of methanolic sodium hydroxide, gave either (μ-Cl)(μ-pz*) complexes or chloro-bridged derivatives containing terminal pyrazolate ligands (68, 69). However, dinuclear pyrazolate-bridged platinum(II) complexes of the type $[Pt_2Cl_2(\mu\text{-pz*})_2(PR_3)_2]$ (Hpz* = Hpz or Hdmpz; $PR_3 = PEt_3$, PMe_2Ph, or $PMePh_2$) were isolated in high yield from the reaction of $[Pt_2Cl_2(\mu\text{-}O_2CCH_3)_2(PR_3)_2]$ with Hpz* (70). A single-crystal structure of the representative complex $[Pt_2Cl_2(\mu\text{-dmpz})_2(PMePh_2)_2]$ was also reported (70).

A trinuclear nickel(II) complex, $[Ni_3(dmpz)_4(acac)_2]$, **43,** has been obtained by reacting $Ni(acac)_2$ with an equimolar amount of Na(dmpz) (71). Its X-ray crystal structure emphasized that the geometry of each nickel atom is square planar and these planes provide the zigzag mode. The terminal and center nickel atoms are bridged by nitrogen atoms of two dmpz groups. Furthermore, the terminal metal centers are coordinated to two oxygen atoms of acac.

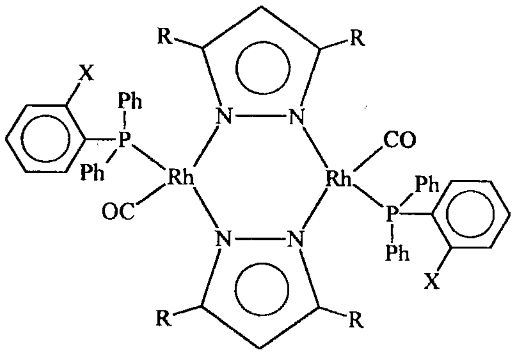
D. Group 9: Co, Rh, or Ir

The dimeric $[Co(dmpz)_2(Hdmpz)]_2$, **44,** and the trimetallic $[Co(dmpz)_2Cl(Hdmpz)]_2Co$, **45,** complexes were synthesized. These complexes were studied magnetically and by single-crystal X-ray diffraction (72). Complex **44** was shown to be isomorphous and isostructural with the zinc analogue $[Zn(dmpz)_2(Hdmpz)]_2$, **31** (42). The IR data for **44** reflect the presence of strong hydrogen bonding in the molecule with the appearance of two broad ν(NH) bands at about 2380 and 1870 cm^{-1}, and a γ(NH) band appearing at 865 cm^{-1}. Complex **45** crystallizes as a trimetallic molecule with the Co^{II} ions in an approximately linear arrangement. The terminal cobalt atoms are linked to the central cobalt by double dmpz bridges. The central cobalt is coordinated by four pyrazolate nitrogen atoms in a pseudotetrahedral fashion. The terminal Co^{II} ions are also coordinated by one Hdmpz and one chloride ion in a distorted tetrahedral manner.

In 1981, Usón et al. (73) reported a general route to the synthesis of pyrazolato bridged dirhodium(I) complexes of the formula $[(PR_3)(CO)Rh(\mu\text{-pz*})]_2$. It consists in the treatment of $[(cod)Rh(\mu\text{-Cl})]_2$ with an alkali pyrazolate followed by reaction with CO and tertiary phosphines (Eq. 2).

$$[(cod)Rh(\mu\text{-Cl})]_2 \xrightarrow{pz^-} [(cod)Rh(\mu\text{-pz})]_2 \xrightarrow{CO}$$

$$[(CO)_2Rh(\mu\text{-pz})]_2 \xrightarrow{PR_3} [(PR_3)(CO)Rh(\mu\text{-pz})]_2 \qquad (2)$$



R = H, X = COOH, **46**

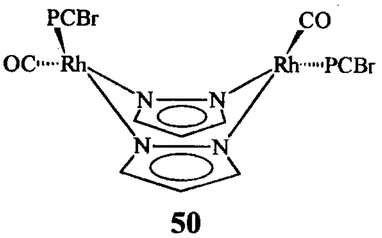
R = Me, X = COOH, **47**

R = H, X = CHO, **48**

R = Me, X = CHO, **49**

The aforementioned synthetic strategy was found also to be applicable to the synthesis of Complexes **46–49** (74, 75). The X-ray crystal structure of **49** was reported (75).

Moreover, it was reported that the complex [Rh(μ-pz)(CO)(PCBr)]$_2$, **50** [PCBr = P(o-BrC$_6$F$_4$)Ph$_2$], prepared, accordingly Eq. 2, by treating [Rh(μ-pz)(CO)$_2$]$_2$ with a stoichiometric amount of PCBr, undergoes orthometalation by a 2c–2e oxidative-addition reaction to give low yields of a new dinuclear compound containing a rhodium–rhodium bond, [Rh$_2$(μ-pz)$_2$(μ-PC)Br(CO)(PCBr)] (**51**). This complex was structurally characterized by X-ray crystallography (76).



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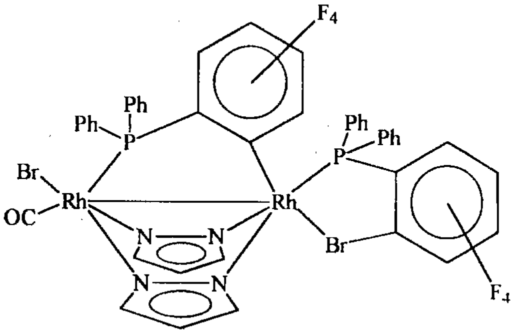


51

These results have been extended to other complexes of the **50** type; it was ascertained that when substituted pyrazolate ligands were used, the orthometalation reaction becomes more selective (77). The X-ray crystal structure of [Rh$_2$(μ-dmpz)$_2$(μ-PC)Br(CO)(PCBr)], **52**, was also reported (77).

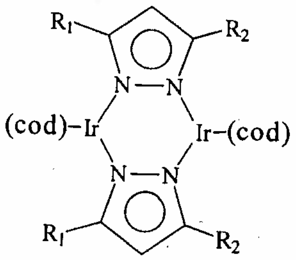
Dinuclear pyrazolate bridged iridium(I) complexes were prepared by employing a synthetic route analogue to that used for the rhodium(I) derivatives, namely, from $[Ir(cod)(\mu\text{-}Cl)]_2$ by Cl displacement by Hpz* in basic medium (78) (Eq. 3):

$$[Ir(cod)(\mu\text{-}Cl)]_2 \xrightarrow[\text{base}]{\text{Hpz*}} [Ir(cod)(\mu\text{-}pz^*)]_2 \qquad (3)$$

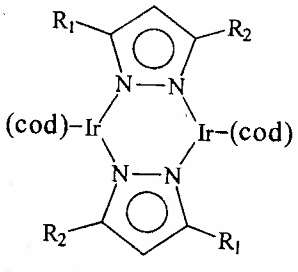
$$(\text{base} = NEt_3,\ K(t\text{-}BuO))$$

$$(\text{Hpz*} = \text{4-MepzH, Hmpz, Hdmpz, Hdppz, 3-Ph-5-MepzH, } 3\text{-}CF_3\text{-5-MepzH, Hdfmpz, Htmpz, 4-ClpzH, 4-IpzH, } 4\text{-}NO_2\text{pzH, 4-CldmpzH, } 3\text{-}CF_3\text{-5-PhpzH})$$

These products were characterized by ^1H and ^{13}C NMR spectroscopy. Among complexes incorporating unsymmetrically substituted bridging pyrazolates, $[Ir(cod)(\mu\text{-mpz})]_2$ and $[Ir(cod)(\mu\text{-}3\text{-}CF_3\text{-5-Mepz})]_2$ exist as diastereoisomeric mixtures (**C** and **D**) with an approximate 1 : 1 ratio, while for $[Ir(cod)(\mu\text{-3-Ph-5-Mepz})]_2$ the diastereoisomer **D** predominates.



C



D

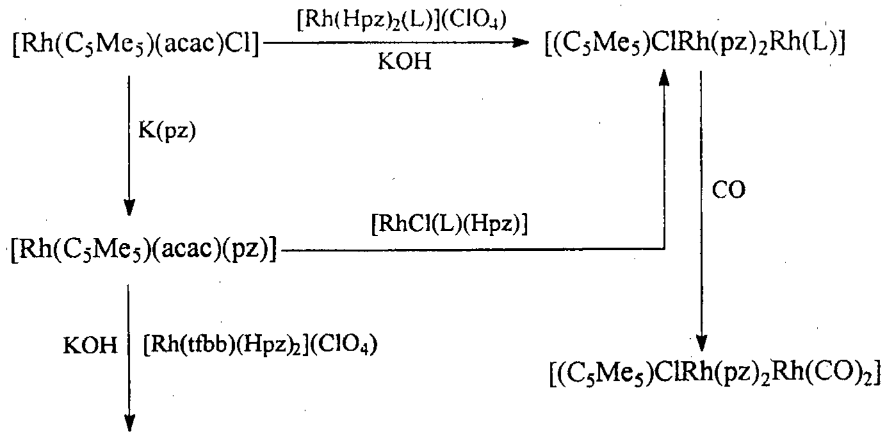
The crystal and molecular structures of the 3-Ph-5-Mepz and tmpz derivatives, as well as the synthesis of the "mixed-bridge" analogue $[Ir(cod)(\mu\text{-pz})(\mu\text{-dfmpz})Ir(cod)]$ and the mixed-metal complex $[Rh(cod)(\mu\text{-pz})_2Ir(cod)]$, were reported (78). The reaction of $[\{Rh(C_5Me_5)\}_2(\mu\text{-OH})_3](ClO_4)$ with an excess of Hpz* and KOH, gave neutral complexes of the formula $[\{Rh(C_5Me_5)(pz^*)\}_2(\mu\text{-}pz^*)_2]$ (Hpz* = Hpz, **53**; 4-BrpzH, **54**) (52). The X-ray structural analysis of Complex **53** confirmed the presence of either exo-bidentate or monodentate pyrazolate groups in the solid state. The addition of $HClO_4$ to Complex **54** resulted in the protonation of the monodentate pyrazolate ligand with formation of $[\{Rh(C_5Me_5)(4\text{-BrpzH})\}_2(\mu\text{-4-Brpz})_2](ClO_4)_2$. Complex **54** can be regenerated on treatment with KOH.

The existence of the well-known acac complex $[Rh(C_5Me_5)(acac)Cl]$ potentially provides a preparative route to dinuclear rhodium(III)–rhodium(I) species with two pz* groups acting as bridging ligands. Thus, its reaction with the cationic complexes $[Rh(Hpz)_2(L)](ClO_4)$ (L = tfbb or cod) in the presence of stoichiometric amounts of KOH, yielded the corresponding neutral complexes $[(C_5Me_5)ClRh(\mu\text{-}pz)_2Rh(L)]$ (79). The latter complexes can be alternatively prepared by reacting the neutral $[(C_5Me_5)Rh(acac)(pz)]$ with $[RhCl(Hpz)(L)]$. The reaction of $[(C_5Me_5)Rh(acac)(pz)]$ with the cationic rhodium(I) complex $[Rh(tfbb)(Hpz)_2](ClO_4)$ in the presence of KOH afforded $[(C_5Me_5)(pz)Rh(\mu\text{-}pz)_2Rh(tfbb)]$, which was reported to contain terminal and bridged pyrazolate groups on the basis of their ^1H NMR spectra. Carbonylation of $[(C_5Me_5)(Cl)Rh(\mu\text{-}pz)_2Rh(L)]$ caused the displacement of the coordinated diolefin and the formation of the carbonyl complex $[(C_5Me_5)(Cl)Rh(\mu\text{-}pz)_2Rh(CO)_2]$, (**55**) (Scheme 2) (79).

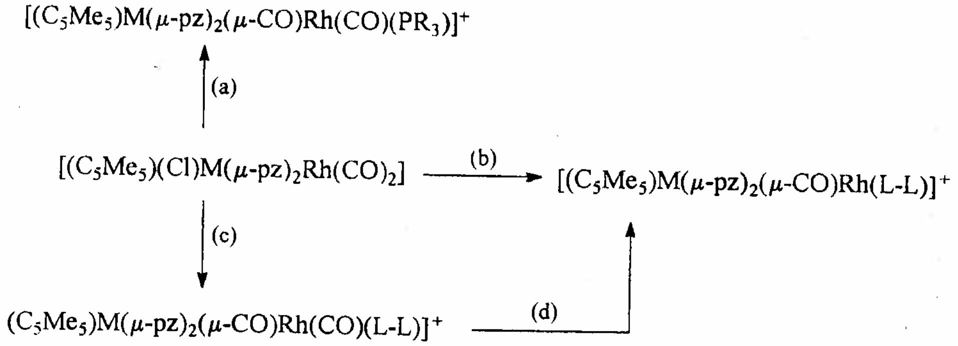
The reactivity of Complex **55**, of the related iodo derivative $[(C_5Me_5)(I)Rh(\mu\text{-}pz)_2Rh(CO)_2]$, **56**, and of the heterobimetallic compound $[(C_5Me_5)(Cl)Ir(\mu\text{-}pz)_2Rh(CO)_2]$, **57**, with monodentate tertiary phosphines, diphosphines, and diarsines was also investigated (Scheme 3) (80–82).

The structure of $[(C_5Me_5)ClRh(\mu\text{-}pz)_2(\mu\text{-}CO)Rh(dppp)](BPh_4)$ was established by X-ray crystallography (81).

Only in the last decade has it become apparent that oxidative addition may result in attachment of substrate fragments at other than a single metal site, although such events have frequently been hypothesized in relation to cooperativity effects in biological systems, as well as in the context of heterogeneous catalytic reactions, especially reorganization of organic molecules at metal surfaces. Around 1980 it was found that doubly bridged pyrazolate iridium(I) dimers undergo facile reactions with halogens or alkyl halides yielding complexes



Scheme 2. The acetylacetonate complex $[Rh(C_5Me_5)(acac)Cl]$ provides a convenient preparative route to doubly bridged Rh(I) pyrazolate derivatives (see text for references).

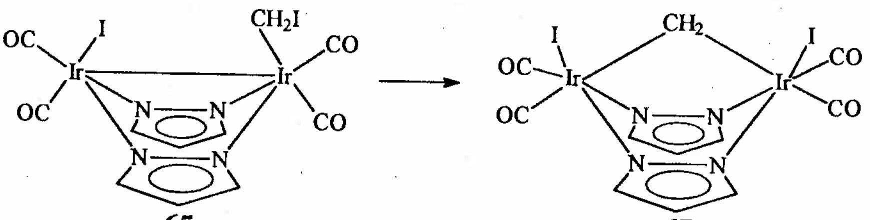


Scheme 3. Reactivity of the species $[(C_5Me_5)(Cl)M(\mu\text{-pz})_2Rh(CO)_2]$. (M = Rh, or Ir) (a) PR_3 (R = Ph or Cy), $NaBPh_4$, MeOH; (b) L—L (dppm, dppp, dppb, or dpae), $AgBF_4$ (c) L—L, $NaBPh_4$, MeOH; (d) acetone or $CHCl_3$ or CH_2Cl_2 (see text for references).

formulated as the products of a two-center oxidative addition (83, 84). In late 1984, Atwood et al. (85) reported the spectral data and the full characterization by X-ray crystallography of the dinuclear complex $[Ir(PPh_3)(CO)(\mu\text{-pz})]_2$, **58.** Reactions of **58** with I_2, Br_2, or Cl_2 gave products formulated as $[Ir(PPh_3)(CO)(X)(\mu\text{-pz})]_2$ (X = Cl, **59;** Br, **60;** I, **61**), having each metal center in a formal II oxidation state (85). In the case of reaction with Cl_2, Cl substitution at the 4-position in the pyrazolyl ring was observed. The X-ray crystal structure analysis for **59** revealed that the Ir—Ir separation had indeed shortened to within bonding distance. Reaction of **58** with MeI was reported to yield a similar 1 : 1 adduct (85).

A series of two fragment, two-center additions of CH_2I_2 to the doubly bridged pyrazolate iridium(I) dimers $[IrL_2(\mu\text{-pz})]_2$ [L_2 = $(CO)_2$, **62;** cod, **63;** CO, PPh_3, **64**] was reported to form 1 : 1 adducts, $[Ir_2(L_2)_2(\mu\text{-pz})_2(I)(CH_2I)]$, which were formulated mainly on the basis of spectroscopic data (86). Interestingly, complexes $[Ir_2(CO)_4(\mu\text{-pz})_2(I)(CH_2I)]$, **65,** and $[Ir_2(CO)_2(PPh_3)_2(\mu\text{-pz})_2(I)(CH_2I)]$, **66,** readily undergo thermal "oxidative isomerization" to the di-iridium(III) methylene species $[Ir_2(CO)_4(\mu\text{-pz})_2(\mu\text{-}CH_2)(I)_2]$, **67,** and $[Ir_2(CO)_2(PPh_3)_2(\mu\text{-pz})_2(\mu\text{-}CH_2)(I)_2]$, **68** (86, 87).

An X-ray crystal structure determination for Compound **68** confirmed that



65 **67**

the two Ir centers lie outside the bonding range at 3.43 Å, with a bridging CH_2 group (87). The isomerization of Complexes **65** and **66** to the di-iridium(III) methylene species **67** and **68** lays emphasis to the remarkable role of the pyrazolate ligands. In fact, it was reported that the oxidative addition of CH_2I_2 to the neutral dinuclear iridium(I) complex $[Ir_2(CO)_4(\mu\text{-}C_5H_4NS)_2]$ (C_5H_4NS = 2-pyridinethiolate) afforded $[Ir_2(CO)_4(\mu\text{-}C_5H_4NS)_2(I)(CH_2I)]$ as the final product, with no formation of a methylene-bridged complex $[\{Ir(\mu\text{-}C_5H_4NS)_2(I)(CO)_2\}(\mu\text{-}CH_2)]$, analogous to **67**, occurring (88).

Kinetic data for two-fragment, two-center addition of MeI to the iridium(I) dimers **62** and **63** were reported (89). Addition of MeI occurs irreversibly to **62** in two kinetically distinguishable steps; by contrast MeI and **63** enter into equilibrium.

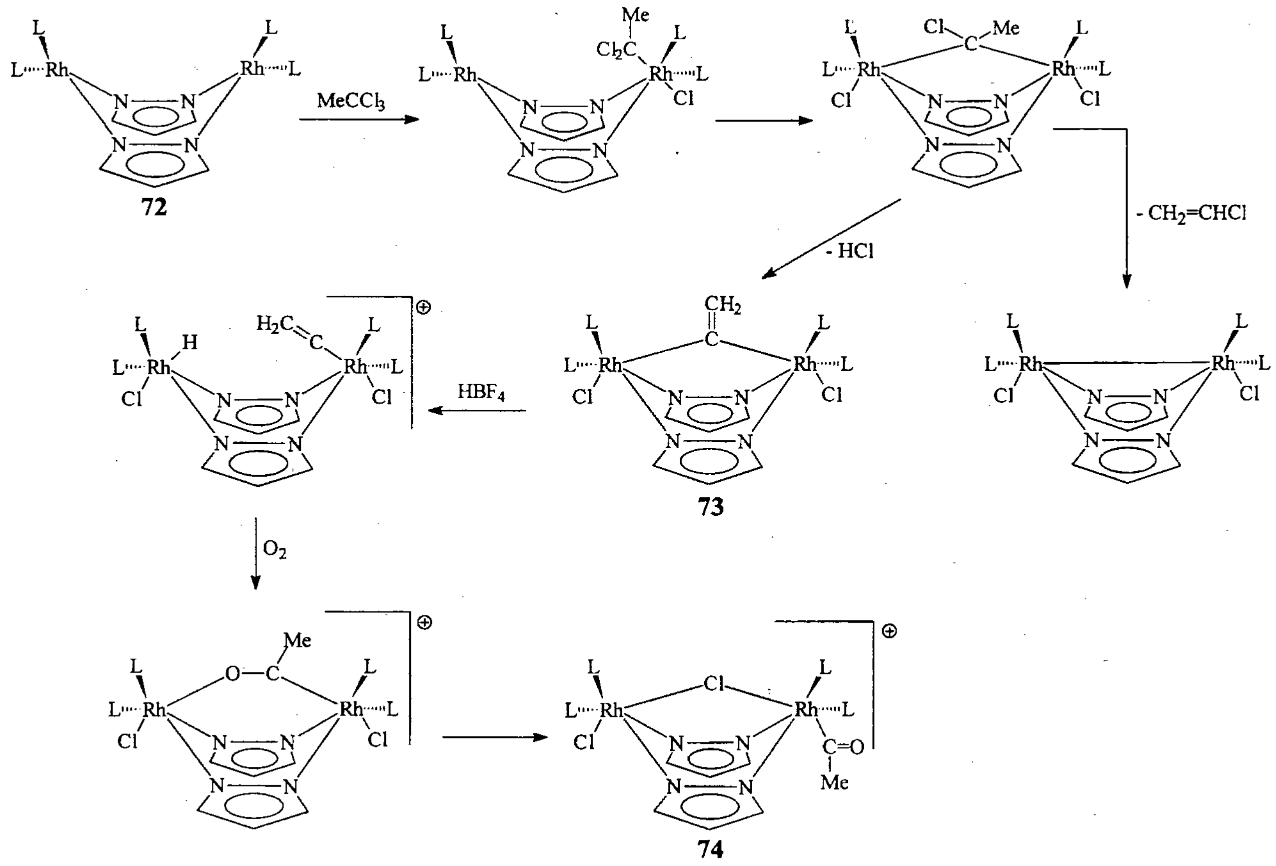
The treatment with gaseous HCl of the cationic nitrosyl-pyrazolate complex $[(cod)(NO)Ir(\mu\text{-}pz)_2Ir(cod)](BF_4)$, **69** (obtained from $[Ir(cod)(\mu\text{-}pz)]_2$ and $NOBF_4$) led to the isolation of $[(cod)(Cl)Ir(\mu\text{-}pz)_2(\mu\text{-}NO)Ir(Cl)(cod)](BF_4)$, **70** (90). Complex **70** has been characterized by X-ray crystal structure determination (90). The reaction affording complex **70** has been described as an unprecedented two-center oxidative addition as a result of which a bent, terminal NO group takes up a bridging position.

Oxidative–addition reaction by iodine carried out in methanol or ethanol on complexes $[(C_5Me_5)(Cl)Rh(\mu\text{-}pz)_2Rh(CO)_2]$, **55**, or $[(C_5Me_5)(Cl)Ir(\mu\text{-}pz)_2Rh(CO)_2]$, **71**, in the presence of sodium salts such as $NaBPh_4$ or $NaI \cdot 2H_2O$, gave the alkoxycarbonyl complex $[(C_5Me_5)M(\mu\text{-}pz)(\mu\text{-}I)_2Rh(I)(CO_2R)(CO)]$ (M = Rh, R = Me or Et; M = Ir, R = Me). The molecular structure of the Ir/Rh derivative was also determined (82).

The alkoxocarbonyl complexes described above are thought to be the products of the nucleophilic attack of MeOH or EtOH on the dinuclear carbonyl Complexs **55** and **71**, which were previously oxidized by iodine, as the latter complex are indefinitely stable in alcohols (82).

The easy three-fragment, four-electron oxidative addition of chloroform and gem-dichloroalkanes to $[Rh(\mu\text{-}pz)(t\text{-}BuNC)_2]_2$, **72**, were prepared in good yield by replacement of cod in $[Rh(\mu\text{-}pz)(cod)]_2$ (91, 92), yielding functionalized methylene bridged complexes (93). Thus, molecules such as $CHCl_2R$ (R = H, Ph, COOMe, or Cl) react with Complex **72** to yield mainly $[\{Rh(\mu\text{-}pz)Cl(t\text{-}BuNC)_2\}_2(\mu\text{-}CHR)]$ and $[Rh(\mu\text{-}pz)Cl(t\text{-}BuNC)_2]_2$ as side products. A definitive proof of the structure of the methylene-bridged complexes comes from their ^1H and ^{13}C NMR spectra (93). No intermediates were observed in these reactions.

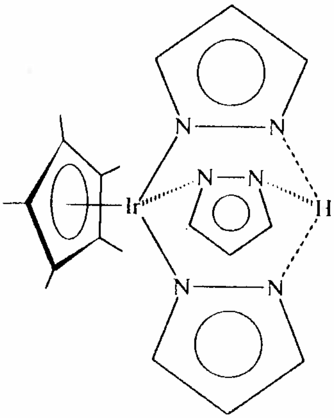
The reaction of **72** with 1,1,1-trichloroethane was also tested (92). A spontaneous elimination of HCl takes place and $[\{Rh(\mu\text{-}pz)Cl(t\text{-}BuNC)_2\}(\mu\text{-}C{=}CH_2)]$, **73**, containing a bridging vinylidene ligand, was obtained and structurally characterized (93). Interestingly, the subsequent reaction of **73** with $HBF_4 \cdot Et_2O$ and O_2 afforded the cationic dinuclear acyl derivative $[\{Rh(\mu\text{-}pz)(t\text{-}BuNC)_2\}_2(\mu\text{-}Cl)Cl(\eta^1\text{-}COCH_3)](BF_4)$, **74** (Scheme 4). The latter reaction in-



Scheme 4. Reaction of $[Rh(\mu\text{-pz})(L)_2]_2$, **72** (L = *t*-BuNC) with $MeCCl_3$ and proposed mechanism for the formation of the acyl derivative **74** (see text). [Adapted from (94).]

volves the oxidation of a vinylidene ligand by molecular oxygen, although the starting complex does not react with O_2 and vinylidene ligands are not easy to oxidize. A plausible mechanism for these reactions was proposed (94).

In 1986, the preparation and characterization of the bis(pyrazolate)pyrazole complex $[C_5Me_5)Ir(pz)_2(Hpz)]$, **75**, was described (95).



75

From a coordination point of view, Complex **75** and the related ruthenium complex $[(\eta^6\text{-}p\text{-cymene})Ru(pz)_2(Hpz)]$, **76** (7), are comparable to protonated polypyrazolylborates $RB(pz)_2(pzH)$ (R = H or pz) (12). The formal similarity between the tris(pyrazolyl)borate anion and the deprotonated form of the iridium complex **75** suggested the preparation of heterodinuclear complexes by using **75** as a building block. Thus, heterodinuclear $(\mu\text{-pz})_2$ complexes of the formula $[(C_5Me_5)(pz)Ir(\mu\text{-pz})_2M(PPh_3)]$ (M = Cu, **77**; Ag, **78**; Au, **79**) were obtained (96).

Complexes **77–79** were characterized by elemental analysis, spectroscopic measurements and, for Complex **78**, by X-ray crystal structure determination. Complexes **77–79** exhibit fluxional properties: At room temperature the $M(PPh_3)$ fragment exchanges fast among the three free nitrogen atoms of the pyrazolate ligands. The crystal structure of Complex **78** shows that, in the solid state, there is a free nitrogen atom whose lone-electron pair can be potentially used to further coordination. In effect, Complex **78** reacts with equimolar amounts of $AgBF_4$ and PPh_3, affording the trinuclear complex $[(C_5Me_5)Ir(\mu\text{-}pz)_3\{Ag(PPh_3)\}_2](BF_4)$, **80.** Spectral data of **80** have been interpreted as the existence of a fluxional process that renders the three pyrazolate and the two $Ag(PPh_3)$ groups equivalent (96).

Iridium–rhodium heterometallic complexes of the formula $[(C_5Me_5)(pz)Ir(\mu\text{-}$

$pz)_2RhL_2]$ [L_2 = cod, **81**; $(CO)_2$, **82**)] were also isolated (96). The free nitrogen atom of Complexes **81** and **82** is again capabale of coordination to the cationic moiety $[Ag(PPh_3)]^+$, which is isolobal to the proton. Consequently, heterotrinuclear complexes, Ir/Ag/Rh, were prepared (96). The dynamic behavior of the heterobimetallic compounds **78**, **80**, and $[(C_5Me_5)(PPh_3)Ir(\mu\text{-}pz)_2\text{-}Ag(PPh_3)](BF_4)$, **83**, were studied by multinuclear NMR spectroscopy (97). The results demonstrated that argentotropism accounts for the observed spectra of Compounds **78** and **80**; in the case of Compound **83**, the dynamic behavior corresponds to a flipping of the central heteroring $Ir{-}[N{-}N]_2{-}Ag$ (97).

An electrochemical study of the behavior of the dinuclear complex $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}dmpz)_2]$, **84**, was described (98). This species undergoes two consecutive oxidation processes at a platinum electrode. The first oxidation gives the corresponding cationic species, $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}dmpz)_2]^+$, as inferred from electrochemical and spectroscopic examination of the oxidized product.

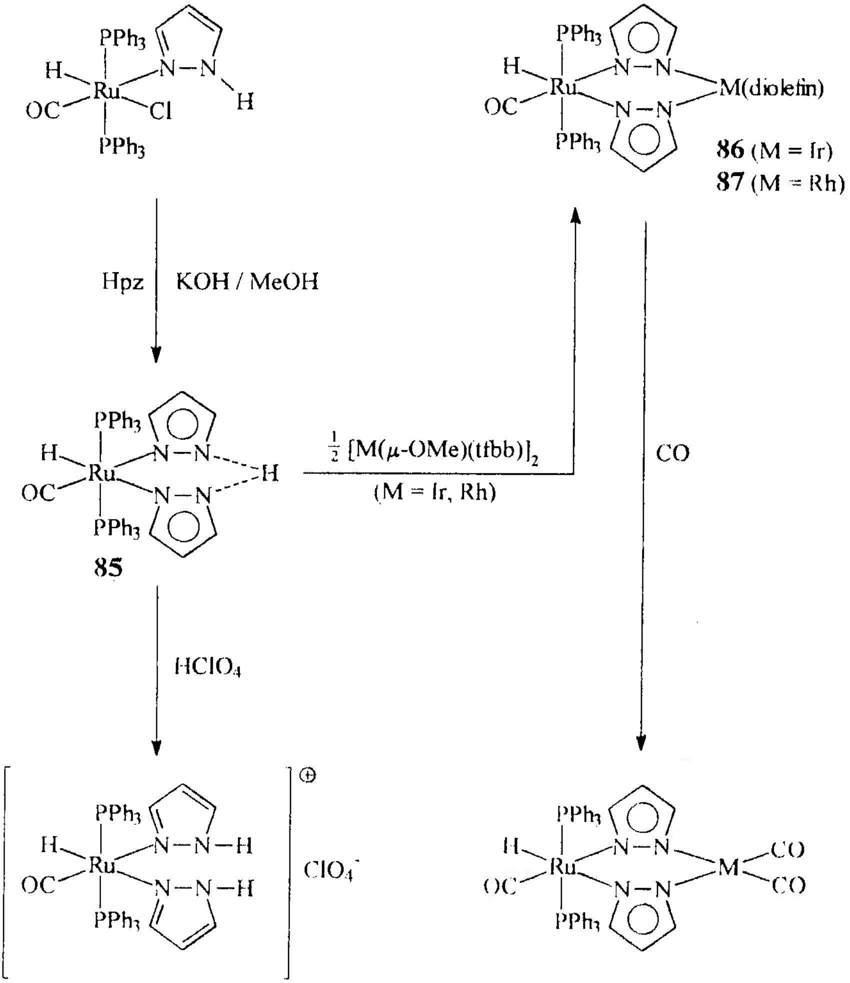
The rates of photoinduced electron transfer (ET) reactions in a series of iridium (spacer)pyridinium complexes, $[Ir(\mu\text{-}dmpz)(CO)(Ph_2PO\text{-}CH_2\text{-}CH_2\text{-}py^+)]_2$ and $[Ir(\mu\text{-}dmpz)(CO)(Ph_2PO\text{-}C_6H_4(CH_2)_n\text{-}py^+)]_2$ ($n = 0 - 3$), have been studied in acetonitrile solution at room temperature (99). The nuclear reorganization energies and electronic couplings in these systems have been evaluated.

The dimeric iridium(I) compound $[Ir(\mu\text{-}dmpz)(CO)(Ph_2PO\text{-}C_6H_5Me)]_2$ has been synthesized by the reaction of $[Ir(\mu\text{-}dmpz)(CO)_2]_2$ with the 4-tolyl-diphenylphosphinite ligand, $Ph_2PO\text{-}C_6H_4Me$ (99) and its X-ray crystal structure has been determined (100). The photophysical and electrochemical properties of this iridium dimer complex have been investigated (100).

E. Group 8: Fe, Ru, or Os

By using $[RuH(Cl)(CO)(Hpz)(PPh_3)_2]$ (101) as the starting reagent, a series of new mono- and dinuclear complexes containing two pyrazole groups can be prepared (102). Thus, treatment of $[RuH(Cl)(CO)(Hpz)(PPh_3)_2]$ with stoichiometric amounts of KOH and Hpz afforded the neutral complex $[RuH(pz)(CO)(Hpz)(PPh_3)_2]$, **85**. The latter complex reacted with $[M(\mu\text{-}OMe)(tfbb)]_2$ yielding the dinuclear compounds $[(PPh_3)_2(CO)HRu(\mu\text{-}pz)_2M(tfbb)]$ (M = Ir, **86**; Rh, **87**). The diolefin tfbb, in Compounds **86** and **87**, can be easily displaced by carbon monoxide yielding $[(PPh_3)_2(CO)HRu(\mu\text{-}pz)_2M(CO)_2]$ (102) (Scheme 5).

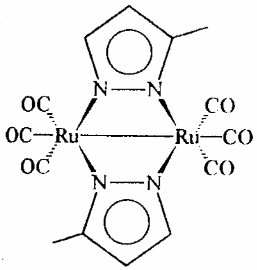
The dinuclear complexes $[Ru_2(\mu\text{-}pz^*)_2(CO)_6]$ (Hpz* = Hpz, **88**; Hdmpz, **89**; 4-MepzH, **90**, Hmpz, **91a**, and **91b**) were prepared by reaction of $RuCl_3 \cdot nH_2O$, the cheapest starting material for ruthenium compounds, with CO followed by reduction with zinc in the presence of Hpz* and CO (103, 104) or, alternatively, by reacting $Ru_3(CO)_{12}$ with the relevant Hpz* (105).



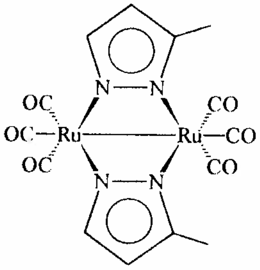
Scheme 5. Synthesis and some reactions of the pyrazole/pyrazolate Ru(II) derivative $[RuH(pz)(CO)(Hpz)(PPh_3)_2]$, **85**. [Adapted from (102).]

These complexes were fully characterized and the X-ray crystal structure of **89** was also reported. The reactivity of these dinuclear complexes toward a variety of nitrogen- and phosphorus-donor ligands was described (104–106) as well as oxidative-addition reaction with iodine (104).

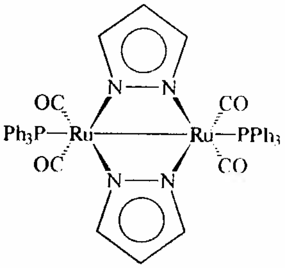
With monodentate phosphines, monosubstituted or disubstituted products such as $[Ru_2(\mu\text{-pz*})_2(CO)_5(PR_3)]$ or $[Ru_2(\mu\text{-pz*})_2(CO)_4(PR_3)_2]$ were obtained depending on the nature of the pyrazolate ligand. Complex **97** (Table II) was



91a



91b



97

alternatively obtained by the reaction of Na(pz) with $[Ru_2(CO)_4(O_2CMe)(MeCN)_2]$ followed by addition of PPh_3 and its X-ray crystal structure was determined (107). A nitrogen-containing ligand such as MeCN or py gave $[Ru_2(\mu\text{-dmpz})_2(CO)_5(L)]$ when it was reacted with **89** (104). The dmpz derivative (**89**) afforded the monosubstituted species even with dppm (Table II) (104). The reaction of **88** or **89** with carboxylic acids affords the carboxylato-bridged dimers $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2(Hpz^*)_2]$ (105). In this process, the heterocyclic bridging ligand is transformed into the monodentate Hpz* group. The unity of the system is maintained by the carboxylato bridges formed. The ligands dppe and cyclop react with **88** to give the diphosphine bridged monosubstitution products **98** and **99**.

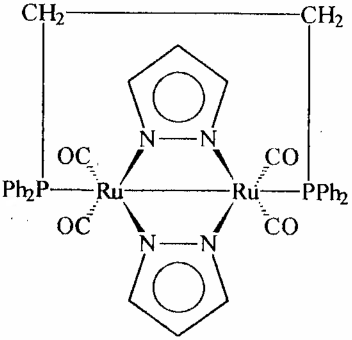
On the contrary, with **89**, the coordination of dppe and cyclop proceed under ortho-metalation of the phenyl group to generate the hydrido clusters **100** and **101** (106). The X-ray crystal structure of **100** evidenced an almost symmetrical position between the Ru atoms for the bridging hydride ligand (106).

Complexes **88** and **89** reacted with I_2 to afford $[Ru_2(\mu\text{-I})(\mu\text{-pz}^*)_2(CO)_6]I_3$ or $[Ru_2I_2(\mu\text{-pz}^*)_2(CO)_6]$ depending on the Ru/I ratio used. The crystal structure of

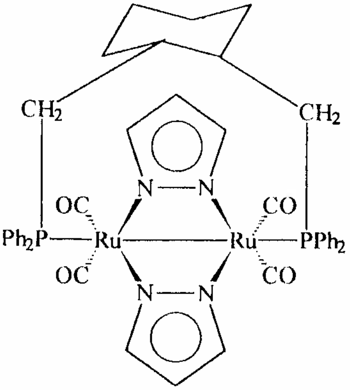
TABLE II

Dinuclear Complexes of Formula $[Ru_2(CO)_4(pz^*)_2(L)(L')]$

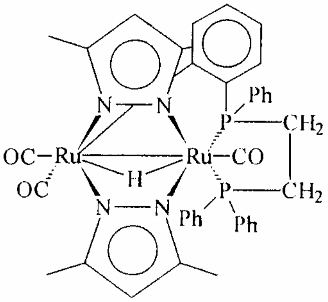
Complex	Hpz*	L	L′	Notes
88	Hpz	CO	CO	
89	Hdmpz	CO	CO	X-ray
90	4-MepzH	CO	CO	
91	Hmpz	CO	CO	Two isomers
92	Hdmpz	CO	MeCN	
93	Hdmpz	CO	py	
94	Hdmpz	CO	PPh_3	
95	Hdmpz	CO	$P(C_6H_{11})_3$	
96	Hdmpz	CO	dppm	
97	Hpz	PPh_3	PPh_3	X-ray



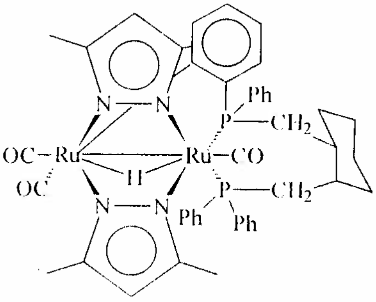
98



99



100



101

89 and [Ru$_2$(μ-I)(μ-dmpz)$_2$(CO)$_6$]I$_3$ were determined by X-ray diffraction methods. The Ru—Ru distance in **89** is consistent with a metal–metal bond (104).

The reaction of the mononuclear ruthenium *p*-cymene pyrazolate complex [(η^6-*p*-cymene)Ru(pz)$_2$(Hpz)], **76**(7) with the halide triphenylphosphine complexes [MCl(PPh$_3$)]$_x$ and KOH led to the corresponding heterodinuclear compounds [(η^6-*p*-cymene)(pz)Ru(μ-pz)$_2$M(PPh$_3$)] (M = Cu, **102**; Ag, **103**; Au, **104**) (108). The ^{1}H and ^{31}P NMR data of **103** are comparable to those of [(C$_5$Me$_5$)(pz)Ir(μ-pz)$_2$Ag(PPh$_3$)], **78**, for which an X-ray crystal structure analysis was performed (96). It is therefore reasonable that both compounds adopt similar structures.

Complex **103** reacted with AgBF$_4$ and PPh$_3$ to yield the heterotrinuclear RuAg$_2$ complex [(η^6-*p*-cymene)Ru(μ-pz)$_3${Ag(PPh$_3$)}$_2$](BF$_4$) (108). The NMR data of this complex can be interpreted by assuming that a fluxional process consisting of the rotation of the two Ag(PPh$_3$) fragments around the three free nitrogen atoms of the (η^6-*p*-cymene)Ru(pz)$_3$ moiety was occurring in a concerted way.

The ruthenium complex **76** reacted with equimolar amounts of [M(acac)L$_2$] (M = Rh, L$_2$ = cod or (CO)$_2$; M = Ir, L = CO) to give the corresponding heterodinuclear complexes [(η^6-*p*-cymene)(pz)Ru(μ-pz)$_2$ML$_2$]. The latter compounds gave cationic derivatives of formula [(η^6-*p*-cymene)(Hpz)Ru(μ-pz)$_2$ML$_2$](BF$_4$) when treated with an equimolar amount of HBF$_4$. An X-ray crystal structure determination was performed for the cationic complex having M = Ir and L = CO (108).

IV. HETEROBRIDGED PYRAZOLATE COMPLEXES

A. Complexes Containing the (μ-pz*)$_a$(μ-X)$_b$(μ-Y)$_c$ Fragment

A variety of heterobridged di- and trinuclear complexes containing, along with pyrazolate ligands, simple anions such as Cl, OH, OR, N$_3$, or SCN, in which single atoms are the bridging groups, were prepared (109–113). Among these complexes, the formation and the chemical properties of mixed-bridged complexes containing the (μ-pz*)(μ-SR) fragment was thoroughly investigated (109–114, 117, 118). The increasing interest for these mixed-bridged systems arises also from the recognized good catalytic activity, under mild conditions, of the homobridged complex [Rh$_2$(μ-S-*t*-Bu)$_2$(CO)$_2${P(OMe)$_3$}$_2$] in the selective hydroformilation of alkenes (115).

A series of dinuclear rhodium(I) and iridium(I) complexes containing the M(μ-pz*)(μ-S-*t*-Bu)M core was obtained according to Eqs. 4 and 5 (109, 117, 118) (Table III):

$$[\mathrm{MCl(Hpz^*)(cod)}] + [\mathrm{M(acac)(cod)}] \xrightarrow{-\mathrm{Hacac}}$$

$$[\mathrm{M_2(\mu\text{-}pz^*)(\mu\text{-}Cl)(cod)_2}] \xrightarrow[-\mathrm{KCl}]{\mathrm{KS}\text{-}t\text{-}\mathrm{Bu}} [\mathrm{M_2(\mu\text{-}pz^*)(\mu\text{-}S\text{-}}t\text{-}\mathrm{Bu)(cod)_2}] \qquad (4)$$

$$[\mathrm{M_2(\mu\text{-}pz^*)(\mu\text{-}S\text{-}}t\text{-}\mathrm{Bu)(cod)_2}] \xrightarrow{\mathrm{CO}} [\mathrm{M_2(\mu\text{-}pz^*)(\mu\text{-}S\text{-}}t\text{-}\mathrm{Bu)(CO)_4}] \xrightarrow{\mathrm{L}}$$

$$[\mathrm{M_2(\mu\text{-}pz^*)(\mu\text{-}S\text{-}}t\text{-}\mathrm{Bu)(CO)_2L_2}] \qquad (5)$$

In complexes containing the (μ-S-*t*-Bu) group, the individual metal centers are joined by one exo-bidentate pyrazolate ligand and one tert-buthylthiol group, in such a way that the cyclic bridged M(μ-pz*)(μ-S-*t*-Bu)M core deviates from planarity, adopting a flexible bent conformation that results in a wide range of intermetallic separations (114).

The crystal and molecular structure of **111** was determined from a single

TABLE III
Homodinuclear Complexes Containing the $M(\mu\text{-pz*})(\mu\text{-S-}t\text{-Bu})M$ Core (M = Rh or Ir)

Complex	Formula	Notes	Reference
105	$[Rh_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(cod)_2]$		117
106	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(cod)_2]$		118
107	$[Ir_2(\mu\text{-dmpz})(\mu\text{-S-}t\text{-Bu})(cod)_2]$		114
108	$[Rh_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(CO)_4]$		117
109	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(CO)_4]$		118
110	$[Ir_2(\mu\text{-dmpz})(\mu\text{-S-}t\text{-Bu})(CO)_4]$		114
111	$[Rh_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(CO)_2\{P(OMe)_3\}_2]$	X-ray	117
112	$[Rh_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(CO)_2\{P(OPh)_3\}_2]$		117
113	$[Rh_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(CO)_2(PPh_3)_2]$		117
114	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(CO)_2\{P(OMe)_3\}_2]$		118
115	$[Ir_2(\mu\text{-dmpz})(\mu\text{-S-}t\text{-Bu})(CO)_2\{P(OMe)_3\}_2]$		114
116	$[Ir_2(\mu\text{-dmpz})(\mu\text{-S-}t\text{-Bu})(CO)_2(PPh_3)_2]$		114
117	$[Rh_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-dppm})(CO)_2]$		110
118	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-dppm})(CO)_2]$		110
119	$[Ir_2(\mu\text{-dmpz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-dppm})(CO)_2]$		110
120	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})I_2(CO)_2\{P(OMe_3)\}_2]$		118
121	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})I_4(CO)_2\{P(OMe_3)\}_2]$		118
122	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-MeO}_2C{-}C{=}C{-}CO_2Me)(CO)_2\{P(OMe_3)\}_2]$	X-ray	118
123	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-MeO}_2C{-}C{=}C{-}CO_2Me)I_2(CO)_2\{P(OMe_3)\}_2]$	X-ray	118
124	$[Rh_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(Me)I(CO)_2\{P(OMe_3)\}_2]$		114
125	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(Me)I(CO)_2\{P(OMe_3)\}_2]$		114
126	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-CH}_2)I_2(CO)_2\{P(OMe_3)\}_2]$	X-ray	114
127	$[Ir_2(\mu\text{-dmpz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-CH}_2I)I(CO)_2\{P(OMe_3)\}_2]$		114
128	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})Cl_2(CO)_2\{P(OMe_3)\}_2]$		114
129	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(SnCl_2I)_2(CO)_2\{P(OMe_3)\}_2]$		114
130	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(SnCl_3)_2(CO)_2\{P(OMe_3)\}_2]$	Two isomers X-ray for one	114
131	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-SnCl}_2)(CO)_2\{P(OMe_3)\}_2]$		114
132	$[Rh_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-dppm})I_2(CO)_2]$		116
133	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-dppm})I_2(CO)_2]$		116
134	$[Ir_2(\mu\text{-dmpz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-dppm})I_2(CO)_2]$		116
135	$[Ir_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-dppm})(\mu\text{-HgCl})Cl(CO)_2]$		116
136	$[Ir_2(\mu\text{-dmpz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-dppm})(\mu\text{-HgCl})Cl(CO)_2]$		116

crystal by X-ray diffraction. This complex is dinuclear, with a pseudomirror plane passing through the S atom and bisecting the pyrazolate ring, with the carbonyl ligands (related to this mirror plane) in a cis conformation, and with the sulfur atom trans to the trimethylphosphite ligands (117).

It is of interest that the heterobridged complexes **108** and **111** were formed by mixing the homobridged complexes $[Rh_2(\mu\text{-pz})_2(CO)_2L_2]$ and $[Rh_2(\mu\text{-S-}t\text{-Bu})_2(CO)_2L_2]$ [L = $P(OMe)_3$ or CO]. No dismutation of the heterobridged complexes was observed (117). The reaction of dppm with Complexes **108–110** quantitatively yields $[Rh_2(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(\mu\text{-dppm})(CO)_2]$, **117**, $[Ir_2(\mu\text{-pz})(\mu\text{-S-}$

t-Bu)(μ-dppm)(CO)$_2$], **118,** and [Ir$_2$(μ-dmpz)(μ-S-*t*-Bu)(μ-dppm)(CO)$_2$], **119,** respectively (110). The structure of these triply heterobridged complexes was assigned on the basis of ^{31}P NMR spectral data. Extensive studies were carried out on the chemical properties of some of the complexes reported above. In particular, attention has been paid to oxidative-addition reactions with alogens (I_2 or Cl_2), methyl iodide, di-iodomethane, and HgX_2 (X = Cl or I).

Compound **114** undergoes stepwise addition of I_2 to yield the complexes [Ir(μ-pz)(μ-S-*t*-Bu)(I)$_n$(CO)$_2${P(OMe)$_3$}$_2$] (*n* = 2, **120** or 4, **121**) (Scheme 6). The increase of the formal oxidation number of the iridium center from I to II and, then to III, is paralleled by the increase of the carbonyl stretching frequency from 1985 to 2040 and 2082 cm^{-1}, respectively (118).

Reaction of complex [Ir$_2$(μ-pz)(μ-S-*t*-Bu)(CO)$_2${P(OMe)$_3$}$_2$], **114,** with the electron-withdrawing alkyne dimethyl-acetylenedicarboxylate ($MeO_2C-C\equiv C-CO_2Me$) gave the triply heterobridged compound [Ir$_2$(μ-pz)(μ-S-*t*-Bu)(μ-$MeO_2C-C{=}C-CO_2Me$)(CO)$_2${P(OMe)$_3$}$_2$], **122** (118). Its X-ray crystal structure evidenced the cis-dimetalated olefinic bonding mode for the unsaturated ligand (118). Complex **122** undergoes further oxidative addition with I_2 affording **123.**

The oxidative addition of MeI to complexes **111** and **114** and of CH_2I_2 to **114** or **115** was also studied. From these reactions, Complexes **124–127** were obtained (111). The spectroscopic data provided the basis of a consistent interpretation of the mechanism of the reaction involving **114** and CH_2I_2.

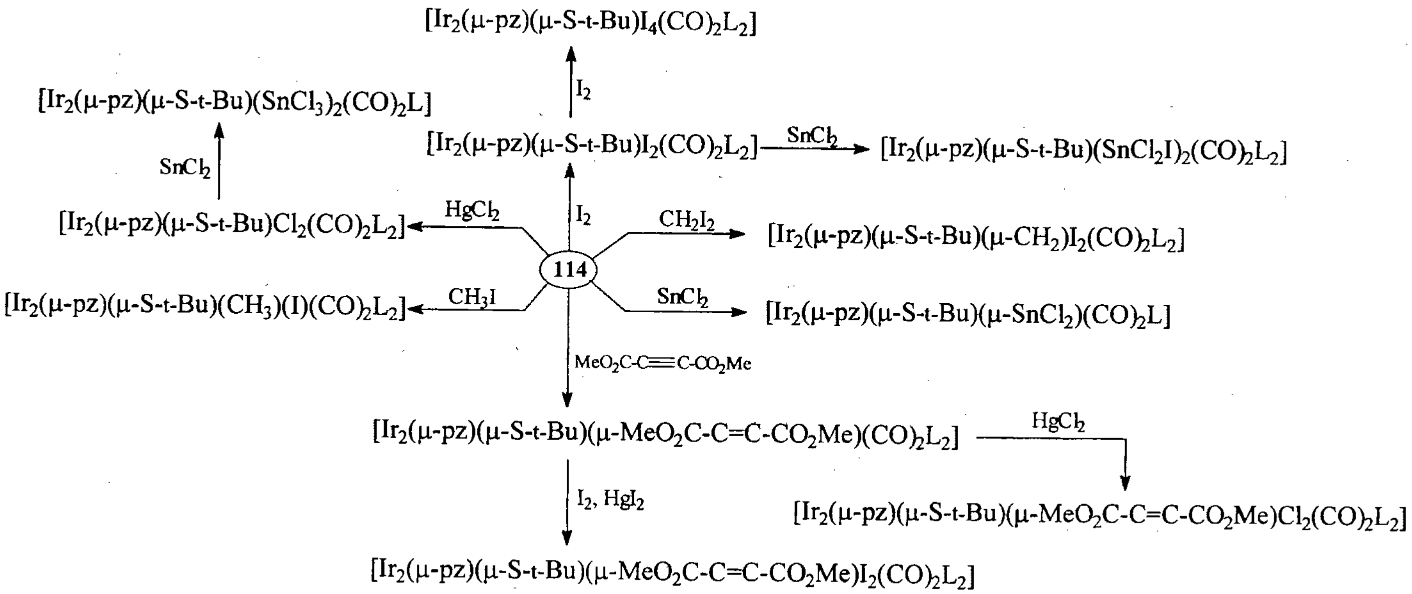
The first step of the reaction is the formation of the intermediate species **E** (Scheme 7) containing a single iridium–iridium bond. The migration of the methylene group leads to the formation of the final Ir^{III}Ir^{III} symmetric complex. The intermediate unsymmetrical species **E** was isolated in the reaction of CH_2I_2 with **115.**

The reaction of **114** with HgX_2 (X = Cl or I) gave the oxidation compounds [Ir$_2$(μ-pz)(μ-S-*t*-Bu)(X)$_2$(CO)$_2${P(OMe)$_3$}$_2$] (X = Cl, **128**; I, **120**). The addition of $SnCl_2$ to the latter complexes involves the insertion of tin(II) into the Ir—X bond and the formation of the trihalogeno/tin derivatives **129** and **130.**

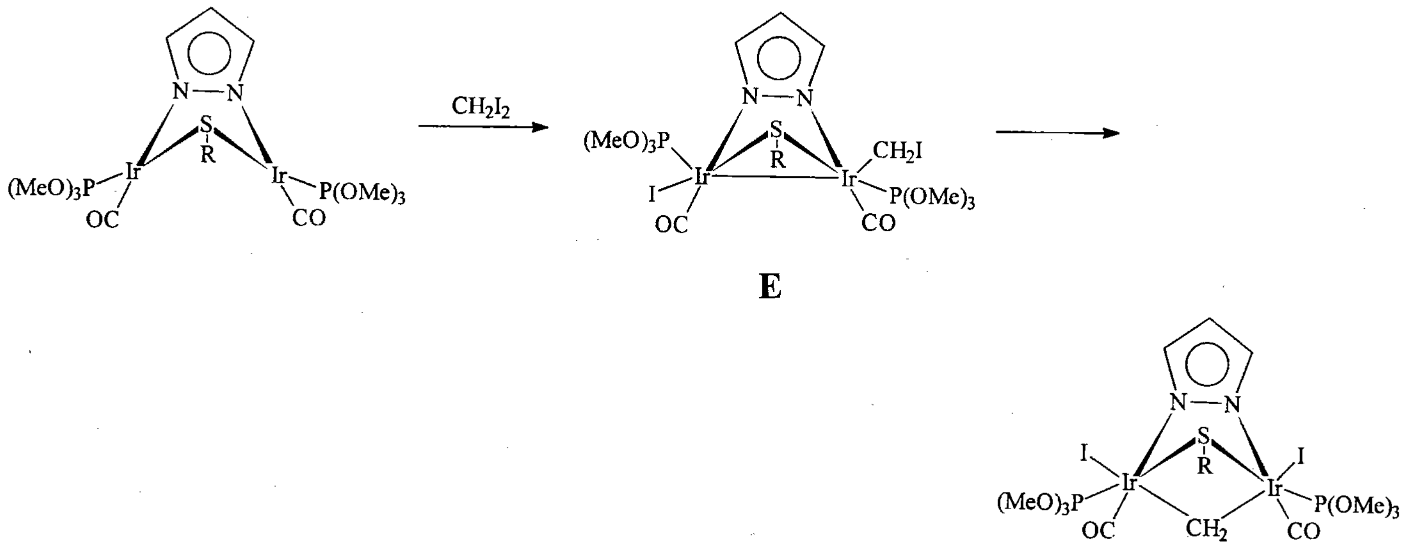
A 1 : 1 adduct (**131**) was obtained on direct treatment of **114** with $SnCl_2$. The formation of these complexes was deduced by IR, ^{31}P, and ^{119}Sn NMR spectroscopy. In solution, [Ir$_2$(μ-pz)(μ-S-*t*-Bu)(SnCl$_3$)$_2$(CO)$_2${P(OMe)$_3$}$_2$] appears to be a mixture of an asymmetric **130a** and a symmetric **130b** isomer.

The crystal structure of **130a,** which was obtained by fractional crystallization, was reported. The Ir—Ir distance (2.72 Å) indicates the presence of a metal-metal bond (114). Complexes **117–119** react readily with an equimolar amount of I_2 to yield **132–134,** respectively, which on the basis of analytical and spectral data were formulated as metal(II)–metal(II) complexes (Table III) (110).

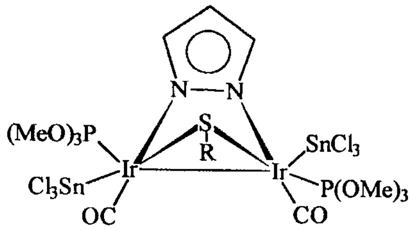
Further confirmation of a symmetrical structure for **132–134** came from their



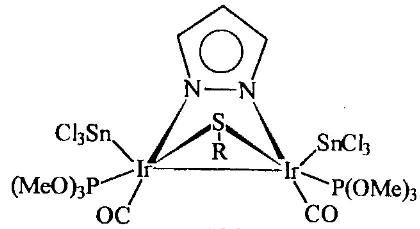
Scheme 6. Oxidative-addition reactions of the Ir(I) dinuclear pyrazolate complex $[Ir_2(\mu\text{-pz})(\mu\text{-S-t-Bu})(CO)_2L_2]$, **114** $[L = P(OMe)_3]$ (see text for references).



Scheme 7. Proposed mechanism for the oxidative addition of CH_2I_2 to $[Ir_2(\mu\text{-pz})(\mu\text{-SR})(CO)_2\{P(OMe)_3\}_2]$, **114** (R = *t*-Bu). [Adapted from (111).]



130a



130b

^{31}P NMR spectra. The terminal iodide ligands in this class of complexes can be removed by reaction with $AgNO_3$ (Scheme 8).

Moreover, Complexes **118** and **119** react with mercury(II) chloride to give the Ir^{III}–Ir^{I} derivatives **135** and **136**, resulting from oxidative addition of $HgCl_2$ to one metal center. A related complex, $[Rh_2(\mu\text{-pz})_2(\mu\text{-HgCl})Cl(CO)_2(PPh_3)_2]$, which exhibits a mercury atom asymmetrically bridging the two rhodium centers, was previously characterized by X-ray diffraction (116).

The synthesis of ruthenium–palladium and ruthenium–rhodium complexes of the formula $[(p\text{-cymene})(X)Ru(\mu\text{-pz*})(\mu\text{-X})M(L_2)]$ (Table IV) were reported (119, 120).

This procedure used involves the reaction of a ruthenium(II) mononuclear pyrazole complex with a second metal acac, as indicated in Eq. 6

$$[(p\text{-cymene})RuX_2(Hpz^*)] + [M(acac)(L_2)] \longrightarrow [(p\text{-cymene})(X)Ru(\mu\text{-pz}^*)(\mu\text{-X})M(L_2)] \quad (M = Pd \text{ or } Rh) \tag{6}$$

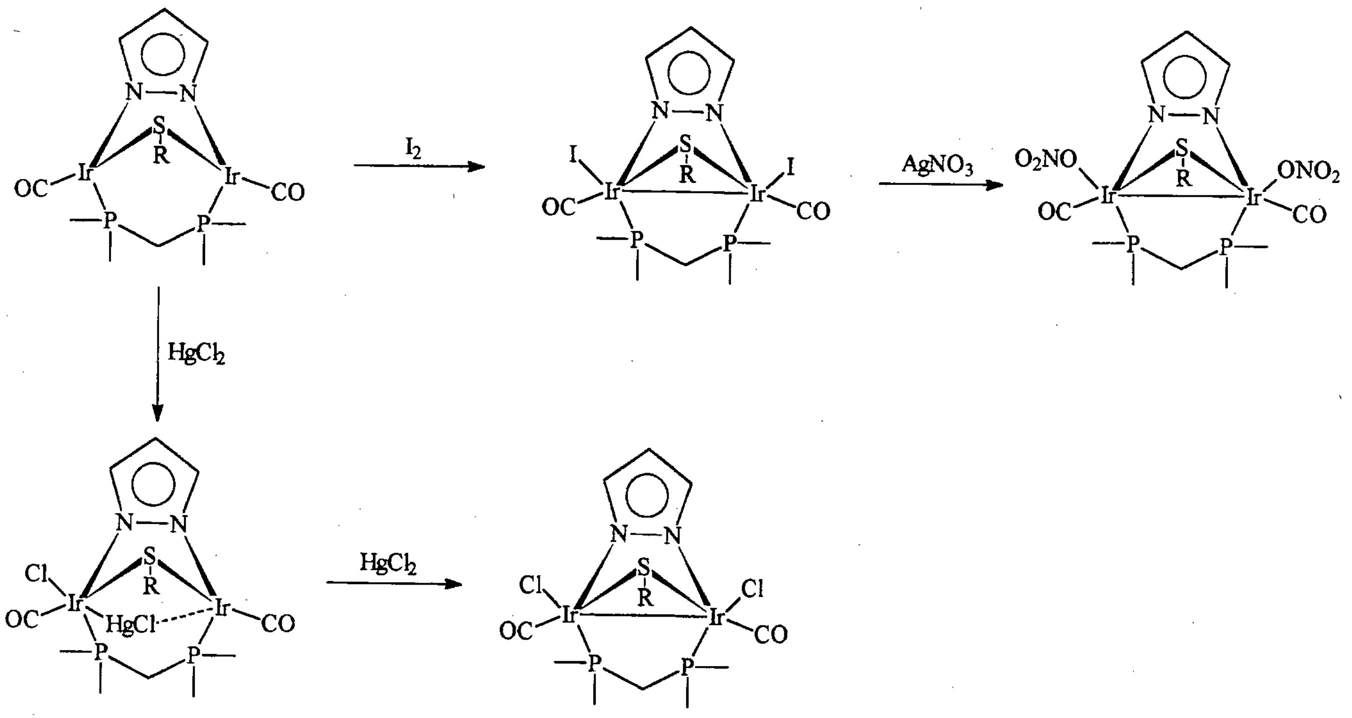
One of the complexes, $[(p\text{-cymene})(Cl)Ru(\mu\text{-pz})(\mu\text{-Cl})Pd(C_8H_{11})]$, **137**, was characterized by single-crystal X-ray diffraction (120).

The X-ray structure of the Ru/Rh derivative $[(p\text{-cymene})(Cl)Ru(\mu\text{-pz})(\mu\text{-Cl})Rh(tfbb)]$, **138** (119), exhibits the triply bridged arrangement $(\mu\text{-pz})(\mu\text{-Cl})_2$,

TABLE IV
Heterodinuclear Complexes of Formula $[(p\text{-Cymene})(X)Ru(\mu\text{-pz*})(\mu\text{-X})M(L_2)]$[a]

M	X	L_2	Hpz*
Pd	Cl	C_3H_5 C_4H_7 C_8H_{11}	Hpz
Rh	Cl	tfbb	Hpz
	I	nbd	Hmpz

[a] References (119) and (120).



Scheme 8. Oxidative-addition reactions of iodine and $HgCl_2$ on $[Ir_2(\mu\text{-pz})(\mu\text{-SR})(\mu\text{-dppm})(CO)_2]$, **118** (R = *t*-Bu). [Adapted from (110).]

in contrast with the doubly bridged arrangement, (μ-pz)(μ-Cl), observed for **137** and for the isoelectronic [(C_5Me_5)(Cl)Rh(μ-pz)(μ-Cl)Rh(tfbb)], **139** (79). A related cationic complex, [(*p*-cymene)(Hpz)Ru(μ-pz)(μ-Cl)Rh(tfbb)](ClO_4), **140**, containing the bridging pyrazolate group as well as the neutral pyrazole ligand, was prepared by treating the cationic complex [(*p*-cymene)RuCl($Hpz)_2$]($ClO_4)_2$ with [Rh(acac)(tfbb)]. The reaction of **140** with Na(acac) afforded the neutral complex [(*p*-cymene)RuCl(μ-pz$)_2$Rh(tfbb)] presumably containing the pyrazolate groups as bridging ligands (120).

The synthetic strategy reported above (Eq. 6) has been previously employed for the preparation of mixed-valence $Rh^{III}Rh^{I}$ complexes containing the (μ-pz*)(μ-Cl) moiety. Treatment of [(C_5Me_5)$RhCl_2$(Hpz)] with [Rh(acac)(tfbb)] afforded **139**, which was characterized by an X-ray crystal structure determination (79). This heterobridged complex contains two rhodium atoms in two different formal oxidation states (Rh^{III} and Rh^{I}), with pseudooctahedral and square planar coordinations, respectively.

Reaction of the ruthenium compounds [RuHCl(CO)($PR_3)_n$] (R = Ph, n = 3; R = *i*-Pr, n = 2) with Hpz afforded the complexes [RuHCl(CO)(HPz)($PR_3)_2$] (101). Treatment of these products with transition metal complexes containing a hydrogen abstractor (MeO^- or $acac^-$), such as [M(μ-OMe)(diolefin)]$_2$ (M = Rh or Ir; diolefin = cod or tfbb) or [Pd(acac)(η^3-C_3H_5)], gave a series of heterodinuclear Ru—Ir, Ru—Rh, and Ru—Pd complexes of the formula [H(CO)($PR_3)_2$Ru(μ-pz)(μ-Cl)M(L_2)] (Table V).

The structure of [H(CO)($PPh_3)_2$Ru(μ-pz)(μ-Cl)Ir(tfbb)], **141**, was also determined (101).

The reaction of [Pt_2Cl_2(μ-Cl$)_2$($PMe_2Ph)_2$] with 1 mol of Hpz in the presence of NaOH afforded the corresponding mono(chloro)-mono(pyrazolate) complex [Pt_2Cl_2(μ-pz)(μ-Cl)($PMe_2Ph)_2$], **142**, from which the (μ-pz)(μ-OMe) derivative was obtained on treatment with an excess of sodium methoxide (68).

Moreover, dinuclear platinum(II) complexes containing both μ-pz and other Group 16 (VI A) donors as bridging ligands were obtained according to Eq. 7.

TABLE V
Heterodinuclear Complexes of the General Formula [H(CO)($PR_3)_2$Ru(μ-pz)(μ-Cl)M(L_2)][a]

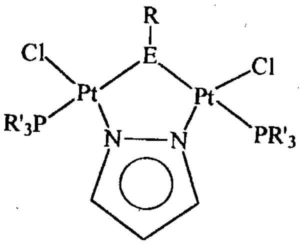
M	R	L_2
Rh, Ir	Ph	cod tfbb
Rh	*i*-Pr	tfbb
Pd	Ph	C_3H_5

[a] See (101).

$$[Pt_2Cl_2(\mu\text{-}ER)(\mu\text{-}Cl)(PR'_3)_2] \xrightarrow{Hpz/NaOH} [Pt_2Cl_2(\mu\text{-}ER)(\mu\text{-}pz)(PR'_3)_2] \quad (7)$$

$$(E = S, Se, \text{ or } Te;\ R = \text{alkyl or aryl})$$

The ^{31}P NMR data seem to indicate that complexes $[Pt_2Cl_2(\mu\text{-}ER)(\mu\text{-}pz)(PR'_3)_2]$ exist in the following cis form (68).



The preparation and properties of trinuclear heterobridged complexes M—Pd—M (M = Rh or Ir) containing the (μ-pz)(μ-X) fragment (X = S-*t*-Bu, Cl) were reported (Table VI) (121–123).

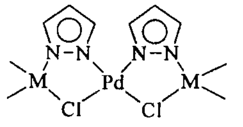
The synthetic route utilized for the preparation of Complexes **146** and **152** employs $[PdCl_2(Hpz)_2]$ and [M(acac)(cod)] as starting materials (Eq. 8).

$$2[M(acac)(cod)] + [PdCl_2(Hpz)_2] \xrightarrow{-2\,Hacac} [Pd\{M(\mu\text{-}pz)(\mu\text{-}Cl)(cod)\}_2] \longrightarrow$$
$$\xrightarrow{2K\text{-}S\text{-}t\text{-}Bu} [Pd\{M(\mu\text{-}pz)(\mu\text{-}S\text{-}t\text{-}Bu)(cod)\}_2] \quad (8)$$

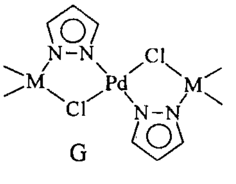
TABLE VI
Trinuclear Species of Formula $[L_2M(\mu\text{-}X)(\mu\text{-}pz)Pd(\mu\text{-}X)(\mu\text{-}pz)ML_2]$

Complex	M	X	L_2	Notes	Reference
143	Rh	Cl	cod		123
144	Rh	Cl	tfbb		123
145	Rh	Cl	$(CO)_2$		123
146	Rh	S-*t*-Bu	cod		124
147	Rh	S-*t*-Bu	$(CO)_2$	X-ray	124
148	Rh	S-*t*-Bu	CO, PPh_3		124
149	Rh	S-*t*-Bu	CO, $P(OMe)_3$		124
150	Ir	Cl	cod		123
151	Ir	Cl	$(CO)_2$		123
152	Ir	S-*t*-Bu	cod		121
153	Ir	S-*t*-Bu	$(CO)_2$		121
154	Ir	S-*t*-Bu	CO, $P(OMe)_3$		121

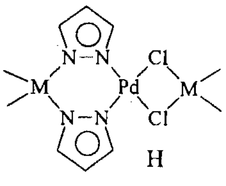
In principle, the heterometallic species **143, 144, 150,** and **151** may give three geometrical isomers:



F



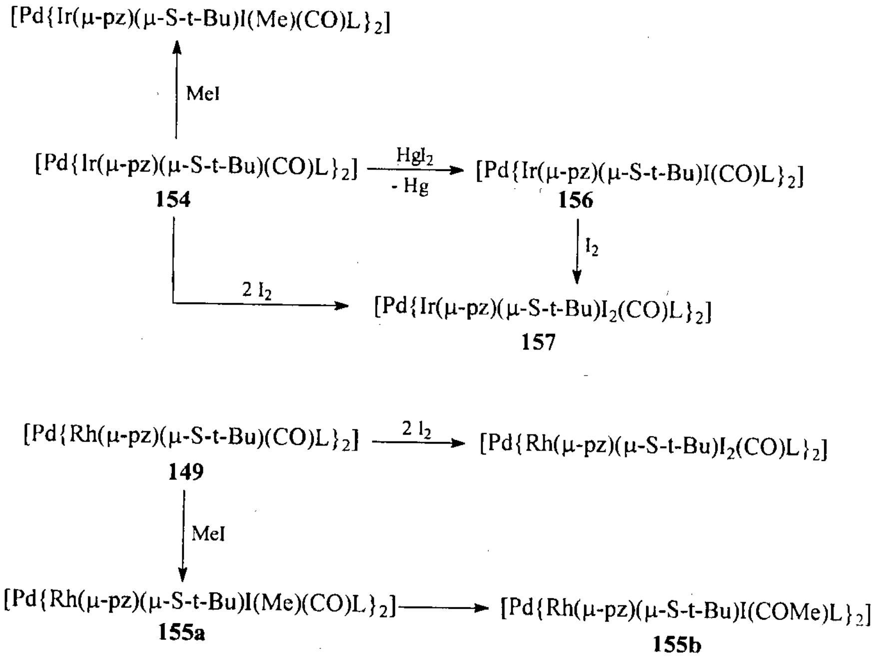
G



H

On the basis of ^1H NMR spectra and taking into account the trans geometry of the starting $[PdCl_2(Hpz)_2]$ complex, the trans arrangement (G) has been considered the most probable structure for this family of trinuclear compounds (123). A trans disposition of the bridging ligands has been observed in the rhodium complex **147.** The same trans conformation was also proposed for Compound **152** (121).

The oxidative–addition reactions carried out on some of the trinuclear complexes reported in Table VI (see Scheme 9) were particularly studied (121, 122, 124).



Scheme 9. Oxidative-addition reactions carried-out on the trinuclear species $[Pd\{Ir(\mu\text{-pz})(\mu\text{-S-t-Bu})(CO)L\}_2$, **154**, and $[Pd\{Rh(\mu\text{-pz})(\mu\text{-S-}t\text{-Bu})(CO)L\}_2]$, **149** (see text for references).

The reaction involving Complex **149** and methyl iodide can be interpreted on the basis of an oxidative addition of a molecule of MeI to each rhodium center (122). The formation of the acetyl derivative **155b** was considered as arising from cis migration of a methyl group in isomer **155a,** as indicated in Scheme 9. It is interesting to point out the different behavior of the related iridium derivative **154,** which did not afford the corresponding acetyl compound. In this case, the formation of a metal–metal bond was explained in terms of a heterolytic addition of the iodide and of the methyl groups (121). Addition of mercury(II) iodide to **154** resulted in the formation of **156** and metallic mercury (Scheme 9). This reaction implies the addition of one iodine atom to each iridium center with concomitant formation of two Ir—Pd bonds (121). Compounds **154** and **156** present a very unusual bonding situation where the iridium(II) centers are candidates to further oxidative-addition reactions. Effectively, Compound **156** reacts with 1 mol of I_2 to yield **157,** which is also obtained by direct addition of 2 mol of iodine to the iridium(I) derivative **154.** Another family of homotrinuclear complexes was derived from two palladium precursors. The reaction of [Pd(acac)(η^3-allyl)] (allyl = C_3H_5 or C_4H_7) with [$PdCl_2(Hpz)_2$] yielded [(η^3-allyl)Pd(μ-pz)(μ-Cl)Pd(μ-pz)(μ-Cl)Pd(η^3-allyl)] (123).

The reactivity of dinuclear anionic hydroxo complexes of the type $[\{R_2M(\mu\text{-}OH)\}_2]^{2-}$ (M = Ni, Pd, or Pt) toward weak acids as pyrazoles was studied extensively. The chemical behavior is consistent with the high-field proton resonances of the OH bridges (65, 66). The (μ-hydroxo)(μ-pyrazolate) or bis(μ-pyrazolate) complexes (the latter are described in Section III.C) were obtained, depending on the reactants molar ratio (M/Hpz* = 1 or 2, respectively) (60–65) (Table VII).

TABLE VII

Anionic Heterobridged Complexes of Formula $[R_2M(\mu\text{-}pz^*)(\mu\text{-}OH)MR_2]$

M	R	Hpz*	Notes	References
Ni	C_6F_5	Hpz	X-ray	60, 61
		Hmpz		60, 61
		Hdmpz		60, 61
Pd	C_6F_5	Hpz		64
		Hmpz		64
		Hdmpz		64
	$C_6F_3H_2$	Hdmpz		63
	C_6Cl_5	Hdmpz		62
Pt	C_6F_5	Hpz		66
		Hmpz		66
		Hdmpz	X-ray	66

The reaction of $[\{R_2Pd(\mu\text{-OH})\}_2]^{2-}$ with Hpz* (1 : 1 molar ratio) did not afford pure (μ-pz*)(μ-OH) complexes because of the persistent presence of impurities of the corresponding bis(μ-pz*) complexes. Nevertheless, their formation is confirmed by IR and NMR data. The dmpz derivatives were prepared, in pure form, by a different strategy (62–64) (Eq. 9; Table VII).

$$[R_2Pd(\mu\text{-Cl})_2PdR_2](NBu_4)_2 + 2(NBu_4)OH + Hdmpz \longrightarrow$$

$$[R_2Pd(\mu\text{-dmpz})(\mu\text{-OH})PdR_2] + 2(NBu_4)Cl + H_2O \qquad (9)$$

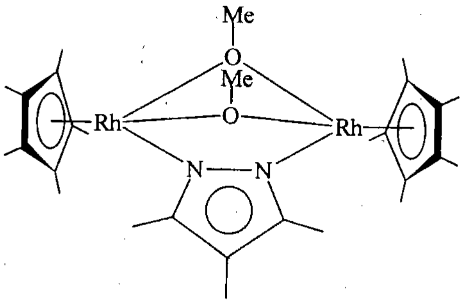
Related dinuclear palladium(II) complexes of formula $[R(PPh_3)Pd(\mu\text{-pz})(\mu\text{-OH})Pd(PPh_3)R]$ ($R = C_6F_5$ or C_6Cl_5) were analogously prepared by reacting $[RPd(PPh_3)(\mu\text{-Cl})]_2$ with $(NBu_4)OH$ and Hpz (125). The NMR data show unambiguously that the (μ-pz)(μ-OH)-palladium(II) complexes exist in solution as the cis isomers, with two equivalent phosphines trans to the bridging OH group.

It has been reported that the 1 : 1 reaction of $[\{Pt(C_6F_5)_2(\mu\text{-OH})\}_2]^{2-}$ with Hpz* (Hpz* = Hpz, Hdmpz, or Hmpz) represents a convenient route for the preparation of the complexes $[\{Pt(C_6F_5)_2\}_2(\mu\text{-pz*})(\mu\text{-OH})]^{2-}$ (66). The latter compounds gave the corresponding mono(methoxo)-mono(pyrazolate) derivatives on treatment with methanol. Spectroscopic (IR, ^1H, and ^{19}F NMR) data were used for structural assignments, and an X-ray structure determination was carried out for $[\{Pt(C_6F_5)_2\}_2(\mu\text{-dmpz})(\mu\text{-OH})](NBu_4)_2$, **158**, which established the dinuclear nature of the anion (66).

Since the Ru^{II}(arene) unit is isoelectronic with the $M^{III}(C_5Me_5)$ (M = Rh or Ir) moieties, studies have been performed in order to obtain ruthenium analogous complexes containing (μ-OH) or (μ-OR) groups as well as pyrazolate ligands but perhaps with new stoichiometries, which were not observed in rhodium or iridium chemistry (126).

The tris(μ-hydroxo)-diruthenium complexes $[\{p\text{-cymene})Ru\}_2(\mu\text{-OH})_3](A)$ ($A = BPh_4$, BF_4, or PF_6) react with equimolar amounts of Hpz* (Hpz* = Hpz, Hdmpz, or Hmpz) to give the heterobridged complexes $[\{(p\text{-cymene})Ru\}_2(\mu\text{-pz*})(\mu\text{-OH})_2](A)$ and/or $[\{(p\text{-cymene})Ru\}_2(\mu\text{-pz*})_2(\mu\text{-OH})](A)$, depending on the nature of Hpz*, the counteranion, and the reaction conditions (126). The tris(μ-OMe)-diruthenium complexes $[\{(p\text{-cymene})Ru\}_2(\mu\text{-OMe})_3](A)$ react in methanol with Hpz* to give the mono(μ-pyrazolate) compounds $[\{(p\text{-cymene})Ru\}_2(\mu\text{-pz*})(\mu\text{-OMe})_2](A)$. The ($\mu$-pz*)$_2$($\mu$-OMe) analogues ($A = BF_4$ or PF_6) were obtained by treating the appropriate tris(μ-OMe) complex with an excess of Hpz*. The structure of $[\{(p\text{-cymene})Ru\}_2(\mu\text{-pz})(\mu\text{-OH})_2](BF_4)$, **159**, was also determined (126). The synthesis and reactions of dinuclear pentamethyl-cyclopentadienyl-rhodium(III) complexes were studied extensively. Although several hydroxobridged compounds were reported, all attempts to isolate related alkoxobridged derivatives were unsuccessful. The latter complexes have been invoked as probable intermediates in the preparation of various hydroxobridged compounds (127). On the contrary, a series of dinuclear rhodium pyrazolate complexes containing the C_5Me_5 group and methoxo- or hydroxobridging ligands was reported (127). These compounds are of interest because there are still relatively few stable and accessible alkoxo- or hydroxocomplexes of the platinum metals.

Dinuclear complexes of formula $[\{Rh(C_5Me_5)\}_2(\mu\text{-pz}^*)(OMe)_2](ClO_4)$ were obtained by treating $[\{Rh(C_5Me_5)\}_2(OH)_3](ClO_4)$ with the appropriate Hpz* in methanol (Table VIII).



It is likely that the intermediate $[\{Rh(C_5Me_5)\}_2(OMe)_3]^+$, formed by reaction of the $(\mu\text{-OH})_3$ derivative with methanol, is protonated by a Hpz* ligand to form a "methanol intermediate," which immediately reacts with the pz* groups to give Complexes **160–165.**

The presence of the bridging pyrazolate group seems to be an essential requirement in order to stabilize the methoxobridges.

Dinuclear complexes of the formula $[\{Rh(C_5Me_5)\}_2(\mu\text{-pz}^*)_2(\mu\text{-OH})](ClO_4)$ (Hpz* = Hpz, **166,** Hmpz, **167**) were obtained by reacting $[\{Rh(C_5Me_5)\}_2(\mu\text{-OH})_3](ClO_4)$ with Hpz* (1:2) (127). The X-ray structural characterization of

TABLE VIII
Dinuclear Complexes of Formula
$[Rh(C_5Me_5)(\mu\text{-pz}^*)(OMe)_2](A)$[a]

Complex	Hpz*	A
160	Hpz	ClO_4
161	Hmpz	ClO_4
162	Hdmpz	ClO_4
163	BrmpH	ClO_4
164	4-BrpzH	ClO_4
165	Hmpz	BF_4

[a] Reference (127).

Complex **166** supported the triple-bridged formulation involving two exo-bidentate pyrazolate ligands and one bridging hydroxo group. The data available for Rh derivatives seem to indicate that complexes containing the (μ-pz*)(μ-OMe)$_2$ fragment are formed for all systems, but (μ-pz*)$_2$(μ-OH) complexes are preferentially obtained when the pyrazoles are unsubstituted or have only a single 3-methyl substituent.

The synthetic strategy used for the preparation of the aforementioned heterobridged rhodium complexes containing pz* and MeO or OH bridging ligands was extended for related C_5Me_5–iridium complexes (128). Thus, complexes of formula [{Ir(C_5Me_5)}$_2$(μ-pz*)$_2$(μ-OH)](BF_4) (Hpz* = Hpz or Hmpz) and [{Ir(C_5Me_5)}$_2$(μ-pz*)(μ-OMe)$_2$](A) (A = ClO_4 or BF_4; Hpz* = Hpz, Hdmpz, or Hmpz) have been prepared.

The complexes [{Ir(C_5Me_5)}$_2$(μ-pz)$_2$(μ-OH)](BF_4) and [{Ir(C_5Me_5)}$_2$(μ-pz)(μ-OMe)$_2$](BF_4) and their rhodium analogues react with HCl to yield the dinuclear chloride complexes [{M(C_5Me_5)}$_2$(μ-pz)$_2$(μ-Cl)](BF_4) and [{M(C_5Me_5)}$_2$(μ-pz)(μ-Cl)$_2$](BF_4) (M = Rh or Ir). These complexes were also prepared from the corresponding neutral species [M(C_5Me_5)(Cl)$_2$(Hpz)] (128, 129). Moreover, addition of NEt_3 to [Rh(C_5Me_5)(Cl)$_2$(Hpz)] afforded [Rh(C_5Me_5)(Cl)(μ-pz)]$_2$, which was crystallographically characterized.

Treatment of [({Rh(C_5Me_5)}$_2$(μ-pz)(μ-Cl)$_2$](BF_4) with excess Zn dust and Cu sand gave a dirhodium(II) complex formulated as [Rh(C_5Me_5)(μ-pz)]$_2$, although this product has not yet been isolated as a pure solid. On the contrary, the C_5H_5 derivative, [Rh(C_5H_5)(μ-pz)]$_2$, was obtained as crystals that were suitable for X-ray diffraction (129). Reaction of the latter rhodium compound with $NOBF_4$ results in reoxidation to a structurally characterized dirhodium(III) nitrosyl complex, [Rh_2(C_5H_5)$_2$(μ-pz)$_2$(μ-NO)](BF_4) (129).

The pyrazolate ligand plays an important role in the addition of $HPPh_2$ to complexes containing the (C_5Me_5)Rh^{III} fragment, allowing new links to the pentamethylcyclopentadienyl–rhodium(III) phosphido chemistry, which is very scarcely represented.

Dinuclear complexes containing pyrazolate and diphenylphosphido bridging ligands were prepared by reacting [{Rh(C_5Me_5)}$_2$(μ-pz*)(μ-OMe)$_2$](BF_4) with $HPPh_2$ (Table IX) (130, 131).

The X-ray crystal structures of [{Rh(C_5Me_5)}$_2$(μ-pz)$_2$(μ-PPh_2)](BF_4), **172**, and [{Rh(C_5Me_5)}$_2$(μ-pz)(μ-Cl)(μ-PPh_2)](BF_4), **176**, obtained by reacting [{Rh(C_5Me_5)}$_2$(μ-pz)(μ-OH)(μ-PPh_2)](BF_4) with hydrochloric acid, were also reported (130, 131).

The rhodium anionic bis(phosphonate) complex [Rh(C_5Me_5)(I){PO-(OMe)$_2$}$_3$]$^-$, can act as a tridentate ligand with the halogen atom as one of the donor centers (132). This behavior can be enhanced by introducing a pz* group instead of the halogen atom. Bimetallic derivatives of the formula [Rh(C_5Me_5){PO(OMe)$_2$}$_2$(μ-pz*)M] (M = Na or Tl) were prepared by addition

TABLE IX

Complexes Containing the $(\mu\text{-pz*})(\mu\text{-PPh}_2)$ Fragment[a]

Complex	Formula	Notes
168	$[\{\mathrm{Rh(C_5Me_5)}\}_2(\mu\text{-dmpz})(\mu\text{-OH})(\mu\text{-PPh}_2)](\mathrm{BF_4})$	
169	$[\{\mathrm{Rh(C_5Me_5)}\}_2(\mu\text{-pz})(\mu\text{-OH})(\mu\text{-PPh}_2)](\mathrm{BF_4})$	
170	$[\{\mathrm{Rh(C_5Me_5)}\}_2(\mu\text{-mpz})(\mu\text{-OH})(\mu\text{-PPh}_2)](\mathrm{BF_4})$	
171	$[\{\mathrm{Rh(C_5Me_5)}\}_2(\mu\text{-pz})(\mu\text{-PPh}_2)_2](\mathrm{BF_4})$	
172	$[\{\mathrm{Rh(C_5Me_5)}\}_2(\mu\text{-pz})_2(\mu\text{-PPh}_2)](\mathrm{BF_4})$	X-ray
173	$[\{\mathrm{Rh(C_5Me_5)}\}_2(\mu\text{-mpz})(\mu\text{-PPh}_2)_2](\mathrm{BF_4})$	
174	$[\{\mathrm{Rh(C_5Me_5)}\}_2(\mu\text{-bmpz})(\mu\text{-OH})(\mu\text{-PPh}_2)](\mathrm{BF_4})$	
175	$[\{\mathrm{Rh(C_5Me_5)}]_2(\mu\text{-bmpz})(\mu\text{-PPh}_2)_2](\mathrm{BF_4})$	
176	$[\{\mathrm{Rh(C_5Me_5)}\}_2(\mu\text{-pz})(\mu\text{-Cl})(\mu\text{-PPh}_2)_2](\mathrm{BF_4})$	X-ray
202	$[\{\mathrm{Rh(C_5Me_5)}\}_2(\mu\text{-H})(\mu\text{-pz})(\mu\text{-PPh}_2](\mathrm{BF_4})$	

[a] References (130, 131).

of NaH to the cationic pyrazole complexes $[\mathrm{Rh(C_5Me_5)}\{\mathrm{PO(OMe)_2}\}\{\mathrm{P(OH)(OMe)_2}\}(\mathrm{Hpz^*})](\mathrm{ClO_4})$ or Tl(acac) to the neutral compounds $[\mathrm{Rh(C_5Me_5)}\{\mathrm{PO(OMe)_2}\}_2(\mathrm{Hpz^*})]$ (Hpz* = Hpz, Hmpz, or Hdmpz).

The sodium or tallium compounds were used as starting materials for the formation of a series of cationic or neutral homo- and heterodinuclear complexes containing the $(\mu\text{-pz*})(\mu\text{-}\{\mathrm{PO(OMe)_2}\})_2$ fragment (Eq. 10a–c) (132):

$$[\mathrm{Rh(C_5Me_5)}\{\mathrm{PO(OMe)_2}\}_2(\mu\text{-pz*})\mathrm{Na}] \xrightarrow{(a)} [\mathrm{Rh(C_5Me_5)}\{\mu\text{-}\mathrm{PO(OMe)_2}\}_2(\mu\text{-pz*})\mathrm{M(C_5Me_5)}](\mathrm{ClO_4}) \tag{10a}$$

$$[\mathrm{Rh(C_5Me_5)}\{\mathrm{PO(OMe)_2}\}_2(\mu\text{-pz*})\mathrm{Na}] \xrightarrow{(b)} [\mathrm{Rh(C_5Me_5)}\{\mu\text{-}\mathrm{PO(OMe)_2}\}_2(\mu\text{-pz*})\mathrm{Ru(arene)}](\mathrm{ClO_4}) \tag{10b}$$

$$[\mathrm{Rh(C_5Me_5)}\{\mathrm{PO(OMe)_2}\}_2(\mu\text{-pz*})\mathrm{Tl}] \xrightarrow{(c)} [\mathrm{Rh(C_5Me_5)}\{\mu\text{-}\mathrm{PO(OMe)_2}\}_2(\mu\text{-pz*})\mathrm{M(CO)_3}] \tag{10c}$$

(a) $[\mathrm{Rh(C_5Me_5)Cl_2}]_2$ or $[\mathrm{Ir(C_5Me_5)Cl_2}]_2$, (b) $[\mathrm{Ru(arene)Cl_2}]_2$, (c) $[\mathrm{Re(CO)_5Br}]$ or $[\mathrm{Mn(CO)_5Br}]$.

Furthermore, similar results were obtained by reacting the neutral pyrazole complex $[\mathrm{Rh(C_5Me_5)}\{\mathrm{PO(OMe)_2}\}_2(\mathrm{Hpz})]$ with the tetrameric platinum(IV) complex $[\mathrm{Pt(Me)_3I}]_4$ in the presence of Tl(OEt), with the neutral complex $[\mathrm{Rh(C_5Me_5)}\{\mu\text{-}\mathrm{PO(OMe)_2}\}_2(\mu\text{-pz})\mathrm{Pt(Me)_3}]$ being formed.

The crystal structure of the cationic heterobimetallic complex $[\mathrm{Rh(C_5Me_5)}\{\mu\text{-}\mathrm{PO(OMe)_2}\}_2(\mu\text{-pz})\mathrm{Ru(Ph)}](\mathrm{ClO_4})$ confirmed that the metal center of the organometallic fragment exhibits a strong tendency to obey the 18-electron rule

(132). In this Rh/Ru complex, the phosphonate anions are coordinated to the rhodium through the phosphorous and to the ruthenium through the oxygen atom. The geometries around the metals are the normal pseudooctahedral three legged piano stool commonly found for six-coordinated $M(C_5Me_5)$ or M(arene) derivatives.

The preparation and properties of dinuclear complexes containing the pyrazolate and azide groups as bridging ligands were reported (113). Representative formulas are $[M_2(\mu\text{-pz})(\mu\text{-}N_3)(CO)_4]$, $[M_2(\mu\text{-pz})(\mu\text{-}N_3)(cod)_2]$ (M = Rh or Ir), $[(CO)_2Rh(\mu\text{-pz})(\mu\text{-}N_3)Rh(cod)]$, $[(CO)_2Rh(\mu\text{-pz})(\mu\text{-}N_3)Ir(CO)_2]$, and $[(\eta^3\text{-}C_3H_5)Pd(\mu\text{-pz})(\mu\text{-}N_3)Rh(CO)_2]$.

The IR spectra (solid state) of the carbonyl compounds were rather complex. This observation, along with the dark color and metallic luster of some of the complexes, suggested extended metal–metal interactions, which were confirmed by the X-ray crystal structure of the Pd/Rh derivative (113).

Two octamolybdenum compounds, containing both bridging pyrazolate and terminal pyrazole ligands, $[Mo_8(pz)_6(O)_{18}(Hpz)_6]$, **177**, and $[Mo_8(pz)_6(O)_{21}(Hpz)_6]$, **178**, were prepared by the reaction of molten pyrazole with molybdenum oxides and their structures were determined by single-crystal X-ray diffraction (133). The overall geometries of **177** and **178** are similar. Both complexes consist of an octametallic framework that may be described as two basally connected flattered trigonal pyramids.

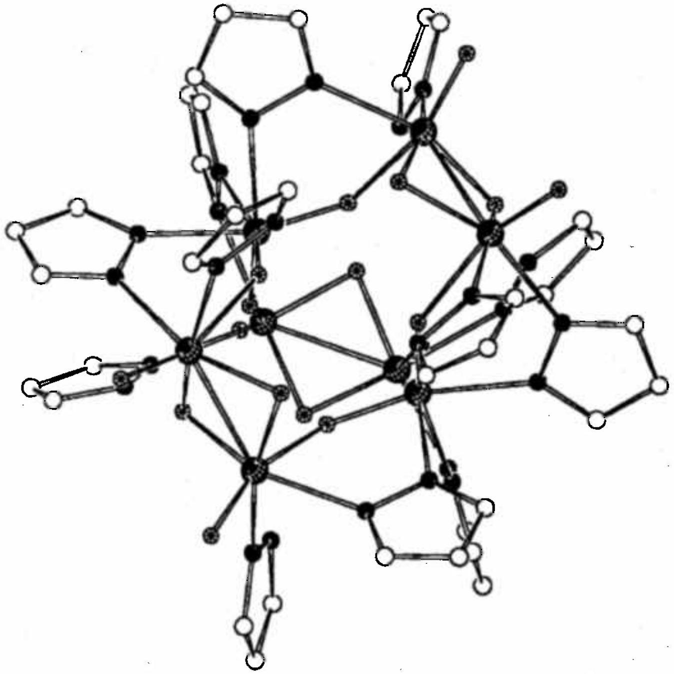
Complex **177** contains both Mo^{VI} and Mo^{V} ions, with the latter linked in pairs by metal–metal single bonds. Compound **178** involves a single-valent molybdenum(VI) octamolybdenum species and is photosensitive.

The complex $[Zn(dmpz)_2(Hdmpz)]_2$, **31**, was reacted with $[Co(MeCN)_6](BF_4)_2$ in the presence of NEt_3 with the aim of obtaining the mixed-cobalt/zinc analogue of the cobalt(II) polymer $[Co(dmpz)_2]_n$ (41), that is, $[CoZn_2(dmpz)_6]_n$ (134). The unexpected formation of the tetranuclear complex $[Co_4(\mu\text{-dmpz})_6(\mu_4\text{-O})]$, **179**, was observed. Its X-ray crystal structure consists of a central O atom around which the four Co^{II} ions are pseudotetraedrally arrayed. The six edges of the tetrahedron are bridged by dmpz ligands (134) (Fig. 8).

The trinuclear copper(II) derivative $[Cu_3(OH)(pz)_3(py)_2Cl_2]\cdot py$, **180**, was obtained by oxidation of the dimeric copper(I) pyrazole complex $[Cu(Hpz)_2Cl]_2$ with molecular oxygen in the presence of pyridine (135). A related compound, $[Cu_3(OH)(pz)_3(HPz)_2(NO_3)_2]$, was previously reported and its X-ray crystal structure was determined (136).

The structure of **180** consists of a triangular arrangement of Cu^{II} atoms connected by μ-pz groups. Three terminal ligands (one Cl and two py) one on each copper atom, and two bridging ligands (μ-Cl and μ_3-OH) complete the coordination spheres of the three metal centers.

Unexpected octanuclear mixed-bridged copper(II)–pyrazolate complexes, $[Cu_8(\mu\text{-OH})_8(\mu\text{-pz*})_8]$ (Hpz* = Hpz, **181**; Hdmpz, **182**), were isolated on treat-



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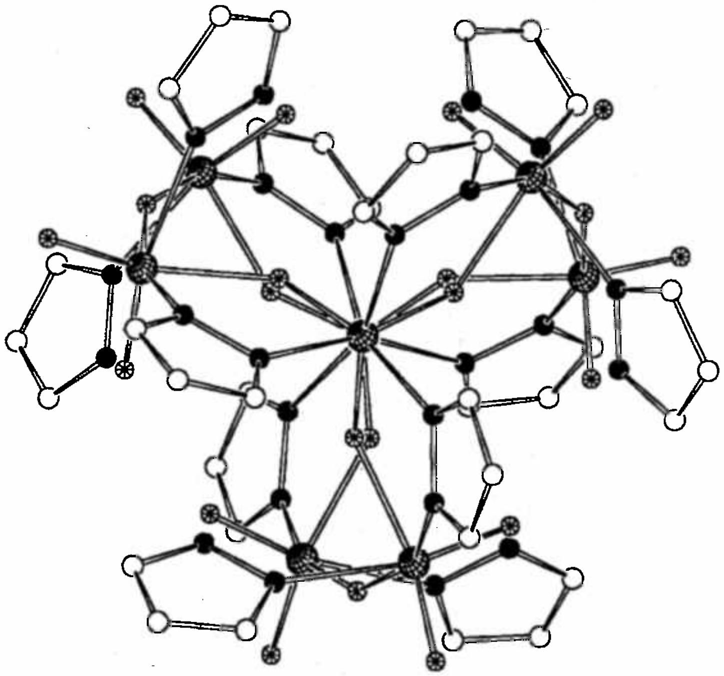


178

Figure 7. Structure drawings of the octanuclear species $[Mo_8(pz)_6(O)_{18}(Hpz)_6]$, **177** and $[Mo_8(pz)_6(O)_{21}(Hpz)_6]$, **178**. [Based on data from (133).]

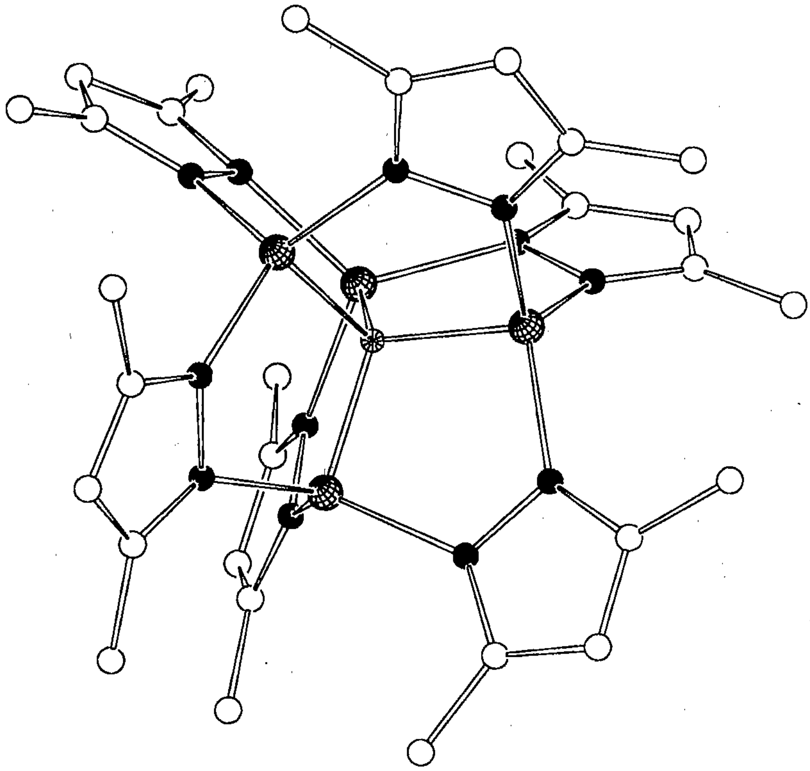


Figure 8. Structure drawing of the tetranuclear cobalt(II) species $[Co_4(\mu\text{-dmpz})_6(\mu_4\text{-O})]$, **179**. [Based on data from (134).]

ment of the binary copper(I) complexes $[Cu(pz)]_n$, **2**, or $[Cu(dmpz)]_3$, **6**, with dioxygen in wet solvents (137). The X-ray crystal structure of **182** was determined. The eight metal atoms, which lie approximately at the vertices of a regular octagon, are connected by μ-OH and μ-dmpz ligands in an alternate "up and down" sequence (Fig. 9) (137).

Complex **182** reacted with PPh_3 at 60°C under an inert atmosphere. This reaction yielded 4 mole of $O{=}PPh_3$ per mole of complex. The metal was recovered in quantitative yield as $[Cu(dmpz)]_3$, according to Eq. 11.

$$[Cu_8(OH)_8(dmpz)_8] + 4PPh_3 \longrightarrow \tfrac{8}{3}\,[Cu(dmpz)]_3 + 4O{=}PPh_3 + 4H_2O \qquad (11)$$

This uncommon behavior was explained by assuming that, in solution, the following equilibrium takes place (Eq. 12).

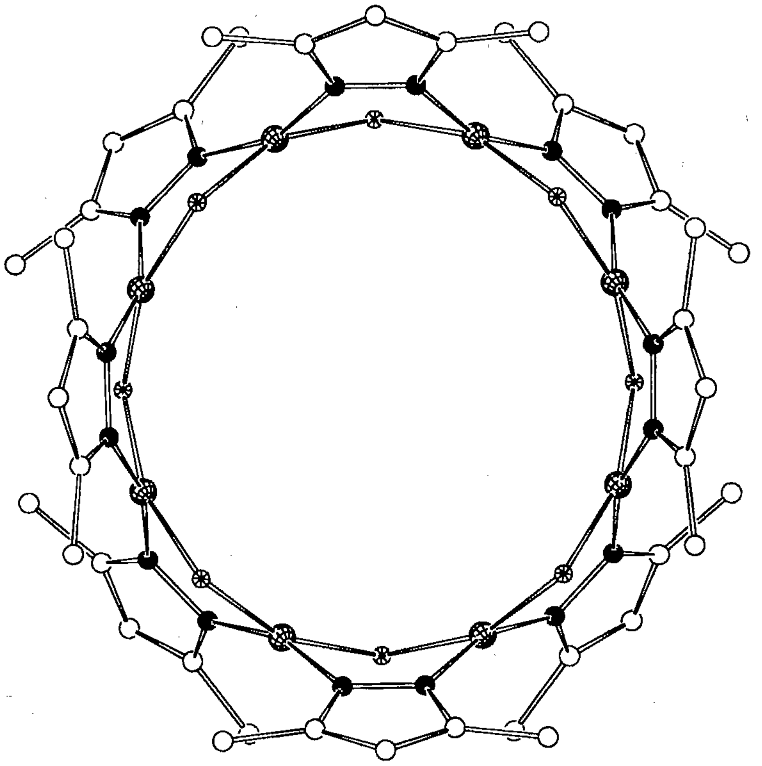


Figure 9. Structure drawing of the octanuclear copper(II) complex $[Cu_8(dmpz)_8(OH)_8]$, **182**. [Based on data from (137).]

$$[Cu_8(OH)_8(dmpz)_8] \rightleftharpoons [Cu_8(dmpz)_8(O)_x(OH)_{8-2x}(H_2O)_x] \quad (x = 1\text{–}4) \qquad (12)$$

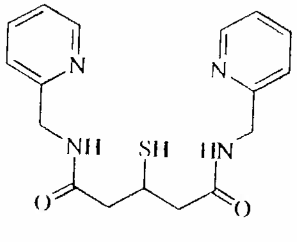
The tautomeric species thus formed were thought to be the plausible active species in the phosphine oxidation. Complex **182** was shown to exhibit catalytic properties in the selective oxidation of various organic substrates (137).

In 1970, the term "dinucleating ligands" was introduced for a series of polydentate ligands capable of simultaneously securing two metasl ions (138). In the past few years, increasing attention has been paid to the synthesis of such ligands and related complexes, resulting in the publication of several papers on this subject (139). Dinuclear copper(II) complexes were especially studied because of the recognized dependence of magnetic exchange within the dinuclear system upon stereochemical factors and the nature of the bridging species. In bis(μ-hydroxo) and bis(μ-alkoxo) bridged dinuclear copper(II) complexes, an increase in the strength of antiferromagnetic exchange coupling with increasing Cu—O—Cu bridging angle in the range 90–105° is well documented (140). More recently, interest in complexes containing larger bridging angles (120–135°) and unsymmetric doubly bridged structures, has stimulated a closer look at the effect of geometry and the nature of the bridging ligands on the strength of the exchange interactions (140). Therefore, the synthesis, structure, and magnetic properties of several dinuclear copper(II) complexes containing bridging pyrazolate ions and neutral or anionic binucleating ligands (Fig. 10) were reported (140–146). It was thus possible to compare data for such complexes to those obtained for single-atom bridged analogues (i.e., OH^-, Cl^-, or OR^-). It was concluded that the order of the decreasing negative coupling constant J, when all is kept constant, is $OR^- \approx pz^* > MeCOO^- \approx OH^- > Cl^-$.

A closer treatment of this topic is out of the realm of this chapter. Representative examples of dinuclear copper(II) complexes employed in such studies are reported in Table X.

Palladium(II) and nickel(II) complexes containing the bridging pyrazolate ion as well as the thiolate based dinucleating ligand H_3L^{12}, $[M_2(L^{12})(pz^*)]$ (Hpz* = Hpz or Hdmpz), were obtained (148). The complexes were easily prepared by treating the $[M_2(L^{12})(CH_3COO)]$ species with Hpz*.

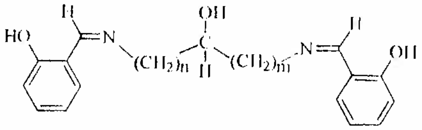
A tetranuclear nickel(II) complex with the dinucleating ligand H_3L^{13} [2,6-bis(salicylideneaminomethyl)-4-methyl-phenol], $[Ni_4(L^{13})_2(pz)_2(MeOH)]$ synthesized and characterized by electronic spectra, magnetic susceptibilities, and X-ray crystal structure analysis (149).



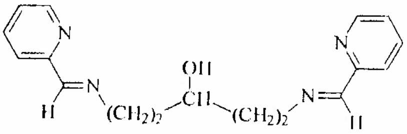
H_3L^{12}

B. Complexes Containing the (μ-pz*)$_a$(μ-H)$_b$ Fragment

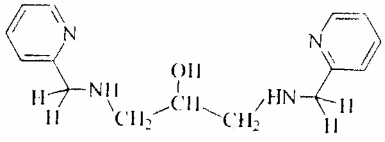
It is well known that hydride derivatives of transition metals can be prepared by hydrogen-transfer reactions from primary and secondary alcohols. Pentamethylcyclopentadienyl (μ-pyrazolate)-(μ-hydrido) complexes of iridium and rhodium were obtained by using propan-2-ol as the hydride source (128, 150).



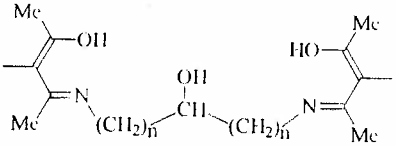
n = 1, m = 1, $\mathbf{H_3L^1}$
n = 2, m = 2, $\mathbf{H_3L^2}$
n = 3, m = 1, $\mathbf{H_3L^3}$



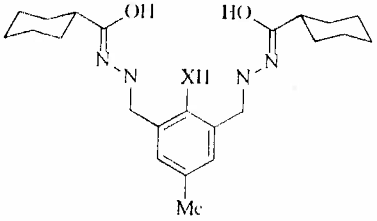
$\mathbf{HL^4}$



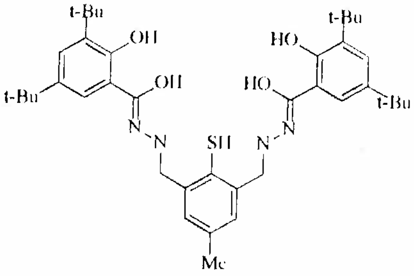
$\mathbf{HL^5}$



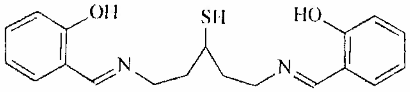
n = 1, $\mathbf{H_3L^6}$ n = 2, $\mathbf{H_3L^7}$



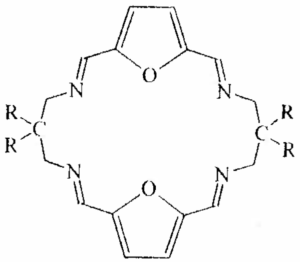
X = O, $\mathbf{H_3L^8}$ X = S, $\mathbf{H_3L^9}$



$\mathbf{H_3L^{10}}$



$\mathbf{H_3L^{11}}$



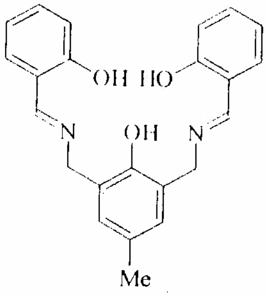
R = H, $\mathbf{L^A}$ R = Me, $\mathbf{L^B}$

Figure 10. Drawing of the dinucleating ligands utilized in the magnetostructural correlations on copper(II) pyrazolato complexes.

TABLE X

Pyrazolate-Bridged Dinuclear Copper(II) Complexes Containing Binucleating Ligands

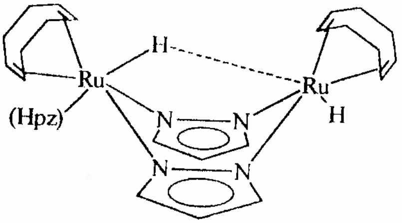
Complex	Formula	Binucleating Ligand	References
183	$[Cu_2(L^3)(pz)]$	H_3L^3	140
184	$[Cu_2(L^4)(pz)](ClO_4)_2$	HL^4	141
185	$[Cu_2(L^5)(pz)](ClO_4)_2$	HL^5	141
186	$[Cu_2(L^1)(pz)]$	H_3L^1	141
187	$[Cu_2(L^2)(pz)]$	H_3L^2	141, 142
188	$[Cu_2(L^6)(pz)]$	H_3L^6	141
189	$[Cu_2(L^6)(dmpz)]$	H_3L^6	141
190	$[Cu_2(L^7)(pz)]$	H_3L^7	141
191	$[Cu_2(L^8)(pz)]$	H_3L^8	145
192	$[Cu_2(L^9)(pz)]$	H_3L^9	145
193	$[Cu_2(L^{10})(pz)]$	H_3L^{10}	145
194	$[Cu_2(L^{11})(pz)]$	H_3L^{11}	147
195	$[Cu_2(L^A)(pz)_2](ClO_4)_2$	L^A	146
196	$[Cu_2(L^A)(dmpz)_2](ClO_4)_2$	L^A	146
197	$[Cu_2(L^B)(dmpz)_2](ClO_4)_2$	L^B	146



H_3L^{13}

Air-stable solids of formula $[\{Ir(C_5Me_5)\}_2(\mu\text{-}H)_2(\mu\text{-}pz^*)](BF_4)$ (Hpz* = Hpz, **198**; Hmpz, **199**; Hdmpz, **200**) were isolated by treating $[\{Ir(C_5Me_5)\}_2(\mu\text{-}OH)_3](BF_4)$ with equimolar amounts of Hpz* in isopropanol (150). The related cationic rhodium complex $[\{Rh(C_5Me_5)\}_2(\mu\text{-}H)_2(\mu\text{-}pz)](BF_4)$, **201**, was analogously obtained (128). Complex **201**, reacted with neutral ligands (L) giving products of the formula $[\{Rh(C_5Me_5)\}_2(\mu\text{-}pz)L_2](BF_4)$ (L = *t*-BuNC or CO), with dihydrogen being displaced (128). Spectroscopic studies on the latter two complexes indicated that CO and *t*-BuNC ligands are moving between terminal and bridging positions. The synthetic route reported above also allowed the preparation of mixed (μ-pz*)(μ-H)(μ-PPh_2) complexes (131). Thus, the reaction of [{Rh(C_5Me_5)}$_2$(μ-OH)$_3$](BF_4) with equimolar amounts of Hpz and $HPPh_2$ in refluxing propan-2-ol afforded [{Rh(C_5Me_5)}$_2$(μ-H)(μ-pz)(μ-PPh_2)](BF_4), **202,** (131).

Treatment of a suspension of [Ru(H)(cod)(NH_2NMe_2)$_3$](PF_6) with Hpz and Et_3N gave [{Ru(H)(pz)(cod)}$_2$(Hpz)], **203,** (151). The X-ray structure of **203** revealed a semibridging hydride ligand in an unsymmetrical dimer with the ruthenium atoms linked by two pyrazolate groups. Both ^1H and ^{13}C NMR spectra showed that this structure persists in solution.

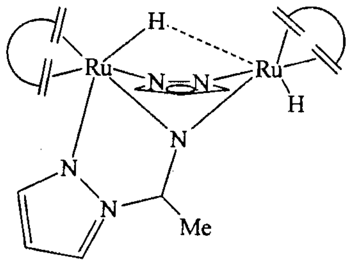


203

Treatment of **203** with PMe_3 affords [{Ru(H)(pz)(cod)}$_2$(PMe_3)], **204,** in which the neutral pyrazole ligand is replaced by trimethylphosphine (151). Further examples of ruthenium complexes containing bridging pyrazolate and hydride ligands were prepared (152, 153) from the ruthenium(II) precursor [Ru(H)(cod)(NH_2NMe_2)$_3$](PF_6).

The dinuclear cationic complex [(cod)(Hpz)Ru(μ-H)(μ-pz)$_2$Ru(Hpz)-(cod)](PF_6), **205,** was synthesized by the reaction of the precursor with Hpz in acetone under reflux (152). A related neutral derivative, [(cod)(Hpz)Ru(μ-H)(μ-pz)$_2$Ru(Cl)(cod)], **206,** formed quantitatively on allowing **203** to stand in CH_2Cl_2. The X-ray crystal structures of both **205** and **206** revealed their close similarity to **203.** An unexpected dinuclear ruthenium complex containing one terminal and one semibridging hydride ligand, [(cod)$_2$Ru$_2$(H)(μ-N=C(Me)pz}(μ-pz)(μ-H)], **207,** was obtained by reacting [Ru(H)(cod)-(NH_2NMe_2)$_3$](PF_6) with excess K[$R_2B(pz)_2$] (R = Et or Ph) in acetonitrile (153). The X-ray crystal structure of **207** confirmed the presence of a semibridging hydride ligand trans to a terminal hydride as well as the presence of a bridging amidine group, formed as the result of the bis(1-pyrazolyl)borate fragmentation followed by a pyrazolate/acetonitrile coupling, and stabilized in an unusual agostic 18-electron, 16-electron diruthenium dihydride complex (153).

The easy dissociation of the acetone molecule of [Ru(H)(η^1-$OCMe_2$)$(CO)_2${P(i-Pr)$_3$}$_2$](BF_4) allowed the synthesis of the cationic complex [Ru(H)$(CO)_2$(Hpz){P(i-Pr)$_3$}$_2$](BF_4), by reaction with pyrazole. The Hpz li-



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gand in the latter species contains an acidic NH group, which is capable of reacting with $[Rh(\mu\text{-OMe})(diolefin)]_2$ to give the heterodinuclear complexes $[(CO)_2\{P(i\text{-Pr})_3\}_2Ru(\mu\text{-H})(\mu\text{-pz})Rh(diolefin)]$ (diolefin = tfbb, **208**; cod, **209**). The presence of a bridging hydride ligand in these compounds is substantiated by ^1H NMR data (154). The existence of a ruthenium–rhodium interaction in **208** and **209** was supported by the X-ray crystal structure of **209**. Reactions between $Ru_3(CO)_{12}$ and Hpz* gave $[Ru_3(\mu\text{-H})(\mu\text{-pz*})(CO)_{10}]$ (Hpz* = Hpz, **210**; Hdmpz, **211**; Hdfmpz, **212**). These compounds, which resulted from the oxidative addition of Hpz* to the ruthenium cluster with concomitant loss of

TABLE XI

Di- and Trinuclear Complexes Containing the $(\mu\text{-pz*})_a(\mu\text{-H})_b$ Fragment

Complex	Formula[a]	Notes	Reference
198	$[\{Ir(C_5Me_5)\}_2(\mu\text{-H})_2(\mu\text{-pz})](BF_4)$	X-ray	150
199	$[\{Ir(C_5Me_5)\}_2(\mu\text{-H})_2(\mu\text{-mpz})](BF_4)$		150
200	$[\{Ir(C_5Me_5)\}_2(\mu\text{-H})_2(\mu\text{-dmpz})](BF_4)$		150
201	$[\{Rh(C_5Me_5)\}_2(\mu\text{-H})_2(\mu\text{-pz})](BF_4)$		128
202	$[\{Rh(C_5Me_5)\}_2(\mu\text{-H})(\mu\text{-pz})(\mu\text{-PPh}_2](BF_4)$		131
203	$[(cod)(Hpz)Ru(\mu\text{-H})(\mu\text{-pz})_2Ru(H)(cod)]$	X-ray	151
204	$[(cod)(PMe_3)Ru(\mu\text{-H})(\mu\text{-pz})_2Ru(H)(cod)]$		151
205	$[\{Ru(cod)(Hpz)\}_2(\mu\text{-H})(\mu\text{-pz})_2](PF_6)$	X-ray	152
206	$[(cod)(Hpz)Ru(\mu\text{-H})(\mu\text{-pz})_2RuCl(cod)]$	X-ray	152
207	$[(cod)(H)Ru\{\mu\text{-N}{=}C(Me)pz\}(\mu\text{-pz})(\mu\text{-H})Ru(cod)]$		153
208	$[(CO)_2\{P(i\text{-Pr})_3\}_2Ru(\mu\text{-H})(\mu\text{-pz})Rh(tfbb)]$		154
209	$[(CO)_2\{P(i\text{-Pr})_3\}_2Ru(\mu\text{-H})(\mu\text{-pz})Rh(cod)]$	X-ray	154
210	$[Ru_3(\mu\text{-H})(\mu\text{-pz})(CO)_{10}]$		155
211	$[Ru_3(\mu\text{-H})(\mu\text{-dmpz})(CO)_{10}]$		155
212	$[Ru_3(\mu\text{-H})(\mu\text{-dfmpz})(CO)_{10}]$	X-ray analysis	155
213	$[Os_3(\mu\text{-H})(\mu\text{-pz})(CO)_{10}]$		156
217	$[Ru_3(\mu\text{-H})_2(\mu\text{-dmpz})(ER_3)_2(CO)_8](cat)$[a]		158

[a] E = Si, R = Et, Ph, or OMe; E = Sn, R = Bu or Ph; cat = Et_4N or PPN.

two CO molecules, do not show any bands assignable to μ-CO ligands in their IR spectra (155). The X-ray crystal structure of the 3,5-bis(trifluoromethyl) complex, $[Ru_3(\mu\text{-}H)(\mu\text{-}dfmpz)(CO)_{10}]$, **212,** was also determined (155).

A related osmium complex, $[Os_3(\mu\text{-}H)(\mu\text{-}pz)(CO)_{10}]$, **213,** was obtained on treatment of $[Os_3(CO)_{10}(Me_3CN)_2]$ with pyrazole (156).

C. Complexes Containing the $(\mu\text{-pz*})_a(\mu\text{-L})_b$ Fragment (L = Neutral Ligand)

The preparation of an unusual heterobridged mixed-valence rhodium complex bridged by one carbonyl group and two pyrazolate ligands was described (157). The complex $[(C_5Me_5)Rh(\mu\text{-}pz)_2(\mu\text{-}CO)Rh(dppp)](BPh_4)$, **214,** was obtained by reacting the heterovalent Rh(III)–Rh(I) complex $[(C_5Me_5)(Cl)Rh(\mu\text{-}pz)_2Rh(CO)_2]$, **55,** with 1,3-bis-(diphenylphosphino)propane (dppp) in methanol in the presence of $NaBPh_4$. The unambiguous characterization of **214** came from its X-ray crystal structure determination (157).

The anionic cluster $[Ru_3(\mu\text{-}dmpz)(\mu\text{-}CO)_3(CO)_7]^-$, **215,** was obtained in high yield, by treating $[Ru_3(\mu\text{-}H)(\mu\text{-}CO)(CO)_{10}]^-$ with Hdmpz (158). Its formulation was proposed on the basis of IR, ^1H, and ^{13}C NMR data. The reactivity of **215** with protic acids, alkynes, tertiary silanes, and tertiary stannanes was described. The already known neutral hydrido derivative $[Ru_3(\mu\text{-}H)(\mu\text{-}dmpz)(CO)_{10}]$, **211,** (155), was obtained from the reaction of **215** with trifluoroacetic acid. The reaction of **215** with diphenylacetylene afforded the anionic complex $[Ru_3(\mu\text{-}dmpz)(\mu_3\text{-}PhC_2)(\mu\text{-}CO)_2(CO)_6]^-$, **216,** in which the alkyne ligand interacts with three ruthenium centers as revealed by an X-ray crystal structure analysis (158). The reaction of **215** with $HSiR_3$ (R = Et, Ph, or OMe) and $HSnR_3$ (R = Bu or Ph) to give the disilyl or distannyl dihydrido derivatives $[Ru_3(\mu\text{-}dmpz)(\mu\text{-}H)_2(ER_3)_2(CO)_8]^-$, **217a–217e,** (E = Si or Sn) was also described (158).

Following the synthesis of the first rhodium(I) complex with an A-frame geometry, $[Rh_2(\mu\text{-}S)(CO)_2(\mu\text{-}dppm)_2]$ (159), several other examples of this type of derivatives in which a $Rh_2(\mu\text{-}L)(\mu\text{-}dppm)$ fragment is present were published. In 1985, the preparation of a series of new A-frame rhodium(I) and rhodium(II) complexes containing a pyrazolate group acting as a capping ligand have been reported (160). These studies were extended to include the synthesis of several additional complexes, including their full characterization and their chemical properties (161–166). Most of these complexes have the basic structure types I and II. Significant examples are listed in Table XII.

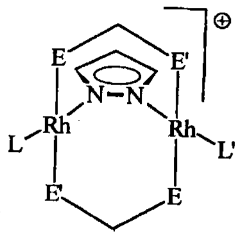
The former type of derivatives (L = L′ = CO) are readily obtained by the addition of $AgClO_4$ and Hpz* to trans-$[Rh_2Cl_2(CO)_2(\mu\text{-}EE')_2]$ in the presence

TABLE XII

Pyrazolate-Bridged Dirhodium Compounds of the General Formulas $[Rh_2(\mu\text{-}EE')(\mu\text{-}pz^*)(L)(L')](A)$ and $[Rh_2(\mu\text{-}EE')(\mu\text{-}pz^*)(L)(L')(Z)_2](A)$

Type	E	E′	L	L′	Hpz*	Z	A	Notes	Referen
I	P	P	CO	CO	Hpz		ClO_4		160
I	P	P	CO	CO	Hdmpz		ClO_4	X-ray	160
I	P	P	CO	Me_3CNC	Hpz		PF_6		163
I	P	P	Me_3CNC	Me_3CNC	Hpz		PF_6		163
I	P	As	CO	CO	Hdmpz		PF_6		163
I	As	As	CO	CO	Hpz		ClO_4		161
I	As	As	CO	CO	Hdmpz		PF_6	X-ray	163
II	P	P	CO	CO	Hpz	I	ClO_4		160
II	P	P	CO	CO	Hdmpz	I	ClO_4	X-ray	160
II	As	As	CO	CO	Hpz	I	ClO_4		161
II	P	P	CO	Me_3CNC	Hpz	I	ClO_4		161
II	P	P	Me_3CNC	Me_3CNC	Hpz	I	BF_4	X-ray	161

of KOH or on direct treatment of pyrazolate ion, $(pz^*)^-$, with $[Rh_2(CO)_2(\mu\text{-}EE')(\mu\text{-}Cl)](PF_6)$.



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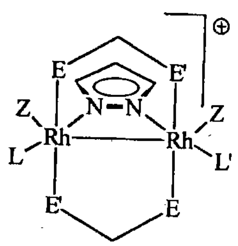
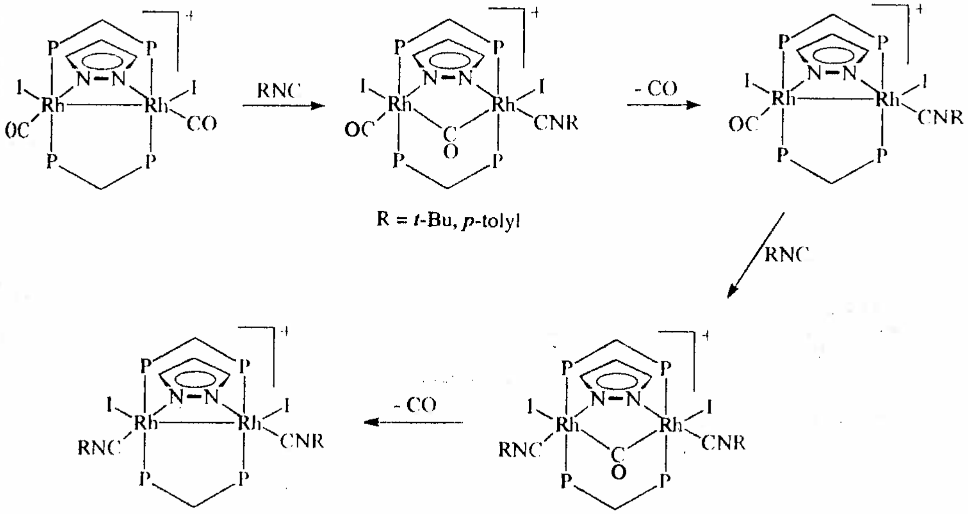


II

When 1 equiv of *t*-BuNC is added to $[Rh_2(CO)_2(\mu\text{-}EE')(\mu\text{-}pz^*)](PF_6)$ a new series of complexes, formulated as containing one CO and one isocyanide ligand, is obtained. The addition of 2 equiv of *t*-BuNC results in the replacement of both CO ligands (163).

Complexes of Type II (Z = Cl, Br, or I; L = L′ = CO) were obtained by bicentric oxidative addition of halogens to the dicarbonyl complexes of Type I (160, 163). In these complexes, the carbonyl ligand can also be gradually substituted by isocyanide ligands. The substitution involves the intermediate formation of species containing a bridging carbonyl ligand, as seen in the case of $[Rh_2(CO)_2(\mu\text{-}dppm)_2(\mu\text{-}pz)(I)_2](ClO_4)$ (Scheme 10) (161).

A related dinuclear heterobridged dirhodium complex triply bridged by two pyrazolate and one dppm ligand $[Rh_2(CO)_2(\mu\text{-}pz)_2(\mu\text{-}dppm)(I)_2]$, was reported



Scheme 10. The stepwise substitution of carbonyl ligands by RNC (R = t-Bu or p-tolyl) in the derivative $[Rh_2(\mu\text{-pz})(\mu\text{-dppm})_2I_2(CO)_2]^+$ is accompanied by the intermediate formation of species containing a bridged carbonyl ligand (see text). [Adapted from (161).]

and its X-ray crystal structure was determined (162). The latter complex was prepared by addition of dppm to $[Rh_2(CO)_4(\mu\text{-pz})_2(I)_2]$.

Extensive electrochemical studies of complexes of Type I were also reported (164–166). It was ascertained that $[Rh_2]^{2+}$ di-isocyanide complexes are more susceptible to oxidation than their dicarbonyl analogues, and that one-electron oxidations of the di-isocyanide complexes produce stable and isolable paramagnetic $[Rh_2]^{3+}$ species (165). In particular, paramagnetic complexes of the type $[Rh_2(\mu\text{-EE}')_2(t\text{-BuNC})_2(\mu\text{-pz}^*)](PF_6)_2$ (EE′ = dppm, dapm, or dpam; Hpz* = Hpz, 4-MepzH, Hdmpz, 4-BrdmpzH, or 3,4,5-BrpzH) containing the $[Rh_2]^{3+}$ core were obtained via controlled potential electrolysis of the parent $[Rh_2]^{2+}$ species $[Rh_2(\mu\text{-EE}')_2(t\text{-BuNC})_2(\mu\text{-pz}^*)](PF_6)$. The X-ray crystal structure of $[Rh_2(\mu\text{-dppm})_2(t\text{-BuNC})_2(\mu\text{-dmpz})](PF_6)_2$ showed a Rh· · ·Rh distance of about 2.83 Å, which is consistent with a bonding order of 0.5 for the $[Rh_2]^{3+}$ core (166).

V. COMPLEXES CONTAINING MONODENTATE PYRAZOLATE GROUPS

The interest for pyrazolate complexes containing the pz* group as a monodentate ligand arises because of their recognized usefulness in the synthesis of dinuclear and trinuclear heterometallic derivatives. The mononuclear complex cis-[$(PPh_3)_2ClPt(dppz)$], **218**, was obtained by reacting cis-$Pt(PPh_3)_2Cl_2$ with Na(dppz) in a 1 : 1 molar ratio (14). The coordination geometry of **218**, which was structurally characterized (14), is very similar to that of the cation in cis-[$PdCl(PEt_3)_2(Hdmpz)$](BF_4), which was reported in 1981 by Busnell et al. (167). The metalloligand **218** is able to bind to various metals such as Cu, Ag, and Au. Three such heterobimetallic derivatives, cis-[$(PPh_3)_2ClPt(\mu$-dppz)AgCl], **219**, cis-[$(PPh_3)_2BrPt(\mu$-dppz)CuCl], **220**, and cis-[$(PPh_3)_2BrPt(\mu$-4-Brdppz)AuBr], **221**, were characterized by single-crystal X-ray analysis (14).

From Vaska's compound, trans-[$Ir(PPh_3)_2(CO)Cl$], the corresponding mononuclear iridium(I) pyrazolate complexes, trans-[$Ir(PPh_3)_2(CO)(pz^*)$], was synthesized on treatment with Hpz* (Hpz* = Hdmpz, 4-NO_2dmpzH, or Hdfmpz) and KOH (168). Evidence for the monodentate nature of the pz* group came from IR and NMR spectra. The presence of a monodentate pyrazolate ligand in trans-[$Ir(PPh_3)_2(CO)(dfmpz)$], **222**, was supported by an X-ray crystal structure determination (168). The iridium(I) pyrazolates undergo oxidative addition by dihydrogen, yielding [$Ir(H)_2(pz^*)(CO)(PPh_3)_2$]. The nitrogen atom not involved in coordination was protonated with HBF_4 to give the corresponding cationic pyrazole complexes [$Ir(CO)(PPh_3)_2(Hpz^*)$](BF_4) (168). The reaction of iridium(I) and iridium(III) pyrazolate complexes [$Ir(PPh_3)_2(CO)(dmpz)$], **223**, and [$Ir(H)_2(dmpz)(CO)(PPh_3)_2$], **224**, with Au(tht)X (X = Cl or Br) afforded the $Ir^{(I)}/Au^{(I)}$ and $Ir^{(III)}/Au^{(I)}$ derivatives [$Ir(PPh_3)_2(CO)(\mu$-dmpz)AuX] and [$Ir(PPh_3)_2(CO)(H)_2(\mu$-dmpz)AuCl], **225** (169). Complex **225** was structurally characterized (169).

Mention is made here to a member of a series of dimeric terpyridine platinum(II) complexes, [$(tpy)Pt(\mu$-pz)Pt(tpy)]($ClO_4)_3$, **226**. These complexes were used to study the effect of the Pt· · ·Pt separation on absorption and emission spectra (170, 171). The X-ray crystal structure of Complex **226** was determined A single pyrazolate ligand bridges two Pt centers. The square planar coordination around each metal is completed by a tridentate terpyridine ligand (170).

In 1979, a series of pyrazolate complexes of the formula [$M(pz^*)_2(L{-}L)$] (M = Pt or Pd; Hpz* = Hpz or Hdmpz; L—L = chelating ligand or diolefin) was described (172). The X-ray crystal structures of [$(dppe)Pt(dmpz)_2$], **227** and [4,4′-Me_2bipy)Pt(dmpz)$_2$], **228**, were reported (173, 174). In all these complexes, the pyrazolate groups are monodentate so that all the molecules described can be considered, at least in principle, bidentate metal-containing ligands. Thus, complexes [$M(pz^*)_2(L{-}L)$] were used as ligands toward selected acceptors, affording bimetallic derivatives containing doubly bridged pyrazolate groups (175, 176).

Recently, the synthesis and X-ray crystal structure of [$Cu(dcmpz)_2(py)_2$], **229**, were reported (40). Complex **229** was obtained either by reacting [$Cu(dcmpz)]_n$, **12**, (27) with dioxygen in pyridine or by the direct reaction of $CuCl_2$ with Hdcmpz in the presence of pyridine. Complexes having two

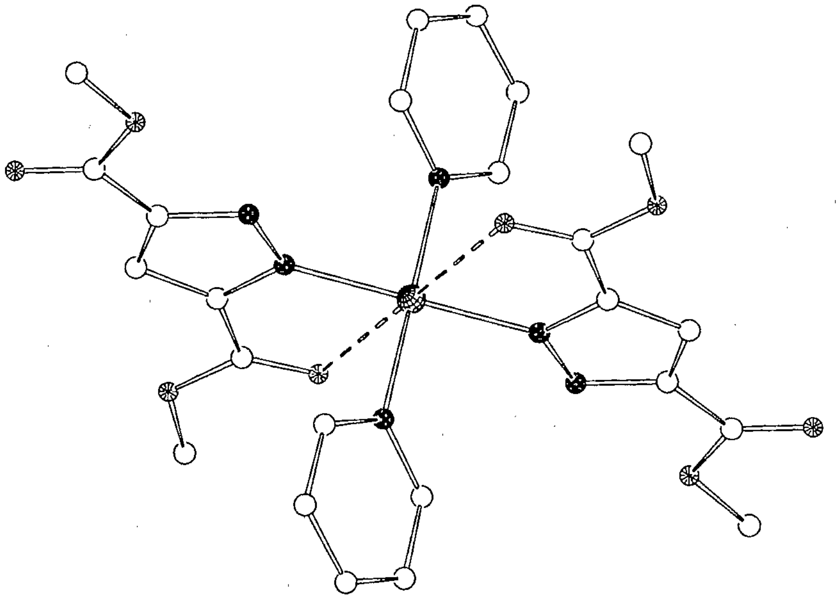


Figure 11. Structure drawing of the mononuclear copper(II) species [Cu(dcmpz)$_2$(py)$_2$], **229**, containing two unidentate 3,5-dicarbomethoxypyrazolate groups in a trans conformation. [Based on data from (40).]

monohapto pyrazolate ligands invariably exhibit a cis-conformation (173). Complex **229** represents the first example of a structurally characterized bis(pyrazolate) species containing two monodentate pyrazolate groups trans to each other (Fig. 11). Since Complex **229** has two nucleophilic nitrogen atoms not yet involved in coordination with metal centers, this complex has the potential of obtaining homo- and heterotrimetallic systems.

The reaction of [{Rh(C$_5$Me$_5$)}$_2$(μ-OH)$_3$](ClO$_4$) with an excess of Hpz or 4-BrpzH, afforded the neutral complexes [{Rh(C$_5$Me$_5$)(pz)}$_2$(μ-pz)$_2$], **230**, and [{Rh(C$_5$Me$_5$)(4-Brpz)}$_2$(μ-4-Brpz)$_2$], **231** (52) in the presence of KOH. An X-ray structural analysis of Complex **230** confirmed the presence of either exo-bidentate or monodentate pyrazolate groups. Interestingly, the addition of HClO$_4$ to **231** causes the protonation of the monodentate 4-Brpz ligand, with formation of [{Rh(C$_5$M$_5$)(4-BrpzH)}$_2$(μ-4-Brpz)$_2$](ClO$_4$)$_2$. The latter easily regenerated **231** on addition of KOH (52). The related mixed-valence rhodium(III)–rhodium(I) complex [(C$_5$Me$_5$)(pz)Rh(μ-pz)$_2$Rh(tfbb)], **232**, was obtained by reacting [Rh(tfbb)(Hpz)$_2$](ClO$_4$) with the appropriate acac complex, [Rh(C$_5$Me$_5$)(acac)Cl], in the presence of KOH (79). The ^{1}H NMR of **232** confirmed the existence of terminal and bridging pyrazolate groups.

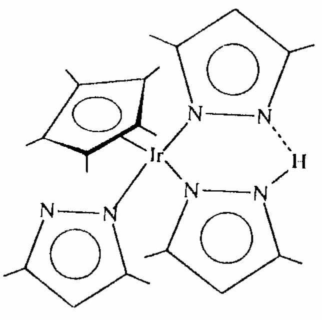
The synthesis and molecular structure of a monomeric vanadium(III) anionic complex, $K[\{HB(dmpz)_3\}VCl_2(dmpz)]$, **233**, were reported. Complex **233** was obtained by reacting VCl_3 with the tris(3,5-dimethylpyrazolyl)borate ligand in solvents other than DMF. The monodentate dmpz group in this species clearly arises from ligand degradation. Several potential pathways for this decomposition have been advanced. These include enhanced hydrolysis of the B—N bond by traces of water in the presence of a strong Lewis acid such as VCl_3 (177).

A trioxo(pyrazolyl)rhenium(VII) complex, $O_3Re(pz)$, of unclarified pz-hapticity, was recently reported (178). This complex was obtained by reacting a frozen solution of Re_2O_7 with solid Na(pz). Its IR spectrum exhibits a strong $\nu(Re{=}O)$ band at 913 cm^{-1}, characteristic of a perrhenate anion, which may indicate that the structure of this compound may be more complex than supposed.

A. Mononuclear Complexes Containing Neutral Pyrazoles and Monodentate Pyrazolate Ligands

In 1986, the preparation and characterization of new mononuclear (pentamethylcyclopentadienyl) iridium(III) complexes containing monodentate pyrazolate ligands as well as neutral pyrazoles, $[(C_5Me_5)Ir(pz)_2(Hpz)]$, **66**, $[(C_5Me_5)Ir(dmpz)_2(Hdmpz)]$, **234**, and $[(C_5Me_5)Ir(dmpz)(Hdmpz)_2](BF_4)$, **235**, were reported (95). Spectroscopic measurements revealed in **66** the equivalence of the pyrazole ligands; this fact has been attributed to an intramolecular proton exchange between the neutral pyrazole and the two anionic pyrazolate ligand. On the contrary, the ^1H NMR spectrum of **234** showed the presence of the Hdmpz ligand sharing the N—H proton with only one dmpz group, whereas the second pyrazolate ligand was free of interaction. An X-ray crystal structure determination confirmed these observations (95). Treatment of **234** with an equimolar amount of HBF_4 afforded the ionic complex **235**. The ^1H NMR of **235** clearly showed that the second proton is bound to the nonchelated ligand.

By taking advantage of the formal similarity between $[RB(pz)_3]^-$ and the deprotonated form of the iridium complex **66**, heterodinuclear complexes, synthesized by using **66** as a building block, were described (96). Ruthenium(II) complexes containing neutral pyrazoles as well as pyrazolate anions as ligands were also described (102, 179). The complex $[Ru(H)(pz)(CO)(Hpz)(PPh_3)_2]$, **80**, was obtained on treatment of $[Ru(H)(Cl)(CO)(Hpz)(PPh_3)_2]$ with the stoichiometric amount of KOH and Hpz (102). The reaction between cis-$[RuCl_2(dmso)_4]$ and $K[H_2B(pz)_2]$ yielded $[Ru(pz)_2(Hpz)_3(dmso)]$, **236**, whose X-ray crystal structure was determined (179). This determination provided evidence in support of the rupture of the boron-nitrogen bond in the dihydrobis(1-pyrazolyl)borate ligand.



234

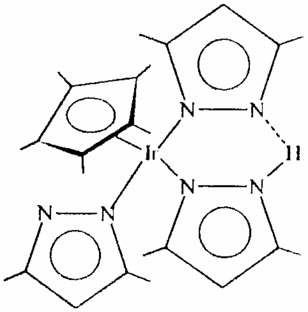
Neutral and cationic ruthenium con
late groups were obtained by using
mene)(acac)Cl], or the dinuclear com
starting material (7) (Scheme 11).

Complex **237** (Scheme 11) could b
second equivalent of KOH, which yi
These complexes were characterized by
studies, and by determination of the X-r
there is an intramolecular hydrogen bo
zoles (Hpz) and the pyrazolate group.
engaged in an intermolecular hydrogen l
ation by NBu_4OH of the pyrazole comple
or $[R_2Pt(Hpz^*)_2]$ ($R = C_6F_5$, Hpz^* =
azolate complexes of the formula $[R_2M($

The IR and NMR data for the latte
ligands were identical. The X-
$[(C_6F_5)_2Pd(pz)(Hpz)](NBu_4)$, **242**, and
tablished the existence of an intramolec
pyrazolyl ligands, the coordination at p
essentially square planar (180).

The synthesis and crystal structures of
complexes of the formula $[M(pz^*)_2(Hpz^*$
= Pd, Hpz* = Hpz, **245**; Hdmpz, **246**
with their IR spectra, the structures of **2**
two monomeric $[M(pz^*)_2(Hpz^*)_2]$ units lin
bridges between the Hpz* and the pz* lig

Complex **246** exhibits high rigidity e
absence of any fluxional behavior (evide



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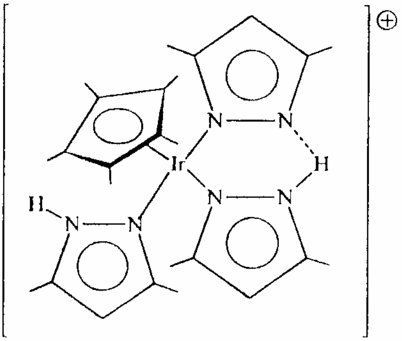


235

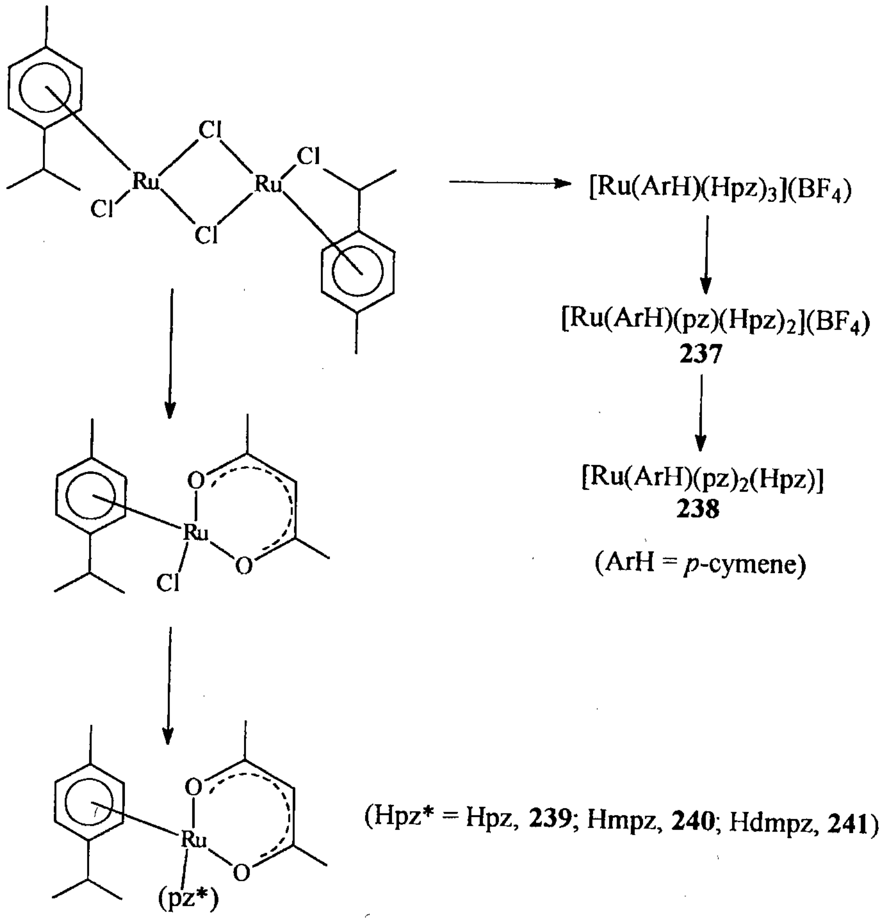
Neutral and cationic ruthenium complexes containing monodentate pyrazolate groups were obtained by using the β-diketonato complex [Ru(p-cymene)(acac)Cl], or the dinuclear complex [{Ru(p-cymene)Cl}$_2$(μ-Cl)] as the starting material (7) (Scheme 11).

Complex **237** (Scheme 11) could be further deprotonated by addition of a second equivalent of KOH, which yielded [Ru(p-cymene)(pz)$_2$(Hpz)], **238.** These complexes were characterized by analytical and IR measurements, NMR studies, and by determination of the X-ray crystal structure of **237.** In the latter, there is an intramolecular hydrogen bond between the NH of one of the pyrazoles (Hpz) and the pyrazolate group. The NH of the second Hpz ligand is engaged in an intermolecular hydrogen bond with the BF_4 anion (7). Deprotonation by NBu_4OH of the pyrazole complexes [R_2Pd(Hpz)$_2$] (R = C_6F_5 or C_6Cl_5) or [R_2Pt(Hpz*)$_2$] (R = C_6F_5, Hpz* = Hpz or Hdmpz) afforded pyrazole–pyrazolate complexes of the formula [R_2M(pz*)(Hpz′)](NBu_4) (180).

The IR and NMR data for the latter species showed that both pyrazolyl ligands were identical. The X-ray structure determinations of [(C_6F_5)$_2$Pd(pz)(Hpz)](NBu_4), **242,** and [(C_6F_5)$_2$Pt(pz)(Hpz)](NBu_4), **243,** established the existence of an intramolecular hydrogen bond between the two pyrazolyl ligands, the coordination at palladium, and platinum centers being essentially square planar (180).

The synthesis and crystal structures of dimeric platinum(II) and palladium(II) complexes of the formula [M(pz*)$_2$(Hpz*)$_2$]$_2$ (M = Pt, Hpz* = Hpz, **244**; M = Pd, Hpz* = Hpz, **245**; Hdmpz, **246**) were reported (44, 45). Consistent with their IR spectra, the structures of **244** and **246** revealed the presence of two monomeric [M(pz*)$_2$(Hpz*)$_2$] units linked by four symmetrical N—H· · ·N bridges between the Hpz* and the pz* ligands (Fig. 12).

Complex **246** exhibits high rigidity even in solution, as indicated by the absence of any fluxional behavior (evidence from ^{1}H NMR measurements at



Scheme 11. Neutral and cationic ruthenium complexes containing unidentate pyrazolate groups have been obtained by using the dinuclear complex [{Ru(*p*-cymeme)Cl}$_2$(μ-Cl)] or the β-diketonato complex [Ru(*p*-cymene)(acac)Cl] as starting materials. [Adapted from (7).]

variable temperature) (45). It was verified that **246** reacts rapidly, in CH_2Cl_2 solution at room temperature, with a number of heterocumulenes, such as CS_2, COS, and *p*-tolylisocyanate (181). The reaction with COS gave [Pd{SC(O)dmpz}$_2$], **247**. The X-ray crystal structure of **247** showed that monomeric, centrosymmetric molecules, containing a square planar trans-PdN_2S_2 chromophore, are formed (Fig. 13) (181).

Interestingly, Complex **246**, reacts, in the solid state, with liquid COS at $-78°C$, yielding a product formulated as [Pd(dmpz)$_2$(Hdmpz)$_2$]$_2$·COS, **248**. The latter compound exhibits a strong, sharp ν_{as}(SCO) IR absorption at 2045 cm^{-1} [ν_{as}(SCO) of free COS = 2062 cm^{-1}]. This absorption was initially at-