

Binuclear and polynuclear complexes of rhodium with nitrogen heterocycles as bridging ligands

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Abstract. A number of binuclear and polynuclear complexes of rhodium(I) with bridging nitrogen heterocycles are known. X-ray crystal structure analysis of some of the complexes has established the bridging nature of the heterocycles. The proximity of the metal atoms is found to considerably influence the electronic spectra of the complexes. Oxidative addition reactions of these compounds are yet to be properly investigated. Some of these compounds are efficient hydrogenation and hydroformylation catalysts.

Keywords. Binuclear complexes; polynuclear complexes; rhodium; nitrogen heterocycles; bridging ligands.

1. Introduction

Binuclear and polynuclear complexes of transition metals have received considerable attention because of the interesting electrical, optical and catalytic properties that could be associated with such systems. Several nitrogen heterocycles have been conveniently employed as bridging ligands in the isolation of such complexes (Coleman *et al* 1982; Lanza 1983; Newkome *et al* 1982; Powers and Meyer 1978; Stobart *et al* 1980; Uson *et al* 1982a). The heterocycles used in this way are bidentate or tetradentate species with the coordinating nitrogen atoms located at positions convenient for bridge formation. They are essentially five- and six-membered rings or their extended forms or their derivatives. While heterocycles derived from six-membered rings and containing two or four nitrogen donor sites can directly bridge two metal centres, those derived from five-membered rings act as bridging ligands in their anionic forms. The heterocycles that have been successfully employed as bridging ligands are depicted in figures 1 and 2.

This review is confined to binuclear and polynuclear complexes of rhodium containing the aforesaid bridging heterocycles. Most of these complexes have the metal atom in the oxidation state +1.

2. General methods of synthesis

The dihalobridged binuclear complexes of the type $L_2Rh(\mu-X_2)RhL_2$ ($X =$ halogen; $L_2 =$ diolefin, $(CO)_2$) are convenient starting materials (Abel *et al* 1959; Chatt and Venanzi 1957; Deeming and Sharratt 1975; Roe and Massey 1971) for the isolation of a majority of rhodium(I) complexes with bidentate or tetradentate bridging hetero-

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A list of abbreviations used appears at the end of the paper.

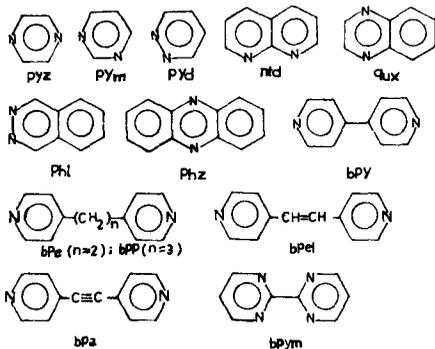


Figure 1. Heterocycles derived from six-membered rings.

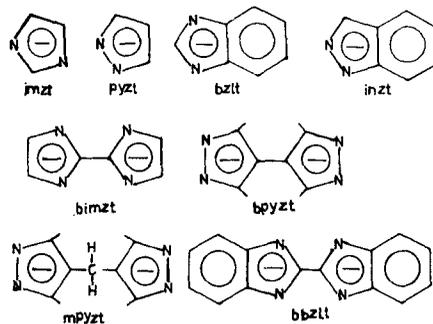
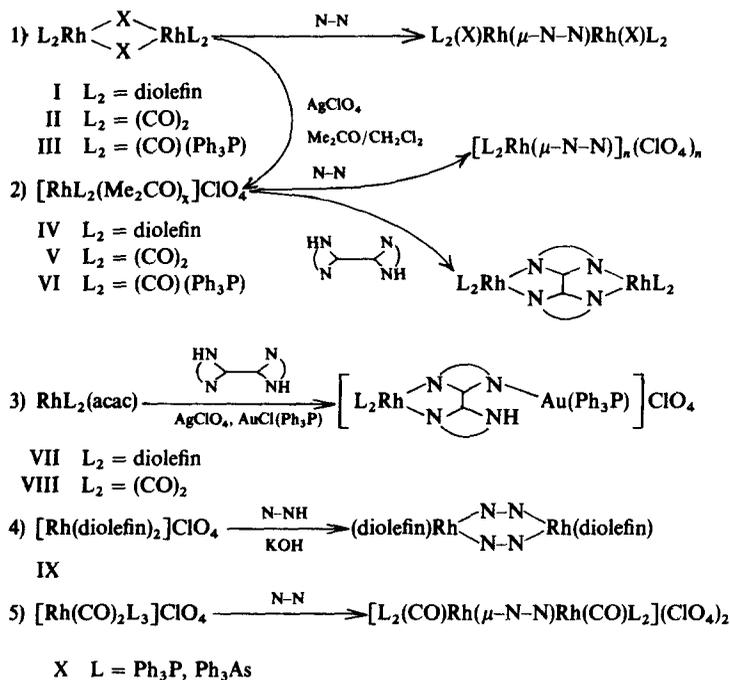
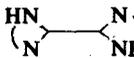


Figure 2. Heterocycles derived from five-membered rings.

cycles*. A few cationic complexes of rhodium(I) also serve as precursors in several reactions. Methods of isolating rhodium(I) complexes with bridging nitrogen heterocycles are summarised below.



*The term "bidentate" generally means "chelate" (*i.e.* endobidentate) and hence a bidentate ligand (N-N or N-NH) which cannot form a chelate but bonds to two metal atoms is termed as an "exobidentate" (Trofimenko 1972). Similarly a tetradentate ligand  which bonds to two metal atoms may be referred to as an "endo-exotetradentate".

3. Complexes containing pyrazine, phenazine and quinoxaline

Pyz and phz react with complex I in acetone to give complexes of the formula (diolefin)-(X)Rh(μ -N-N)Rh(X)(diolefin) (diolefin = cod, nbd; N-N = pyz, phz) (Halesha *et al* 1983; Siedle *et al* 1983). In the cod complexes pyz can be replaced by the more bulkier ligands like phz. Endobidentate ligands such as bipy and phen, however, cleave the pyz bridge in cod containing compounds to form mononuclear ionic complexes. In benzene, the binuclear complexes undergo substitution of the diolefin with carbon monoxide to give (CO)₂(X)Rh(μ -N-N)Rh(X)(CO)₂. The latter complexes can also be isolated by treating complex II in benzene with the bridging heterocycles (Balch and Cooper 1979; Halesha *et al* 1983; Siedle *et al* 1983). The pyz bridged bromo carbonyl is, however, very unstable. Qux behaves similar to the above mentioned heterocycles in its reaction with complex I (X = Br; diolefin = cod). However the compound is not as stable as its pyz or phz analogs probably due to the less symmetric nature of the bridging heterocycle. Carbonyls of the type (CO)₂(X)Rh(μ -qux)Rh(X)(CO)₂ are made by reacting complexes II with qux. The stability of the carbonyl complexes follows roughly the order pyz < qux < phz (Halesha and Reddy, Unpublished results). IR and PMR data of some of these complexes are listed in table 1.

X-ray crystal structure analysis of (cod)(Cl)Rh(μ -pyz)Rh(Cl)(cod) has unequivocally established the dinuclear nature of the complex with the two metal atoms bridged *via* the pyz nitrogens (Rh-N = 2.1 Å). The pyz ring is virtually planar and makes an angle of 56.9° to the coordination plane of the metal atoms due to steric effects arising from bulky chlorine atoms which are located *trans* to each other (figure 3; Halesha *et al* 1983).

Table 1. IR and PMR spectral data of pyz, phz and qux complexes.

Complex	PMR data (δ)/ ν_{CO} (cm ⁻¹)
(cod)ClRh(μ -pyz)RhCl(cod)	1.80, 2.49, 4.21 (cod); 8.67 (pyz)
(OC) ₂ ClRh(μ -pyz)RhCl(CO) ₂	8.82 (pyz)/2015, 2105
(cod)BrRh(μ -pyz)RhBr(cod)	1.80, 2.49, 4.21 (cod); 8.69 (pyz)
(OC) ₂ BrRh(μ -pyz)RhBr(CO) ₂	—/2016, 2095
(OC) ₂ ClRh(μ -phz)RhCl(CO) ₂	8.12, 9.43 (phz)/2005, 2085
(OC) ₂ BrRh(μ -phz)RhBr(CO) ₂	—/2005, 2085
(OC) ₂ ClRh(μ -qux)RhCl(CO) ₂	—/2005, 2090
(OC) ₂ BrRh(μ -qux)RhBr(CO) ₂	—/2010, 2080
[(OC) ₂ ClRh(μ -pyz)RhCl(CO) ₂] _{4.2}	—/2015, 2105
[(OC)Rh(μ -pyz)Rh(CO)] _n (ClO ₄) _{2n}	—/2050, 2120
[(OC)Ph ₃ PRh(μ -pyz)] _n (ClO ₄) _n	—/2010

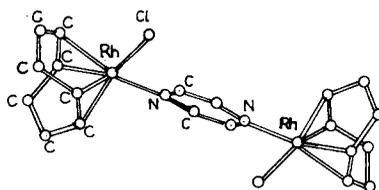


Figure 3. Molecular structure of (cod)ClRh(μ -pyz)RhCl(cod).

The qux and phz complexes may be expected to show more tilting of the bridging ligand with respect to the coordination plane. In fact molecular model studies for the monomeric complex $\text{RhCl}(\text{cod})\text{phz}$ indicate that non-bonded repulsions between the phz peri-hydrogen atoms and the halogen and cod groups cause the heterocycle to twist so that its molecular plane is perpendicular to the rhodium plane (Siedle *et al* 1983). A similar orientation of phz molecule may be expected in the binuclear complex $(\text{cod})\text{ClRh}(\mu\text{-phz})\text{RhCl}(\text{cod})$. In this orientation the phz π^* and *trans* olefin π^* orbitals do not overlap with and compete for electron density from the same filled metal $4d$ orbital. This sterically enforced twisting of the phz ligand would lead to strong metal-nitrogen bonds. The dinuclear complexes (containing cod and pyz or phz) are good hydrogenation catalysts for the conversion of alkenes to alkanes, and nitro compounds to amino compounds (Leelamani *et al*, Unpublished results).

For the carbonyl complex $(\text{CO})_2\text{ClRh}(\mu\text{-pyz})\text{RhCl}(\text{CO})_2$, on the basis of molecular models, it is suggested that the two $\text{Rh}(\text{CO})_2\text{Cl}$ planes can be coplanar with the pyz ligand. The molecule is thus expected to be flat and may be able to stack in such a way that one rhodium(I) site lies over another. In the uv-visible region, the complex shows absorption bands at 300, 375, 415 and 650 nm, and the spectrum, with the exception of the longest wavelength band, is analogous to that of the phz isolog. However the longest wavelength band is suggested to be similar to that found for rhodium(I) complexes wherein the metal atoms are held in close proximity by bridging isocyanides (Mann *et al* 1980). Attempts to oxidise the above carbonyl with iodine have produced a black compound of the composition $[(\text{CO})_2\text{ClRh}(\mu\text{-pyz})\text{RhCl}(\text{CO})_2]\text{I}_{4.2}$ in which the metal ion continues to remain in the +1 oxidation state *vide infra* (table 1). It is likely that the iodo compound is a partially oxidised derivative of the parent compound (Siedle *et al* 1983). In the carbonyls of the formula $(\text{CO})_2\text{XRh}(\mu\text{-phz})\text{RhX}(\text{CO})_2$ the heterocyclic ring may be expected to be positioned perpendicular to the $\text{Rh}(\text{CO})_2\text{X}$ planes so that there is little opportunity for intermolecular interaction.

Reaction of complex IV (diolefin = cod, nbd, tfb) with pyz gives polynuclear cationic species $[(\text{diolefin})\text{Rh}(\text{pyz})]_n(\text{ClO}_4)_n$ containing bridging pyz. The diolefin in these complexes may be completely replaced by carbon monoxide to yield the carbonyl complex $[(\text{CO})_2\text{Rh}(\mu\text{-pyz})]_n(\text{ClO}_4)_n$. This carbonyl may also be obtained by employing the chloro carbonyl dimer (II) as the precursor and the reaction proceeds *via* the formation of complex V. The above carbonyl reacts with Ph_3P , in stoichiometric quantities to produce the mononuclear complex $[\text{Rh}(\text{CO})\text{pyz}(\text{Ph}_3\text{P})_2]\text{ClO}_4$. The polynuclear complex $[\text{Ph}_3\text{P}(\text{CO})\text{Rh}(\mu\text{-pyz})]_n(\text{ClO}_4)_n$ has, however, been made by the following reaction (Uson *et al* 1981b).



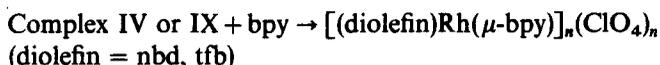
Yeh *et al* (1979) have prepared a mixed metal binuclear complex $(\text{NH}_3)_5\text{Rh}(\mu\text{-pyz})\text{Fe}(\text{CN})_5$ by treating $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ with $[\text{Rh}(\text{NH}_3)_5(\text{pyz})]^{3+}$ under argon. In the electronic spectrum of the complex an absorption band at 570 nm is observed and this is assigned to metal-to-ligand charge-transfer transition. The metal ions in the complex have well-defined oxidation states, *i.e.* Rh(III)-Fe(II), in contrast to trapped valences in the corresponding Ru-Fe complex, *i.e.*, Ru(III)-Fe(II) or Ru(II)-Fe(III), or a delocalised situation.

4. Complexes containing 4,4'-bipyridyl, 1,2-bis(4-pyridyl)ethane and related heterocycles

Mononuclear five-coordinate cationic complexes of the formula $[\text{Rh}(\text{CO})_2\text{L}_3]\text{ClO}_4$ ($\text{L} = \text{Ph}_3\text{P}, \text{Ph}_3\text{As}$) react with bpy in ethanol to yield binuclear heterocycle bridged complexes of the type $[\text{L}_2(\text{CO})\text{Rh}(\mu\text{-bpy})\text{Rh}(\text{CO})\text{L}_2](\text{ClO}_4)_2$ where the metal ion has coordination number four. Under similar conditions with pyz, only mononuclear complexes of the formula $[\text{Rh}(\text{CO})\text{L}_2(\text{pyz})]\text{ClO}_4$ are obtained. While the bpy complexes are 1:2 electrolytes in nitrobenzene, the pyz complexes are 1:1 electrolytes (Reddy and Ramesh 1975).

The exobidentate nitrogen heterocycles, bpy, bpe and bpeI react with complex I in acetone to produce yellow products of the composition $(\text{cod})\text{XRh}(\mu\text{-N-N})\text{RhX}(\text{cod})$ ($\text{N-N} = \text{bpy}, \text{bpe}, \text{bpeI}$). The bpy complex ($\text{X} = \text{Cl}$) is found to be a good catalyst for the hydrogenation of 1-heptene to heptane and some organic nitro compounds to amino compounds (Leelamani *et al*, Unpublished results). It is observed that the bpy complexes, on treatment with endobidentate ligands bipy and phen, undergo bridge cleavage reaction to yield mononuclear ionic complexes. The cod groups in the parent binuclear complexes can be replaced by CO. The carbonyl $(\text{CO})_2\text{ClRh}(\mu\text{-bpy})\text{RhCl}(\text{CO})_2$ may also be obtained by the reaction of bpy either with complex II ($\text{X} = \text{Cl}$) in benzene or carbonylated alcoholic solution of rhodium trichloride (Halesha *et al* 1983; Halesha and Reddy, Unpublished results). The ligand bpp, which may be considered as similar to bpy, reacts with complex II ($\text{X} = \text{Cl}$) to give yellow binuclear complex $(\text{CO})_2\text{ClRh}(\mu\text{-bpp})\text{RhCl}(\text{CO})_2$ which shows an absorption band at 343 nm in acetone (Balch and Cooper 1979). IR data of the above complexes (table 2) suggest *cis* positions for the carbonyl groups in the square planar geometry around the metal ion.

Polynuclear complexes with bridging bpy are formed according to the following reaction. The diolefins in these complexes undergo



substitution with carbon monoxide in dichloromethane to afford the polynuclear

Table 2. IR and PMR spectral data of bpy, bpe, bpp and bpeI complexes.

Complex	PMR data (δ)/ ν_{CO} (cm^{-1})
$(\text{cod})\text{ClRh}(\mu\text{-bpy})\text{RhCl}(\text{cod})$	1.86, 2.52, 4.21 (cod); 7.46, 8.86 (bpy)
$(\text{cod})\text{BrRh}(\mu\text{-bpy})\text{RhBr}(\text{cod})$	1.83, 2.48, 4.25 (cod); 7.44, 8.86 (bpy)
$(\text{cod})\text{ClRh}(\mu\text{-bpe})\text{RhCl}(\text{cod})$	1.83, 2.50, 4.14 (cod); 2.90, 7.20, 8.62 (bpe)
$(\text{cod})\text{ClRh}(\mu\text{-bpeI})\text{RhCl}(\text{cod})$	1.85, 2.49, 4.18 (cod); 7.22, 7.40, 8.66 (bpeI)
$(\text{nbd})\text{ClRh}(\mu\text{-bpy})\text{RhCl}(\text{nbd})$	1.33, 3.87, 4.02 (nbd); 7.50, 8.59 (bpy)
$(\text{OC})_2\text{ClRh}(\mu\text{-bpy})\text{RhCl}(\text{CO})_2$	—/2000, 2090
$(\text{OC})_2\text{BrRh}(\mu\text{-bpy})\text{RhBr}(\text{CO})_2$	—/2020, 2080
$(\text{OC})_2\text{ClRh}(\mu\text{-bpp})\text{RhCl}(\text{CO})_2$	—/1997, 2091
$[(\text{OC})_2\text{Rh}(\mu\text{-bpy})]_n(\text{ClO}_4)_n$	—/2040, 2100
$[\text{Ph}_3\text{P}(\text{OC})\text{Rh}(\mu\text{-bpy})]_2(\text{ClO}_4)_2$	—/2000
$[\text{Ph}_3\text{As}(\text{OC})\text{Rh}(\mu\text{-bpy})]_2(\text{ClO}_4)_2$	—/1995
$[\text{Ph}_3\text{P}(\text{OC})\text{Rh}(\mu\text{-bpy})]_n(\text{ClO}_4)_n$	—/2000

carbonyl complex $[(\text{CO})_2\text{Rh}(\mu\text{-bpy})]_n(\text{ClO}_4)_n$. One carbonyl group per metal atom in the latter compound may be replaced by Ph_3P with the retention of the polynuclear structure. Further addition of Ph_3P in stoichiometric quantities produces the binuclear complex $[(\text{Ph}_3\text{P})_2(\text{OC})\text{Rh}(\mu\text{-bpy})\text{Rh}(\text{CO})(\text{Ph}_3\text{P})_2](\text{ClO}_4)_2$ (Uson *et al* 1981b; Reddy and Ramesh 1975).

A mixed metal binuclear complex $(\text{NH}_3)_5\text{Rh}(\mu\text{-bpy})\text{Fe}(\text{CN})_5$ has been obtained by reacting $[\text{Rh}(\text{NH}_3)_5(\text{bpy})]^{3+}$ with $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$. The complex shows an absorption band at 515 nm due to metal-to-ligand charge-transfer transition. As in the pyz analog, the metal ions in the complex possess well-defined oxidation states (Yeh *et al* 1979).

5. Complexes containing 1,8-naphthyridine

Reaction of complex II ($X = \text{Cl}$) with ntd in benzene produces green needles of the binuclear species $(\text{CO})_2\text{ClRh}(\mu\text{-ntd})\text{RhCl}(\text{CO})_2$ (figure 4a). In the electronic spectrum of the complex, the longest wavelength band located at 422 nm has been assigned to metal-to-ligand spin allowed ($d_{z^2} \rightarrow \pi^*$) transition. The corresponding absorption band in the mononuclear complex $\text{Rh}(\text{CO})_2\text{Cl}(\text{ntd})$ is found at 335 nm. The shifting of the $d_{z^2} \rightarrow \pi^*$ band to longer wavelength (or lower energy) is attributed to the close proximity of the metal centres in the binuclear complex (Balch and Cooper 1979). Such an observation has also been made in several binuclear rhodium(I) complexes (Mann *et al* 1980).

Complex II ($X = \text{Cl}$) also reacts with $\text{Ir}(\text{CO})_2\text{Cl}(\text{ntd})$ in benzene to give deep blue crystals of the heterobinuclear species $(\text{CO})_2\text{ClRh}(\mu\text{-ntd})\text{IrCl}(\text{CO})_2$ (figure 4b). For this complex, the $d_{z^2} \rightarrow \pi^*$ band occurs at 465 nm.

6. Complexes containing imidazolate, benzimidazolate and their derivatives

Noriaki *et al* (1977) have synthesised trinuclear rhodium complexes of the type $[\text{L}_2\text{Rh}(\mu\text{-N-N})]_3$ ($\text{L}_2 = \text{cod}$; $\text{N-N} = \text{imzt}$, bzlt ; $\text{L} = \text{C}_2\text{H}_4$; $\text{N-N} = \text{imzt}$) by treating $[\text{L}_2\text{Rh}(\mu\text{-Cl})]_2$ ($\text{L}_2 = \text{cod}$, $(\text{C}_2\text{H}_4)_2$) with butyl lithium/hexane and N-NH in thf. The imidazolate bridged trimer having cod is also obtained by reacting either complex VII with imztH in acetone or complex I with $\text{Au}(\text{imzt})(\text{Ph}_3\text{P})$ in dichloromethane (Uson *et al* 1981c). This complex is found to be an active hydroformylation catalyst for the conversion of olefins to aldehydes (Tanaka *et al* 1977). A number of other tri- and tetranuclear species containing the derivatives of imzt and bzlt have also been synthesised (Tiripicchio *et al* 1982; scheme 1). The trimeric and tetrameric nature of the above complexes has been proposed on the basis of molecular weight determinations in chloroform. The tetrameric structure for the compound $[(\text{OC})_2\text{Rh}(\mu\text{-2-Me-imzt})]_4$ has been confirmed by x-ray diffraction studies (figure 5; mean $\text{Rh-N} = 2.06 \text{ \AA}$).

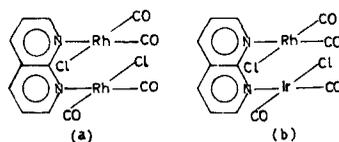
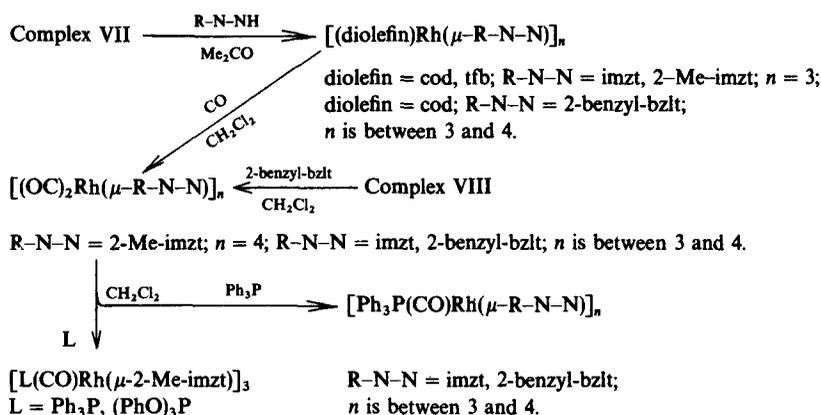
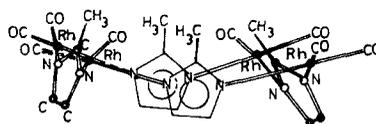


Figure 4. Proposed structures of ntd complexes.

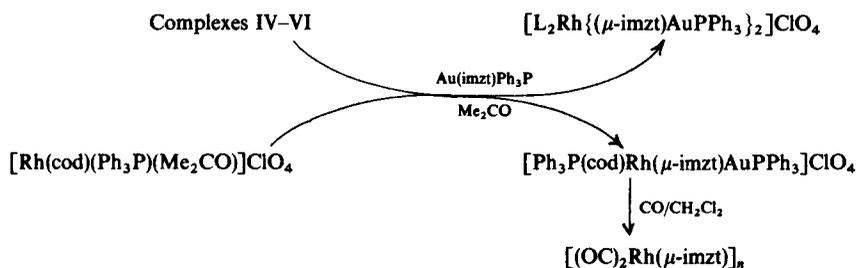


Scheme 1

Figure 5. Structure of $[(\text{OC})_2\text{Rh}(\mu\text{-2-Me-imzt})]_4$.

Oro *et al* (1983) have obtained yellow cationic complexes of the type $[(\text{diolefin})\text{Rh}(\mu\text{-bbzdH}_2)\text{Rh}(\text{diolefin})](\text{ClO}_4)_2$ (diolefin = cod, tfb) by the addition of the benzimidazole derived ligand bbzdH_2 either to complex IV in acetone or to complex IX in dichloromethane. On the other hand, bbzdH_2 reacts with complex I (X = Cl) in methanol to yield the neutral binuclear complex $(\text{diolefin})\text{ClRh}(\mu\text{-bbzdH}_2)\text{RhCl}(\text{diolefin})$. The tfb containing compound of the latter series in the presence of triethylamine in methanol, undergoes elimination of HCl to produce light yellow tetrameric complex of the composition $[(\text{tfb})\text{Rh}(\mu\text{-bbzd})\text{Rh}(\text{tfb})]_2$. Bubbling carbon monoxide through a solution of this complex in chloroform gives an impure polymeric complex $[(\text{OC})_2\text{Rh}(\mu\text{-bbzd})\text{Rh}(\text{CO})_2]_n$ which on addition of Ph_3P in stoichiometric quantities produces $[\text{Ph}_3\text{P}(\text{CO})\text{Rh}(\mu\text{-bbzd})\text{Rh}(\text{CO})\text{Ph}_3\text{P}]_n$. The parent tetrameric complex also reacts with $[\text{AuL}(\text{Me}_2\text{CO})_x](\text{ClO}_4)$ (L = Ph_3P) to yield $[(\text{tfb})\text{Rh}(\mu\text{-bbzd})\text{Rh}(\text{tfb})\text{Au}_2\text{L}_2]_n(\text{ClO}_4)_{2n}$ which with CO in chloroform undergoes displacement of tfb to afford the yellow complex $[(\text{OC})_2\text{Rh}(\mu\text{-bbzd})\text{Rh}(\text{CO})_2\text{Au}_2\text{L}_2]_n(\text{ClO}_4)_{2n}$. The last complex with L (Rh/L = 1/1) loses one CO group per metal atom to give $[\text{Ph}_3\text{P}(\text{CO})\text{Rh}(\mu\text{-bbzd})\text{Rh}(\text{CO})(\text{Ph}_3\text{P})\text{Au}_2\text{L}_2]_n(\text{ClO}_4)_{2n}$.

Uson *et al* (1981c) have reported that heteronuclear complexes with Rh-heterocycle-Au bridges are formed when complexes IV–VI and $[\text{Rh}(\text{cod})(\text{Ph}_3\text{P})(\text{Me}_2\text{CO})]\text{ClO}_4$ are treated with $\text{Au}(\text{imzt})\text{Ph}_3\text{P}$ in acetone as illustrated below. Molecular weight measurements on the last polymeric carbonyl complex indicate that the value of n is between 3 and 4. Reaction of complex III with $\text{Pt}(\text{imzt})\text{dppe}$ in acetone produces heterotetranuclear complex $[(\text{cod})\text{Rh}(\mu\text{-imzt})_2\text{Pt}(\text{dppe})]_2(\text{ClO}_4)_2$ in which the cod groups can be substituted by carbon monoxide.



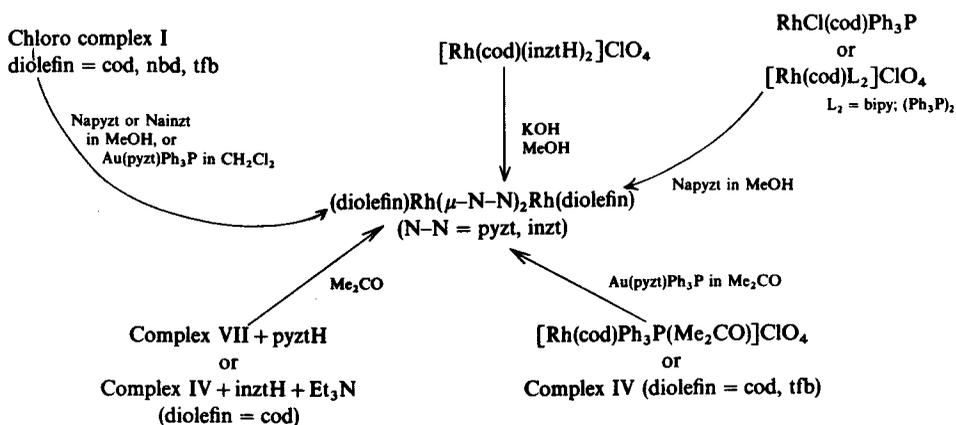
7. Complexes containing pyrazolate, indazolate and their derivatives

PyztH reacts with $[(\text{C}_2\text{H}_4)_2\text{Rh}(\mu\text{-Cl})]_2$ in methanol to give the red complex $(\text{C}_2\text{H}_4)_2\text{Rh}(\mu\text{-pyzt})_2\text{Rh}(\text{C}_2\text{H}_4)_2$ (Uson *et al* 1981a). Complexes of the formula $(\text{diolefin})\text{Rh}(\mu\text{-N-N})_2\text{Rh}(\text{diolefin})$ (N-N = pyzt, inzt) are obtained from several routes (Uson *et al* 1981a, 1982e) and some of these are visualised below (scheme 2).

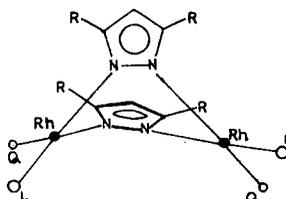
The marked stability of the pyzt bridges in these complexes is reflected in their non-reactivity towards Ph_3P or $(\text{PhO})_3\text{P}$. The diolefin in some of these complexes can be displaced partially or completely by CO to get either $(\text{cod})\text{Rh}(\mu\text{-inzt})_2\text{Rh}(\text{CO})_2$ or $(\text{OC})_2\text{Rh}(\mu\text{-inzt})_2\text{Rh}(\text{CO})_2$ and the reactions are reversible. The diolefin containing carbonyl is also formed when $[\text{Rh}(\text{diolefin})(\text{inztH})]_2\text{ClO}_4$ (diolefin = cod, nbd, tfb) is reacted with either complex V or VIII in the presence of Et_3N . On the other hand, when the above cationic complex of inztH is treated with either $\text{Rh}(\text{CO})\text{Ph}_3\text{P}(\text{acac})$ or complex VI, in the presence of Et_3N , it yields $(\text{diolefin})\text{Rh}(\mu\text{-inzt})_2\text{Rh}(\text{CO})\text{Ph}_3\text{P}$ from which the diolefin can be displaced by CO. The carbonyl dimers (N-N = pyzt, inzt) are conveniently prepared by reacting complex II (X = Cl) with the heterocycles in the presence of Et_3N (Borkett and Bruce 1974; Uson *et al* 1982e).

Trofimenko (1971) is the earliest to report the synthesis of $\text{L}_2\text{Rh}(\mu\text{-3,5-Me}_2\text{pyzt})_2\text{RhL}_2$ ($\text{L}_2 = \text{cod}, (\text{CO})_2$) starting from complex I or II (X = Cl) and 3,5-Me₂-pyztH. According to molecular models the metallocycles are not planar but puckered in the boat form (Trofimenko 1972). Complex II also reacts with $\text{Au}(3,5\text{-Me}_2\text{-4-NO}_2\text{-pyzt})\text{Ph}_3\text{P}$ in benzene to give the corresponding heterocycle bridged rhodium carbonyl dimer (Minghetti *et al* 1979). Similar carbonyl dimers are probably formed when CO is bubbled through dichloromethane solutions of $(\text{diolefin})\text{Rh}(\mu\text{-pyzt})_2\text{Rh}(\text{diolefin})$ complexes since these on addition of a tertiary phosphine produce $\text{L}(\text{CO})\text{Rh}(\mu\text{-pyzt})_2\text{Rh}(\text{CO})\text{L}$ ($\text{L} = \text{Ph}_3\text{P}, p\text{-tolyl}_3\text{P}, (p\text{-ClC}_6\text{H}_4)_3\text{P}, (p\text{-OMeC}_6\text{H}_4)_3\text{P}, (\text{PhO})_3\text{P}$) (Uson *et al* 1981a). The Ph_3P complex can also be obtained by treating $\text{Rh}(\text{CO})\text{L}(\text{acac})$ with pyztH in $\text{Me}_2\text{CO-CH}_2\text{Cl}_2$. The inzt analog is also known (Uson *et al* 1982e). Such complexes have also been made by reacting $[(\text{OC})_2\text{Rh}(\mu\text{-R-pyzt})]_2$ ($\text{R} = 3,5\text{-Me}_2, 3,5\text{-Ph}_2$) with tertiary phosphite, phosphines or arsine (Powell *et al* 1982). The x-ray crystal structure of $(\text{PhO})_3\text{P}(\text{OC})\text{Rh}(\mu\text{-pyzt})_2\text{Rh}(\text{CO})\text{P}(\text{OPh})_3$ complex (figure 6; $\text{R} = \text{H}; \text{Q} = \text{CO}; \text{L} = (\text{PhO})_3\text{P}$) has been determined (Uson *et al* 1981a). This complex as well as complexes of the type $(\text{cod})\text{Rh}(\mu\text{-R-pyzt})_2\text{Rh}(\text{cod})$ ($\text{R} = \text{H}, \text{Me}, \text{Me}_2$) are shown to serve as catalysts for the hydroformylation of 1-heptene (Uson *et al* 1982b).

Red crystalline solids of the composition $\text{L}(\text{SC})\text{Rh}(\mu\text{-R-N-N})_2\text{Rh}(\text{CS})\text{L}$ ($\text{L} = \text{Ph}_3\text{P}; \text{R-N-N} = \text{pyzt}, 3\text{-Me-pyzt}, 3,5\text{-Me}_2\text{-pyzt}, \text{inzt}$) are obtained by the action of



Scheme 2

Figure 6. Structure of $\text{L}(\text{Q})\text{Rh}(\mu\text{-R}_2\text{-pyzt})_2\text{Rh}(\text{Q})\text{L}$.

alkaline methanol on $[\text{Rh}(\text{CS})(\text{R-N-NH})\text{L}_2]\text{ClO}_4$ in ether. Other methods to get these complexes involve the reaction of R-N-NH with $\text{RhCl}(\text{CS})\text{L}_2$ or $[\text{Rh}(\text{CS})\text{L}_2(\text{Me}_2\text{CO})_x]\text{ClO}_4$ in the presence of an alkali. The structure of the 3,5- Me_2 -pyzt complex is confirmed by x-ray diffraction analysis (Uson *et al* 1982d) *vide* figure 6 ($\text{R} = \text{Me}$; $\text{Q} = \text{CS}$; $\text{L} = \text{Ph}_3\text{P}$). Thus the complexes $[(\text{PhO})_3\text{P}(\text{CO})\text{Rh}(\mu\text{-pyzt})]_2$ and $[\text{Ph}_3\text{P}(\text{SC})\text{Rh}(\mu\text{-3,5-Me}_2\text{-pyzt})]_2$ conceive almost the same geometry with an average Rh-N distance of 2.10 Å. The N-N bond length of the heterocycles is in the range 1.35–1.39 Å, and is slightly lengthened in the complexes when compared to that found for pyztH (1.35 Å; Berthou *et al* 1970). The two pyzt rings in both the complexes are planar and nearly perpendicular to each other; the angle formed by the two rings is 80.6° for the former whereas it is 82.3° for the latter. In both the cases the coordination around each metal atom is approximately square planar and the dihedral angle between the two square planes 86.2° (former) and 71.1° (latter) gives a bent configuration for the complex where the CO/CS and $(\text{PhO})_3\text{P/Ph}_3\text{P}$ ligands are in *trans*. For the former complex the intramolecular Rh-Rh distance is 3.568 Å as against 3.22 Å for the latter.

Powell *et al* (1982) have carried out oxidative addition reactions of $\text{L}(\text{OC})\text{Rh}(\mu\text{-R-pyzt})\text{Rh}(\text{CO})\text{L}$ with iodine or 1,2-diiodoethane. From these reactions they have isolated Rh(II) and Rh(III) (formal oxidation state) complexes of the formulae $\text{LI}(\text{OC})\text{Rh}(\mu\text{-3,5-Me}_2\text{-pyzt})_2\text{Rh}(\text{CO})\text{IL}$ ($\text{L} = (\text{PhO})_3\text{P}, \text{PhMe}_2\text{P}, \text{Ph}_2\text{MeP}, \text{PhMe}_2\text{As}$)

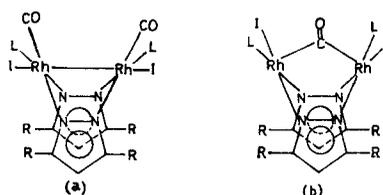


Figure 7. Proposed structures of
(a) $\text{LI}(\text{CO})\text{Rh}(\mu\text{-}3,5\text{-Me}_2\text{-pyzt})_2\text{Rh}(\text{CO})\text{IL}$ and
(b) $\text{LIRh}(\mu\text{-CO})(\mu\text{-R}_2\text{-pyzt})_2\text{RhIL}$ complexes.

and $\text{LIRh}(\mu\text{-CO})(\mu\text{-R-pyzt})_2\text{RhIL}$ ($\text{R} = 3,5\text{-Me}_2$; $\text{L} = \text{Ph}_3\text{P}$; $\text{R} = 3,5\text{-Ph}_2$; $\text{L} = \text{Ph}_2\text{MeP}$, Ph_2MeAs). While the Rh(II) complexes show IR bands in the range $2070\text{--}2000\text{ cm}^{-1}$ corresponding to terminal CO groups, the Rh(III) complexes exhibit an IR band at $ca\ 1790\text{ cm}^{-1}$ indicating bridging CO moiety. Based on IR and preliminary x-ray diffraction results the following structures have been proposed for the complexes (figure 7). In the solution, the Rh(II) complex ($\text{L} = \text{PhMe}_2\text{P}$) on standing for several days gets converted into Rh(III) complex. The latter complex is regarded as containing 16e with approximately square-pyramidal coordination around each metal atom. These observations support the remarkable stability of the heterocycles towards bridge cleavage reactions.

Reaction of complex IV with $\text{pt}(\text{pyzt})_2\text{dppe}$ produces heterobinuclear complex, $[(\text{cod})\text{Rh}(\mu\text{-pyzt})_2\text{Pt}(\text{dppe})]\text{ClO}_4$ which undergoes displacement of cod with CO. One of the carbonyl groups in the resultant complex can be replaced by Ph_3P or $(\text{PhO})_3\text{P}$ (Uson *et al* 1981c). By contrast, Ph_3P instead of displacing CO, cleaves the heterocycle bridges in the ionic compound $[(\text{OC})_2\text{Rh}(\mu\text{-pyzt})_2\text{Pt}(\text{bipy})][\text{Rh}(\text{CO})_2\text{Cl}_2]$ which in turn is prepared by mixing complex II and $\text{Pt}(\text{pyzt})\text{bipy}$ in ether (Bandini *et al* 1979). Treatment of $[\text{Rh}(\text{CS})\text{L}_2(\text{Me}_2\text{CO})_x]\text{ClO}_4$ ($\text{L} = \text{Ph}_3\text{P}$, Cy_3P) with $\text{Au}(\text{pyzt})\text{Ph}_3\text{P}$ in $\text{Me}_2\text{CO-CH}_2\text{Cl}_2$ affords orange or pink crystals of $[\text{L}_2(\text{SC})\text{Rh}(\mu\text{-pyzt})\text{AuPPh}_3]\text{ClO}_4$ (Uson *et al* 1982d).

It may be noted that most of the above cited binuclear complexes invariably involve two of the exobidentate heterocycles. Perhaps location of the two nitrogen donor atoms of the heterocycle in adjacent positions and the fact that the heterocycle behaves as an anionic ligand necessitates the use of two such ligands for bridge formation.

8. Complexes containing 2,2'-bimidazolate and related heterocycles

Synthesis of the dinuclear complex $(\text{cod})\text{Rh}(\mu\text{-bimzt})\text{Rh}(\text{cod})$ by reacting $[(\text{cod})\text{Rh}(\mu\text{-OMe})]_2$ with bimztH_2 or $\text{Rh}(\text{cod})$ (bimztH) in dichloromethane, has been reported by Rasmussen and coworkers (Kaiser *et al* 1976a). x-ray diffraction studies on the complex have indicated the planarity of the tetradentate bimzt dianion and the dihedral angle between the two rings, nearly 0° (as against 1.2° for bimztH_2 ; Mitchell *et al* 1969). The geometry about each metal atom is approximately square-planar with the coordination polyhedron defined by two N atoms from bimzt ($\text{Rh-N} \sim 2.14\text{ \AA}$) and the midpoints of two olefin bonds from the cod ring (figure 8a). The cod groups are easily displaced on passing CO through a benzene solution of the above complex to give the tetranuclear complex $[(\text{OC})_2\text{Rh}(\mu\text{-bimzt})\text{Rh}(\text{CO})_2]_2$ which may also be prepared by treating

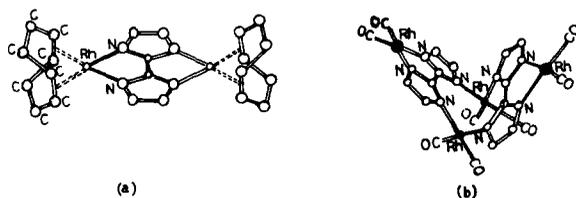


Figure 8. Structures of (a) $(\text{cod})\text{Rh}(\mu\text{-bimzt})\text{Rh}(\text{cod})$ and (b) $[(\text{OC})_2\text{Rh}(\mu\text{-bimzt})\text{Rh}(\text{CO})_2]_2$ complexes.

complex VIII with bimztH_2 . Crystal structure of this complex has been elucidated by x-ray diffraction analysis (Kaiser *et al* 1976b). It is found that each of the bimzt ligands coordinates simultaneously in a bidentate manner through both rings to one metal atom and also in a unidentate manner through each imidazolate ring to two metal atoms (figure 8b). The geometry about each rhodium is approximately squareplanar with the coordination polyhedron defined by two C atoms from CO groups and two N atoms from the bimzt groups; Rh-N distances are in the range 2.055–2.087 Å. The two rings of one bimzt ligand are nearly coplanar making a dihedral angle of 4° with each other. Metal-metal interactions of the bridging rhodium atoms (Rh-Rh = 2.975 Å) are thought to be the driving force toward the tetranuclear structure in preference to a dinuclear structure. It is also likely that changing the terminal ligand from cod to carbonyls has so modified the electron density on the rhodium atom that significant changes in molecular geometry are required to stabilise the system. Preparation of mixed-ligand complex $[(\text{cod})\text{Rh}(\mu\text{-bimzt})\text{Rh}(\text{CO})_2]_2$ has also been reported and the complex is expected to have structure similar to the aforesaid carbonyl.

Chloro complexes I and II react with the heterocycles, bpyztH_2 and mpyztH_2 in methanol to yield $\text{L}_2\text{ClRh}(\mu\text{-YH}_2)\text{RhClL}_2$ ($\text{L}_2 = \text{cod, nbd, tfb, (CO)}_2$; $\text{Y} = \text{bpyzt}$; $\text{L}_2 = \text{tfb, (CO)}_2$; $\text{Y} = \text{mpyzt}$) complexes. Addition of Et_3N to the above reaction systems, however, results in the formation of polynuclear complexes of the type $[\text{L}_2\text{Rh}(\mu\text{-Y})]_n$ ($\text{L}_2 = \text{cod, nbd, tfb, (CO)}_2$; $\text{Y} = \text{bpyzt, mpyzt}$). In the case of bpyzt complexes, the molecular weight measurements in chloroform indicate the value of n between 3 and 4. The dinuclear and polynuclear carbonyl complexes are also obtained by bubbling CO through dichloromethane solutions of the corresponding tfb containing complexes. Treatment of *trans*- $\text{RhClQ}(\text{Ph}_3\text{P})_2$ ($\text{Q} = \text{CO}$), CS in benzene/toluene with alkaline methanolic solutions of bpyztH_2 also affords polynuclear complexes, $[(\text{Ph}_3\text{P})_2\text{QRh}(\mu\text{-bpyzt})]_n$ (νCO , 1990, 1970; νCS , 1290 cm^{-1}) (Uson *et al* 1982c).

Recently a report on the preparation of mixed-metal complexes of the composition $[\text{L}_2\text{Rh}(\mu\text{-Y})\text{Ru}(\text{Cp})\text{Ph}_3\text{P}]_n$ ($n = 1$ for $\text{L}_2 = \text{tfb}$; $\text{Y} = \text{bimzt, bbzlt}$; $\text{L}_2 = \text{cod, nbd, (CO)}_2$; $\text{Y} = \text{bbzlt}$; $n = 2$ for $\text{L}_2 = \text{nbd, (CO)}_2$; $\text{Y} = \text{bimzt}$) starting from $\text{RhL}_2(\text{acac})$ and $\text{Ru}(\text{Cp})(\text{YH})\text{Ph}_3\text{P}$ is made by Uson *et al* (1983a). Uson *et al* (1983b, 1983c) have also synthesised a wide range of hetero bi- and tri-nuclear cationic complexes of the formulae $[\text{L}_2\text{Rh}(\mu\text{-bbzlt})\text{M}(\text{dppe})]\text{ClO}_4$ ($\text{L}_2 = \text{cod, (CO)}_2, (\text{CO})(\text{Ph}_3\text{P})$; $\text{M} = \text{Pd, Pt}$), $[\text{L}_2\text{Rh}(\mu\text{-bbzlt})\text{Au}_2\text{Q}_2]\text{ClO}_4$ ($\text{L}_2 = \text{cod, (CO)}_2, (\text{CO})(\text{Ph}_3\text{P})$; $\text{Q}_2 = (\text{Ph}_3\text{P})_2, \text{dppe, dppm}$; $\text{L}_2 = (\text{CO})_2, (\text{CO})(\text{Ph}_3\text{P})$; $\text{Q} = (\text{MeO})_3\text{P}$) and $[\text{L}_2\text{Rh}(\mu\text{-bbzltH})\text{AuQ}]\text{ClO}_4$ ($\text{L}_2 = \text{cod, nbd, (CO)(Ph}_3\text{P), (CO)(MeO)}_3\text{P}$; $\text{Q} = (\text{MeO})_3\text{P, Ph}_3\text{P}$). A majority of these complexes have been prepared by employing the reactions described

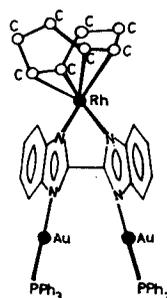


Figure 9. Structure of $[(\text{cod})\text{Rh}(\mu\text{-bbzlt})\text{Au}_2(\text{Ph}_3\text{P})_2]^+$ cation.

previously for similar complexes. The hetero trinuclear complex $[(\text{cod})\text{Rh}(\mu\text{-bbzlt})\text{Au}_2(\text{Ph}_3\text{P})_2]\text{ClO}_4 \cdot \text{CHCl}_3$ has been studied by x-ray crystallography (Uson *et al* 1983c). Accordingly the geometry around the Rh atom is approximately square-planar with the polyhedron defined by the two N atoms of bbzlt (Rh-N \sim 2.1 Å) and the midpoint of the two olefinic bonds of cod (figure 9). The two benzimidazole moieties of bbzlt ligand are slightly twisted and make a dihedral angle of 17.6° with each other.

9. Complexes containing 2-(2'-pyridyl)benzimidazole

The ligand pbzltH has features of a five-membered as well as a six-membered heterocycle. It reacts with complexes VII in dichloromethane to form Rh(diolefin) (pbzlt) (diolefin = cod, nbd). Treatment of these mononuclear complexes, in stoichiometric amounts, with AuClL or L in the presence of AgClO_4 in acetone yields hetero dinuclear cationic complexes of the formula $[(\text{diolefin})\text{Rh}(\mu\text{-pbzlt})\text{ML}]\text{ClO}_4$ (M = Au; L = Ph_3P , $(\text{MeO})_3\text{P}$; M = Ag; L = Ph_3P). However, on reaction of the mononuclear complexes with only AgClO_4 in the mole ratio 2:1, trinuclear cationic complexes of the type $[(\text{diolefin})\text{Rh}(\mu\text{-pbzlt})\text{Ag}(\mu\text{-pbzlt})\text{Rh}(\text{diolefin})]\text{ClO}_4$ are formed. The mononuclear complexes also react with $\text{AuCl}(\text{tht})$ in dichloromethane to yield neutral complexes of the composition $(\text{diolefin})\text{Rh}(\mu\text{-pbzlt})\text{AuCl}$. In dichloromethane, the diolefin in the above complexes can be displaced by carbon monoxide to get the corresponding carbonyls (Uson *et al* 1983d).

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Abbreviations

acac	acetylacetonate
bbzdH ₂	1,6-bis(2'-benzimidazolyl)-2,5-dithiahexane
bbzlt	2,2'-bibenzimidazolate dianion
bimzt	2,2'-biimidazolate dianion
bipy	2,2'-bipyridyl
bpa	1,2-bis(4-pyridyl)acetylene
bpe	1,2-bis(4-pyridyl)ethane
bpel	1,2-bis(4-pyridyl)ethylene
bpp	1,3-bis(4-pyridyl)propane
bpy	4,4'-bipyridyl
bpym	2,2'-bipyrimidine

bpyzt	3,3',5,5'-tetramethyl-4,4'-bipyrazolate dianion
bzlt	benzimidazolate
cod	cycloocta-1,5-diene
Cp	cyclopentadienyl
dppe	1,2-bis(diphenylphosphino)ethane
dppm	1,1-bis(diphenylphosphino)methane
imzt	imidazolate
inzt	indazolate
mpyzt	4,4'-methylene bis(3,5-dimethylpyrazolate) dianion
nbd	norborna-2,5-diene
ntd	1,8-naphthyridine
pbzltH	2-(2'-pyridyl)benzimidazole
phen	1,10-phenanthroline
phl	phthalazine
phz	phenazine
pyd	pyridazine
pym	pyrimidine
pyz	pyrazine
pyzt	pyrazolate
qux	quinoxaline
thf	tetrahydrofuran
tht	tetrahydrothiophen
tfb	tetrafluorobenzobarrelene