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Controlling the molecular architecture of low nuclearity rhodium and iridium complexes using bridging N–C–X (X = N, O, S) ligands

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Abstract

The controlled synthesis of low nuclearity rhodium and iridium complexes by using bridging ligands containing N–C–X or X–C–N–C–X (X = N, O, S) groups is reviewed. The geometry and electronic characteristics of these N–C–X ligands allow the incorporation of a wide variety of additional metals and permit the preparation of several types of polynuclear complexes which frequently exhibit unusual molecular architectures and chemical reactivities.

Keywords: Rhodium; Iridium; Polynuclear; Bridging ligands; Nitrogen ligands; Oxidative-addition

1. Introduction

The control of the molecular architecture of polynuclear metal complexes where the metals are held in close proximity, is basic in the search for cooperative effects and new reactivity modes and it is an important objective because of their potential relevance in multimetallic catalysis. Low nuclearity complexes are useful for testing the distinctive reactivity patterns of the multimetallic systems. In this context there is an increasing interest in dinuclear complexes containing rhodium and iridium centers in close proximity. Two types of bridging ligands have been used in such complexes: (i) anionic bridging ligands capable of promoting flexible open-book structures such as thiolate bridging ligands [1], extensively studied by Poilblanc and others, amido bridging ligands [2] or azolate bridging ligands, mainly studied by Stobart [3] and our group [4] (Fig. 1), and (ii) neutral bidentate bridging ligands such as bis(diphenylphosphino)methane [5] or 2-(diphenylphosphino)pyridine [6], studied by Balch, Cowie and others, capable of promoting a face-to-face disposition of the metal coordination planes (Fig. 2). The reported studies have revealed that the above mentioned groups act as strong but flexible bridging ligands capable of maintaining two metal fragments in close proximity, both within and beyond the requirements of metal–metal interactions or bonds.

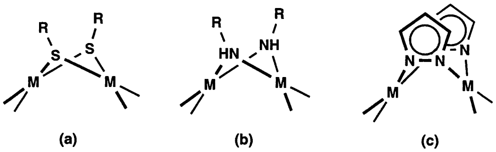


Fig. 1. Anionic bridging ligands leading to dinuclear open-book structures.

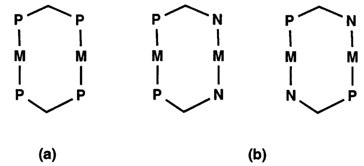
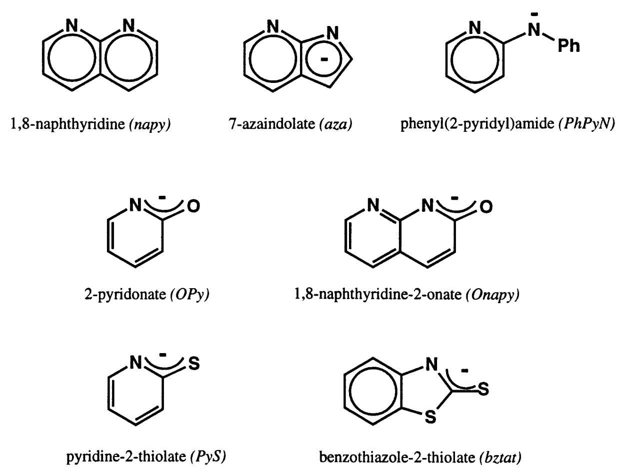


Fig. 2. Neutral bidentate bridging ligands leading to dinuclear face-to-face structures.



1,8-naphthyridine *(napy)* 7-azaindolate *(aza)* phenyl(2-pyridyl)amide *(PhPyN)*

2-pyridonate *(OPy)* 1,8-naphthyridine-2-onate *(Onapy)*

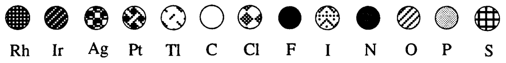
pyridine-2-thiolate *(PyS)* benzothiazole-2-thiolate *(bztat)*

Fig. 3. Bridging ligands having the N–C–X (X = N, O, S) structural unit.

In recent years we have used a variety of related ligands having a N–C–X (X = N, O, S) structural unit to construct polynuclear complexes. The greater part of these binucleating ligands are anionic and all of them present the two donor atoms, N and X connected by a single bridgehead carbon atom in a structural disposition similar to that of the neutral bridging ligands bis(diphenylphosphino)methane or 2-(diphenylphosphino)pyridine. Furthermore, the presence of several lone electron pairs (O or S) could favour acting as five-electron donors and therefore allowing the construction of complexes of higher nuclearity. Another useful strategy for the controlled construction of complexes of higher nuclearity is the increase in the number of donor atoms to create polydentate ligands containing X–C–N–C–X moieties. This short-bite situation, with the donor atoms in close proximity, favours metal–metal interactions in the resulting polynuclear complexes.

This review will deal with the chemistry of di- and polynuclear rhodium and iridium complexes containing bridging N–C–X or X–C–N–C–X units. These bridging ligands, shown in Fig. 3, are capable of maintaining two or more rhodium or iridium metals in close proximity and have allowed, in many cases, the control of the nuclearity of the final complexes. They have also provided useful information for the understanding of bi- and poly-metallic reactivity. A closely related approach for the construction of polynuclear clusters with polydentate phosphine ligand backbones has been developed by Balch [7]. In addition, comprehensive reviews on the coordination chemistry of 2-pyridonate [8] and N–C–S ligands [9] have recently appeared.

The organization of this review is based on a nuclearity criterion. The synthesis of dinuclear complexes using N–C–X ligands is described first and comprises heterocyclic N–C–N type ligands, such as the neutral 1,8-naphthyridine and the anions derived from N-2-pyridylaniline and 7-azaindole, anionic N–C–O type ligands such as 2-pyridonate and 1,8-naphthyridine-2-onate and also anionic



Scheme 1.

N–C–S type ligands such as pyridine-2-thiolate and benzothiazole-2-thiolate. In the following section, the controlled synthesis of angular and linear trinuclear complexes supported by the N–C–S and 1,8-naphthyridine-2-onate ligands, respectively, is described. The straightforward synthesis of tetranuclear complexes can be achieved, in favourable cases, as a result of the assembling of dinuclear complexes. However, the rational design of new bridging ligands, such as 2,6-dithiolpyridine and benzimidazole-2-thiol, provides a smart alternative pathway to homo- and heterotetranuclear complexes. In addition, useful strategies for the synthesis of high nuclearity complexes are presented. Finally, some interesting results on the oxidative-addition reactions of dinuclear rhodium and iridium complexes supported by N–C–S ligands are discussed.

The following scheme is a key for the atom symbols used in the Chem3D representation of the molecular diagrams in the figures (Scheme 1).

2. Dinuclear complexes with bridging N–C–X ligands

2.1. Complexes with neutral N–C–N ligands

The 1,8-naphthyridine ligand is a versatile and neutral bidentate ligand capable of acting as an *endo*- or as *exo*-bidentate ligand. The small chelate bite (2.2 Å) [10] and the unfavourable orientation of the nitrogen lone pairs for chelation of 1,8-naphthyridine ligand (napy) produces high coordination numbers in mononuclear complexes of the first-row transition metals as found in $[Fe(napy)_4]^{2+}$ [10] and $[Ru(napy)_4]^{2+}$ [11]. These characteristics, and the rigidity of the skeleton comprising the N-donor atoms, confer to 1,8-naphthyridine and its methyl derivatives the ability to bridge two metal atoms in close proximity. Earlier structural evidence of the binucleating behaviour of this ligand was found in $[Cu_2(\mu\text{-}Cl)_2Cl_2(\mu\text{-}napy)_2]$ [12] and in the mixed-valence complexes $[Ni_2Br_2(\mu\text{-}napy)_4]BPh_4$ and $[Cu_2(\mu\text{-}Cl)Cl_2(\mu\text{-}napy)_2]$, reported by Sacconi group [13,14]. Carbonyl rhodium and iridium mononuclear complexes of formula $[MCl(CO)_2(napy)]$ result from the reactions of $[\{MCl(CO)_2\}_2]$ with 1,8-naphthyridine in benzene [15]. The molar ratio of ligand:starting material in this reaction is essential to give either these square-planar complexes with a monodentate napy ligand or the green dinuclear complex $[Rh_2Cl_2(CO)_4(\mu\text{-}napy)]$.

A variety of cationic rhodium complexes are obtained starting from the solvated species $[Rh(diolefin)(Me_2CO)_x]^+$ and 2,7-dimethyl-1,8-naphthyridine (R_2napy), 2-methyl-1,8-naphthyridine (Rnapy) or napy [16]. Diolefin dinuclear cationic complexes of formula $[Rh_2(\mu\text{-}Rnapy)_2(diolefin)_2]^{2+}$ (R = H, Me) are obtained by reacting the solvated species $[Rh(diolefin)(Me_2CO)_x]^+$ (diolefin = 2,5-norbornadi-

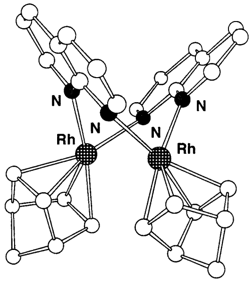


Fig. 4. Molecular structure of $[Rh_2(\mu\text{-napy})_2(NBD)_2]^{2+}$.

ene (NBD) or tetrafluorobenzobarrelene (TFB)) with napy or Rnapy. The intense red or purple colour of the dinuclear complexes indicates that the rhodium atoms are in close proximity [16]. Thus, the X-ray crystal structure of the $[Rh_2(\mu\text{-napy})_2(NBD)_2]^{2+}$ derivative (Fig. 4) shows a Rh-Rh separation of 2.916(3) Å, suggesting a metal–metal interaction, confirmed by the deviation of the metals from square-planar coordination towards the other metal atom.

However, the dinuclear entities (Fig. 5(a)) having diolefin ligands are not robust towards fragmentation. They dissociate into mononuclear species (Fig. 5(b)), in dilute solutions, and give bridge splitting reactions with an excess of Rnapy yielding the mononuclear cationic complexes $[Rh(diolefin)(Rnapy)_2]^+$ (Fig. 5(c)). The formation of mononuclear complexes is favoured by steric effects either from substituents on the rings of the bridging ligands or the bulkiness of the diolefin ligand, or both. Thus, yellow mononuclear complexes with chelating napy ligands $[Rh(R_2napy)(diolefin)]^+$ (diolefin = 1,5-cyclooctadiene (COD), NBD, TFB) and [Rh(Rnapy)(COD)] (R = H, Me) result under identical reaction conditions. Moreover, replacement of COD by less sterically demanding carbonyl ligands in these mononuclear complexes leads to a change in the nuclearity yielding the red complexes $[Rh_2(\mu\text{-Rnapy})_2(CO)_2]^{2+}$.

The napy ligands were shown to possess different coordination modes with little configurational barrier, which could be appropriate for the design of homogeneous catalysts having site-opening and -closing functions, as recently proposed for the mononuclear ruthenium complexes $[Ru(bipy)_2(napy)]^{2+}$ [17]. Therefore, napy can be considered to be both a potentially binucleating ligand and a mononucleating

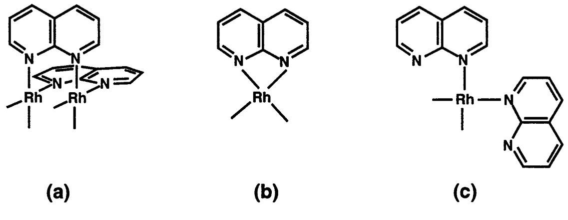


Fig. 5. Dinuclear and mononuclear type complexes with 1,8-naphthyridine ligands.

ligand. Recent studies on the catalytic activity of several ruthenium complexes with napy ligands for primary and secondary alcohol oxidation indicate that the dinuclear complexes are less active than the mononuclear complexes (or dinuclear which become mononuclear in aqueous solution) [18]. Although recent reports have shown napy to act as a bridging ligand in complexes of copper [19], and platinum [20] leading to short metal–metal distances, the interest is focused on substituted polyfunctional napy ligands, as discussed in 3.2 and 4.2.

2.2. Complexes with anionic N–C–N ligands

In the search for stable dinuclear entities we turned our attention to uncommon anionic binucleating ligands containing a N–C–N skeleton such as the anions derived from 7-azaindole (Haza) and N-2-pyridylaniline (PhPyNH) by removing the pyrrole NH and the amine protons respectively. These ligands were promising candidates because they had been shown to bridge in quadruply bonded dimolybdenum complexes with a short metal–metal separation [21,22]. Neutral $[M_2(\mu\text{-aza})_2(\text{diolefin})_2]$ complexes are prepared by reaction of $[M_2(\mu\text{-Cl})_2(\text{diolefin})_2]$ with a mixture of 7-azaindole and potassium hydroxide in methanol [23]. The $[Ir_2(\mu\text{-aza})_2(COD)_2]$ (COD = 1,5-cyclooctadiene) complex is more conveniently obtained by protonation of the methoxo ligands in $[Ir_2(\mu\text{-OMe})_2(COD)_2]$ with 7-azaindole ($pK_a = 4.54$) [24]. Deprotonation of PhPyNH first requires a strong base to form the anion, which then reacts with $[Rh_2(\mu\text{-Cl})_2(NBD)_2]$ and $[Rh_2(\mu\text{-Cl})_2(CO)_4]$ to give the corresponding dinuclear complexes $[Rh_2(\mu\text{-PhPyN})_2(L_2)_2]$ [25].

The X-ray crystal structures of the red $[Rh_2(\mu\text{-aza})_2(NBD)_2]$ (Fig. 6(a)) and $[Rh_2(\mu\text{-PhPyN})_2(NBD)_2]$ (Fig. 6(b)), show intermetallic distances of 3.207(3)Å and 2.959(1)Å respectively and consist of two 'Rh(NBD)' moieties bridged by two azaindolate or two phenyl(2-pyridyl)amido anions coordinated through the two N atoms in a relative *cis*-disposition.

A comparison of the metal–metal separation in these complexes reflects the binucleating bite angles of the bridging ligands, bigger for the aza ligand due to the angles imposed by the five-membered ring. A weak metal–metal interaction in $[Rh_2(\mu\text{-PhPyN})_2(NBD)_2]$ is suggested by the deviation of the rhodium atoms from square-planar coordination towards the other metal atom [25]. The 7-azaindolate ligand is disordered and distributed in two positions, as the pyrrole and the pyridine N atoms in each ligand can be interchanged by coordination to the metals [23]. Thus, two isomers, head-to-head (HH) and head-to-tail (HT) in a 2:3 ratio are observed in the solid state. The related iridium complexes $[Ir_2(\mu\text{-aza})_2(L_2)_2]$ (L_2 = COD, L = CO) also exist in solution as a mixture of the HH and HT isomers in relative proportions 1:5 and 1:3, respectively. For $[Rh_2(\mu\text{-PhPyN})_2(NBD)_2]$, only the HT isomer is found in the solid state [25] whereas a mixture of both isomers HT and HH isomers is observed in solution.

Two-dimensional H,H-COSY NMR spectroscopy is a useful tool to characterize and differentiate the HH and HT isomers of the diolefin complexes in solution [24]. This method relies on the observation of couplings between the diolefin protons, which are inequivalent for the HT isomer. In addition this technique, along with

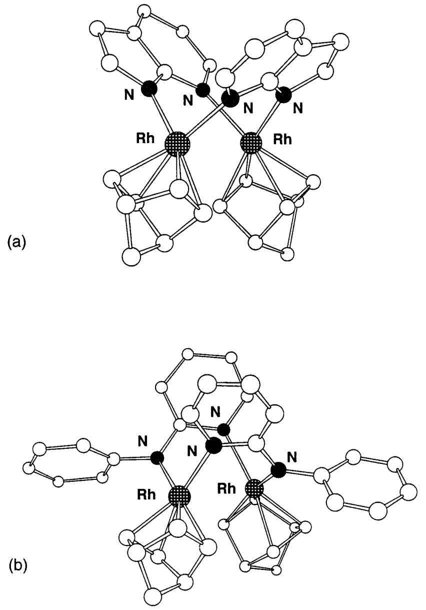
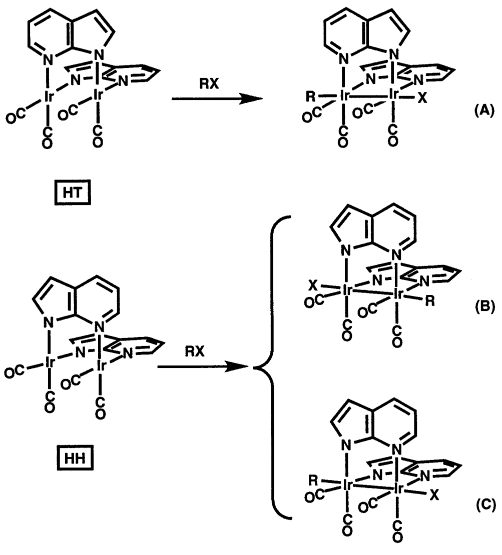


Fig. 6. Molecular structures of $[Rh_2(\mu\text{-aza})_2(NBD)_2]$ (a) and $Rh_2(\mu\text{-PhPyN})_2(NBD)_2]$ (b).

nuclear Overhauser effect (nOe) measurements, allows the assignment of the olefinic resonances in favourable cases.

Carbon monoxide replaces the coordinated diolefin in the above mentioned complexes to give the related *cis*-$[M_2(\mu\text{-aza})_2(CO)_4]$ ($M = Rh$, Ir) compounds [23,26]. Interestingly, the compound $[Ir_2(\mu\text{-aza})_2(CO)_4]$ is very reactive and very easily oxidised [26]. Thus, oxidation by silver tetrafluoroborate in a coordinating solvent such as acetonitrile gives the yellow cationic species $[Ir_2(\mu\text{-aza})_2(CO)_4\text{-}(MeCN)_2]^{2+}$, which was not isolated. However, oxidation with the silver salt of a coordinating anion, such as acetate, leads to the isolation of the neutral complex $[Ir_2(\mu\text{-aza})_2(O_2CMe)_2(CO)_4]$, which shows the two monodentate acetato ligands *trans* to the Ir–Ir bond. Both the HH and HT isomers of $[Ir_2(\mu\text{-aza})_2(CO)_4]$ are oxidized and undergo two-electron, two-fragment, binuclear oxidative-addition reactions with a variety of substrates [26]. Reactions with halogens yield the diiridium(II) complexes $[Ir_2(\mu\text{-aza})_2X_2(CO)_4]$ ($X = Cl$, Br, I). For iodine and bromine the diiridium (II) complexes do not undergo a further oxidation of the metals with an excess of the halogen. However, an additional reaction is the selective bromination at the C3 of the five-membered ring in the aza bridges affording $[Ir_2(\mu\text{-azaBr})_2Br_2(CO)_4]$,. Iodine does not react further although chlorine produces a mixture of complexes which are yet to be identified.

Iodomethane, polyiodomethanes, chloroform or carbon tetrachloride add to $[Ir_2(\mu\text{-aza})_2(CO)_4]$ giving $[Ir_2(\mu\text{-aza})_2(X)(R)(CO)_4]$ ($X = I$, $R = Me$, CH_2I or CHI_2; $X = Cl$, $R = CHCl_2$ or CCl_3) complexes as a mixture of three isomers (one from the parent HT isomer, and two from the HH isomer) (Scheme 2). The relative



Scheme 2.

disposition, HT or HH is maintained in these two-fragment dinuclear oxidative-addition reactions.

The double-bridged azaindolate complex, with three atoms in the bridge, is more rigid than related doubly bridged thiolate and pyrazolate (Pz) complexes, with one and two atoms in the bridges, which accommodate a wide range of metal–metal separations. These three ligand types are shown in Fig. 7.

Thus, on reaction with iodine or diiodomethane, the iridium complexes $[Ir_2(\mu\text{-}SR)_2(CO)_2(PR_3)_2]$ and $[Ir_2(\mu\text{-}Pz)_2(CO)_2(PPh_3)_2]$ are able to give both Ir(II) metal–metal bonded complexes [27–29] and Ir(III) methylene-bridged compounds [30,31], whereas identical reactions with $[Ir_2(\mu\text{-aza})_2(CO)_4]$ stop at the iridium (II) complexes. The rigidity imposed by the double azaindolate bridge and the face to face orientation of the square-planar environments seems to have two effects. First, it prevents the migration of fragments from one metal centre to the other and, second, the proximity of the metals causes a strong interaction of the metallic orbitals that lie perpendicular to the square-planar environments on each metal. This interaction, responsible for the photoreduction of alkyl halides, is associated with a strong band in the visible region ($\lambda_{max} = 530$ nm). Indeed, the reactions of $[Ir_2(\mu\text{-}$

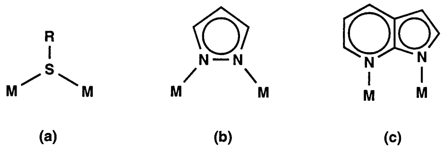


Fig. 7. Molecular framework in bridged dinuclear thiolate, pyrazolate and 7-azaindolate complexes.

aza)$_2$(CO)$_4$] with chlorocarbons are very slow in the absence of light although they proceed very quickly under direct sunlight, revealing that the iridium complex is a strong photoreductor, as predicted by Gray for d^8–d^8 dimers [32].

7-Azaindolate has not been much used as a bridging bidentate ligand in spite of its high synthetic potential. Quite recently, lantern-type multiple-bonded dinuclear 7-azaindolate niobium and tungsten complexes have been described by Cotton et al [33]. This ligand can also act as a bridging between three metal atoms, as found in ruthenium and osmium trimetallic clusters [34,35]. Furthermore, extensive studies on catalytic hydrogenation of acetylenes promoted by triruthenium clusters face-bridged by the deprotonated form of 2-amino-6-methylpyridine have been carried out [36].

On the other hand, non heterocyclic nitrogen-donor ligands containing the structural unit N–C–N have also proved to be versatile ligands for the construction of dinuclear entities. In particular, dinuclear rhodium complexes supported by anionic ligands derived from acetamidine [37], formamidine [38] and benzamidine [39] have been described. Interestingly, the nuclearity of *N,N′*-diphenylbenzamidinate rhodium and iridium complexes is strongly dependent on the ancillary ligands. Thus, the 1,5-cyclooctadiene complex [M{CPh(NPh)$_2$}(COD)] is mononuclear, whereas the 2,5-norbornadiene and tetrafluorobenzobarrelene complexes [M$_2${CPh-(NPh)$_2$}$_2$(diolefin)$_2$] (diolefin = NBD, TFB; M = Rh, Ir) are dinuclear [39].

2.3. Complexes with N–C–O and N–C–N–C–O ligands

The double bridging 2-pyridonate (OPy) system is more flexible in comparison with that of 7-azaindazolate due to the possibility that the square-planar coordination planes of each metal can slide over the other in the former case, leading to a range of metal–metal separations for the *cis*-HT arrangements, as shown by the structures of [Ir$_2$(μ-OMePy)$_2$(COD)$_2$] [40], [Rh$_2$(μ-OMePy)$_2$(COD)$_2$] [41] and [Rh$_2$(OClPy)$_2$(NBD)$_2$] [42]. The diolefinic complexes [M$_2$(μ-OPy)$_2$(diolefin)$_2$] can be easily prepared by reacting the appropriate chloro-derivatives [M$_2$(μ-Cl)$_2$(diolefin)$_2$] with an equimolar mixture of 2-hydroxypyridine and potassium hydroxide in methanol [43]. Carbonylation of [M$_2$(μ-OPy)$_2$(diolefin)$_2$] under atmospheric pressure gives the complexes [M$_2$(μ-OPy)$_2$(CO)$_4$] in high yields. The dinuclear tetracarbonyl complex [Rh$_2$(μ-OPy)$_2$(CO)$_4$], which crystallizes as dichroic dark-blue needles having a copper-like appearance, shows the arrangement of the binuclear units stacked to form an infinite zig-zag chain (Fig. 8) with intramolecular and intermolecular Rh–Rh separations of 2.899(2) and 3.410(2) Å, respectively

In the solid state, the bridging 2-pyridonate ligands are arranged in a *cis*-head-to-head disposition in such a way that the chemical environments of the two rhodium atoms in the binuclear unit are different [43], while both isomers HH and HT, in roughly 1:1 molar ratio, are present in solution. A comparison of the structures of the diolefin and carbonyl complexes clearly exemplifies the influence of steric factors on the metal–metal separation in the rhodium(I) and iridium(I) dinuclear 2-pyridonate complexes ranging from 3.367(1) Å for the sterically demanding COD

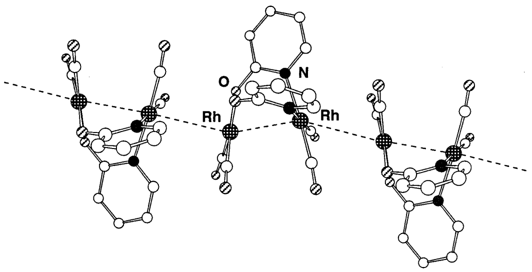
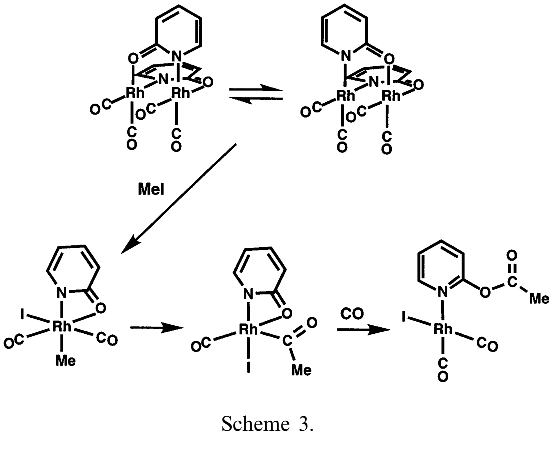


Fig. 8. Molecular structure of $[Rh_2(\mu\text{-}OPy)_2(CO)_4]$.

ligands in $[Rh_2(\mu\text{-}OMepy)_2(COD)_2]$ to 2.899(2) Å for the above-mentioned carbonyl complex.

Oxidation to the paramagnetic cations $[Rh_2(\mu\text{-}OXPy)_2(NBD)_2]^+$ (X = Cl, Me) seems to be the only reaction in which the dinuclear entity is preserved [44]. Oxidative addition of MeI to $[Rh_2(\mu\text{-}OPy)_2(CO)_4]$ is a complex reaction which requires the presence of carbon monoxide to give isolable products [43]. Under these conditions the mononuclear yellow complex $[RhI(PyCO_2Me)(CO)_2]$, containing the 2-acetoxypyridine ligand, is obtained in good yield. This complex was characterized by comparison of its chemical and spectroscopic properties with an authentic sample prepared by an alternative method. The generation of the 2-acetoxypyridine ligand involves an initial oxidative-addition of MeI to the starting complex followed by the insertion of a carbonyl ligand into the Rh–Me bond to give an acyl complex and a further attack of the acetyl ligand to the oxygen of the 2-pyridonate ligand. Most probably the mechanism of the reaction involves mononuclear complexes, as tentatively proposed in Scheme 3.

The anionic polydentate ligands 1,8-naphthyridine-2-onate (Onapy) and 5,7-dimethyl-1,8-naphthyridine-2-onate (OMe_2napy) should display the binucleating ability of the parent 1,8-naphthyridine and that of the related 2-pyridonate ligands.



Scheme 3.

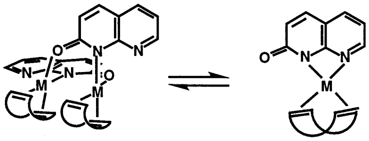


Fig. 9. Equilibrium between mono-and dinuclear Onapy complexes (M = Rh, Ir) with COD as ancillary ligand.

In this way, these ligands offer a multiple choice of coordination possibilities in mono and dinuclear complexes.

Reactions of $[Rh_2(\mu\text{-}Cl)_2(diolefin)_2]$ with HOnapy or $HOMe_2napy$ and potassium hydroxide yield mono- or dinuclear complexes $[Rh(OR_2napy)(diolefin)]_x$ ($x = 1, 2$) [45]. Alternatively, these compounds and $[Ir(\mu\text{-}OR_2napy)(COD)]_x$ ($x = 1, 2$) result from the reactions of the appropriate methoxy complex $[M_2(\mu\text{-}OMe)_2(diolefin)_2]$ with HOnapy or $HOMe_2napy$ in dichloromethane, respectively [46]. The protonation of the methoxy group in $[M_2(\mu\text{-}OMe)_2(COD)_2]$ by the HOR_2napy ligands is an equilibrium due to the low acidity of the latter and requires the removal of methanol to drive the reaction to completion. The nuclearity of the complexes $[M(OR_2napy)(diolefin)]_x$ in the solid state and in solution is influenced by various factors ranging from steric reasons to the variability of the coordination modes and even the nature of the solvent or the crystallization conditions. It should be noticed that the complexes with sterically demanding COD ligands and those with 5,7-dimethylnaphthyridine-2-onate are mononuclear in polar solvents, but those complexes with Onapy and NBD or TFB are dinuclear, probably because the repulsions between the diolefin ligands in the dinuclear complexes are smaller than those for COD. Moreover, the complexes $[M(\mu\text{-}OMe_2napy)(COD)]_x$ crystallize as yellow or purple solids (M = Ir) and as a yellow or an orange form (M = Rh) [46]. These crystalline forms are completely interconvertible, by simply dissolving in an appropriate solvent. One remarkable difference between the two forms concerns the IR $\nu(C{=}O)$ bands of the bridging ligands; the yellow forms show a broad band at 1640 cm^{-1}, as in the free ligand, while the red or orange forms show two bands at 1615 and 1590 cm^{-1}. This shift of $\nu(C{=}O)$ to lower frequencies is important because it suggests the coordination through the oxygen. The behaviour of these compounds in solution is also confusing because they show solvent and temperature dependence. In toluene, at low temperature, the complexes are dinuclear with head-to-tail (HT) disposition of the bridging ligands, as deduced from the H,H-COSY spectra; however in chloroform they are mononuclear. Moreover, a fluxional process involving mono and dinuclear species makes the olefinic protons equivalent (Fig. 9).

X-ray diffraction studies [46] on the yellow and orange crystalline forms of $[Rh(OR_2napy)(COD)]_x$ indicate that the former is a mononuclear complex in which the OMe_2napy ligand acts as chelating ligand through the two N atoms, while the orange form consists of dinuclear complexes in which the bridging ligands are coordinated by the central N and the O atoms in a HT disposition (Fig. 10).

Reaction of the complexes $[M(OR_2napy)(diolefin)]_x$ (R = H or Me; M = Rh or Ir) with carbon monoxide gives the air-sensitive, black-violet tetracarbonyl com-

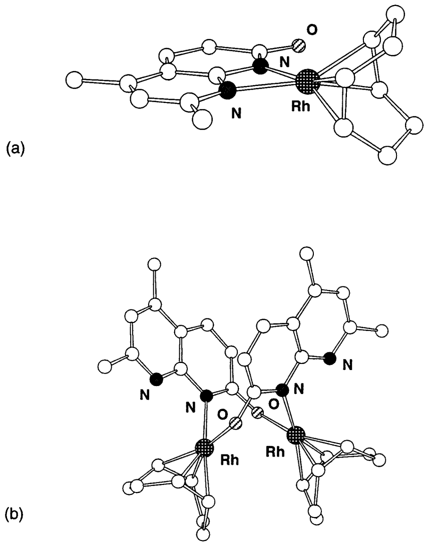


Fig. 10. Molecular structures of [Rh(OMe$_2$napy)(COD)] (a) and [Rh$_2$(μ-OMe$_2$napy)$_2$(COD)$_2$] (b).

plexes [M$_2$(μ-OR$_2$napy)$_2$(CO)$_4$]. The structure of the [Rh$_2$(μ-Onapy)$_2$(CO)$_4$] complex (Fig. 11) [47] shows the two *cis*-Onapy ligands bridging the two metals through the N atoms in a HT fashion with a distance between the bridged Rh atoms of 2.880(2) Å.

In contrast, the coordination of the related bridging 5-methyl-7-phenyl-1,8-naphthyridine-2-onate (OMePhnapy) ligands in the *cis*-HT dinuclear complex [Rh$_2$(μ-OMePhnapy)$_2$(CO)$_4$] recently reported by Sheldrick [48] is μ$_2$-(1κN,2κO) probably as consequence of the steric effect of the bulky phenyl ligands in the bridges.

Although there is no clear reason why the metals are in close proximity, bonded to consecutive donor atoms in the ligand instead of separating and coordinating the N and O donor atoms at the extremes of the ligand, an additional stabilization associated with the metal–metal interaction appears to be present. The apparent attraction between the metals results in both being displaced towards each other from their square-planar environments.

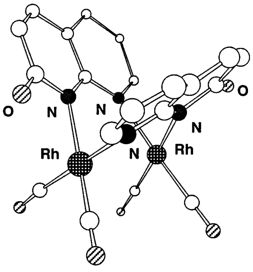


Fig. 11. Molecular structure of [Rh$_2$(μ-Onapy)$_2$(CO)$_4$]

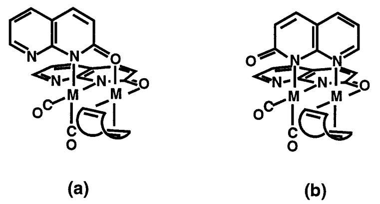


Fig. 12. Isomers of the mixed-ligand complexes $[M_2(\mu\text{-}OMe_2napy)_2(CO)_2(COD)]$ (M = Rh, Ir).

In contrast, for the dinuclear diolefin complexes, the rigidity of the framework in a μ_2-(1κN, 2κN) coordination, retaining a face-to-face structure, would result in COD ligand overlap. Therefore, the μ_2-(1κN, 2κO) coordination is preferred due to its flexibility, since the sliding of one of the square-planar environments relative to the other keeps the COD ligands apart, as observed in $[Ir_2(\mu\text{-}OPy)_2(COD)_2]$ and related 2-pyridonate complexes [40].

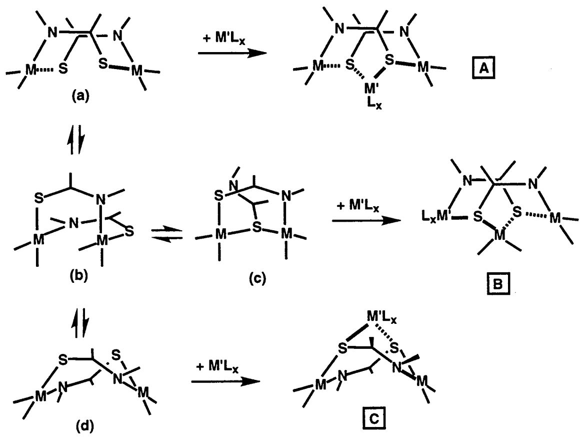
The replacement of 1,5-cyclooctadiene in $[M(OR_2napy)(COD)]_x$ (M = Rh, Ir) by carbon monoxide is reversible and can be carried out stepwise. Thus, the mixed–ligand complexes $[M_2(\mu\text{-}OMe_2napy)_2(CO)_2(COD)]$ are isolated by refluxing the appropriate tetracarbonyl complex with COD in dichloromethane. Both compounds are fluxional and exist as the *cis,cis* -HH and one unsymmetrical isomer in solution (Fig. 12) as determined by H,H-COSY spectra at low temperature.

The heterometallic mixed-ligand dinuclear complexes $[RhIr(\mu\text{-}OMe_2napy)_2(CO)_2\text{-}(COD)]$ result from the reaction of equimolecular mixtures of $[M(OMe_2napy)\text{-}(COD)]_x$ (M = Rh, Ir) and $[IrCl(CO)_2(NH_2\text{-}p\text{-tolyl})]$ or $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$. One of them, $[(COD)Rh(\mu\text{-}OMe_2napy)_2Ir(CO)_2]$, was isolated and fully characterized by NMR methods as a mixture of the two isomers similar to those depicted in Fig. 12 for the mixed-ligand homonuclear complexes.

2.4. Complexes with N–C–S ligands

Our interest for testing bifunctional ligands with soft and hard donor atoms, which in addition should be able to coordinate electronically different metals, led us to initiate, some years ago [49], a comprehensive exploration of the coordination possibilities of the deprotonated form of pyridine-2-thione (PyS^-). This ligand possesses a structural disposition of the donor atoms identical to 2-pyridonate but the sulfur atom can also bridge two metal centres, which is an important feature of aryl and alkyl thiolate ligands [50], opening the possibility to act as a bridging trinucleating ligand. Since then, a plethora of polynuclear complexes with this and related thioamide complexes has been reported [9].

Dinuclear complexes $[Rh_2(\mu\text{-}PyS)_2(diolefin)_2]$ can be prepared by reaction of LiPyS with $[Rh_2(\mu\text{-}Cl)_2(diolefin)_2]$, and show a fluxional behaviour in solution associated with the bridging ligands [51]. These dinuclear complexes have a very flexible eight-membered ring *cis*-$M_2(N\text{–}C\text{–}S)_2$, which can adopt several conformations (see Scheme 4(a–d)). However, the pyridine-2-thiolate can bridge the metal



Scheme 4.

centres through the sulfur atom only or dissociate into mononuclear complexes, allowing a complex fluxional behaviour. Equilibria between dinuclear and mononuclear chelate complexes producing a dynamic behaviour has been observed [52] for palladium complexes of the type $[Pd_2(\mu\text{-}PyS)_2(PR_3)_2]$. On the other hand, the thiolate coordination of the pyridine-2-thiolate ligand has been found in the X-ray crystal structure of the tetrafluorobenzobarrelene rhodium complex which strongly supports the involvement of the equilibrium shown in Fig. 13 in the fluxional behaviour of these dinuclear complexes.

The crystal structure of $[Rh_2(\mu\text{-}PyS)_2(TFB)_2]$ shows one pyridine-2-thiolate bonded through the N and S atoms, but the other is bridging through the sulfur atom only (Fig. 14(a)). In contrast the related carbonyl complex $[Rh_2(\mu\text{-}PyS)_2(CO)_4]$ shows [51] the presence of bonded N–C–S units in a head-to-tail disposition (Fig. 14(b)).

The related benzothiazole-2-thiolate (bztat$^-$) diolefin complexes can also be prepared by similar methods. Carbon monoxide easily replaces the diolefin in the above mentioned complexes to give $[Rh_2(\mu\text{-}PyS)_2(CO)_4]$ and $[Rh_2(\mu\text{-}bztat)_2(CO)_4]$; the latter is apparently rigid in contrast with the pyridine-2-thiolate derivative and exists in solution as the head-to-tail and head-to-head isomers [51]. Substitution of the carbonyl groups by PPh_3 can be carried out stepwise, and the following dynamic equilibrium can be observed:

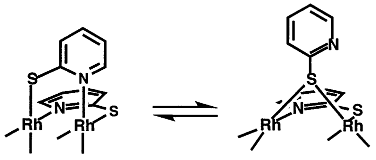


Fig. 13. Possible fluxional motion of pyridine-2-thiolate and related ligands.

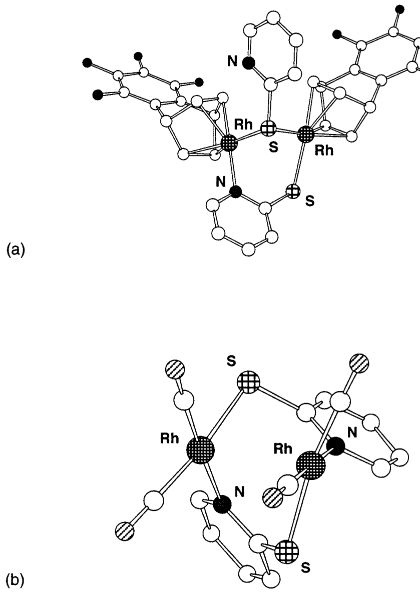


Fig. 14. Molecular structures of $[Rh_2(\mu\text{-PyS})_2(TFB)_2]$ (a) and $[Rh_2(\mu\text{-PyS})_2(CO)_4]$ (b).

$$2[Rh_2(\mu\text{-bztat})_2(CO)_3(PPh_3)]$$
$$\rightleftharpoons [Rh_2(\mu\text{-bztat})_2(CO)_4] + [Rh_2(\mu\text{-bztat})_2(CO)_2(PPh_3)_2]$$

Scrambling experiments between dinuclear benzothiazole-2-thiolate and 6-methylbenzothiazole-2-thiolate rhodium complexes suggest that the observed redistribution reactions can be explained by an associative mechanism through tetranuclear intermediates formed by interaction between two dinuclear units, where an interchange of the bridging N–C–S ligands takes place [53].

The dark-red $[Ir_2(\mu\text{-PyS})_2(COD)_2]$ and orange $[Ir_2(\mu\text{-bztat})_2(COD)_2]$ iridium complexes result from the reactions of $[Ir_2(\mu\text{-Cl})_2(COD)_2]$ with the lithium salts LiPyS and Li(bztat) prepared 'in situ'. They are non-rigid showing broad resonances in the ^{1}H-NMR spectrum. However, on carbonylation under atmospheric pressure, the deep purple air-sensitive carbonyl complexes $[Ir_2(\mu\text{-PyS})_2(CO)_4]$ [54] and $[Ir_2(\mu\text{-bztat})_2(CO)_4]$ [55], are formed, respectively, which are found to be mixtures of the HH and HT isomers in solution.

3. Trinuclear complexes with bridging N–C–X ligands

The above mentioned mono- and dinuclear complexes with OR$_2$napy ligands still have at least one uncoordinated ketonic oxygen atom or a nitrogen atom and are therefore potential ligands to build larger assemblies. Moreover, the three donor atoms (N, N, and O) are coplanar and the ligands are useful for the design of rigid, linear trimetallic complexes in which the metals are within cooperative distances. Another approach consists of the use of the above dinuclear complexes with bidentate N–C–S ligands (pyridine-2-thiolate and benzothiazole-2-thiolate) as metallaligands using all the lone electron pairs on the sulfur for coordination. In this way, the N–C–S and N–C–N–C–O ligands act as five-electron donors, allowing the controlled synthesis of trinuclear angular and linear aggregates, respectively. Although dinuclear complexes of rhodium and iridium are quite common, trinuclear complexes, especially the linear ones, are very infrequent. Some examples such as $[M_3^{II}(dpa)_4Cl_2]$ (M = Rh, Ru; dpa = bis(dipyridy)lamido)) and $[Rh_3(pqdi)_4(pqdi)_2]^+$ (pqdi = 9,10-phenanthroquinonediimine) have recently been reported [56,57]

3.1. Angular trinuclear complexes with N–C–S ligands

A general view of the flexibility of the eight-membered dimetallacycles *cis*-M_2(N–C–S)$_2$ in the dinuclear complexes $[M_2(\mu\text{-N–C–S})_2(L_2)_2]$ and a possible fluxional movement involving the bridging ligands are shown in Scheme 4(a–d). From this picture the addition of a metal fragment $M'L_x$ to the dinuclear complexes can take place in several ways.

Starting from the dinuclear complexes $[M_2(\mu\text{-N–C–S})_2(L_2)_2]$ (M = Rh, L_2 = diolefin, $(CO)_2$ or $(CO)(PPh_3)$; M = Ir, L_2 = COD) a variety of homotrinuclear angular aggregates of general formula $[M_3(\mu\text{-N–C–S})_2(L_2)_3]^+$ have been prepared by addition of the appropriate mononuclear species $[ML_2(Me_2CO)_x]^+$. X-ray diffraction studies show that the two N–C–S ligands act as triple bridges through the nitrogen and one sulfur atom interacting with all the three metals which are in a bent arrangement in relatively close proximity [58,59]. From these reactions the isomer of the type A (Scheme 4), derived from conformation (a), is the preferred structure observed in the products. However, NMR spectroscopic studies on the complex $[Rh_3(\mu\text{-bztat})_2(CO)_2(TFB)_2]$ suggest that its structure is of type B, derived from (c). In addition, one compound, the heterotrinuclear $[(\eta^3\text{-allyl})_2Pd_2(\mu\text{-PyS})_2Rh(\mu\text{-PyS})_2]^+$, illustrating isomer C, has been reported [60].

The trinuclear diolefinic complexes $[M_3(\mu\text{-N–C–S})_2(diolefin)_3]^+$ show two strong absorptions in the visible region of the UV-vis spectrum and are non-fluxional, in contrast with the parent dinuclear complexes which are fluxional. This blocking of the fluxionality allows an easy structural characterization by NMR methods [58,59], which can be attributed to a full involvement of the electron pairs on the sulfur in bonding.

Heterotrinuclear complexes of formula $[(Ph_3P)_2(OC)_2Rh_2(\mu_3\text{-bztat})_2ML_2]^+$ [ML_2 = Ir(COD) or Pd(allyl)], $[(COD)_2M'_2(\mu_3\text{-bztat})_2AgX]^{n+}$ (n = 0, X = ClO_4, Cl, NO_3 or BF_4; n = 1, X = PPh_3 or pyridine), $[(COD)_2M'_2(\mu_3\text{-bztat})_2M'Cl]$ (M′ = Rh, Ir; M′ = Cu or Au) have been prepared by reaction of the dinuclear complexes with appropriate mononuclear cationic or neutral species. All these heterotrinuclear complexes possess the structure of the isomer A, confirming the proposed pathway of formation involving the actuation of the dinuclear starting complexes as chelating metallaligands through the sulfurs as donor atoms.

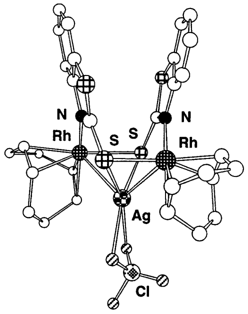


Fig. 15. Molecular structure of $[(COD)_2Rh_2(\mu_3\text{-bztat})_2AgO_2ClO_2]$

The structure of the complex $[(COD)_2Rh_2(\mu_3\text{-bztat})_2AgO_2ClO_2]$ (Fig. 15) exemplified the bent arrangement of the metals (see Scheme 4(A)) with two molecules of benzothiazole-2-thiolate interacting with the three metals (Rh–Ag: 2.796(3) Å); interestingly, the four-coordinate Ag atom completes the coordination with two oxygen atoms from a perchlorate anion. The structures of the trinuclear complexes Rh_2ML (ML = CuCl, AgCl, AuCl or $Ag(PPh_3)$) should involve three coordinate copper, silver or gold [59].

Attempts to prepare the heterotrinuclear complex $[(Ph_3P)_2(OC)_2Rh_2(\mu_3\text{-bztat})_2MCl_2]$ by reaction of $[Rh_2(\mu\text{-bztat})_2(CO)_2(PPh_3)_2]$ with $MCl_2(COD)$ (M = Pt or Pd) were unsuccessful. Instead, the new diamagnetic heterodinuclear complexes $[(Ph_3P)M(\mu_3\text{-bztat})_2RhCl(CO)]$ were obtained through a complicated process. A more direct route involves the reaction of *trans*-$[Pt(bztat)_2(PPh_3)_2]$ with $[Rh_2(\mu\text{-Cl})_2(CO)_4]$. The X-ray structure of $[(Ph_3P)Pt(\mu_3\text{-bztat})_2RhCl(CO)]$ (Fig. 16) shows the two metal atoms joined by a short metal–metal bond (2.6266(4) Å), and bridged by the two benzothiazole-2-thiolate groups mutually *trans* and in a head-to-head fashion [61].

A vacant coordination position on the rhodium atom *trans* to the metal–metal bond is primarily due to steric effects dictated by two protons of the benzothiazole-2-thiolate groups. The inertness of this coordination position is not surprising since there is no room even for a small ligand such as carbon monoxide. In addition, these compounds are rare examples of dinuclear complexes containing just two

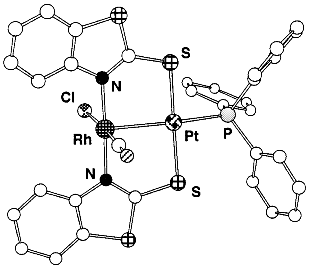


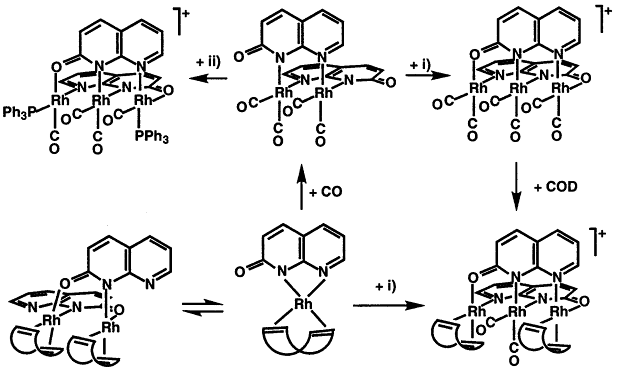
Fig. 16. Molecular structure of $[(Ph_3P)Pt(\mu_3\text{-bztat})_2RhCl(CO)]$.

anionic short-bite ligands in a *trans* disposition. A *trans* arrangement is usually found in $M_2(dppm)_2$ complexes whereas for the $M_2(\mu\text{-N–C–X})_2$ complexes a *cis*-arrangement is generally preferred.

3.2. Linear trinuclear complexes with bridging N–C–N–C–O ligands

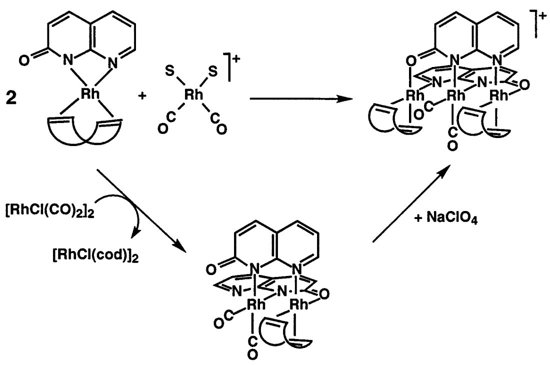
The complexes $[M(OR_2napy)(COD)]_x$ ($M = Rh$, Ir; $x = 1, 2$) and $[Rh_2(\mu\text{-}OR_2napy)_2(CO)_4]$ are able to act as metallaligands towards other metals behaving thus as building blocks for trinuclear complexes with a linear disposition of the metal atoms. Thus, reactions of the tetracarbonyl complexes $[Rh_2(\mu\text{-}R_2Onapy)_2(CO)_4]$ with the solvated species $[Rh(CO)_2(Me_2CO)_x]^+$ or $[Rh(CO)(PPh_3)_2(Me_2CO)]^+$ give the trinuclear complexes $[Rh_3(\mu_3\text{-}R_2Onapy)_2(CO)_6]^+$ and $[Rh_3(\mu_3\text{-}R_2Onapy)_2(CO)_4(PPh_3)_2]^+$, respectively (Scheme 5). The former reacts with diolefins to give the complexes $[Rh_3(\mu_3\text{-}R_2Onapy)_2(CO)_2(diolefin)_2]^+$ [45]. Analogously, $[Rh(CO)_2(Me_2CO)_x]^+$ reacts directly with $[Rh(OMe_2napy)(COD)]_x$ to give the trinuclear complexes $[Rh_3(\mu_3\text{-}OMe_2napy)_2(CO)_2(COD)_2]^+$ in a one-pot reaction. The preference of the sterically undemanding $[Rh(CO)_2]^+$ fragment to coordinate the central nitrogen atoms and to occupy the middle of the metal chain becomes evident from the above reactions.

A further insight into these reactions comes from the reaction between $[Rh(OMe_2napy)(COD)]_x$ and $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$, which gives the mixed-ligand dinuclear complex $[Rh_2(\mu\text{-}OMe_2napy)_2(CO)_2(COD)]$ and $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ (Scheme 6). This reaction demonstrates that 'Rh(CO)$_2$' and 'Rh(COD)' fragments are readily interchangeable. Further addition of a poor-donor anion, such as perchlorate, to this mixture gives selectively the trinuclear complex $[Rh_3(\mu_3\text{-}OMe_2napy)_2(CO)_2(COD)_2][ClO_4]$. The fragment 'Rh(COD)' added to the mixed-ligand dinuclear complex occupies the required vacant metal for a selective synthesis



$i) = [Rh(CO)_2(Me_2CO)_2]^+$; $ii) = [Rh(CO)(PPh_3)(Me_2CO)_2]^+$

Scheme 5.



Scheme 6.

performed by the easy mobility of the bridging ligands [46]. In view of this information, the one-pot synthesis previously reported [45] should be described as a stepwise mechanism from the mononuclear to the trinuclear complexes.

Similarly, reaction of $[Ir(OMe_2napy)(COD)]_x$ with $[IrCl(CO)_2(NH_2\text{-}p\text{-tolyl})]$ and further addition of sodium perchlorate yields $[Ir_3(\mu_3\text{-}OMe_2napy)_2(CO)_2(COD)_2][ClO_4]$. In these trinuclear complexes the OMe_2napy bridging ligands are coordinated to the three metals through all the donor atoms in a *cis,cis*-HT arrangement as found for the related complex $[Rh_3(\mu_3\text{-}Onapy)_2(CO)_2(COD)_2][ClO_4]$ by X-ray diffraction [62]. Fig. 17 shows the approximately linear arrangement of the three Rh atoms with intermetallic distances of about 2.91 Å.

The above procedure represents a general method for the preparation of the deep coloured heterotrinuclear complexes with the $[Rh_2Ir]^{3+}$ core $[Rh_2Ir(\mu_3\text{-}OR_2napy)_2(CO)_2(diolefin)_2]A$ (R = Me, diolefin = COD, TFB or NBD; R = H, diolefin = COD) from the appropriate $[Rh(OR_2napy)(diolefin)]_x$ complex, $[IrCl(CO)_2(NH_2\text{-}p\text{-tolyl})]$ and sodium perchlorate or tetrafluoroborate (A); the orange mixed-ligand heterodinuclear complexes $[(diolefin)Rh(\mu\text{-}OMe_2napy)_2Ir(CO)_2]$ are intermediates in these syntheses [30]. These trinuclear complexes are fluxional but the low-temperature ^1H- and $^{13}C\{^1H\}$-NMR spectra correspond to the isomer *cis,cis*-HT, which is found in the solid state for $[Rh_2Ir(\mu_3\text{-}$

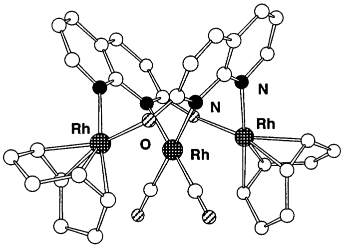


Fig. 17. Molecular structure of $[Rh_3(\mu_3\text{-}Onapy)_2(CO)_2(COD)_2]^+$.

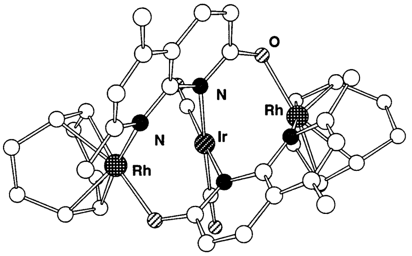


Fig. 18. Molecular structure of $[Rh_2Ir(\mu_3\text{-}OMe_2napy)_2\ (CO)_2(COD)_2]^{2+}$.

$OR_2napy)_2(CO)_2(COD)_2]BF_4$. Complexes with the $[RhIr_2]^{3+}$ core of the type $[RhIr_2(\mu_3\text{-}OR_2napy)_2(CO)_2(COD)_2]BF_4$ (R = Me or H) are more unstable than the homologous $[Rh_2Ir]^{3+}$ complexes but can be prepared by similar methods.

All the homo- and heterotrinuclear complexes $[M_3(\mu_3\text{-}OR_2napy)_2L_6]^+$ undergo two reversible one-electron oxidations at a platinum bead electrode to give the di- and tri-cations. The values of E_1° for the first oxidation process, in the range 0.590–0.145 V, suggest the feasibility of a chemical oxidation while the isolation of the tricationic complexes is out of the question since E_2° for the second oxidation process, in the range 1.340–0.923 V, is too high [46,63]. The relative values of E_1° and E_2° depend on the metal core and the bridging and ancillary ligands, being smaller for iridium than for rhodium in general. In particular, the deep-blue mixed-valence dications $[M_3(\mu_3\text{-}OMe_2napy)_2(CO)_2(COD)_2](X)_2$ (M = Rh, Ir; X = BF_4, ClO_4), $[Rh_2Ir(\mu_3\text{-}OMe_2napy)_2(CO)_2(COD)_2](BF_4)_2$, and $[RhIr_2(\mu_3\text{-}OMe_2\text{-}napy)_2(CO)_2(COD)_2](BF_4)_2$, result from oxidation of the appropriate complexes with $AgClO_4$ or with a solution of $[N(p\text{-}BrC_6H_4)_3]BF_4$ in dichloromethane. Rapid recrystallisation and storage at −20°C under nitrogen is required to avoid decomposition. These paramagnetic complexes were characterized [46] by electrochemical methods, UV-vis spectroscopy and a X-ray diffraction study for $[Rh_2Ir(\mu_3\text{-}OMe_2napy)_2(CO)_2(COD)_2](BF_4)_2$. The values of the g factor in the e.s.r. spectra, different from those for the free electron, are indicative that the unpaired electron is largely localized on the trimetallic core.

Fig. 18 displays a view of the structure of the cations $[Rh_2Ir(\mu_3\text{-}OMe_2napy)_2(CO)_2(COD)_2]^+$ and $[Rh_2Ir(\mu_3\text{-}OMe_2napy)_2(CO)_2(COD)_2]^{2+}$ which resemble the closely related homometallic rhodium complex $[Rh_3(\mu_3\text{-}Onapy)_2(CO)_2(COD)_2]^+$. Each complex has essentially linear metallic backbones with the rhodium atoms at the extremes of the molecule and the iridium atom positioned in the centre, while the tridentate OMe_2napy ligands bridge the metals in a HT disposition. Although they are structurally very similar, a significant difference in the intermetallic separations is observed, appearing shorter for the oxidised product (2.848(1) vs. 2.770(2) Å, average values). Shortening of the intermetallic non-bonded Rh···Rh distance upon oxidation has been observed [44] in related 2-pyridonate dinuclear rhodium complexes.

A synthetic and structural study on rhodium and iridium complexes containing OR_2napy ligands shows that homo- and heterotrinuclear cationic complexes are readily accessible when a sterically undemanding ML_2 fragment occupies the central position in the preferred *cis,cis*-HT disposition of the molecular framework. To fulfil this requirement the migration of ML_2 fragments is frequently observed. Interestingly, the interchange of ancillary ligands between different metallic centres also occurs to achieve this special arrangement. This behaviour should be related to the multiple coordination possibilities of the OR_2napy ligands and, in particular, with the easy switch between the different coordination modes as has been shown in related dinuclear complexes [46].

4. Tetranuclear complexes with bridging N–C–X and X–C–N–C–X ligands

4.1. Assembling dinuclear complexes

Some dinuclear complexes with ancillary ligands capable of acting as bridges may give rise to species of higher nuclearity just by producing controlled coordination vacancies. Thus, elimination of a ligand is a typical procedure for the synthesis of metal clusters starting from mono- or dinuclear metal carbonyl compounds [64]. In this context, the tetranuclear complex $[Rh_4(\mu\text{-OPy})_4(\mu\text{-CO})_2(CO)_4]$ results from the reaction of $[Rh_2(\mu\text{-OPy})_2(CO)_4]$ with trimethylamine-N-oxide in methanol [65]. The release of one carbonyl ligand from the dinuclear complex causes a terminal carbonyl to become bridging along with an arrangement of the 2-pyridonate bridges to form the tetranuclear complex. This process is reversible in the presence of carbon monoxide to give the dinuclear complex.

The structure of the 60-electron tetranuclear cluster (Fig. 19) shows a planar ring of four metal atoms formed by two binuclear halves '$Rh_2(\mu\text{-OPy})(\mu\text{-CO})(CO)_2$' bridged by 2-pyridonate groups. This structure closely resembles that of the related 64-electron cluster $[Rh_4(\mu\text{-Cl})_2(\mu\text{-aza})_2(\mu\text{-CO})_2(CO)_2(NBD)_2]$, in which two binuclear halves '$Rh_2(\mu\text{-aza})(\mu\text{-CO})(CO)(NBD)$' are bridged by two chloro ligands to form a tetrametallic planar hexagonal ring (Fig. 20) [66].

Both structures have in common a metal–metal bond bridged by a carbonyl group within the binuclear halves (Rh···Rh separations 2.6197(8) and 2.686(2) Å,

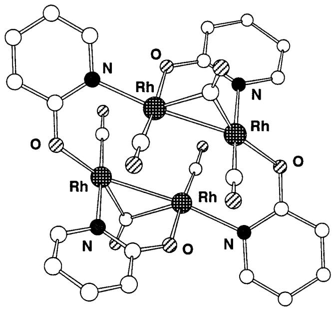


Fig. 19. Molecular structure of $[Rh_4(\mu\text{-OPy})_4(\mu\text{-CO})_2(CO)_4]$.

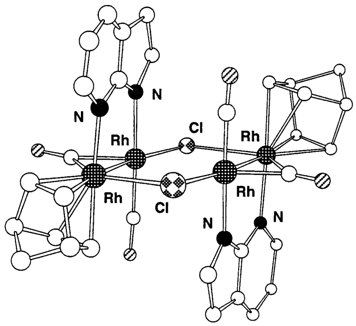


Fig. 20. Molecular structure of $[Rh_4(\mu\text{-}Cl)_2(\mu\text{-}aza)_2(\mu\text{-}CO)_2(CO)_2(NBD)_2]$.

respectively) but differ in the two metal–metal interactions, which occur along the long edges of the rectangle for the pyridonate complex (3.0325(7) Å) and along a diagonal in the hexagon for the 7-azaindolate cluster (3.156(2) Å). The second main difference between these two compounds is the pentacoordination of two metals, excluding the metal–metal bonds, in the 7-azaindolate complex versus the tetracordination of the metals in the 2-pyridonate cluster, which leads to the difference in the electron counts.

Interestingly, the complex $[Rh_4(\mu\text{-}Cl)_2(\mu\text{-}aza)_2(\mu\text{-}CO)_2(CO)_2(NBD)_2]$ can be generated from a variety of routes ranging from redistribution reactions between dinuclear complexes to reactions between appropriate mononuclear complexes. However, attempts to isolate similar tetranuclear complexes containing diolefins other than NBD by similar routes were unsuccessful [66]. The simplest synthetic method consists of a deprotonation of $[RhCl(NBD)(azaH)]$ with $[Rh(acac)(CO)_2]$ or deprotonation of $[RhCl(CO)_2(azaH)]$ with $[Rh(acac)(NBD)]$. The removal of acetylacetone is essential to create coordination vacancies to form the carbonyl and aza bridges. Careful comparison of the structure of the tetranuclear complex with those of their parent complexes, $[Rh_2(\mu\text{-}Cl)_2(NBD)_2]$ and $[Rh_2(\mu\text{-}aza)_2(CO)_4]$, indicates a complete redistribution of the terminal and bridging ligands, when obtained from them. The most simple explanation would suggest the dissociation of the starting dinuclear complexes into mononuclear species, but it should be followed by a further and suspicious symmetrical aglommeration into the tetranuclear complex. Regardless of the mechanism of such reactions, the tetranuclear complex could be a model for the intermediate in redistribution reactions between dinuclear complexes to give mixed-ligand complexes, such as:

$$[Rh_2(\mu\text{-}L)_2(\text{diolefin})_2] + [Rh_2(\mu\text{-}L)_2(CO)_4] \rightarrow 2[(\text{diolefin})Rh(\mu\text{-}L)_2Rh(CO)_2]$$

4.2. Tetranuclear complexes resulting from a rational design of the bridging ligands

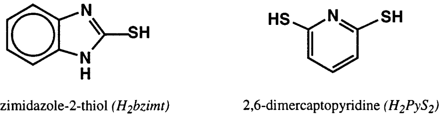
Going from dinuclear to polynuclear complexes generally requires the development of new synthetic strategies in which the design of the bridging ligands plays an important role; an increase of the number of donor atoms in the bridging ligands or the presence of several lone electron pairs on them (O or S for example) are useful approaches. In addition, the framework in which the donor atoms are placed should be carefully chosen to produce small 'bites' and to avoid undesired coordination modes. Ligands of these characteristics are, for example, 1,8-naphthyridine-2,7-dicarboxylate [67], bis(diphenylphosphinomethyl)phenylphosphine (dpmp) [7,68] bis(diphenylphosphinomethyl)phenylarsine (dpam) [7] and 2,6-bis(diphenylphosphino)pyridine [7] which give rise to controlled synthesis of homo and heterotrinuclear and tetranuclear complexes.

Other attempts to obtain complexes of high nuclearity by using promising polydentate ligands such as 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine (dpnapy) [69] and 2-mercapto-7-methyl-1,8-naphthyridine [70] have met with little success so far since only dinuclear complexes have been isolated. However, very recently the trinuclear complex $[Cu_3(\mu\text{-dpnapy})_3(CH_3CN)][ClO_4]_3$ showing a linear Cu–Cu–Cu array has been reported [71]. In addition, similar bridging ligands capable of binding several metal atoms such as 6-(diphenylphosphino)-2-pyridonate are found to form metal–metal bonded heterotetranuclear Mo–Pd and Cr–Pt complexes [72]. Remarkably, the related ligand 2,7-bis(diphenylphosphino)-1,8-naphthyridine (ppnapy) forms gold(I) and silver(I) bi- and trimetallic metallocriptands which exhibit interesting photophysical properties [73].

One of our approaches consists of using anionic ligands containing three donor atoms (N and S) such as 2,6-dithiolpyridine (H_2PyS_2) and benzimidazole-2-thiol (H_2bzimt) (Fig. 21). 2,6-Dithiolpyridine combines the properties of both thiolate and doubly functionalized pyridine ligands at positions 2 and 6 such as 2,6-bis(-diphenylphosphino)pyridine. On the other hand, benzimidazole-2-thiol shows the characteristics of both imidazole and thioamide systems.

Tetranuclear diolefin complexes of the general formula $[M_4(\mu_4\text{-PyS}_2)_2(\text{diolefin})_4]$ [M = Rh, diolefin = COD, NBD or TFB; M = Ir, diolefin = COD) are prepared in high yield by reaction of the appropriate complex $[M_2(\mu\text{-Cl})_2(\text{diolefin})_2]$ with the salt Li_2PyS_2 generated 'in situ' from dimercaptopyridine. This method is also used to prepare $[Pd_4(\mu_4\text{-PyS}_2)_2(\text{allyl})_4]$. Alternative syntheses for these complexes have also been described [74]. The structure of the complex with COD (Fig. 22) shows the tetranuclear complex with two *S*,*N*,*S*-tridentate 2,6-pyridinedithiolate ligands bridging all the four metallic centres. The two S atoms of each bridging ligand exhibit different coordination modes, while one is bonded to one metal, the second one is coordinated to two different rhodium centres. The shortest Rh···Rh separation is 3.1435(5) Å.

Carbonylation of the rhodium diolefin complexes under atmospheric pressure gives $[Rh_4(\mu_4\text{-PyS}_2)_2(CO)_8]$, which maintains the molecular framework. Further



benzimidazole-2-thiol *(H_2bzimt)* 2,6-dimercaptopyridine *(H_2PyS_2)*

Fig. 21. New bridging ligands for the synthesis of high nuclearity complexes.

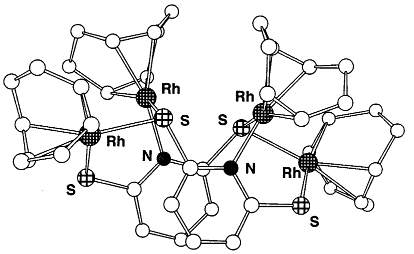
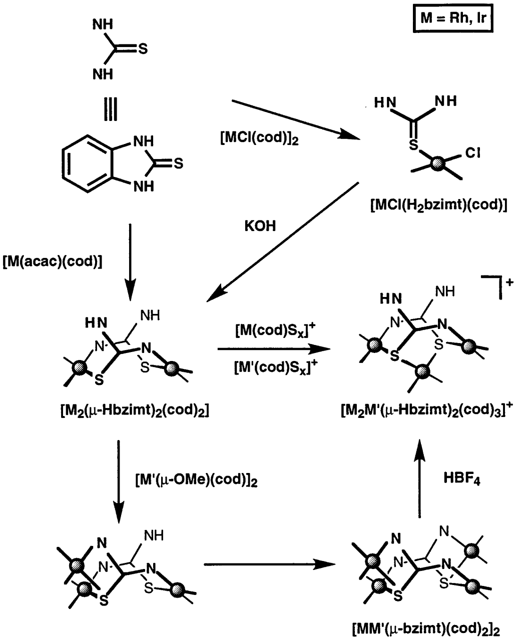


Fig. 22. Molecular structure of $[Rh_4(\mu_4\text{-}PyS_2)_2(COD)_4]$.

reaction of the carbonyl complex with PPh_3 gives $[Rh_4(\mu_4\text{-}PyS_2)_2(CO)_4(PPh_3)_4]$. The diolefinic and carbonyl complexes are fluxional. Variable temperature ^1H- and $^{13}C\{^1H\}$-NMR spectra combined with H,H-COSY experiments led to the assignment of the olefinic resonances and concluded that the two diolefins at the inner part of the complexes are rigid but the two external diolefins undergo the fluxional behavior due to an inversion at the terminal sulfur donor atoms. This is also the origin of the fluxionality of the carbonyl complex [74]. The rhodium complexes undergo two reversible one-electron oxidations at a platinum bead electrode in dichloromethane, separated by approximately 0.4 V at potentials, $E°$, in the ranges 0.0–0.4 and 0.4–0.8V. The electrochemical behaviour of the iridium complex is more complicated undergoing two similar one-electron oxidations followed by a chemical reaction.

A stepwise construction of polynuclear complexes of rhodium and iridium can be carried out starting from the mononuclear complexes of benzimidazole-2-thiol, $[MCl(H_2bzimt)(COD)]$, through deprotonation and addition of the appropriate metal fragments [75,76]. Reactions of $[M_2(\mu\text{-}Cl)_2(COD)_2]$ (M = Rh, Ir) with benzimidazole-2-thiol afford the mononuclear complexes $[MCl(H_2bzimt)(COD)]$ for which a S-coordination of the ligand is proposed. The dinuclear complexes $[M_2(\mu\text{-}Hbzimt)_2(COD)_2]$ are isolated from the reaction of [M(acac)(COD)] and benzimidazole-2-thiol. They contain the monodeprotonated ligand ($Hbzimt^-$) bridging the two metals in a μ_2-(1κN, 2κS) coordination mode and in a relative *cis*,*cis*-HT arrangement. (Scheme 7). These dinuclear complexes react with the appropriate species $[M(COD)(Me_2CO)_2]^+$ to afford the trinuclear cationic aggregates $[M_3(\mu\text{-}Hbzimt)_2(COD)_3]^+$ and with the $[M'_2(\mu\text{-}OMe)_2(COD)_2]$ compounds to give the homo- and hetero-tetranuclear complexes $[MM'(\mu\text{-}bzimt)(COD)_2]_2$ (M = M′ = Rh or Ir; M = Ir, M′ = Rh) containing the dideprotonated ligand ($bzimt^{2-}$). Interestingly, the trinuclear neutral complexes $[M_3(\mu\text{-}bzimt)(\mu\text{-}Hbzimt)(COD)_3]$ are intermediates detected in the synthesis of the tetranuclear complexes.

The molecular structure of the tetranuclear compound $[Rh_4(\mu\text{-}bzimt)_2(COD)_4]$ [75] shows a complex bonding mode of the two doubly deprotonated $bzimt^{2-}$ tridentade ligands. Each ligand is bonded to only three of the rhodium atoms acting as *N*,*S*-chelating to one rhodium and as N,S-bridging to two others (1κN, 1:2κS, 1κN′) (Fig. 23).



Scheme 7.

Reaction of the dinuclear complex $[Rh_2(\mu\text{-Hbzimt})_2(COD)_2]$ with $[Rh_2(\mu\text{-}Cl)_2(COD)_2]$ gives the neutral tetranuclear complex $[Rh_4(\mu\text{-Hbzimt})_2Cl_2(COD)_4]$ in dichloromethane and the trinuclear cationic complex $[Rh_3(\mu\text{-Hbzimt})_2(COD)_3]Cl$ in methanol, respectively. The ionization ability of the solvent seems to be the driving force to give either one or the other complex. Analogous tetranuclear complexes $[M_4(\mu\text{-Hbzimt})_2Cl_2(\text{diolefin})_4]$ (M = Rh, diolefin = TFB; M = Ir, diolefin = COD) are isolated from the reactions of the appropriate complexes $[MCl(H_2bzimt)(\text{diolefin})]$ and $[M(acac)(\text{diolefin})]$ in acetone. An X-ray diffraction study on $[Rh_4(\mu\text{-Hbzimt})_2Cl_2(COD)_4]$ shows the $Hbzimt^-$ ligands bridging two rhodium atoms through the sulfurs, forming a basic four-membered '$Rh_2(\mu$-

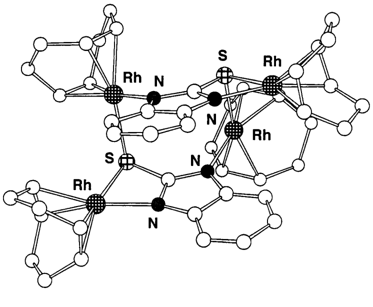


Fig. 23. Molecular structure of $[Rh_4(\mu\text{-bzimt})_2(COD)_4]$.

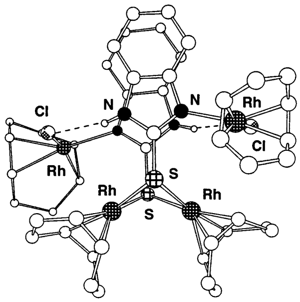


Fig. 24. Molecular structure of $[Rh_4(\mu\text{-Hbzimt})_2Cl_2(COD)_4]$.

(1:2κS)-Hbzimt)$_2$' ring along with two 'RhCl(COD)' moieties bonded to the nitrogen atoms (Fig. 24). Two intramolecular hydrogen bonds between the chloro ligands and the acidic NH protons should stabilize the *syn-exo* disposition of the bridging ligands as a simple thiolate mode.

Replacement of the olefin in $[Rh_4(\mu\text{-Hbzimt})_2Cl_2(COD)_4]$ by carbon monoxide gives $[Rh_4(\mu\text{-Hbzimt})_2Cl_2(CO)_8]$. In contrast with the parent diolefin complex its X-ray structure shows the Hbzimt$^-$ ligands in an unusual 'HT-Rh$_2$(μ-(1κN, 2κS)-Hbzimt)$_2$' disposition with two 'RhCl(CO)$_2$' fragments coordinated to the sulfur atoms (Fig. 25). In addition, two tetranuclear units are associated in a dimer through four intermolecular hydrogen bonds. This association occurs even in solution, where the two species can be observed spectroscopically. The equilibrium constant for the dissociation fits a linear plot of $\ln(K_{eq})$ versus $1/T$, which gives: $\Delta H = 43.3$ kJ mol^{-1} and $\Delta S = 114.7$ J K^{-1} mol^{-1} [76].

5. Going to higher nuclearities

Polydentate bridging ligands containing multiple coordination sites generally produces low nuclearity complexes since the disposition of the donor atoms plays an important role both in the geometry and nuclearity of the resulting complexes.

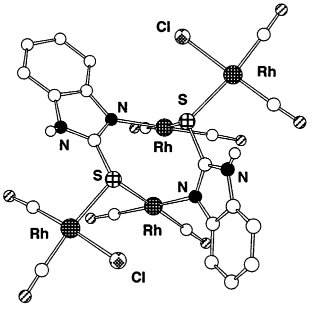


Fig. 25. Molecular structure of $[Rh_4(\mu\text{-Hbzimt})_2Cl_2(CO)_8]$.

However, high nuclearity complexes have been recently obtained using the pentadentate ligand *N*,*N*′-bis(2′-pyridyl)-2,6-diaminopyridine (bpda). The disposition of the nitrogen-donor atoms in the ligand allows the stabilisation of linear cobalt and nickel pentametallic chains in the complexes $[Co_5(\mu_5\text{-bpda})_4(NCS)_2]$ and $[Ni_5(\mu_5\text{-bpda})_4Cl_2]$ [77]. However, increasing the number of donor atoms might not be necessary to get higher nuclearity. Following our stepwise synthetic approach to polynuclear complexes, we have also succeeded in the preparation of high nuclearity complexes. Thus, the tetranuclear complexes $[M_4(\mu_4\text{-PyS}_2)_2(COD)_4]$ (M = Rh, Ir) and $[Rh_4(\mu\text{-Hbzimt})_2Cl_2(CO)_8]$ are convenient precursors for the synthesis of heteropentanuclear and hexanuclear complexes respectively.

The homotetranuclear rhodium and iridium complexes $[M_4(\mu_4\text{-PyS}_2)_2(COD)_4]$ (M = Rh, Ir) behave as encapsulating agents for the thallium(I) ion through the formation of cationic pentametallic species. Thus, the reaction of $[M_4(\mu_4\text{-PyS}_2)_2(COD)_4]$ with $TlPF_6$ gives the heterobimetallic complexes $[TlM_4(\mu_5\text{-PyS}_2)_2(COD)_4][PF_6]$ [78]. The cation $[TlRh_4(\mu_5\text{-PyS}_2)_2(COD)_4]^+$ consists of a boat shaped pentametallic chain supported by two 2,6-pyridinedithiolate groups acting as *S*,*N*,*S*′-tridentate ligands (Fig. 26). The 2,6-pyridinedithiolate ligands are bonded to the four rhodium atoms exclusively through the sulfur atoms which coordinate in a μ_2-fashion, i.e. as thiolate ligands. The structure shows an almost linear Rh–Tl–Rh bonded subunit with Tl–Rh separations of 2.7686(9) and 2.7706(9) Å, the unusual saw-horse coordination environment of the thallium atom is completed by binding to two pyridinic nitrogens.

The Tl(I) encapsulation seems to be determined by subtle electronic factors, and involves an important structural reorganization driven not only by multiple coordination possibilities of the doubly deprotonated 2,6-dimercaptopyridine ligands but also by the existence of d^8–s^2–d^8 bonding interactions which contribute to the stabilization of the structure. This interaction is supported by theoretical calculations although it can also be understood in terms of the '*metallophilic attraction*' between closed-shell metal cations [79]. Taking into account the structure of the precursor, the formation of $[TlRh_4(\mu_5\text{-PyS}_2)_2(COD)_4]^+$ could be envisaged as a structural reorganization process involving the breaking of the Rh–N bonds and formation of new Rh–S and Tl–N bonds (Fig. 27). In such a manner the molecular framework provides the proper spatial requirements to accommodate the Tl(I) atom, and the Rh–Tl and Rh–N bonds the necessary energetic stabilization.

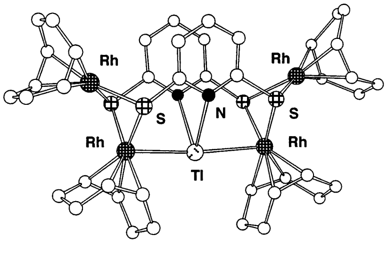


Fig. 26. Molecular structure of $[TlRh_4(\mu_5\text{-PyS}_2)_2(COD)_4]^+$.

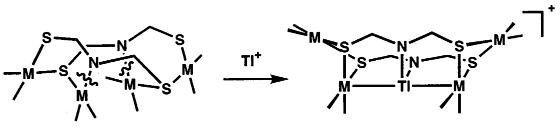


Fig. 27. Framework reorganization leading to the encapsulation of Tl$^+$ into the $[M_4(\mu_5\text{-}PyS_2)_2(COD)_4]$ tetranuclear structures.

The complex $[Rh_4(\mu\text{-}Hbzimt)_2Cl_2(CO)_8]$ still has two acidic hydrogens which can be abstracted by basic rhodium compounds to produce high nuclearity clusters [76]. Thus, the deprotonation of $[Rh_4(\mu\text{-}Hbzimt)_2Cl_2(CO)_8]$ with $[Rh_2(\mu\text{-}OMe)_2(COD)_2]$ gives the hexanuclear complex $[Rh_6(\mu\text{-}bzimt)_2(\mu\text{-}Cl)_2(COD)_2(CO)_8]$. The molecular structure of the complex (Fig. 28) shows the ability of the dideprotonated bzimt^{2-} ligands to interact with four metallic centres acting as a tridentade ligand. Each ligand is bridging two rhodium atoms through the sulfur atom and is bound to two other rhodium atoms through both deprotonated nitrogen atoms. Both complexes show identical conformation of the eight-membered 'HT-$Rh_2(\mu\text{-}(1\kappa N, 2\kappa S)\text{-}bzimt)_2$' metallacycle and identical configuration of the sulfur atoms. However, the molecular structure shows the coordination of the incoming 'Rh(COD)' fragments to the sulfur donor atoms instead of to the deprotonated nitrogen atoms.

A rationalization for the formation of the hexanuclear complex is as follows. The deprotonation of $[Rh_4(\mu\text{-}Hbzimt)_2Cl_2(CO)_8]$ leads to migration of the '$Rh(CO)_2Cl$' fragment bonded to the sulfur to the adjacent nitrogen in a first step. This sulfur then coordinates the 'Rh(COD)(MeOH)' fragment formed in the deprotonation. A further replacement of the coordinated methanol by the chloro ligand renders the compound as a single isomer. This process provides further evidence for the mobility of the metal fragments in the tetranuclear complexes owing to the presence of acidic hydrogens, the conformational nonrigidity of the eight-membered 'HT-$Rh_2(\mu\text{-}(1\kappa N,2\kappa S)\text{-}bzimt)_2$', and the presence of potentially bridging donor atoms such as chlorine and sulfur atoms.

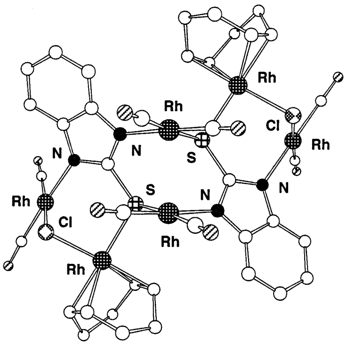


Fig. 28. Molecular structure of $[Rh_6(\mu\text{-}bzimt)_2(\mu\text{-}Cl)_2(COD)_2(CO)_8]$.

6. Additional comments on oxidative-addition reactions of low nuclearity rhodium and iridium complexes.

One aspect of the structural interest in the dinuclear complexes with anionic N–C–X ligands concerns the effects of these ligands, which incorporate three atoms in the bridge, on the tilt of the coordination planes, studied by Cowie [80], and on the rigidity of these systems. Closely related with this tilt and with the electronic density on the metals is their reactivity with small molecules and their photochemical properties. The effect of a larger tilt, when compared with systems incorporating two pyrazolate and thiolate ligands, on the subsequent chemistry has already been mentioned in Section 2.2 for quite rigid complexes with 7-azaindolate ligands as bridges. Such a tilt could hinder the access by molecules of the substrate to the bridging site between the metals. However, what is not so clear is the importance of an initial attack between the metals in dinuclear complexes. Moreover, this attack may easily take place at the *exo* vacant coordination side of the complex. Furthermore, for complexes with 2-pyridonate and pyridine-2-thiolate a subsequent rearrangement can occur due to the flexibility of the bridging system allowed by a sliding of the coordination planes.

The rhodium and iridium complexes with bridging N–C–S ligands behave in quite a different way in dinuclear oxidative-addition reactions. For both elements the anionic ligands confer properties of electron-rich metal centres to the complexes, which undergo facile oxidation reactions, exemplified by their reactions with iodine. Typically, the rhodium complexes are oxidized to the corresponding Rh(III)–Rh(III) species whereas identical reactions for iridium end with the formation of the diiridium(II) compounds possessing a metal–metal bond. Moreover, the reactions with iridium are highly photosensitive while those for rhodium are not noticeable photosensitive.

Iodomethane adds to $[Rh_2(\mu\text{-N–C–S})_2(CO)_2L_2]$ ($L = CO$ or PPh_3) affording the diacetyl complexes $[Rh_2(\mu\text{-N–C–S})_2(COMe)_2(I)_2L_2]$ as a result of the addition of one MeI molecule to each metal followed by migratory insertion [51,81]. An unusual change in the coordination mode of the bridging ligands from binucleating μ-1κN, 2κS to μ-1κN, 1:2κS accompanies this reaction. The crystal structure of the complex $[Rh_2(\mu\text{-bztat})_2(COMe)_2(I)_2(PPh_3)_2]$ (Fig. 29) shows the rare coordination mode μ-1κN, 1:2κS of the bridging ligands consisting of the bond through the exocyclic sulfur atoms to both rhodium atoms while the azolate nitrogen maintains a weak bonding interaction with one of the metals [81]. This compound exists in solution as a mixture of two species, most probably the dinuclear and one mononuclear complex resulting from the breaking of the sufur bridges.

Comparison of the double oxidative-addition and insertion reactions of MeI to the complexes $[Rh_2(\mu\text{-N–C–S})_2(CO)_2L_2]$ with the deactivation after the single addition of MeI at the thiolate complex $[Rh_2(\mu\text{-SBu}^t)_2(CO)(PMe_2Ph)_2]$ [82] indicates a higher reactivity of the former, which could be associated with the switch between different coordination modes along with the presence of a second donor atom, rendering a high flexibility to the doubly bridging N–C–S system.

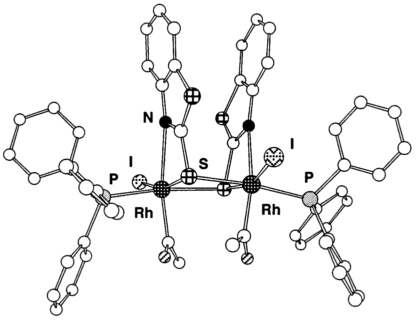


Fig. 29. Molecular structure of [Rh_2(μ-bztat)$_2$(COMe)$_2$(I)$_2$(PPh$_3$)$_2$].

The reaction of [Rh_2(μ-bztat)$_2$(CO)$_2$(PPh$_3$)$_2$] with iodine gives an insoluble solid formulated as the rhodium(III) complex [Rh(bztat)(I)$_2$(CO)(PPh$_3$)]. In contrast, the reactions of [Ir_2(μ-S–C–N)$_2$(CO)$_4$] with iodine, iodomethane or diiodomethene give diiridium(II) complexes. These reactions with [Ir_2(μ-PyS)$_2$(CO)$_4$] require sunlight irradiation to rapidly give the complexes [Ir_2(μ-PyS)$_2$(I)(X)(CO)$_4$] (X = I, CH_3 or CH_2I), otherwise, they require long reaction times in the dark [54]. The structure of the iodo-iodomethyl complex [Ir_2(μ-PyS)$_2$(I)(ICH$_2$)(CO)$_4$] (Fig. 30) shows two iridium atoms bridged by two pyridine-2-thiolate ligands in a head-to-tail disposition at a distance of 2.695(2)Å, corresponding to an Ir–Ir bond.

Although the above iodomethyl complex remains unaltered, even under reflux in toluene, the related iodomethylpyrazolate complex [Ir_2(μ-Pz)$_2$(I)(CH$_2$I)-(CO)$_2$(PPh$_3$)$_2$] undergoes an oxidative-isomerization [31] to the corresponding methylene-bridged diiridium(III) complex [Ir_2(μ-Pz)$_2$(μ-CH$_2$)(I)$_2$(CO)$_2$(PPh$_3$)$_2$]. This lack of reaction suggests that the iodomethyl ligand, *trans* to the metal–metal bond in this complex, is unable to access the bridging position between the iridium atoms, most probably because of the strength of the metal–metal bond.

The reaction of the complex [Ir_2(μ-bztat)$_2$(CO)$_4$] with iodine gives outstanding information on dinuclear oxidative-addition reactions. An intermediate in this reaction is the tetranuclear complex [Ir_4(μ-bztat)$_4$(I)$_2$(CO)$_8$], isolated as a dichroic golden-green or purple solid, in high yield, if the reaction is carried out in toluene.

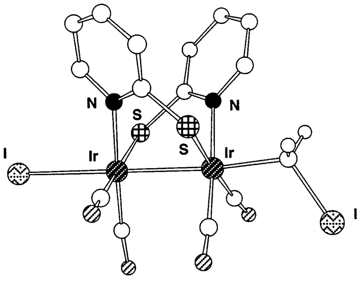


Fig. 30. Molecular structure of [Ir_2(μ-PyS)$_2$(I)(ICH$_2$)(CO)$_4$].

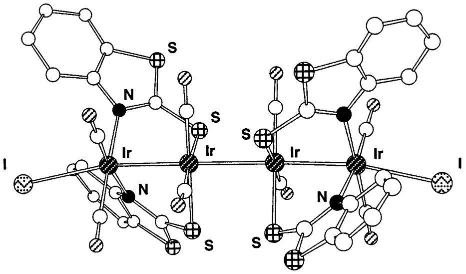


Fig. 31. Molecular structure of $[Ir_4(\mu\text{-bztat})_4(I)_2(CO)_8]$.

A further reaction of $[Ir_4(\mu\text{-bztat})_4(I)_2(CO)_8]$ with iodine requires exposure to sunlight affording the diiridium (II) complex $[Ir_2(\mu\text{-bztat})_2(I)_2(CO)_4]$ [55]. The dinuclear complex is the single product if the reaction is carried out in a solvent such as dichloromethane under sunlight irradiation. The structure of the unique mixed-valent tetranuclear cluster $[Ir_4(\mu\text{-bztat})_4(I)_2(CO)_8]$ (Fig. 31) shows an almost linear chain of three Ir–Ir bonds formed by two dinuclear units connected through an unsupported metal–metal bond. In the dinuclear units two benzothiazole-2-thiolate ligands bridge the metals in a *cis* and head-to-head disposition with the S atoms bonded to the inner iridium in the chain and the N atoms to the outer iridium. On the other hand, this compound is the first precedent of a new family of iridium blues, closely related to the well known platinum blues [83,84].

Regarding the reaction, the structure of the tetranuclear complex suggests that iodine attacks one of the metal centres in the parent dinuclear iridium complex to give presumably the radical complex $[Ir_2(\mu\text{-bztat})_2I(CO)_4]^\bullet$ having an Ir–Ir bond, which dimerizes rapidly. Isomerization from the HT to the HH disposition of the bridging ligands occurs in the formation of the tetranuclear complex and from HH to HT in the further reaction of this compound with iodine to give the diiridium(II) complex $[Ir_2(\mu\text{-bztat})_2I_2(CO)_4]$ (Ir–Ir: 2.676(2)Å) (Fig. 32).

The isolation of the linear tetrametallic complex in a dinuclear oxidative-addition reaction poses the question as to whether tetranuclear species are frequent intermediates in this type of reactions.

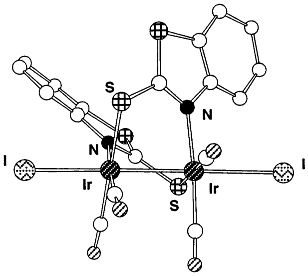


Fig. 32. Molecular structure of $[Ir_2(\mu\text{-bztat})_2I_2(CO)_4]$.

7. Concluding remarks

N-based bridging ligands containing the N–C–X (X = N, O, S) groups have been proven to be adequate supporting ligands for the controlled synthesis of low nuclearity rhodium and iridium complexes, maintaining the metal centres in close proximity. The geometric and electronic characteristics of these N-based ligands allow the incorporation of a wide variety of additional metals and permit the preparation of several types of polynuclear complexes which frequently exhibit unusual architectures and chemical reactivities. The above mentioned stepwise construction of mono- di- tri- tetra- and hexa-nuclear complexes, by using benzimidazole-2-thiol and diprotonated ligands, is a representative example of the potential of these synthetic approaches. Polynuclear building blocks such as the homotetranuclear complexes $[M_4(\mu_4\text{-}PyS_2)_2(\text{diolefin})_4]$ should be capable not only of encapsulating single metals such as thallium(I), but should also be appropriate starting blocks for the preparation of polynuclear complexes containing selected transition metals as connectors. Finally, application of metallophilic attraction concepts should also be useful for the design of novel heteropolynuclear complexes. We anticipate that new types of polynuclear complexes, with unusual properties, will be found through further study of the coordination chemistry of N–C–X ligands. A full exploration of the mentioned preparative strategies towards transition metals is waiting for further development.

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