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Phosphine-pyridyl and related ligands in synthesis and catalysis

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Contents

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Abstract

This review summarizes the advances produced in the last 5 years in the use of mixed ligands containing at least one phosphino and one pyridyl or related group (bipyridyl, quinolyl, etc.) bonded to the same or different metals. In this period the publications have doubled since the last review on this topic. The present paper covers the structural applications of these ligands, and also the catalytic applications of the complexes produced with them.

Keywords: Hemilabile ligands; Phosphine; Pyridine; Catalysis; Transition metals

1. Introduction

Some years ago Rauchfuss introduced the concept of *hemilabile* for ligands possessing a combination of soft and hard donor atoms [1]. This term was originally used for phosphine–amine and phosphine–ether ligands that 'would bind well enough to permit isolation but would readily dissociate the hard end component, thus generating a vacant site for substrate binding'. Since then, there has been an increasing interest in the synthesis and use of this kind of ligand, as the different features associated with each donor atom confer unique reactivity to their metal complexes [2].

One important property of these potentially multidentate ligands is that they can stabilize metal ions in a variety of oxidation states and geometry. Moreover, the hard ends are weakly coordinated to soft metal centers and can be easily dissociated in solution, affording a vacant site whenever demanded, whereas their chelate effect confers stability to the catalyst precursor in the absence of substrate. This kind of versatility is of interest both in basic research and for applications (catalysis).

A distinguished family of hemilabile ligands is that combining phosphorus and nitrogen atoms. These ligands can display quite different coordination modes compared to the P–P or N–N ligands. The π-acceptor character of the phosphorous ligand can stabilize a metal center in a low oxidation state, while the nitrogen σ-donor ability makes the metal more susceptible to oxidative addition reactions. This can help to stabilize intermediate oxidation states or geometries during a catalytic cycle.

Very recently attention has been focused on P–N chiral ligands: they have been used very successfully in asymmetric catalytic reactions such as allylic substitution [3], hydrosilylation [4], hydroboration of olefins [5], and hydrogen transfer on ketones [6]. The reason for their good performance is twofold: steric factors, but also the electronic asymmetry induced by the presence of very different donor atoms on the metal (Faller has called this *electronic differentiation* [7]).

On the other hand, polydentate ligands having both hard and soft donors are excellent candidates for the preparation of heterobimetallic compounds containing a hard and a soft metal center. Compounds comprised of more than one metal center in close proximity might exhibit different properties, compared to the monometallic fragments that constitute them: cooperative reactivity patterns, stabilization of unusual ligand coordination modes, higher catalytic activity or different selectivity than the corresponding mononuclear moieties [8].

The number of publications in this area has been increasing very quickly, which makes it necessary to update the reviews which are available. One very representative and most widely used group of heterofunctional phosphines is that of pyridylphosphines, which have been reviewed twice before. One review is more general [9], and the other treats the chemistry of the metal complexes of 2-(diphenylphosphino)pyridine [10] exclusively, but both cover the literature only until 1993. In the last 5 years the number of publications which have appeared is comparable to those which appeared up to 1993.

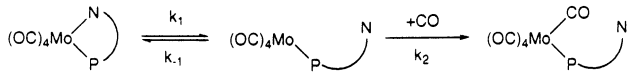
Thus the present review will focus on the structure, reactivity and catalytic behavior of complexes containing P–N ligands, N being included in a pyridine ring. Those already mentioned in the previous reviews are not commented here. Moreover we will limit ourselves to the presentation of the complexes where at least one P and one N simultaneously play an active role, permanently or at some point of a reaction sequence. The material is organized according to a few dominant structural types, as shown in the content index, trying to keep an order of increasing size of the spacer between the P and the N donor. As far as possible, the compounds are grouped by the ligand. The most common ligands are highlighted in bold type the first time they appear, in order to help for a fast search of each section. For short the most common 2-pyridyl group will be represented as **Py**. P–N ligands where N is not coming from a pyridyl group will be presented in forthcoming reviews. The figures are adapted from the corresponding references given in the text. This review covers the literature appearing up to September–October 1998.

2. Mononuclear complexes

The formation of complexes where the P–N ligand acts as chelate depends very much on the stability of the chelate ring formed. In general four-membered rings are strained, whereas seven- or longer membered rings are not so much geometrically favored, so five- and six-membered chelates are expected to be the best. This is very well exemplified by the rates of dissociative substitution (involving a ring-opening preequilibrium) in $[Mo(CO)_4(P–N)]$ for the phosphines Ph_2PNHPy, Ph_2PCH_2Py, $Ph_2P(CH_2)_2Py$ or $Ph_2P(CH_2)_3Py$ [11]. The reaction rates increase with increasing size of chelate ring (Scheme 1).

2.1. Compounds with non-asymmetric ligands

The ligand 2-(diphenylphosphino)pyridine (**PPh_2Py**), although better suited to



Scheme 1.

bridge two metal centers (see Section 3), also has the ability to form stable four-membered chelate rings with a metal.

[Mo(η^3-allyl)Br(CO)$_2$(PPh$_n$Py$_{3-n}$-P,N)] ($n = 1, 2$) were synthesized as racemic mixtures by substitution of MeCN by PPy$_{3-n}$ in [Mo(η^3-allyl)Br(CO)$_2$(NCMe)$_2$] [12]. These chiral complexes undergo racemization in solution via a novel 'pivoted double switch' mechanism in which the P atom always remains coordinated *trans* to the allyl group, whereas the bromo ligand exchanges its equatorial position with an uncoordinated pyridyl arm (Scheme 2).

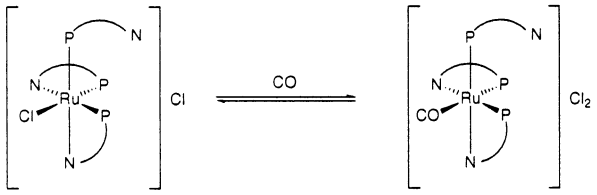
The reaction between [TcCl$_2$(NO)Cl$_4$](Bu$_4$N) and a 3-fold excess of PPh$_2$Py yields a Tc(I) neutral complex [TcCl$_2$(NO)(PPh$_2$Py-P,N)(PPh$_2$Py-P)] which was characterized by X-ray analysis [13]. In this complex, one phosphine is monodentate (through P), while the other is bidentate.

The complex *cis*-[Fe(CO)$_2$(PPh$_2$Py-P,N)$_2$][ClO$_4$]$_2$ has been prepared by reaction of *trans*-[Fe(CO)$_3$(PPh$_2$Py)$_2$] with Fe(ClO$_4$)$_3$ [14]. This Fe(II) cationic complex is formed by the oxidation of Fe(0) by Fe(III), and is the first example of a first row transition metal complex with two planar four-membered rings involving P and N donor atoms. Its X-ray structure has been determined.

The reaction of [RuCl$_2$(cod)]$_n$, (**cod** = 1,5-cyclooctadiene) with PPh$_2$Py (1:3) affords the first example of a mononuclear complex with three short bite ligands, although only two are chelating, as shown in Scheme 3 [15]. By bubbling CO, an equilibrium is established with a dicationic complex which has not been isolated. Upon standing in a solution of chlorinated solvents the complex is converted into the neutral [Ru(PPh$_2$Py)$_2$Cl$_2$], the structure of which has been determined by X-ray diffraction.

The isoelectronic neutral compounds [(η^6-C$_6$H$_6$)Ru(PPh$_2$Py)Cl$_2$] and [(η^5-C$_5$Me$_5$)Rh(PPh$_2$Py)Cl$_2$] contain a monodentate P-coordinated ligand, as found in the crystal structure of the Rh compound. Upon treatment with AgPF$_6$ (1:1) one chloride is removed and the cationic compounds [(η^6-C$_6$H$_6$)Ru(PPh$_2$Py)Cl]PF$_6$ and [(η^5-C$_5$Me$_5$)Rh(PPh$_2$Py)Cl]PF$_6$, where PPh$_2$Py is P, N coordinated, are obtained [16].

Scheme 2.



Scheme 3.

The synthesis, characterization and reactivity of Ru(II) complexes containing P,N,N′ coordinated ligands of the general type $PPh_{3-n}Py_n$ ($n = 2,3$), including the X-ray crystal structures of $[RuCl(PPh_3)_2(PPh_{3-n}Py_n\text{-}P,N,N')]PF_6$ ($x = 2, 3$), have been reported recently [17]. This coordination mode was previously unknown for 2-pyridylphosphines. The structure of $[RuCl(PPh_3)_2(PPhPy_2\text{-}P,N,N')]PF_6$ is depicted in Fig. 1. This highly strained coordination mode tends to release the strain. Thus chloride or CO reversibly displace one coordinated pyridyl arm. No evidence of decoordination of the second pyridyl group was found. A relative ordering of π-acceptor ability is established, through the carbonyl compounds synthesized.

The preparation of PPh_2Py–Ru complexes incorporating an unprecedented three-center dihydrogen bond (Ru–H···HPy_2) has very recently been reported [18]. The reactions and equilibria between the existent Ru species are outlined in Scheme 4. The complexes 4-**1** and 4-**2** are obtained by reaction of three equivalents of PPh_2Py with $[RuCl_2(bpzm)(cod)]$ or [RuClH(bpzm)(cod)], respectively (**bpzm** = bis(pyrazol-1-yl)methane). Complex 4-**2** exists as two isomers *fac* and *mer* in equilibrium. Addition to 4-**2** of three equivalents of CF_3COOH transforms both isomers to 4-**3**. Only one proton has been transferred to 4-**3** from CF_3COOH. This proton is in fast exchange between the two dangling pyridyl arms and there is also

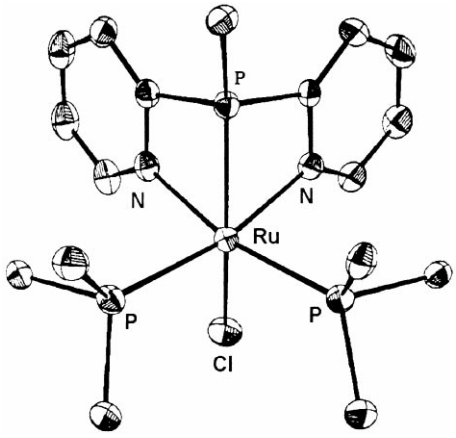
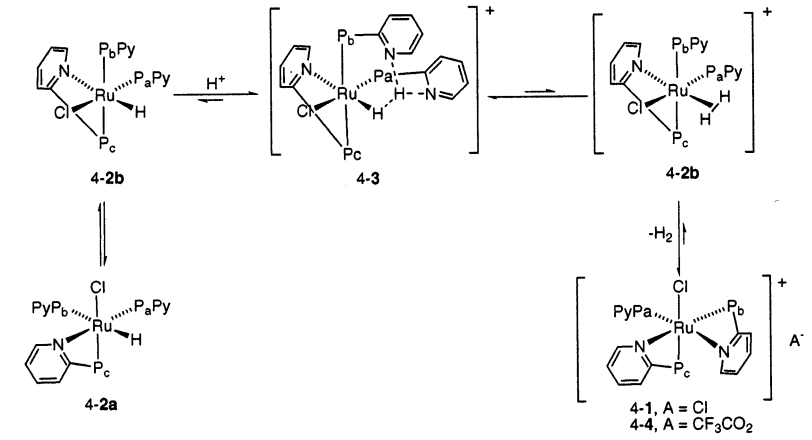


Fig. 1.



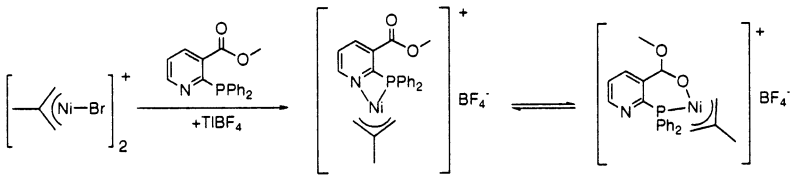
Scheme 4.

exchange between the hydride and the pyridinium proton. Above room temperature H_2 is lost and 4-**3** converts to 4-**4**. The complex 4-**2b** (but not 4-**2a**) is very active in the D^+-H_2 interchange process.

A ligand analogous to PPh_2Py is 2-(dimethylphosphino)pyridine (**PMe_2Py**). The first example of PMe_2Py acting as a chelating ligand was reported in 1990 [19]. The four-membered chelate ring in the complexes $[PdX(PMe_2Py)_2]Y$, (X = Cl, Br, I; $Y = ClO_4$, PF_6) was confirmed by X-ray analysis of one (X = Cl; $Y = ClO_4$). One of the phosphines is P,N chelated, while the other is monocoordinated through P. The crystal structure of a neutral Pd complex with two ligands coordinated through P is also reported.

The potentially P,N,O ligand methyl **2-(diphenylphosphino)nicotinate** was synthesized and used for the preparation of a cationic nickel complex [20]. The X-ray structure of this complex surprisingly revealed a four-membered chelate ring with P,N coordination instead of the expected P,O coordination [20b]. It seems that preferred coordination of N in respect to O counterbalances the ring strain. In solution an equilibrium between the P,N and P,O chelated complexes takes place (Scheme 5).

Five-membered chelate rings are usually obtained using P,N ligands derived from 8-phosphinoquinoline, or phosphines linked to a 2-pyridyl group through a



Scheme 5.

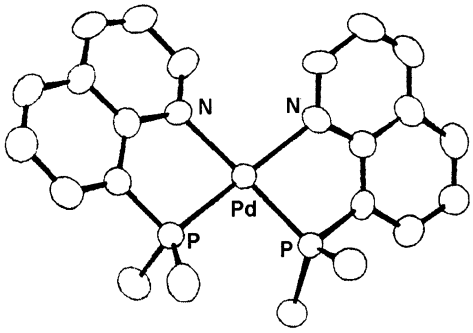


Fig. 2.

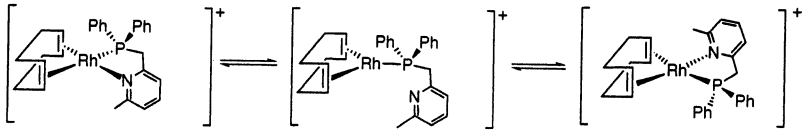
methylene unit. The first report on chelated complexes of 8-(diphenylphosphino)quinoline **(PQN)** just mentioned the preparation of two complexes of the type $[MBr_2(PQN)_2]$ (M = Co, Ni) [21].

The complexes $[Pd(PN)_2](BF_4)_2$ (PN = PQN, **PePy**; PePy = 1-(diphenylphosphino)-2-(2-pyridyl)ethane) were prepared from $[Pd(CH_3CN)_4](BF_4)_2$ [22] and characterized by IR, ^1H, and $^{31}P\{^1H\}$. The ligands are chelated in both cases. The PQN complex adopts a *cis* conformation.

The reactions of PQN with Ru(II), Rh(III), Pd(II) and Pt(II) have also been investigated together with other N–N and N–As ligands [23]. The structure of the compounds has been proposed on the basis of IR spectra, magnetic moments and conductivity measurements. The reaction with $[RuCl_2(Me_2SO)_4]$ did not afford any Ru–(PQN) complex. The reaction with $RhCl_3{\cdot}3H_2O$ yielded a paramagnetic Rh(II) square-planar complex $[RhCl_2(PQN)]$ ($\mu_{eff} = 2.17\ \mu_B$). This behavior is attributed to a compromise between the tendency of P to stabilize the +1 oxidation state and that of N to stabilize the +3 oxidation state. For the same reasons the Rh(I) anion $[RhCl_2(CO)_2]^-$ affords a diamagnetic Rh(II) dimer $[RhCl_2(PQN)(CO)]_2$. Pd and Pt yielded the expected $[MCl_2(P–N)]$ compounds.

The synthesis and coordination behavior of 8-(dimethylphosphino)quinoline (**Me_2PQN**) with Pd(II), and the X-ray structure of the cationic complex *cis* $[Pd(Me_2PQN)_2](BF_4)_2$ have been reported (Fig. 2) [24]. Binuclear compounds have also been reported (see Section 3).

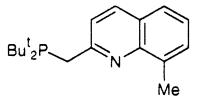
Recently the ligand **2-methyl-6-((diphenylphosphino)methyl)pyridine** was prepared together with other asymmetric ligands [25]. Its reaction with $[Rh(cod)(thf)_2][BF_4]$ results in the formation of a major compound $[Rh(cod)(P,N)][BF_4]$, fluxional in solution. The ^1H-NMR and $^{31}P\{^1H\}$-NMR spectra reveal that a reversible opening



Scheme 6.

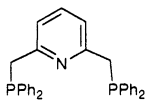
of the Rh–N bond is occurring, as shown in Scheme 6. The X-ray structure of the complex [Rh(cod)(P,N)][BF_4] was solved.

The coordination chemistry of the ligand (8-methyl-2-quinolylmethyl)di-*t*-butylphosphine (**MQP**), (1), has been reported by Deeming et al. [26]. The ligand displays P-monodentate (as in [$PdCl_2(MQP)_2$]), and bidentate (as in [$PdCl_2(MQP)$]) coordinations. It can also be 3-metallated. The crystal structure of [$PdCl_2(MQP)$] reveals some distortions in respect to the square planar ideal geometry because of the steric hindrance of the methyl group in the plane. This favors easy decoordination of the quinolyl moiety. In the complex [RhCl(CO)(MQP)] the ligand is also chelated with CO *cis* to the P atom. These chelated compounds take part in a number of reactions and equilibria that involve mono-coordinated or dimeric species (see Section 3).



(1)

The terdentate ligand 2,6-bis(diphenylphosphinomethyl)pyridine (**PNP**) (2) has been used for the preparation of complexes [$M(PNP)X_2$] (M = Fe(II), Co(II), Ni(II); X = Br, I, NCS) [27]. The compounds were characterized by IR and UV–vis spectroscopy, conductivity and magnetic susceptibility measurements, and distorted square-pyramidal structures were proposed for all of them. The Fe complexes are high-spin in all temperature ranges studied, whereas Co and Ni change depending on the temperature. For the Ni complexes a low-spin↔high-spin equilibrium was proposed.



(2)

The cationic complexes [Rh(PNP)(olefin)]BF_4 (olefin = ethylene, styrene) have been reported and their X-ray crystal structures studied [28]. The former reacts with LiR to give the corresponding [RhR(PNP)] (R = Me, Ph) [29]. With secondary amines and in the presence of excess ethylene an equilibrium is established with the [$Rh(PNP)(HNR_2)$]BF_4 complex, and nucleophilic attack of the amine to the coordinated olefin is not observed. This attack is, however, observed in the similar dicationic [Pd(PNP)(olefin)]$(BF_4)_2$ (olefin = ethylene, styrene), where the olefin is more activated, to give [$Pd(PNP)(CHR'CH_2NR_2)$](BF_4). The dicationic olefin complexes, the X-ray structure of one of which is reported, are remarkable for the stability of an olefin complex in a highly charged complex. It is suggested that steric protection by the PNP ligand might have a role in this stabilization [30]. The X-ray structure of [Rh(PNP)ClH(MeCN)]SO_3CF_3, obtained by the reaction of [RhCl(PNP)] with HSO_3CF_3, has also been reported (Fig. 3) [29].

The ligand PePy is the most common among those making six-membered cycles. It was used long ago for the preparation of Ni(II), Co(II), and Zn(II) tetrahedral 1,1-complexes. Cu(I) complexes were also prepared [31].

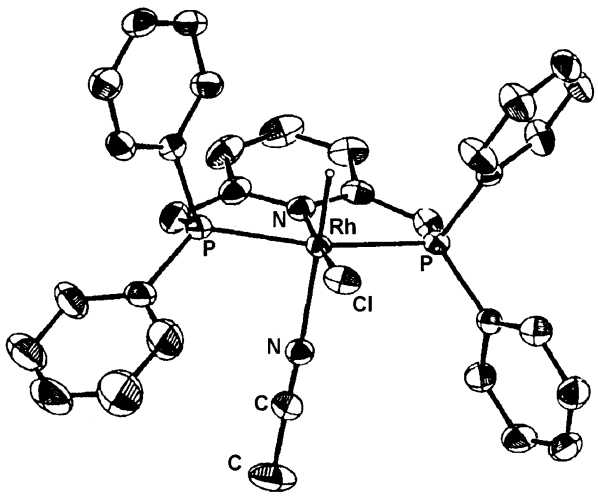
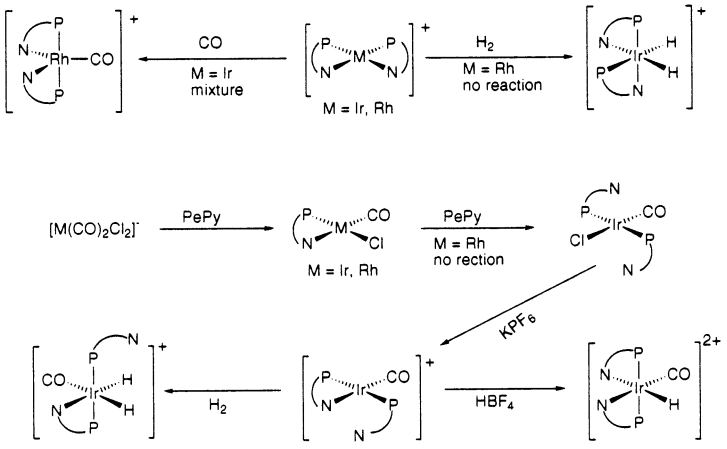


Fig. 3.

Nickel cyanide complexes of the type $[Ni(CN)_2(PePy)_2]$ can be four or five-coordinated [32]. In the five-coordinated compounds both P,N chelated and P monocoordinated ligands exist, while in the four-coordinated the ligand is P-monodentate.

The solution behavior of Ru (II) [33] and Os (II) [34] with PePy has been investigated by $^{31}P\{^1H\}$-, $^{13}C\{^1H\}$-NMR, UV–vis spectroscopy and conductivity measurements. Reaction of the $[MX_2(PePy\text{-}P,N)_2]$ species (M = Ru, X = Cl, Br, I; M = Os, X = Cl, Br) with CO in low polarity solvents yields neutral carbonyl compounds $[MX_2(CO)(PePy\text{-}P)(PePy\text{-}P,N)]$ by rupture of one M–N bond. The second pyridyl arm is not displaced by CO. In polar solvents halide dissociation from $[MX_2(PePy\text{-}P,N)_2]$ is favored. This results in five-coordinate cations $[MX(PePy\text{-}P,N)_2]^+$, in equilibrium with hexacoordinated X-bridged dimers. Its reaction with CO gives hexacoordinated cationic monocarbonyls. The kinetic products, in which the P atom is *trans* to CO, are converted at room temperature to the thermodynamic ones in which the P atoms are *cis* to CO. The chemistry of the Os(II) complexes of PePy closely parallels that of Ru(II). The rates of isomerization of Os complexes are slower than for the corresponding Ru. Some compounds were characterized by X-ray diffraction.

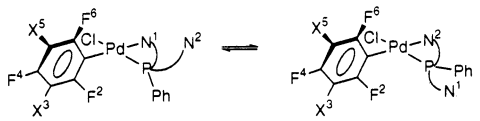
The cationic Ir(I) complex $[Ir(PePy)(cod)]PF_6$ [35] and other Rh and Ir complexes [36] have been reported. The structure of [Ir(PePy)(CO)Cl] was determined by X-ray analysis. The compound is a slightly distorted square-planar complex in which both P and N are coordinated. The π-acceptor ligands, CO and P are positioned *trans* to the σ-donors, the N atom being *trans* to CO. The single crystal X-ray analysis of the square-planar $[Rh(PePy)_2]BF_4$ revealed a *cis* bis-chelate structure. The reactivity pattern and interconversions of these compounds are presented in Scheme 7.



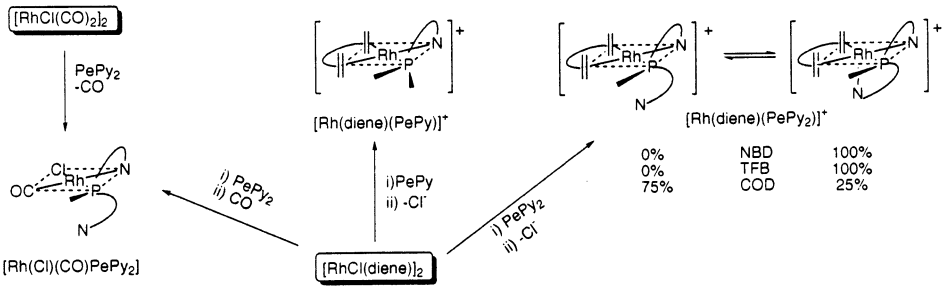
Scheme 7.

The ligands PePy, $P(CH_2CH_2Py)_2Ph$, (**PePy$_2$**) and $P(CH_2CH_2Py)_3$, (**PePy$_3$**) yielded neutral mononuclear compounds of the general type $[PdRCl(PePy_n)]$ upon reaction with the dimeric Pd compounds $[Pd_2(\mu\text{-}Cl)_2(R)_2(tht)_2]$, $R = C_6F_5$, $C_6Cl_2F_3$; tht = tetrahydrothiophene) [37]. In all these complexes the ligands act as P,N chelates with the P coordinated *cis* to the fluoroaryl ring. Their dynamic behavior in solution was studied by ^{1}H-, $^{31}P\{^1H\}$-, and ^{19}F-NMR spectroscopy. The PePy compounds undergo a conformational inversion of the six-membered metallacycle formed by the chelating ligand, without N decoordination. The $PePy_2$ and $PePy_3$ compounds show exchange between the free and coordinated pyridyl arms (Scheme 8).

Several complexes $[RhCl(CO)(PePy_2)]$, $[Rh(diene)(PePy_2)]^+$ and $[Rh(diene)(PePy)]^+$ (diene = norbornadiene (NBD), tetrafluorobenzobarrelene (TFB) or cyclooctadiene (cod)) have been prepared and studied by NMR spectroscopy [38]. The ligands act as bidentate or tridentate P,N-chelating ligands and in solution the complexes adopt square-planar and trigonal-bipyramidal geometries. The complex $[Rh(diene)(PePy_2)]^+$ exists in solution as a mixture of isomers, one square-planar and one pentacoordinated. The exchange between them has been studied. The general reaction pattern is shown in Scheme 9. The ancillary ligands, as well as the charge of the complex determine which species is more stable between the four- and the five-coordinated. The five-coordinated is favored in the order NBD > TFB > cod. Three independent movements can be seen: (a) rotation of the olefin (fast); (b)



Scheme 8.



Scheme 9.

exchange between the free and coordinated pyridyl arms (associative); (c) inversion of the chelate ring conformation. The X-ray structure of the complex $[Rh(NBD)(PePy_2)](BF_4)$ has been studied and is shown in Fig. 4.

The bis-chelate Cu(I) and Ag(I) complexes $[M(PePy)_2]PF_6$ have been prepared [39]. The cation rearranges in solution by inversion at the tetrahedral metal center as shown by variable temperature NMR experiments. Au(I) forms a complex with two ligands mono-coordinated, which has been determined by X-rays.

A number of P,N ligands with terminal 2-pyridyl groups have been synthesized and used in reactions with Ni(II), Pd(II) and Pt(II) [40]. The phosphines are of the type $Py(CH_2)_2P(R')(CH_2)_mPR_2$, **(PPN)**, $Py(CH_2)_2P[(CH_2)_mPR_2]_2$ **(PPPN)** and $(CH_2)m[P(R')(CH_2)_2Py]_2$ **(PPNN)**. Some of the PPN ligands form square planar Ni(II), Pd(II) and Pt(II) compounds $[MX_2(PPN)]$ in which the coordinated P is chiral (Scheme 10, complexes 10-**1**). The PPPN ligands form cationic square-pyramidal complexes [MX(PPPN)]X, (M = Ni, Pd; X = Cl, Br) (3, complexes **2**). The X-ray structure of the complex [NiBr(PPPN)]Cl has been determined. The ligand

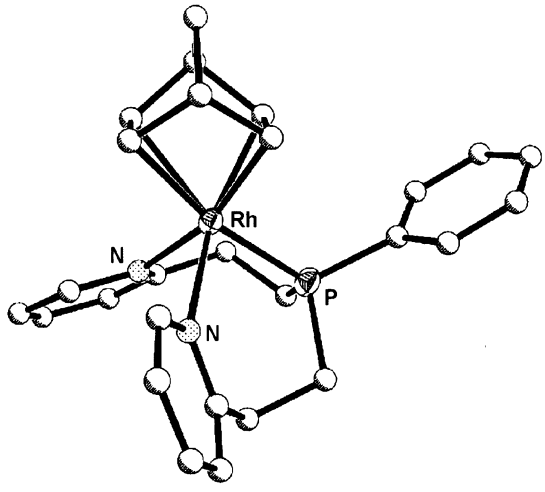
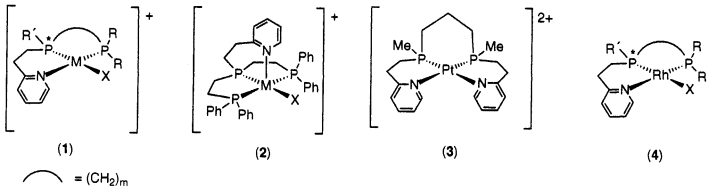


Fig. 4.

PPNN forms Ni, Pd and Pt complexes of the type $[MX_2(PPNN)]$ (M = Ni, X = Br; M = Pd, Pt, X = Cl), which for Pd and Pt exhibit dynamic behavior in solution, due to Py exchange. Halogen abstraction from the Pt compound results in the tetracoordination of the ligand (3, complex **3**). With $[RhCl(cod)]_2$ the PPN ligands yield products [RhCl(PPN)] (3, complexes **4**), and the structure of one of them has been determined by X-ray crystallography.

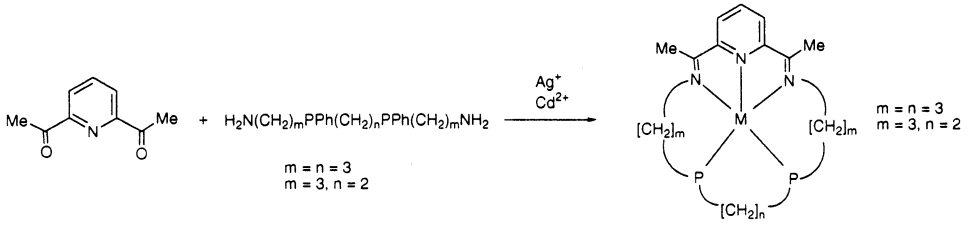


(3)

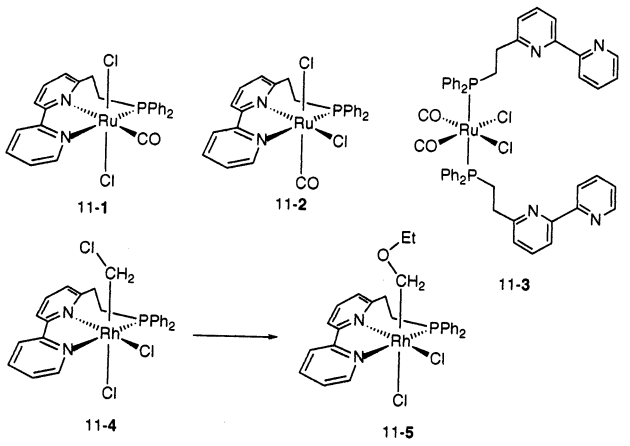
Phosphorus–nitrogen macrocycles have been synthesized through template synthesis (Scheme 10) [41]. It is assumed that all five atoms are coordinated to the metal, but the products are poorly characterized.

Three coordination modes were found for the tridentate ligand **6-(2-diphenylphosphinoethyl)-2-2′-bipyridine** (L) [42]. Tridentate-meridional coordination is observed for two Ru(II) complexes *trans*-Cl_2-$[RuCl_2(L)(CO)]$ (11-**1**) and *cis*-Cl_2-$[RuCl_2(L)(CO)]$(11-**2**), prepared from $[\{RuCl_2(CO)_2\}_n]$ in NEt_3/MeOH. The electrochemical properties of these compounds have been studied. An example of monodentate coordination is found in *cis*-Cl_2-*trans*-P,P-*cis*-$(CO)_2[RuCl_2(L)_2(CO)_2]$ (11-**3**), which can be regarded as a multisite metallo-synthon for the preparation of metallomacrocycles (Scheme 11). The X-ray structures of the complexes 11-**1** and 11-**3** have been determined. Reaction of the same ligand with $[\{RhCl(C_2H_4)_2\}_2]$ yields a Rh(I) intermediate which activates dichloromethane under ambient conditions to give 11-**4**. Chemical transformation of the coordinated CH_2Cl fragment to give 11-**5** happens with retention of the coordination (Scheme 11).

The multifunctional ligand ***N*-(2-diphenylphosphinobenzylidene)-2-(2-pyridyl)-ethylamine** has recently been synthesized together with its Pd and Pt complexes [43]. It is potentially tridentate and a tridentate coordination is found in ionic complexes of the type [(PNN)Pd(R)]Y (Scheme 12). CO insertion on the cationic [(PNN)PdMe]Cl (12-**1**) gives the neutral [(PNN)Pd(C(O)Me)Cl] where the ligand is coordinated in a bidentate mode through P and the imino N, with the

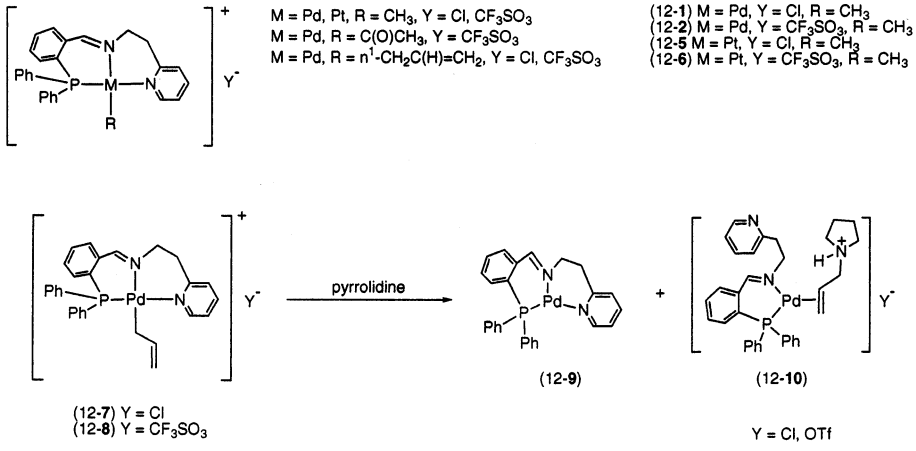


Scheme 10.



Scheme 11.

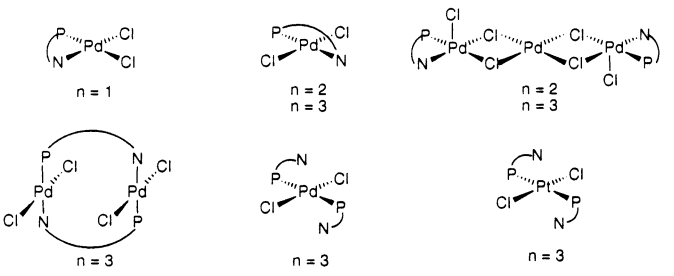
chloride also coordinated, whereas the same reaction with (12-**2**) results in the cationic [(PNN)Pd(C(O)Me)](CF_3SO_3) where the ligand acts as tridentate. The enhanced π-accepting abilities of the imino and pyridyl groups favors the stabilization of zerovalent palladium complexes and in fact a Pd(0) compound (12-**9**) stabilized just with this ligand has been prepared. This is important for catalytic applications through Pd(II)–Pd(0) species without additional stabilizing ligands. A bidentate coordination mode is also observed with this ligand in [(PNN)Pd-(η^3-$Me_2CCMeCMe_2$)]Cl. The crystal structures of the complexes [(PNN)PdMe]Cl (12-**1**), [(PNN)PdMe](CF_3SO_3) (12-**2**) and [(PNN)Pd(C(O)Me)Cl] (12-**5**) have been determined. The reactivity of some of these compounds towards CO and others with similar aminophosphine species are compared. The catalytic activity of



Scheme 12.

compound (12-**7**) in allylic alkylation reactions has been investigated (see Section 5).

Some bidentate P,N ligands *o*-$Ph_2PC_6H_4CH_2O(CH_2)_nPy$ (**PON**, $n = 1, 2, 3$), bearing different spacers [44], are capable of *trans* chelation. These complexes are expected to demonstrate unique behavior as catalysts. When $n = 1$ the *cis* complex is formed, but for $n = 2, 3$ it is the *trans* products that are mainly formed (4). The *trans* chelated neutral Pd complexes of $Ph_2PC_6H_4CH_2O(CH_2)_3Py$ are easily transformed to the cationic *trans*-$[Pd(PON)(MeCN)_2](PF_6)_2$ [45]. Binuclear and trinuclear compounds are also obtained. For Pt it was not possible to obtain the *trans* chelating compound. The different behavior between Pd and Pt is attributed to their different softness. Fig. 5 shows the first X-ray structure of a Pd(II) *trans* chelated PON species, together with that of the *cis* complex with $n = 1$ [44].



(4)

The stereoselective formation of (*E*)-σ-alkenyl palladium complexes with this PON ligand ($n = 1$) has been described (Scheme 13) [46]. The X-ray structure of the complex $[Pd(PON)\{\eta^1\text{-}(E)\text{-}(EtO_2C)C=C(OMe)(CO_2Et)\}][PF_6]$, where the ether linkage has become stereochemically active, was determined. The ability of the ligand to bind in a tridentate mode seems to be crucial for the isolation of the (*E*)-σ-alkenyl compound. For PON ($n = 3$) where a five- and a seven-membered ring should be formed, ring strain probably prevents tricoordination and the desired complexes are not formed.

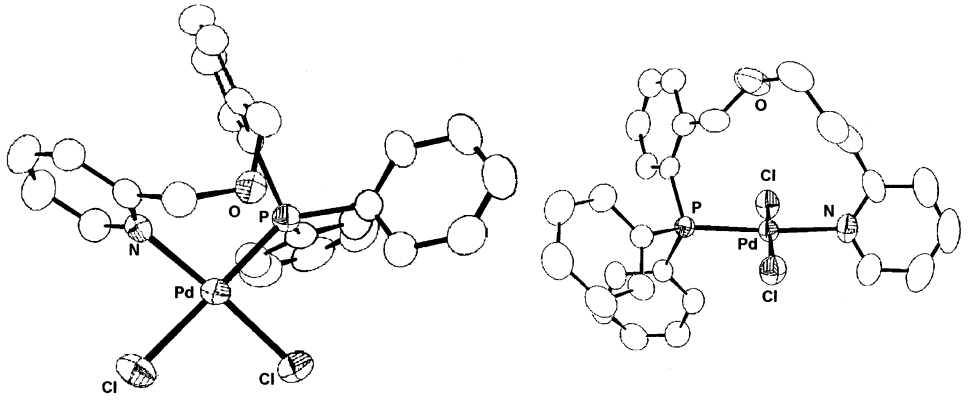
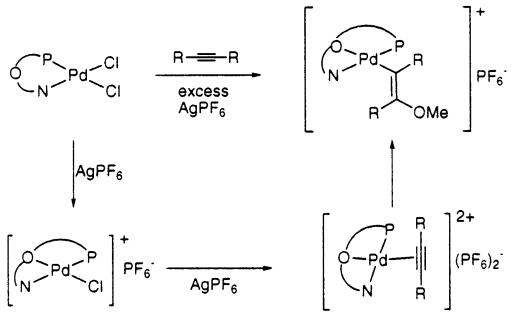


Fig. 5.



Scheme 13.

The reaction of $Cd(O_3SCF_3)_2$ with **2,6-($Ph_2PCH_2CH_2SCH_2)_2C_5H_3N$** yields an unusual seven-coordinate compound $[Cd\{(Ph_2PCH_2CH_2SCH_2)_2C_5H_3N\}(O_3SCF_3)_2]$ [47]. Its crystal structure is depicted in Fig. 6. The coordination geometry is a distorted pentagonal bipyramid. The complex is highly distorted due to the constraints that the pentadentate ligand imposes. The same ligand acts as a tetracoordinate PSSP ligand towards Ag(I).

The reaction of 8-azidoquinoline (**8-AZQ**) with $[Mo(CO)_3(dppm)(CH_3CN)]$ (dppm = bis(diphenylphosphino)methane) results in formation of a phosphine phosphoranimine chelate, the structure of which has been determined by X-ray crystallography [48]. A mechanism is proposed, in which the formation of the phosphine phosphoranimine chelate occurs via chelate ring opening followed by intramolecular attack of one dangling phosphine on a bent-nitrene intermediate. The steps of the proposed mechanism are shown in Scheme 14.

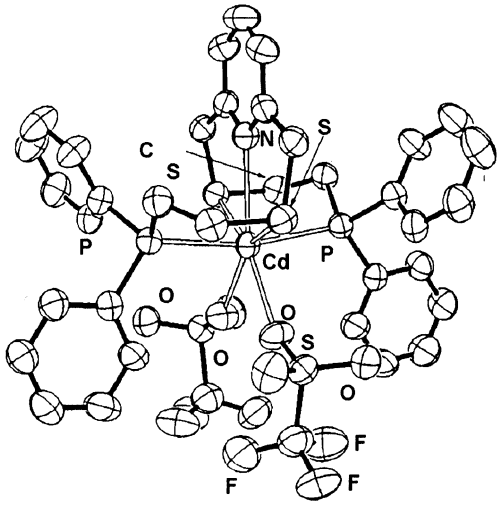
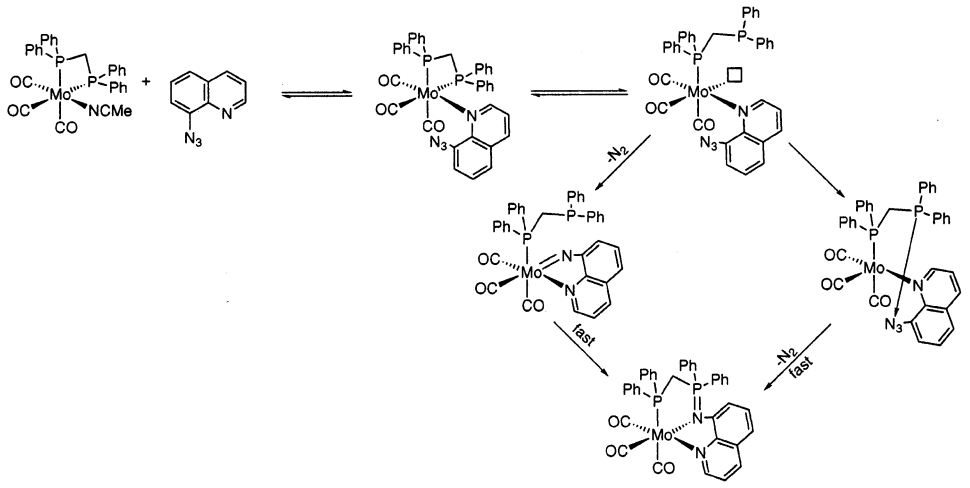


Fig. 6.



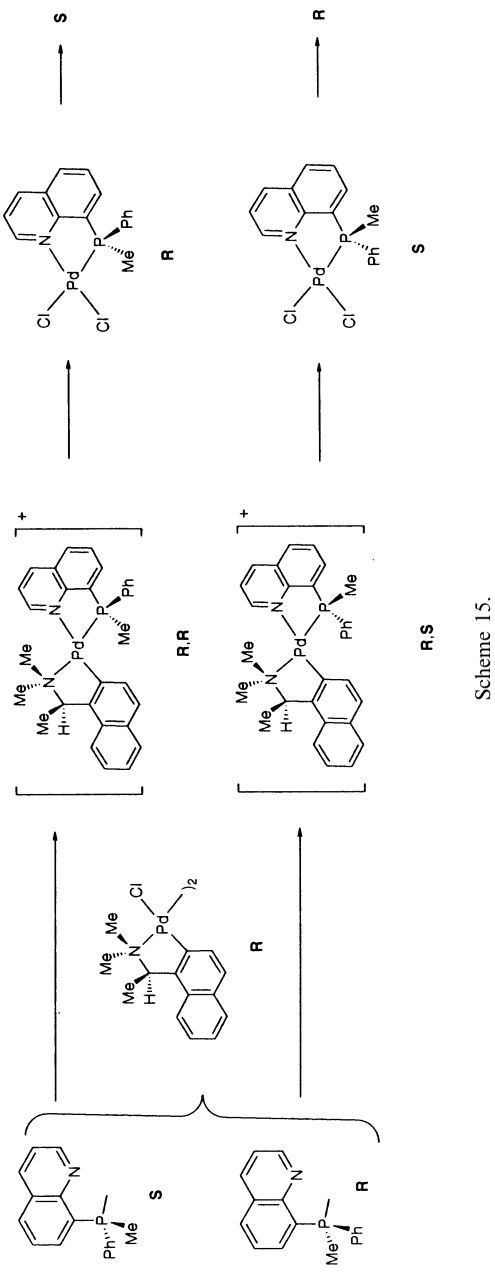
Scheme 14.

2.2. Compounds with asymmetric ligands

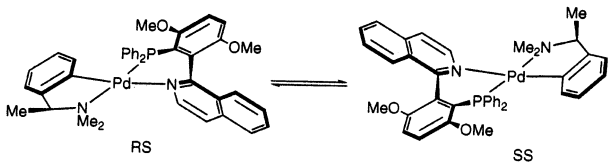
The synthesis and resolution of the two enantiomers of the chiral ligand **methylphenyl(8-quinolyl)phosphine** and its arsenic analog was reported in the early 80's [49](293). The resolution of the enantiomers was achieved by fractional crystallization of a pair of internally diastereoisomeric Pd(II) complexes containing the chelated (P,N) ligand and an optically active *ortho*-metallated (*R*)-(+)-dimethyl(1-(1-naphthyl)ethyl)amine (Scheme 15) This is a quite general method for the resolution of chiral ligands. The molecular structure and absolute configuration of (+)-(*R*,*S*) complex was determined by X-ray diffraction.

One decade later, the behavior in solution of cationic complexes of the same phosphine and arsine ligands was studied by variable temperature NMR spectroscopy [50]. The complexes were square planar $[M(P^*N)_2](PF_6)_2$ and square pyramidal [MCl(P*N)] (M = Pd, Pt). The *cis* coordinated complexes undergo an intermolecular redistribution of the ligands, faster for Pd. The square pyramidal complexes show in addition an axial chloro site exchange which is even faster.

The chelating P,N ligand **1-(2′-diphenylphosphino-3,6′-dimethoxyphenyl)-isoquinoline**, has been prepared as a racemic mixture [51]. This ligand gives the corresponding racemic complex $Pd(P,N)Cl_2$, for which the X-ray analysis confirmed the *cis* chelating coordination. Attempts at resolving the ligand through the enantiomerically pure palladium complex derived from (*S*)-(+)-dimethyl(1-phenylethyl)amine, revealed that the diastereomeric complexes were interconverting in solution. (Scheme 16). This epimerization requires a prior dissociation of one of the coordinating atoms (probably the N). The rapid racemization of the free ligand was also confirmed by NMR magnetization transfer experiments.



Scheme 15.



Scheme 16.

The chiral ligand 1-(2′-diphenylphosphino-1-naphthyl)-isoquinoline (**QUINAP**) could be resolved through its complexation to Pd containing the chiral agent (*R*)-(+)-dimethyl(1-(1-naphthyl)ethyl)amine [52]. The X-ray structure of the (*R*,*R*) diastereoisomer is shown in Fig. 7). This complex turns out to be the less stable in solution. The X-ray structure of the more stable (*S*,*R*) complex was determined later [53]. The free ligands were regenerated from the Pd complexes by treatment with 1,2 bis(diphenylphosphino)ethane.

Several allylpalladium complexes of the ligand S-QUINAP were prepared (Scheme 17) [54]. Their NMR spectra reveal that they all exist as a mixture of diastereomers, except (17-**4**) which is a single diastereomer with CPh_2 *trans* to P,

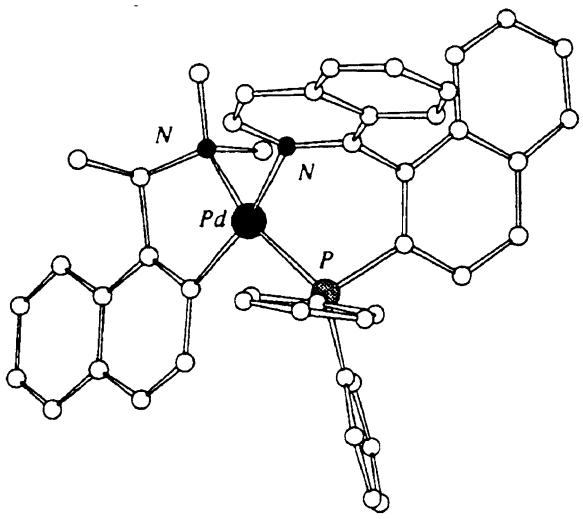
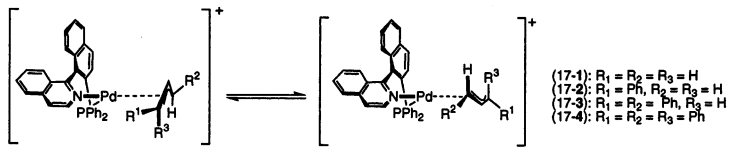
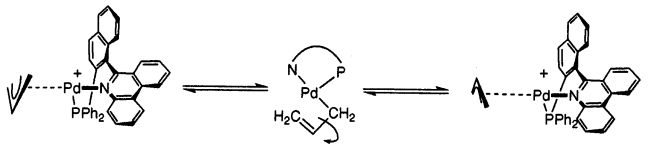


Fig. 7.



Scheme 17.



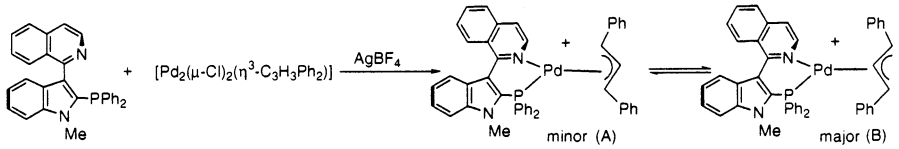
Scheme 18.

but with unknown configuration. The diastereomers interconvert in solution at various rates. These NMR studies were made to assist with the elucidation of the mechanism of asymmetric alkylation in which allylpalladium complexes are involved (see Section 5).

The resolution of the related ligands (*R*)- and (*S*)-6-(2′-diphenylphosphino-1′-naphthyl)phenanthridine (**PHENAP**) was made by the methodology mentioned previously [55]. The (*R*,*S*) diastereomer is P,N coordinated and the (*R*,*R*) monocoordinated through P. Both of them were characterized by X-ray. In contrast to the QUINAP allylpalladium complex (17-**1**) (Scheme 17), for which it was necessary to reduce the temperature to 220 K in order to slow down the interconversion between the two diastereomers and observe them in a ratio almost 1:1 [54], the PHENAP analog at room temperature is a mixture of two diastereomers (6:1). They interconvert by the pathway shown in Scheme 18, which implies that only the σ-allyl intermediate in which the Pd–C bond is *trans* to nitrogen is accessible. Intrusion of the phenanthridine C-ring into the coordination sphere is probably responsible for the discrimination between the two diastereomers. The η^3-cyclohexenyl complex is present as a single diastereomer.

Another related ligand is **1-methyl-2-diphenylphosphino-3-(1′-isoquinolyl)indole** (Scheme 19), for which rapid racemization is observed [56]. The 1,3-diphenylallyl complex of this ligand was isolated as a 30:1 mixture of two racemic diastereomers (Scheme 19). The X-ray structure of what was assumed to be the major component is presented in Fig. 8. The allyl group is significantly twisted in a way that the C_c-C_b bond is on the P–Pd–N plane. In addition the C_c–Pd bond is significantly shorter than the C_a–Pd bond. This is quite an extreme case of twisting, although it is not unique. The ground-state geometry is interesting in relation to the catalysis of the asymmetric allylic alkylation (see Section 5) and all the NMR evidence indicates that this distortion is retained in solution.

The importance of the choice of the resolving agent used to resolve these chiral ligands has been discussed on the basis of the different conformational rigidity that can exist between analogues with closely related structures. The superiority of the



Scheme 19.

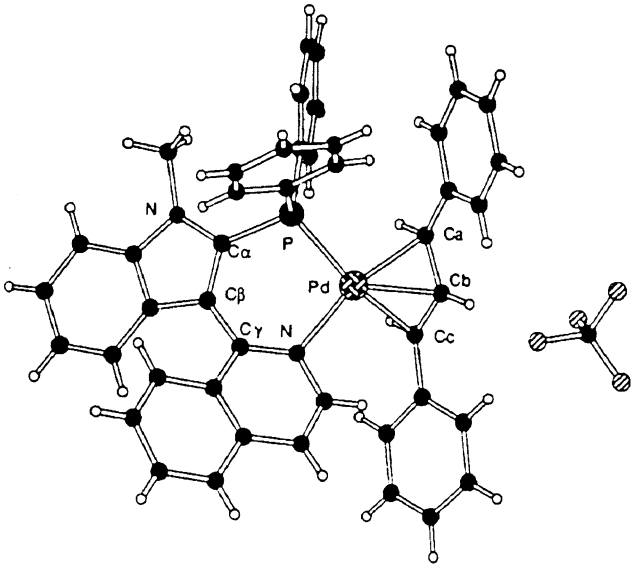
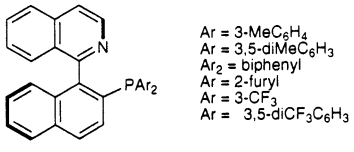


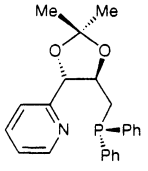
Fig. 8.

Pd resolving complex of (*R*)-(+)-dimethyl(1-(1-naphthyl)ethyl)amine, over that with (*S*)-(+)-dimethyl(1-phenylethyl)amine, is explained on the basis of steric influences [53]. A series of phosphines presented in 5, in which the aryl substituents are varied, have been prepared and resolved [57].

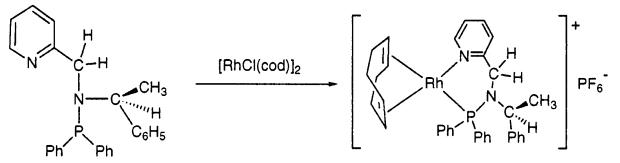


(5)

The chiral ligand (−)-(4*S*,5*R*)-4-(2-pyridyl)-5-(diphenylphosphino)methyl-2,2-dimethyl-1,3-dioxolane (**PYDIPHOS**), (6), and their complexes [Pd(PYDIPHOS)Cl_2], [Pt(PYDIPHOS)Cl_2], [Pt(PYDIPHOS)($SnCl_3$)Cl] and [Rh(PYDIPHOS)(CO)Cl] have been synthesized and characterized [58]. The structure of [Pd(PYDIPHOS)Cl_2] has been determined by X-ray analysis. In all compounds the ligands act as P,N-chelates. The Rh complex is formulated as square-planar with CO coordinated *trans* to N, but the available experimental data cannot exclude a dinuclear symmetric species.



(6)

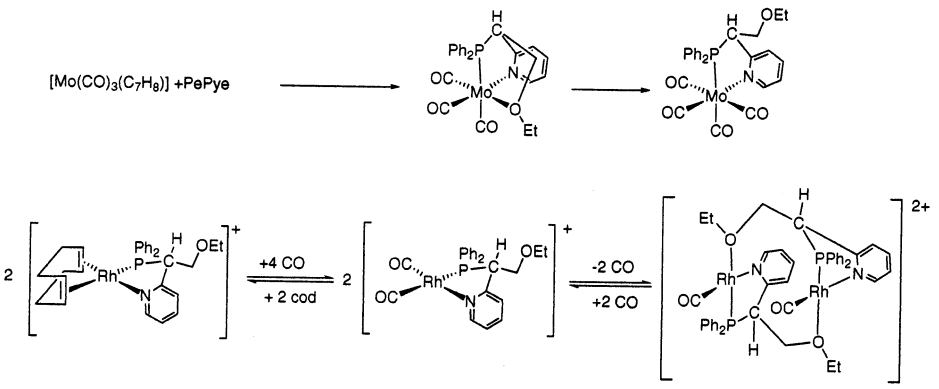


Scheme 20.

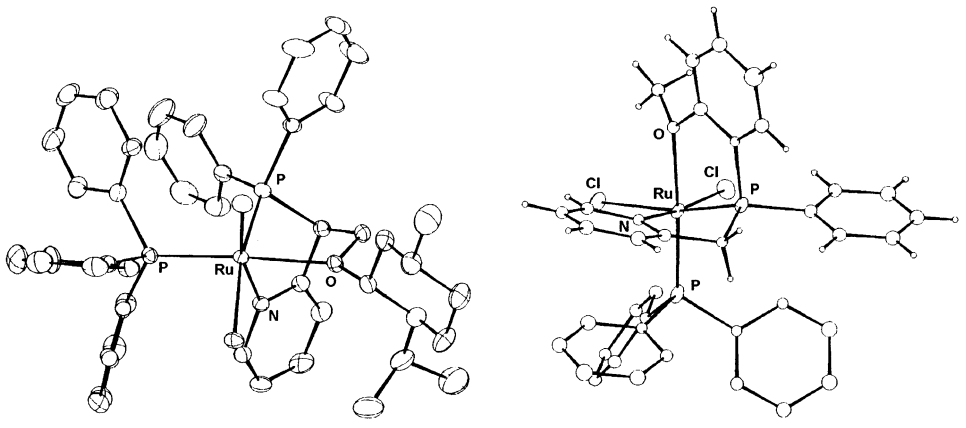
A number of new optically active P–N ligands were prepared among which the pyridylaminophosphine (*S*)-***N*-(diphenylphosphino)-*N*-(1-phenylethyl)-2-pyridinmethanamine**, which forms the Rh complex shown in Scheme 20 [59]. These complexes together with the ones prepared from the other P–N ligands were tested in the catalytic asymmetric hydrosilylation of acetophenone (see Section 5).

The trifunctional P,N,O ligand 1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)-ethane (**PePyE**), with two hemilabile centers (N,O), and various Mo(0), Rh(I) and Ru(II) complexes have been described [60]. Some reactions are outlined in Scheme 21. The reaction of PePyE with $Mo(CO)_3(C_7H_8)$ results in the initial formation of *fac*-[$Mo(CO)_3$(PePyE)] in which the ligand is P,N,O coordinated. Instability in solution leads to decomposition products and [$Mo(CO)_4$(PePyE)]. In [Rh(cod)(PePyE)]ClO_4 the ligand is P,N coordinated and reaction with CO rapidly results in [$Rh(CO)_2$(PePyE)]ClO_4, stable only under CO. Removal of CO results in the formation of a dinuclear complex. The complex all-*cis*-[$RuCl_2$(PePyE)$_2$] was isolated in two diastereoisomeric forms. In polar solvents it converts to the ionic species [RuCl(PePyE-P,N,O)(PePye-P,N)]BPh_4 in which one of the ether groups has been displaced from the coordination sphere. Reaction with CO displaces the second ether group yielding [RuCl(CO)(PePyE)$_2$]BPh_4.

The related ligands (*S*)-(phenyl(2-anisyl)phosphino)(2-pyridyl)methane (**1**), (*R*)-1-(diphenylphosphino)-2-((1*R*,2*S*,5*R*)-menthoxy)-1-(2-pyridyl)-ethane (**2R**), and (*S*)-1-(diphenylphosphino)-2-((1R,2S,5R)-menthoxy)-1-(2-pyridyl)-ethane (**2S**) (7), as well as PePyE, give complexes [$RuCl_2(PPh_3)$L] where L acts as a trifunctional



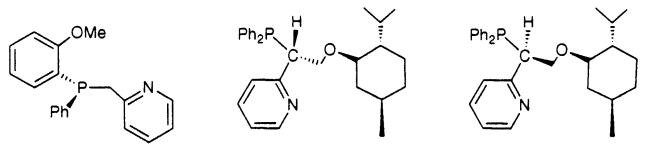
Scheme 21.



4b 5

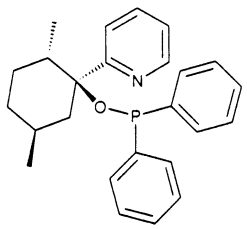
Fig. 9.

P,N,O donor [61]. Their structures have been assigned based on those solved by X-rays for two of the complexes with the ligands **1** and **2S** (Fig. 9). Some of the complexes showed fluxionality which was shown to be related to the dissociation of the bond *trans* to the PPh_3 ligand, whether this was N–Ru or O–Ru.



1 **2R** **2S** (7)

The ligand **2-[1-(1*S*,2*S*,5*R*)-(−)menthoxydiphenylphosphino]pyridine** (L), (8) reacts with $[Rh(C_8H_{12})(solv)_2]ClO_4$ to give $[Rh(C_8H_{12})(L)]ClO_4$, whose structure has been determined by X-ray analysis [62]. Bubbling CO through a CH_2Cl_2 solution containing this complex and 1 equivalent of PPh_3 yielded $[Rh(CO)(PPh_3)(L)]ClO_4$ in which, according to ^{31}P-NMR data, the two P atoms are in *trans* positions. The two compounds were tested as catalysts in the asymmetric hydroformylation of olefinic substrates (see Section 5).



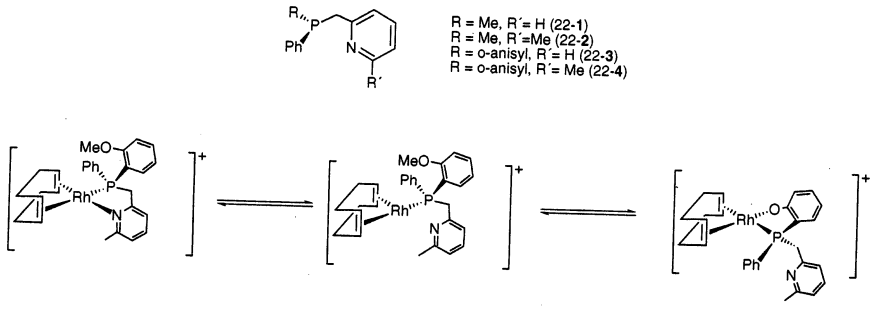
(8)

The examples of optically active pyridylphosphines containing a resolved tertiary phosphorus stereocenter are rare [63]. The interest of these ligands for asymmetric catalysis is due to the fact that the chiral center is directly attached to the metal center. Their scarcity is associated to the difficulty of their synthesis and resolution. However, a series of polydentate ligands chiral at P, and their bonding properties towards $[Rh(cod)]^+$, have been reported [25]. The ligands are shown in Scheme 22. Introduction of a methyl group at the two-position of the pyridyl ring induces the formation of a bis-chelated complex. Due to the initial difficulty of N to coordinate, coordination of two ligands by P, and finally binding of the N with subsequent elimination of cod occurs. The replacement of Me by Ph increases the steric hindrance on P, restoring the coordinating ability of N. The dynamic behavior in solution of the P,N,O ligands is summarized in Scheme 22. The X-ray structure of the complex [Rh(cod)(22-**1**)][BF_4] is reported, allowing one to establish the S_P configuration to the free ligand (22-**1**).

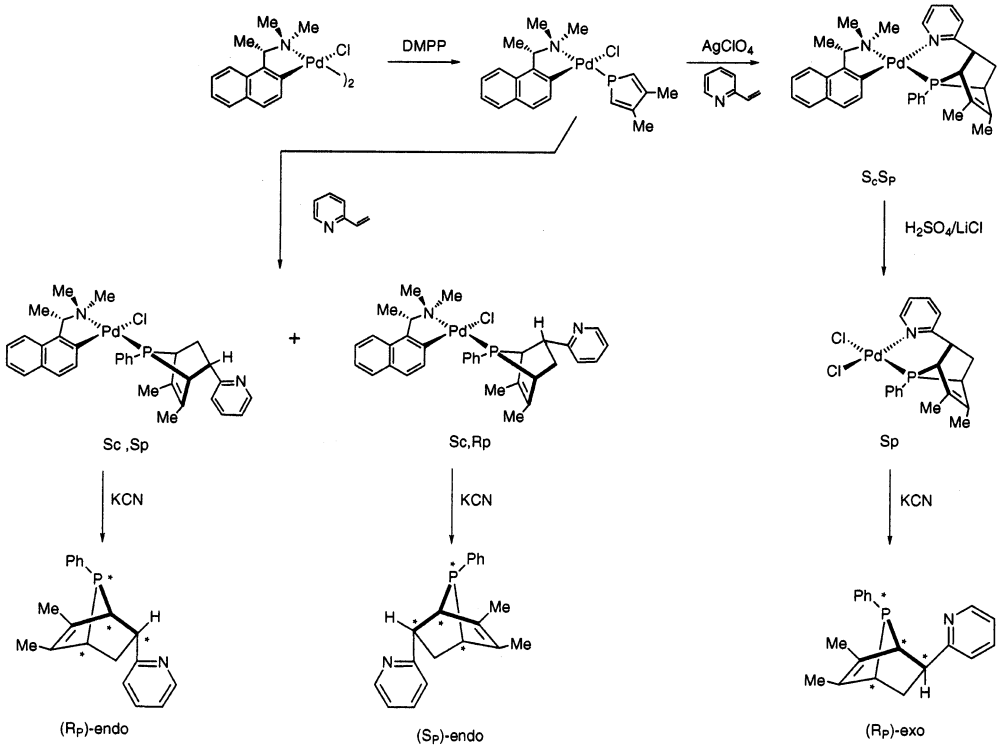
The P-chiral phosphines presented in Scheme 23 are the product of an *exo-endo* stereochemically controlled asymmetric Diels–Alder reaction in which the chiral complex, [(*R*)-1-[dimethylamino)ethyl]-2-naphthalenyl-C,N]dipalladium (II), plays both the role of the promoter and the stereochemical controller (Scheme 23) [64]. The *exo* isomers can chelate to a metal center whereas the endo isomers are necessarily monodentate or bridging. In the exo cycloaddition the P,N R_P-*exo* ligand is exclusively produced, but in the *endo*-, a pair of diastereoisomeric palladium complexes (Sc,Sp and Sc,Rp) are produced, which after separation can liberate the two endo phosphines. The crystal structures of complexes Sc,Sp and Sp have been determined.

Chiral ferrocene derivatives have attracted considerable interest due to their applications in asymmetric catalysis [65]. Not many pyridyl containing ferrocenylphosphines have been reported, in contrast to amino-ferrocenylphosphines [66], oxazoline-ferrocenylphosphines [67] or pyrazole ferrocenylphosphines [68].

The reaction of $[M(cod)Cl]_2$, (M = Rh, Ir) with the ligand **[Fe{η^5-C_5H_4Py}(η^5-$C_5H_4PPh_2$)]** and $AgPF_6$ yields cationic complexes with the same formula, $[M(cod)L]PF_6$, but different structures [69]. The Rh complex is square-planar. During irradiation experiments, spin saturation transfers between the signals of the



Scheme 22.



Scheme 23.

β-protons of the cyclopentadienyl ring of the PPh_2 group, as well as those of the cyclopentadienyl ring of the Py group indicate that these protons exchange slowly in solution according to the equilibrium shown in Scheme 24. The NMR spectrum of the Ir compound reveals the presence of a hydridic proton *cis* to P, indicating that an Ir(II) hydride has been formed by oxidative addition of C–H of the Py-substituted Cp to the Ir(I) center. The Rh complex presents just a weak C–H···M interaction. Thus these two complexes constitute an example of C–H activation by transition metals in which the oxidative addition product as well as a course for an oxidative addition of an intramolecular C–H bond can be visualized. The X-ray structure determinations verified the proposed structures.

Pyridylphosphinines are structurally related to bipyridines by replacement of a pyridine by a phosphinine. Weaker σ-donor as well as enhanced π-acceptor

Scheme 24.

properties make these phosphorus analogues of bipyridines good candidates to stabilize low oxidation states. Two recent publications concerning the phosphorus analogues of bipyridines review the work that has been done in this quite new field [70].

The synthesis and use of ferrocenes that contain a pyridylphosphinine moiety (9) have been reported [71]. The ligand **2(2′-pyridyl)-3,4-dimethylphosphaferrocene**, upon reaction with $[W(CO)_5(thf)]$ eventually yields the complex $[W(CO)_4(P,N)]$, characterized by X-ray analysis. Reaction of the same ligand with $[Cu(MeCN)_4]BF_4$ gives $[Cu(MeCN)_2(P,N)]BF_4$. Further replacement of the remaining acetonitrile ligands by PPh_3 yields $[Cu(PPh_3)_2(P,N)]BF_4$.

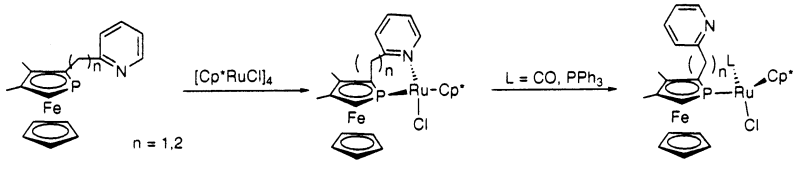
2(2′-pyridyl)-3,4-dimethylphosphaferrocene 2(8′-quinolyl)-3,4-dimethylphosphaferrocene (9)

The ligands **2-[(3,4-dimethylphosphaferrocene-2-yl)methyl]pyridine** and **2-[(3,4-dimethylphosphaferrocene-2-yl)ethyl]pyridine** (Scheme 25), have been reported in enantiomerically pure forms [72]. The two ligands react with $[Cp^*RuCl]_4$ ($Cp^* = C_5Me_5$) to give the corresponding chelate complexes [Cp*RuCl(P,N)] with high diastereoselectivity (higher in the case of the five-membered ring). The reaction of $[(C_3H_5)PdCl]_2$ with the ligand 2-[(3,4-dimethylphosphaferrocene-2-yl)methyl]-pyridine gave a poorly characterized polymeric product, while with 2-[(3,4-dimethylphosphaferrocene-2-yl)ethyl]pyridine the complex $[(C_3H_5)Pd(P,N)]PF_6$ was isolated and its crystal structure determined (Fig. 10).

3. Binuclear complexes

3.1. Homobimetallic complexes

PPh_2Py is a useful building block for the synthesis of homo- or hetero-bimetallic compounds. Moreover, because of the rigidity induced by the small bite angle of the ligand, the formation of a M–M bond is strongly favored. The early research made by Balch and co-workers is commented in the two previously mentioned reviews [9,10].



Scheme 25.

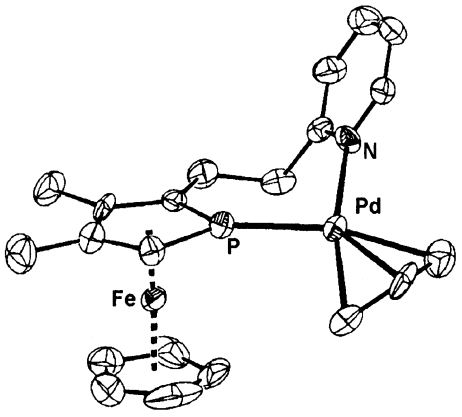


Fig. 10.

Treatment of $[Mo_2(O_2C\text{-}t\text{-}Bu)_3(MeCN)_2](BF_4)$ with one equivalent of PPh_2Py yielded $[Mo_2(\mu\text{-}O_2C\text{-}t\text{-}Bu)_2(\mu\text{-}PPh_2Py)_2](BF_4)_2$ [73], for which a head-to-tail structure has been proposed with a quadruple Mo–Mo bond and a *cis* arrangement of the two carboxylates.

The reaction of $Ru_3(CO)_9(PPh_2Py)_3$ with CdI_2 resulted in the formation of the homobimetallic head-to-head $[I(CO)_2Ru(\mu\text{-}PPh_2Py)_2Ru(CO)_2I]$ (Fig. 11) [74].

Dinuclear compounds of Ru(I) with the ligands PPh_2Py, **PQN**, and 6-diphenylphosphino-2,2′-bipyridine (**dpbipy**) are obtained by reaction with $[\{Ru_2[\mu\text{-}\eta^{2-}OC(R)O]_2(CO)_4\}_n]$ (R = H,Me,Et) [75]. One carboxylate ligand is readily displaced in the presence of two molar equivalents of PPh_2Py, or PQN, NH_4PF_6, and CO to give cationic dimeric species $[Ru_2\{\mu\text{-}\eta^{2-}OC(R)O\}(CO)_4(P,N)_2]PF_6$ (**1**). Under more vigorous conditions dpbipy affords compounds of the type (**2**) (10). The X-ray structures of the compounds $[Ru_2\{\mu\text{-}\eta^{2-}OC(H)O\}(CO)_4(\mu\text{-}PPh_2Py)_2]PF_6$, and $[Ru_2\{\mu\text{-}\eta^{2-}OC(Me)O\}(CO)_4(\mu\text{-dpbipy})_2]PF_6$, have been re-

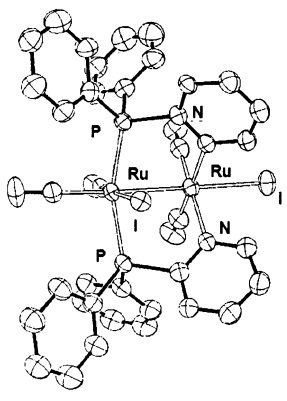
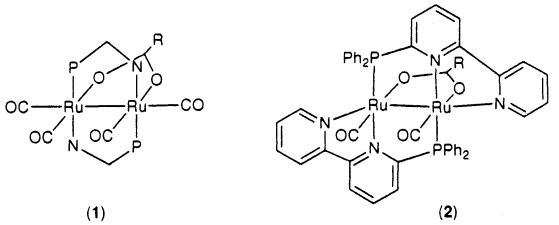


Fig. 11.

ported, as well as that of the $[Ru_2\{\mu\text{-}\eta^{2-}OC(Me)O\}_2(CO)_4(PPh_2Py)_2]$ in which the PPh_2Py is P-monocoordinated.



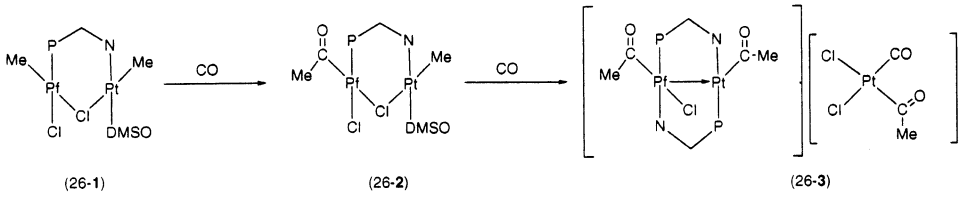
(1) (2) (10)

$[MeClPt(\mu\text{-}Cl)(\mu\text{-}PPh_2Py)PtMe(DMSO)]$ (26-**1**) inserts CO to yield (26-**2**) [76]. The fact that the insertion does not take place on the other metal center is considered to have a kinetic origin due to the ability of the soft P ligand to facilitate the uptake of CO and the formation of a five-coordinate species. Complex (26-**2**) changes slowly to (26-**3**) (Scheme 26). The X-ray analysis of a crystalline species obtained, revealed the co-existence of compounds (26-**2**) and (26-**3**) in a 1:1 ratio, while semi-empirical MO calculations for the cation support the dative nature of the $Pt^{II} \rightarrow Pt^{II}$ bond.

The first Cu(I) complexes containing PPh_2Py were reported in 1989 [77]. The complexes are of the type $[Cu_2(\mu\text{-}PPh_2Py)_2(MeCN)n](BF_4)_2$ ($n = 2, 4$) and $[Cu_2(\mu\text{-}PPh_2Py)_3L_n](BF_4)_2$ ($n = 0, 1, 2$; L = N- or P-monodentate ligands). The crystal structure of $[Cu_2(\mu\text{-}PPh_2Py)_3(MeCN)](BF_4)_2$, (Fig. 12) is the first example of a new structural type of bimetallic PPh_2Py bridged complexes. The two Cu(I) atoms have a different coordination number and they are bridged by three, instead of the commonly encountered, two PPh_2Py ligands.

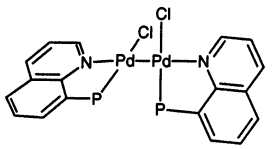
Compared to PPh_2Py, the related ligand methyl 2-(diphenylphosphino)nicotinate (Scheme 5) has less tendency to form dinuclear complexes [20b]. Thus, reaction of $[(\mu\text{-}Br)Ni(\eta^3\text{-methallyl})]_2$ with PPh_2Py and $AgBF_4$ yields the dinuclear $[Ni(\mu\text{-}PPh_2Py\text{-}P,N)(\eta^3\text{-methallyl})]_2(BF_4)_2$, with a head to tail bridging arrangement of the ligand, while as already described before, the same reaction with methyl 2-(diphenylphosphino)nicotinate yields the mononuclear P,N chelate.

The Pd(I) complex $[Pd_2Cl_2(Me_2PQN)_2]$ (11) was obtained by reaction among $PdCl_2(PhCN)_2$, Me_2PQN and $[Pd_2(dba)_3]\cdot CHCl_3$ (**dba** = 1,5-diphenyl-1,4-pentadien-3-one) [24]. The X-ray structure of this compound, shows an unsupported Pd–Pd bond.



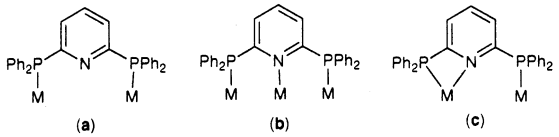
(26-1) (26-2) (26-3)

Scheme 26.



(11)

A recent review treats the synthesis of polynuclear complexes making use of polyphosphine ligands [78], amongst them 2,6-bis(diphenylphosphino)pyridine, **$(Ph_2P)_2Py$**. Binuclear complexes using P and N donor atoms are reported, as well as compounds of higher nuclearity, homo- and heterometallic. The work mentioned in that review is not discussed here. Three modes of coordination have been reported for $(Ph_2P)_2Py$ (12). The most common is (**a**) [9,79]. There are several examples of the coordination mode (**b**) [9], but just one example of (**c**) has been reported [80].



(12)

Another coordination mode for $(Ph_2P)_2Py$ was reported recently in which the ligand bridges the two metal atoms through P and N, leaving the other P atom free [81]. The synthesis, X-ray structure and reactivity of a molybdenum and two

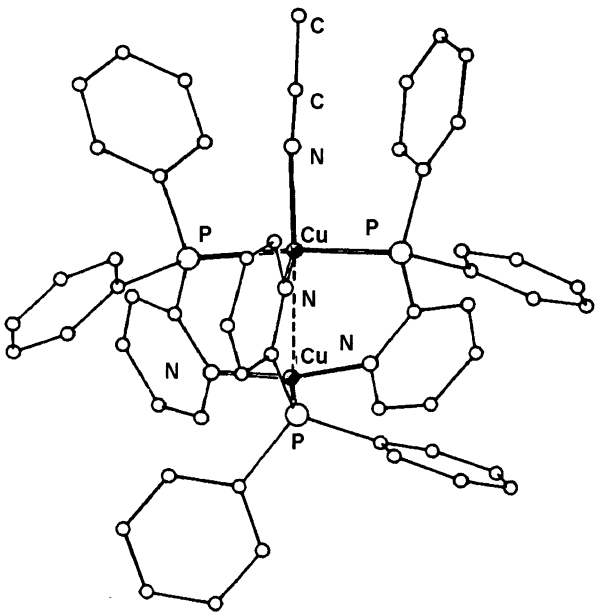
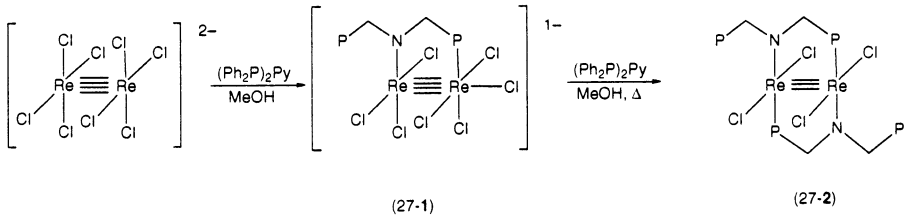


Fig. 12.



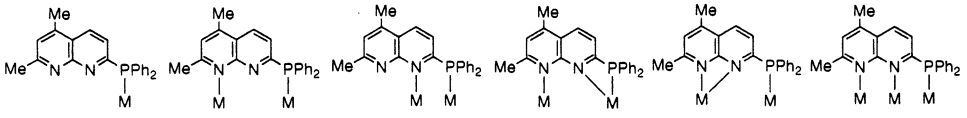
(27-1) (27-2)

Scheme 27.

rhenium complexes containing $(Ph_2P)_2Py$ are described. The reaction for Re (Scheme 27) not only results in ligand substitution but also in a reduction of Re(III) to Re(II). Complexes (27-**1**) and (27-**2**) exhibit typical electrochemical behavior for the cores Re_2^{4+} and Re_2^{6+}.

Reaction of **MQP**, (1) with $[RhCl(CO)_2]_2$ gives $[(CO)_2Rh(\mu\text{-}Cl)_2(CO)(MQP\text{–}N,P)]$ [26]. NMR data indicate the chelation of the ligand and a $CH_3\cdots Rh$ interaction with the CH_3 group of the quinolyl moiety.

The ligand 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine (**dpnapy**) [82] has a rigid skeleton and combines the structural features of 1,8 naphthypyridine and PPh_2Py, and a quasi-linear disposition of the phosphorus and the two nitrogen binding sites. All the coordination modes shown in 13 have been realized [82–84].



(13)

The product of the reaction of $[RhCl(cod)]_2$ with dpnapy depends on the ratio between the reactants [82]. The mononuclear compound [Rh(cod)(dpnapy)Cl], is formed when the ratio is 1:2, and the binuclear compound $[\{Rh(cod)Cl\}_2(\mu\text{-dpnapy})]$ when the ratio is 1:1. [Rh(cod)(dpnapy)Cl] exhibits fluxional behavior in solution, attributed to: (a) fast intramolecular exchange of the cod protons, through a five-coordinate intermediate; and (b) a slower dynamic equilibrium between [Rh(cod)(dpnapy)Cl] and $[\{Rh(cod)Cl\}_2(\mu\text{-dpnapy})]$ with loss of dpnapy. The reaction between $[RhCl(CO)_2]_2$ and dpnapy results in the formation of *cis*,*cis*-$[Rh(CO)(\mu\text{-dpnapy})Cl]_2$ (Fig. 13). The same ligand fails to give a similar metallacycle with *cis*-$[Ir(CO)_2(p\text{-toluidine})Cl]$ [85]. The complex *trans*-$[Ir(CO)(\mu\text{-dpnapy})_2Cl]$, where the ligand is monocoordinated through P, was the main product of this reaction. With $[IrCl(CO)_2]_2$ dpnapy gives two different products, depending on the metal to ligand ratio. [Ir(cod)(μ-dpnapy)Cl], with the ligand coordinated through P only, exhibits rapid exchange of the cod protons in the NMR, occurring via a fast intramolecular associative mechanism involving the N closer to P. The dimer $[\{Ir(cod)Cl\}_2(\mu\text{-dpnapy})]$ (Fig. 14), where the ligand is bridging the two metal centers, is formed by using a ratio Ir:dpnapy = 1:0.5. This dimer is also involved in a dynamic process assigned to the interchange between two stereoisomers.

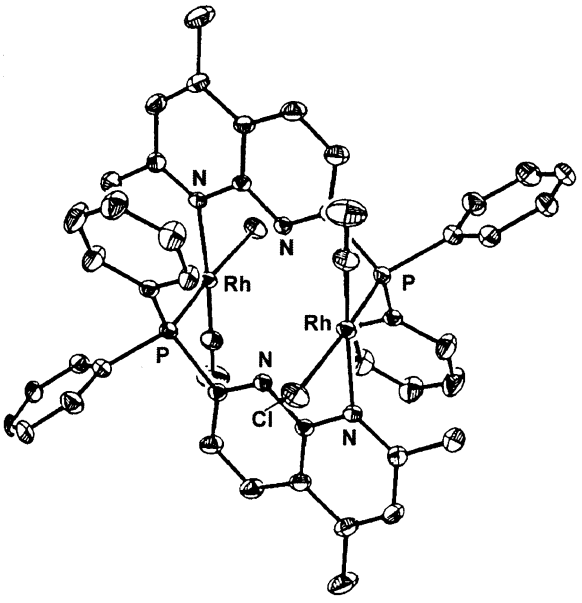


Fig. 13.

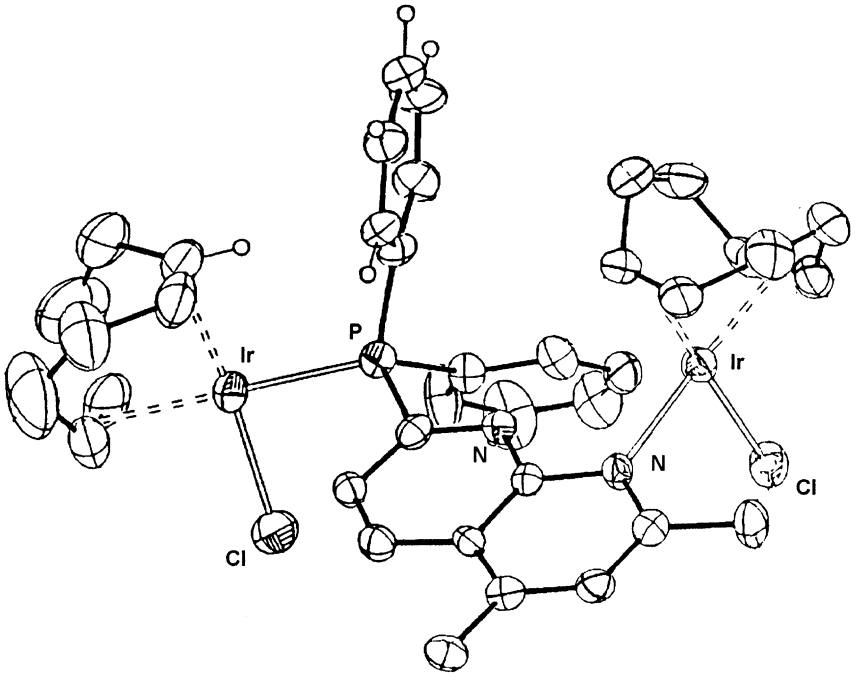


Fig. 14.

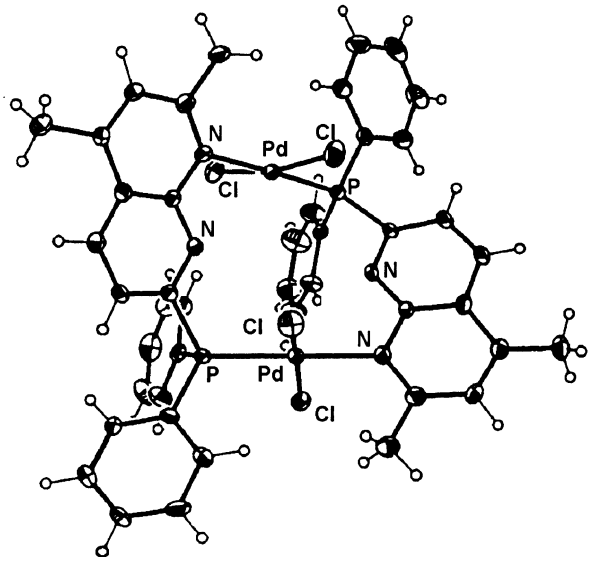


Fig. 15.

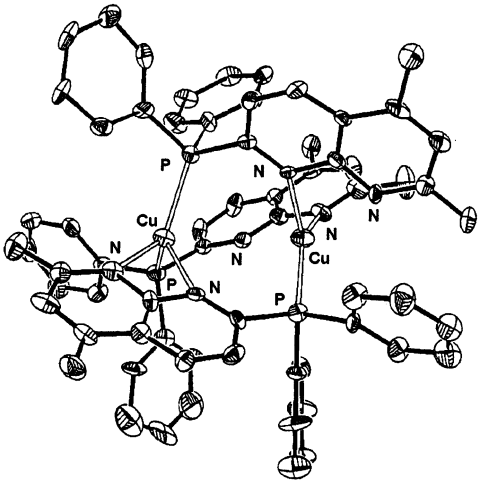


Fig. 16.

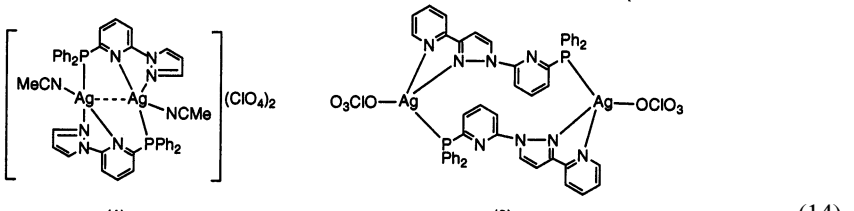
The compound *trans*,*trans*-[{Pd(μ-dpnapy)Cl_2}$_2$] shows a head-to-tail arrangement of the two dpnapy ligands (Fig. 15) [83]. The cavity of this metallamacrocycle was expected to be a good host for metal ions, but attempts at including species such as $HgCl_2$, $SnCl_2$ or Ag^+ failed, probably due to the asymmetry of the ligand as well as the large distance between the two free nitrogen atoms. Efforts to prepare heterometallic compounds starting from complexes [MCl_2(dpnapy)$_2$] (M = Pd, Pt) and [{Rh(cod)Cl}]$_2$ also failed.

The complex $[Cu_2(\mu\text{-dpnapy})_3][ClO_4]$ was prepared by reaction of the trinuclear compound $[Cu_3(\mu\text{-dpnapy})_3(CH_3CN)][ClO_4]_3$ (see Section 4) with PPh_3 [84]. Its X-ray structure (Fig. 16) reveals that all three dpnapy ligands are coordinated in a distinct mode.

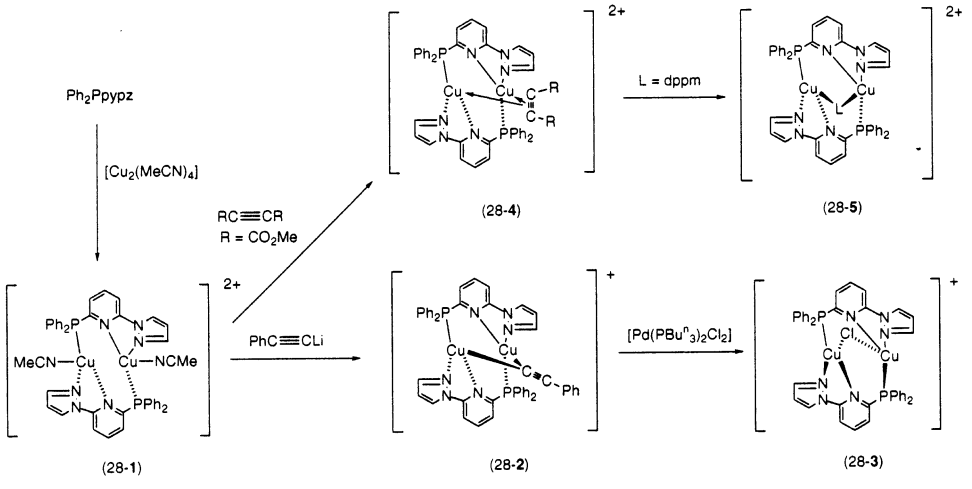
The ligand 2-diphenylphosphino-6-(pyrazol-1-yl)pyridine (**Ph_2PPypz**) is potentially tridentate. The synthesis and reactivity of $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(CH_3CN)_2][ClO_4]_2$ (28-**1**) was reported recently [86]. The ligand binds in a tridentate P,N,N′ mode. The general reactivity pattern is outlined in Scheme 28. The structures of the compounds 28-**1,2,** and **3** were determined by X-ray analysis. Other compounds reported within this system are $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu\text{-X})](ClO_4)$ (X = Cl, I, OAc, pyrazolate) and $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(CH_3CN)_2][Fe(CO)_4]$. The last three species have been characterized by X-ray [87].

The first structurally characterized complex with a μ-1,1-N_3 bridging ligand, $[Cu_2(\mu\text{-}Ph_2PPypz)_2(\mu\text{-}1,1\text{-}N_3)][ClO_4]$, contains two N,N′ chelating N,P head-to-tail bridging Ph_2PPypz ligands. $[Cu_2(\mu\text{-}Ph_2PPypz)_2(\mu\text{-}1,1\text{-SCN})][ClO_4]$ is the second binuclear Cu(I) complex that presents a μ-1,1-SCN coordination mode [88].

The reactions of $[Ag(MeCN)_4]ClO_4$ with Ph_2Ppypz and with the related polydentate new ligand 2-diphenylphosphino-6-[3-(2′-pyridyl)-pyrazol-1-yl]pyridine give **1** and **2**, respectively (14), the structures of which have been determined by X-ray analysis [89]. A weak metal–metal interaction is present in **1**.



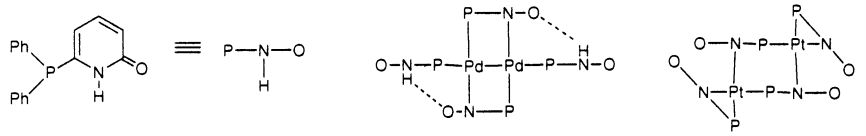
(14)



Scheme 28.

The ligand 3-diphenylphosphino-2,2′-bipyridyl (**Ph_2Pbipy**) can be considered as a tridentate equivalent of Ph_2PPy. The di-copper compounds $[Cu_2(\mu\text{-}Ph_2Pbipy)_2(MeCN)_2]^{2+}$ and $[Cu_2(2,2'\text{-bipy})(\mu\text{-}Ph_2Pbipy)_2]^{2+}$ show a head-to-tail coordination and a head-to-head coordination, respectively (Fig. 17) [90].

The potentially tridentate P,N,O ligand 6-(diphenylphosphino)-2-pyridonate (**Pyphos**) is depicted in 15 in its protonated form (**PyphosH**). The synthesis and X-ray structure of the dinuclear complexes of Pd(I) $[Pd_2(Pyphos)_2(PyphosH)_2]$ (**1**) and Pt(II) $[Pt_2(Pyphos)_4]$ (**2**) have been reported [91]. Both show head-to-tail P,N bridged structures, the former with a Pd–Pd bond.



(15)

Bi- and trinuclear compounds with the ligands PON were presented in Scheme 14. The compound $[Pd_2Cl_4\{\mu\text{-}o\text{-}Ph_2C_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]$ was obtained by isomerization through heating, of a solution of the mononuclear $[PdCl_2\{\mu\text{-}o\text{-}Ph_2C_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}]$ [44a]. The two bridging ligands are in a head-to-tail arrangement and take *trans* sites on each Pd atom. The cationic Pd(I) complex $[Pd\{\mu\text{-}o\text{-}Ph_2C_6H_4CH_2O(CH_2)_3C_5H_4N\text{-}2\}_2]X_2$, ($X = BF_4$, PF_6) shows the ligand as O,N-chelating P,O-bridging, and is obtained in low yield by reaction of the Pd(II) complex with the corresponding AgX salt in the presence of more phosphine (probably acting as the reducing agent) [45]. The N atoms are in *trans* position to the Pd–Pd bond.

The trifunctional P,N,O ligand **PePyE** with two hemilabile centers (N,O) was presented in Scheme 21 [60]. The reaction of $[Rh(cod)(PePyE)]ClO_4$ with CO rapidly results in $[Rh(CO)_2(PePyE)]ClO_4$, stable only under CO. Removal of CO

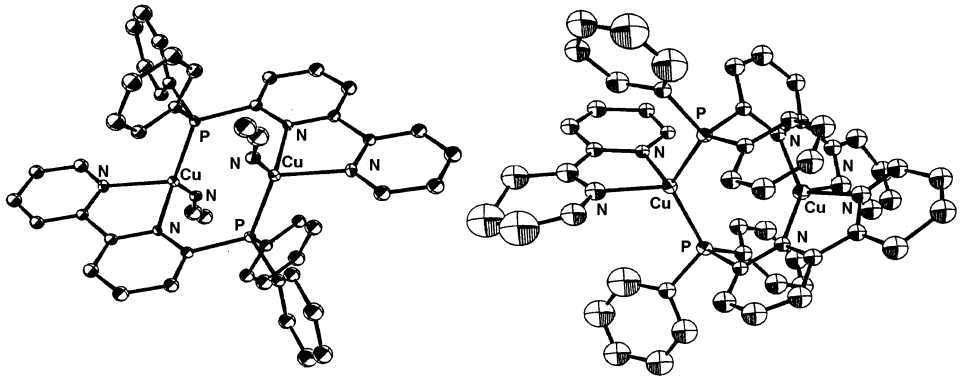
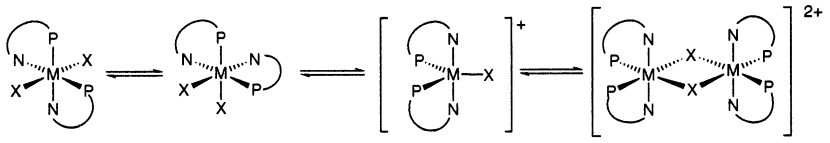


Fig. 17.



Scheme 29.

results in the formation of a dinuclear complex in which the two Rh centers are bridged by the P and the ether function (Scheme 21) [60].

The solution behavior of Ru(II) [33] and Os(II) [34] with PePy, has been mentioned previously in the mononuclear compounds. The equilibria between monomers and dimers in solution, are shown in Scheme 29.

Until 1996 no dinuclear species with PePy acting as a bridge had been reported. The silver(I) cationic dinuclear complex $[Ag(\mu\text{-PePy})_2](PF_6)_2$ has been prepared and its structure determined by X-ray analysis [92]. The cation forms a 12-membered $Ag_2P_2N_2C_6$ ring in which the silver is tricoordinated through the P of one ligand, the N of the second, and the oxygen of a coordinated acetone. The dimension of the cavity, estimated by the Ag···Ag distance, is 5.077(1) Å.

The neutral mononuclear compounds of the general type $[PdRCl(PePy_n)]$, ($n = 1, 2, 3$; $R = C_6F_5$, $C_6Cl_2F_3$), have been mentioned in the mononuclear compounds section. Halogen abstraction from the $n = 2, 3$ complexes yields the corresponding binuclear products $[Pd_2R_2(PePy_n)_2](BF_4)_2$ [37] in which the $PePy_n$ ligands act as chelating and bridging units. The bridges are labile and exchange experiments on mixtures of complexes with different R groups reveal equilibration between the dimeric 'pure' complexes and the mixed complexes $[Pd_2(C_6F_5)(C_6Cl_2F_3)(PePy_n)_2]^{2+}$. The X-ray structure of complex $[Pd_2R_2(PePy_2)_2](BF_4)_2$ is shown in Fig. 18.

The complexes $[Rh(diene)(PePy_2)]^+$ that were shown in Scheme 9 react with CO to give $[Rh_2(CO)_2(PePy_2)_2][BF_4]_2$, shown by X-ray diffraction to have a structure very similar to that found for the Pd complex in Fig. 18, although the structure could not be fully refined [38]. The complex is also obtained by reaction of $[RhCl(CO)_2]_2$ with $PePy_2$ followed by Cl removal. The dimeric structure of the compound is retained in solution, but an equilibrium between two isomers exists, shown in Scheme 30. The IR spectrum indicates that, in contrast to what is found in the solid state, the *trans* isomer is the predominant species in solution.

3.2. Heterobimetallic complexes

Heterobimetallic complexes are ideal candidates for enhanced reactivity, due to the possible cooperation between two different metals [93]. Moreover, as transition metals in low oxidation states have non-bonding electron density available, they can form donor bonds to Lewis acid metal centers [94]. There has been particular interest on this kind of compound which can exert a synergistic interaction when used in some catalytic reactions. There are many synthetic methods for the directed synthesis of heteronuclear complexes [95]. A common synthetic strategy is the coordination of an organometallic multidentate ligand to another metal center.

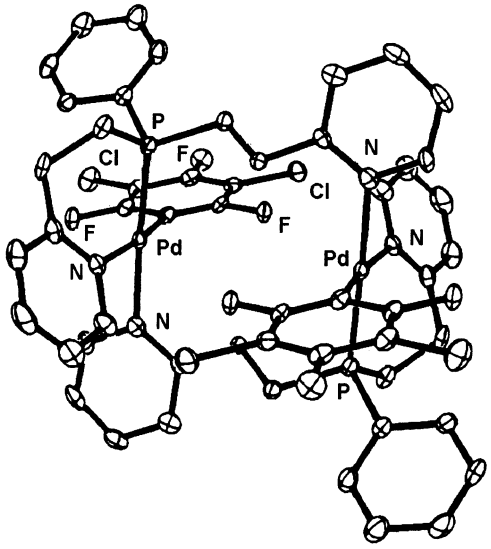
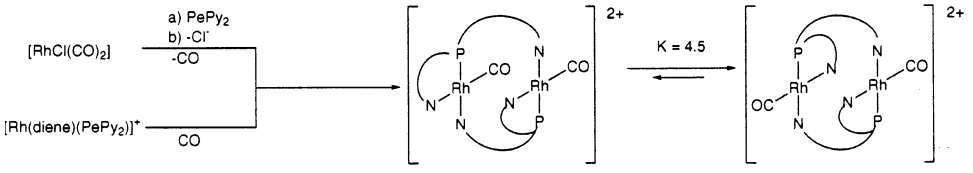


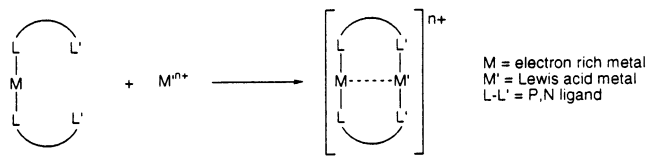
Fig. 18.



Scheme 30.

Ph_2PPy has been widely used for the synthesis of heterobinuclear compounds [10]. The uncoordinated Py groups of a mononuclear compound, in which the ligand is monocoordinated through P, can displace ligands from another metal center to produce a binuclear species, with or without a donor–acceptor metal–metal bond. Another approach is the oxidative addition method, in which a mononuclear P-only coordinated species of the general type $MX_2(PPh_2Py\text{-}P)$ captures another metal center by the free N groups, and in a subsequent oxidative addition of the M–X bond to the metal center a binuclear bridge is formed [10].

trans-$[Fe(CO)_3(PPh_2Py)_2]$ (**L**) [96] having a basic iron center and two pendant pyridyl nitrogen arms, has been widely used by Zhang et al. and the early results of this research have been already reported elsewhere [10]. The general approach is depicted in Scheme 31. The crystal structures of the following complexes have been reported: $[CuL(Me_2CO)]ClO_4$, $[CuL(H_2O)]ClO_4$, $[HgL(H_2O)(OClO_3)]ClO_4$, and $[AgL(PPh_2Py)]ClO_4$ [14]. The bimetallic complexes contain a metal–metal bond and the rings formed by the two metals and L are five-membered. In the neutral binuclear complexes of the type $[(CO)_3Fe(\mu\text{-}PPh_2Py)_2MX_n]$ (M = Mn(II), Co(II),



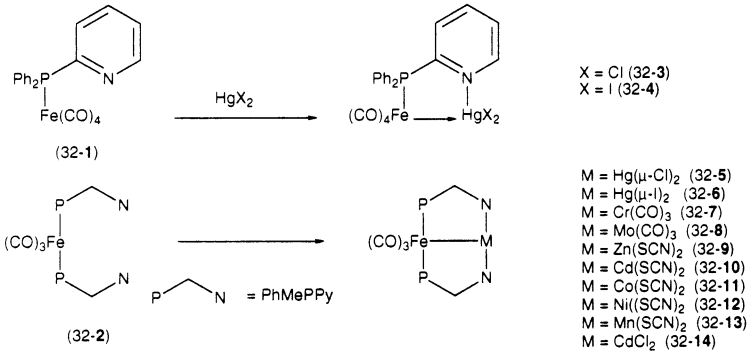
Scheme 31.

Ni(II), Mo(0), Zn(II), Cd(II), Hg(II), Ag(I), Sn(II)) there is also metal–metal bond, as suggested by their Mössbauer and electron-absorption spectra. The structure of $[(CO)_3Fe(\mu\text{-}PPh_2Py)_2HgI_2]$ was determined by single crystal X-ray diffraction [97].

The X-ray structures of the complexes $[XFe(CO)_2(\mu\text{-}PPh_2Py)_2HgX]$ (X = SCN, Cl) have also been determined. These are Fe(I)–Hg(I) complexes formed from *trans*-$[Fe(CO)_2(CS_2)(PPh_2Py)_2]$ and HgX_2 [98] and show a head-to-head arrangement with the two P atoms *trans* on the Fe center and the two CO ligands mutually *cis*.

$[Fe(CO)_4(PPh_2Py)]$ (32-**1**) and *trans*-$[Fe(CO)_3(PPhMePy)_2]$ (32-**2**) were used in the synthesis of heterobimetallic complexes (Scheme 32) [99] PPhMePy is less bulky and more basic than PPh_2Py and therefore *trans*-$[Fe(CO)_3(PPhMepy)_2]$ is more basic than *trans*-$[Fe(CO)_3(PPh_2Py)_2]$. This is the reason for the synthesis of compound (32-**7**) with $Cr(CO)_6$ which cannot be obtained by the analogous reaction with *trans*-$[Fe(CO)_3(PPh_2py)_2]$. The crystal structures of (32-**3**), (32-**5**) and (32-**6**) are described. The synthesis of *trans*-$[Fe(CO)_3(PEtPhPy)_2]$ and its reactivity with $Mo(CO)_6$ and $M(SCN)_2$ (M = Mn, Fe, Co, Ni, Zn, Cd, Hg) have been reported also [100], together with the X-ray structures of the dinuclear neutral complexes $[(CO)_3Fe(\mu\text{-}PEtPhPy)_2Cd(SCN)_2]$ and $[(CO)_3Fe(\mu\text{-}PEtPhPy)_2Mo(CO)_3$.

The ligand *trans*-$[Fe(CO)_3(Ph_2Ppym)_2]$ (pym = 2-pyrimidyl), very similar to *trans*-$[Fe(CO)_3(Ph_2PPy)_2]$, was synthesized and its structure determined by X-ray diffraction, as well as that of four complexes of this ligand with HgX_2 (X = Cl, Br, I, SCN) of the general type $[Fe(CO)_3(Ph_2Ppym)_2HgX_2]$. The organometallic ligand acts in a mono-, di-, and tridentate mode [101]. The variation of the molecular



Scheme 32.

structure by the use of different HgX_2 compounds is attributed to the difference of the acid strength of Hg(II) and the base strength of the N atoms of the ligand. In all compounds the Fe–Hg distances are consistent with the existence of a donor–acceptor metal–metal bond.

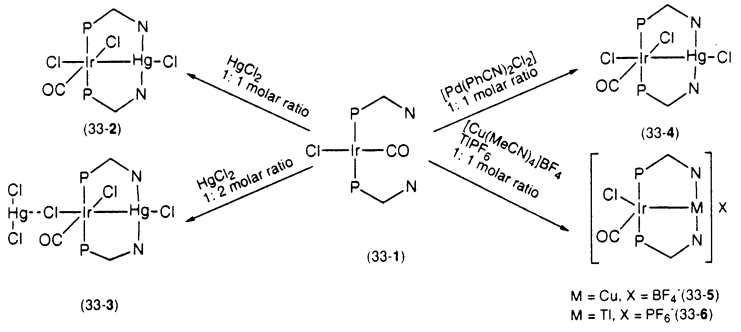
Similarly *trans*-[$Ru(CO)_3(PPh_2Py)_2$] reacts with a variety of Lewis acids ($ZnCl_2$, $CdCl_2$, $Cd(ClO_4)_2$, $HgCl_2$) [102] to give the corresponding heterobimetallic complexes *trans*-[$Fe(CO)_3(\mu\text{-}Ph_2Ppym)_2MX_2$]. Their X-ray structures were reported. From the change of $\nu(C{\equiv}O)$ with respect to *trans*-[$Ru(CO)_3(PPh_2Py)_2$] it is concluded that the Ru–M donor–acceptor interaction decreases with the hardness of the Lewis acid. Comparison with the $\Delta\nu(C{\equiv}O)$ of Fe–M complexes [97] finds the Ru–M values larger, which is explained by the higher basicity of Ru.

The neutral trinuclear cluster [$Ru_3(CO)_9(PPh_2Py)_3$] reacts with two equivalents of $HgBr_2$ yielding *cis*-[$Ru(CO)_3(\mu\text{-}PPh_2Py)(HgBr)_2$]. [$Os_3(CO)_{11}(PPh_2Py)$] reacts with $HgCl_2$ producing *cis*-[$Os(CO)_3(\mu\text{-}PPh_2Py)(HgCl)_2$]. The cleavage of the metal–metal bonds in the clusters is the result of two successive oxidative additions of HgX_2 to two cluster metal centers. The crystal structures of both complexes are reported [74].

[$(\eta^6\text{-}C_6H_6)Ru(PPh_2Py)Cl_2$] reacts with *cis*-[$Pt(DMSO)_2Cl_2$] to give [$(\eta^6\text{-}C_6H_6)Ru(PPh_2Py)(\mu\text{-}Cl)Pt(DMSO)Cl_2$]Cl, whereas the reaction between [$(\eta^5\text{-}C_5H_5)Rh(CO)(PPh_2Py)$] and [$\{(C_8H_{12})Ru\text{-}Cl_2\}_n$] in a 1:1 molar ratio is complicated, and work-up of the reaction mixture gives [$(C_8H_{12})RuCl(\mu\text{-}Cl)(\mu\text{-}PPh_2Py)Rh(\eta^5\text{-}C_5H_5)$] [16].

[Ir(CO)Cl(PPh_2Py)] reacts with CdI_2 in the presence of CO, affording the first Ir(I)–Cd(II) complex structurally characterized, *trans*,*trans*-[$I(CO)_2Ir(\mu\text{-}PPh_2Py)\text{-}CdI_2$]. IR data suggest that the Ir^I–Cd^{II} bond is donor–acceptor with reduction of the electron density on Ir. A red emission with quite a long lifetime, related to a 3MLCT excitation, occurs at room temperature when a solid sample of this complex is irradiated with UV light [103].

The ligand *trans*-[$Ir(PPh_2Py)_2Cl(CO)$] (33-**1**) was prepared recently and its reactivity with a variety of substrates was studied, among them SO_2, halogens, HCl, and CH_3I [104]. It was also used successfully for the synthesis of the heterobimetallic



Scheme 33.

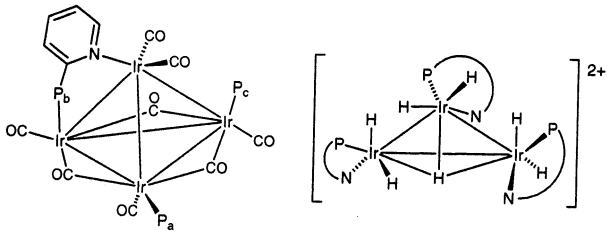
complexes shown in Scheme 33. The ligand adopts a head-to-head coordination mode, which is not usual for analogous complexes of electron rich metals.[9,10] In complexes 33-**4** and 33-**2** there is a change in the formal oxidation states of the metals, reflected in the ν(C≡O) values, whereas the formation of 33-**5** and 33-**6** is proposed to occur from the nucleophilic attack of the free Py nitrogens on the second metal center. The crystal structures of 33-**4** and 33-**3** have been determined.

4. Polynuclear compounds

The interest about molecular architectures is growing rapidly [105]. Polyfunctional rigid pyridylphosphine ligands with small bite angles and some ability to select the metal centers to which they bind can be used in the synthesis of polymetallic structures, such as linear chains or more complex polynuclear structures [78].

4.1. Homometallic

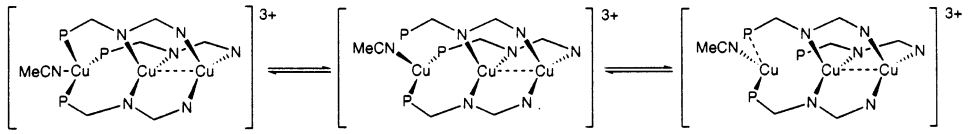
The cluster $Ir_4(CO)_{12}$ reacts with PPh_nPy_{3-n} to give $[Ir(\mu\text{-}CO)_3(CO)_5(\mu\text{-}PPh_n\text{-}Py_{3-n}\text{-}P,N)(PPh_nPy_{3-n}\text{-}P)_2]$ [106]. The schematic structure of these compounds is depicted in 16(**a**). An X-ray study of the PPh_2Py complex confirmed the proposed structure. The geometry of the clusters is retained in solution, the pyridyls do not exchange and carbonyl scrambling is not observed by NMR in the temperature range studied.



(16)

The polyhydrido cluster $[Ir_3(PePy)_3(H)_7](PF_6)_2$ was obtained by hydrogenation of $[Ir(PePy)(cod)](PF_6)$ in methanol (polyhydrido clusters have been isolated from catalytic hydrogenations using $[IrL_2(cod)]^+$ (L = tertiary phosphine or pyridine)), and characterized by X-ray crystallography [35]. Its schematic structure is shown in 16(**b**). The hydride positions were inferred by IR and NMR data, which also indicate that the structure is retained in solution.

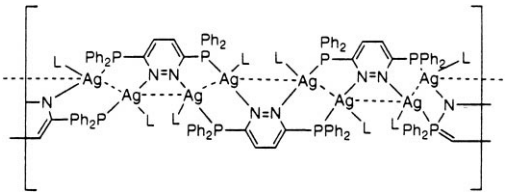
The already mentioned ligand dpnapy (see 13) reacts with $[Cu(MeCN)_4](ClO_4)$ affording $[Cu_3(\mu\text{-dpnapy})_3(MeCN)](ClO_4)_3$ [84]. This compound is one of the few Cu(I) complexes with a linear array of copper atoms. Its X-ray structure shows that only two of the copper atoms are connected through a metal–metal bond. The complex exhibits in solution a dynamic behavior due to the on and off switching of



Scheme 34.

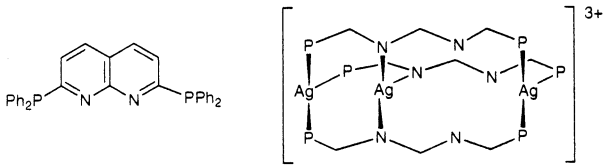
the P donors (Scheme 34). The trinuclear complex reacts with PPh_3 and 2,2′-bipyridine to give $[Cu_2(\mu\text{-dpnapy})_2](ClO_4)_2$ which. has been mentioned in the previous chapter, and $[Cu(bpy)(dpnapy)_2](ClO_4)$ which has been shown by X-rays to have the dpnapy ligand monocoordinated.

The reaction of $[Ag(MeCN)_4]ClO_4$ with 3,6-bis-(diphenylphosphino)pyridazine (**dppyaz**) leads to a polymeric product of $\{[Ag(MeCN)_2(\mu\text{-dppyaz})]\}_n(ClO_4)_n$ (17) [107]. Its structure was determined by X-ray analysis. The repeating structural unit is $Ag_2(MeCN)_2(\mu\text{-dppyaz})$. Successive dppyaz ligands lie on alternate sides of a zig-zag Ag(I) chain. Each silver is coordinated to the P of one dppyaz and the N of the other, and the centers of the eight-membered rings are inversion centers. The ability of dppyaz to act as a tetranucleating ligand with donor atoms that cannot coordinate to the same metal atom due to their linear arrangement is the reason for the self-assembly of this coordination polymeric chain. In contrast, $[Ag(MeCN)_4]ClO_4$ forms a polymeric species with $(Ph_2P)_2Py$ whose chain is linear, without coordination of the nitrogen.



(17)

The ligand 2,7-bis(diphenylphosphino)-1,8-naphthyridine **(dppnapy)** reacts with $AgClO_4$ to give $[Ag_3(dppnapy)_3](ClO_4)_3$ (18) [108]. The structure of the complex was established by partial X-ray crystal analysis. Upon photoexcitation at 300–400 nm it exhibits room temperature emission of a lifetime of 5.0 μs.



(18)

4.2. Heterometallic

The ligand **$(Ph_2P)_2Py$**, which at first sight fulfills the prerequisites for the synthesis of mixed-metal trinuclear species (soft and hard donor atoms, rigid

skeleton), presents problems mainly connected to its rigidity that imposes restrictions to the metal–metal separation. A recent review covers its chemistry in respect to the formation of polynuclear complexes [78].

Reaction of $[Ir_4(CO)_{11}Br]NEt_4$ with **PPh_2Py** in a 1:2 molar ratio affords $[Ir_4(CO)_{10}(PPh_2Py\text{-}P)_2]$. The pendant nitrogen atoms can then act as donors towards coordinatively unsaturated metals or naked metal ions. Thus, with $[Cu(NCMe)_4]BF_4$ or $AgPF_6$ the compounds $[Ir_4M(CO)_{10}(PPh_2Py)_2]X$ ($M = Cu$, $X = BF_4$; $M = Ag$, $X = PF_6$) [109]. The crystal structure of the copper compound is shown in Fig. 19.

The ligand **dppnapy** was presented in 18. The synthesis of the complex $[Au_2K(dppnapy)_3](ClO_4)_3$ has been reported together with its X-ray structure [108]. This metallamacrocycle contains a potassium cation strongly bound to three nitrogens, and shows room temperature emission upon photoexcitation at 300–400 nm.

The tridentate ligand 6-(2-diphenylphosphinoethyl)-2,2′-bipyridine (**L**) has been reported in two publications [110,42] and has been mentioned previously (Scheme 11). The X-ray structure and self-assembling properties of the metallosynthon complex *cis*-Cl_2-*trans*-P,P-*cis*-$(CO)_2[RuCl_2(L)_2(CO)_2]$ (11-**3**) for the preparation of metallamacrocycles have been reported. Copper(I)-induced self-organization of the metallamacrocycle $[\{Ru^{II}(L\text{-}P,N,N')_2(CO)_2Cl_2\}Cu^{I}]_2(ClO_4)_2$ was accomplished by reaction of (11-**3**) with $[Cu(MeCN)_4]ClO_4$ in a 1:1 molar ratio. This species forms a 36-membered $Ru_2Cu_2P_4N_8$ ring (Fig. 20). The *trans*-P,P stereochemistry of (11-**3**) prevents the bipyridine units from wrapping around just one metal center, and the fact that these units are substituted in the α-position makes (11-**3**) suitable for trapping pseudo-tetrahedral metal ions. The wrapping of (11-**3**) around two copper

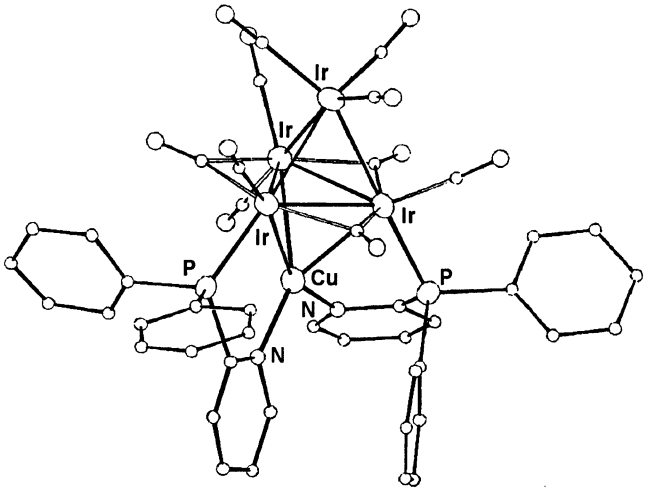


Fig. 19.

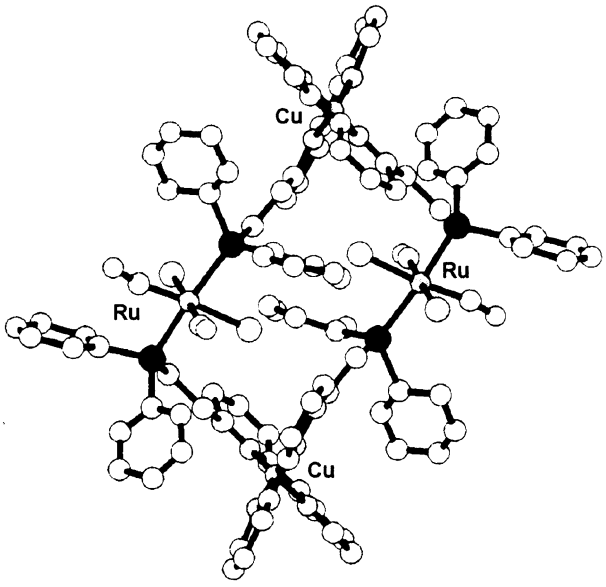


Fig. 20.

centers leads to an achiral complex and not to a double-stranded helix. The electrochemical properties of (11-**3**) and $[\{Ru^{II}(L\text{-}P,N,N')_2(CO)_2Cl_2\}Cu^{I}]_2(ClO_4)_2$ have been studied [42].

trans-$[Rh(CO)(Ph_2PPyOMe)_2Cl]$ (**Ph_2PPyOMe** = 2-(diphenylphosphino)-6-methoxypyridine) or *cis*-$[Rh(CO)_2(Ph_2PPyOMe)Cl]$ react with $[Cu(MeCN)_4]BF_4$ to yield the trinuclear compound $[Rh_2Cu(CO)_2(Ph_2PPyOMe)_2(\mu\text{-}Cl)_2]BF_4$ (Fig. 21)

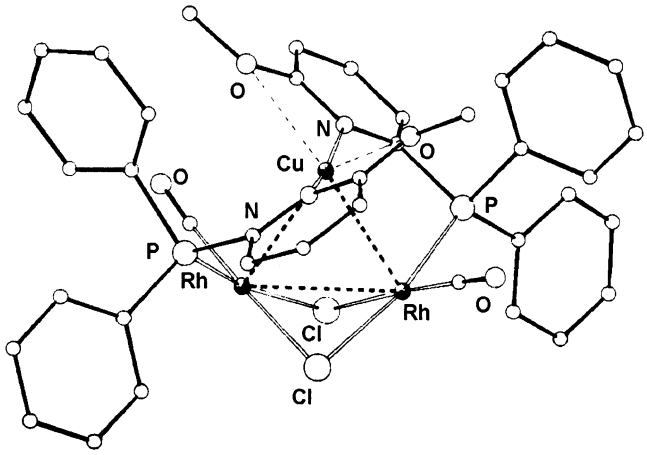
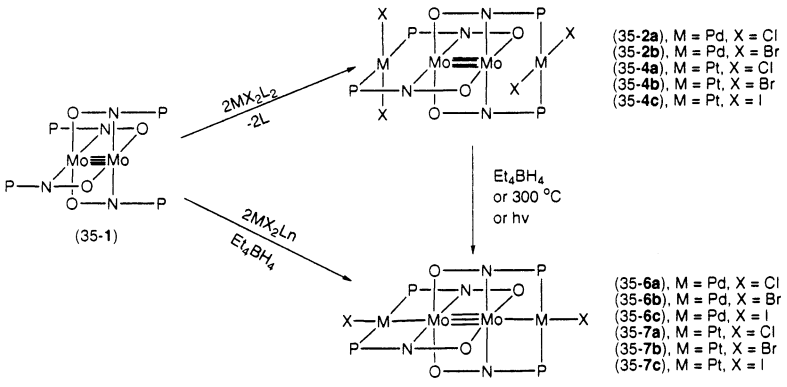


Fig. 21.

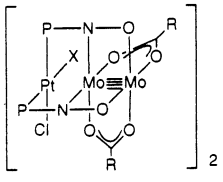


Scheme 35.

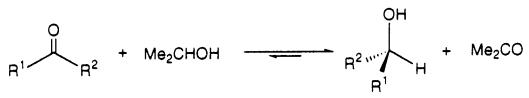
[111]. The formation of this compound can be visualized as a process in which the Cu^{+} ion is incorporated into a framework of *trans*-$[Rh(CO)(Ph_2PPyOMe)(\mu\text{-}Cl)]_2$. Attempts to obtain the analogous Au (I) compound failed, probably due to the bigger size of Au^{+}.

Low-dimensional materials present interesting magnetic, electronic and optical properties. Addition of metal ions to the *axial* position of a metal–metal bond, provides a new methodology for the formation of straight linear tetranuclear metal–metal compounds according to Scheme 35 [112]. The ligand (**Pyphos**), which has three coordination sites supported linearly by a rigid pyridone ring, has been revealed to be very powerful to support this kind of arrangement, and a large number of complexes have been prepared starting from $[Mo_2(Pyphos)_4]$ (35-**1**). Following the strategies summarized in Scheme 35, tetranuclear complexes with and without Mo–M′ bonds can be obtained. Many of them are supported by X-ray diffraction studies. Electrochemical studies on some of the systems indicate a strong electronic coupling between all the atoms of the linear system, which allows two well distinguished one electron redox processes.

The trinuclear Pt···Mo–Mo complexes $[Mo_2PtX_2(Pyphos)_2(O_2CR)_2]_2$ ($R = CH_3$, $C(CH_3)_3$; X = Cl, Br, I) have also been made (19) [113], and the structures of four of them determined by X-ray diffraction studies. Their electronic absorption spectra and the cyclic voltamograms depend on the halogen atom attached to Pt(II). The Pt···Mo interactions are sensitive to the halo ligands and the alkyl group, whereas the Mo–Mo bond is not affected by these substitutions.



(19)



Scheme 36.

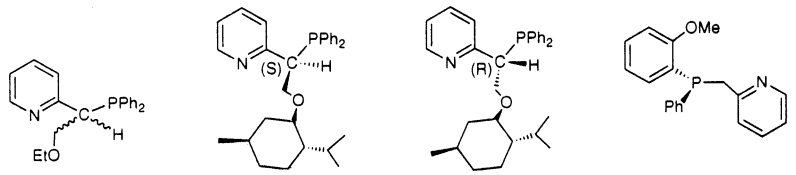
5. Catalytic studies

The catalytic activity of complexes containing phosphinopyridyl ligands is now reported briefly, and ordered by the type of catalytic process involved. The reviews in Refs. [9] and [10] also report on the catalytic activity of many of these compounds.

5.1. Asymmetric transfer hydrogenation

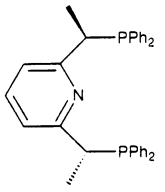
Transition metal catalyzed transfer hydrogenation of ketones with isopropanol (Scheme 36) has received much attention due to the low cost of the reducing agent and its operational simplicity [114]. In the asymmetric version high enantioselectivitiy has been achieved in some cases [115].

The potentially tridentate ligand **1** is shown in 20. The complex $[RuCl_2(PPh_3)(\mathbf{1})]$, which has already been mentioned in Section 2 [61], exhibited unprecedented activity in the transfer hydrogenation of ketones by 2-propanol [116]. Under the conditions employed, the transformation of cyclohexanone to cyclohexanol occurred with a turnover rate of 118 800 h^{-1}. This is probably the highest activity reported for a Ru catalyst in this reaction. High rates were also achieved with cyclopentanone and acetophenone, whereas for ethyl phenyl ketone the activity was low. The authors attribute this high activity to the presence of the hemilabile ether arm. However it has been argued that this is quite improbable in an alcoholic reaction medium [6b]. The similar chiral ligands 45-**2a**, **2b** and **3** were used for the preparation of the corresponding asymmetric complexes of the general type $[RuCl_2(PPh_3)(L)]$, which did not induce any significant enantiomeric excess (ee), although their activities were comparable to that of $[RuCl_2(PPh_3)(\mathbf{1})]$ [61]. Decreasing the temperature from 80°C results in the increase of the ee, but the activity decreases, suggesting that the reversibility of the reaction must be important with these catalysts.



(1) (2a) (2b) (3) (20)

The tridentate ligand (1R,1R′)-2,6-bis[1-(diphenylphosphino)ethyl]pyridine (21) can bind metals in a planar geometry and create a well defined C_2 symmetric chiral environment. It has been used in the in situ formation of a Ru catalytic system for the asymmetric transfer hydrogenation of aromatic ketones [117]. Asymmetric hydrogenation of various substrates was achieved with conversions between 33 and 98% and ee between 30 and 74%.

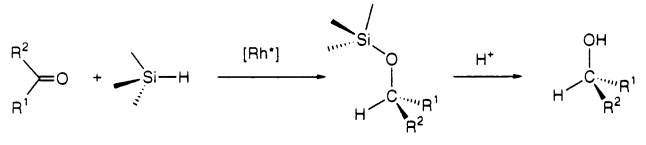


(21)

5.2. Asymmetric hydrosilylation

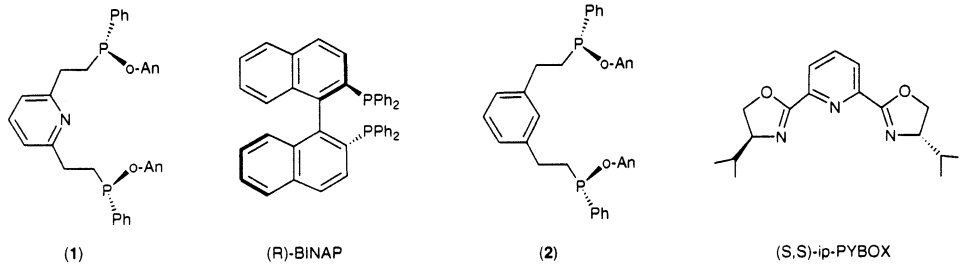
Hydrosilylation is the addition reaction of organic and inorganic silicon hydrides mainly to C–C, C–O, or C–N multiple bonds. The best known catalyst is a chloroplatinic acid known as Speier's catalyst [118]. Although most classical catalytic cycles involve the insertion of an olefin into a M–H bond [119], there are also postulates proposing an olefin insertion into a M–Si bond followed by C–H reductive elimination [120]. Rhodium–phosphine complexes are usually active in the asymmetric hydrosilylation of alkenes, ketones and aldehydes giving rise to optically active alkoxysilanes of high purity. Chiral Rh complexes predominate in the hydrosilylation of prochiral ketones (Scheme 37) [121].

A variety of optically active pyrroliminephosphines, aminophosphines and the pyridineaminophosphine (*S*)-*N*-(diphenylphosphino)-*N*-(1-phenylethyl)-2-pyridinmethanamine and their cationic Rh complexes were reported by Brunner. The pyridineamine phosphine and the corresponding Rh compound were presented in Scheme 22. The activity of both the isolated complexes and in situ prepared catalysts in the asymmetric hydrosilylation of acetophenone with diphenylsilane was investigated [59]. The ee was in the best case 19.6% in (*R*)-1-phenylethanol, with a pyrrolimine phosphine complex prepared in situ. The pyridineamine phosphine, although very active, gave only 4.4% (*R*) as the best ee. The activity and the ee depend on the Rh:ligand ratio, the Rh:substrate ratio, the reaction temperature and the solvent.



Scheme 37.

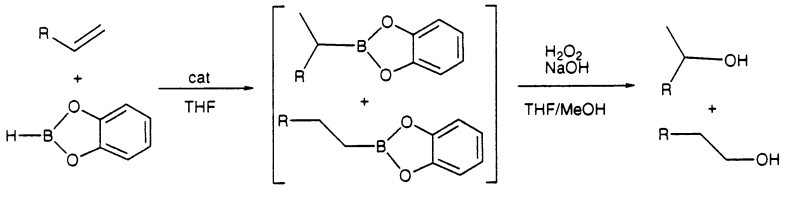
The chiral tridentate ligand **1**, presented in 22, was used for the in situ preparation of a Ru catalyst that catalyzes the asymmetric hydrosilylation of a variety of ketones with diphenylsilane [122]. In contrast to some Rh-systems with chiral bidentate nitrogen ligands that need a 10-fold excess of ligand in order to achieve high enantioselectivity, in the present case two equivalents of ligand per Ru are enough to achieve maximum enantioselectivity, which corresponds to 54% for acetophenone as a substrate. Although the enantioselectivity is much lower than those achieved with some Rh catalysts, this result is the best obtained with a Ru system. The ligands (*R*)-BINAP (**2**) and (*S*,*S*)-ip–PYBOX were tested for comparative purposes, and produced much lower ee, showing that the presence of the pyridine is crucial to achieve relatively high enantioselectivity. In a previous study on the asymmetric allylic alkylation catalyzed by Pd with the same ligands the pyridine-N seemed not to play any role [123].



(22)

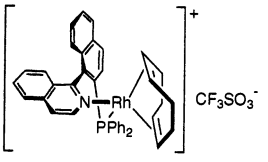
5.3. Asymmetric hydroboration

The hydroboration of unsaturated hydrocarbons is very useful for the functionalization of organic compounds. The use of transition metal complexes provides several advantages over the non-catalyzed reaction [124]. Milder conditions can be employed and, furthermore, in many cases the chemo-, regio-, and stereoselectivity can be reversed. Catecholborane (**HBCat**) is the boron hydride used in most of the cases for the metal catalyzed hydroboration. The general reaction is outlined in Scheme 38. The first examples of catalytic hydroboration have been reported by Burgess [125] and Suzuki [126] with 1,1- and 1,2-substituted olefins as substrates and in situ formed Rh complexes with chiral phosphine ligands as catalysts. The detailed mechanism is not known but it is consistent with a cycle in which the addition of borane to Rh occurs first [127].



Scheme 38.

A (*S*)-QUINAP Rh complex **1** (23) was used for the catalyzed asymmetric hydroboration of several vinyl arenes. The hydroboration followed by oxidation afforded the corresponding 1-aryletanols in up to 99% chemoselectivity and 94% ee [128]. A comparison of the performance in the asymmetric hydroboration of several alkenes of **1** and of the corresponding complexes with (*R*)-PHENAP (**2**) (Scheme 18) [129], showed that in general the ee obtained with **2** is lower than with **1**. The most interesting results [130] were obtained for two substrates for which **2** gave better results than **1**, demonstrating that steric effects in the substrate and the ligand have an important influence on the stereoselectivity. The two ligands, as well as BINAP (22) catalyze the reaction with the same sense of relative asymmetric induction. The striking differences between **1** and **2** indicate that the phenanthridine moiety of **2** participates to control the diastereoselectivity in the stereochemically defining transition-state for hydride transfer from Rh to carbon. The same complex **1** has been applied to amination reactions starting with a catalytic hydroboration of the vinylarenes [131]. This has developed into a one-pot asymmetric synthesis of primary amines [132]. The ee achieved reflect those of the enantioselectivity of the hydroboration step, and ranged from 77 to 98%.

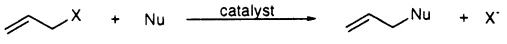


(23)

5.4. Allylic substitution

The allylic substitution reaction is the substitution by a nucleophile of an appropriate leaving group in an allylic position (Scheme 39) [133]. Metal complexes of nickel, palladium, platinum, rhodium, iron, ruthenium, molybdenum and tungsten have been used as catalysts. Palladium is by far the metal of preference. The catalytic cycle involves a π-allyl metal complex as a key intermediate, formed by oxidative addition of an allylic substrate to a Pd(0) species. The π-allyl metal complex then undergoes attack of a nucleophile on the π-allyl group, in a rate-determining step, to give the allylic substitution product.

Metal-catalyzed **asymmetric** C–C and C–N bond forming allylic substitutions confer additional interest to the use of this reaction in synthesis. The reaction occurs with retention of the configuration at carbon. In the last years spectacular improvements have been achieved and enantiomeric excesses greater than 95% are quite usual. The chiral catalyst often consists of a Pd complex containing a chiral chelating ligand, or it can be generated in situ from $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ or



Scheme 39.

$[Pd_2(dba)_3]\cdot CHCl_3$ and the chiral ligand. The donor atoms of the chiral ligand can be P–P [134], P–S [135], P–N [136], P–O [137], N–N [138] N–S [139]. The bond breaking and bond forming reactions occur away from the metal, in contrast to the majority of asymmetric reactions in which the stereogenic center is formed within the coordination sphere of the metal. The creation of a deep chiral pocket surrounding the substrate was proposed by Trost [140]. For chiral bidentate ligands these pockets can be created by increasing the bite angle of the chelating ligand. Application of this idea has led to very efficient catalysts.

The ligand *N*-(2-(diphenylphosphino)benzylidene)(2-(2-pyridyl)ethyl)amine and several Pd complexes of it were presented in the previous section and in Scheme 12 [43b]. Complex 12-**7** has been used as a catalyst precursor for allylic alkylation, in order to compare its activity that displayed by other catalysts employed in the asymmetric version of the reaction. The rates with 12-**7** are much higher than with the corresponding asymmetric catalysts. The authors attribute the higher rates to the presence of the chelated imino-N, the π-accepting properties of which increase the electrophilicity of the η^3-allyl intermediate species, hence increasing its susceptibility to nucleophilic attack.

Pd complexes of the previously mentioned ligand QUINAP (Scheme 17) are highly reactive catalysts (comparable to the catalysts obtained from phosphinoaryloxazolines) [135,136b] for the reaction of (*E*)-1,3-diphenyl-2-propenyl acetate with dimethyl malonate [54]. The enantiomeric excess ranges from 67 to 98%. 2-Cyclohexenyl acetate and 1.1.3-triphenyl-2-propenyl acetate gave lower ee, 67 and 47%, respectively. The interconversion between various $[Pd(P,N)^*(allyl)]^+$ diastereoisomeric complexes in solution has been studied by NMR. When the nucleophile attacks the allylpalladium complex, bond reorganization is taking place, as the allylic moiety changes its hapticity, from η^3 to η^2. Partial bonding of the nucleophile to the free carbon causes the rehybridization of the later towards sp^3. Interactions between the ligand and the allyl fragment during this rearrangement are decisive for the outcome of the reaction. From crystallographic, NMR, and catalytic evidences it is proposed that the reaction proceeds through a late transition-state in which the nucleophilic attack happens preferentially on the predominant diastereoisomer and on the carbon *trans* to the P of the chelate ligand. Other authors for other P–N asymmetric ligands also have reached the conclusion that the nucleophilic attack happens preferentially on the carbon *trans* to P, though through a different rationalization that takes into account electronic as well as steric effects induced by the ligand [135]. In Fig. 22 the 3-D molecular models of (**A**) the favored and (**B**) the disfavored diastereomer (as seen by NMR data), are shown. As it can be seen, in a late transition state, attack *trans* to N brings about steric congestion between the allyl and one P phenyl group in both diastereomers, so attack *trans* to P is favored. In the minor isomer (**B**), this attack produces important steric hindrance between the H-3 of isoquinoline and the vicinal Ph group of the allyl moiety.

A comparison of the catalytic activity of the ligands QUINAP (Scheme 17) and PHENAP [55] (Scheme 18) showed that, although the PHENAP complex exhibits higher diastereoselectivity upon complexation with the 1,3 diphenylallyl moiety (as

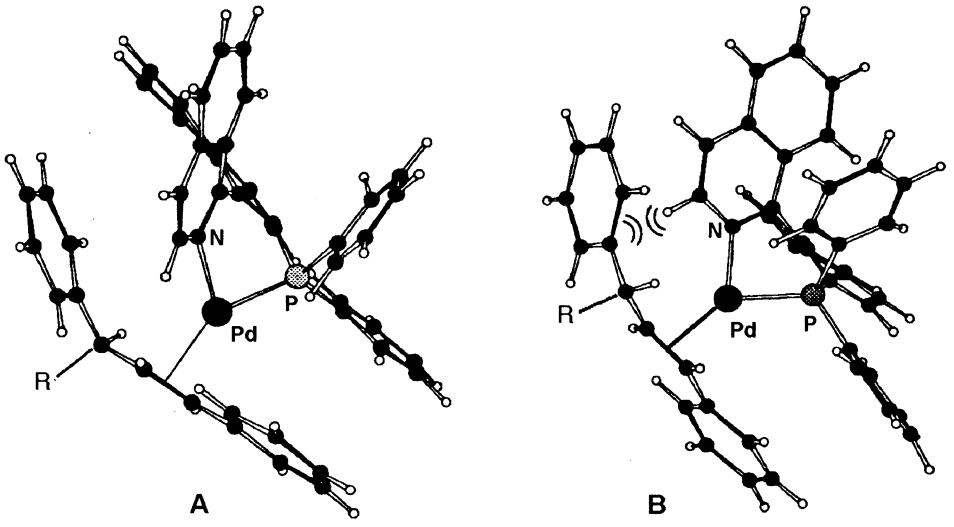
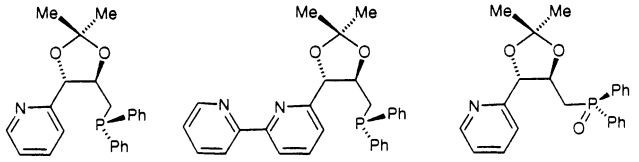


Fig. 22.

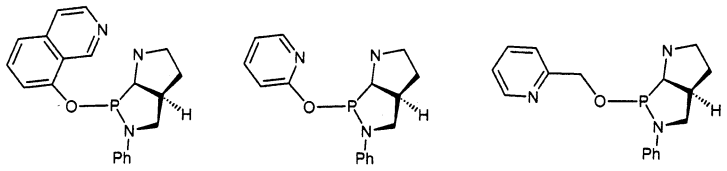
discussed in a previous chapter), it gives a lower ee in the reaction of 1,3 diphenylallyl acetate. Despite the high level of recognition in the cyclohexenyl complex of PHENAP, there was no allylic alkylation of cyclohex-3-en-1-yl acetate under standard conditions.

The catalytic activity of a homochiral pyridylphosphine ligand derived from L-(+)-tartaric acid, PYDIPHOS, was examined in the allylic alkylation of 1,3 diphenyl-2-propenyl acetate with dimethyl malonate [136,58]]. The catalyst used was [(PYDIPHOS)Pd(η^3-C_3H_5)]PF_6, preformed or prepared in situ with from [Pd(η^3-C_3H_5)Cl]$_2$ and PYDIPHOS (Pd:PYDIPHOS = 1:2). The catalysts were effective giving high yield of product, but the enantioselectivity was low (ee < 10% (*R*)). The ligand is presented in 24 together with its phosphine-oxide and its bipy analog. The ligands **1** and **2** have been used for other catalytic reactions (see Section 5.7).



(24)

The ligands that are shown in 25 are chiral on P and have been used in the allylic substitution of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate [137]. The complexes used as catalysts were formed in situ from [Pd(η^3-C_3H_5)Cl]$_2$ and the ligands in various Pd:ligand ratios. Ligand **1** was used for the optimization of the conditions. The best ee obtained was 85% (*R*). Under the best conditions ligands **2** and **3** gave almost the same results as **1**.



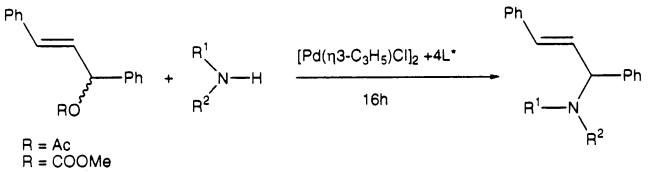
(25)

The same ligands shown in 25 were used for the enantioselective allylic amination according to the reaction shown in Scheme 40 [143]. The amines used as nucleophiles were phenylamine, veratrylamine and morpholine. The enantioselectivities were up to 94% (*S*), **1** and **3** giving the best results.

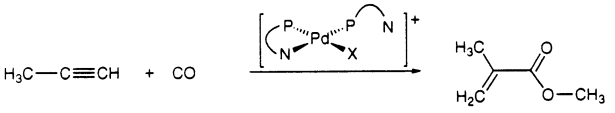
The pyridyl-substituted phosphaferrocenes shown in Scheme 25 were tested in the allylic alkylation of 1,3-diphenyl acetate with sodium malonate as nucleophile in the presence of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$. The yields ranged from 65 to 80%, but the ee were low ($< 20\%$ (*R*)) [72].

5.5. Carbonylations

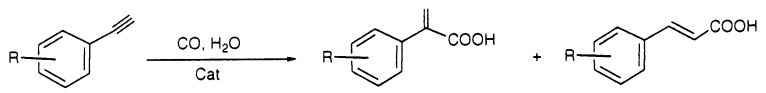
Methoxycarbonylation of propyne leads to the production of methyl methacrylate with unprecedented activity and almost complete regioselectivity, using as a catalyst palladium acetate in combination with phosphines and methanesulfonic acid (Scheme 41) [144]. Upon replacement of PPh_3 with 2-$PyPPh_2$, even at much milder conditions, a spectacular increase both in rate (from 10 to 40 000 $mol_{sub}(mol_{Pd})^{-1}\ h^{-1}$), as well as in selectivity (from 89 to 98.9%) takes place. 3-$PyPPh_2$ did not produce such a big rate increase and 4-$PyPPh_2$ gave results very similar to PPh_3. The acids that promote the reaction are strong acids with a weakly coordinating anion. A methyl substituent at the six-position of the 2-pyridyl groups raised the selectivity to 99.95% with conservation of the catalytic activity, whereas substitution at the four-position did not affect the selectivity. Increasing the number



Scheme 40.



Scheme 41.



Scheme 42.

of pyridyl groups does not affect the selectivity of the catalyst while it provokes a drop in activity. Similar results were obtained on other alkynes as substrates and other nucleophilic reagents apart from methanol, giving rise to a variety of unsaturated carboxylic acids, esters and amides. It is proposed that complexes of the type shown in Scheme 41 play a key-role.

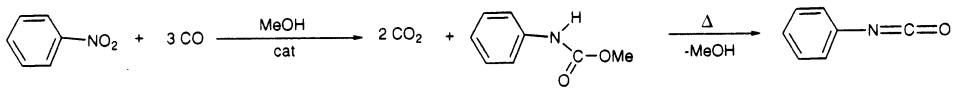
The same catalytic system was employed successfully for the production of 2-arylpropenoic acids by hydrocarbonylation of the corresponding 1-alkynes (Scheme 42) [145]. The conversions are very high under 30 bar of CO, but they are acceptable even at atmospheric pressure. The regioselectivity is also high, e.g. over 98% towards atropic acid against less than 2% of the isomeric cinnamic acid.

The hydrocarboethoxylation of styrene was studied employing as catalysts [Pd(PYDIPHOS)Cl_2] [58] and the in situ formed species from $PdCl_2$ and PY-DIPHOS or its derivative **1** of 24 [141]. The preformed complex presented satisfactory activity [141,142], and the ee was 20%(*R*) [141], but the in situ formed complexes did not function satisfactorily. This behavior is attributed to the difficult complexation of the ligands in a chelating mode. The fact that the branched ester is the only product also suggests that the ligands bind in a monodentate way.

5.6. Reductive carbonylation of nitro group

This is a one-step process in which the nitro function reacts directly with CO in the presence of a catalyst. The carbamate, which is the main product if the reaction is carried out in an alcohol, is then converted to the corresponding isocyanate if desired (Scheme 43).

Several bidentate P–N ligands have been used in the palladium-catalyzed reductive carbonylation of nitrobenzene [22]. The catalysts were used either as preformed complexes [Pd(bidentate ligand)$_2$](BF_4)$_2$ with 3 equivalents of free ligand, or generated in situ using $Pd(OAc)_2$, the ligand in a ratio ligand:Pd = 10, and adding 2,4,6-trimethylbenzoic acid as cocatalyst for the replacement of the acetate ions. Several bidentate nitrogen ligands and bidentate phosphorus ligands were tested for comparison. The imine containing P–N ligands were found to be inactive. The PePy and PQN ligands gave moderately active systems.



Scheme 43.

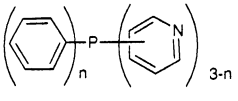
5.7. Hydroformylation

Mixed ligands such as PePy, PPh_2Py and $PPh_2(CH_2)_nNMe_2$, ($n = 1,2,3$), were tested in the Rh catalyzed hydroformylation of olefins (styrene, 1-decene, α-methylstyrene) under mild conditions (600 psi of *syn*-gas, 80°C) [147]. The catalysts were prepared in situ from $[RhCl(cod)]_2$. The P–N ligands are superior to the monophosphines and biphosphines used for comparison both in yield (up to 87% for styrene) and in selectivity towards the branched isomer for styrene (up to 98:2). Using the corresponding phosphine oxide derivatives of the above mentioned ligands yields ranging from 23 to 100% and a selectivity more or less constant (87–92% towards the branched aldehyde) were found for the hydroformylation of styrene [148].

Reaction of $[Ru(PPh_2Py)_3Cl]Cl$ (**a**) (Scheme 3) with $[RhCl(CO)_2]_2$ or $[IrCl(CO)_2(p\text{-toluidine})]_2$ afforded $[Ru(PPh_2Py)_3Cl][RhCl_2(CO)_2]$ (**b**) and $[Ru(PPh_2Py)_3Cl][IrCl_2(CO)_2]$ (**c**), respectively [15]. These three complexes and $[RhCl_2(CO)_2](AsPh_4)$ were used as catalysts for the hydroformylation of styrene at the temperature range 45–100°C and under 20–60 atm of $CO:H_2 = 1:1$ [15]. The bimetallic complex (**b**) is much more active than the mononuclear complexes $[RhCl_2(CO)_2](AsPh_4)$ and $[Ru(PPh_2Py)_3Cl]Cl$, which indicates a cooperative effect between the anionic Rh and the cationic Ru moieties and implies that both metals take part in the reaction. Compound (**c**) showed negligible activity.

The complexes 33-**1**, **5** and **6** shown in Scheme 33 catalyze the hydroformylation of styrene at temperatures of 60 and 80°C and under 60 and 80 atm of $CO:H_2 = 1:1$ [104]. PPh_2Py causes a pronounced effect on the catalytic activity of 33-**1**, since Vaska's complex displays negligible activity under the same experimental conditions. A catalytic cycle is proposed in which protonation of one of the uncoordinated Py occurs at the beginning of the catalytic cycle. The final step is the protonolysis of an Iridium(I) acyl species by this protonated pyridyl group, giving the aldehyde and regenerating (33-**1**). Complexes (33-**5**) and (33-**6**) showed a catalytic activity comparable to the one of (33-**1**), and it was proven by IR and NMR data that, under catalytic conditions, the Cu–N and Tl–N bonds are broken to give (33-**1**).

A variety of mixed ligands, among which the pyridylphosphines shown in 26, were tested in the Rh-catalyzed hydroformylation of 1-octene [149]. The catalysts were prepared in situ using $[Rh(acac)(CO)_2]$ in a ratio ligand:Rh = 1:2. The pyridylphosphines showed reaction rates up to twice faster than PPh_3 (**3** = **2** = **1** = PPh_3). This is attributed to the electron-withdrawing nature of the pyridyl group, since the pyridyl-N is placed in *meta*- or *para*- positions and cannot chelate. No effect on selectivity was observed. This system is not suitable for 'true' biphasic catalysis, and in an attempted two-step recycling process the pyridylphosphine catalysts decomposed during the acidic extraction step [150].



(**1**) n = 2, 4-pyridyl
(**2**) n = 2, 3-pyridyl
(**3**) n = 1, 3-pyridyl

(26)

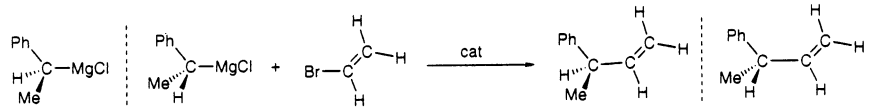
The ligand 2-[1-(1*S*,2*S*,5*R*)-(−)menthoxydiphenylphosphino]pyridine was presented in a previous section and was shown in 8. The complexes obtained with this ligand, $\{Rh(C_8H_{12})[(-)menthoxy\text{-}PPy]\}ClO_4$ (**1**) and $\{Rh(CO)(PPh_3)[(-)menthoxy\text{-}PPy]\}ClO_4$ (**2**), were tested in the hydroformylation of styrene, 2-vinylnaphthalene, methacrylate and vinylacetate [62]. In the hydroformylation of styrene **1** is less effective than **2**. The chemoselectivity and regioselectivity for branched to linear aldehyde is high, but the enantioselectivity is low (ee = 6% (*R*)). The hydroformylation of 2-vinylnaphthalene with **2** took place with 100% conversion and the branched aldehyde was the only product with a high enantioselectivity (ee = 78% (*R*)). The highest ee (92% (*R*)) was achieved in the hydroformylation of methylacrylate using **2** as catalyst precursor, under 60 atm of CO/H_2 and at 60°C for 16 h. The temperature affects the ee strongly. As far as vinylacetate is concerned, **2** exhibits 100% conversion and 100% regioselectivity for the branched product, but the enantioselectivity is low (ee = 12% (*R*)).

The ligand PYDIPHOS (24) and its P-oxide were employed in the Rh catalyzed enantioselective hydroformylation of styrene. The catalyst was formed in situ from $[Rh(CO)_2(acac)]$ and the ligand in a ratio 1:2.5 [151]. The addition of the phosphine reduces the catalytic activity of $[Rh(CO)_2(acac)]$, whereas the phosphine-oxide enhances the reaction rate (97% in 5 h). The enantioselectivity is always less than 1%. The difference is attributed to the ability of the P-oxide to form an eight-membered (N,O) chelate. The weakly interacting group (O) can produce a vacant coordination site, promoting the oxidative-addition of H_2.

The hydroformylation of styrene was also investigated with the preformed complexes [Rh(PYDIPHOS)(CO)Cl] and $[Pt(PYDIPHOS)(SnCl_3)Cl]$ [58]. Compared to the in situ catalytic runs, where there was practically no asymmetric induction, in the reaction with [Rh(PYDIPHOS)(CO)Cl] much lower catalytic activity was observed, but the ee was about 30% [141]. The authors suggest that the concentration of the catalytic active species bearing the chiral ligand is too low and the reaction is mainly catalyzed by the more active unmodified Rh carbonyl complexes that are dominant under hydroformylation conditions. Similar results were obtained with the ligands **1** and **2** of 24 used in situ. The complex $[Pt(PYDIPHOS)(SnCl_3)Cl]$ reduces the regioselectivity while the ee was 31% (*R*).

5.8. Decarbonylation of aldehydes

Cationic diphosphine complexes of Rh and Ir have good catalytic activities in the decarbonylation of aldehydes, and mechanistic studies have shown that M–P bond cleavage is the rate limiting step. Considering that usually M–N bonds are more labile than M–P bonds, it was expected that P–N ligands would induce higher catalytic activities. In addition oxidative-addition to more electron rich complexes of the type $[M(PN)_2]^+$ should be easier. Pignolet et al. demonstrated that $[Rh(PN)_2]BF_4$ complexes (PN = PePy) were inferior catalysts for the decarbonylation of benzaldehyde, compared to $[Rh(dppp)_2]BF_4$ while the iridium analogs $[Ir(PN)_2]PF_6$ were better than $[Ir(dppp)_2]PF_6$ [36]. Assuming that the mechanisms



Scheme 44.

for these two catalysts was the same as for $[Rh(dppp)_2]^+$, then the increased rates of $[Ir(PN)_2]PF_6$ could result from the increased lability of the Ir–N bond relative to Ir–P. The most probable reason for the behavior of the $[Rh(PN)_2]BF_4$ is the slower oxidative addition, although a slow Rh–N bond cleavage cannot be ruled out completely.

5.9. Cross-coupling

Several N–N, P–P and P–N ligands, including (*S*)-*N*-(diphenylphosphino)-*N*-(1-phenylethyl)-2-pyridin-methanamine (Scheme 20), were used with $NiCl_2$ as in situ catalysts for the enantioselective cross-coupling of 1-phenylethylgrignard and vinyl-bromide (Scheme 44) [152]. The pyridylphosphine ligand gave a very low ee (1.4% (*S*)). Using PYDIPHOS (24) and $NiCl_2$ the enantioselectivity, though still not satisfactory, was much higher (26% (*R*)) [146].

5.10. Ethylene oligomerization

The use of cationic and neutral Ni compounds with the chelating ligands methyl 2-(diphenylphosphino)nicotinate and 2-(diphenylphosphino)nicotinic acid in ethylene oligomerization, with and without methylalumoxane (**MAO**), has been reported [20a]. The cationic compounds of methyl 2-(diphenylphosphino)nicotinate were presented in Scheme 5. The neutral complexes yielded linear α-olefins, whereas the cationic complexes oligomerized the substrate to a mixture of linear and branched olefins. Oligomerization of the branched olefins lead to branched products. Addition of MAO resulted in a dramatic increase of the activity, but with complete loss of chemoselectivity.

Acknowledgements

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Appendix A. Abbreviations

Py	2-pyridyl group

PPh_2Py	2-(diphenylphosphino)pyridine
cod	1, 5-cyclooctadiene
bpzm	bis(pyrazol-1-yl)methane
PMe2Py	2-(dimethylphosphino)pyridine
PQN	8-(diphenylphosphino)quinoline
PePy	1-(diphenylphosphino)-2-(2-pyridyl)ethane
Me_2PQN	8-(dimethylphosphino)quinoline
MQP	(8-methyl-2-quinolylmethyl)di-*t*-butylphosphine
PNP	2,6-bis(diphenylphosphinomethyl)pyridine
$PePy_2$	$P(CH_2CH_2Py)_2Ph$
$PePy_3$	$P(CH_2CH_2Py)_3$
NBD	norbornadiene
TFB	tetrafluorobenzobarrelene
PPN	$Py(CH_2)_2P(R')(CH_2)_mPR_2$
PPPN	$(CH_2)_2P[(CH_2)_mPR_2]_2$
PPNN	$(CH_2)_m[P(R')(CH_2)_2Py]_2$
PON	o-$Ph_2PC_6H_4CH_2O(CH_2)_nPy$, ($n = 1, 2, 3$)
8-AZQ	8-azidoquinoline
QUINAP	1-(2′-diphenylphosphino-1-naphthyl)-isoquinoline
PHENAP	6-(2′-diphenylphosphino-1′-naphthyl)penanthridine
PYDIPHOS	(−)-(4*S*,5*R*)-4-(2-pyridyl)-5-(diphenylphosphino)-methyl-2,2-dimethyl-1,3-dioxolane
PePyE	1-(diphenylphosphino)-2-ethoxy-1-(2-pyridyl)ethane
dpbipy	6-diphenylphosphino-2,2′-bipyridine
dba	1,5-diphenyl-1,4-penta-dien-3-one
$(Ph_2P)_2Py$	2,6-bis(diphenylphosphino)pyridine
dpnapy	7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine
Ph_2Ppypz	2-diphenylphosphino-6-(pyrazol-1-yl)pyridine
Ph_2Pbipy	3-diphenylphosphino-2,2′-bipyridyl
Pyphos	6-(diphenylphosphino)-2-pyridonate
dppyaz	3,6-bis-(diphenylphosphino)pyridazine
dppnapy	2,7-bis(diphenylphosphino)-1,8-naphthyridine
$Ph_2PPyOMe$	2-(diphenylphosphino)-6-methoxypyridine
HBCat	catecholborane
MAO	methylalumoxane

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