Coordination Chemistry Reviews 236 (2003) 143–206

COORDINATION CHEMISTRY REVIEWS

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Structural diversity in coordination chemistry of tridentate and tetradentate polyphosphines of Group 6 to 10 transition metal complexes

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Received 7 March 2001; accepted 30 August 2002

Contents

Abstract

Tridentate and tetradentate polyphosphines offer a huge variety of coordination modes to transition metals which lead, depending on the metal, to very different structural features in the resulting complexes. Steric effects being crucial in metal–phosphine

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PII: S0010-8545(02)00221-7

complexes reactivity, a good knowledge of the molecular structures of the species is required both in the solid state and in solution. This article reviews from a structural point of view the monometallic and symmetrical homobimetallic complexes of the transition elements of Group 6 to 10 with tridentate and tetradentate phosphines. Concerning the classical triphosphines and tetraphosphines, emphasis was put on advances reported after the year 1994, since comprehensive reviews have covered the former period. Several anterior relevant results are, however, briefly mentioned when necessary. A second part is devoted to nitrogen- and sulfur-containing derivatives potentially tridentate and tetradentate ligands, and their coordination to the above-mentioned metals. The last part describes the complexes obtained with the less classical ferrocenyl polyphosphine ligands or their nitrogen-containing derivatives: each ligand having a potential tridentate or tetradentate coordination from either phosphorus or nitrogen donor atoms. The literature cutoff date was during the second half of 2000, but in a few cases, references to important work appearing during 2001 were made; however such coverage should be completed in a future compilation. An exhaustive quoting of catalytic applications and reaction chemistry was beyond the scope of this article mainly devoted to structural works. Nevertheless, in order to illustrate the importance of this chemistry, efforts were made to provide the reader with recent references that have marked the field, even in the absence of X-ray structural characterization.

Keywords: Polyphosphines complexes; Tridentate phosphines; Tetradentate phosphines; Nitrogen-containing phosphines; Sulfur-containing phosphines; Ferrocenyl phosphines; Group 6 to 10; Transition metals; Crystal structures

1. Introduction

The coordination chemistry of polyphosphine ligands has been experiencing, since the 1960s [1], increasing development in the structural design of novel metal complexes and their application in some of the major chemical reactions of homogeneous catalysis. Bidentate phosphines such as bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe) or 1,3-bis(diphenylphosphino)propane (dppp), have attracted considerable attention due to their excellent ligating properties to almost all transition metals of the periodic table [2–4]. Following this interest, higher-rank potential polydentate phosphines such as tridentate, tetradentate or hexadentate polyphosphines were synthesized and their coordination chemistry and reactivity intensively examined. In 1992, a detailed review by Cotton and Hong appeared, covering the syntheses, structural aspects and some applications of polydentate phosphines [5]. This work was completed later by Mayer and Kaska, who reviewed the reaction chemistry of polydentate metal complexes, including non-transition metals [6]. Other related articles with more specific purposes were also recently published: (i) Bianchini et al. have developed the selectivity control of organometallic reactions via tripodal polyphosphines ligands [7], (ii) Woollins et al. have reviewed the bis(diphenylphosphino)amine chemistry [8], and (iii) bidentate medium-sized ring phosphine compounds has been reviewed by Alder and co-authors [9]. Several other reports from the 1980s on the reaction chemistry of polyphosphine can provide the reader with a useful background [10–13].

One interest of our group is focused on novel molecular architectures of polydentate phosphines-containing transition metal complexes more specifically with ferrocenyl polyphosphines [14–16]. We review here from a structural viewpoint the monometallic or homobimetallic complexes of the transition elements of Group 6 to 10 containing tridentate or tetradentate phosphines ligands. A few compounds containing metals of Group 11 (Cu, Ag, Au) or 12 (Hg) are quoted for comparison, or because of particularly intriguing geometries.

The relevant advances since 1994 concerning classical tridentate and tetradentate polyphosphines are described on the basis of the Cotton and Hong [5], and the Kaska and Mayer reviews [6]. Nevertheless, for reasons of brevity the earlier principal results have only been briefly reported. The second part of this review is devoted to the tridentate and tetradentate phosphine-derivatives in which nitrogen or sulfur donor atoms substitute one or several phosphorus atoms. A final part deals with the ferrocenyl polyphosphines and the nitrogen/phosphorus ferrocenyl derivatives, for which a potential tri- or tetradentate coordination mode has been reported. The crystal structures of the resulting coordination complexes obtained with transition metals are also described.

In view of the extensive literature, we reference almost exclusively only those species characterized by single crystal X-ray diffraction studies. However, some recent relevant papers that contain spectroscopically identified complexes were quoted in order to illustrate the importance of polyphosphine metal chemistry. Consequently, the literature referenced in this case constitutes only selected examples to provide the reader with a substantial basis. Also excluded were the trinuclear and heterobimetallic polyphosphine complexes as well as the cluster, macrocyclic derivatives, and catenated compounds. Moreover, due to our structural interest, only complexes with at least biligate ligands were mentioned, except for Section 4.2 where a few complexes containing monoligate 1N/2P donor ligands are quoted for information. A systematic approach leads one to present the referenced complexes listed either by metals [6] or by ligands (family type of ligands) [5]; this last option was retained in the current review. The terms monoligate, biligate, triligate or tetraligate are preferred to monodentate, tridentate or tetradentate in order to account for the actual number of donor atoms involved in bonding of the tridentate or tetradentate ligands described here.

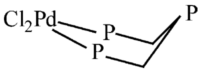
2. Linear, tripodal and other simple tridentate phosphines and their metal complexes

2.1. Linear triphosphines

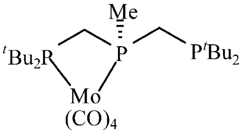
A large number of linear triphosphines are known. They lead to various modes of coordination depending on: (i) the substituents present on the phosphorus atoms, (ii) the other ligands bonded to the metal, and mostly (iii) the backbone length of the phosphine. The most commonly used linear triphosphines represented in Scheme 1 are [$(Ph_2PCH_2)_2PPh$] bis[(diphenylphosphino)methyl]phenylphosphine (dpmp), [$(Ph_2PCH_2CH_2)_2PPh$] bis[2-(diphenylphosphino)ethyl]phenylphosphine (etp) and [$(Ph_2PCH_2CH_2CH_2)_2PPh$] bis[3-(diphenylphosphino)propyl]phenylphosphine (ttp). The parent compound eptp (Scheme 1) has been much less studied.

The ligands that contain methylene linkages (type dpmp) bonded to one metal are generally biligate and form six- or four-membered metallacycles, as shown for instance in Schemes 2 and 3, respectively, with $PdCl_2(dpmp)$ [17] and $Mo(CO)_4[(^tBu_2PCH_2)_2PMe]_2$ [18]. These modes of coordination leave a free phosphorus donor, allowing thus the potential formation of polynuclear species, as shown in Scheme 4 [19].

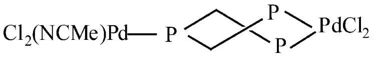
Interestingly, combined modes of coordination were found. Balch et al. have shown that, for a 1:2 ratio metal:ligand, complexes containing two dpmp ligands can adopt a structure with one six-membered and one four-membered ring [20]. In the cation $[Pd(dpmp)_2]^{2+}$, the palladium atom is in a square-planar environment. The six-membered ring formed adopts a pseudo chair geometry. The related iridium complex $[Ir(dpmp)_2CO]^+$ displays a five-coordinate geometry, the two dpmp ligands forming also one six-membered and one four-membered chelating ring (Scheme 5) [21]. One major interest of these structures, is the possibility to stabilize very original dinuclear and trinuclear mixed species in a controlled way, through further chelate ring opening of the metal complexes.



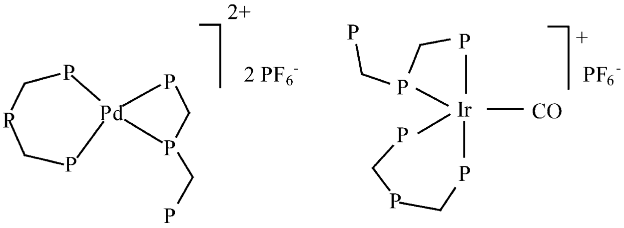
Scheme 2.



Scheme 3.

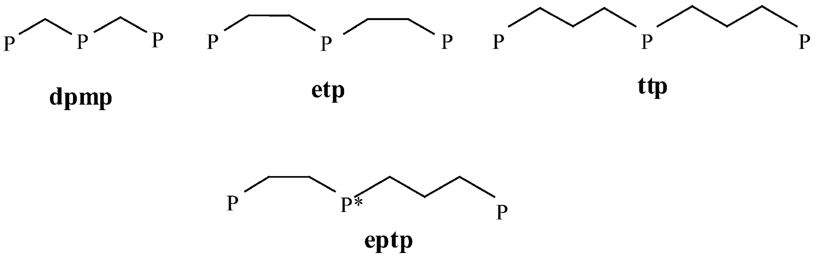


Scheme 4.

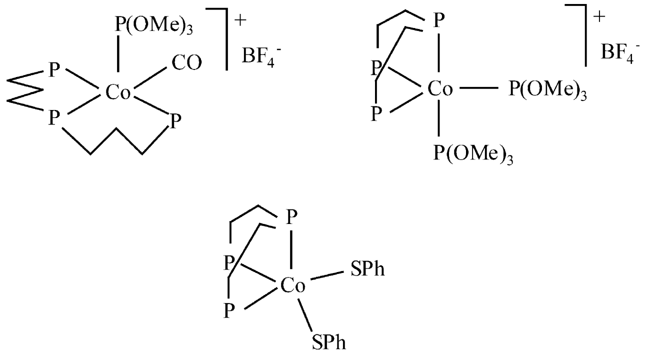


Scheme 5.

Linear triphosphines with a longer backbone are more flexible and thus are most often triligate. Depending mainly on the nature of the metal, and on the resulting “chelate bite angles” formed by the phosphorus atoms with the metal, tetrahedral, trigonal-bipyramidal, square-pyramidal or octahedral geometries were identified. Coordination complexes of cobalt with ttp and etp were known for a long time [22,23]. The longer ttp ligand leads in five-coordinate Co(I) cationic species to a square-pyramidal geometry, while the ligand etp in similar conditions leads to *fac*-trigonal-bipyramidal cations (Scheme 6). The thiolate Co^{II} complex $[Co(etp)(SPh)_2]$ reported by Liu et al. is a five-coordinate compound, with a *fac*-configuration of the triphosphine, the geometry around cobalt being intermediate



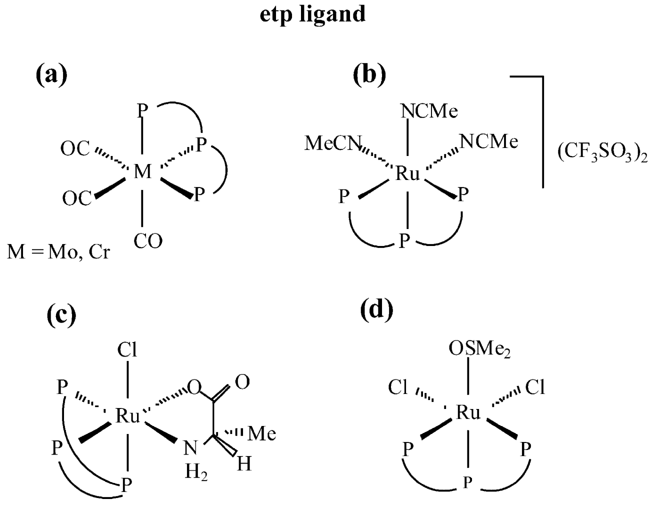
Scheme 1.



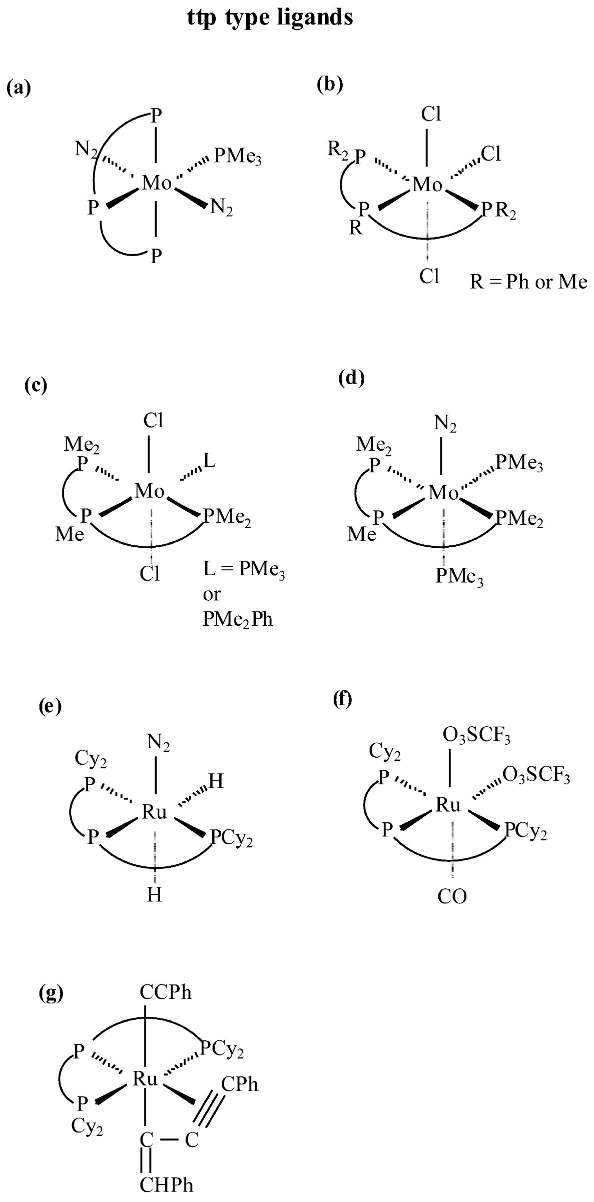
Scheme 6.

between square-pyramidal and trigonal-bipyramidal (Scheme 6) [24].

Rhodium complex geometry with ttp type ligands were thoroughly reviewed [5]: they classically present a square-planar environment around the rhodium. The structural characterization of RhCl(etp) [25] confirms the monomeric square-planar geometry initially expected [26], while it had been later suggested that one of the phosphine appendages was bridging to another rhodium atom to generate polynuclear complexes [27]. In the case of rhodium, and contrary to cobalt, the steric congestion of etp as compared to ttp does not change the square-planar geometry around the four-coordinate rhodium atoms: the P–Rh–P_{cis} angles are simply smaller than those found in analogous Rh(ttp) complexes (83.08(3) and 83.98(3)° compared with 90±1°) [20]. With the etp triphosphine, the allyl iridium complex [Ir(σ-allyl)$_3$(etp)] has recently been obtained in high yield from the reaction of [Ir(η-allyl)$_3$] with etp [28]. The complex has an octahedral environment around the iridium atom, with a *fac*-coordination of the phosphine ligand. Interestingly, in contrast to its rhodium analogue, [Ir(η-allyl)$_3$] gives stable adducts with phosphorus ligands, with no tendency to undergo hydrocarbon elimination reactions.

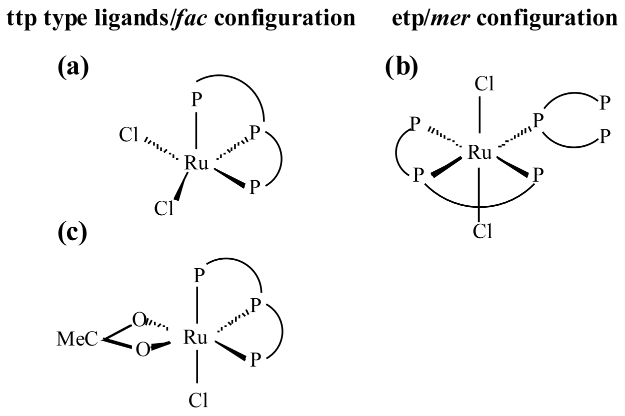


Scheme 7.



Scheme 8.

The molybdenum and ruthenium complexes containing the same ligands lead to octahedral hexacoordination, as shown in some relevant examples (Schemes 7 and 8). In pseudo-octahedral complexes the ligands of the etp type favor the facial coordination *fac* [29–32] ((**a**), (**b**), (**c**), (**d**) in Scheme 7 respectively), while the meridional coordination *mer* is more usual for ttp [33–37] (Scheme 8). However, it seems that this general behavior can be overcome. Indeed, *fac*-coordination has been found for ttp in the five-coordinate RuCl$_2$(ttp) [30], this complex having a geometry intermediate between square-pyramidal and trigonal-bipyramidal ((**a**) Scheme 9). Upon reaction with two equivalents of Ag[CF$_3$SO$_3$]

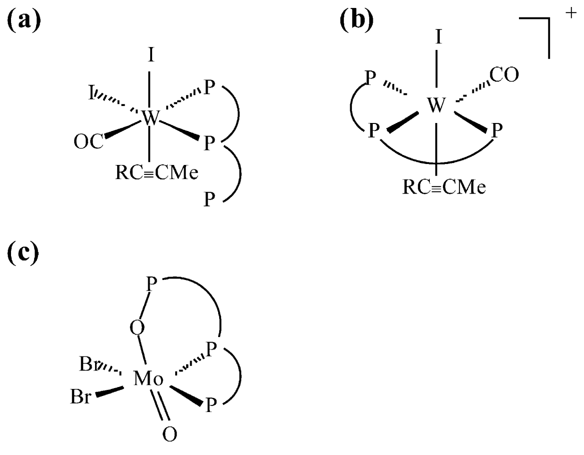


Scheme 9.

in acetonitrile, an octahedral *fac*-[Ru(MeCN)$_3$(ttp)]-[CF$_3$SO$_3$]$_2$ complex is formed in which the facial coordination for ttp is retained, as suggested from NMR measurements. Another strategy to obtain an unexpected *mer*-ruthenium/etp compound has been to change the metal:ligand ratio of starting products; RuCl$_2$(etp)$_2$ has been obtained from RuCl$_2$(PPh$_3$)$_2$ reacted with *two* equivalents of etp [38]. As shown in (**b**) Scheme 9, the resulting compound has a unique meridional chelate arrangement for one etp ligand, while only the central phosphorus of the second ligand coordinates the metal. Another ruthenium compound with etp is the homobimetallic [Ru$_2$(μ-Cl)$_3$(etp)$_2$]$^+$ cation, which displays a cofacial bioctahedral coordination with three bridging chlorine atoms and the etp ligand in *fac*-coordination mode [30].

Pietsch and Dahlenburg have established a meridional-octahedral arrangement for ttp ligands in [Mo(N$_2$)$_2$(ttp)(PMe$_3$)], with the dinitrogen molecules in *trans* position ((**a**) Scheme 8) [33]. The same *trans*-octahedral coordination geometry was also found for [Mo(Cl)$_2$(tdmme)(PMe$_3$)] and [Mo(Cl)$_2$(tdmme)(PMe$_2$Ph)] (tdmme is the methylated derivative of ttp, e.g. bis[3-(dimethylphosphino)propyl]methylphosphine ((**c**) Scheme 8) [34]. The authors later prepared from *mer*-[MoCl$_3$(tdmme)] ((**b**) Scheme 8) under N$_2$ in the presence of an excess of PMe$_3$ the *cis*,*mer* isomer of [Mo(N$_2$)(PMe$_3$)$_2$(tdmme)] ((**d**) Scheme 8) [35]. The complexes containing the parent ligand bis[3-(dicyclohexylphosphino)propyl]phenylphosphine (ttpcy) used by Meek et al. have been reviewed ([6] and references therein). The ttpcy ligand gives mainly *mer*-configured ruthenium hydride octahedral complexes (see for instance (**e**) Scheme 8 [37]). The first *mer*-configured ruthenium hydride with molecular dihydrogen as ligand [Ru(H)$_2$(η^2-H$_2$)(ttpcy)] has been synthesized by Meek and Jia [39], and characterized by NMR spectroscopy. The meridional stereochemistry still predominates in the final products of the reaction of *cis*-*mer*-[Ru(H)$_2$(CO)-(ttpcy)] with an excess of HX (X = BF$_4$, O$_3$SCF$_3$); the X-ray structures of *cis*-*mer*-[Ru(X)$_2$(CO)(ttpcy)] were reported ((**f**) Scheme 8) [40]. As mentioned above for [RuCl$_2$(ttp)], five-coordinate ruthenium complexes with ttp-type ligands are known in a *fac*-geometry [41,42]. Careful tuning of experimental conditions allows one to isolate either facial or meridional isomers of [RuCl$_2$(ttpcy)]; the formation of the *mer*-isomer seems to be kinetically favored while the *fac*-isomer dominates in longer time reactions [41]. A series of acetate ruthenium complexes were obtained [43], and among them, *fac*-[RuCl(O$_2$CMe)(ttpcy)] was characterized by X-ray crystallography ((**c**) Scheme 9). The ruthenium atom lies in the center of a strongly distorted octahedral geometry due to the small bite angle of the chelate acetato group (O–Ru–O angle 58.9(1)°). It was observed that *fac*-[RuCl(O$_2$CMe)(ttpcy)] is more stable than *mer*-[RuCl(O$_2$CMe)(ttpcy)], which slowly isomerizes into *fac*-[RuCl(O$_2$CMe)(ttpcy)] in methanol. In general, while the facial geometry is electronically preferred for the linear triphosphines, due to the *trans*-influence of the ancillary ligands, steric interactions would favor the meridional arrangement around the metal. Thus, the observation of one or the other configuration, for a given triphosphine, gives an indication of the predominant influence of electronic or steric factors.

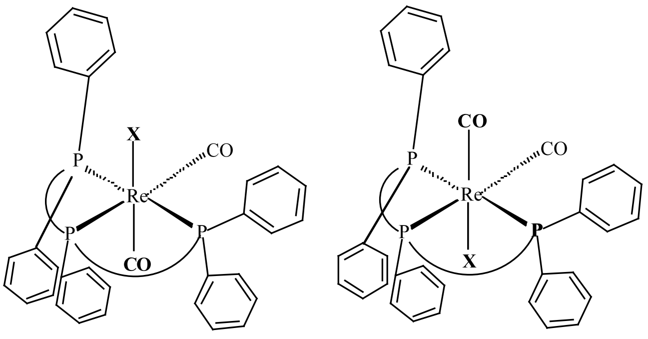
Baker et al. have used bis(alkyne) tungsten complexes to synthesize, from reaction with etp, original biligate-triphosphine alkyne complexes with a dangling arm containing the third phosphorus donor atom [44,45]. The molecular structures of the original [W(I)$_2$(CO)(etp-*P*,*P′*)(η^2-MeC≡CR)] (R = Me or Ph) were crystallographically determined [44]. In both complexes the coordination pattern about the metal is octahedral with one phosphorus atom *trans* to an iodide ligand and one phosphorus *trans* to the carbonyl ligand in the equatorial plane ((**a**) Scheme 10). These complexes were used as precursors to prepare a number of new di- and trinuclear molybdenum or tungsten species. Several at-



Scheme 10.

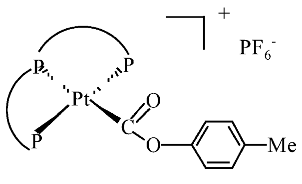
tempts to coordinate the unattached phosphorus donor to the metal center were unsuccessful. Later, the authors were able to convert these biligate-triphosphines $[\mathrm{M(X)_2(CO)(etp\text{-}}P,P')(\eta^2\text{-}\mathrm{MeC{\equiv}CR})]$ complexes into ionic tridentate complexes of the type $[\mathrm{M(X)(CO)(etp\text{-}}P,P',P'')(\eta^2\text{-}\mathrm{MeC{\equiv}CR})]\mathrm{Y}$ (where M = Mo or W; X = Cl, Br or I; R = Me or Ph; Y = $\mathrm{W_6O_{19}}$, Br, $\mathrm{BF_4}$ or $\mathrm{BPh_4}$) [46]. In this report are described the unexpected complexes $[\mathrm{WI(CO)(etp\text{-}}P,P',P'')(\eta^2\text{-}\mathrm{MeC{\equiv}CMe})]_2[\mathrm{W_6O_{19}}]$ ($\mathrm{W_6O_{19}^{2-}}$ is a dianion) and $[\mathrm{Mo(Br)_2(O)\{Ph_2P(CH_2)_2\text{-}PPh(CH_2)_2POPh_2\text{-}}P,P',O\}]$, which were characterized by X-ray diffraction measurements. These species were isolated from refluxing acetonitrile solutions of, respectively, $[\mathrm{W(I)_2(CO)(etp\text{-}}P,P')(\eta^2\text{-}\mathrm{MeC{\equiv}CR})]$, and $[\mathrm{MoBr(CO)(etp\text{-}}P,P',P'')(\eta^2\text{-}\mathrm{MeC{\equiv}CR})]\mathrm{Br}$ in air. The crystal structure of $[\mathrm{WI(CO)(etp\text{-}}P,P',P'')(\eta^2\text{-}\mathrm{MeC{\equiv}CMe})]\mathrm{BPh_4}$, was also reported [46]. The structures of the cationic tungsten species $[\mathrm{WI(CO)(etp\text{-}}P,P',P'')(\eta^2\text{-}\mathrm{MeC{\equiv}CMe})]\mathrm{BPh_4}$ and $[\mathrm{WI(CO)(etp\text{-}}P,P',P'')(\eta^2\text{-}\mathrm{MeC{\equiv}CMe})]_2[\mathrm{W_6O_{19}}]$ are equivalent. The geometry around the W atom can be described as a distorted octahedron with the triphosphine ligand in a meridional arrangement ((**b**) Scheme 10). One apical position is occupied by the iodide atom *trans* to the alkyne ligand. The last equatorial position is occupied by the carbonyl ligand *trans* to the central phosphorus of etp. The free phosphorus donor atom in the neutral precursor has displaced the second iodide atom to give the stereochemistry of the cation. In the parent molybdenum product $[\mathrm{Mo(Br)_2(O)\{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2\text{-}}P,P',O\}]$ one of the terminal phosphorus atoms of the etp ligand was oxidized. The metal is bonded to this tridentate ligand in a facial arrangement of a distorted octahedral geometry ((**c**) Scheme 10). Two phosphorus atoms are *trans* to the two bromo ligands, and the oxygen atom that is bonded to the third phosphorus is *trans* to the oxo ligand. The rearrangement which occurs from the presumed *mer*-configured precursor to the *fac*-configured product could be a relevant example of changes from a steric preference to an electronic preference due to modified mutual *trans* effects in the molecule. The ligand $\mathrm{Ph_2P(CH_2)_2PPh(CH_2)_2POPh_2}$ was already reported; it was found, in a facial configuration, in the crystallographically characterized molybdenum complex *fac*-$[\mathrm{Mo(SeC_6H_2Me_3\text{-}2,4,6)_2(O)\{Ph_2P(CH_2)_2\text{-}PPh(CH_2)_2POPh_2\text{-}}P,P',O\}]$ [47]. This latter observation supports the above hypothesis of an electronic effect stabilizing the facial arrangement of this phosphine ligand. Finally, concerning this metal group, the synthesis of the dinuclear $[\mathrm{Mo_2(OAc)Cl_3(etp)}]$ complex [48], which shows a chelating and bridging triligate structure *similar* to an original tetraphosphine dimolybdenum complex (see more details in Section 3.2 on tripodal tetraphosphines) should be mentioned.

Pentacarbonyl manganese and rhenium halides were used to prepare the *cis*,*mer*-$[\mathrm{MX(CO)_2(etp)}]$ complexes (where M = Mn or Re; X = Cl or Br) [49]. The crystal structure of *cis*,*mer*-$[\mathrm{ReCl(CO)_2(etp)}]$ shows that this octahedral compound adopts two diastereoisomeric forms, in which the etp ligand has the same meridional triligate arrangement. However, this arrangement generates a cavity formed by three phenyl rings on one side of the rhenium atom (Scheme 11). Consequently, the geometries of the complexes differ by the interchange of the mutually *trans* chloro and carbonyl ligands. *cis*,*fac*-$[\mathrm{ReCl(CO)_2(etp)}]$ as well as *fac*-$[\mathrm{Re(CO)_3(etp)}]\mathrm{Cl}$ and the dimeric species $[\mathrm{ReCl(CO)_2(etp)}]_2$ (with bridging etp) were identified as minor products, demonstrating the existence of complicated and isomerically-rich systems.



Scheme 11.

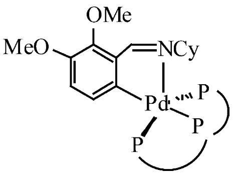
Group 10 metals are known classically to form four coordinate square-planar complexes with linear triphosphines with the phosphine ligand triligate [5,6,50–56]. The reaction of $[\mathrm{Pt(etp)Cl}]\mathrm{Cl}$ with $\mathrm{NaOC_6H_4}$-*p*-Me in the presence of $\mathrm{NaPF_6}$ yields the aryloxy complex $[\mathrm{Pt(etp)(OC_6H_4}$-*p*-Me$)]\mathrm{PF_6}$, which upon reaction with carbon monoxide leads to the aryloxycarbonyl complex $[\mathrm{Pt(etp)(C(O)OC_6H_4}$-*p*-Me$)]\mathrm{PF_6}$ (Scheme 12) [54]. This compound with a square-planar geometry, was the first aryloxycarbonyl complex to be characterized by an X-ray structural determination. The authors have compared in details its structure with those of related alkoxycarbonyl platinum complexes bearing monophosphine ligands. The most noticeable differences are the short C–O bond distance of 1.08(1) Å (alkoxycarbonyl C–O bond distances are in the range 1.19–1.23 Å), and the (aryloxy)carbonyl group adopting a geometry that is tilted 75.4(9)° regarding the $\mathrm{PtP_3C}$ plane while comparable alkoxycarbonyls have a perpendicular orientation. Kinetic studies have shown that the mechanism of formation proceeds via a classical concerted migratory insertion of the aryloxide ligand to coordinated carbon



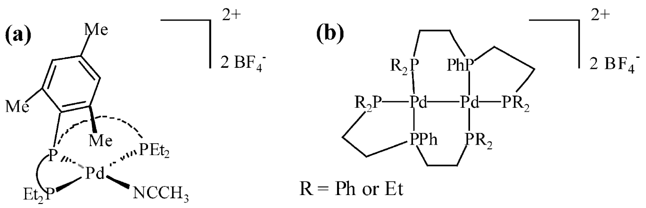
Scheme 12.

monoxide [54–57]. Sevillano et al. have found that the square-planar geometry of [Pd(etp)Cl]Cl and [Pt(etp)Cl]Cl is conserved upon reaction of these complexes with [Au(thiodiglycol)Cl], which lead to the formation of the heterobimetallic compounds [$PtAu(etp)Cl_3$] and [$PdAu(etp)Cl_3$] [55]. The etp ligand changes from a triligate bis-chelating arrangement on the Pt (or Pd) to a biligate chelating bonding on the same nucleus, the third phosphine binding the Au–Cl moiety. Recently, a five-coordinate palladium/etp complex with a very original structure was isolated and characterized [58] (Scheme 13). Indeed, [Pd{3,4-$(MeO)_2C_6H_2C(H)$=NCy}(etp)]PF_6 contains three five-membered rings at palladium: two comprising the triphosphine ligand, and the palladacycle from the C,N-bonded ligand. The geometry was found in the solid state as trigonal-bipyramidal from a single crystal X-ray diffraction and ^{31}P-NMR, while in chloroform solution NMR evidences point to a square-pyramidal geometry. In analogous reactions with mono- and diphosphines the authors only obtained four-coordinate compounds with a common square-planar environment for the palladium atom [58]. This is a relevant example where the use of tri or tetraphosphines provides a strategy to modify the coordination number as well as the geometry at the metal center, leading to unusual molecular structures.

Very useful derivatives of etp were prepared for various purposes. The linear triphosphine bis[2-(diethylphosphino)ethyl]mesithylphosphine (called MesetpE) contains a mesityl substituent on the central phosphorus atom, and the analogous compound with a trimethoxybenzene substituent was also prepared [59]. The objective was to obtain palladium complexes displaying a square-planar structure with one methyl group of the central mesityl substituent blocking one potential coordination site above the plane. Indeed, it was found that [$Pd(L)(CH_3CN)$][BF_4]$_2$ complexes (where L is a linear triphosphine such as etpE = [$(Et_2PCH_2CH_2)_2PPh$] or etpCy = [$(Cy_2PCH_2CH_2)_2PPh$]) catalyze the electrochemical reduction of CO_2 to CO in acidic dimethylformamide or acetonitrile solutions [60]. The mechanistic studies raise the question of the existence of a five-coordinate or a six-coordinate palladium(I) complex as the transition-state species for the rate-determining step in the catalytic cycle. Thus, the [Pd(MesetpE)(CH_3CN)][BF_4]$_2$ complex was prepared that precludes the formation of six-coordinate transition states due to the steric bulk of the mesityl group [59]. An X-ray diffraction study of this complex confirms that the [Pd(MesetpE)(CH_3CN)]$^{2+}$ cation has a square-planar structure with one methyl group of the mesityl substituent blocking a potential coordination site above the basal-plane ((**a**) Scheme 14). The rate-constant associated with [Pd(MesetpE)(CH_3CN)][BF_4]$_2$ in the electrochemical reduction of CO_2 to CO supports a five-coordinate transition state for the rate-determining step in which CO_2 approaches along the axis perpendicular to the plane of the complex. This excellent work shows the potential to correlate structures and catalytic reactivities by modifying the architecture of the tridentate phosphines. The authors also reported in the course of their catalytic studies the structures of the decomposition products [Pd(etp)]$_2$[BF_4]$_2$ and [Pd(etpE)]$_2$[BF_4]$_2$ [60]. The complexes are palladium(I) dimers that consist of two approximately square-planar molecules joined by Pd–Pd bonds (Pd–Pd distances around 2.6 Å, see (**b**) Scheme 14).

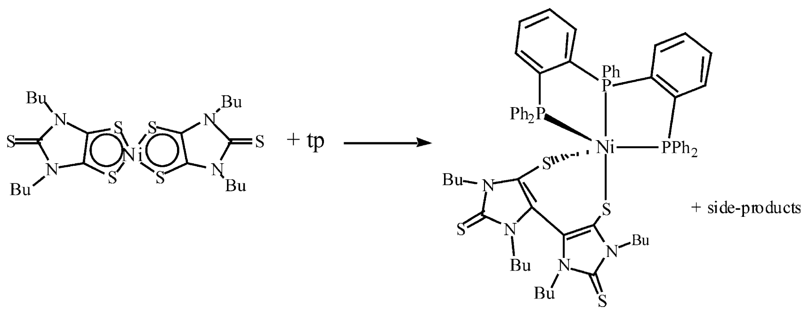


Scheme 13.



Scheme 14.

An interesting variation of the etp ligand is the chiral unsymmetrical triphosphine {[2-(diphenylphosphino)-ethyl][3-(diphenylphosphino)propyl]}phenylphosphine, [$(Ph_2PCH_2CH_2CH_2)PPh(CH_2CH_2PPh_2)$], (named eptp, see Scheme 1). This ligand was first reported by Meek et al. [61,62], then Roscoe and Dyer gave an improved synthetic method involving phosphonium salts and phosphine oxides as intermediates [63]. The ligand eptp contains a chiral phosphorus center and three non-equivalent phosphorus nuclei. Nickel(II) and palladium(II) complexes [M(X)(eptp)]Y (where M = Ni or Pd; X = Br or I; Y = I, PF_6, or ClO_4) were obtained as diamagnetic crystalline species, which adopt in solution square-planar geometry, according to NMR studies [63]. Interestingly, X-ray crystallographic analyses were carried out on [Ni(I)(eptp)]I, which revealed a five-coordinate complex in a slightly distorted square-pyramidal environment. The Ni–I bond lengths show that the second iodide ligand, in apical position, is only weakly held which explains the square-planar environment detected in solution (distances Ni–I_e = 2.544(2) Å and Ni–I_a = 2.974(2) Å). The crystal consists of regular arrays of alternating *R*- and *S*-enantiomers, consequently not optically active. A trigonal-bipyramidal geometry was also found at the nickel atom for the nickel thiolate compound Ni(tp)(Bu_4btimdt), as represented in Scheme 15 ([Bu_4btimdt = 5,5′-bis-(1,3-dibutyl-

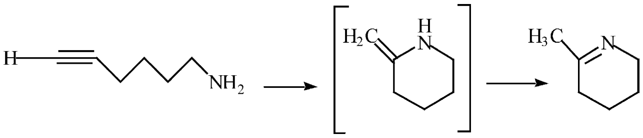


Scheme 15.

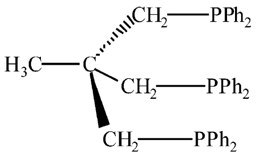
4-imidazolidine-2-thione-4-thiolate] being generated in situ) obtained with the linear triphosphine named tp (tp = bis[2-(diphenylphosphino)phenyl]phenylphosphine) [64].

It is worth to note that, with the emergence of liquid biphasic processes, the water-soluble triphosphine prepared by Katti and co-workers: $PhP[CH_2CH_2P(CH_2OH)_2]_2$. This ligand was obtained from the formylation of etp, and was used to form platinum, rhodium, palladium and rhenium complexes identified by NMR studies [65,66].

In order to illustrate a selected part of the applications of the polyphosphines chemistry with transition metals, recent catalytic studies from Müller's [67], and Bianchini's [68] groups are of interest. The intramolecular addition of amines to alkynes was achieved using $[Pd(etp)][BF_4]_2$ [67]. The cyclization of 6-aminohex-1-yne to 2-methyl-1,2-dehydropiperidine is observed in the presence of palladium salts (Scheme 16). The stability of the catalytic species is increased when the etp linear triphosphine is added, allowing the use of higher temperatures without noticeable catalyst decomposition. In contrast, the use of bidentate phosphines results into a dramatic drop in catalytic activity of the palladium center, suggesting the importance of the structural features provided by the triphosphine. The catalyst stability improvement induced by stereochemical control coming from polydentate ligands was also experienced in the hydroformylation reaction. The hydroformylation of hex-1-ene in the presence of the Rh^I catalyst precursor $[Rh(CO)(etp)]PF_6$ has shown effective results, and the involvement of phosphine free "Rh–CO" species in the catalytic mechanism was ruled out, even under high partial pressure of CO [68].



Scheme 16.



tdpme

Scheme 17.

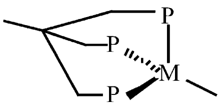
2.2. Tripodal triphosphines

A second class of polyphosphines, called tripodal phosphines, lead to different geometries due to their branched structures. Numerous tripodal polyphosphines are known; the most commonly used one, (Scheme 17), is $[CH_3C(CH_2PPh_2)_3]$ 1,1,1-tris[(diphenylphosphino)methyl]ethane (tdpme, also called sometimes triphos). We deal first with the tdpme ligand itself, and then the several derivatives obtained in recent years. Sterically small polyphosphine podands (for instance $[HC(PPh_2)_3]$, sometimes called tripod) have led to cluster chemistry, not described here, but well documented before 1994 in Ref. [6].

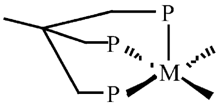
The chemistry of the tripodal phosphines with transition metals is very rich and many metal complexes containing tdpme and related ligands have marked the importance of this chemistry in homogeneous catalysis over the last 30 years (see for instance [7] and references therein). In general, tdpme is triligate on the metal center, occupying the facial position in square-pyramidal, trigonal-bipyramidal and octahedral arrangements, and generating several free *cis*-positions for the co-ligands. Consequently, tdpme is an excellent phosphine for the stabilization of a variety of reactive species on metals, and is also appropriately structured for NMR studies, with easily identifiable ^{31}P-NMR patterns. As underlined by Mayer and Kaska ([6] and references quoted therein), acyl, alkyl, aryl, carbon monoxide, hydride, olefin and alkyne containing complexes were obtained. Among the species stabilized in the past decades are the *cyclo*-E_3 pnictogen species (E = P or As) with Group 9 metals [6,69], such as the X-ray characterized $[(tdmpe)Co\{\eta^3\text{-}cyclo\text{-}P_2P(CH_3)\}]BF_4$ [69]. Complexes containing aromatic and cycloaliphatic hydrocarbons as well as alkyne dimeric-species have also been isolated [6,70–72]. Among them, the crystal structures of the acetylene cyclotrimerization catalysts (or intermediates) [(tdpme)Rh(η^2-C_4H_4)Cl] and [(tdpme)Ir(η^4-C_6H_6)]$^+$ were reported [70], as well as the ethyne-bridged [(tdpme)Rh(μ-η^2,η^2-C_2H_2)Rh-(tdpme)]BPh_4 [71].

Examples from the recent studies have shown the formation of: (i) hydride and thiolate/thiophene ruthenium, rhodium and iridium complexes [73–82] (the species [(tdpme)RuH{BH_3(*o*-S(C_6H_4)CH_2CH_3)}] [73] and [(tdpme)RhH(μ-H){μ-*o*-S(C_6H_4)CH_2CH_3}W$(CO)_4$] [76,77] were identified by X-ray analysis), (ii) isonitrile, isocyanide, cyanide, nitrile and alkyne cobalt complexes [83] (the compounds [(tdpme)Co^{II}$(CN)_2$], [(tdpme)Co^{I}-(CN^{t}Bu)$_2$][PF_2O_2], [(tdpme)Co^{II}(CNC_6H_{11})$_2$][PF_2O_2]$_2$, [(tdpme)Co^{I}(NCO)] and [(tdpme)Co^{II}$(NCS)_2$] were identified by X-ray analysis), (iii) bisalkynyl and diyne cobalt complexes [84] (the complex [(tdpme)Co^{I}-(η^2-^{t}BuC≡CC≡C^{t}Bu]PF_6 was authenticated by X-ray), and (iv) quinones, semiquinones and catecholates containing cobalt, rhodium and iridium complexes [85,86]: the oxygen adduct complex [(tdpme)Ir–(O_2)–(PhenSQ)]BPh_4 (PhenSQ = 9,10-phenanthrene semiquinonate) was prepared and identified by X-ray analysis [85]. The iridium atom is hexacoordinated by the

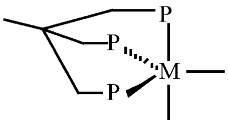
tdpme ligand L



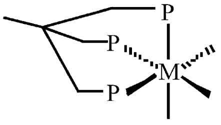
Co(NCO)L (83)
[Co(η^2-^{t}BuC≡CC≡C^{t}Bu)L](PF_6) (84)
Ni(SO_2)L (87)
NiIL (88)
Ni(CF_2CF_2)L (89)
Cu(S_2CSnMe_3)L (90)



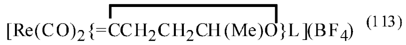
[Co(CNC_6H_{11})$_2$L](PF_2O_2)$_2$, Co(CN^{t}Bu)$_2$L](PF_2O_2) (83)
Co$(NCS)_2$L , Co$(CN)_2$L (83)
Co(SO_4)L , Co(SeO_4)L , Ni(SO_4)L, Ni(SeO_4)L (91)
Co(π-CS_2)L (92)
Co(O_2SO)L (93)
[Rh(Se_2CO)L]$(BPh_4)_2$ (94)
[Rh(η^4-SCHCHCH(CH_2CPh_3)L](PF$_6$) (95)



[Co(*O*,*O*′-$O_2C_6H_2O_2CH_2$)L](BF$_4$) (86)
Co(BH_4)L (87)
[Co(ac)L](BPh$_4$) (96)
IrCl(CO)L (97)
RhMe(CO)L (98)
[CoCl(PMe_3)L](BPh$_4$) (99)
[CoCl(NH_3)L](BPh$_4$) (99)
[CoCl(CH_3CN)L](BPh$_4$) (99)

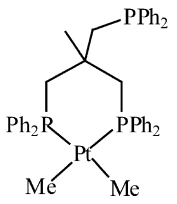


[Co{η^3-cyclo-$P_2P(CH_3)$}L] (69)
[Ru(H){BH_3(*o*-S(C_6H_4)CH_2CH_3}L] (73)
[RhH(μ-H){μ-*o*-S(C_6H_4)CH_2CH_3}L]W$(CO)_4$ (76)
[Ir(O_2)(PhenSQ)L](BPh$_4$) (85)
Co(η^3-cyclo-P_3)L (100,101)
Rh$(H)_3$L (102)
Rh(H)(η^2-DMFU)L (103)
Ir(η^4-$C_6H_6^+$)L , RhCl(C_2H_4)L , RhH(C_2H_4)L (70,104,105)
[RhCl(S_2CHPEt_3)L]$(BPh_4)_2$ (106)
[Ir(η^3-S(Me)CH=CHCH=CH_2)L](BPh4) (107)
ReCl$_3$L (108)
Re$(CO)_2$HL (109)
CrCl$_3$L (110)
RhCl(η^2-CSe_2)L (111)
[Re$(CO)_2${=C=C(H)Ph}L](BF$_4$) (112)
[Re$(CO)_2${=C(OEt)CH_3}L](BPh$_4$) (112)



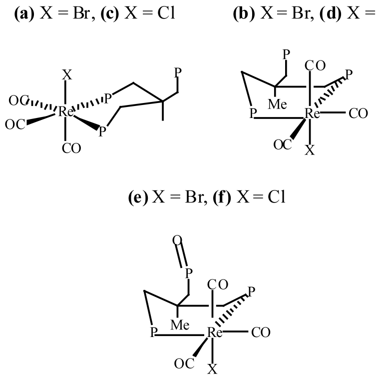
[Re$(CO)_2${=$\overbrace{\text{CCH}_2\text{CH}_2\text{CH(Me)O}}$}L](BF$_4$) (113)
[Re$(CO)_2${=C(OMe)CH=CHMe}L](OTf) (114)

Scheme 18.



Scheme 19.

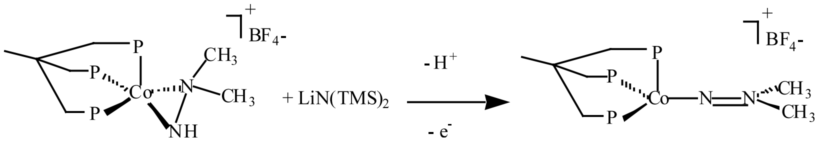
phosphorus atoms and by three oxygen atoms, one from O_2 and two from the catecholate ligand transformed into a semiquinonate. The four dinuclear compounds $[(tdpme)Co{-}L{-}Co(tdpme)][BF_4]_2$ (where $L = C_6X_2O_4^{2-}$, X = H, Cl or Br, a dianion derived from 2,5-dihydroxy-1,4-benzoquinone, or $L = C_2O_4^{2-}$, oxalate) were prepared and identified by X-ray diffraction measurements, as well as the mononuclear $[(tdpme)Co{-}L]BF_4$ (L = 4,5-methylenedioxycatecholato) [86]. Scheme 18 summarizes the general types of geometries authenticated by X-ray structural studies for mononuclear complexes containing *one* tdpme; references to selected structural data are also given to illustrate the diversity of the existing compounds [69,70,73,76,83–114]. However, Walton and co-workers, and Bianchini et al. have also identified by NMR rhenium polyhydrides complexes exhibiting high coordination numbers such as $[Re(tdpme)H_5]$, $[Re(tdpme)H_7]$, $[Re(tdpme)(PPh_3)H_3]$ and $[Re(tdpme)(CO)H_3]$ [6,115,116]. Tdpme was also occasionally found biligate in monometallic compounds, as described for $[PtMe_2(tdpme\text{-}P,P')]$ (Scheme 19) [117]. In this square-planar compound, the biligate geometry with the third dangling phosphine moiety was shown both in the solid state and in solution. More recently, Gibson et al. have synthesized new rhenium carbonyl complexes showing a biligate coordination of tdpme (Scheme 20) [118]. The X-ray structure determination of *fac*-$[ReBr(CO)_3(tdpme\text{-}P,P')]$ showed that two isomeric forms were obtained in the solid state (see (**a**) and (**b**) Scheme 20) [118]. In one isomer, the six-membered metallacyclic ring ReP_2C_3 adopts a chair conformation such as previously described for the known analogous chloro-complex *fac*-$[ReCl(CO)_3(tdpme\text{-}P,P')]$ ((**c**) Scheme 20) [119]. The second isomer displays an original boat conformation of the metallacyclic ring. The two isomers were obtained in 1:1 ratio from the reaction of tdpme with $[Re(CO)_5Br]$ in methanol, and were separated owing to their differences of solubility in acetone. The synthesis from $[ReCl(CO)_5]$ and tdpme has led to comparable yields of isomeric species (see (**c**) and (**d**) Scheme 20) [118]. The crystal structure of the phosphine oxide minor derivatives of the “boat” complexes *fac*-$[ReBr(CO)_3(tdpme\text{-}P,P')]$ ((**e**) Scheme 20) [118] and *fac*-$[ReCl(CO)_3(tdpme\text{-}P,P')]$ ((**f**) Scheme 20) [120] were also reported, the specific conformation being retained upon oxidation. Molecular modeling and energy calculations of these rhenium complexes would probably be of interest.


(**a**) X = Br, (**c**) X = Cl (**b**) X = Br, (**d**) X = Cl

(**e**) X = Br, (**f**) X = Cl

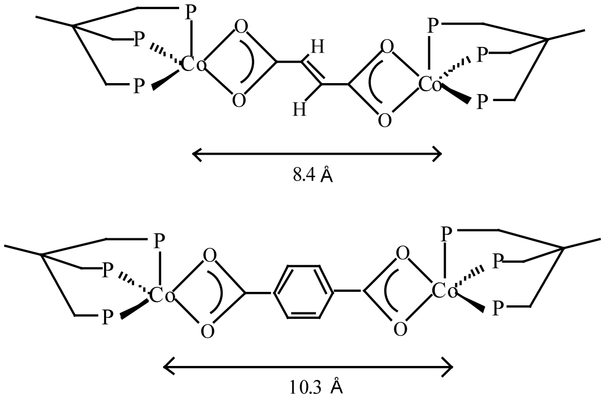
Scheme 20.

In recent years, Huttner and co-workers have reported several important advances in the field of tripodal phosphine chemistry. The template Co(tdpme) was used to stabilize species containing N_2R_x type co-ligands (R = H or Me, $x = 2$–4) [121]. In particular, the authors report the conversion of $[Co(tdpme)(\eta^2\text{-}NHNMe_2)]^+$ into $[Co(tdpme)(\eta^1\text{-}NNMe_2)]^+$ (Scheme 21); both compounds were characterized by X-ray measurements. The overall reaction combines a deprotonation and a redox process (i.e. coupled loss of an electron plus a proton). In this reaction, the fundamental interest is the analogy existing with the biochemical process postulated for N_2 fixation (i.e. coupled transfer of protons and electrons). The chemistry of $CoCl_2$ with tdpme led to a huge variety of cobalt complexes; among them, X-ray structures were obtained for the cations $[Co(tdpme)Cl(L)]^+$ ($L = PMe_3$, NH_3 or CH_3CN) with a borate counter-anion [99]. These cobalt complexes present a similar distorted trigonal-bipyramidal environment around the metal center. Huttner et al. have also shown the existence of an equilibrium in solution between a five-coordinate and a tetrahedral form for $[Co(tdpme)Cl_2]$; for the solid-state stable five-coordinate isomer a distorted trigonal-bipyramidal geometry was identified by single X-ray diffraction [99]. The Co(I) complex [Co(tdpme)Cl] has a four-coordinate

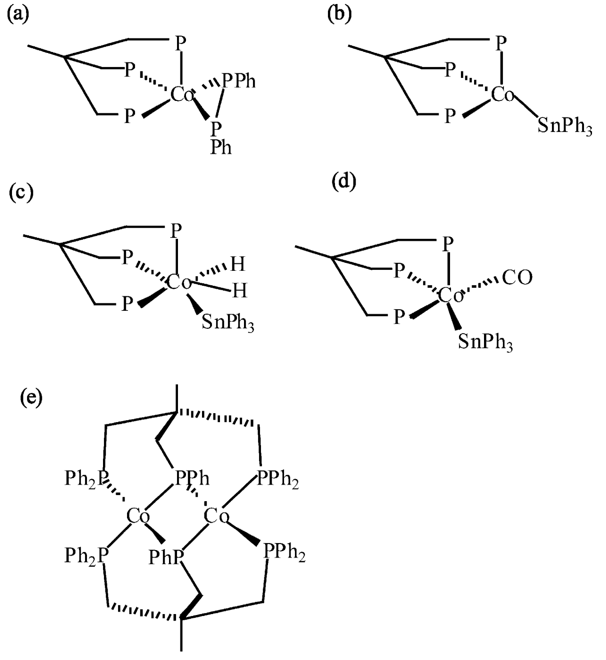


Scheme 21.

molecular structure confirmed by an X-ray crystallographic determination, which shows a pseudo-tetrahedral geometry around the metal. Small P–Co–P angles (around 90°) and larger P–Co–Cl (around 120°), which are classical features for [(tdpme)MX] species, were observed due to the steric constraint of the tridentate tdpme (see Ref. [99] and references therein). The solid-state structure of the homobimetallic dinuclear species [(tdpme)Co(μ-Cl_2)Co(tdpme)][Zn_2Cl_6] was reported, as well as those of the dissymmetric compounds [(tdpme)Co(μ-Cl_2)$CoCl_2$] and [(tdpme)-Co(μ-Cl_2)$FeCl_2$]. These three complexes were obtained by reacting the monomeric species [Co(tdpme)Cl_2] with various Lewis acids ($ZnCl_2$, $CoCl_2$, $FeCl_2$) in different solvents [99]. The template Co(tdpme) was also used by Huttner et al. to stabilize two dinuclear homobimetallic complexes of the type [{(tdpme)Co}$_2$(μ-dicarboxylato)][BF_4]$_2$ [122], where the dicarboxylato anions derive from either fumaric acid or terephtalic acid (Scheme 22). The objective was to observe the long-distance magnetic interaction between the metal centers separated by the carboxylato organic spacers. Antiferromagnetic exchanges were detected in spite of the 8–10 Å distances between the cobalt atoms. The geometry around the cobalt atoms is best described as distorted square-pyramidal with a phosphorus of tdpme in the apical position. Obviously, the distortion arises from the P–M–P angles around 90 ± 3 °C. The different cobalt complexes described above by Huttner et al. illustrate that five-coordinate complexes with tdpme tripodal ligand type can hardly adopt the ideal structures known, e.g. trigonal-bipyramidal or square-pyramidal. In general, it was possible in most of the cases to assign a distorted trigonal-bipyramidal or square-pyramidal structure (see Ref. [122] and references therein); sometimes the structure of the cation depends on the nature of the counter-anion. For instance [(tdpme)Co(μ-Cl_2)Co(tdpme)][BPh_4]$_2$ shows a square-pyramidal environment at the cobalt centers, while [(tdpme)Co(μ-Cl_2)Co(tdpme)][Zn_2Cl_6] displays a trigonal-bipyramidal geometry [99]. The oxidative addition of compounds containing P–H or Sn–H functions was achieved *under argon*, starting from [(tdpme)$CoCl_2$] in the presence of strong reducing agents such as KC_8 [123]; the following species, [(tdpme)Co(η^2-PhP=PPh)](**a**) from $PhPH_2$ or PhPHNa, [(tdpme)Co($SnPh_3$)](**b**) from Ph_3SnH, [(tdpme)Co(H)$_2$($SnPh_3$)](**c**) from addition of H_2 to [(tdpme)Co($SnPh_3$)], [(tdpme)Co(CO)($SnPh_3$)](**d**) from addition of CO to [(tdpme)Co($SnPh_3$)], were obtained and characterized in the solid-state by crystallographic studies ((**a**), (**b**), (**c**) and (**d**) in Scheme 23). The geometry about cobalt in (**a**) is distorted square-pyramidal, distorted tetrahedral in (**b**), and intermediate between trigonal-bipyramidal and square-pyramidal in (**d**). The environment of cobalt in (**c**) displays a very strong distortion from the ideal octahedron usually observed in Co^{III} compounds ([123] and references therein), since all the angles involving the Sn center deviate from the ideal values by 20–30°. Interestingly, agostic interactions between the cobalt-bonded hydrides and the tin atom were suggested as a major factor, since steric constraints cannot alone be responsible for this distortion. *Under N_2*, the reduction of [(tdpme)$CoCl_2$] by activated magnesium or of [(tdpme)CoCl] by KC_8 led to the isolation of the complex [(tdpme)Co–N≡N–Co(tdpme)] (structural data referenced in Ref. [124]). The reduction of [(tdpme)$CoCl_2$] also produces the intriguing dephenylated minor by-product [Co_2{$CH_3C(CH_2PPh_2)_2$-CH_2PPh}$_2$] ((**e**) Scheme 23) [123]. This last compound was identified by X-ray diffraction analysis. [Co_2{$CH_3C(CH_2PPh_2)_2CH_2PPh$}$_2$] contains a di-cobalt unit bridged by two μ^2-phosphido CH_2PPh^- groups, each of these phosphido groups belonging to a tripodal



Scheme 22.



Scheme 23.

entity coordinating each a cobalt center by a CH_2PPh_2 group. The cobalt atoms are, thus, in a four-coordinate environment best described as distorted tetrahedral, the P–Co–P angles ranging between 92.5 and 126.9°. Finally, the authors also reported the formation of the homobimetallic dinuclear complex [(tdpme)Co(μ-NH_2)$_2$Co(tdpme)][BPh_4]$_2$ [123], whose crystal structure is isotypical with that of the previously discovered [[(tdpme)Co(μ-OH)$_2$Co(tdpme)][BPh_4]$_2$ [96,125]. A compilation of the reference codes of the tripodal metal templates type $CH_3C(CH_2X)(CH_2Y)(CH_2Z)CoL_x$ (where X,Y and Z are donor groups, L are the various co-ligands associated and $x = 2$ or 3) registered in the Cambridge structural database [126] was published in 1996. The analysis of the conformational data related to these structures leads to several basic *regularities* whatever the system observed. Thus, the *conformation* of the tripodal metal templates is governed by the forces acting within them, and not by the forces imposed on them by their unique chemical or crystallographic environment. This important conclusion is valuable whatever the metal center involved.

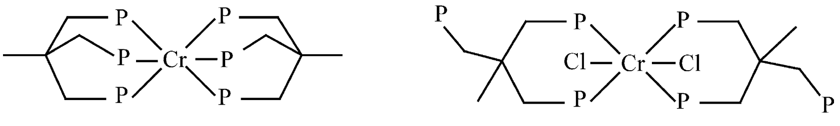
Among the recently reported rhodium complexes, the original [Rh{η^4-SCHCHCH(CH_2CPh_3)}(tdpme)]PF_6 presents a distorted square-pyramidal geometry with one phosphorus atom occupying the apical position, while the two other P atoms, plus the two C–S and C–C bonds of the η^4-ligand, can be considered as occupying the basal sites (Scheme 18) [95].

Bianchini and co-workers initiated a general study of the organometallic chemistry of rhenium in combination with the tdpme ligand [109]. The reaction of [ReCl(CO)$_3$(PPh_3)$_2$] with tdpme gives [ReCl(CO)$_2$(tdpme)], which is converted into the hydride [ReH(CO)$_2$(tdpme)] by treatment with $LiAlH_4$. The X-ray diffraction analysis showed that the rhenium atom is octahedrally coordinated by the triphosphine in a facial position, and by two carbonyl groups and a terminal hydride (Scheme 18). The first rhenium–carbene complexes, stabilized by the tripodal phosphine tdpme, were isolated [112]: [Re(CO)$_2${=C=C(H)Ph}(tdpme)]BF_4 and [Re(CO)$_2${=C(OEt)CH_3}(tdpme)]BPh_4 (Scheme 18) present the rhenium atom octahedrally coordinated by a *fac*-tdpme ligand, two *cis* terminal carbonyl and by the organyl ligand. Later the formation of the 2-oxacyclopentylidene derivative was reported: [Re(CO)$_2${=CCH_2CH_2CH(Me)O}(tdpme)]BF_4 formed by the rhenium-assisted ring-closure of the alkynol HC≡$CCH_2CH(OH)CH_3$ reacting with [Re(CO)$_2$(η^2-H_2)}(tdpme)]BF_4 (Scheme 18) [113]. Single crystal X-ray analyses have shown a structure similar to the first rhenium–carbene complexes with a facial tripodal ligand and two *cis* carbonyl groups. The existence of the analogous rhenium species with 2-oxacyclohexylidene and with the original 2-oxacycloheptylidene was shown by NMR measurements; these syntheses proceed via a similar mechanism [113]. [Re(CO_2)(OTf)(tdpme)] reacts with the secondary propargyl alcohol HC≡CCH(Me)OH in the presence of methanol, to give the stable carbene complex [Re(CO_2){=C(OMe)CH=CHMe}(tdpme)][OTf] authenticated by an X-ray diffraction analysis (Scheme 18) [114].

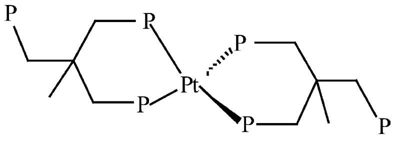
In the case of tripodal ligands, as noticed previously for linear polyphosphines, the use of a different metal:ligand ratio permitted one to isolate different species [110] (Scheme 24). The zerovalent chromium complex [Cr(tdmpe)$_2$] (where tdmpe is the ligand [CH_3C(CH_2PMe_2)$_3$] 1,1,1-tris[(dimethylphosphino)methyl]ethane) is the first example of a structurally characterized hexakis(trialkylphosphine)-coordinated Cr(0) compound. The complex is obtained from the reduction of [$CrCl_2$(tdmpe)$_2$] by a Na/Hg amalgam in tetrahydrofuran, [$CrCl_2$(tdmpe)$_2$] being prepared from the reaction of $CrCl_2$ with *2 molar equivalents* of tdmpe. In [$CrCl_2$(tdmpe)$_2$] the two tripodal ligands are biligate each with an uncoordinated PMe_2 moiety (Scheme 24). While the coordination geometry around the Cr atom in [$CrCl_2$(tdmpe)$_2$] is octahedral with *trans* chlorine atoms, the molecular geometry of [Cr(tdmpe)$_2$] is best described as a trigonal antiprism due to the two triligate tripodal ligands which severely constrain the angles of the molecule. The trigonal distortion is explained by the values of the two angles subtended by *one* unique tripodal ligand: P–Cr–P = 83.6(3) and 83.3(4)°. The values of the angles at Cr between the phosphorus atoms of two different tripodal ligands are far from the ideal 90° value (P–Cr–P′ = 96.4(4) and 96.7(4)°) [110].

Another complex, [Pt(tdpme)$_2$], with a stoichiometry of one metal to two tdpme ligands, was isolated by Meek et al. [127] (Scheme 25). The tripodal ligand is biligate, leaving a PPh_2 dangling group. In this compound, the zerovalent platinum center is in a distorted tetrahedral environment contrary to the common four-coordinate Group 10 complexes, which usually display a square-planar arrangement (see for instance [$PtMe_2$(tdpme-*P*,*P′*)] in Scheme 19) [117].

Many useful variations on the tdpme triphosphine were obtained in recent years. Beside the results concerning the template Co(tdpme), Huttner has reported the synthesis of relevant variations of this

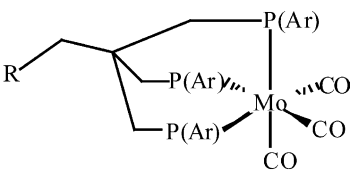


Scheme 24.



Scheme 25.

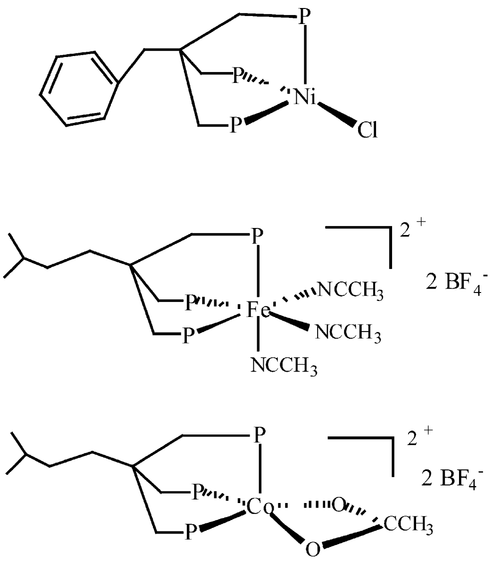
tripodal triphosphine. (i) Tripodal ligands $RCH_2C[CH_2P(Ar)_2]_3$ (Ar = aryl) were transformed into the trilithiotriphosphide $RCH_2C[CH_2P(Ar)(Li)]_3$. Reaction of this latter tripodal phosphide leads to $RCH_2C[CH_2P(Ar)(H)]_3$ with water, to $RCH_2C[CH_2P(Ar)(R')]_3$ with alkyl halides R′X and to $[RCH_2C[\{CH_2P(Ar)(Li)\}]_3Mo(CO)_3]$ with $[Mo(CO)_3(CH_3CN)_3]$ [128]. X-ray analyses of the three compounds of the type $[RCH_2C\{CH_2P(Ar)(benzyl)\}_3Mo(CO)_3]$ (where Ar = Ph, R = Me; Ar = 3,5-$Me_2C_6H_3$, R = Me; Ar = Ph, R = Ph), which can be obtained either by reacting $RCH_2C[CH_2P(Ar)(benzyl)]_3$ with $[Mo(CO)_3(CH_3CN)_3]$ or $[RCH_2C\{CH_2P(Ar)(Li)\}_3Mo(CO)_3]$ with the alkyl halide $ClCH_2Ph$, were reported and indicate closely similar octahedral structures (Scheme 26). (ii) Tripodal ligands of the type $HOCH_2C(CH_2PPh_2)(CH_2Y)(CH_2Z)$ are difficult to convert into the corresponding ether without protection of the donor functions PR_2, Y, Z. The coordination of these phosphines to the $Mo(CO)_3$ template was shown to efficiently protect the donor groups and reduce the steric hindrance around the CH_2OH group by fixing the arms of the tripodal species to the metal center [129]. Consequently, ether-ligands of the type $ROCH_2C(CH_2PPh_2)(CH_2Y)(CH_2Z)$ were obtained coordinated to Mo, after deprotonation of the alcohol and reaction with an electrophile R^+. The ether-tripod can be liberated from the molybdenum center by UV irradiation in the presence of pyridine *N*-oxide. (iii) Huttner has also obtained functionalized tripodal ligands of the type $[RC(CH_2PPh_2)_3]$ (where R = benzyl, $^{n}C_{12}H_{25}$ or $(CH_3)_2CHCH_2CH_2)$ from their corresponding triols, $RC(CH_2OH)_3$, reacted successively with $SOCl_2$ and $KPPh_2$ [130]. The crystallographic structures of $(benzyl)C(CH_2PPh_2)_3$ as well as the nickel complex $[(benzyl)C(CH_2PPh_2)_3NiCl]$ were obtained; in this compound the nickel center is in a classical tetrahedral environment (Scheme 27). The X-ray analyses of the $[\{(CH_3)_2CHCH_2CH_2C(CH_2PPh_2)_3\}Fe(NCMe)_3][BF_4]_2$, and $[\{(CH_3)_2CHCH_2CH_2C(CH_2PPh_2)_3\}Co\{O(O)CCH_3\}]BF_4$ complexes were also reported [130]: the iron compound displays an octahedral geometry at the metal center, and the cobalt complex a five-coordinate distorted square-pyramidal geometry (Scheme 27). (iv) A chiral tripodal ligand with three different donor groups, $L = CH_3C(CH_2PR_2)(CH_2PR_2')(CH_2PR'_2)$, was also obtained by Huttner and co-workers [131]. From this ligand with R = 2-tolyl, R′ = 4-tolyl, R″ = Ph the complex $[(L)Fe(NCMe)_3][BF_4]_2$ was isolated and characterized by X-ray diffraction crystallography (Scheme 28); the complex shows a classical octahedral coordination at the iron center. (v) More recently, Friesen and co-authors have described the synthesis and the characterization, in the solid state and in solution, of the new silyl tripodal phosphine $HC[Si(CH_2)_2PPh_2]_3$ which displays a rigid conformation due to significant barriers to rotation of the dimethylsilyl arms [132]. (vi) Venanzi et al. have reported the synthesis and the X-ray diffraction analysis of the rhodium complex $[Rh(nbd)\{td(CF_3)pme\}][CF_3SO_3]$ (nbd = norbornadiene), where $td(CF_3)pme$ represents the CF_3 substituted triphosphine $CH_3C[CH_2P(m\text{-}CF_3C_6H_4)_2]_3$ (Scheme 29) [133]. In the cation $[Rh(nbd)\{td(CF_3)pme\}]^+$, as well as in the tdpme



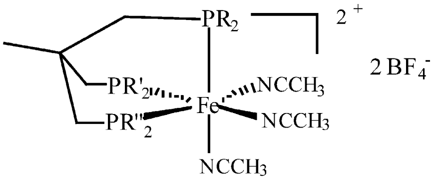
P = P(Benzyl)

(**a**) Ar = Ph, R = Me
(**b**) Ar = 3,5-$Me_2C_6H_3$, R = Me
(**c**) Ar = Ph, R = Ph

Scheme 26.

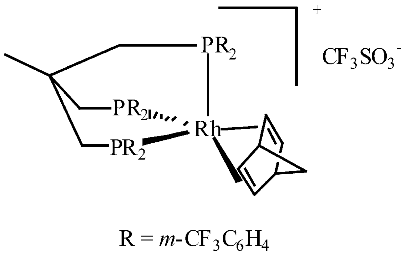


Scheme 27.



R = 2-tolyl, R'= 4-tolyl, R''= Ph

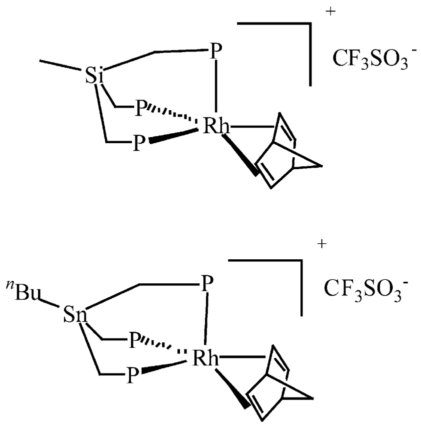
Scheme 28.



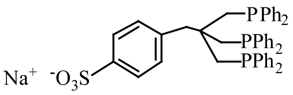
Scheme 29.

parent compound, severe distortions are caused by the nbd bite angle: nevertheless, the CF_3 substituted five-coordinate rhodium complex displays a greater deviation of its square-pyramidal geometry towards a trigonal-bipyramidal arrangement. This compound has shown a lower sensitivity to oxygen compared to the tdpme analogous complex, presumably due to stabilizing electronic effects of the six CF_3 substituents. The same fluorinated ligand was used to form complexes with ruthenium and iridium [134]. This kind of complex is active in catalytic acetalization of benzophenone with better results than the analogous compounds with tdpme [135]. (vii) Venanzi had previously developed synthetic methodologies to produce the original tripodal phosphines $CH_3Si(CH_2PPh_2)_3$ and $^{n}BuSn(CH_2PPh_2)_3$ [136]. The related ligand $CH_3Si(CH_2PMe_2)_3$ had already been reported by Becker et al. [137]. The crystal structures of the rhodium complexes [Rh(nbd)(triphosph)][CF_3SO_3] obtained from triphosph = $CH_3Si(CH_2PPh_2)_3$ and $^{n}BuSn(CH_2PPh_2)_3$ were reported and display similar distorted trigonal-bipyramidal geometries (Scheme 30) [136].

Bianchini and co-authors reported in 1995 an important result in the field of tripodal polyphosphine chemistry [138]. The modification of the phosphine ligand tdpme, with the aim to make its metal complexes exclusively soluble in light alcohols and water has lead to the new ligand [$Na^+, {}^-O_3S(C_6H_4)CH_2C(CH_2PPh_2)_3$] (abbreviated sulphos). This compound with a hydrophilic tail (see Scheme 31) opens triphos type ligands to

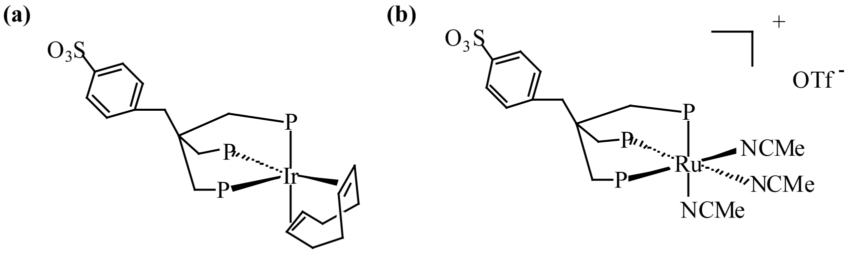


Scheme 30.



Scheme 31.

their use in liquid biphasic catalysis. Further detail on their surprising catalytic performances, for example in hydroformylation of hex-1-ene, which results from the use of the zwitterionic rhodium complexes [(sulphos)Rh(cod)] and [(sulphos)Rh$(CO)_2$] (cod = cycloocta-1,5-diene) is beyond the scope of this review. However, we mention the possibility of the exclusive production of alcohols, in certain conditions, in contrast to the classical aldehyde formation of traditional rhodium/triphosphine systems. The catalytic activity of [(sulphos)Rh(cod)] for the selective hydrogenation or hydrogenolysis reactions of the benzo[*b*]thiophene to 2,3-dihydrobenzothiophene or 2-ethylthiophenolate (in presence of NaOH), respectively, in liquid-biphase comprising MeOH or MeOH/H_2O mixtures as the polar phase and *n*-heptane as the organic phase, was reported [139]. The complex was used also for isomerization of allylic and homoallylic alcohols into the corresponding aldehyde or ketone in liquid-biphase [140]. An uncertainty remains concerning the geometry in the solid state of [(sulphos)Rh(cod)] and [(sulphos)Rh$(CO)_2$], due to the lack of suitable single crystals for X-ray diffraction [141]. The solution NMR studies are in favor of five-coordinate complexes. They can adopt a more or less distorted (depending on the co-ligands) either square-pyramidal or trigonal-bipyramidal conformation, due to the geometrical constraints of the tripodal phosphine. Nevertheless, the authors have reported the X-ray characterization of [(sulphos)Ir(cod)] for which a distorted trigonal-bipyramidal geometry was established [141] (see (**a**) Scheme 32). Interesting applications of this type of compound are reported by Bianchini et al. in the field of heterogenization of homogeneous catalysts: immobilization procedures, based on the ability of the sulfonate tail to link silanol groups on silica via hydrogen bonding, were developed [141]. The sulphos ligand was also used to form ruthenium complexes as soluble catalysts in polar phases [142,143]. The dimer Na[$\{O_3S(C_6H_4)CH_2C(CH_2PPh_2)_3Ru\}_2(\mu\text{-}Cl)_3$] (identified by NMR) is a catalyst precursor for the liquid-biphase hydrogenation of the double bond in various alkene (hex-1-ene, dec-1-ene, allylbenzene, styrene) as well as the heteroaromatic ring in benzo[*b*]thiophene and quinoline [142]. Recently, the ruthenium complex [$(O_3S(C_6H_4)CH_2C(CH_2PPh_2)_3Ru(NCMe)_3][O_3SCF_3]$, was immobilized on silica via hydrogen bonding between the silanol groups of the support and the SO_3^- groups from the sulphos ligand and the triflate counter-anion [143]. In the solid state this ruthenium compound was characterized by an X-ray diffraction study. The



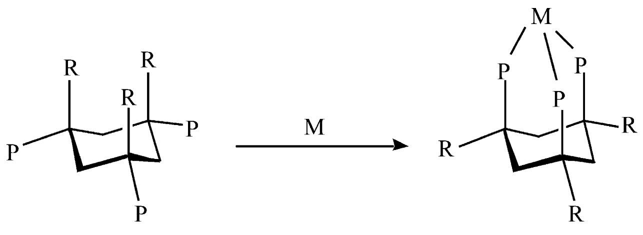
Scheme 32.

structure consists of complex cations and triflate anions with interspersed MeCN and water molecules. The metal center is in a classical octahedral environment (three phosphorus and three nitrogen atoms) distorted by the constraints of the tripodal ligand (see (**b**) Scheme 32). The supported hydrogen-bonded complex is a selective catalyst for the hydrogenation of benzylidene–acetone to benzylacetone and of benzonitrile to benzylidenebenzylamine. In all cases of these biphasic liquid catalyses the ruthenium remains in the polar phase at the end of the catalytic reactions thus allowing an easy separation of the catalyst and the substrate [142,143]. The comparison between the reactivity of the aqueous-biphase catalyst and the homogeneous analogue $[(tdpme)Ru(NCMe)_3][CF_3SO_3]_2$, shows that the silica-supported catalyst is slightly less active but much more selective and recyclable [143]. In this relevant example, the goal of combining, by heterogenization, the advantages of homogeneous catalysis (high selectivity) and heterogeneous catalysis (stability, easy catalyst recovering) is successfully reached. Other water-soluble triphosphines were reported in the last few years: the linear triphosphine $PhP[CH_2CH_2P(CH_2OH)_2]_2$ (see Section 2.1) or the polymer-like tripodal *cis*,*cis*-1,3,5-$(PPh_2)_3$-1,3,5-$[CH_2(OCH_2CH_2)_xOCH_3]C_6H_6$ (xix range from 30 to 160) (see Section 2.3.1).

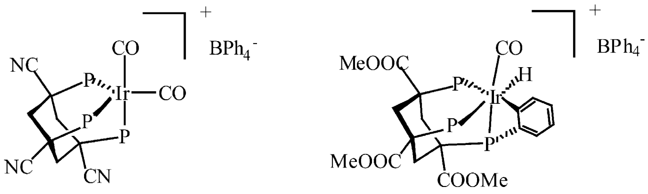
2.3. Other tridentate phosphines

2.3.1. Triphosphines with a cyclohexane ring backbone

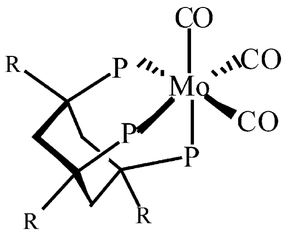
In the early 1990s Mayer and co-workers synthesized a novel family of tridentate polyphosphines with a cyclohexane frame as backbone, substituted in positions 1,3,5 by either PPh_2 or CH_2PPh_2 moieties, plus eventually other groups at the same positions [6,144,145] (Scheme 33). The ligands *cis*,*cis*-1,3,5-$(PPh_2)_3$-1,3,5-$R_3C_6H_6$ with R = H, COOMe, CN (respectively tdppcy, tdppcyme, tdppcycn) were synthesized. Among them, the structure of tdppcyme in the solid state was reported from X-ray diffraction measurements [146]. These ligands were used to form carbonyl-containing iridium coordination complexes; $[(tdppcycn)Ir(CO)_2]BPh_4$ and the orthometallated species [(tdppcyme-P,P',P'',C_{Ph})-IrH(CO)]BPh_4 (Scheme 34) were authenticated by X-ray analysis [144]. Other functionalizations of the cyclohexane backbone of the tripodal phosphines were achieved, and molybdenum complexes containing these new ligands were isolated: two of them were characterized by X-ray diffraction (Scheme 35, R = CH_2OCH_3, $C(O)NH(CH_2)_2NH_2$ [145]. In these complexes the stereochemical constraints of the tridentate coordination impose a facial arrangement at the molybdenum center which leads to adamantane-type structures. Three carbonyl ligands complete the octahedral environment around the molybdenum atoms. In each complex, the three functional groups of the phosphines (R) are oriented equatorially at the *ipso*-positions of the cyclohexane ring [145]. In the comparable octahedral adamantane-type complexes (molybdenum or iridium complexes) the conformation of the cyclohexane ring



Scheme 33.



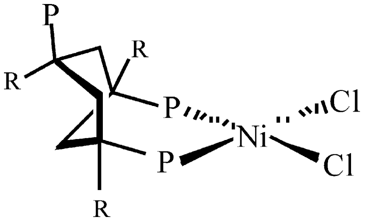
Scheme 34.



R = CH_2OCH_3 or $C(O)NH(CH_2)_2NH_2$

Scheme 35.

is more or less distorted from an ideal chair conformation by a flattening of the ring. In the iridium complex with tdppcycn the arrangement around the metal center is trigonal-bipyramidal, the phosphine ligand being in facial position [144]. The coordination sphere is completed by two mutually *cis* carbonyl ligands. The geometry around the iridium atom in the orthometallated complex with tdppcyme (Scheme 34) is best described as a distorted octahedron [144]. A carbonyl group, a hydride and the α-carbon atom of the metallated phenyl ring occupy each a position *trans* to a phosphorus atom of the tdppcyme ligand. The formation of the four-membered ring causes only slight deformations of the orthometallated ring, the benzene and the metallaphosphacyclobutane showing only minor deviations from planarity. The CO group is bent toward the hydride. These recently reported structures are interesting to compare with that of a previously described iridium complex containing the ligand *cis*,*cis*-1,3,5-tris(diphenylphosphinomethyl)-1,3,5-trimethylcyclohexane (tdppmtmcy) (Scheme 36) [147]. This ligand contains the more flexible CH_2PPh_2 moiety (an X-ray structure determination is given). In spite of its higher flexibility, only two phosphines of tdppmtmcy are coordinated to the iridium metal center, while the third one remains uncoordinated (Scheme 36), and a very rare coordination of a central carbon atom of the cyclohexane ring resulting from a C–H activation is observed. The X-ray structural characterization of the iridium complex $[(tdppcy)IrCl_3]$ has revealed a more classical octahedral adamantane-type geometry [148]; in contrast with this result, a biligate coordination for tdppcyme was observed for $[(tdppcyme)NiCl_2]$, a square-planar arrangement around the metal being preferred (Scheme 37) [149]. The X-ray diffraction analysis showed for the complex the chlorine atoms in a *cis*-configuration; the cyclohexane backbone displays a boat conformation. The tripodal phosphine ligands of tdppcyme-type are coordinated in an η^2-fashion to Group 10 metals, despite the stability provided by the adamantane-type polyhedron formed when the three phosphines bind the metal center. Considering their rather rigid backbone these ligands have shown an interesting variety of coordination modes, which depend mainly on the length of their podand chains and of the geometric requirement of the metal involved.

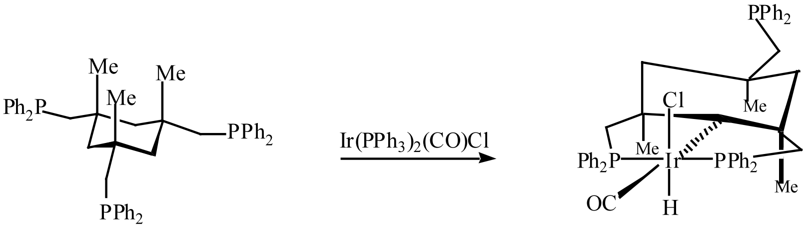


Scheme 37.

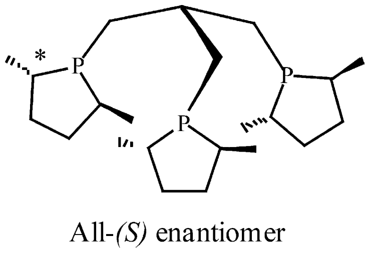
It is worth mentioning the powerful application of $[Mo(CO)_6]$ in synthetic chemistry related to the complexes displayed in Scheme 35. The $Mo(CO)_3$ template was used as an organometallic protection of the phosphorus center while functionalization of the tripodal phosphine was carried out [145]. Upon irradiation of the resulting molybdenum carbonyl complexes, solutions in the presence of N_2O or pyridine *N*-oxide the new polyphosphines are released. This methodology opens a potential novel route to the synthesis of chiral polyphosphines, and has already been used to prepare a water-soluble polymer-like triphosphine [150]. The cyclohexane backbone of tdppcy-type phosphine was functionalized with polyethylene glycol groups to form the *cis*,*cis*-1,3,5-$(PPh_2)_3$-1,3,5-$[CH_2(OCH_2CH_2)_x$-$OCH_3]_3C_6H_6$ (*x* range from 30 to 160). The alcohol $[Mo(CO)_3\{$*cis*,*cis*-1,3,5-$(PPh_2)_3$-1,3,5-$(CH_2OH)_3C_6H_6\}]$ was converted to the corresponding alcoholate, then to the polyethylene derivative in a polyaddition reaction with oxirane. The degree of polymerization was controlled by adjusting the ratio of oxirane to alcohol molybdenum complex in the range 90:1 to 500:1. After methylation of the hydroxylic end groups, and photochemical demolybdenation, the water-soluble ligand was reacted with a rhodium precursor. The resulting water-soluble rhodium carbonyl hydrido complex was used in biphasic (hex-1-ene/water) hydroformylation of hex-1-ene, with a comparable catalytic activity to the single-phase system hex-1-ene/methanol.

2.3.2. Miscellaneous triphosphines

Among tridentate chiral phosphines, few of them, or of their metal complexes, were structurally authenticated by X-ray crystal structures. The most common tridentate chiral phosphines are chiral at the phosphorus center due to all different substituents, so that in the ligands employed, the asymmetry is restricted to the

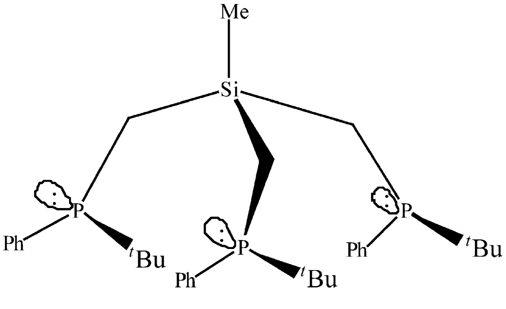


Scheme 36.



Scheme 38.

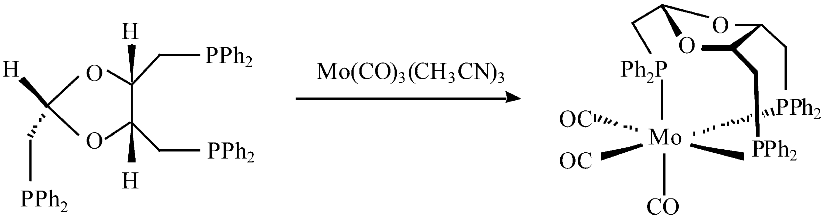
phosphorus atom while the backbone remained C_3-symmetric [131,151–156]. Chiral tripodal ligands with three different donor groups, $L = CH_3C(CH_2PR_2)(CH_2PR'_2)(CH_2P''R_2)$ [131], obtained by Huttner and co-workers as tdpme variations, are described in Section 2.2. Burk et al. have reported the first examples of homochiral C_3-symmetric polydentate phosphine, as well as the preparation and structural characterization of rhodium complexes bearing these ligands [154,155]. The chiral C_3-symmetric all-(*S*) triphosphine ligand, abbreviated CP_3 (Scheme 38), was reacted with $[(cod)_2Rh][SbF_6]$ to yield the complex all-(*S*)-$[(cod)Rh(CP_3)][SbF6]$. The X-ray structural study indicates that the triphosphine imposes a C_3-symmetric environment to the metal. The rhodium complex was shown to react as a catalyst precursor for the enantioselective hydrogenation of various unsaturated substrates, such as for instance dimethyl itaconate (50 °C, 95% e.e.). Ward et al. have reported the synthesis and characterization of a silane C_3-symmetric tripodal phosphine bearing chirality on the phosphorus atoms: $MeSi[CH_2P(^tBu)Ph]_3$ (abbreviated (*RRR*)-Siliphos, see Scheme 39) [156]. The chiral triphosphine is obtained from borane-removal in the precursor compound (*RRR*)-Siliphos-borane. An X-ray structure of this precursor compound was reported, as well as the X-ray structure of the rhodium complex obtained with the Siliphos ligand: $[Rh(nbd)\{(RRR)\text{-Siliphos}\}][CF_3SO_3]$. The coordination geometry around the metal atom is distorted square-pyramidal and similar to that found by Venanzi and co-workers in $[Rh(nbd)(tdpme)]^+$ [133].



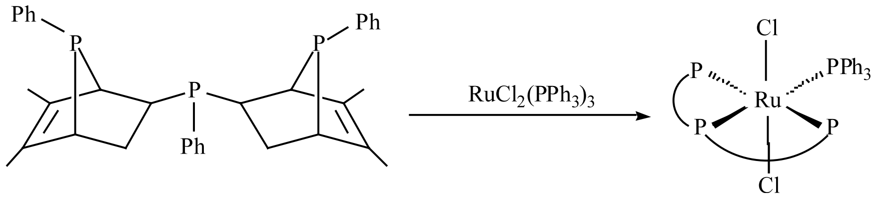
Scheme 39.

Börner and co-workers in 1998 reported the formation of an octahedral complex of molybdenum from the reaction of $[Mo(CO)_3(CH_3CN)_3]$ with the (*S*,*R*) stereoisomer of the chiral phosphine presented in Scheme 40 [157]. The crystal structure of the resulting complex shows that the three phosphorus atoms are bound to the metal in a facial mode. Three carbonyl ligands occupy the face opposite to the polyphosphine. The species present two eight-membered and one seven-membered metallacycles. Nevertheless, the general selectivity in the chemistry reported remains troublesome, since, under equivalent reaction conditions, related chiral polyphosphines (homologues with long chain $-(CH_2)_m-PPh_2$, $m = 2–6$, linked to the quaternary carbon) have yielded mixtures of numerous molybdenum complexes difficult to characterize even by NMR.

A very original type of conformationally rigid tridentate phosphine was reported (Scheme 41) [158]; this bisphosphabicyclo phosphine (L) is obtained as a result of two Diels–Alder cycloadditions of divinylphenylphosphine to 1-phenyl-3,4-dimethylphosphole assisted by anhydrous nickel dibromide. The ligand L can be removed from nickel, and was used to form the *mer*-ruthenium complex $[LRuCl_2(PPh_3)]$. X-ray diffraction analysis characterized both the ruthenium complex and the new polyphosphine ligand. The geometry of the coordination sphere around the ruthenium atom is a severely distorted octahedron, where the apical positions are occupied by two *trans* chloride ligands. Two fused five-membered chelate rings Ru–P–C–C–P are equatorially disposed, the last equatorial coordination position being occupied by the triphenylphosphine group. The phosphanorbornene rings of L in the complex are strained: the C–P–C angles made by the bridgehead carbons and the 7-phospha phosphorus being small,



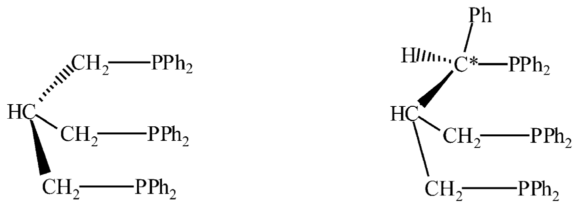
Scheme 40.



Scheme 41.

79.5(2) and 79.1(2)°. The double bonds are well localized with a mean bond length of 1.321(5) Å; other bond distances and angles in the triphosphine are in a classical range.

The chiral triphosphine modification of tripod named heliphos (Scheme 42) is particular since the stereogenic center is neither one phosphorus atom, neither an atom of the ancillary groups attached to phosphorus, nor the central carbon atom of the tripodal compound [159].



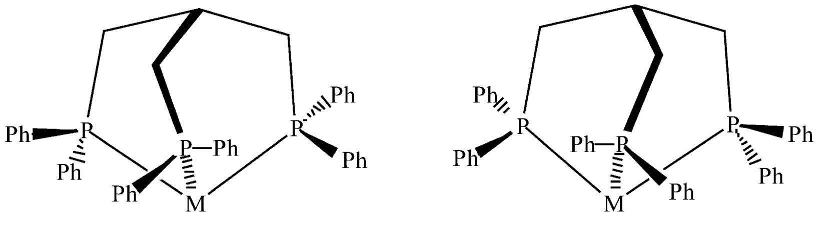
tripod

(*S*)-heliphos

Scheme 42.

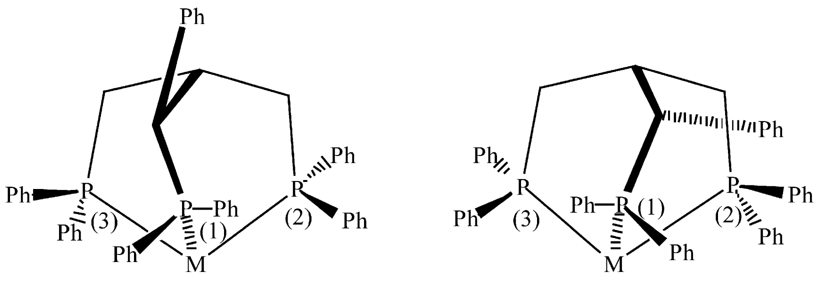
The absolute configuration of the stereogenic center allows control of an element of chirality usually neglected, e.g. the helical conformations adopted by the tripodal phosphine upon coordination to metal centers (see Scheme 43). The crystal structure of [Rh((*R*)-heliphos)(nbd)]ClO_4 was determined by X-ray diffraction; with (*R*)-heliphos a left-handed helical conformation was obtained, which minimized the steric repulsions existing between the phenyl ring on the asymmetric carbon and the phenyl rings on P(2). The reverse situation was suggested upon coordination with (*S*)-heliphos (right-handed conformation). Thus, these steric repulsions dictate the final conformations of (*R*)- or (*S*)-heliphos.

It is worth noting, as a conclusion, that compared to Group 6 to 10, only a few multidentate polyphosphine complexes with transition metals of other groups have been reported (see for example the zirconium/etp-derivative compound synthesized by Edwards et al. [160]). Thus, this chemistry still remains a relevant field for further investigations.



Left-handed conformation

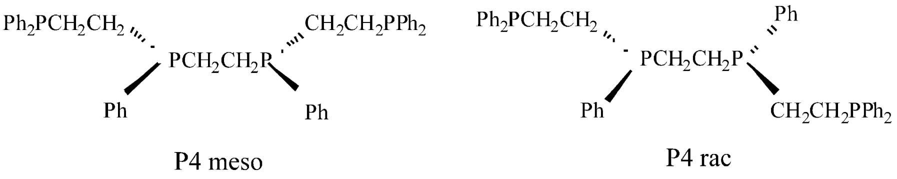
Right-handed conformation



Left-handed conformation

Right-handed conformation

Scheme 43.



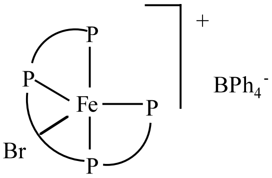
Scheme 44.

3. Linear, tripodal and other simple tetradentate phosphines and their metal complexes

3.1. Linear tetraphosphines

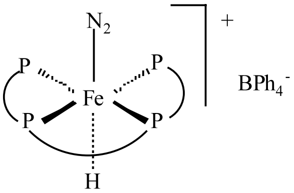
Linear tetraphosphines of the general formula R_2P–$(CH_2)_2$–$PR(CH_2)_m$–$PR(CH_2)_2$–PR_2 are known for $m=1$ as eLTTP (ethyl-substituted linear tetratertiary phosphine, R = Et) derivatives and for $m=2$ as P4 (hexaphenyl-1,4,7,10-tetraphosphadecane, R = Ph) derivatives. A compilation of other exotic linear tetraphosphines is available in Ref. [5], the principal variations noted being: (i) the number of methylene groups between the phosphorus atoms ($m=1$, 2, 3, 6 or 10), and (ii) the differences in the alkyl substituents (R = H, Me, ^{i}Pr, ^{t}Bu) on the phosphorus between the central and terminal phosphorus atoms and of course a combination of these two parameters. The phosphine P4 (also called tetraphos I) prepared by King and co-workers was the first linear tetratertiaryphosphine obtained [161,162]. P4 exists as two possible sets of diastereoisomers: the meso R,S form and the racemic R,R and S,S pair (Scheme 44) [161,162].

Monometallic and homobimetallic complexes with various structural features were obtained using P4, more structural data being now available concerning mononuclear species. The $[Fe(P4)Br]^+$ group in the complex $[Fe(P4)Br]BPh_4$ displays a trigonal-bipyramidal geometry with two phosphorus in axial positions, and the two others in equatorial positions (Scheme 45) [163,164]. Treatment of these species with sodium tetrahydroborate under nitrogen gives the hydrido-dinitrogen–iron(II) complex $[FeH(N_2)(P4)]Br$, which then presents a distorted octahedral environment at the iron atom with the four phosphorus atoms in the equatorial plane, the axial positions being occupied by the hydrogen atom and one nitrogen of the N_2 ligand (Scheme 46) [165]. In the structurally characterized *meso*-form compound, the iron atom is shifted out of the equatorial plane towards the N_2 ligand by 0.34 Å.

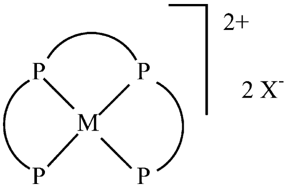


Scheme 45.

The dicationic species of Group 10 metals with a general formula $[M(P4)]^{2+}$ adopt a more or less distorted square-planar geometry due to the steric constraints exerted by the three five-membered chelating rings (Scheme 47). Brüggeller and co-workers have thoroughly studied the formation of platinum, palladium and nickel compounds with P4 [166–169], focusing on crystal structure characterization by X-ray to distinguish the complexes with either a diastereomeric *rac*- or *meso*-form for P4. In 1990, these authors have described the crystallographic structure of *rac*-$[Pt(P4)][BPh_4]_2$ as the first one obtained with *chiral* P4; all the previously-known structures of complexes containing P4 being *meso*-forms [166]. In the $[Pt(P4)]^{2+}$ moiety the distorted Ph_2P–Pt–PPh_2 angles are of 84.3±1.8°, and the Pt atom is only shifted out of the phosphorus plane by 0.0039 Å. A comparison with the known structures (see above the shift of Fe for $[FeH(N_2)(P4)]Br$, or the shift of 0.12 Å in *meso*-$[RuCl_2(P4)]$ [170]) shows that *meso*-P4 and *rac*-P4 lead to significant different deviations of the metal from planar MP4 configuration. This is a result of their respective different angular requirements in occupying a planar position. This observation was later confirmed by the authors with the crystal structure determination of the *meso*-$[Pt(P4)][BPh_4]_2$ form where the platinum atom is 0.161 Å out of the phosphorus plane [167]. In 1995 they also described the first X-ray structure of a palladium–P4 complex [168]: the *meso*-$[Pd(P4)]Cl_2$ complex shows a strongly distorted square-planar geometry where the Pd atom deviates 0.231 Å from the best plane through the phosphorus atoms.

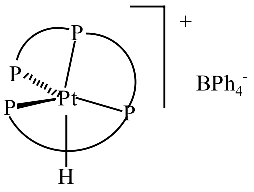


Scheme 46.

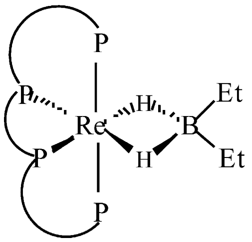


Scheme 47.

Despite many attempts, the complex *rac*-[Pd(P4)]Cl_2 has not be obtained (the exclusive formation of the five-coordinate [PdCl(P4)]Cl was observed). According to Brüggeller, in some platinum or palladium P4 complexes the deviations from square-planar coordination are so important that one of the diastereomeric forms *rac* or *meso* is destabilized, creating thus a stereoselective reactivity of P4 in the formation of these complexes [168]. The more recent report of the X-ray crystal structure of *rac*-[Ni(P4)]Cl_2 shows for the Ni atom a square-planar environment distorted towards a tetrahedral P4 arrangement. The nickel atom deviates only 0.034 Å from the mean plane of the phosphorus atoms. The tetrahedral distortion is very similar to that detected in *rac*-[Pt(P4)][BPh_4]$_2$ and seems dominated, in this case too, by the steric requirements of *rac*-P4 and not by the metallic center. With platinum, crystallographic structures of P4 compounds of trigonal-bipyramidal geometry have also been described: [PtH(P4)]BPh_4 was prepared from the addition of $NaBH_4$ on [Pt(P4)][BPh_4]$_2$. The compound adopts in the solid state a strongly distorted trigonal-bipyramidal coordination towards a square-pyramidal geometry, where the hydride ligand is in an axial position and the chiral P4 is in a tetrahedral configuration around the platinum center (Scheme 48) [171,172]. The *rac*-[Re(H_2BEt_2)(P4)] complex (Scheme 49) was obtained from [$ReCl_3$(P4)] by reaction with a mixture of ($LiBHEt_3$/$LiBEt_4$/$LiBH_2Et_2$) in THF [173]. The X-ray structure determination shows that the compound has a two-fold symmetry axis along the Re–B bond, and that two hydrides bridge the rhenium and bore atoms. The environment around the metal center is best described as distorted trigonal-bipyramidal with two phosphorus in axial position and the equatorial plane occupied by two phosphorus and the boron atom.

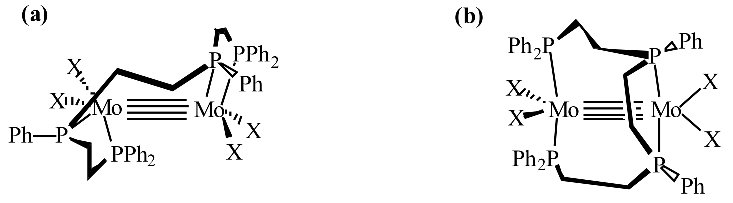


Scheme 48.



Scheme 49.

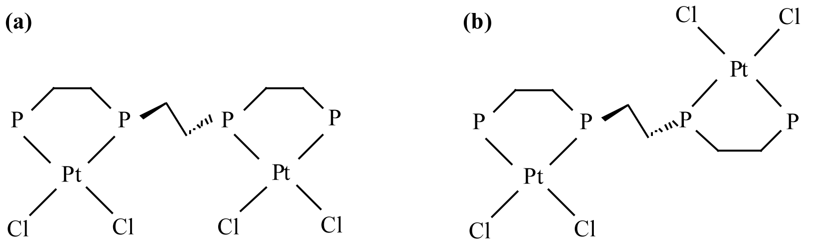
The ligand P4 can also act as virtually two independent diphosphines to form homobimetallic ethylene-bridged species (Scheme 50). This behavior was first noted by Cotton et al. [5,174,175] through X-ray characterization of [Mo_2X_4(P4)] complexes (X = Cl or Br). Interestingly, *rac*-[Mo_2X_4(P4)] displays a bis-chelating single-bridging mode of coordination for P4 ((**a**) Scheme 50), while *meso*-[Mo_2X_4(P4)] exhibits a chelating double-bridging coordination mode for P4 ((**b**) Scheme 50) [5,175]. In 1992, the structure of *cis,rac*-[Pt_2Cl_4(P4)] was reported [176]. The features of *rac*-[Mo_2X_4(P4)], and *rac*-[Pt_2Cl_4(P4)] are very different: while the geometry around the molybdenum atoms derived from pentacoordination, the platinum atoms environment is square-planar ((**a**) Scheme 51). The average distances Mo–Mo in [Mo_2X_4(P4)] compounds (2.154 Å for racemic and 2.190 Å for meso diastereomers, respectively) infer quadruple metal–metal bonds [175], whereas the Pt centers lie 6.338(1) Å from each other. The flexibility of P4 allows this difference based on the orientation of the C–P bonds at the ethylene-bridge; thus, an open-mode structure is observed for the dinuclear platinum complex, while the molybdenum complex adopts a close-mode structure [5]. The diastereomeric *cis,meso*-[Pt_2Cl_4(P4)], structurally characterized later, also shows an open-mode structure with a Pt–Pt distance of 6.916(1) Å and a *cis* P4 configuration ((**b**) Scheme 51) [177]. *cis,rac*-[Pt_2Cl_4(P4)] displays an identical orientation of the two coordination units containing a platinum, two phosphorus and two chlorine atoms with the Cl pointing in the same direction. On the contrary *cis,meso*-[Pt_2Cl_4(P4)] is a completely different rotational isomer where the two coordination units point in opposite directions, presumably to minimize



rac-bischelating single bridging mode (X = Cl, Br, average Mo-Mo = 2.154 Å)

meso-chelating double bridging mode (X = Cl, Br, average Mo-Mo = 2.190Å)

Scheme 50.

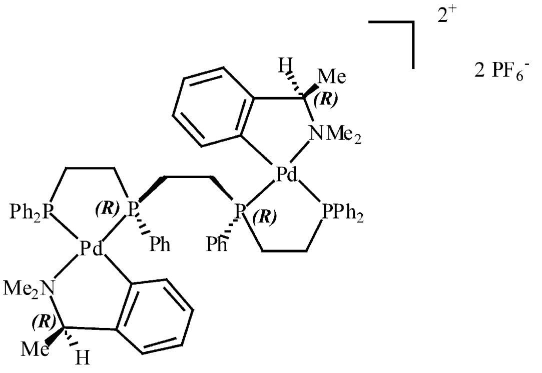


Cis-rac $Pt_2Cl_4P_4$ (Pt-Pt = 6.338(1)Å)   *Cis*-meso $Pt_2Cl_4P_4$ (Pt-Pt = 6.916(1)Å)

Scheme 51.

the steric interactions. The X-ray structure of *cis*,*rac*-$[Ni_2Cl_4(P4)]$ reveals an open-mode dimer with the P4 ligand coordinating in a similar manner as in *cis*,*rac*-$[Pt_2Cl_4(P4)]$ [169]. Whereas the deviations from ideal square-planar angles are larger in the nickel complex than in the platinum one, the Ni–Ni distance of 6.339(1) Å is identical to the Pt–Pt distance of 6.338(1) Å. Another parameter obviously very similar in the two complexes is the respective orientation of the two coordination units containing one metal center, two phosphorus and two chlorine atoms pointing in the same direction. The two coordination planes in *cis*,*rac*-$[Ni_2Cl_4(P4)]$ include an angle of 7.2°, within the standard deviations, the same value was found (7.3°) in the platinum analogue. Considering these similarities and the intrinsic differences of nickel and platinum atoms, it seems likely that the very nature of the *rac*-P4 ligand dominates the stereochemistry of *cis*,*rac*-$[Pt_2Cl_4(P4)]$ and *cis*,*rac*-$[Ni_2Cl_4(P4)]$.

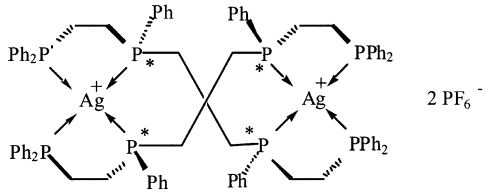
Wild and co-workers have separated, by extraction using benzene/methanol mixtures, the *meso* and *rac* diastereomeric forms of P4. The commercial product was first equilibrated as a 1:1 *rac*/*meso* mixture by heating it at 200 °C for 2 h [178]. The resolution of the *rac*-P4 diastereomer was achieved by complexation to an enantiomerically pure dimeric (*R*,*R*)-palladium complex. The resulting diastereomeric dinuclear (*R*,*R*,*R*,*R*)- and (*R*,*R*,*S*,*S*)-palladium(P4) species were separated by fractional crystallization. A crystal structure of the (*R*,*R*,*R*,*R*)-palladium complex (Scheme 52) was reported. The enantiomers (*R*,*R*)- and (*S*,*S*)-P4 were liberated by reaction of the palladium complexes with HCl and NaCN successively. When reacted with silver perchlorate and an excess of $NaPF_6$, optically pure (*S*,*S*)-P4 spontaneously self-assembles into a dimeric helical silver complex: (*R*,*R*,*R*,*R*)-$[Ag_2(P4)_2][PF_6]_2$ [179]. The X-ray structure determination has revealed both double helix and side-by-side helix conformers of the disilver cations in the unit cell (see Scheme 53). The coordination of the phosphine to the metal is stereospecific with retention of configuration at phosphorus, the apparent inversion is just a consequence of the classical rules for assigning chiral center configurations.



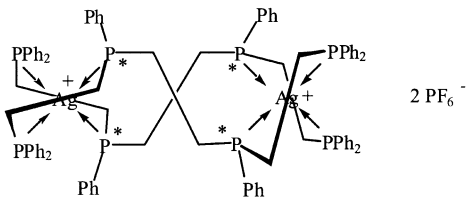
Scheme 52.

The ligand eLTTP is also a chiral tetraphosphine with *rac* and *meso* forms (Scheme 54). Contrary to P4 for which mononuclear crystallographic structures were described, it seems that eLTTP leads preferentially to dinuclear species, acting as two virtually independent diphosphines. Due to the methylene-bridging units, the metallic centers are generally closer to each other in the complexes described compared with P4-containing dinuclear complexes.

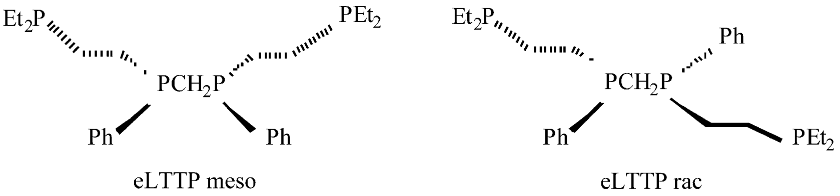
Schematic side-elevation of the all-*(R)* double-stranded double helix conformer



Schematic side-elevation of the all-*(R)* side-by-side helix conformer



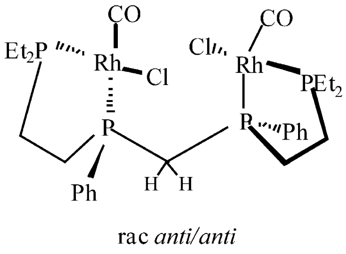
Scheme 53.



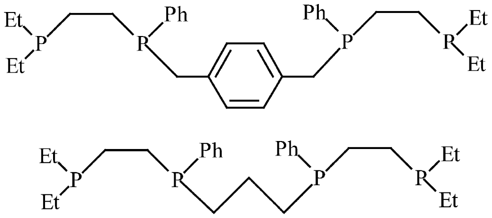
Scheme 54.

The reaction of eLTTP with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ yielded the dimeric complex *rac*-$[Rh_2Cl_2(CO)_2(eLTTP)]$ [5,180] (Scheme 55). X-ray diffraction studies have revealed that only the chiral *R*,*R*- and *S*,*S*-eLTTP diastereomer was present. The coordination geometry about the metal center is distorted square-planar due to the two five-membered chelating rings. The general rotational orientation of each half of the complex with respect to the central methylene-bridge hydrogen atoms can be described as *anti* or *syn*. *syn* will refer to the case in which a metal atom is on the same side of the eLTTP ligand as the hydrogen atoms of the central methylene-group, while *anti* will indicate that the metal atom is on the opposite side. The *rac*-rhodium complex adopts in the solid state an *anti–anti* open-mode conformation where the Rh–Rh bond distance is 5.813(2) Å. A similar *anti–anti* conformation was found for *rac*-$[Ni_2Cl_4(eLTTP)]$ with a Ni–Ni bond distance of 5.417(1) Å, the P–CH_2–P angles being more open than in the rhodium complex with 119.3(3)° compared to 113(1)° [5,181]. The complex *meso*-$[Ni_2Cl_4(eLTTP)]$ prefers to adopt a different conformation identified as *syn–anti* where the Ni–Ni bond distance is longer 6.272(1) Å (Scheme 56) [181]; the square-planar local coordination geometry about each nickel center is very similar to that found for the mononuclear compound $[NiCl_2(dppe)]$ [182]. A shorter distance between metal centers was reported for the dimeric cobalt species *meso*-$[Co_2(\mu\text{-}CO)_2(CO)_2(eLTTP)]$, where a Co–Co bond of 2.513(4) Å is observed [5,183].

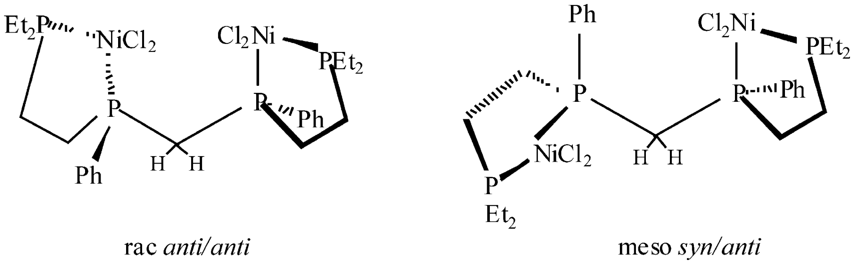
Stanley and co-workers have reported an important contribution to dinuclear rhodium complex chemistry using eLTTP and eLTTP derivatives as ligands (Scheme 57) [184]. The basic idea of the work was to keep a close distance between the metal centers in the new dinuclear complexes for studying cooperative behavior and promoting novel reactivity in homogeneous catalysis. The dicationic homobimetallic complex *rac*-$[Rh_2(nbd)_2(eLTTP)][BF_4]_2$ (Scheme 58) was successfully shown to be a precursor of a highly active and regioselective catalyst for the hydroformylation of alk-1-enes [184,185]. An X-ray diffraction structure showed that the Rh–Rh distance was 5.5058(6) Å, with each rhodium center in a square-planar environment. Several observations are consistent with bimetallic cooperation involving a dicationic active species of the type *rac*-$[Rh_2H_2(\mu\text{-}CO)_2(CO)_2(eLTTP)][BF_4]_2$ for the catalyst. Monometallic model complexes built as “half” the active dimeric compounds were very poor catalysts, as were dinuclear complexes formed with spacers-containing eLTTP derivatives (see in Scheme 57). In the course of the studies to improve their catalytic hydroformylation reactions, Stanley et al. have recently reported the



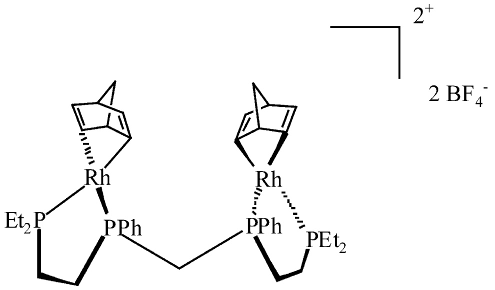
Scheme 55.



Scheme 57.



Scheme 56.



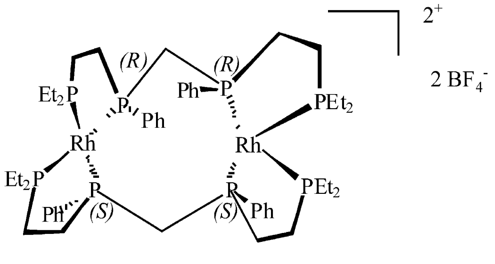
Scheme 58.

X-ray structure of one stereoisomer of a Rh(I) homobimetallic complex with two eLTTP ligands: $[Rh_2(R,R\text{-eLTTP})(S,S\text{-eLTTP})][BF_4]_2$ (Scheme 59) [186]. The geometry at the rhodium atoms is tetrahedrally-distorted square-planar with Rh–Rh distances of 5.4555(11) Å. However, the spectroscopic data show that this novel species is not involved in the hydroformylation catalytic process.

3.2. Tripodal tetraphosphines

The tripodal tetraphosphines, as illustrated in Scheme 60, display one central phosphorus atom and three peripheral (or terminal) phosphorus atoms. Among these branched polyphosphines the most commonly used as ligand are: $[P(CH_2CH_2PPh_2)_3]$ the tris[2-(diphenylphosphino)ethyl]phosphine (PP_3, sometimes called also tetraphos II), $[P(CH_2CH_2CH_2PMe_2)_3]$ the tris[3-(dimethylphosphino)propyl]phosphine (TPm), and $[P(o\text{-}C_6H_4PPh_2)_3]$ the tris[*o*-(diphenylphosphino)phenyl]phosphine (QP).

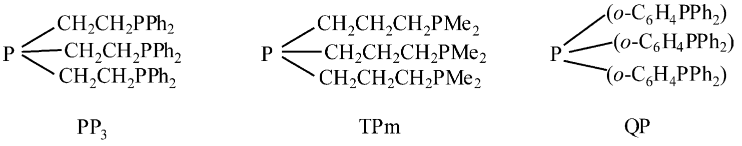
The flexibility of these podand ligands provides a tetradentate coordination in the majority of complexes. To illustrate the possible modes of coordination of these tripodal tetraphosphines, a selection of the complexes identified by X-ray diffraction analysis are listed in Scheme 61, together with their geometry [187–222].



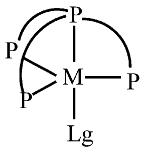
$[Rh_2(R,R\text{-eLTTP})(S,S\text{-eLTTP})][BF_4]_2$

Scheme 59.

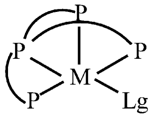
Trigonal-bipyramidal, square-pyramidal and octahedral more or less distorted geometries were reported for five- or six-coordinate complexes. As previously detailed by Hong and Cotton [5], all the compounds with trigonal-bipyramidal geometry described in the last decades have their co-ligands Lg located in an apical position, the *trans* position being occupied by the central phosphorus atom of the tripodal tetraphosphine. This arrangement avoids bridges between phosphorus atoms to span angles of greater than 90 °C. The central phosphorus of the podands compared with the terminal phosphorus, displays a shorter P–M bond length to the metal. The crystallographic structures of the original complexes reported after 1990 confirm these general observations. Stoppioni and co-workers have synthesized and fully characterized the rhodium/tetraphosphines complexes with hydrochalcogenide ligands $[Rh(XH)(PP_3)]$, where X = S, Se, Te [197]. The geometry of these isomorphous compounds consists of a classical trigonal-bipyramidal environment at the metal with the terminal phosphorus atoms of the polydentate ligand in the equatorial plane and the central phosphorus atom and the chalcogen atom in the axial positions. The chalcogen, rhodium and the central phosphorus atom of the PP_3 ligand lie on a 3-fold symmetry axis. In $[Rh(XH)(PP_3)]$ the Rh–P distances involving the central P are significantly shorter (respectively for X = S, Se, Te: 2.198(3), 2.187(7), 2.194(8) Å) than the ones involving a terminal phosphorus (respectively for X = S, Se, Te: 2.326(2), 2.320(4), 2.316(5) Å). These compounds are the first rhodium complexes with SeH and TeH as ligand while molecular structures of iron and nickel complexes with SH were already known (Scheme 61) [193]. In spite of the increased nucleophilicity at the rhodium center provided by the polyphosphine ligand, the authors have proposed that further electrophilic attack on the hydrochalcogenide complexes will occur preferentially on a lone pair of the chalcogen atom than on the rhodium. They have investigated the reaction of these complexes with the electrophilic reagents H^+ and CH_3^+ [219]. In particular, the complex $[Rh(H)(SeCH_3)(PP_3)]BPh_4$ was obtained from the attack of CH_3^+ at the nucleophilic chalcogen atom of $[Rh(SeH)(PP_3)]$. The trigonal-bipyramidal transient cation $[Rh(HSeCH_3)(PP_3)]^+$ is formed in the first step. The subsequent intramolecular oxidative addition of the $HSeCH_3$ ligand produced the stable



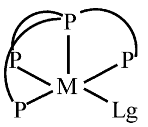
Scheme 60.



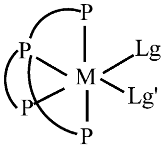
$CoH(PP_3)$ (187)
$[Co(P(OMe)_3)(PP_3)]BF_4$ (188)
$[CoH_2(PP_3)]PF_6$ (189)
$[CoN_2(PP_3)]BPh_4$ (190)
$[Co(C{=}C(H)Ph)(PP_3)]BPh_4$ (191)
$[Fe(NO)(PP_3)]BPh_4$ (192)
$[Fe(SH)(PP_3)]BPh_4$ (193)
$[FeBr(PP_3)]BPh_4$ (194)
$[Fe(C{\equiv}CPh)(PP_3)]BPh_4$ (195)
$[Ni(P(OMe)_3)(PP_3)][AsF_6]_2$ (188)
$[Ni(SH)(PP_3)]BPh_4$ (193)
$[NiBr(PP_3)]PF_6$ (196)
$Rh(SH)(PP_3)$, $Rh(SeH)(PP_3)$, $Rh(TeH)(PP_3)$ (197)
$Rh(SC{=}SCH_3)(PP_3)$ (198)
$[PdCl(PP_3)]Cl$, $[PdBr(PP_3)]Br$, $[PdI(PP_3)]I$ (199)
$Pt(PO(OMe)_2)(PP_3)$ (200)
$[PtH(PP_3)]BPh_4$ (201)
$[CoCl(QP)]BPh_4$ (202,203)



$[CoBr(PP_3)]PF_6$ (204)
$[Ni(Py)(PP_3)][BF_4]_2$ (205)



$[Co(OH)(PP_3)]BF_4$ (206)
$[Co(H_2O)(PP_3)][BF_4]_2$ (206)
$[RuCl(PP_3)]BPh_4$ (207)



$RuH(C_6H_3Me_2\text{-}3,4)(PP_3)$ (208)
$RuH(C_6H_3Me_2\text{-}3,5)(PP_3)$ (208)
$RuH(C_6H_4Me\text{-}3)(PP_3)$ (208)
$RuH(C_6H_4CF_3)(PP_3)$ (209)
$[Ru(\eta^3\text{-}(SiMe_3)C_3CH(SiMe_3))(PP_3)]BPh_4$ (210)
$[RuH(\eta^1\text{-}ClTl)(PP_3)]PF_6$ (211)
$RuH(CCPh)(PP_3)$ (212)
$RuH(\eta^1\text{-}C(MeO_2C){=}CH(CO_2Me))(PP_3)$ (212)
$Ru(CCPh)_2(PP_3)$ (212)
$[RuH(\eta^2\text{-}H_2)(PP_3)]BPh_4$ (213)
$[FeH(\eta^2\text{-}H_2)(PP_3)]BPh_4$, $[FeH(CO)(PP_3)]BPh_4$ (213)
$[Fe(PP_3)(O_2CCH_2CH_2C{\equiv}CH)]BPh_4$ (214)
$[FeCl(PPh_3)(PP_3Me)]BPh_4$ (215)
$[Fe(\eta^3\text{-}PhCCC{=}CHPh)(PP_3Me)]BPh_4$ (216)
$[OsH(\eta^2\text{-}H_2)(PP_3)]BPh_4$ (217)
$[Rh(H)_2(PP_3)]BF_4$ (218)
$[RhH(SeCH_3)(PP_3)]BPh_4$ (219)
$FeCl_2(TPm)$ (220)
$RuH(Cl)(TPm)$ (221)
$Ru(H)_2(TPm)$ (222)

Scheme 61.

octahedral Rh^{III} hydride $[Rh(H)(SeCH_3)(PP_3)]^+$. In the structure of this complex the arrangement of the non-hydrogen atoms at the metal center is approximately square-pyramidal, with the Se atom, the central phosphorus and two peripheral phosphorus atoms located in the equatorial plane. The apical phosphorus atom forms a longer Rh–P bond by an average of 0.09 Å. The hydride ligand, which has not been located from X-ray diffraction data, likely lies in *trans* position to the apical phosphorus, in agreement with NMR data, completing thus a distorted octahedral geometry.

Bianchini et al. have isolated from the reaction of the cationic fragment $[Co(PP_3)]^+$ with terminal alkynes HC≡CR, either π-alkyne adducts of the type $[Co(\eta^2\text{-}HC{\equiv}CR)(PP_3)]^+$, or hydride alkynyl species $[Co(H)(C{\equiv}CR)(PP_3)]^+$, or vinylidene complexes $[Co\{C{=}C(H)R\}(PP_3)]^+$ (where $R = H$, Ph, $n\text{-}C_3H_7$, $n\text{-}C_5H_{11}$, CMe_3, $SiMe_3$) depending on the temperature conditions [191]. Two species resulting from 1-hydride alkyne to vinylidene tautomerization were authenticated in the solid state by X-ray diffraction measurements: the vinylidene $[Co\{C{=}C(H)Ph\}(PP_3)]BPh_4$ and the hydride alkynyl $[Co(H)(C{\equiv}CSiMe_3)(PP_3)]BPh_4$ complexes. The coordination geometry at the cobalt atom in the carbene complex $[Co\{C{=}C(H)Ph\}(PP_3)]BPh_4$ is trigonal-bipyramidal with classical apical positions for the central phosphorus atom P_c from the PP_3 ligand and for the co-ligands. The sequence P_c–Co–C_α–C_β is not linear: P_c–Co–C_α is 167(1) or 162(1)° (two marginally different molecules are present in the asymmetric unit); some other vinylidene complexes have shown similar slight bending [191]. The presence of the vinylidene ligand is supported by all the bond length and angle values. The angle C_α–C_β–C_{Ph} has a value of 128(3) or 131(3)°, reasonable for sp^2 hybridization, and the C_α–C_β bond length (1.34(5) Å, average) is in agreement with the value expected for a $C(sp^2)=C(sp)$ double bond; X-ray characterizations of a mononuclear vinylidene complex of a first-row transition element are scarce. Despite the poor diffracting properties of the crystals of $[Co(H)(C\equiv CSiMe_3)(PP_3)]BPh_4$ obtained (R factor = 0.11), the resolution is good enough to show the quasi-collinearity of the vector P_c–Co–C_α–C_β–Si (P being the central phosphorus atom of PP_3). The value of 178° for the C_α–C_β–Si angle excludes an sp^2 hybridization of the carbon in β-position of the Co and thus confirms an hydride alkynyl complex rather than a vinylidene one. One of the angles at the cobalt atom determined by two peripheral phosphorus atoms is opened to a value of 150°, indicating a sufficient area for the hydride ligand to sit. In this case a pseudo-octahedral structure with an equatorial hydride ligand is expected. Finally, this is the first example of metal–hydride alkynyl to metal–vinylidene rearrangement occurring in the solid state [191]. The two above examples of vinylidene and hydrochalcogenide phosphine complexes show that the strong stability provided by the tripodal tetraphosphines leads to the formation and isolation in the solid state of complexes with rather unusual co-ligands and above all allows an interesting reactivity focused especially on these ancillary ligands.

The first stable iron(I) σ-alkynyl complexes of general formula $[Fe(C\equiv CR)(PP_3)]$, as well as iron(II) analogous species $[Fe(C\equiv CR)(PP_3)]BPh_4$, were synthesized and characterized by Bianchini and co-workers (R = Ph, $SiMe_3$, n-C_3H_7, n-C_5H_{11}, CMe_3) [195]. The X-ray structures of the 17- and 16-electrons complexes forming the redox couple $[Fe(C\equiv CPh)(PP_3)]/[Fe(C\equiv CPh)(PP_3)]BPh_4$ were reported. The Fe^{II} complex displays a quasi-regular trigonal-bipyramidal structure with the alkynyl ligand occupying the classical position *trans* to the bridgehead phosphorus atom (bond angle P_c–Fe–C = 177.2(6)°). The Fe(I) complex assumes a strongly distorted trigonal-bipyramidal structure with P_c–Fe–C = 170.3(3)° and equatorial bond angles of 102.4(1), 111.1(1), and 143.9(1)° [195].

Five-coordinate trigonal-bipyramidal palladium(II) complexes of formula $[PdX(PP_3)]X$ (where X = Cl, Br or I) were studied by Funahashi et al. [199,223]. The authors have determined the X-ray structures of these halide complexes, and a space group correction has later been reported [224]. The three structures with a central phosphorus in axial position show similar features, except obviously for the Pd–X distances [199].

The five-coordinate complexes with a square-pyramidal geometry identified by X-ray crystallography are less numerous. They can display an environment at the metal atom where the apical position of the pyramid is occupied by either a central phosphorus, or a terminal phosphorus (Scheme 61). The complexes $[Co(Br)(PP_3)]PF_6$, $[Co(OH)(PP_3)]BF_4$ and $[Co(H_2O)(PP_3)][BF_4]_2$ display these structural features [204,206]. Concerning $[Co(Br)(PP_3)]PF_6$, the geometry deviates so strongly from a trigonal-bipyramid that it is best described as a distorted square-pyramid where the metal lies 0.37 Å above the mean plane through the four basal atoms [204]. Strong distortions were noticed, as well, for the complexes $[Co(OH)(PP_3)]BF_4$ and $[Co(H_2O)(PP_3)][BF_4]_2$, since in these compounds the metal atom lies above the mean plane by 0.37 and 0.34 Å, respectively [206].

In the structure [207] of the distorted square-pyramidal ruthenium(II) compound $[RuCl(PP_3)]BPh_4$ the largest deviation from the idealized geometry is represented by a P–Ru–P angle of 154.5(1)° significantly closed with respect to the expected value of 180°. The ruthenium(I) complex $[RuCl(PP_3)]$ was generated, from the previous one, by one-electron electrochemical reduction, and is expected to retain the square-pyramidal geometry. Other electrochemical studies have shown the possibility of electrogeneration of Fe(I), Ru(I) and Os(I) five-coordinate complexes from deprotonation of $[MH(Cl)(PP_3)]$ (M = Fe, Ru or Os) [225]. Among these complexes, a square-pyramidal geometry was assigned to $[Os^ICl(PP_3)]$ by spectroscopic comparison with its precursor $[Os^{II}Cl(PP_3)]BPh_4$.

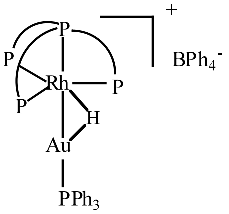
Concerning Group 10, the crystal structure of the complex $[Ni(py)(PP_3)][BF_4]_2$ (where py is a pyridine ligand) was also reported. A geometry intermediate between trigonal-bipyramidal and square-pyramidal, was found [205] where the metal atom lies 0.66 Å above the best mean plane through the four basal atoms.

Many recently reported structures of octahedral tripodal tetraphosphines complexes contain ruthenium (Scheme 61). The general features of these compounds invariably are that three *fac* positions are occupied by three phosphorus of the tripodal ligand, the fourth atom lying in an adjacent coordination position, thus giving rise to two *cis*-positions for the co-ligands. Usually the co-ligands are located in the equatorial plane of the octahedron formed around the metal, together with the central and one terminal phosphorus of the polyphosphine. Several novel complexes have been structurally characterized since the first ruthenium–hydride tripodal tetraphosphines species were reported by Dahlenburg and co-workers [208,209,221,222]. A study by Bianchini et al. of the catalytic properties of $[Ru(H)(H_2)(PP_3)]BPh_4$ and $[Ru(H)(N_2)(PP_3)]BPh_4$ toward the metal-assisted dimerization of terminal alkynes to alkenynes has led the authors to isolate the intermediate complex (*E*)-[Ru{η^3-(SiMe$_3$)C$_3$CH(SiMe$_3$)}(PP$_3$)]BPh$_4$ [210]. The coordination around ruthenium is strongly distorted due to the η^3-coordinate butenynyl ligand, but the bond distances between ruthenium and the C atoms are consistent with the values reported for other butenynyl complexes [210]. These authors have also reported a detailed study of the use of the *cis*-dihydride Ru^{II} complex [Ru(H)$_2$(PP$_3$)] as catalyst precursor for the regio- and stereoselective dimerization of HC≡CPh to (*Z*)-PhC≡C–CH=C(H)Ph [212]. Extensive comments on this exciting work are beyond the scope of this review, nevertheless several organometallic compounds of interest stabilized by PP$_3$ were reported and structurally characterized: the complexes [RuH(C≡CPh)(PP$_3$)]·C$_6$H$_6$, [Ru(C≡CPh)$_2$(PP$_3$)] and (*E*)-[RuH{η^1-(MeO$_2$C)-C=CH(CO$_2$Me)}(PP$_3$)]·EtOH display in the solid state the distorted octahedral geometry with the phosphine and the co-ligands at the classical positions mentioned above. In [RuH(C≡CPh)(PP$_3$)] the Ru–P distances (2.228(2)–2.335(2) Å) are non-equivalent but lie in the range of the values reported in the literature. The *trans* influence of the hydride to the terminal phosphorus in the equatorial plane results in the largest separation between this P atom and the ruthenium center. The Ru–H bond distance value of 1.57(8) Å is classical while the Ru–C separation, 2.078(8) Å, is shorter than the value expected for a Ru–C(*sp*) single bond (Ru–C$_{calcd}$ = 2.127 Å); according to the authors this difference may be attributed to back donation from dπ(metal) to π*(alkynyl) orbitals. [Ru(C≡CPh)$_2$(PP$_3$)] is the first *cis*-dialkynyl ruthenium complex authenticated by an X-ray diffraction determination; it was obtained by thermal treatment of the [RuH(C≡CPh$_2$)(PP$_3$)] hydride alkynyl species in the presence of an excess of HC≡CPh. The structure consists of discrete molecules of [Ru(C≡CPh)$_2$(PP$_3$)] with no solvent molecules in the lattice. The overall geometry is analogous to its precursor [RuH(C≡CPh)(PP$_3$)], the only difference being a phenylethynyl group in the place of the hydride. The largest Ru–P separation (2.347(4) Å) is found, once again, for the terminal phosphorus in the equatorial plane, suggesting that the *trans* influence of the ethynyl ligand is comparable to that of the hydride ligand in [RuH(C≡CPh)(PP$_3$)]. The interatomic distance between the two ruthenium bonded C(sp), 2.94(2) Å, preclude any interaction between the two alkynyl ligands. Finally, reaction of [Ru(H$_2$)(PP$_3$)] with MeO$_2$CC≡CCO$_2$Me results in stereoselective *cis* insertion of the disubstituted alkyne into the Ru–H bond *trans* to the central phosphorus. The X-ray analysis of the resulting vinyl hydride complex (*E*)-[RuH{η^1-(MeO$_2$C)C=CH(CO$_2$Me)}(PP$_3$)] shows that, as in the previous compounds, the principal distortion of the octahedral environment at the metal center is due to the axial P–Ru–P angle which closes up to 149.85(7)°. The Ru–P bond distances, as for the previous compounds, are consistent with the presence of a *trans* hydride ligand. The C=C bond and one C=O ester function lie coplanar to the equatorial plane of the octahedral polyhedron, while the other ester function is in a virtually perpendicular plane. Interestingly, the geometry with different orientations of the carboxylate substituents is apparently retained by the complex in solution in the temperature −80 to +60 °C range. Bianchini and co-workers have assigned a distorted octahedral structure to the complexes [RuH(η^2-H$_2$)(PP$_3$)]BPh$_4$, [FeH(η^2-H$_2$)(PP$_3$)]BPh$_4$ and [FeH(CO)(PP$_3$)]BPh$_4$ on the basis of their single-crystal X-ray diffraction analyses, multinuclear NMR studies in solution and theoretical calculations [213]. The authors reported that complexes of general formula [MH(L)-(PP$_3$)]BPh$_4$ (where M = Ru, L = H$_2$ or C$_2$H$_4$ and M = Fe, L = H$_2$, C$_2$H$_4$, CO or N$_2$) display an octahedral structure where the hydride, *trans* to a terminal phosphorus donor, and the L ligand occupy classical mutually *cis* positions. The calculations have indicated in the dihydrogen–hydride species that the H$_2$ ligand, difficult to localize by X-ray diffraction, is placed in a plane parallel to the P$_T$–M–H plane. The kinetics of formation of [FeH(η^2-H$_2$)(PP$_3$)]$^+$ from reaction of [Fe(H$_2$)(PP$_3$)] with HX acids in THF was electrochemically studied by Basallote et al. [226].

In the same Group 8 of elements an osmium complex was described [217]; the structure of the *cis*-hydride–η^2-dihydrogen complex [OsH(η^2-H$_2$)(PP$_3$)]BPh$_4$ was established in solution by variable-temperature NMR measurements and the determination of the solid-state geometry of the compound was shown to be consistent with this “non-classical” assignment, namely a distorted octahedral environment generally observed for ruthenium complexes; in this case a terminal hydride ligand and a H$_2$ molecule are located mutually *cis* in the equatorial plane completed by the bridgehead phosphorus and one peripheral phosphorus atom of PP$_3$. In fact, while the refinement procedure clearly confirmed the presence of a “classical” hydride *trans* to the peripheral phosphorus in the equatorial plane of the molecule, it was not possible to separate the other electron density spots into the two H components of the “non-classical” H$_2$ ligand molecule. As a consequence, only a hypothetical position for the η^2-H$_2$ ligand based on the spectroscopic information was retained to complete the structure. The photochemistry of [Os(H)$_2$(PP$_3$)] and [Ru(H)$_2$(PP$_3$)] was studied by means of laser flash photolysis and NMR by Perutz et al. [227]. From the ruthenium complex, the photochemical elimination of dihydrogen under selected gaseous conditions leads to species such as [Ru(C$_2$H$_4$)(PP$_3$)] or [Ru(CO)(PP$_3$)]. The compounds [RuH(SiEt$_3$)(PP$_3$)] or [RuH(Ph)(PP$_3$)] were also obtained by photolysis in THF or THF/benzene. From [Os(H)$_2$(PP$_3$)], the species [OsH(Ph)(PP$_3$)],

$[OsH(2\text{-}C_4H_7O)(PP_3)]$ or $[OsH(OTf)(PP_3)]$ then $[OsH(Me)(PP_3)]$ can be synthesized by either photolysis or thermolysis in solution. The previous results establish that the structural features obtained to date, for iron, ruthenium and osmium complexes with tetradentate polyphosphines are very similar, and thus more influenced by the polyphosphine ligand itself than by the properties of the metallic centers or of the ancillary ligands.

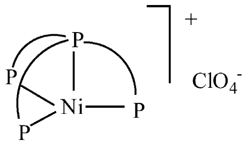
The rhodium species $[Rh(H)_2(PP_3)]BF_4$ reported by Bianchini et al., displays in the solid state and in solution below 183 K the same octahedral arrangement with a C_{2v} symmetry, in which the equatorial positions are occupied by two phosphorus (classically: one central, one terminal) and two *cis*-hydride ligands [218]. In solution *above 183 K* the geometrical change of the fragment from C_{2v} to C_{3v} symmetry detected by NMR suggests the formation of a transient trigonal-bipyramid structure with a dihydrogen ligand in an apical position. This study could have provided the first evidence for a *cis*-dihydride$\leftrightarrow\eta^2$-H_2 exchange with rhodium phosphine species; this could be very relevant information since rhodium is one of the most active metals for catalytic homogeneous hydrogenation. Concerning cobalt complexes, Bianchini et al. have reported that $[CoH_2(PP_3)]^+$ has either a dihydrogen or a dihydride structure in the solid state, depending on the nature of the counter anion employed (the PF_6 salt crystallizes as a dihydrogen complex while the BPh_4 salt adopts a dihydride structure) [228,229]. However, the structural and dynamical behavior studies by Heinekey and van Roon, using partial deuteration, lead in contrast to the conclusion that the cationic complexes $[RhH_2(PP_3)]^+$ and $[CoH_2(PP_3)]^+$ are correctly formulated as dihydrides whatever the temperature conditions [230]. In this same Group 9, the isolobal analogy between H^+ and $Au(PPh_3)^+$ was investigated with rhodium hydride complexes [231]. The reaction of the electrophilic fragment $Au(PPh_3)^+$ with the monohydride $[RhH(PP_3)]$ has led to the dinuclear complex $[(PP_3)Rh(\mu\text{-}H)\{Au(PPh_3)\}]BPh_4$. The geometry of the coordination polyhedron around the rhodium approximates a trigonal-bipyramid with the bridgehead phosphorus in axial positions and an intact $HAu(PPh_3)$ group *transoid* to each other (Scheme 62). The interesting (μ-H) ligand was localized mainly from NMR spectroscopy, and its position was confirmed by some geometrical features affecting the crystal structure of the $[(PP_3)RhAu(PPh_3)]$ assembly; especially the short Rh–Au distance of 2.690(1) Å matches well the values observed in rhodium–gold clusters containing a (μ-H) ligand.



Scheme 62.

Field and co-workers have used the methylated phosphine TPm and $[P(CH_2CH_2PMe_2)_3]$ (tris[2-(dimethylphosphino)ethyl]phosphine abbreviated PP_3Me) to study both iron and ruthenium hydride complexes [232–234]. They have reported high-yield tripodal tetraphosphine syntheses comprising photochemical reaction steps; in particular the PP_3Me ligand was synthesized in a one-step reaction by the photochemical addition of three equivalents of dimethyl phosphine to trivinylphosphine [234]. The subsequent synthesis and characterization of new iron(II) chloride, hydride and methyl complexes $[Fe(X)(Y)(PP_3Me)]$ was reported ($X = Cl$, H, Me, CO or PPh_3, $Y = Cl$, H, Me, CO or Cl) [215]. In the salt $[FeCl(PPh_3)(PP_3Me)]BPh_4$ (Scheme 61) the five phosphorus atoms of the phosphine ligands and the chloro ligand are arranged in a distorted octahedron. The distortion is mostly due to the bite angle of PP_3Me which is less than the required 90°, but it is also noticeable in the angle between the *trans* phosphine ligands found of 161.07°, nearly 20° below the ideal value for octahedral angle. With PP_3Me, Field et al. have also described the synthesis of a family of iron(II) hydride complexes of the type $[FeH(X)(PP_3Me)]$ ($X = Br$, I, N_3, CO, N_2 or PPh_3) [235]. The neutral iron(0) compounds $[Fe(CO)(PP_3Me)]$ and $[Fe(N_2)(PP_3Me)]$ can be obtained by deprotonation of $[FeH(CO)(PP_3Me)]^+$ and $[FeH(N_2)(PP_3Me)]^+$, respectively (with BPh_4^- as counter-ion). The insertion of CO_2, CS_2 and COS into iron(II)–hydride bonds of PP_3Me-containing complexes was recently investigated [236]. In 1999, the preparation and characterization of the (η^3-but-1-en-3-yn-2-yl) Fe^{II} complex containing PP_3Me was reported [216]; $[Fe\{\eta^3\text{-}PhC{\equiv}C{-}C{=}CHPh\}(PP_3Me)]BPh_4$ has a very similar structure to that detailed above for $[Ru\{\eta^3\text{-}(SiMe_3)C{\equiv}C{-}C{=}CH(SiMe_3)\}(PP_3)]BPh_4$ [210]. A similar stereochemistry was found for the complexes with the alkyne bond *trans* to the central phosphorus.

Another interesting modification of PP_3, the tris[2-(dicyclohexylphosphino)ethyl]phosphine, $[P(CH_2CH_2PCy_2)_3]$ (abbreviated PP_3Cy), was used in the synthesis of dihydrogen complexes of iron(II) and ruthenium(II); this chemistry was reviewed in Ref. [6]. The complex $[FeCl(PP_3Cy)]BPh_4$ displays a trigonal-bipyramidal environment around the iron metal, in which only small deviations from the ideal 120° value for the equatorial bond angles are observed [237]. The chloro ligand is in a classical apical position and the Fe^{II} is displaced by 0.312(3) Å out of the equatorial plane, a displacement value of the metal atom in agreement with

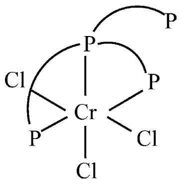


Scheme 63.

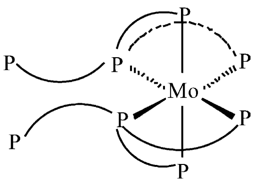
those previously reported for PP_3 containing complexes [193,197].

The apparent uniformity of coordination of tripodal tetraphosphines does show some exceptions, already in part reviewed [5]: the nickel complex $[Ni(PP_3)]ClO_4$ has a trigonal-pyramid geometry whose vertices are occupied by the phosphorus atoms, the central one being at the apex of the pyramid (Scheme 63) [238,239].

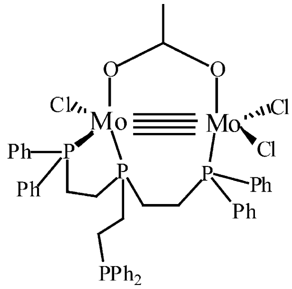
Rare crystallographic examples of *triligate* coordination, thus leaving a dangling peripheral phosphorus, have also been reported: for instance $[Cr(Cl)_3(PP_3)]$ adopts a *mer*-configuration with the central phosphorus in the axial position and two terminal phosphorus atoms mutually *trans* in the equatorial plane (Scheme 64) [240]. The reaction of *trans*-$[Mo(N_2)_2(PPh_2Me)_4]$ with *one* molar equivalent of PP_3 yields after recrystallization in benzene the complex $[Mo(PP_3)_2]$ [241]. The complex has a distorted octahedral MoP_6 fragment with two PP_3 acting as triligate ligands. Both PP_3 ligands coordinate through the central phosphorus atom and two terminal phosphorus atoms in a *fac*-configuration with the two central phosphorus atoms in position *cis* from each other, and lying in the equatorial plane of the molecule (Scheme 65). The strong distortion arises from the P–Mo–P angles which range from 77.8(1) to 107.3(1)°, the chelating rings severely closing up from the ideal angle value of 90°. The structure of the dimolybdenum complex *rac*-$[Mo_2(OAc)Cl_3(PP_3)]$ reveals that the PP_3 tetraphosphine ligand coordinates to the molybdenum centers in a triligate mode, as found for the etp triphosphine analogous complex (Scheme 66) [48]. The structures of the etp- and PP_3-containing complexes are similar, the only difference being that with etp the central phosphorus atom is coordinated with a phenyl group instead of a dangling $-CH_2CH_2P$ unit. This type of chelating/bridging bonding mode for PP_3 was first discovered by Cotton and Hong in the complex *rac*-$[Mo_2Cl_4(PEt_3)(PP_3)]$ [242]. In *rac*-$[Mo_2(OAc)Cl_3(PP_3)]$, as in *rac*-$[Mo_2Cl_4(PEt_3)(PP_3)]$, the central phosphorus of PP_3 becomes chiral upon coordination of the ligand to the molybdenum atoms, so that a *R* and *S* racemic mixture was obtained [48]. The PP_3 ligand forms one five-membered chelating ring on a molybdenum atom, and one six-membered bridging ring with the dinuclear moiety. The six-membered ring adopts a *boat* configuration.



Scheme 64.



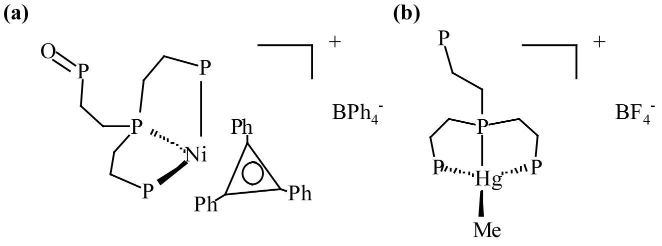
Scheme 65.



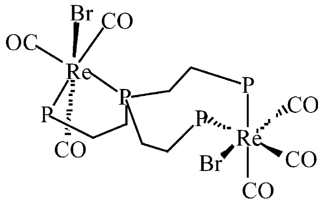
Scheme 66.

From an acetone/butanol solution of the nickel complex $[Ni(\eta^3\text{-}C_3Ph_3)(PP_3)]BPh_4$ exposed to air, the new derivative $[Ni(\eta^3\text{-}C_3Ph_3)(PP_2PO)]BPh_4$ was obtained, in which PP_2PO is the phosphine resulting from the oxidation of one of the terminal phosphorus of the parent-PP_3 ((**a**) Scheme 67) [243]. The tetraphosphine is coordinated by the three non-oxidized phosphorus atoms. The NiP_3 resulting fragment is bound to a cyclopropenium in a staggered conformation. The $-CH_2CH_2PO$ dangling arm is involved in strong hydrogen bonding (O···O, 2.67 Å) with the butanol solvent molecule. The X-ray structure of the mercury complex $[Hg(Me)(PP_3)]BF_4$, which displays a tricoordinated tetraphosphine PP_3, was also reported ((**b**) Scheme 67) [244].

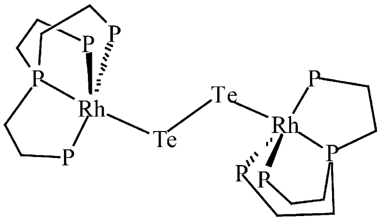
Finally, there are X-ray structures for several dinuclear compounds containing the tripodal tetradentate PP_3. The rhenium complex $[Re_2Br_2(CO)_6(PP_3)]$ (Scheme 68) [245] consists of two "$Re(CO)_3Br$" units unsymmetrically connected by the PP_3 ligand; the coordination



Scheme 67.



Scheme 68.



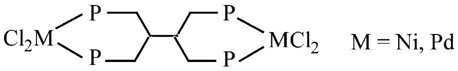
Scheme 69.

about both rhenium center is distorted octahedral. The reaction of Rh(PP_3) cationic species in a polytelluride THF solution yields the symmetrical homobimetallic complex [Rh(PP_3)Te–Te(PP_3)Rh] (Scheme 69) [246]. In the elegant dinuclear gold complex, [Au_2(μ-PP_3)$_2$]Cl_2, reported by Balch and Fung (Scheme 70) [5,247], each ligand is coordinated to one gold center by three phosphorus: one central and two terminal ones. In both PP_3 ligands the last terminal phosphorus bridges the other gold atom, creating a virtually symmetric pattern of two gold ions and two phosphine ligands. NMR measurements in chloroform solution indicate that the complex retains its dinuclear structure with two equivalent phosphine ligands.

3.3. Other tetradentate phosphines

Several new tetraphosphines were synthesized in the last decade with the view to investigate their possible coordination modes on transition metals. These polyphosphines built on various backbones such as butane, cyclobutane or benzene moieties, were expected at first sight to lead to various monometallic or homobimetallic species, depending on the reaction conditions. Interestingly, in almost all the cases described below the tetradentate phosphines act as two independent diphosphines leading to very stable bis-chelating complexes.

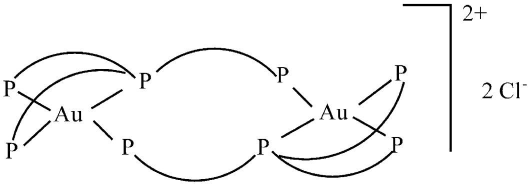
The synthesis of the 2,3-bis[(diphenylphosphino)-methyl]-1,4-bis(diphenylphosphino)butane (dpmdpB) was reported by Verkade and co-workers [248]. Starting from the palladium and nickel dichloride salts the complexes [Pd_2Cl_4(dpmdpB)] and [Ni_2Cl_4(dpmdpB)] (Scheme 71) were prepared and structurally characterized.



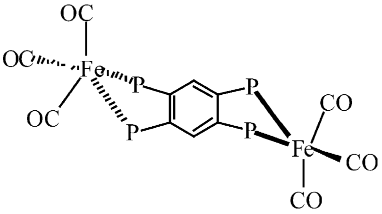
Scheme 71.

The ligand dpmdpB coordinates in a bis(biligate) manner to two metals with the formation of two six-membered chelate rings. In both structures each palladium or nickel atom is in an essentially square-planar environment comprised of two chloride ligands and two phosphorus donor atoms. The formation of the isomeric product displaying two seven-membered chelate rings (from the chelation of phosphines mutually separated by four carbon atoms instead of three carbons) was not detected for the nickel complex. However, it was suggested to form in minor amounts for the palladium one, on the basis of ^{31}P-NMR analysis. All the attempted syntheses of monometallic complexes of Ni^{II} or Pd^{II} yielded mixtures which exhibit complex behavior in solution. Only the exposure to air for 5 days of the reaction solution of [(dpmdpB)Pd_2Cl_4] in the presence of one molar equivalent of dpmdpB led to the formation of the biligate mononuclear complex [{(Ph_2PCH_2)$_2$CHCH-($CH_2P(O)Ph_2$)$_2$}$PdCl_2$] where the two uncoordinated phosphorus are in an oxidized form as phosphoryl groups. This complex has a square-planar geometry where the palladium lies 0.034 Å out of the P_2Cl_2 plane. According to the authors, steric and structural limitations of dpmdpB preclude the formation of tetraligate monometallic complexes of Ni^{II} and Pd^{II}; thus, further work could consider the removal of these steric and structural limitations in derivatives with the view to yield a novel class of branched tetradentate phosphine ligands [248].

Hogarth has reported the synthesis of the 1,2,4,5-tetrakis(diphenylphosphino)benzene which reacts with an excess of diiron nonacarbonyl to give the dimeric complex [di-μ-{(Ph_2P)$_2C_6H_2$(PPh_2)$_2$}{$FeCO_3$}$_2$] (Scheme 72) [249]. The molecule consists of two iron tricarbonyl units linked via the 1,2,4,5-tetrakis(diphenylphosphino)benzene ligand in such a way that each iron atom is chelated by a pair of adjacent phosphines,



Scheme 70.

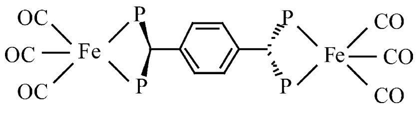


Scheme 72.

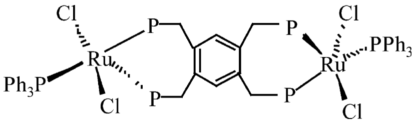
three CO ligands completing the coordination sphere around the metal. The five-coordinate geometry at each iron center can be considered as intermediate between distorted trigonal-bipyramidal (where one the phosphorus occupies an equatorial site and the other an axial position) and square-pyramidal (with one carbon at the apex). In the solid state structure, the tetraphosphine ligand is rigorously planar while the five-membered rings formed are bent at the iron atoms, one iron lying above the plane and the other below this plane.

The tetradentate phosphine α,α,α′,α′-tetrakis-(diphenylphosphino)-*p*-xylene (called ddpx) reacts with $Fe_2(CO)_9$ to afford the bridged bis-chelated complex $[Fe(CO)_3(dppx)Fe(CO)_3]$, which was characterized by X-ray diffraction studies (Scheme 73) [250]. The dppx ligand is non-planar, with the diphosphinomethane groups at dihedral angles of approximately 60° with respect to the xylyl ring. The geometry about the iron atom is distorted trigonal-bipyramidal: the phosphorus and the carbon atom occupying the axial sites are related by an angle of 162.1(6)°. The atoms located at the three sites of the idealized equatorial plane are nearly coplanar, but form angles of 109.1(5), 111.8(8) and 137.3(6)°. The distance between the iron atoms is about 15.6 Å.

Van Koten et al. have described the closely related tetradentate polyphosphine 1,2,4,5-tetrakis[(diphenylphosphino)methyl]benzene [251]. The aim of the authors was to isolate dinuclear ruthenium complexes with a coordination *P*,*C*,*P′* analogue to the well-known *N*,*C*,*N′*-triligate coordination of van Koten's “pincer” ligands. The reaction of this phosphine with $[RuCl_2(PPh_3)_4]$ in CH_2Cl_2 afforded, in fact, the dinuclear complex $[\{(Ph_2PCH_2)_2C_6H_2(CH_2PPh_2)_2\}\text{-}\{RuCl_2PPh_3\}_2]$ (Scheme 74). The X-ray crystal structure of the compound shows that the polyphosphine bridges two identical five-coordinate ruthenium centers with a distorted square-pyramidal geometry. The molecule has an inversion center positioned in the aromatic ring of the tetraphosphine. The square-pyramidal environment involves two *trans*-Cl atoms and two *trans*-phosphorus atoms (one from the tetradentate phosphine, one from the PPh_3 ligand) in the basal plane, the apical position being occupied by a second phosphorus of the tetradentate phosphine. The bridging phosphine employs two mutually *ortho*-CH_2PPh_2 fragments to coordinate each metal center, thus forming two seven-membered metallated rings. The expected coordination of two mutually *meta*-CH_2PPh_2 groups which would have lead to eight-membered chelate rings and possibly a bis(triligate) *P*,*C*,*P′*-cyclometallated complex does not occur. The main reason is the larger conformational flexibility provided by the two seven-membered rings when compared to eventual eight-membered ring closures. As a consequence the C_{aryl}–H bond of the central aromatic ring cannot approach the metal center for intramolecular activation and subsequent C–Ru bond formation, as observed in *N*,*C*,*N′* “pincers”.

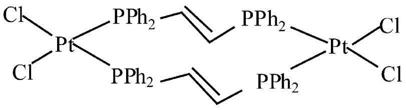


Scheme 73.

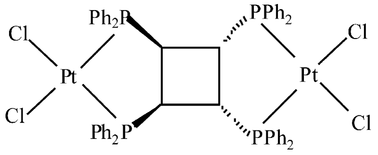


Scheme 74.

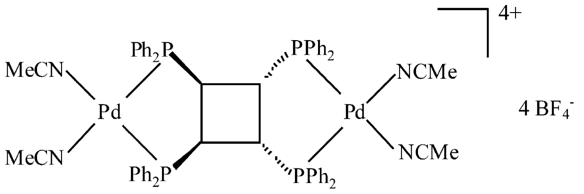
Brüggeller and co-workers have shown that the intramolecular [2+2] photocycloaddition of the two olefinic diphosphine-bridges in the dinuclear complex $[Pt_2Cl_4$*trans*-(dppen)$_2]$ (where dppen is the 1,2-bis(diphenylphosphino)ethene, see Scheme 75) produces the original $[Pt_2Cl_4(dppcb)]$ (where dppcb is the in situ-formed new tetradentate phosphine *cis*,*trans*,*cis*-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane) (Scheme 76) [252]. The new polyphosphine cyclobutane based ligand can be obtained as a pure product after treatment of the platinum complex with NaCN. The crystal structure of the dinuclear platinum complex $[Pt_2Cl_4(dppcb)]$ consists of molecules displaying two different conformations (A and B) in equal amounts. These different conformations likely arise from an energetic competition between the steric demands of dppcb and an ideal square-planar environment for the platinum atom. However, the differences remains marginal: the conformation B presents a square-planar environment closer to the ideal for Pt^{II} ions (P–Pt–P angles of 89.11(10)° against 85.19(11)° for A) while the five-membered chelate rings in conformation A are released of some steric pressure due to the larger envelope-folding (153.1 against 168.3° in B). The cyclobutane rings in both conformations are rigorously planar and other bond lengths and bond angles of these rings show no differences within statistical difference. It is noteworthy that in the absence of a metallic promoter, such as platinum or palladium, no



Scheme 75.



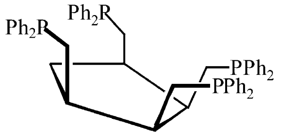
Scheme 76.



Scheme 77.

cycloaddition reaction was observed; consequently, the authors have described a relevant metal-assisted synthesis of novel tetradentate phosphines. This *cyclo*-tetraphosphine dppcb was used by Bianchini and co-workers to synthesize rigid palladium(II) catalysts for the alternating copolymerization of CO and ethene [253]. The complexes $[(MeCN)_2Pd(dppcb)Pd(NCMe)_2][X]_4$ ($X = PF_6$ or BF_4) were obtained (Scheme 77). The X-ray crystal structure of $[(MeCN)_2Pd(dppcb)Pd(NCMe)_2][BF_4]_4$ shows that a planar cyclobutane ring connects two equivalent $(-PPh_2)_2Pd(NCMe)_2$ moieties. The bond distances and angles in the cyclobutane ring are close to those of an ideal square, and the palladium atoms environment is slightly distorted square-planar. Previous studies on the catalytic properties of palladium/diphosphine complexes had correlated the *greater activity* of the diphosphine dppp complexes to the *higher flexibility* of its backbone as compared to that of more rigid dppe [253]. One particular interest of this work is that, on the contrary, the *high rigidity* of the ligand is a structural feature that improves CO/ethene copolymerization Pd^{II} catalysts.

Another recent interesting catalytic application of original tetraphosphines was reported by Doucet and Santelli [254]. Their system with the tetraphosphine *cis,cis,cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane (abbreviated tedicyp) (see Scheme 78), and the dimeric $[PdCl(\eta^3\text{-}C_3H_5)]_2$ precursor catalyzed the amination of allyl acetates (Scheme 79) with a very low ratio of catalysts (0.0001%). The authors attribute these excellent results (especially compared with classical mono and diphosphine) to the stability of the complexes obtained: this stability is probably provided by the four phosphinoalkyl groups stereospecifically bound to the same face of the Cp ring.



tedicyp

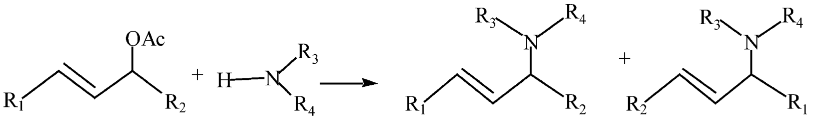
Scheme 78.

Finally, there have been studies on cyclocarba- and cyclodicarba-tetraphosphines (Scheme 80) [255]. In particular, the X-ray diffraction structures of $(PhP)_4CH_2$ [256], and $CH_2(PhP)_4CH_2$ (1,2,4,5-tetraphenylcyclo-3,6-dicarba-1,2,4,5-tetraphosphine) are available [255]. The 1,2,4,5-tetraphenylcyclo-3,6-dicarba-1,2,4,5-tetraphosphine presents a highly folded chair conformation where the dihedral angles between the P_4 plane and the P–C–P is between 99.2 and 104.5° (dihedral angles of 129° for the chair form of cyclohexane).

The organic chemistry of polyphosphines has provided some new branched-species tetraphosphine. However, from a structural point of view, the stabilization resulting from the dinuclear bis(chelating) behavior of these tetraphosphines often leads to "stereotyped" complexes with comparable homobimetallic structures. The influence of the steric rigidity (or flexibility) of the polyphosphine ligands upon catalytic applications remains, still, an essential parameter to be developed; indeed, contrasting results were obtained depending on the type of phosphine and on the type of reaction examined.

4. Tri- and tetradentate sulfur- or nitrogen-containing polyphosphines ligands and their metal complexes

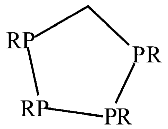
Compared to the tridentate and tetradentate polyphosphines we have examined previously, the replacement of one or several phosphorus atoms by other donor atoms such as nitrogen or sulfur in these polydentate ligands leads to different molecular architectures, coordination modes and catalytic properties. The main purpose of this chapter is to provide an overview from a structural perspective of the diversity of coordination modes to transition metal centers reported for this relevant alternative to polyphosphine ligands. The



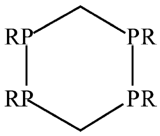
R_1 = H, Ph or *n*-Pr
R_2 = H or Ph

R_3 = Et, *n*-Pr, *n*-C_8H_{17}, $CH_2CH{=}CH_2$ or ^{i}Pr
R_4 = Et, *n*-Pr, *n*-C_8H_{17}, $CH_2CH{=}CH_2$ or ^{i}Pr
$R_3 - R_4$ = $-(CH_2)_4-$ or $-(CH_2)_2O(CH_2)_2-$

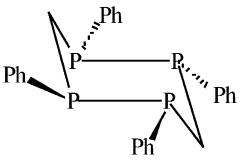
Scheme 79.



Cyclocarba-tetraphosphine



Cyclodicarba-tetraphosphine



Scheme 80.

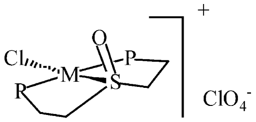
description of their catalytic reactivity is beyond the scope of this article. However, as a general remark most of the articles that accurately describe the species obtained, unfortunately, mention little of the reaction chemistry of their complexes (this is especially true of the sulfur derivatives). Consequently, this field of investigation is promising. When appropriate, some available catalytic results are briefly discussed.

4.1. Tri- and tetradentate sulfur/phosphorus ligands

The linear tridentate phosphinothioether 1,5-bis-(diphenylphosphino)-3-thiapentane, (Ph_2**P**CH_2CH_2)**S**-(CH_2CH_2**P**Ph_2) (abbreviated PSP) acts as a triligate or a biligate ligand depending on the metal involved [257–262]. Group 10 metals form with this phosphine triligate bis-chelating complexes such as [PtCl(PSP)]ClO_4, [PtI-(PSP)]I or [NiI_2(PSP)], while a biligate complex was isolated with mercury(II) iodide (Scheme 81).

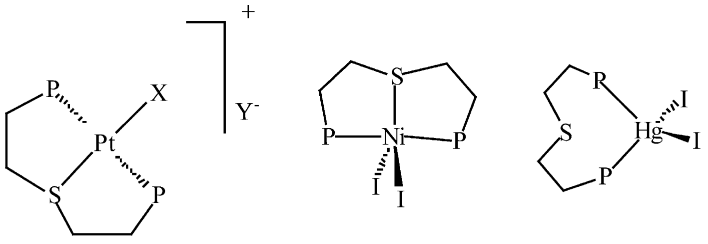
An X-ray analysis has shown that the mercury cation is not only coordinated to two iodide ions but also bonded to two phosphorus atoms of one molecule of the PSP ligand in a distorted tetrahedral arrangement. An eight-membered puckered chelate ring is formed where the Hg–S distance, 3.71(1) Å, is not a contact distance [259]. The angles in the tetrahedron vary from 97 to 123° probably due to the steric hindrance provided by the chelate ring. In the compound [NiI_2(PSP)] the nickel atom is five-coordinated to two iodine atoms, and the three donor atoms of PSP [258]. The environment at the nickel atom is intermediate between square-pyramidal and trigonal-bipyramidal; in the description of the square pyramid one iodo ligand is at the apex, and the four other atoms form the basal plane. In terms of a trigonal bipyramid the two phosphorus lie in axial positions while the three other atoms occupy the equatorial positions. The Ni–S and the two Ni–P distances are very close to each other: 2.190(3), 2.185(3) and 2.192(3) Å, respectively. The crystal structures of [PtCl(PSP)]ClO_4 and [PtI(PSP)]I reveal that the platinum center is square-planar, distorted towards a tetrahedron due to the bis-chelating tridentate PSP ligand. In [PtI(PSP)]I, the larger iodide atoms cause an even greater distortion [257]. Almost no difference is noted between the Pt–S distances in the two complexes (respectively 2.254(1) and 2.258(6) Å) despite the *trans* influence of the iodide ligand. On the other hand the *trans* influence of the chelating sulfur donor is reflected in long platinum–halogen distances (Pt–Cl: 2.347(1) Å, Pt–I: 2.613(2) Å). The sulfoxide derivative of PSP, $(Ph_2PCH_2CH_2)_2SO$ was synthesized by Leung et al., and forms with palladium and platinum triligate square-planar complexes [260]. An X-ray crystal structure of the complex [PtCl{$(Ph_2PCH_2CH_2)_2SO$}]ClO_4 was reported, and no Pt–O bond is involved in the molecule (Scheme 82).

In the homobimetallic silver halide complexes [Ag_2(μ-X)$_2$(PSP)$_2$] (X = Cl, I) each PSP ligand is bonded through two phosphorus atoms to a silver center, two bridging halides completing a distorted tetrahedral arrangement around the silver atoms (Scheme 83) [261,262].



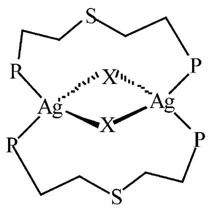
M = Pt, Pd

Scheme 82.



X=Cl, Y^-=ClO_4^-
X=I, Y^-=I^-

Scheme 81.

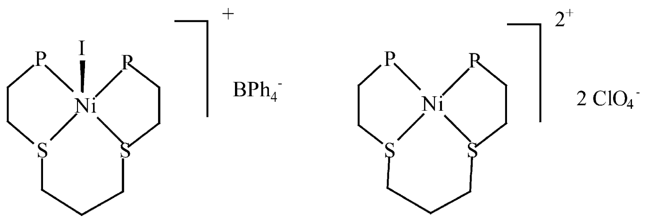


X = Cl, (Ag–Ag = 3.708(3) Å)
X = I, (Ag–Ag = 3.852(2) Å)

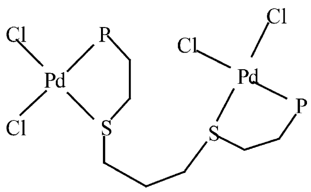
Scheme 83.

The linear tetradentate ligand 1,9-bis(diphenylphosphino)-3,7-dithianonane, $(Ph_2\mathbf{P}CH_2CH_2)\mathbf{S}(CH_2)_3\mathbf{S}(CH_2CH_2\mathbf{P}Ph_2)$ (abbreviated PSSP), in which two sulfur atoms are separated by three methylene units, offers an additional donor atom compared to PSP [263]. The increased-length of the ligand chain favors a polynuclear coordination. However, when this PSSP ligand reacts with nickel it forms the mononuclear five-coordinate complex $[NiI(PSSP)]BPh_4$ (Scheme 84) [263]. A square-pyramidal arrangement was observed around Ni for $[NiI(PSSP)]BPh_4$, in which the PSSP ligand occupies the basal plane and the iodine atom the apical position. In this compound the Ni atom takes part in three chelating fused rings: two five-membered $NiPC_2S$, and one six-membered $NiSC_3S$. The Ni atom is located 0.26 Å outside the mean plane formed by the phosphorus and sulfur atoms in direction of I. The ligand keeps its meridional coordination in the four-coordinate complex $[Ni(PSSP)][ClO_4]_2$ which is square-planar (Scheme 84) [264]. The tetraligate coordination mode is very similar to the previously described Ni compound with slightly shorter Ni–P and Ni–S distances.

Beside the mononuclear tris-chelating tetraligate coordination of PSSP on Ni, palladium provides a bridging bis-chelating tetraligate coordination mode leading to a dinuclear species (Scheme 85) [265]. The complex $[Pd_2Cl_4(PSSP)]$ shows a square-planar environment at each palladium atom, and the PSSP ligand acts as two independent bidentate phosphines on the two Pd centers: P and S occupy mutual *cis* positions of the square-plane while the coordination sphere around the metal is completed by two Cl atoms. The previous reports do not describe the syntheses of the products, which could confirm whether the species obtained can be modified with the stoichiometry of the ligand.



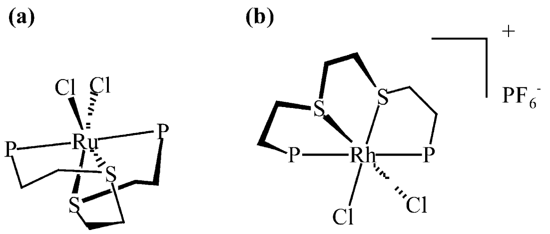
Scheme 84.



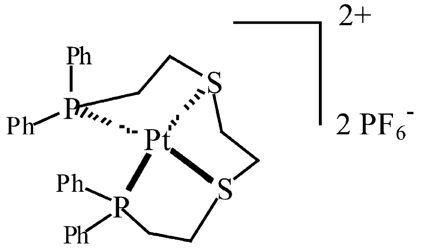
Scheme 85.

More recently, another related tetradentate ligand, 1,8-bis(diphenylphosphino)-3,6-dithiaoctane, $(Ph_2\mathbf{P}CH_2CH_2)\mathbf{S}(CH_2)_2\mathbf{S}(CH_2CH_2\mathbf{P}Ph_2)$ (abbreviated P_2S_2), was used by Reid and co-workers. With respect to Groups 8 and 9, studies were reported on the neutral ruthenium(II) compound $[RuCl_2(P_2S_2)]$ and the ionic rhodium(III) and iridium(III) compounds $[MCl_2(P_2S_2)]PF_6$ (M = Rh, Ir) [266]. The X-ray structural characterizations of $[RuCl_2(P_2S_2)]$ and $[RhCl_2(P_2S_2)]PF_6$ show comparable environments at the metal centers: the P_2S_2 ligand being attached by all the four donor atoms with the two phosphorus occupying mutually *trans* sites, and two *cis*-chloro ligands completing the octahedral co-ordination sphere (Scheme 86). With respect to Group 10, a series of square-planar ionic palladium(II) and platinum(II) complexes involving P_2S_2 were obtained [267]. The X-ray structure of $[Pt(P_2S_2)][PF_6]_2$ shows a rather strained geometry with the methylene groups all directed to one side of the coordination plane and the metal ion displaced out of the best mean square-plane by 0.19 Å in the opposite direction (Scheme 87).

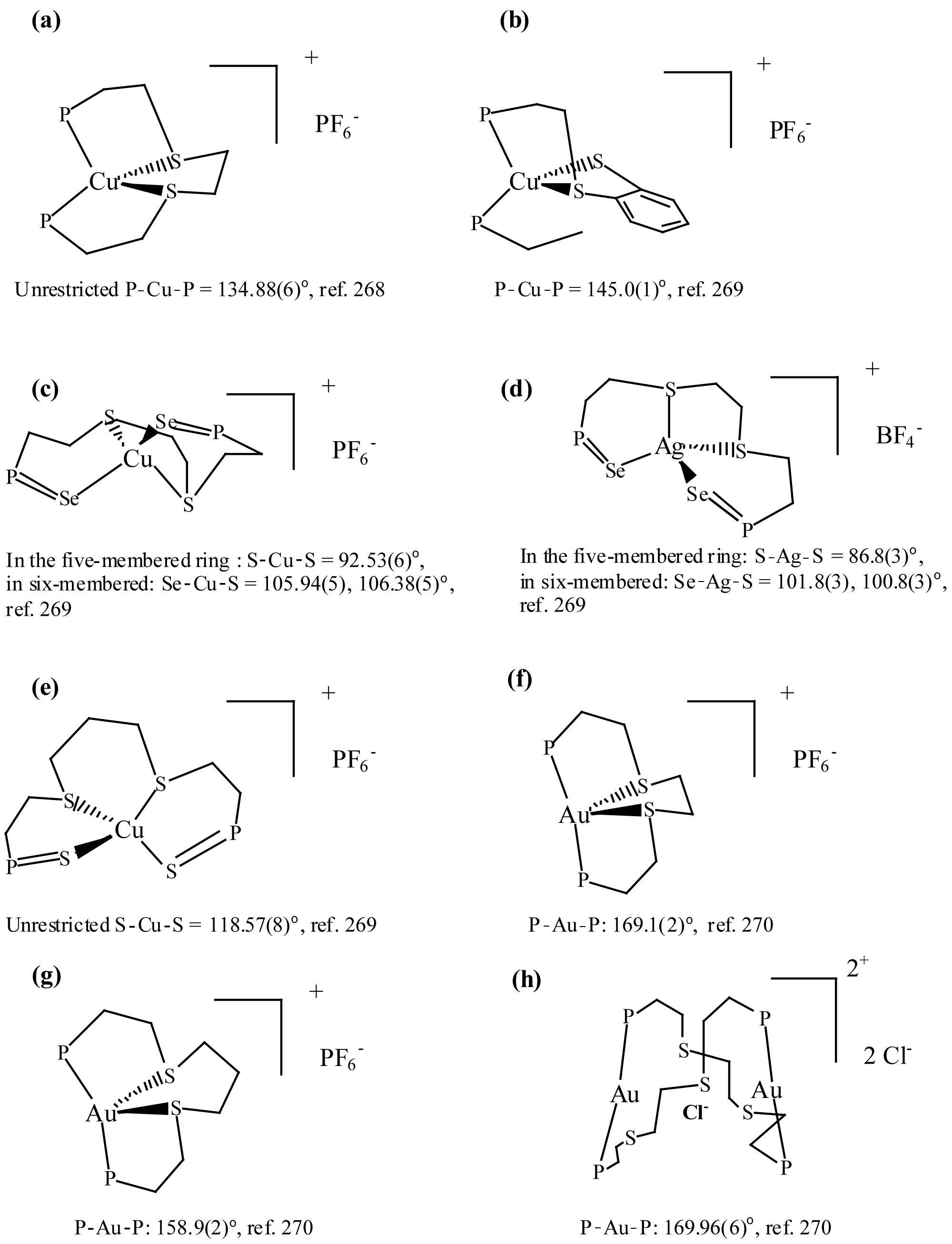
Copper, silver and gold complexes containing P_2S_2 or PSSP, or the parent tetradentate phosphines $(Ph_2\mathbf{P}CH_2CH_2)S(o\text{-}C_6H_4)S(CH_2CH_2\mathbf{P}Ph_2)$, $\{Ph_2(\mathbf{Se}{=})\mathbf{P}CH_2$



Scheme 86.



Scheme 87.



(a) Unrestricted P-Cu-P = 134.88(6)°, ref. 268

(b) P-Cu-P = 145.0(1)°, ref. 269

(c) In the five-membered ring : S-Cu-S = 92.53(6)°, in six-membered: Se-Cu-S = 105.94(5), 106.38(5)°, ref. 269

(d) In the five-membered ring: S-Ag-S = 86.8(3)°, in six-membered: Se-Ag-S = 101.8(3), 100.8(3)°, ref. 269

(e) Unrestricted S-Cu-S = 118.57(8)°, ref. 269

(f) P-Au-P: 169.1(2)°, ref. 270

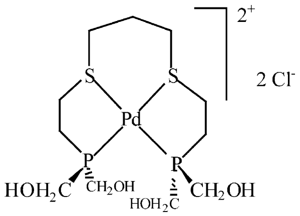
(g) P-Au-P: 158.9(2)°, ref. 270

(h) P-Au-P: 169.96(6)°, ref. 270

Scheme 88.

$CH_2\}\mathbf{S}(CH_2)_2\mathbf{S}\{CH_2CH_2\mathbf{P}(=\mathbf{Se})Ph_2\}$ and $\{Ph_2(\mathbf{S}=)\text{-}\mathbf{P}CH_2CH_2\}\mathbf{S}(CH_2)_3\mathbf{S}\{CH_2CH_2\mathbf{P}(=\mathbf{S})Ph_2\}$ were also X-ray characterized by Reid and co-workers (see Scheme 88) [268–270]. These four-coordinate mononuclear complexes display more or less distorted (flattened) tetrahedral geometries at the metal center. Scheme 88 summarizes the geometry of x-ray authenticated complexes with characteristical angles values.

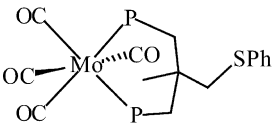
A recent advance was reported by Katti and co-workers with the synthesis of the related *water-soluble* ligand 1,9-bis(dihydroxymethylphosphino)-3,7-dithianonane, $\{(HOH_2C)_2\mathbf{P}CH_2CH_2\}\mathbf{S}(CH_2)_3\mathbf{S}\{CH_2CH_2\mathbf{P}\text{-}(CH_2OH)_2\}$ (abbreviated $PSSP_{OH}$) [271]. In contrast with the dinuclear palladium complex obtained with PSSP, the structure of $[Pd(PSSP_{OH})]Cl_2$ reveals a mononuclear compound where the thiophosphine ligand is tetraligate providing a square-planar arrangement at the palladium center (Scheme 89). This complex was obtained in quantitative yield from a biphasic mixture water/dichloromethane of $PSSP_{OH}$ and $[PdCl_2(PhCN)_2]$. Analogous platinum species were formed in a similar manner from $[PtCl_2(cod)]$. This new class of water-stable complexes indicates the propensity of $PSSP_{OH}$ to form mononuclear species via tetradentate interactions with



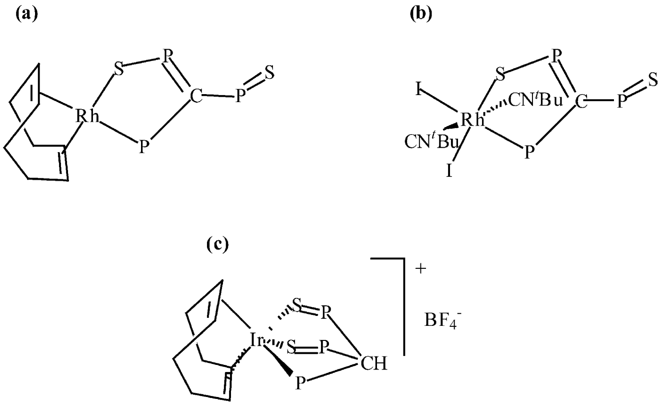
Scheme 89.

the Group 10 transition metals. The difference of behavior compared with PSSP might be attributed to the substituents on the phosphorus: the hydroxymethoxy group in $PSSP_{OH}$ provides a hydrogen bonding network with water molecules in the lattice, which presumably stabilizes the mononuclear structure in the solid state.

Tripodal phosphorus/sulfur ligands are also known and offer various coordination modes. Peng and coworkers reported a tdpme variation: the tripodal 2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane ($CH_3C(CH_2SPh)(CH_2PPh_2)_2$, abbreviated P_2S) [272]. The carbonyl complexes of Group 6 metals $[M(CO)_4(P_2S)]$ (where M = Cr, Mo, W) were prepared, and spectroscopic data indicate that the P_2S ligand is biligate in the complexes. This result was confirmed by the crystal structure of the octahedral $[Mo(CO)_4(P_2S)]$, showing two phosphorus in a mutual *cis*-position as a part of a six-membered ring in a twisted-boat conformation (Scheme 90). Dixon et al. have studied the coordination chemistry with Group 9 transition metals of the potentially triligate anionic ligand $[(Ph_2P)C\{Ph_2P(=S)\}_2]^-$, to confirm that these phosphine/sulfur ligands promote catalytic activity at some metal centers (Ir, Rh) [273]. The complexes $[Rh(cod)\{P,S\text{-}(Ph_2P)C\{P(S)Ph_2\}_2\}]$ (see (**a**) Scheme 91) and $[RhI_2({}^tBuNC)_2\{P,S\text{-}(Ph_2P)C\{P(S)Ph_2\}_2\}]$ ((**b**) Scheme 91) both contain biligate *P*,*S* bonded ligands with a dangling –P=S group [273]. However, they constitute, respectively, Rh^I and Rh^{III} species with very different geometries. $[Rh(cod)\{P,S\text{-}(Ph_2P)C\{P(S)Ph_2\}_2\}]$ displays a virtual square-planar coordination at rhodium with the phosphorus and sulfur atoms in *cis* positions, completed by the two double bonds of the cycloocta-1,5-diene ligand. In $[RhI_2({}^tBuNC)_2\{P,S\text{-}(Ph_2P)C\{P(S)Ph_2\}_2\}]$ the two iodide ligands and the P/S donor atoms form an equatorial plane, the octahedral arrangement being completed by the isocyanide ligands in the axial positions. The bond angles within the octahedron all lie in the range 86–95°. NMR studies have shown that the iridium/cod analogous complex with a biligate coordination mode was also readily obtained. The protonated neutral derivative tripodal ligand $[(Ph_2P)CH\{Ph_2P(=S)\}_2]$ also reacts with rhodium, iridium, palladium or platinum, and provided the first X-ray structural confirmation of triligate coordination with a d^8 metal for this family of ligands [274]. The complex $[Ir(cod)\{P,S,S\text{-}(Ph_2P)CH\{P(S)Ph_2\}_2\}]BF_4$ is five-coordinate with a *P*,*S*,*S*-triligate coordination mode for the ligand, the two double bonds of the cycloocta-1,5-diene completing an irregular geometry ((**c**) Scheme 91) [274]. The structural parameters of the sulfur-containing phosphine $[(Ph_2P)CH\{Ph_2P(=S)\}_2]$ [274] show only marginal changes upon coordination to iridium, except for a narrowing of the P–C–P angles required to achieve triligate coordination (from an average of 114° for the free ligand to an average of 107° in the complex) [274]. This lower mean value provides good evidence for the protonation at the central carbon atom; indeed, in the case of a flattening of the arrangement at carbon due to an anionic $C(P)_3^-$ unit, the P–C–P angles average value should increase above 114°. Thus, for this kind of tripodal neutral ligand, the preferred mode in d^8 metal complexes is triligate -*P*,*S*,*S* coordination; the sp^3 geometry of the central carbon in the protonated ligand more easily accommodates a tripodal coordination than the almost planar arrangement of the anions (sp^2 hybridization approach).

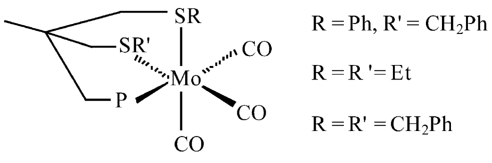


Scheme 90.



Scheme 91.

Huttner et al. have recently published several strategies for the preparation of tripodal ligands with mixed P/S donor sets such as $MeC(CH_2\mathbf{P}Ph_2)(CH_2\mathbf{S}R)(CH_2SR')$ (where R = R′ = Et, or R = Ph and R′ =



Scheme 92.

CH_2Ph, or $R = R' = CH_2Ph$) [275]. The coordination abilities of these ligands were studied with molybdenum. Complexes were structurally characterized which show a triligate coordination of the mixed P/S tripodal phosphines (Scheme 92). All the compounds $[Mo(CO)_3\{MeC(CH_2\mathbf{P}Ph_2)(CH_2\mathbf{S}R)(CH_2\mathbf{S}R')\}]$ show an octahedral geometry where the thiophosphine ligand occupies facial positions. As noticed in the third part, this arrangement is rather common in phosphorus "only" tripodal analogous ligands and leads to three fused six-membered rings. An important result of the chemical reactivity of these complexes is the apparent versatility of one of the sulfur donors, which under one bar of carbon monoxide gives way to a κ^2-coordination of the ligand, the dangling sulfur moieties being replaced by a carbonyl group. This interesting work sheds light on the large open field of research of the coordination chemistry of tripodal phosphines with different donor groups and their resulting reactivity.

4.2. Tridentate nitrogen/phosphorus ligands: 1N/2P and 2N/1P

An important class of mixed nitrogen/phosphorus-containing polyphosphine ligands which include a great number of species will not be described here (nor in the next part); phosphine–pyridyl and related NP_2, N_2P, N_2P_2, NP_3, N_3P ligands were the subject of a recent excellent review article from Espinet and Soulantica [276]. This article also highlights the advantages of having multidentate ligands (particularly with various donor atoms), and provides much information concerning their catalytic applications.

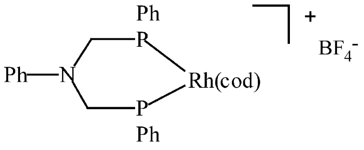
Similarly to the polyphosphine ligands examined in the previous parts, nitrogen-containing phosphines can be listed as linear or tripodal ligands. Three-, five- and seven-membered linear chains of the PNP type are known. A large number of ligands with a directly connected PNP sequence (called here, three-membered linear chains) were reported. These bis(phosphino)amines and amides can be conveniently divided in the *four* following families: the ligands containing tertiary phosphine only, of the type (i) $R-N-\{P(R')_2\}_2$ and their deprotonated anionic analogues (ii) $^-N-\{P(R)_2\}_2$. The ligands which contain two (or sometimes *one*) phosphorus with P(V) high oxidation degree: (iii) $R-N-\{P(=R')(R'')_2\}_2$ and their anionic parent compounds (iv) $^-N-\{P(=R')(R'')_2\}_2$. Indeed, the bis(phosphino)amines with PNP backbones can be easily oxidized at one phosphorus atom to form a series of heterofunctional P,R′ ligands with a soft P^{III} and a relatively harder chalcogenyl center ($R' = S$ or Se).

A query to the Cambridge Structural Database (CSD) on the molecular structures which include the P–N–P moiety and a transition metal yields more than 340 positive answers in the period 1970–2001. Among them, macrocyclic and linear alternating N_xP_y chain ligands (with $x > 1$ and/or $y > 2$) were detected and excluded from this review. The heterobimetallic as well as the cluster compounds, and the known Cu, Ag, Au and Hg species have also been excluded from Tables 1 and 2, which attempt to summarize the references describing structurally characterized complexes together with their corresponding PNP ligands. Table 1 refers to the Groups 6 to 10 complexes containing PNP ligands of the type $R-N-\{P(R')_2\}_2$, while Table 2 collects species including the ligands of the type $\{P^V(=R')(R'')_2\}-N\mathbf{R}-\{P^{III}(R'')_2\}$, $\{P^V(=R')(R'')_2\}-N^--\{P^{III}(R'')_2\}$ and $^-N-\{P(R'')_2\}_2$. The ligands with two P(V) phosphorus $R-N-\{P(=R')(R'')_2\}_2$ and their anionic parent compounds $^-N-\{P(=R')(R'')_2\}_2$ were also excluded since they form complexes bonded only via the two R′ donors ($R' = O$, S, or Se).

The complexes referenced in Table 1 are either mononuclear with a *P*-monoligate or a *P*,*P*-chelating biligate mode of coordination for the PNP ligands, or they are dinuclear with, most often, a *P*,*P*-bridging coordination mode for the ligands. As shown in Table 1, complexes were synthesized which can contain from one to four ligand molecules [277–352]. The steric constraint on the ligands seems to be too important to lead to a *N*,*P*-mode of coordination, whether the nitrogen atom is di- or tri-substituted. In addition to the ligands and complexes described in Table 1, other structures have been reported. For example, the unsymmetrical diphosphazane $Ph(Me)P-N(^iPr)-PPh_2$ was used to form a square planar palladium(II) iodide complex [353]. The symmetrical diphosphazane ligand $(CH_2O)_2P-N(Et)-P(OCH_2)_2$, containing the cyclic moieties $-POCH_2CH_2O-$, provides the structurally unsymmetrical dimeric cobalt complex $[Co_2(CO)_4\{\mu\text{-}(CH_2O)_2P\text{-}N(Et)P(OCH_2)_2\}_2]$, which has a trigonal-bipyramidal environment at one cobalt atom and a distorted square-pyramidal one at the other cobalt atom [354].

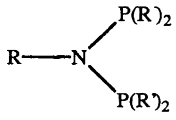
The studies summarized in Table 2 [293,347,351,355–364], mainly employed the noble metals of Group 9 and 10, namely palladium, platinum and rhodium (square planar complexes). Octahedral complexes of rhenium have also been reported. Two modes of coordination in mononuclear species are predominant: the *P*-monoligate and *P*,*R′*-chelating biligate bonding modes. To our knowledge, X-ray structures of nitrogen-bonded species of this type have not been reported.

With respect to five-membered linear chains, Reetz and coworkers describe a biligate coordination mode in



Scheme 93.

Table 1

PNP Ligand	R	R'	Metal centre(*)	Number of PNP units in the complexes$^{a,b\text{ or }c}$(*)/References
	H	Ph	Mo (M and D)	$1^{a\text{ or }b}$(M)/ 277, 2^{c}(D)/ 278-280
			W (D)	2^{c} / 281
			Mn (M)	1 / 282
			Re (M and D)	1^{a}(M)/283, 1^{b}/283-285, 2^{b}/ 285, 2^{c}(D)/286,287
			Fe (M and D)	1(M) / 282, 1^{c}(D) or 2^{c}(D) / 288
			Ru (M)	1^{b} / 289,290
			Co (D)	1^{c}/ 291,294, 2^{c}/ 292,293
			Ni (D)	2^{c} / 295, 296
			Pd (D)	2^{c} / 297, 298
			Pt (M)	1^{b} / 299, 2^{b} /300
	Me	Ph	Mo (D)	2^{c} / 301-304
			Co (M and D)	1^{b}(M) / 305, 1^{c}(D)/ 306
			Pd (M)	2^{b} / 307, 1^{b}/ 308
			Pt (M)	1^{b}/ 308,309, $2^{a\text{ or }b}$/300
		OMe	W (D)	$3^{a\,\&\,b}$ / 310, 2^{b} / 311
			Fe (D)	1^{c} / 312
			Ru (M)	1^{b} / 310
			Co (D)	2^{c} / 313
			Rh (D)	$4^{b\&c}$ / 314-316
			Ir (M)	1^{b} / 314
		$OCH_2(CF_3)$	Co (D)	3^{c} / 317
		$OCH(CF_3)_2$	Co (D)	1^{c} / 306
		OPh	Co (M)	2^{b} / 317
			Pd (D)	3^{c} / 318
		F	W (D)	2^{b} / 319
			Cr (M)	1^{b} / 320
			Re (D)	1^{c} / 321
			Fe (M)	$4^{a\&b}$ / 320
			Co (D)	3^{c} / 320,322, 1^{c} / 306
			Rh (D)	3^{c} / 323-325
			Pt (D)	3^{c} / 326
	Et	Ph	Fe (M and D)	1^{b}(M) / 327, 1^{c}(D)/ 328
			Pd (M)	1^{b}/ 329
		OMe	Ru (D)	2^{c}/ 330,331
			Co (D)	2^{c} / 332
			Rh (D)	2^{c} / 333
		O–^{i}Pr	Ru (D)	2^{c} / 330, 334-338
		OPh	Fe (D)	2^{c} / 339,340
	CH_2–^{i}Pr	Ph	Co (M)	2^{b} / 341
			Fe (M)	1^{b} / 342
			Ru (M)	2^{b} / 343
	^{i}Pr	Ph	W (M)	1^{b} / 344
	CH(Me)(Ph)	Ph	Pd (M)	1^{b} / 345
			Pt (M)	1^{b} / 346
	CH(Me)(COOMe)	Ph	Pd (M)	1^{b} / 347
			Pt (M)	1^{b} / 347
	Ph	OPh	Mo (M)	1^{b} / 344
			W (M)	1^{b} / 348
			Pd (D)	2^{c} / 318
		NH(Ph)	Mo (M)	1^{b} / 349
		F	Mo (D)	2^{c} / 350
	o-(OMe)C_6H_4	Ph	Mo (M)	1^{b} / 351
			Ru (M)	2^{b} / 351
			Pd (M)	1^{b} / 351
	$N(Me)_2$	Ph	Fe (M)	1^{b} / 352

(*) = (M), mononuclear species or (*) = (D), dinuclear species.

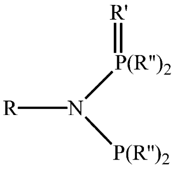
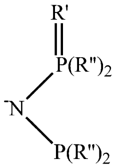
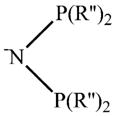
[a] *P*-Monoligate bonding mode.

[b] *P,P*-Chelating biligate bonding mode.

[c] *P,P*-Bridged species.

a rhodium/aminophosphine complex, despite the longer-chain ligand of the type **P**–C–**N**–C–**P** [365]. In the complex [Rh(cod){$PhN(CH_2PPh_2)_2$}]BF_4 (Scheme 93) the rhodium center lies in a square-planar environment with two *cis* phosphorus atoms. The six-membered metallacycle adopts an approximate chair conformation with a Rh···N distance of 3.797(5) Å confirming the *P*,*P*-biligate only coordination. The complex was used

Table 2

PNP Ligand	R	R'	R''	Metal centre	Number of PNP units in the complexes$^{a,b\text{ or }c}$ / References
	H	O	Ph	Re Rh Pd Pt	1^{b} / 355 1^{a} / 356, 1^{b} / 357 1^{b} / 358,359 $2^{a\text{ or }b}$ / 360, 1^{a} / 361
	CH(Me)(COOMe)	O	Ph	Pd	1^{b} / 347
	H	Se	Ph	Pt	2^{b} / 362
	Ph	S	Ph	Pt	1^{b} / 363
	o-(OMe)C_6H_4	S	Ph	Pt	1^{b} / 351
	/	O	Ph	Re Ru Ir Pd Pt	1^{b} / 355 1^{b} / 357 1^{b} / 356 1^{b} / 356,359, 2^{c}(D)* / 358 1^{b} / 361, 2^{b} / 360, 2^{a}(D)* / 361
	/	Se	Ph	Pt	2^{b} / 362
	/	/	Ph	Pd Co	1^{b} / 364 1^{c}(D)* / 293

(D)* = dinuclear species.

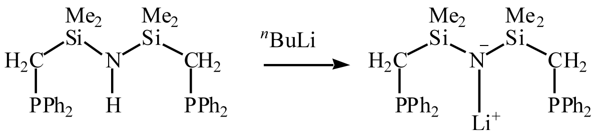
[a] *P*-Monoligate bonding mode.

[b] *P,R'*- or P,P-chelating biligate bonding mode.

[c] *P,R'*-Bridged species.

to carry out hydroformylation catalysis experiments on oct-1-ene and 2-vinylnaphtalene; the results clearly show an enhancement of the catalytic activity attributed to the presence of the nitrogen in the backbone of the ligand. Kinetic studies could be helpful to understand the exact role of the nitrogen donor atom in the mechanism. Balch et al. had previously reported the X-ray crystal structure of the similar square-planar *P*,*P*-biligate palladium complex [$PdCl_2\{PhN(CH_2PPh_2)_2\}$] [366]. The cyclohexyl-substituted derivative of the chain type **P**–C–**N**–C–**P**, $MeN(CH_2PCy_2)_2$ was used by Kemmitt and co-workers to obtain the palladium(0) complex [Pd(dba)$\{MeN(CH_2PCy_2)_2\}$] from tris(dba)dipalladium (Cy = cyclohexyl, dba = dibenzylidene acetone) [367]. Later the authors reported the X-ray structures of the square-planar *P*,*P*-biligate platinum(II) halide compounds: [$PtCl_2\{MeN(CH_2PCy_2)_2\}$] and [$PtI_2\{MeN(CH_2PCy_2)_2\}$] [368].

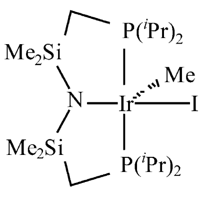
In the early 1980s, Fryzuk and MacNeil initiated studies on a new class of mixed-donor multidentate ligands with a seven-membered linear chain of the **P**–C–Si–**N**–Si–C–**P** type: the neutral 1,3-bis[(diphenylphosphino)methyl]tetramethyldisilazane, $(Ph_2PCH_2SiMe_2)_2NH$ (abbreviated PSiN(H)SiP), and the corresponding anion $(Ph_2PCH_2SiMe_2)_2N^-$ (abbreviated PSiNSiP) [369]. $Ph_2PCH_2SiMe_2)_2N^-$ was obtained from the lithium salt $(Ph_2PCH_2SiMe_2)_2NLi$, produced after lithiation of $(Ph_2PCH_2SiMe_2)_2NH$ (Scheme 94). The detailed syntheses of PSiN(H)SiP and PSiNSiP were reported [370], as well as the synthesis of the parent compounds $(Me_2PCH_2SiMe_2)_2N^-,Li^+$ and $\{(^iPr)_2PCH_2SiMe_2\}_2N^-,Li^+$ [371]. These nitrogen/phosphorus containing ligands successfully led to the synthesis and characterization of many coordination compounds, with virtually all the transition metals of the periodic table. Most often, the complexes were obtained from metathetical reaction between the lithium salt and a transition metal halide. Review articles by Fryzuk and co-authors are available concerning (i) Groups 3, 4,



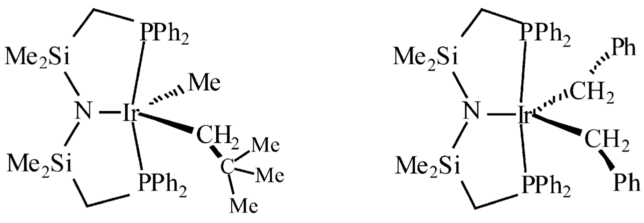
Scheme 94.

lanthanides and actinides [372,373], (ii) Groups 8, 9 and 10 [372,374], and (iii) the lithium derivatives containing these mixed-donor ligands [375]. Among the species which concern the present review, the complexes of Group 10 were first obtained [369,370,376–378]; the structures of [M^{II}Cl(PSiNSiP)] (M = Ni and Pd) show that the coordination of the (PSiNSiP) ligand is N,P,P-triligate to the metal centers in a square-planar environment [369,370]. On the contrary, the neutral ligand PSiN(H)SiP led to the biligate tetrahedral [Ni^{II}Cl$_2$(PSiN(H)SiP)] [370]. Peculiar CO migratory insertion behavior was detected for the nickel derivatives [376–378]; the carbonylation of [Ni^{II}R(PSiNSiP)] (R = Me, CH=CH$_2$, CH$_2$CH=CH$_2$ and Ph) results in a rearrangement to produce zerovalent nickel dicarbonyl compounds that contain the N,O-disilylimidate moiety [Ni^0(CO)$_2${RC=N(SiMe$_2$CH$_2$PPh$_2$)OSiMe$_2$CH$_2$PPh$_2$}] [377]. Loss of one CO ligand from the vinyl derivative produced the X-ray structurally authenticated η^2-acryloyl compound [Ni^0(CO){(η^2-C$_2$H$_3$)C=N(SiMe$_2$CH$_2$PPh$_2$)OSiMe$_2$CH$_2$PPh$_2$}]. Intermediates of these processes are the acyl [Ni(COR)(PSiNSiP)]; the X-ray molecular structure of the phenyl derivative acyl complex [Ni(COC$_6$H$_5$)(PSiNSiP)] was reported [378].

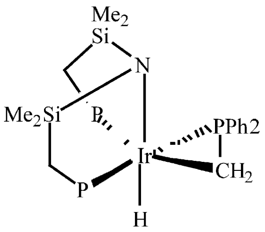
The following studies were concerned with Group 9 transition metals complexes [372,379–394]: (i) iridium hydride, alkyl and alkenyl species were described [380–382], the X-ray diffraction structures of the complexes [Ir^{III}(H)(CH$_3$)I{NH[SiMe$_2$CH$_2$P(^{i}Pr)$_2$]$_2$}] [381,386], [Ir^{III}{C(Me)=CH$_2$}{η^2 - Al,N - (Me)$_2$AlN[SiMe$_2$CH$_2$P(Ph)$_2$]$_2$}] [382] and [Ir^{III}(CH$_3$)I{N[SiMe$_2$CH$_2$P(^{i}Pr)$_2$]$_2$}] are available [384]. This late five-coordinate compound presents in the solid state, and in solution, a distorted square-pyramidal geometry, the apical position being occupied by the methyl group (Scheme 95). Thus, the **P**–C–Si–**N**–Si–C–**P** type ligand is in a meridional conformation and forms two fused five-membered chelating rings including the iridium center, the *mer* conformation for this family of tridentate 1N/2P ligand being more common. (ii) The formation and the X-ray structure of the square-planar iridium methylidene [Ir^I(=CH$_2$)(PSiNSiP)] was reported [383]. (iii) From the square-pyramidal alkyl halides previously mentioned, dialkyl iridium complexes were also obtained [385,390]. The X-ray diffraction structures of the methyl neopentyl [Ir^{III}(CH$_3$){CH$_2$C(CH$_3$)$_3$}(PSiNSiP)] [385] and the dibenzyl [Ir^{III}(CH$_2$Ph)$_2$(PSiNSiP)] compounds [390] show that these five-coordinate dialkyl compounds have, in the solid state and in solution, a distorted trigonal-bipyramidal geometry (Scheme 96), while square-pyramidal geometries were expected. (iv) Rhodium and iridium dihydride complexes were synthesized, which present common structural features indicated by the molecular structures of [Rh^{III}H$_2$I{NH[SiMe$_2$CH$_2$P(^{i}Pr)$_2$]$_2$}] and [Ir^{III}H$_2$Cl{NH(SiMe$_2$CH$_2$PPh$_2$)$_2$}] [386]; octahedral environments around metal centers, and intramolecular N–H···X hydrogen bonding were observed (H···I = 2.80(4) Å in the rhodium compound, and H···Cl = 2.76(6) Å in the iridium one). (v) The iridium diphenylphosphido complex [Ir^{III}(CH$_3$)(PPh$_2$)(PSiNSiP)] generates, due to thermally induced rearrangement, the octahedral hydride complex *fac*-[Ir^{III}H(η^2-CH$_2$PPh$_2$)(PSiNSiP)]: the X-ray structure shows that the tridentate ligand has isomerized to a facial coordination with the nitrogen *trans* to the hydride ligand and the cyclometallated η^2-CH$_2$PPh$_2$ moiety occupying the remaining *cis* sites (Scheme 97) [391,393]. (vi) The crystal structure and the NMR spectral data reveal that the tridentate ligand PSiNSiP in the buta-1,3-diene complex [Ir(η^4-C$_4$H$_6$)(PSiNSiP)] is coordinated, as well, in a quasi facial manner [392]. For the buta-1,3-diene ligand a η^4-π bonding mode was found with, however, some σ-π^2 component present. (vii) Later, the X-ray structure of the previously mentioned methyl diphenylphosphido [Ir^{III}(CH$_3$)(PPh$_2$)(PSiNSiP)] was reported and the geometry at the iridium center is described as distorted square-pyramidal with the phosphido group in apical position [393]. (viii) The synthesis of the iridium vinylidene [Ir^I(=C=CH$_2$)(PSiNSiP)] was reported [394]: the square-planar complex was structurally identified by X-ray diffraction studies and displays a rather short distance for the iridium–carbon bond, 1.806(4) Å, compared with the related distance of 1.868(9) Å found in the methylidene complex [Ir^I(=CH$_2$)(PSiNSiP)] [383].



Scheme 95.



Scheme 96.



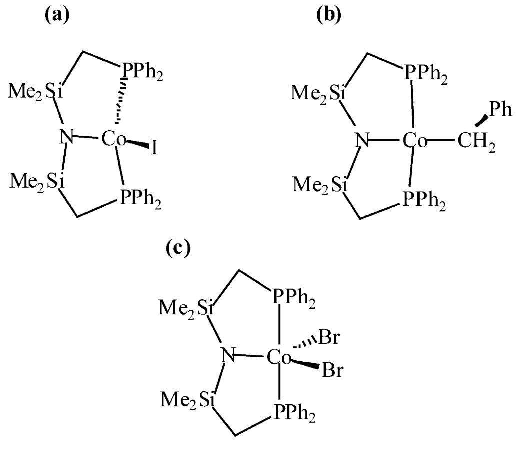
Scheme 97.

The vinylidene complex reacts with a variety of electrophiles ER_3 such as for instance, $AlMe_3$ or $GaMe_3$ to give $[Ir^{III}(AlMe_2)(CMe{=}CH_2)(PSiNSiP)]$ or $[Ir^{III}(GaMe_2)(CMe{=}CH_2)(PSiNSiP)]$ by oxidative addition reactions [394]. These complexes have isostructural distorted square-pyramidal geometries with the isopropenyl ligand in the equatorial plane and an apical EMe_2 group bridging to the nitrogen atom. Oxidative addition of methyl iodide led to the X-ray characterized $[Ir^{III}(\eta^3\text{-}C_3H_5)I(PSiNSiP)]$ complex, as final product, after rearrangement of $[Ir^{III}I(CMe{=}CH_2)(PSiNSiP)]$. The crystallographic data for $[Ir^{III}(CH_3)I_2\{PSiN(H)SiP\}]$ have also been reported [394]; curiously this complex was obtained from the previous vinylidene compound using an excess of CH_3I.

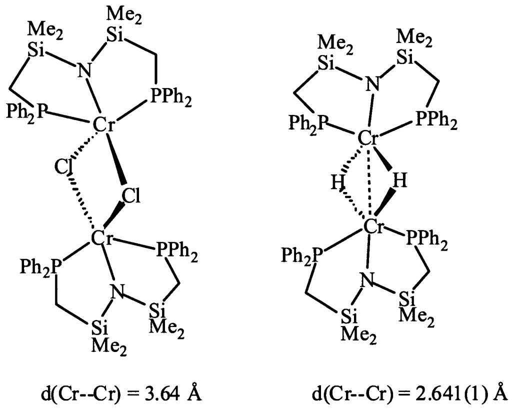
Cobalt complexes with tetrahedral geometry of the type $[Co^{II}X(PSiNSiP)]$ (where X = Cl, Br, I) can be prepared. Structural data for [CoI(PSiNSiP)] ((**a**) Scheme 98) were reported [395]. Reaction of these halide complexes with alkyllithium or sodium reagents leads to $[Co^{II}R(PSiNSiP)]$ (where R = CH_3, CH_2Ph, CH_2SiMe_3, C_5H_5); the X-ray structure of the cobalt benzyl complex $[Co(CH_2Ph)(PSiNSiP)]$ confirms that this kind of complex is monomeric with a square-planar geometry ((**b**) Scheme 98). Reaction of benzyl bromide in large excess with $[Co^{II}Br(PSiNSiP)]$ led to the complex $[Co^{III}Br_2(PSiNSiP)]$ and formation of dibenzyl ($PhCH_2CH_2Ph$). The structural analysis of this complex reveals a nearly perfect trigonal-bipyramidal environment at the Co center ((**c**) Scheme 98). Of the few structurally characterized five-coordinate cobalt(III) complexes, the majority have square-pyramidal geometry [395].

Fryzuk and co-workers have studied the synthesis, structure and reactivity of iron(II) and iron(III) complexes containing PSiNSiP [396]. Halide or alkyl iron(II) complexes of the formula [FeX(PSiNSiP)] were prepared (where X = Cl, Br, CH_2SiMe_3 or $CH(SiMe_3)_2$, for X = Me or CH_2Ph the species are thermally unstable). The X-ray diffraction study of $[Fe^{II}\{CH(SiMe_3)_2\}(PSiNSiP)]$ show a distorted tetrahedral geometry for the complex (the bond angles ranges from 87.03(5) to 131.20(7)°). In the preparation of the chloride $[Fe^{II}Cl(PSiNSiP)]$ the side product $[Fe^{II}(PSiNSiP)_2]$ is formed in low yield. The molecular structure of this compound reveals a tetrahedral coordination around the iron atom, with each tridentate PSiNSiP *biligate* through the nitrogen atom and one phosphorus. The reaction of $[Fe^{II}Cl(PSiNSiP)]$ with NaCp·DME led to $[Fe(\eta^5\text{-}C_5H_5)(PSiNSiP)]$ with a tetrahedral geometry. The trivalent iron complexes $[Fe^{III}X_2(PSiNSiP)]$ can be obtained directly from the halides FeX_3 by reaction with Li(PSiNSiP). The crystal structure of $[FeBr_2(PSiNSiP)]$ shows an almost regular trigonal-bipyramidal geometry for the complex.

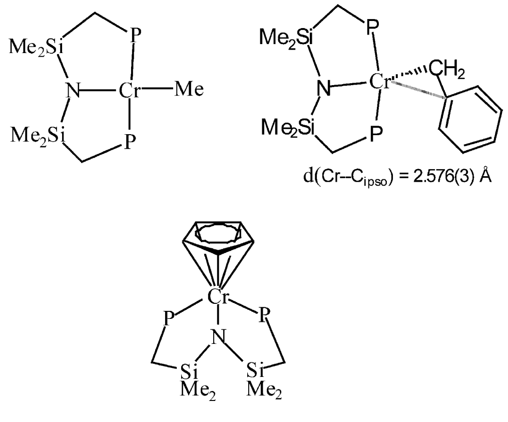
The coordination chemistry of the PSiNSiP ligand was also studied with chromium [397–400]. Two dinuclear chromium(II) complexes of the formula $[\{(PSiNSiP)Cr\}_2(\mu\text{-}Cl)_2]$ and $[\{(PSiNSiP)Cr\}_2(\mu\text{-}H)_2]$ were synthesized and structurally characterized (Scheme 99) [397]. Five-coordinate slightly distorted trigonal-bipyramidal geometries were found around each chromium center: a larger distortion is observed in the hydrido-bridged dimer than in the chloride bridged-dimer due to the smaller bridging atoms. The chloro-



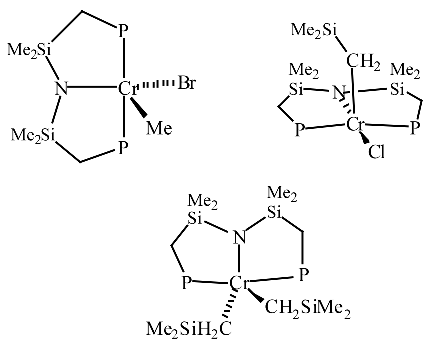
Scheme 98.



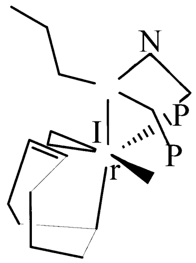
Scheme 99.



Scheme 100.

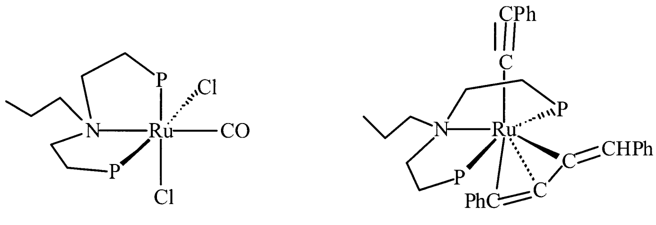


Scheme 101.

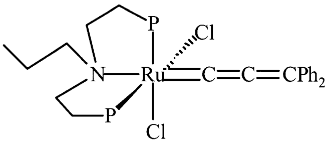


Scheme 102.

bridged dimer was used as starting material to form the alkyl complexes [$Cr^{II}R$[(PSiNSiP)] (where R = Me, CH_2Ph, C_5H_5) [398]. Rather different X-ray crystal structures were obtained for the products: while [CrMe(PSiNSiP)] has a square-planar geometry and [Cr(η^2-CH_2Ph)(PSiNSiP)] shows a distortion towards a tetrahedron, [Cr(η^3-C_5H_5)(PSiNSiP)] presents a pseudo-octahedral three legged “piano-stool”-like geometry (Scheme 100). Chromium(III) complexes have also been reported by Fryzuk and co-workers: the thiolate complex [Cr^{III}Me(SPh)(PSiNSiP)] displays a distorted square-pyramidal geometry, with the methyl group in an apical position [399]. Unusual examples of five-coordinate chromium(III) alkyl-halide and dialkyl complexes were characterized by X-ray measurements: [Cr(CH_3)Br(PSiNSiP)], [Cr(CH_2SiMe_3)Cl(PSiNSiP)] and [Cr(CH_2SiMe_3)$_2$(PSiNSiP)] show distorted five-coordinate geometries that can be described as square-pyramidal or trigonal-bipyramidal (Scheme 101) [400]. The chromium(III) complexes, despite the presence of an open coordination site compared to well-known octahedral Cr^{III} complexes, did not show any activity in ethylene polymerization.



ref. 403



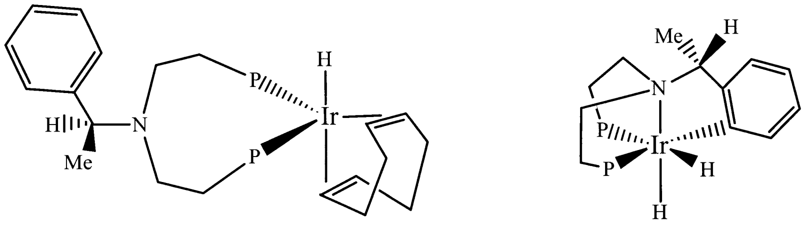
ref. 404

Scheme 104.

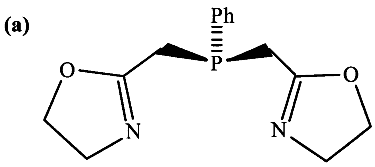
Symmetric and asymmetric seven-membered linear PNP chains of the **P**–C–C–**N**–C–C–**P** type were studied by Bianchini and co-workers [401,402]. Iridium complexes of the family of the *N*,*P*,*P*-triligate trigonal-bipyramidal [Ir{^{n}Pr-N($CH_2CH_2PPh_2$)$_2$}(σ,η^2-C_8H_{13})] complex (Scheme 102), for which a crystal structure was reported, show catalytic activity for selective reduction of α,β-unsaturated ketones to allylic alcohols [401]. The (*R*) and (*S*) chiral aminodiphosphine {PhC(H)Me}N($CH_2CH_2PPh_2$)$_2$ (abbreviated PNP*) were synthesized separately, and coordinated to iridium for the catalytic enantioselective reduction of α,β-unsaturated ketones [402]. Among the intermediates possibly involved, the *P*,*P*-biligate trigonal-bipyramidal (*R*)-[IrH(cod)(PNP*)] and the *C*,*N*,*P*,*P*-tetraligate orthometallated octahedral (*R*)-[IrH_2(PNP*)] (an X-ray crystal structure is available for this complex) (Scheme 103). Ruthenium organometallic complexes containing ^{n}Pr-N($CH_2CH_2PPh_2$)$_2$ were also described with either a meridional or a facial coordination at the metal center (Scheme 104) [403,404].

The X-ray structure of the ionic nickel phosphorane imino complex [NiCl(PMe_3){*o*-$Ph_2P(C_6H_4)N$=PMe_3}]PF_6 was reported [405]. The NP_2 ligand is *P*,*N*-biligate, leaving a dangling PMe_3 group, and the nickel center is in a square-planar environment.

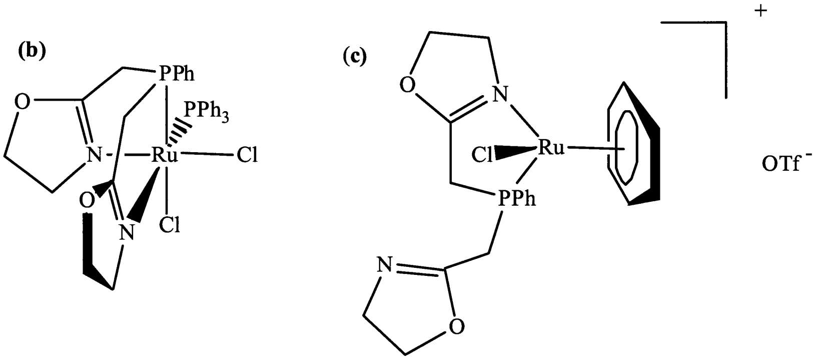
With respect to N_2P ligands, the bis(2-oxazolin-2-ylmethyl)phenylphosphine synthesized by Braunstein et al. is a novel seven-membered linear NPN ligand ((**a**)



Scheme 103.



NPN bis-oxazolin-phosphine ligand



Scheme 105.

Scheme 105), forming several ruthenium complexes which show catalytic activity towards transfer hydrogenation reactions between propan-2-ol and ketones [406]. The ligand was either found triligate (*fac*-coordination) or *N*,*P*-biligate with a dangling oxazoline ring. The X-ray structural determination of the octahedral complex [RuCl$_2$(PPh$_3$)(NPN)] and of the ionic species [RuCl(η^6-C$_6$H$_6$){*N*,*P*-(NPN)}][OTf], which adopts a "piano-stool" type of geometry, were reported (see (**b**) and (**c**) Scheme 105).

Shaw and Perera have developed a family of hydrazone, $R_2\mathbf{N}'{-}\mathbf{N}{=}C(R')CH(R'')\mathbf{P}Ph_2$, and azine, $R_2C{=}\mathbf{N}{-}\mathbf{N}{=}C(R')CH_2\mathbf{P}Ph_2$, linear ligands with 2N/1P donor atoms [407–415]. Complexes of these ligands were reported with Group 6 carbonyl complexes, Group 9 iridium and rhodium chloro/carbonyl complexes, Group 10 halide complexes, and recently with [RuCl$_2$(PPh$_3$)$_3$]. Scheme 106 summarizes representative examples of the species obtained and characterized by X-ray diffraction. These examples illustrate the diversity of coordination modes and structures provided by these N$_2$P ligands: *N*,*P*- and *N′*,*P*-biligate molybdenum and palladium hydrazone complexes (respectively (**a**), (**f**), and (**b**), (**c**), (**e**) in Scheme 106), *P*-monoligate palladium hydrazone complexes (106**g**), *C*,*N*,*P*-triligate orthometallated azine iridium (106**d**), *C*,*N*,*O*,*P*-tetraligate azine rhodium (106**h**), *N*,*P*-biligate azine molybdenum complexes (106**i**), and *F*,*N*,*P*-triligate azine ruthenium species (106**j**).

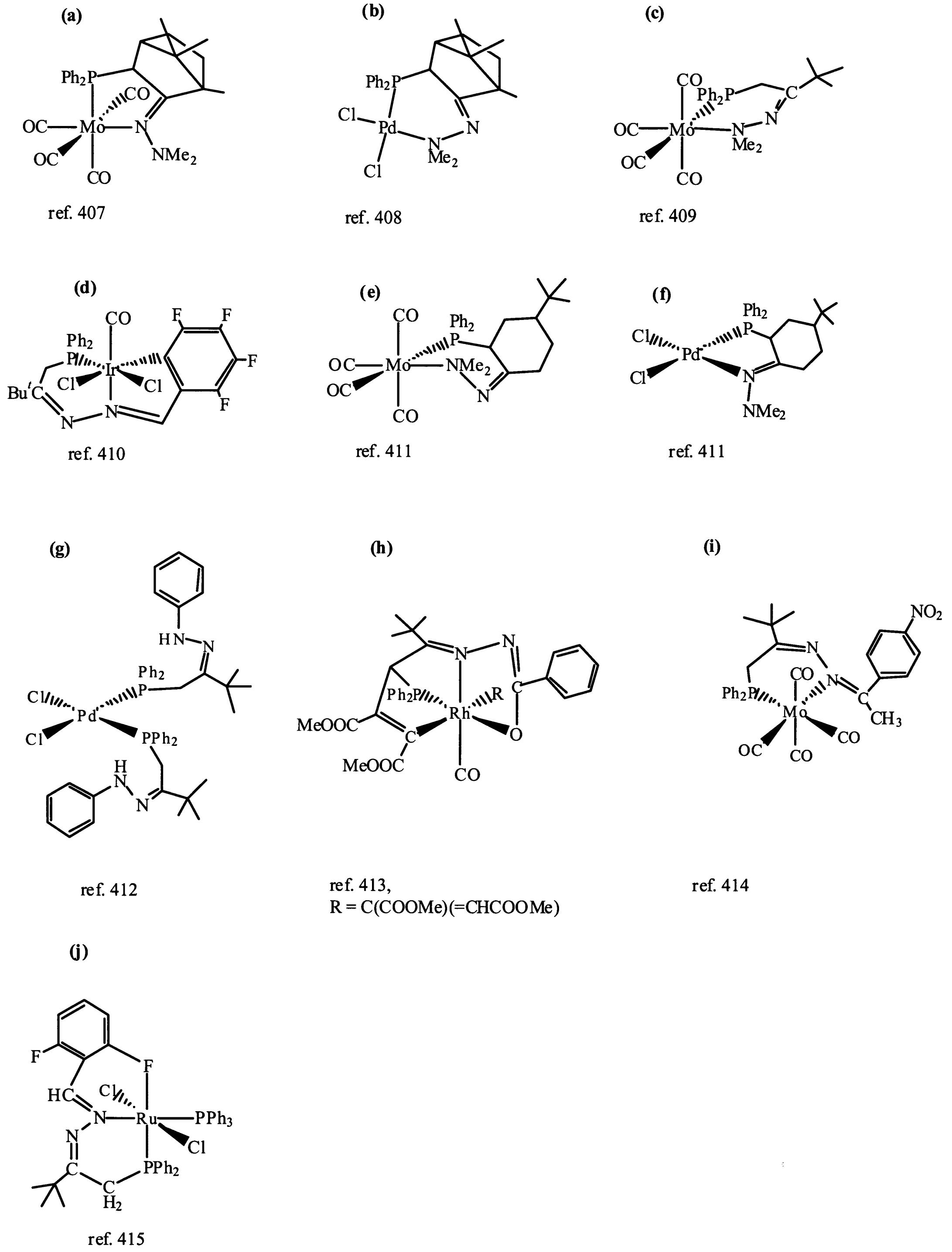
All the previous structural data concerning linear N/P mixed donor ligand show the flexibility provided by longer N/P linear chains. These data show that, as found for the linear triphosphines, the triligate or the biligate coordination mode of tridentate N/P ligands are strongly directed by the length of the chains between the donor atoms, especially when the seven-membered linear chains are compared with three- and five-membered ones.

Concerning tripodal mixed nitrogen/phosphorus ligands, Liu and co-workers reported photochemical substitution reactions of [Fe(CO)$_2$Cp)]I with the amino-phosphines $CH_3C(CH_2\mathbf{N}H_2)(CH_2\mathbf{P}Ph_2)_2$ and $HC(CH_2\mathbf{N}H_2)(CH_2\mathbf{P}Ph_2)(\mathbf{P}Ph_2)$ [416]. The complexes obtained, of the type [FeCp(NP$_2$)]I, were easily converted into the imino-species displayed in Scheme 107. X-ray structure characterizations confirm the triligate coordination of the N/P ligand at the iron center. The investigations carried out by Huttner et al. on the reactivity of the tripodal $CH_3C(CH_2\mathbf{N}Me_2)(CH_2\mathbf{P}Ph_2)_2$ with [Rh(cod)Cl]$_2$ have shown the formation of the *P*,*P*-biligate complex [Rh(cod){CH$_3$C(CH$_2$NMe$_2$)(CH$_2$PPh$_2$)$_2$}]PF$_6$ (Scheme 108) [417]. In this complex the phosphine ligand forms a six-membered chelate ring in a chair conformation, the coordination of the metal center completed by the cycloocta-1,5-diene co-ligand, being pseudo square-planar. This report has shown the preference of this type of tripodal *NP$_2$* ligand for a *P*,*P*-biligate coordination mode, with a left pendant nitrogen-containing arm [417]. This is in contrast with the general behavior of the parent compound tdpme. Studies on rhodium catalyzed hydrogenation of diphenylacetylene were reported to test the activity of new tripodal hemilabile ligands of that kind [417].

4.3. Tetradentate nitrogen/phosphorus ligands: 2N/2P, 1N/3P

4.3.1. Nitrogen/phosphorus ligands: 2N/2P

The contribution from Sacconi and co-workers concerning these polydentate phosphines and their metal



ref. 407

ref. 408

ref. 409

ref. 410

ref. 411

ref. 411

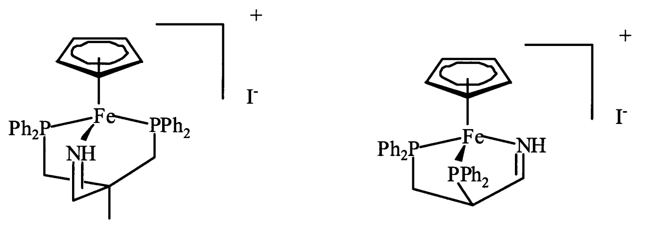
ref. 412

ref. 413,
R = C(COOMe)(=CHCOOMe)

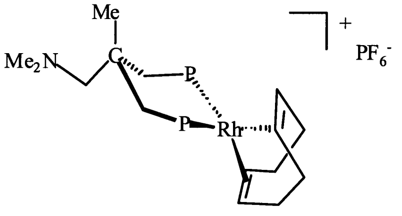
ref. 414

ref. 415

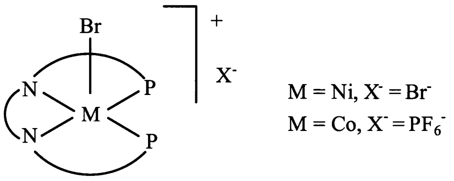
Scheme 106.



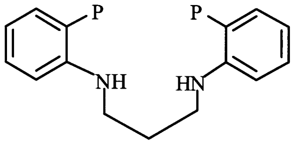
Scheme 107.



Scheme 108.



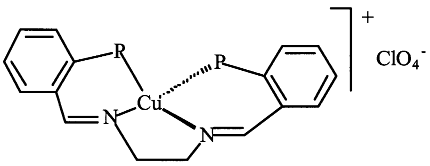
Scheme 109.



Scheme 110.

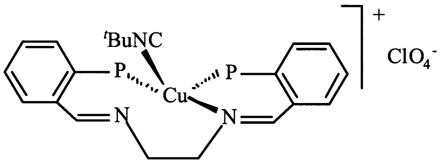
complexes was decisive since at an early stage they described nickel and cobalt complexes with the linear tetradentate $Ph_2P(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2PPh_2$ (called pnnp) [418]. The complexes [NiBr(pnnp)]Br and [CoBr(pnnp)]PF_6 show for their metallic cation the same square-pyramidal environment in which the pnnp ligand occupies the basal plane and the bromide the apical position (Scheme 109).

Amino-polyphosphine ligands including two phosphorus and two nitrogen atoms in a linear chain were used to prepare Groups 10 and 11 complexes. *N*,*N′*-Bis[2-(diphenylphosphino)phenyl]-propane-1,3-diamine (called H_2dppd, see Scheme 110) forms complexes with a tetraligate coordination mode to nickel [419], and copper [420,421], while a *P*,*P*-biligate coordination was found for rhodium [419] (Scheme 111). In contrast to the nickel and rhodium complexes which are square-planar, the coordination sphere of the Cu^I center in the complex [Cu(H_2dppd)]BF_4 is severely distorted tetrahedral [421]; indeed the bond angles at the metal for this complex range between 87.4(3) and 131.6(3)°. The tetraligate coordination of H_2dppd leads to a tricyclic (five-, six-, five-membered rings) system around copper with the six-membered ring in a twist-boat conformation. The two five-membered rings are roughly perpendicular to each other and hydrogen bonding with the BF_4^- counter ion is present in the molecule. These structural characteristics are very different from the first crystallographically identified copper/H_2dppd complex: [Cu(η^1-$OClO_3$)(H_2dppd)]ClO_4 [420] (Scheme 111). In this complex, H_2dppd behaves as a tetraligate chelating ligand, producing along with the η^1-$OClO_3$ unit a square-pyramidal arrangement around the Cu^{II} center. The copper atom lies 0.24 Å above the mean basal plane formed by the N_2P_2 atoms.

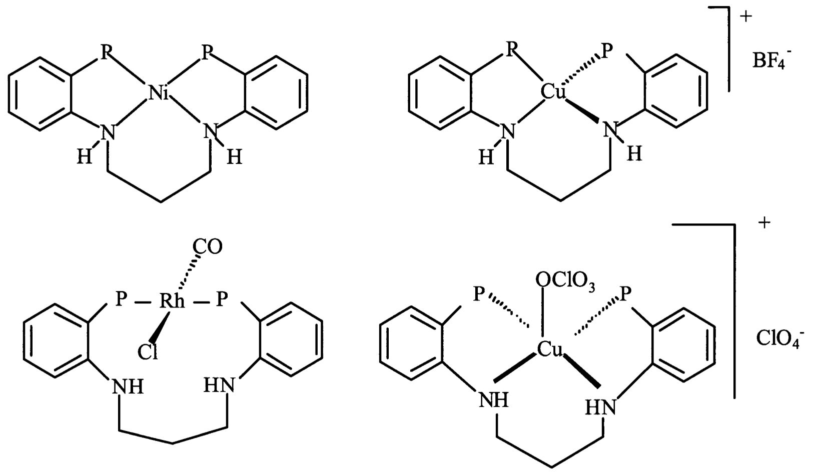


Scheme 112.

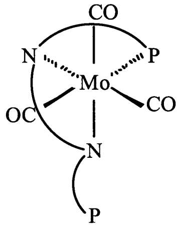
A related imino-phosphine N_2P_2 ligand, *N*,*N′*-bis[*o*-(diphenylphosphino)benzylidene]-ethane-1,2-diamine forms a copper complex with a tetraligate coordination at the Cu center from the four donor atoms (Scheme 112) [422]. The X-ray crystal structure of the complex [Cu(N_2P_2)]ClO_4, obtained from [Cu(MeCN)$_4$]ClO_4, shows a very distorted tetrahedral environment at copper due to the three fused chelating rings, the constraint being amplified by the short imine C=N bond. Interestingly, a ^{t}BuNC co-ligand added to the coordination sphere does not lead to a five-coordinate



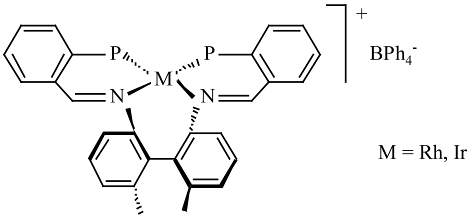
Scheme 113.



Scheme 111.



Scheme 114.

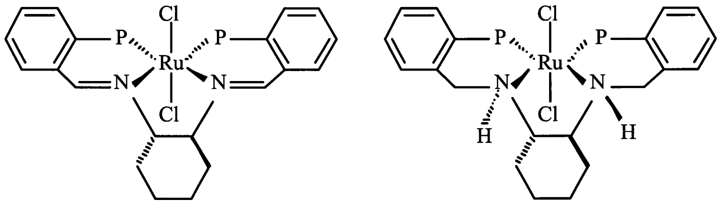


Scheme 115.

compound (Scheme 113), instead the N_2P_2 hemilabile donor group becomes *N*,*P*,*P*-triligate conserving thus the tetrahedral arrangement around the copper and showing the ability of the ligand to vary its coordination mode. The complex formed by the displacement of an internal donor contains a unique nine-membered chelate ring. A structural consequence of the replacement of one of the imine nitrogen atoms coordinated to copper by the isocyanide group is the obvious relief of some angular strain at the tetrahedral coordination. The fused six- and nine-membered chelate rings are more likely a consequence of a geometric requirement rather than a preference of the copper for phosphine over imine donors. The tetrahedral geometry better accommodates 6,9 fused chelating rings than 6,5 rings due to the preference for a large "bite" angle at the metal. In an octahedral complex with a preferred smaller "bite" angle, fused six- and five-membered rings should be obtained as in the case of the analogous molybdenum(0) complex (Scheme 114) [422]. This complex is *N*,*N*,*P*-triligate confirming, thus, the versatility of coordination provided by this ligand.

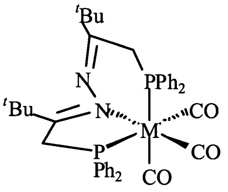
Pignolet et al. and Noyori et al. have synthesized chiral versions of the previous ligand, and produced rhodium, iridium or ruthenium precursors to examine their performance in asymmetric catalysis of the resulting complexes [423,424]. The reaction of the asymmetric mixed N/P ligand 2,2′-bis[{*o*-(diphenylphosphino)benzylidene}amino]-6,6′-dimethylbiphenyl (called PPNN) with $[Rh(cod)Cl]_2$ or $[Ir(PPh_3)_2(N_2)Cl]$, after treatment with $NaBPh_4$, leads respectively to the racemic $[Rh(PPNN)]BPh_4$ and the isostructural $[Ir(PPNN)]BPh_4$ (Scheme 115) [423]. The crystal structures show that in both complexes the PPNN ligand is tetraligate and the metal adopts a slightly distorted square-planar geometry. Only marginal differences were detected between the two rhodium and iridium complexes, resulting mainly from the radius difference between the two elements. In the structure a large twist between the two phenyl rings of the biphenyl is detected and the dihedral angle between the least-square planes of these two phenyl rings is 69.68°. This twist is the direct cause of the chirality of the resolved complexes since any rotation is prevented by the 6,6′-methyl substituents. The reactivity studies have shown that the rhodium complex does not react with H_2 and only partially with CO whereas the iridium one has shown rapid and complex reactivity with H_2 and CO. The CO adduct with iridium was found to have a bond between the metal atom and a methyne carbon atom of the PPNN ligand to give an Ir(PPNC) core.

Noyori and co-workers have synthesized *trans*-$Ru^{II}Cl_2$ complexes with *N*,*N*′-bis[*o*-(diphenylphosphino)benzylidene]cyclohexane-1,2-diamine (dpbc, imine type ligand) or with *N*,*N*′-bis[*o*-(diphenylphosphino)benzyl]cyclohexane-1,2-diamine (H_2dpbc, amine type ligand) ligands [424] (Scheme 116). The (*S*,*S*)-ruthenium diamine complex, in contrast to the analogous (*S*,*S*)-diimine one, acts as a very good catalyst precursor in asymmetric transfer hydrogenation of acetophenone to 2-phenyl-ethanol (93% yield in 97% e.e.). In the selected conditions (45 °C for 7 h) the limiting reversibility of the reaction is found to be uncommonly low. The ruthenium complexes are structurally similar with an octahedral arrangement at the Ru center for which the equatorial positions are occupied by the tetraligate P_2N_2 ligand and the axial positions by two chloro ancillary ligands. The differences in reactivity between the diamine and diimine ruthenium complexes can hardly be explained by geometrical parameters since they remain very similar between the



S,S-Ru/Diimine (dpbc) *S,S*-Ru/Diamine (H_2dpbc)

Scheme 116.



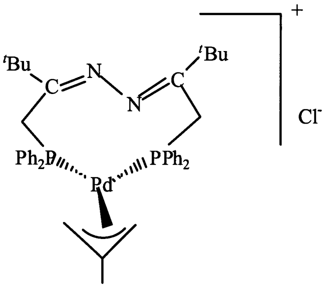
M = Cr, Mo, W

Scheme 117.

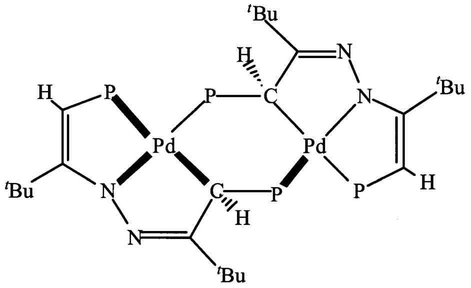
two species. The authors have postulated that the NH functions in the diamine ligand are responsible for the high activity of the complex [424].

Shaw and co-workers have synthesized the azine diphosphine Z,Z-$PPh_2CH_2C(^tBu)=N-N=C(^tBu)$-$CH_2PPh_2$ and reacted it with Group 6 carbonyl metals [425]. The complexes $[M(CO)_3\{N,P,P\text{-}(PPh_2CH_2C(^tBu)=N-N=C(^tBu)CH_2PPh_2)\}]$ (with M = Cr, Mo, W, see Scheme 117) were obtained, and the X-ray crystal structure of the molybdenum compound was reported. Octahedral geometries of the complexes were determined, where the triligate azine diphosphine has changed from Z,Z- to E,Z-configuration upon its *fac*-coordination. The treatment of the azine diphosphine with methylallyl palladium chloride gives the ionic complex $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)\{P,P\text{-}(PPh_2CH_2C(^tBu)=N-N=C(^tBu)CH_2PPh_2)\}]Cl$ (Scheme 118) [426]. The crystal structure of the compound shows that the P,P-*biligate* azine has adopted an E,Z-configuration with a C–C=N–N=C–C backbone mostly planar.

The neutral palladium complex $[PdCl\{N,P,P\text{-}[\mathbf{P}Ph_2CH=C(^tBu)-\mathbf{N}-N=C(^tBu)CH_2\mathbf{P}Ph_2]\}]$, which contains a triligate nitrogen-deprotonated azine ligand, reacts with 2 equiv. $Li[N(SiMe_3)_2]$, to form the dinuclear compound $[\{Pd[PPh_2CH=C(^tBu)-N-N=C(^tBu)CH\text{-}PPh_2)]\}_2]$ (Scheme 119) [427]. The azine diphosphine ligands are coordinated in a tetraligate manner to one palladium each, through one nitrogen, one phosphorus and the carbon in the α-position of the second phosphorus; the second phosphorus bridging the other palladium atom. This arrangement gives four five-membered rings and a central fused six-membered ring in a puckered conformation. Mononuclear palladium halide compounds bearing this type of azine ligand were found to be proper catalysts for Heck reactions of aryl halides [428]. Shaw et al. have also reacted Z,Z-$PPh_2CH_2C(^tBu)=N-N=C(^tBu)CH_2PPh_2$ with $[RuCl_2(CO)_2]_x$ to yield the complex *fac,cis*-$[RuCl_2(CO)\{N,P,P$ - $(PPh_2CH_2C(^tBu)=N-N=C(^tBu)CH_2PPh_2)\}]$ where the azine is triligate in a E,Z-configuration [429]; a facial arrangement of the ligand with the nitrogen atom *trans* to the CO was indicated by an X-ray determination. A parent enantiomerically pure azine diphosphine (R-(+)-camphor azine) was used by Shaw and co-workers to synthesize complexes with Group 6 carbonyl metals [430]; the X-ray structure of the *fac*-$[W(CO)_3)\{N,P,P\text{-}(R)\text{-camphor azine}\}]$ (see Scheme 120) was described. The synthesis of an azine dioxide derivative was recently described, and the crystal structure of the $^iPr_2P(O)CH_2C(^tBu)=N-N=C(^tBu)$-$CH_2P(O)^iPr_2$ compound is available [431]. This kind of ligand generated dinuclear palladium complexes bearing the η^3-2-methylpropenyl co-ligand.



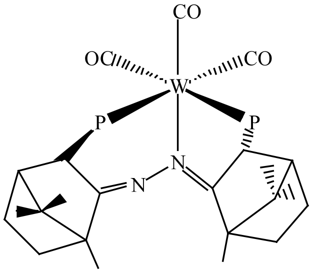
Scheme 118.



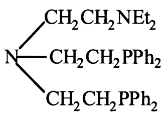
Scheme 119.

A family of linear N_2P_2 bis(iminophosphorane), $RN=P(R')_2CH_2P(R')_2=NR$ ($R = Ph$ or $C_6H_3^iPr_2$, $R' = Me$ or Ph) ligands and their deprotonated lithium salts were used with cobalt and nickel halides precursors to form the complexes $[CoCl_2\{CH_2(Ph_2P=NPh)_2\}]$ and $[NiBr\{HC(Ph_2P=NC_6H_3\text{-}2,6\text{-}^iPr_2)_2\}]$ [432]. $[CoCl_2\{CH_2(Ph_2P=NPh)_2\}]$ has a tetrahedral geometry with a N,N-biligate coordination mode of the iminophosphorane. $[NiBr\{HC(Ph_2P=NC_6H_3^iPr_2)_2\}]$ has a square-planar geometry where the ligand is C,N,N-triligate. The use of the compounds in ethylene polymerization has shown a modest activity for the cobalt complex, and no activity for the nickel complex.

The X-ray structure of the new silylated iminophosphorane $Me_3Si-N=P(Ph_2)-N(R)-PPh_2$ was reported

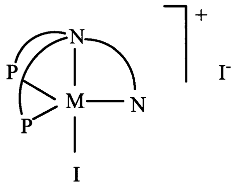


Scheme 120.



NP_2N

Scheme 121.



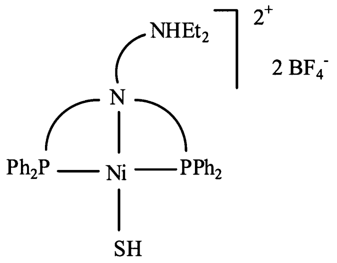
M = Co, Ni

Scheme 122.

(with $R = {}^{n}Pr$) [433]. The silylated iminophosphorane containing $R = {}^{n}Pr$, ${}^{n}Bu$ and Et react with rhodium(I), palladium(II) and platinum(II) complexes to give metallacycles via biligate phosphorus and nitrogen coordination.

Beside the linear four donor atoms nitrogen/phosphorus polyphosphine ligands, tripodal ligands have been studied. Sacconi et al. used *N*,*N*-bis-(2-diphenylphosphino-ethyl)-*N′*-(2-diethylaminoethyl)amine (called NP_2N, Scheme 121) to form the isomorphous complexes $[Co^I(NP_2N)]I$ and $[Ni^I(NP_2N)]I$ [434] whose geometry is trigonal-bipyramidal with tetraligate coordination of the amino-polyphosphine ligand. The central nitrogen atom and the iodo ligand lie in the apical positions, while the equatorial positions are occupied by the two phosphorus and the terminal nitrogen atom (Scheme 122). The major difference between the two structures is a distortion towards an elongated square-pyramidal geometry for the nickel compound, while the geometry of the cobalt complex shows distortion towards a tetrahedral geometry. The long distance between the apical nitrogen and the cobalt center 2.440(15) Å led Sacconi et al. to consider a “semi-coordination” for this nitrogen atom and thus a distortion towards a tetrahedron.

The same ligand NP_2N can be triligate as well: NP_2N was used to yield stable thiol/nickel complexes where it acts on the nickel center as a *N*,*P*,*P*-tridentate ligand [435]. The terminal nitrogen is quaternized by the uptake of a proton from the reactant H_2S. The X-ray structure determination of $[Ni(SH)(NP_2NH)][BF_4]_2$ has shown that the metal atom is coordinated by one nitrogen and two phosphorus atoms from the polyphosphine and by a sulfur atom forming a distorted square-planar arrangement (Scheme 123). The P–Ni–P and N–Ni–S angles slightly close up with values less than 180° (respectively 157.0(1) and 170.1(2)°), leading to a small distortion towards a tetrahedral coordination. Structural evidence for the quaternization of the terminal nitrogen is that *both* BF_4 anions lie close to the non-chelating chain of the tripodal ligand, forming several short contacts with it (N···F non-bonding distance 2.90 Å).

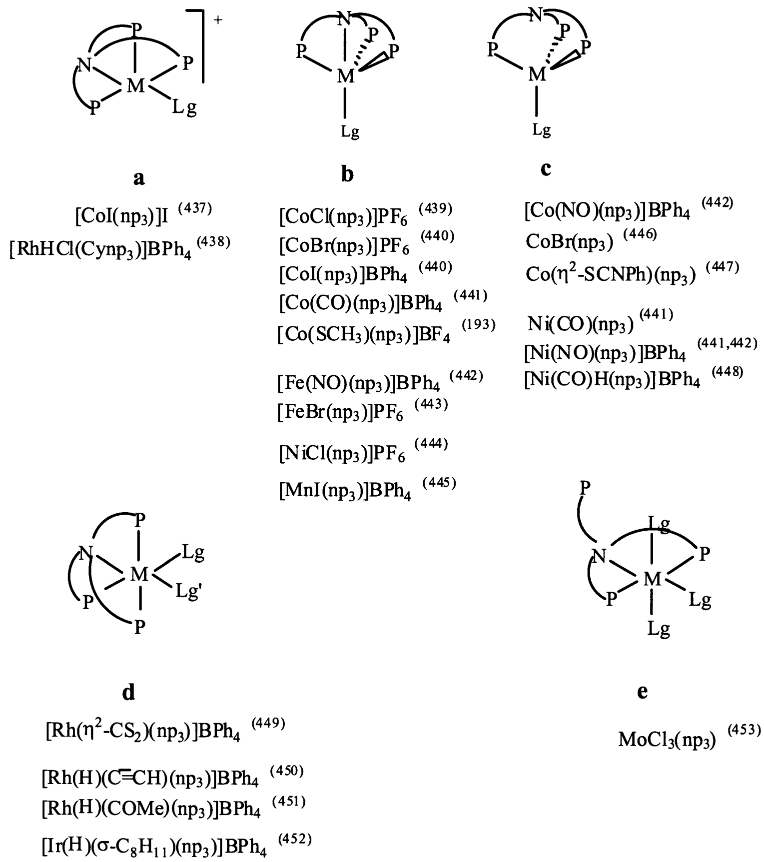


Scheme 123.

4.3.2. Nitrogen/phosphorus ligands: 1N/3P

The mixed N/P tripodal polyphosphine ligand tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$ (np_3) was extensively studied and compared with the analogous $P(CH_2CH_2PPh_2)_3$ ligand containing only phosphorus atoms as potential donors. One of the main reasons is that this class of mixed polydentate ligands can favor catalytic reactions which need open sites at the metal center by dissociation of either a phosphine or a nitrogen donor (hemilabile behavior) [7]. Thus, even if crystallographic structures have not been systematically reported, numerous X-ray diffraction studies of complexes with np_3 as ligand are known for late transition metals: Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt. Mayer and Kaska have reported the reaction chemistry of these complexes [6]. Classically, np_3 can act as a tetraligate or a triligate ligand and in the latter case, most of the time, the nitrogen donor remains uncoordinated. The coordination mode seems governed by the electronic demand of the metal and by the co-ligands. A review of the bonding capabilities of the ligand np_3 was reported in 1992 by Mealli et al. [436], indicating at this time more than 60 structures reported by the group of Sacconi. Scheme 124 is an attempt to illustrate the diversity of structures obtained with np_3 when co-ligands are involved: square-pyramidal with np_3 tetraligate geometry type (**a**) [437,438]; bipyramid-trigonal type (**b**) [193,439–445] when np_3 is tetraligate, and type (**c**) [441,442,446–448] when triligate; octahedral type (**d**) [449–452] when np_3 is tetraligate and type (**e**) [453] when triligate.

More recently the np_3 ligand was used by George and co-workers to stabilize and structurally characterize dinitrogen and carbonyl iron(II) hydride complexes [454]. The ionic compounds $[FeH(L)(np_3)]BPh_4$ (where $L = N_2$ or CO) are isostructural, the environment at the iron center being distorted octahedral with a tetraligate np_3; three phosphorus atoms and a hydride ligand defining an equatorial plane (Scheme 125). Orlandini et al. have described a palladium/tellurium dimer where each palladium center is four-coordinated by two bridging tellurium atoms and by two phosphorus atoms



a

$[CoI(np_3)]I$ (437)
$[RhHCl(Cynp_3)]BPh_4$ (438)

b

$[CoCl(np_3)]PF_6$ (439)
$[CoBr(np_3)]PF_6$ (440)
$[CoI(np_3)]BPh_4$ (440)
$[Co(CO)(np_3)]BPh_4$ (441)
$[Co(SCH_3)(np_3)]BF_4$ (193)
$[Fe(NO)(np_3)]BPh_4$ (442)
$[FeBr(np_3)]PF_6$ (443)
$[NiCl(np_3)]PF_6$ (444)
$[MnI(np_3)]BPh_4$ (445)

c

$[Co(NO)(np_3)]BPh_4$ (442)
$CoBr(np_3)$ (446)
$Co(\eta^2\text{-}SCNPh)(np_3)$ (447)
$Ni(CO)(np_3)$ (441)
$[Ni(NO)(np_3)]BPh_4$ (441,442)
$[Ni(CO)H(np_3)]BPh_4$ (448)

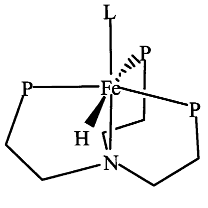
d

$[Rh(\eta^2\text{-}CS_2)(np_3)]BPh_4$ (449)
$[Rh(H)(C{\equiv}CH)(np_3)]BPh_4$ (450)
$[Rh(H)(COMe)(np_3)]BPh_4$ (451)
$[Ir(H)(\sigma\text{-}C_8H_{11})(np_3)]BPh_4$ (452)

e

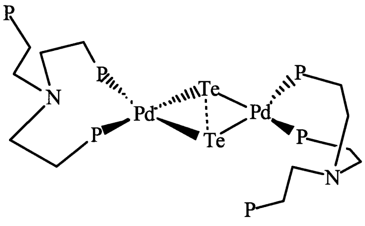
$MoCl_3(np_3)$ (453)

Scheme 124.



L = N_2, CO

Scheme 125.



d (Te–Te) = 2.919(2) Å

Scheme 126.

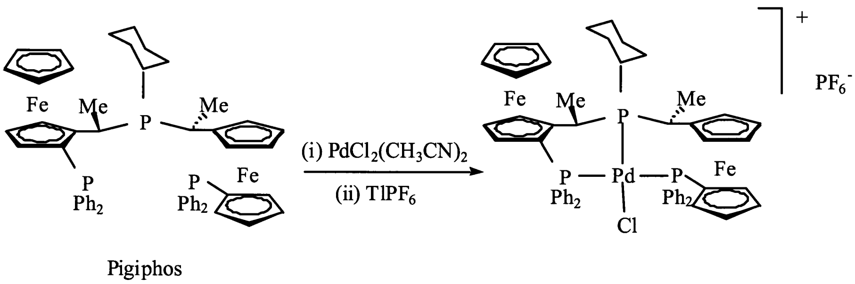
of the np_3 ligand, the third phosphorus remaining uncoordinated (Scheme 126) [455].

The X-ray structures of molybdenum complexes containing the tris(diphenylphosphinomethyl)amine ligand, $N(CH_2PPh_2)_3$, and its nitrogen quaternized protonated-derivative, $HN^+(CH_2PPh_2)_3$, were reported: $[MoCO_3\{N(CH_2PPh_2)_3\}]$ and $[MoCO_3\{HN(CH_2\text{-}PPh_2)_3\}]BPh_4$ show the polyphosphine *P*,*P*,*P*-triligate to the metal center [456].

Burk et al. have reported the chiral C_3-symmetric all-(*S*) triphosphine ligand, abbreviated CP_3 (see Section 2.3.2 and Scheme 38), and simultaneously the analogous C_3-symmetric all-(*S*) triphospholanamine ligand NP_3^* [154]. The all-(*R*) C_3-symmetric rhodium complex $[Rh(CO)(NP_3^*)]Cl$ was characterized by X-ray crystallography revealing that the rhodium center has a trigonal-bipyramidal geometry. The rhodium atom is located 0.2 Å above the equatorial plane defined by the three phosphorus atoms, the apical positions being occupied by the carbonyl ligand and the nitrogen atom.

5. Complexes with ferrocenyl tri- and tetradentate polyphosphines or nitrogen/phosphorus ligands

Since the synthesis of 1,1′-bis(diphenylphosphino)ferrocene (dppf) in 1965, which has probably been the most intensively studied ferrocenyl phosphine compound to date, the reaction chemistry of ferrocenyl polyphosphine has received much attention [457]. Among these com-

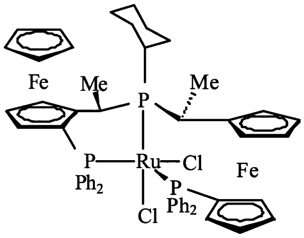


Scheme 127.

pounds the interest in tridentate and tetradentate ferrocenyl phosphines has appeared rather recently from ever growing research for novel homogeneous catalytic properties. One driving force for these studies is indisputably the potential route to asymmetric catalysis opened by the chiral polyphosphines obtained. The two following sections concern the structural advances described by our team and others since the early 1990s concerning tri- and tetraphosphines incorporating ferrocenyl moieties.

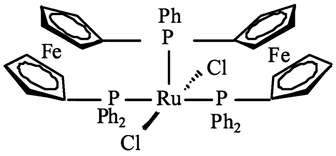
5.1. *Triphosphine ferrocenyl ligands*

Until now, few ferrocenyl phosphines with three phosphorus atoms potentially coordinating to metal were characterized by X-ray structural studies. Nevertheless among those reported, some display various elegant tricoordinate geometries. In 1995, Barbaro and Togni have described the synthesis and characterization of the bis{(*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl}cyclohexylphosphine named Pigiphos, which is constituted of two diphenylphosphino-substituted ferrocene moieties bridged by a diethyl(cyclohexyl)phosphino group (displayed as the ligand in Scheme 127) [458]. The polyphosphine is obtained from the reaction of cyclohexylphosphine and *N*,*N*-dimethyl-(*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine in acetic acid and proceeds with retention of configuration on the stereogenic centers, leading thus to a (*S*,*R*) configuration on both ferrocenyl units. Pigiphos reacts with palladium and other d^8-metal centers to form meridional coordinate complexes. $[PdCl(Pigiphos)]PF_6$ was obtained from $[PdCl_2(NCCH_3)_2]$ reacting with Pigiphos in the presence of $TlPF_6$. The $[PdCl(Pigiphos)]^+$ cation adopts a square-planar environment around the Pd^{II} center (Scheme 127). In the complex the chlorine atom and the cyclohexyl phosphorus atom are in a mutual *trans* positions. The distortion from the ideal square-planar geometry is indicated by the 0.18 Å distance of the Pd out of the mean plane. Barbaro et al. later described the complex $[RuCl_2(Pigiphos)]$ formed from the reaction in toluene of Pigiphos and $[RuCl_2(PPh_3)_3]$ [459]. The coordination geometry around the metal center is distorted square-pyramidal: the apical position is occupied by the phosphorus of one PPh_2 group while the basal positions are occupied by the other phosphorus and the two Cl in *cis* mutual positions (Scheme 128). The ruthenium atom lies 0.36(7) Å above the best coordination plane comprising the basal donor atoms of an idealized square-pyramidal geometry. The Pigiphos ligand, in this case, adopts a facial coordination. The asymmetric catalytic reaction chosen to test the complex properties was the reduction of prochiral acetophenone to chiral 1-phenylethanol via hydrogen transfer from propan-2-ol; the enantiomeric excess of this specific complex is low (i.e. 5.5% e.e., a better result of 72% e.e. was obtained with a Ru/Pigiphos acetonitrile derivative) for a type of reaction known to give excellent results (e.e. > 90%) with Ru^{II} chiral complexes [459,460]. Pigiphos was also used to yield rhodium and nickel complexes as catalyst precursors for acetalization of aldehydes and ketones with glycols [461].



Scheme 128.

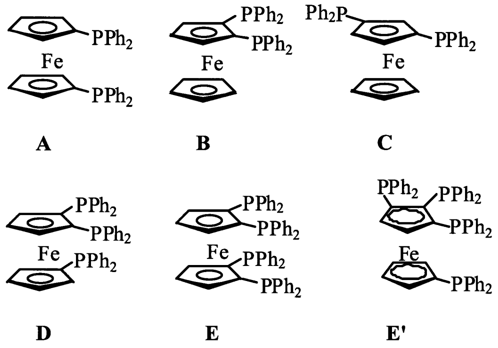
Butler et al. have reported the synthesis of the bis-1-(1′-diphenylphosphinoferrocenyl) phenylphosphine, called triphosfer, obtained from 1,1′-dibromoferrocene after two successive reactions with ^{n}BuLi and $PPhCl_2$. Triphosfer reacts with $[RuCl_2(PPh_3)_3]$ to give the complex $[RuCl_2(triphosfer)]$ (Scheme 129) [462]. Interestingly, just as $[RuCl_2(Pigiphos)]$, the complex has a distorted square-pyramidal five-coordinate geometry.



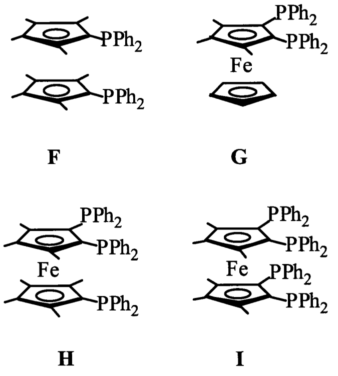
Scheme 129.

However, several important differences can be noticed: the first is that in the case of [$RuCl_2$(triphosfer)] the apical position is occupied by the phosphorus atom shared by the two ferrocenyl groups. In Butler's compound the chlorine atoms are *trans* to each other, which is extremely rare for $M(PPP)L_2$ square-pyramidal species or even $M(PPP)L_3$ octahedral species (see Section 2); even in [$RuCl_2$(Pigiphos)] the Cl atoms are in mutual *cis* positions [459]. One of the phenyl hydrogens of one of the PPh_2 groups in the basal plane makes a close approach to the metal from the opposite side of the phosphorus. The Ru···H distance of about 2.89 Å provides a pseudo-octahedral environment around the ruthenium atom. This contact is relevant in that it could block the vacant octahedral site of the metal center. A similar situation observed for [$RuCl_2(PPh_3)_3$] was suggested to give extra stability to the electron "deficient" metal center. Finally, the likely more constrained geometry of [$RuCl_2$(triphosfer)] results in an important intrinsic structural difference from [$RuCl_2$(Pigiphos)], since triphosfer lacks the flexibility provided to Pigiphos by the methylene bridges between the ferrocene and the central phosphorus. Unfortunately, no catalytic behavior was described for the ruthenium triphosfer complex in this report [462].

New synthetic procedures were recently developed by Butler and co-workers leading to various ferrocenyl polyphosphines alternative to dppf (i.e. 1,1′-bis(diphenylphosphino)ferrocene, **A** in Scheme 130), for instance: 1,2-bis(diphenylphosphino)ferrocene, **B**, 1,3-bis(diphenylphosphino)ferrocene, **C**, 1,1′,2-tris(diphenylphosphino)ferrocene, **D** or 1,1′,2,2′-tetrakis(diphenylphosphino)ferrocene, **E**, [463,464]. In parallel to this work Broussier et al. have obtained the permethyl-analogues noted **F**, **G**, **H**, **I** in Scheme 131 [465]. Among these polyphosphines the tridentate **D** and **H**, which were mainly characterized by NMR studies, are the most relevant in the present discussion. The strategies to obtain the triphosphines **D** and **H** were different: Butler et al. started from the ferrocene backbone already formed with 1,1′-dibromoferrocene which undergoes successive lithiation and electrophilic quenching with $ClPPh_2$ [463]. Broussier and co-workers first formed the appropriate phosphine-substituted cyclopentadienyl rings [466], and then obtained the ferrocenyl compounds from reaction with $FeCl_2$ [465]. Unfortunately, and contrary to the tetradentate analogues (see Section 5.2), solid-state structural data for complexes formed with these ferrocenyl phosphines are not yet available. Investigation of the coordination behavior of **D** towards transition metals would be of interest. Preliminary results from Broussier et al., have shown the reactivity of **H** towards [$Cr(CO)_4$(nbd)] leading to a 1,2-biligate coordination to chromium despite the possibility of tridentate coordination, leaving thus the 1′-phosphine atom non-coordinated. The complex [$Cr(CO)_4$(**H**)] should be very similar to the complexes [$W(CO)_4$(**G**)] and [$Cr(CO)_4$(**G**)] formed with the diphosphine **G**. For [$W(CO)_4$(**G**)] a crystal structure was solved [465]. An application of this biligate coordination behavior would be to take advantage of the pendant phosphine to form heterobimetallic architectures, and to use the potential cooperative effect between metals to tune the catalytic activity in various reactions.



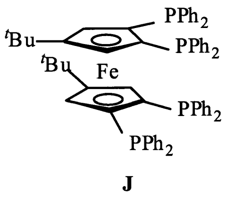
Scheme 130.



Scheme 131.

5.2. Tetraphosphine ferrocenyl ligands

The ferrocenyl tetraphosphines derived from dppf and their metal complexes, unknown until the pioneering work of Broussier and Butler, have developed rapidly. The 1,1′,2,2′-tetrakis(diphenylphosphino)-3,3′,4,4′,5,5′ hexamethylferrocene, **I**, (Scheme 131) [465], 1,1′,2,2′-tetrakis(diphenylphosphino)ferrocene, **E** (Scheme 130) and 1,1′,2,3-tetrakis(diphenylphosphino)ferrocene **E′** [464] were the first ferrocenyl tetraphosphines of this



Scheme 132.

type to be described. Another tetraphosphine species was recently obtained: 1,1′,2,2′-tetrakis(diphenylphosphino)-4,4′-di-*tert*-butylferrocene, **J** (Scheme 132) [467,468].

I was obtained in 85% yield from $FeCl_2$ by reaction with two equivalents of the 1,2-bis(diphenylphosphino)-3,4,5-trimethylcyclopentadienyllithium anion in toluene [465]. The molecular structure of **I** shown in Fig. 1 exhibits a centrosymmetric structure at the iron center. The 1,2-substitutions on the cyclopentadienyl rings lead to phosphorus atoms having a greater displacement from the ring plane outside the iron atom compared to known phosphine-mono-substituted Cp rings: 0.38 and 0.09 Å (*exo*-type), while a deviation of 0.07 Å was, for instance, detected for the phosphorus atom in the case of the mono-substituted $[C_5Me_4PPh_2]_2Fe$ complex. From the orientation of the adjacent phosphorus on the same Cp ring, a repulsion of the lone electron pairs is expected. That may partly explain the 0.38 Å displacement of one phosphorus atom out of the Cp plane. The four phenyl groups of two PPh_2 substituents on the same Cp ring form two pairs of virtually parallel cycles. The shortest distance between two phenyl planes is around 3.4 Å, which is in the range of the distances recorded between two parallel π-systems. The other bond distances and bond angles of the molecule compare well to those of classical ferrocenyl phosphine structures described earlier (dppf) [457]. From NMR data in solution, this phosphine in $[Cr(CO)_4(\mathbf{I})]$ is apparently 1,2-biligate such as in the case of the 1,1′,2-tridentate analogue (see Section 5.1 above), one of the Cp rings thus having two potential phosphine sites free for coordination [465].

The tetraphosphine ligands 1,1′,2,2′-tetrakis(diphenylphosphino)ferrocene, **E**, and 1,1′,2,3-tetrakis(diphenylphosphino)ferrocene, **E**′ (Scheme 131), were characterized in solution by spectroscopic methods [464], and the NMR data compare well with those obtained for **I**. Their transition metal coordination chemistry and reactivity are still under investigation.

The idea to synthesize the ferrocenyl tetraphosphine **J**, with a tertiary butyl substituent in the 4-position on the cyclopentadienyl ring, has arisen from the aim to direct a 1,2-phosphine di-substitution on the Cp ring *without* the need to block all the other positions (3,4,5).

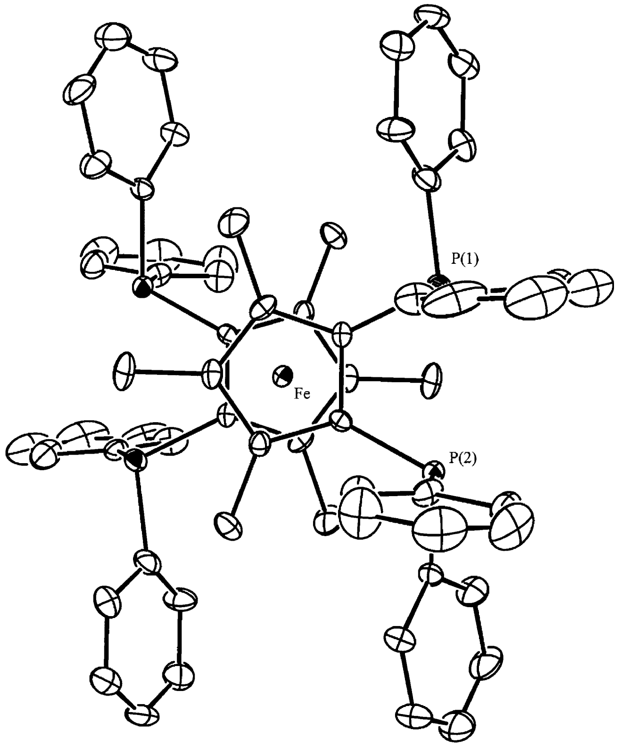


Fig. 1. Molecular structure of **I**.

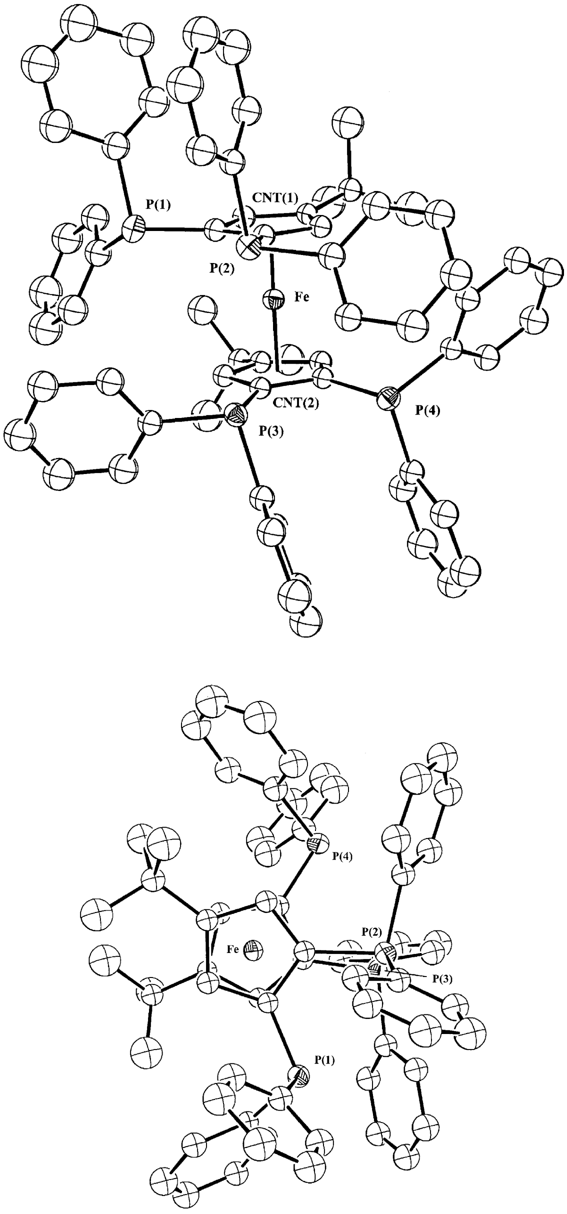


Fig. 2. ORTEP view of **J**.

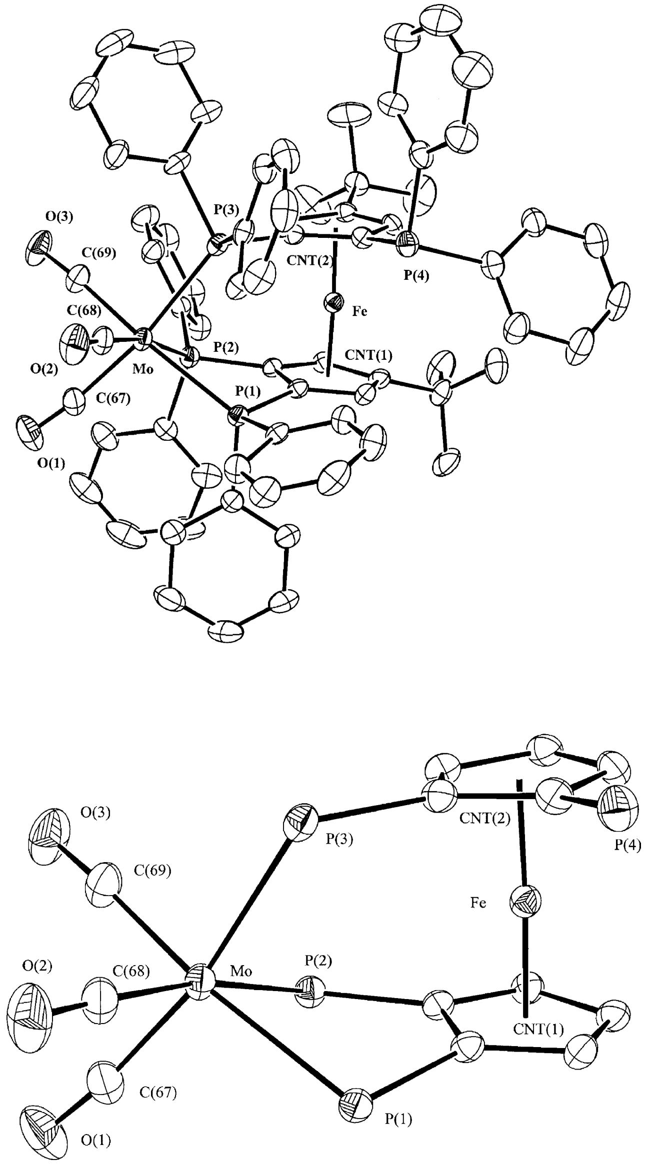
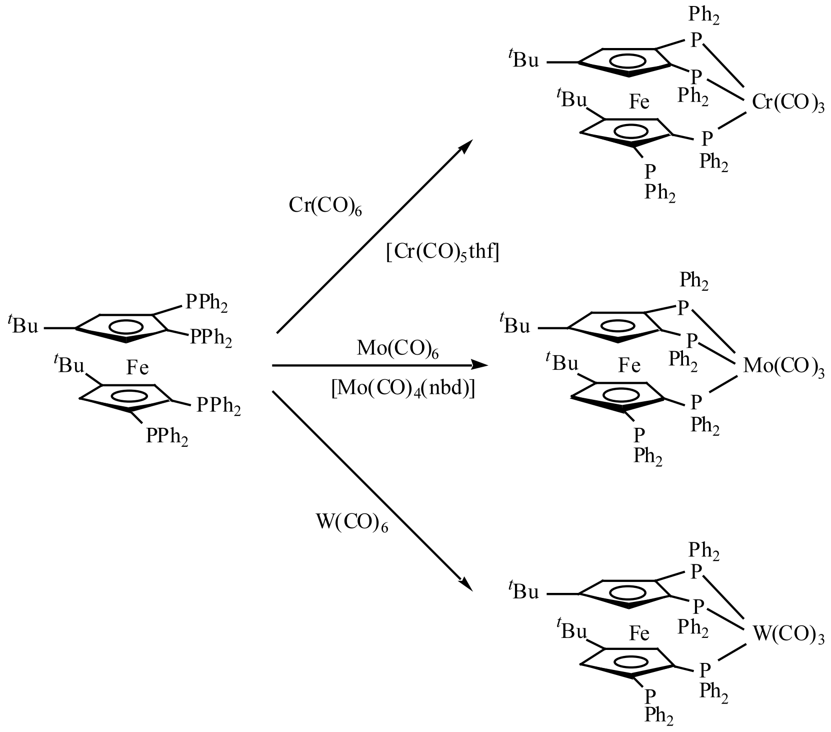


Fig. 3. ORTEP views of [Mo(CO$_3$)**J**].

Indeed, without a prior appropriate blocking of positions on Cp the 1,3-phosphine di-substituted Cp is invariably obtained [15]. In contrast, successive lithiations and reactions with ClPPh$_2$ of the ^{t}BuCp ring direct the phenylphosphine substituents β of the bulky tertiary butyl group, yielding thus the 1,2-diphenylphosphino-4-*tert*-butylcyclopentadienyl lithium salt [15]. **J** was obtained in 70% yield when FeCl$_2$ reacts with two equivalents of the 1,2-bis(diphenylphosphino)-4-tertiary butylcyclopentadienyllithium anion in toluene at reflux [467]. The molecular structure of **J**, displayed in Fig. 2, is an example of conformational chirality (atropoisomerism).

The absence of any symmetry plane or symmetry center, in contrast to **I**, results in the potential existence of two enantiomers. This interesting stereoisomerism is a direct result of the different orientations adopted by the two Cp groups in the polyphosphine. The conformational preference for minimum energy configuration leads to the tertiary butyl groups in staggered positions. The eight phenyl-groups on the phosphorus atoms are tightly interlocked generating an arrangement with four pairs of almost parallel and orthogonal rings. The phosphorus atoms display a large *exo* deviation outside the Cp plane of 0.186(2) Å for P(1) and 0.254(2) Å for P(2). It is useful to compare the relative arrangement of the phosphorus atoms in **J** with the one in **I**. While in the tetraphosphine **I** the two phosphorus of one Cp ring are as distant as possible from the two others phosphorus on the second Cp ring, this is no longer the case for **J**. Indeed, in **J** the arrangement seems oriented by the ^{t}Bu groups which adopt a position minimizing the steric interactions. As a consequence the tetraphosphine **J** should more easily allow a higher coordination number than the biligate coordination detected in **I**. Preliminary results with Group 6 metals have shown a 1,1′,2-triligate coordination at the metal center for the carbonyl complexes [M(CO)$_3$**J**] (M = Mo, Cr, W) (Scheme 133) [468]. The molybdenum complex is displayed in Fig. 3 [468]. Interestingly, from the precursor complex [Mo(CO)$_4$(nbd)] a biligate compound (such as [Mo(CO)$_4$**I**]) was expected more than a triligate [Mo(CO)$_3$**J**] complex. Similarly, from [Cr(CO)$_5$(thf)] a monodentate complex was expected with the substitution of the thf molecule. However, in both cases the triligate polyphosphine complex was obtained as a single product even when the reaction was carried out in the presence of one more equivalent of M(CO)$_6$. These reactions occur despite the strong geometric constraints undergone by the different moieties in the resulting complexes. Comparison of the crystalline structure of **J** and of [Mo(CO)$_3$**J**] shows that the ferrocenyl backbone displays only minor modifications: the ^{t}Bu Cp rings are slightly less staggered than in **J** (twist angle 58°), and the Cp rings parallel in **J** lean towards each other in the molybdenum complex (inclination angle 7°). On the other hand, the octahedral environment at the Mo center is severely distorted. The angle P(1)–Mo–P(2) of 75.68(3)° results directly from the adjacent 1,2-positions of the phosphorus on the Cp ring. The angles P(1)–Mo–P(3) 87.85(3)° and P(2)–Mo–P(3) 98.84(4)° are very different and result from the impossibility of P(3) finding a symmetric position with regard to P(1) and P(2). Finally, the four phosphorus centers remain in the *exo* position, with a deviation from the Cp plane of 0.35 Å for P(1) and 0.25 Å for P(4), the deviation from the Cp planes being insignificant for P(2) and P(3) (respectively 0.05 and 0.03 Å). It is interesting to note that Long and co-workers have obtained an analogous *S*,*S*,*S*-triligate bonding mode to tungsten with their elegant tetradentate 1,1′,2,2′-tetrakis(methylthio)ferrocene (TMSF) ligand [469,470]; the structure of [W(CO)$_3$(TMSF)] is rather similar to that of

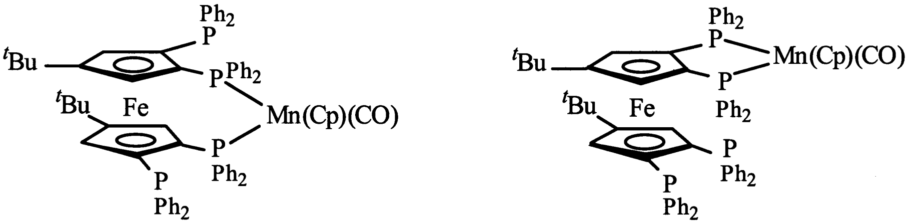


Scheme 133.

$[Mo(CO)_3$**J**$]$ [469], suggesting that this kind of constrained geometry with tetradentate ferrocenyl ligands might not be so unusual.

The reactivity of the tetraphosphine **J** under irradiation with the manganese precursor $[MnCp(CO)_3]$ was also studied [468]. The two biligate phosphine complexes [MnCp(CO)**J**] shown in Scheme 134 were identified. From fractional crystallization, single crystals of a 1,1′-biligate heteroannular complex were isolated. The molecular structure of this complex is described in Fig. 4 [468]. Analogous structures were reported with dppf by Onaka et al. which display very similar features [471]. The inclination angle between the two Cp rings is 4.5(5)°. The *exo* deviation from the Cp plane of the phosphorus atoms is P(1) 0.52 Å, P(2) 0.07Å, P(3) 0.20 Å, P(4) 0.17 Å, and the unique position of P(1) might be explained by a weak interaction with the oxygen atom of the carbonyl group (distance P···O 3.39 Å). The Mn metal center lies in a distorted tetrahedral environment where the angles range from 88.2(3)° for C(77)–Mn–P(3) to 124.4° for CNT(3)–Mn–P(3). The P(2)–Mn–P(3) angle ranges in classical value with 98.86(9)°.

Tetradentate ferrocenyl polyphosphines have shown great diversity in structural architecture; mononuclear and homodinuclear complexes of transition metals with either monoligate, 1,1′- or 1,2-biligate, and 1,1′,2-triligate coordination were identified. This versatility can be somewhat directed by substitution of bulky groups on the Cp rings with a view to block the rotational abilities of the ferrocenyl ligands. Several studies are in progress to characterize Group 9 (rhodium, iridium) and Group 10 (nickel, palladium) metals with ferrocenyl tetraphosphines and their behavior in various catalytic reactions. The specific geometry of ferrocene with the independence between the two Cp rings as well as the relative flexibility at the iron center, and the rotational mobility of the Cp rings will likely give access in the future to other original structures and coordination modes for polyphosphine substituted ferrocenyl species.



Scheme 134.

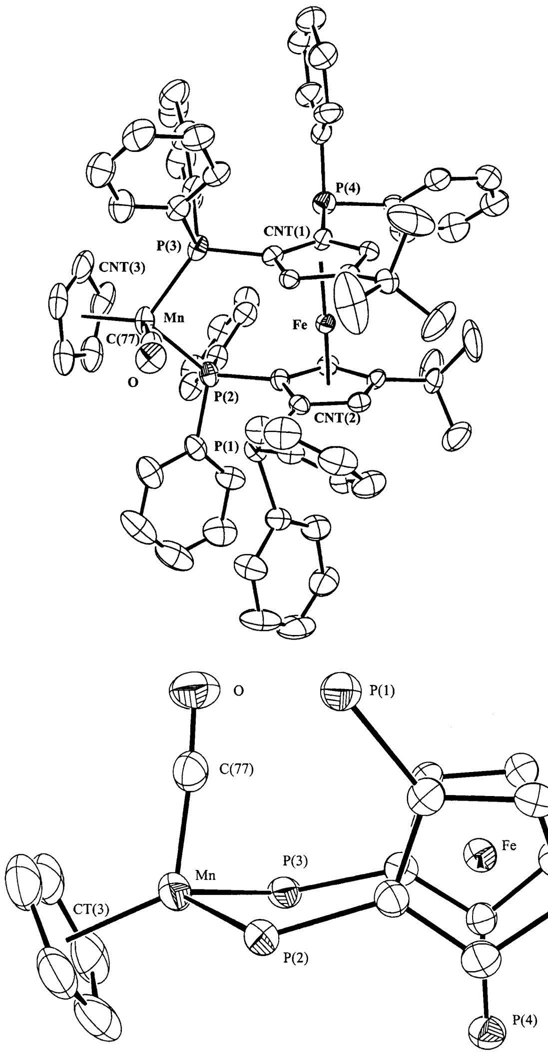
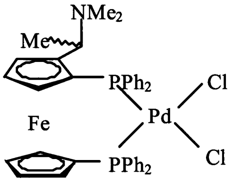


Fig. 4. ORTEP views of [MnCp(CO)**J**].

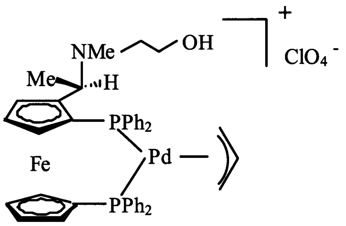
5.3. Nitrogen-containing phosphine ferrocenyl ligands

5.3.1. Ligands with 1N/2P

An interesting route for tuning the properties of ferrocenyl polyphosphines can be to exchange one or several phosphorus atoms by other donor atoms such as nitrogen or sulfur. X-ray diffraction studies of several Group 10 complexes containing amino-ferrocenyl diphosphines were conducted. The various species displayed similar general features. In 1987, Hayashi and co-workers isolated [$PdCl_2$(BPPFA)] (Scheme 135), in which BPPFA is the racemic (*S*)-*N*,*N′*-dimethyl-1-[(*R*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine ligand, bearing two phosphorus and one nitrogen potential donor atom [472]. The authors later reported an allyl–palladium complex incorporating a chiral ferrocenylphosphine parent of BPPFA (Scheme 136) [473]. More recently, Landis and co-workers prepared [PtMeI(*rac*-BPPFAPh)] by reaction of [Pt(Me)I(cod)] with *rac*-BPPFAPh (where BPPFAPh is the name for 1,1′-bis(diphenylphosphino)-2-[1((1-hydroxy-2-phenyl)-amino)ethyl]-ferrocene) [474] (Scheme 137). The geometry of all these complexes is obviously governed by the palladium and platinum demand for a square-planar environment. As a consequence the phosphorus atoms adopt a chelating 1,1′-biligate coordination on the metal while the co-ligands occupy the two remaining mutual *cis*-position. The dangling aminoalkyl side chains on the Cp rings introduce a chiral center which reinforces the planar asymmetry of the ferrocenyl ligand; these complexes were used by the authors in asymmetric catalytic reactions: Grignard cross-coupling or allylic amination [472–474].



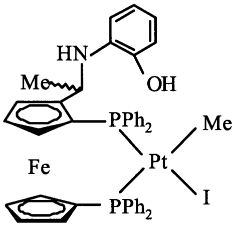
Scheme 135.



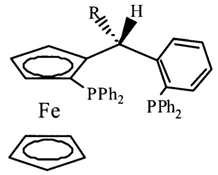
R-(*S*-ferrocenyl) isomer

Scheme 136.

Knochel et al. have described the synthesis from ferrocene of a family of chiral ferrocenyl ligands with two phosphanyl substituents in the α,ε positions (Scheme 138) [475]. These ligands associated with ruthenium were highly efficient for the enantioselective hydrogenation of β-ketoesters (e.e. > 95%). Using the rhodium precursor [$Rh(nbd)_2$]BF_4 with this class of ferrocenyl phosphine, the enantioselective hydrogenation of methylacetamido cinnamate Ph(H)C=C{N(H)Ac}(COOMe) into the amino acid derivative $PhCH_2$–CH(NHAc)(COOMe) proceeds with e.e. ≥ 92%. In the rhodium complex (Scheme 139) [475] the ligand is triligate and forms two six-membered metallo-

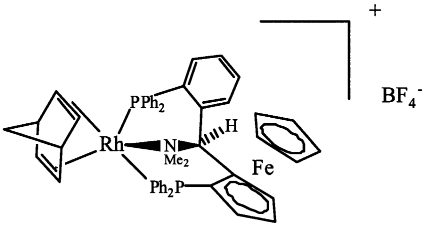


Scheme 137.



R = NMe$_2$, N-pyrrolidyl

Scheme 138.



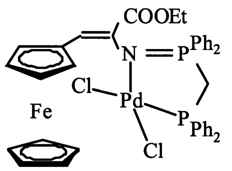
Scheme 139.

cycles, and the rhodium center is in an unusual five-coordinate environment. Interestingly, hydrogenation using a parent ligand with a R = ^{i}Pr moiety instead of the coordinated R = NMe$_2$ amino group (see Scheme 138) gives comparable enantioselectivities, questioning, thus, the role of the nitrogen coordination in the catalytic process.

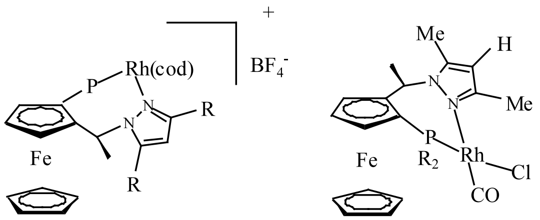
Molina and co-authors have described an original ferrocenyl derivative displaying a nitrogen/phosphorus biligate coordination mode on palladium (Scheme 140) [476]. In this particular nitrogen/diphosphine ligand the phosphorus atom is not directly bonded to the Cp ring. The Pd^{II}-metallacycle obtained, for obvious steric constraints, forms a five-membered heterocycle with a central P^{V} phosphorus atom (double-bonded to the nitrogen) which is not available to form a metal–phosphorus bond. The complex represents the first example of a ferrocene derivative containing an iminophosphorane phosphine ligand. The palladium atom is surrounded by a distorted square-planar environment with the chloride atoms in mutual *cis*-positions.

5.3.2. Ligands with 2N/1P

Chiral mixed ferrocenyl ligands with one phosphorus and two nitrogen donor atoms were prepared by Togni and co-workers; the ligands contain a phosphine group in position 1 of one Cp ring, and in position 2 the side chain contains a pyrazolyl group [477]. The rhodium complexes in Scheme 141 were easily obtained via a substitution reaction involving the precursor complexes [Rh(cod)$_2$]BF$_4$ or [Rh(CO)$_2$Cl]$_2$ and the appropriate N$_2$P ferrocenyl ligand. The various species displayed very similar conformational features. The rhodium center lies in a distorted square-planar environment and is connected to the phosphorus atom and to one nitrogen atom of the pyrazolyl group, thus leading to a biligate *N*,*P*-coordination mode. The co-ligands occupy the remaining mutual *cis*-positions. The bonding parameters fall in the expected range of values. Finally, in this work, hypotheses were provided to correlate the structural and electronic features of the different complexes with their reactivity in the rhodium-catalyzed enantioselective hydroboration of styrene [477].



Scheme 140.



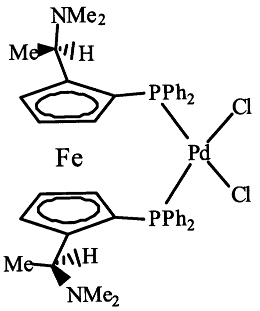
R = CF$_3$
or CH$_3$

R = 3,5-Me$_2$-Ph
or 4-Me-Ph

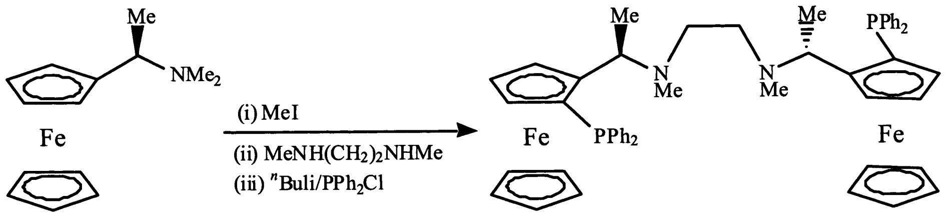
Scheme 141.

5.3.3. Ligands with 2N/2P

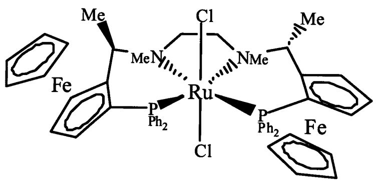
Hayashi and co-workers have prepared the chiral N$_2$P$_2$ ferrocenyl phosphine ligand 2,2′-bis[1-(*N*,*N*′-dimethylamino)ethyl]-1,1′-bis(diphenylphosphino)ferrocene (called **BPPFAII**) [478]. An X-ray diffraction study of the complex [PdCl$_2$(BPPFA**II**)] showed a *P*,*P*-biligate coordination mode for BPPFA**II** and a square-planar geometry at the palladium center with *cis* chlorine atoms (Scheme 142). Compared with the complex [PdCl$_2$(BPPFA)] (Scheme 135) [472], quoted above, [PdCl$_2$(BPPFA**II**)] has a larger P–Pd–P angle value of 103.43(5)°. The location of (1-dimethylamino)ethyl side chains on BPPFA**II** in [PdCl$_2$(BPPFA**II**)] is different from that of BPPFA in [PdCl$_2$(BPPFA)]: both of the side chains are directed apart from the PdCl$_2$



Scheme 142.



Scheme 143.



Scheme 144.

moiety, while with BPFFA the chain is directed toward $PdCl_2$. This results from different twist angles of the Cp rings in the two ligands.

Kim et al. have described the synthesis of chiral N_2P_2 C_2-symmetric bisferrocenyldiamines, prepared from the chiral template *N*,*N*-(dimethylamino)-1-(*R*)-ferrocenylethylamine (usually named (*R*)-FA) by reaction with MeI, followed by nucleophilic substitution with *N*,*N′*-dimethylenediamine and ortholithiation/phosphination (Scheme 143) [479]. This N_2P_2 ligand reacts with $[RuCl_2(DMSO)_4]$ to give the tetraligate *N*,*N*,*P*,*P*-ruthenium complex displayed in Scheme 144. The metal center is in a distorted octahedral environment with *trans* chloride ligands in axial positions. This ruthenium compound is an efficient catalyst for the asymmetric cyclopropanation of olefins such as β-methylstyrene or indene (high *trans*:*cis* selectivity 98:2, with e.e. > 80%).

6. Concluding remarks

In the present review the structural diversity of the important tridentate and tetradentate polyphosphine ligands was illustrated with emphasis on results of the last decade. A good knowledge of the structural characteristics of these species is the first step towards the understanding and control of the reaction chemistry, and thus towards catalytic activity, which remains for the moment, the principal application of these polyphosphines complexes. Promising areas of research currently under study include: modification of polyphosphines for water-soluble ligands, novel chiral polyphosphines for asymmetric catalysis, ferrocenyl polyphosphines and their heterobimetallic Fe/M complexes, and polyphosphines' reactivity enhanced by heteroelement substitution at the phosphorus.

BPPFA	*N*,*N′*-dimethyl-1-[1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine
BPPFAII	1,1′-bis(diphenylphosphino)-2,2′-bis[1-(*N*,*N′*-dimethylamino)ethyl]-ferrocene
BPPFAPh	1,1′-bis(diphenylphosphino)-2-[1((1-hydroxy-2-phenyl)amino)ethyl]-ferrocene
ddpx	α,α,α′,α′-tetrakis-(diphenylphosphino)-*p*-xylene
dpbc	*N*,*N′*-bis[*o*-(diphenylphosphino)benzylidene]cyclohexane-1,2-diamine
dpmdpB	2,3-bis[(diphenylphosphino)methyl]-1,4-bis(diphenylphosphino)butane
dpmp	bis[(diphenylphosphino)methyl]-phenylphosphine, $(Ph_2PCH_2)_2PPh$
dppcb	*cis*,*trans*,*cis*-1,2,3,4-tetrakis(diphenylphosphino)cyclobutane
dppe	1,2-bis(diphenylphosphino)ethane
dppen	1,2-bis(diphenylphosphino)ethene
dppf	1,1′-bis (diphenylphosphino)ferrocene
dppm	bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
eLTTP	ethyl-substituted linear tetratertiary phosphine, $Et_2P{-}(CH_2)_2{-}PEt(CH_2){-}PEt(CH_2)_2{-}PEt_2$
eptp	[2-(diphenylphosphino)ethyl][3-(diphenylphosphino)propyl]-phenylphosphine, $(Ph_2PCH_2CH_2CH_2)$-$PPh(CH_2CH_2PPh_2)$
etp	bis[2-(diphenylphosphino)ethyl]-phenylphosphine, $(Ph_2PCH_2CH_2)_2$ PPh
etpCy	$(Cy_2PCH_2CH_2)_2PPh$
etpE	$(Et_2PCH_2CH_2)_2PPh$
H_2dpbc	*N*,*N′*-bis[*o*-(diphenylphosphino)-benzyl]cyclohexane-1,2-diamine
H_2dppd	*N*,*N′*-bis[2-(diphenylphosphino)-phenyl]-propane-1,3-diamine
MesetpE	bis[2-(diethylphosphino)ethyl]-mesithylphosphine, $(Et_2PCH_2CH_2)_2$-$P(2,4,6\text{-}Me_3C_6H_2)$
NP_2N	*N*,*N*-bis-(2-diphenylphosphino-ethyl)-*N′*-(2-diethylaminoethyl)amine
np_3	tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$
P_2S	2,2-bis(diphenylphosphinomethyl)-1-phenylthiopropane, $CH_3C(CH_2SPh)$-$(CH_2PPh_2)_2$

P_2S_2	1,8-bis(diphenylphosphino)-3,6-dithiaoctane $(Ph_2PCH_2CH_2)S(CH_2)_2S(CH_2CH_2PPh_2)$
P4	Hexaphenyl-1,4,7,10-tetraphosphadecane, $Ph_2P{-}(CH_2)_2{-}PPh(CH_2)_2{-}PPh(CH_2)_2{-}PPh_2$, also called Tetraphos I
Pigiphos	bis{(*S*)-1-[(*R*)-2-(diphenylphosphino)-ferrocenyl]ethyl}cyclohexylphosphine
pnnp	$Ph_2P(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2PPh_2$
PNP*	$\{PhC(H)Me\}N(CH_2CH_2PPh_2)_2$
PP_3	tris[2-(diphenylphosphino)ethyl]phosphine, $P(CH_2CH_2PPh_2)_3$, or Tetraphos II
PP_3Cy	tris[2-(dicyclohexylphosphino)ethyl]phosphine, $P(CH_2CH_2PCy_2)_3$
PP_3Me	tris[2-(dimethylphosphino)ethyl]phosphine, $P(CH_2CH_2PMe_2)_3$
PPNN	2,2′-bis[{*o*-(diphenylphosphino)benzylidene}amino]-6,6′-dimethylbiphenyl
PSiN(H)SiP	1,3-bis[(diphenylphosphino)methyl]tetramethyldisilazane, $(Ph_2PCH_2SiMe_2)_2NH$
PSP	1,5-bis(diphenylphosphino)-3-thiapentane, $(Ph_2PCH_2CH_2)S(CH_2CH_2PPh_2)$
PSSP	1,9-bis(diphenylphosphino)-3,7-dithianonane, $(Ph_2PCH_2CH_2)S(CH_2)_3S(CH_2CH_2PPh_2)$
$PSSP_{OH}$	1,9-bis(dihydroxymethylphosphino)-3,7-dithianonane
QP	tris[*o*-(diphenylphosphino)phenyl]phosphine, $P(o\text{-}C_6H_4PPh_2)_3$
(*RRR*)Siliphos	$MeSi[CH_2P(^tBu)Ph]_3$
sulphos	$[Na^+, {}^-O_3S(C_6H_4)CH_2C(CH_2PPh_2)_3]$
$td(CF_3)pme$	$CH_3C[CH_2P(m\text{-}CF_3C_6H_4)_2]_3$
tdmme	bis[3-(dimethylphosphino)propyl]methylphosphine, methyl derivative of ttp
tdmpe	1,1,1-tris[(dimethylphosphino)methyl]ethane, $CH_3C(CH_2PMe_2)_3$
tdpme	1,1,1-tris[(diphenylphosphino)methyl]ethane, $CH_3C(CH_2PPh_2)_3$, or triphos
tdppcy	*cis*,*cis*-1,3,5-$(PPh_2)_3$-C_6H_{12}
tdppcycn	*cis*,*cis*-1,3,5-$(PPh_2)_3$-1,3,5-$R_3C_6H_6$ (R = CN)
tdppcyme	*cis*,*cis*-1,3,5-$(PPh_2)_3$-1,3,5-$R_3C_6H_6$ (R = COOMe)
tdppmtmcy	*cis*,*cis*-1,3,5-tris(diphenylphosphinomethyl)-1,3,5-trimethylcyclohexane
tedicyp	*cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane
tp	bis[2-(diphenylphosphino)phenyl]phenylphosphine
TPm	tris[3-(dimethylphosphino)propyl]phosphine, $P(CH_2CH_2CH_2PMe_2)_3$
triphosfer	bis-1-(1′-diphenylphosphinoferrocenyl)phenylphosphine
tripod	$HC(PPh_2)_3$
ttp	bis[3-(diphenylphosphino)propyl]phenylphosphine, $(Ph_2PCH_2CH_2CH_2)_2PPh$
ttpcy	bis[3-(dicyclohexylphosphino)propyl]phenylphosphine, $(Cy_2PCH_2CH_2CH_2)_2PPh$

Acknowledgements

We thank the referees for their helpful comments. The authors are also thankful to Dr. Ph. Richard, Ms. S. Royez-Gourier and Ms. G. Delmas for their assistance which made this work much easier.

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