



## Review

## Polydentate phosphines

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## ABSTRACT

Phosphines are one of the most important classes of ligands in chemistry, in both the industrial and academic spheres. This review deals with the design and properties of polydentate phosphines, an original and broad class of multidentate ligands. The multidentate nature of these species has led to special properties, in which the spatial proximity of phosphorus atoms is crucial. The first part gives an overview of oligodentates polyphosphines in which is discussed the types and the basic routes for their synthesis. The review continues with the most important synthetic routes for obtaining complexes. Because of huge amount of literature data this review is not exhaustive, but it collects the most relevant findings in this area. The restriction to structural and spectroscopic properties allows us for a well organized handling of the complex material.

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## 1. Introduction

Phosphines are easy to synthesize and are excellent ligands for transition metals. As a consequence, the steric attributes of the

phosphine ligand are easily controlled. This ability to control the bulk of the ligand permits one to tune the reactivity of the metal complex. For example, if the dissociation of a phosphine ligand is the first step in a reaction, the reaction can be accelerated by

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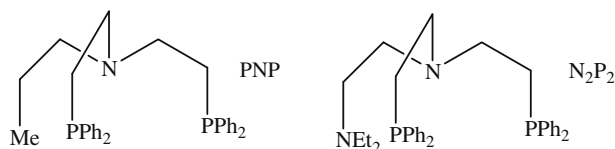


Fig. 1. Example of tripodal phosphines.

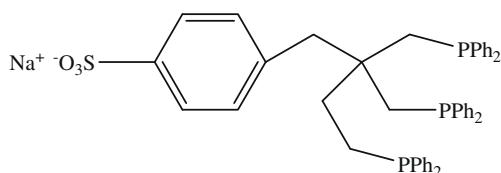


Fig. 2. Structure of sulphos.

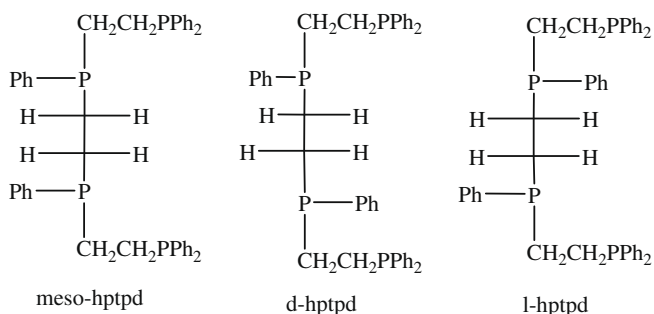


Fig. 3. Linear tetraphosphines.

utilizing a larger phosphine ligand. Likewise, if dissociation is a problem, then a smaller phosphine can be used.

Since the 1960s [1] the rich transition metal chemistry of phosphine ligands has evolved from a desire to exploit the general utility of the phosphine to the increasing development in the structural design [2] of novel metal complexes and their application. Starting from bidentate phosphines which attracted attention because of their excellent ligating properties to almost all transi-

tion metals, tridentate, tetradentate or hexadentate polyphosphine ligands were synthesized and the chemistry of their complexes were studied extensively. Therefore, the organic chemistry of polyphosphines has provided some new branched-species. However, from a structural point of view, the influence of the steric rigidity (or flexibility) of the polyphosphine ligands upon their applications remain an essential parameter to be developed; contrasting results were obtained depending on the type of phosphine and on the type of reaction examined.

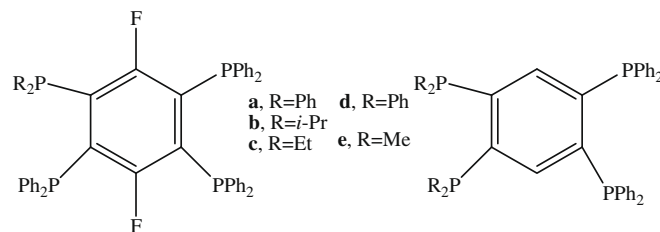
In 1992, Cotton et al. review the synthesis, structural aspects and some applications of polydentate phosphines [3]. The work was completed in 1994 by Mayer et al. who reviewed the reaction chemistry of transitional and non-transitional metal complexes with polyphosphine ligands [4]. Later in 2003, Hierso and co-workers, focused the attention on the molecular architectures of polydentate phosphines (nitrogen or sulfur donor atoms substitute one or several phosphorus atoms)-containing transition metal complexes of the transition elements of Group VIB to XB [5].

The interest of our group was to study the structure of polyphosphines, basic routes of synthesis and  $^{31}\text{P}$  NMR properties of polyphosphines complexes containing transition metal. We focused also our attention on the ferrocenyl polyphosphines ligands and their complexes with transition metals.

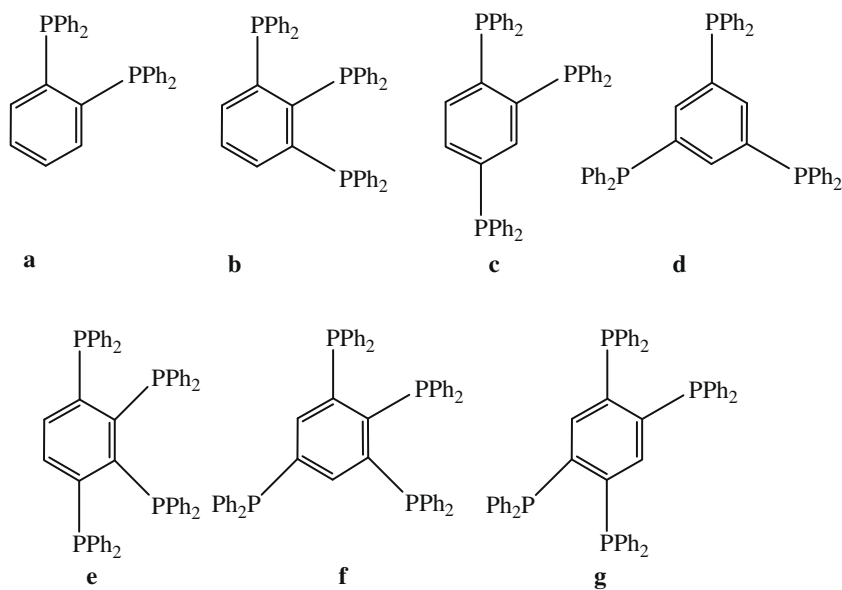
## 2. Structure of ligands

### 2.1. Tripodal phosphines

Tripodal polyphosphines have proven to be useful and versatile ligands in inorganic and organometallic chemistry. The first X-ray



Scheme 2. Structure of tetrakis(phosphino)benzenes.



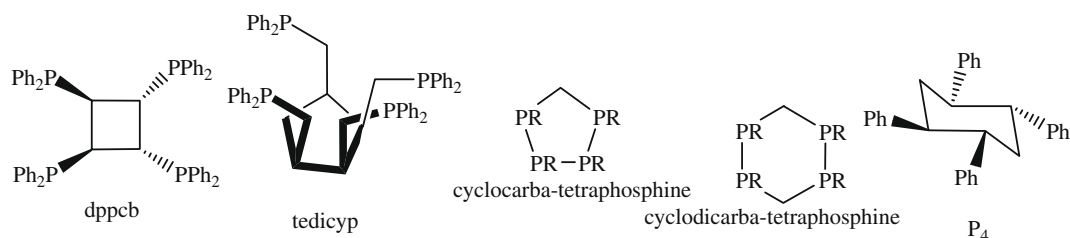
Scheme 1. Phosphinobenzenes.

of a small polyphosphine podands  $\text{HC}(\text{PPh}_2)_3$ , shown that the free molecule has the phosphorus atom lone pairs in a *trans* orientation. Polydentate organophosphines promote the formation of metal clusters upon formation of radial metal–ligand bonds, the metal atoms being located at the center of the molecule 1,1,1-tris-(diphenylphosphinomethyl)ethane which is not only able to stabilize high coordination numbers acting as a tripodal ligand, but also forms tetrahedral or square-planar complexes acting as a bidentate ligand. Ph-triphos [bis(2-diphenylphosphinoethyl)phenylphosphine], was first prepared by King in 1971 [6,7]. In general, phosphine is triligate on the metal center, occupying the facial position in square-pyramidal, trigonal-bipyramidal and octahe-

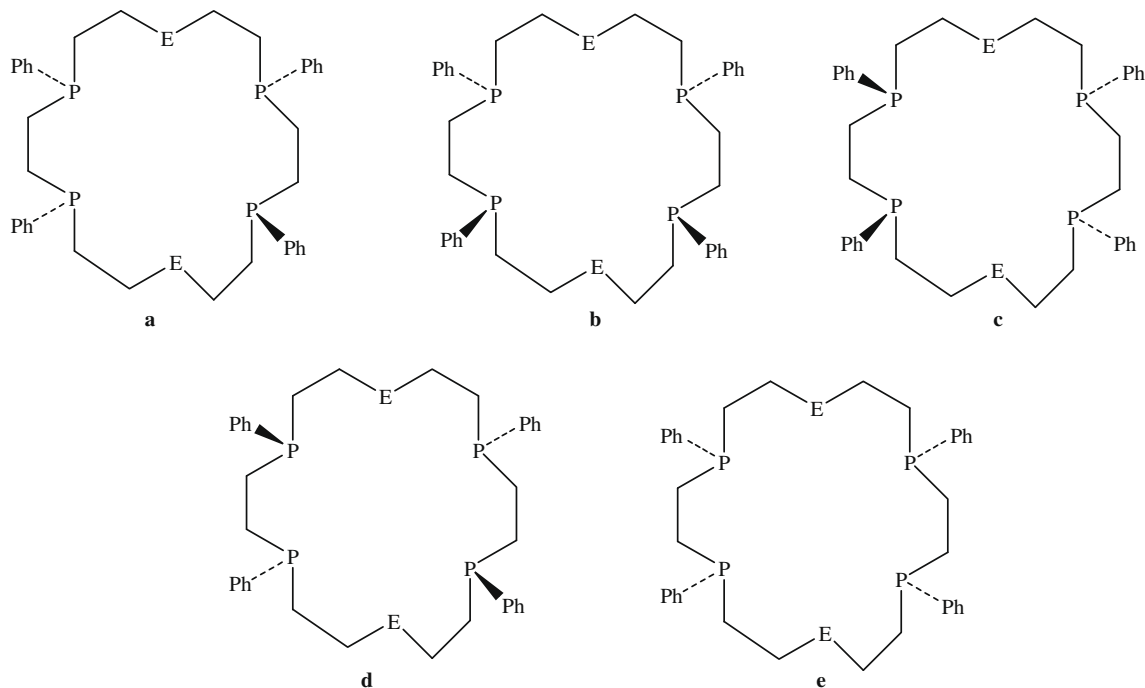
dral arrangements, and generating several free *cis*-positions for the coligands [8].

Studies performed by Jiang include the 1,1,1-tris(diphenylphosphinomethyl)ethane (tdppme), and the tetraphosphines 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane (hptpd). These phosphines are versatile multidentate ligands for transition metals in a variety of oxidation states, and their complexes have been the subject of studies of catalysis, structure–bonding relationships and spectroscopy [9].

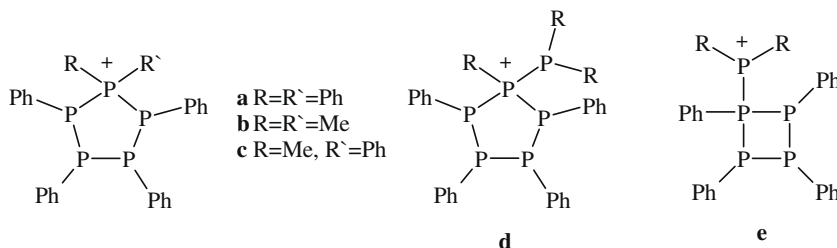
The remarkable aptitude of tripodal polyphosphines, either in the tetradentate  $\text{NP}_3$  and  $\text{PP}_3$  form or in the tridentate triphos assembly to stabilize mono- and (homo-/hetero-)bi-nuclear metal



Scheme 3. Cyclocarba- and cyclodicarba-tetraphosphines.



Scheme 4. Macrocyclic phosphino-ligands.



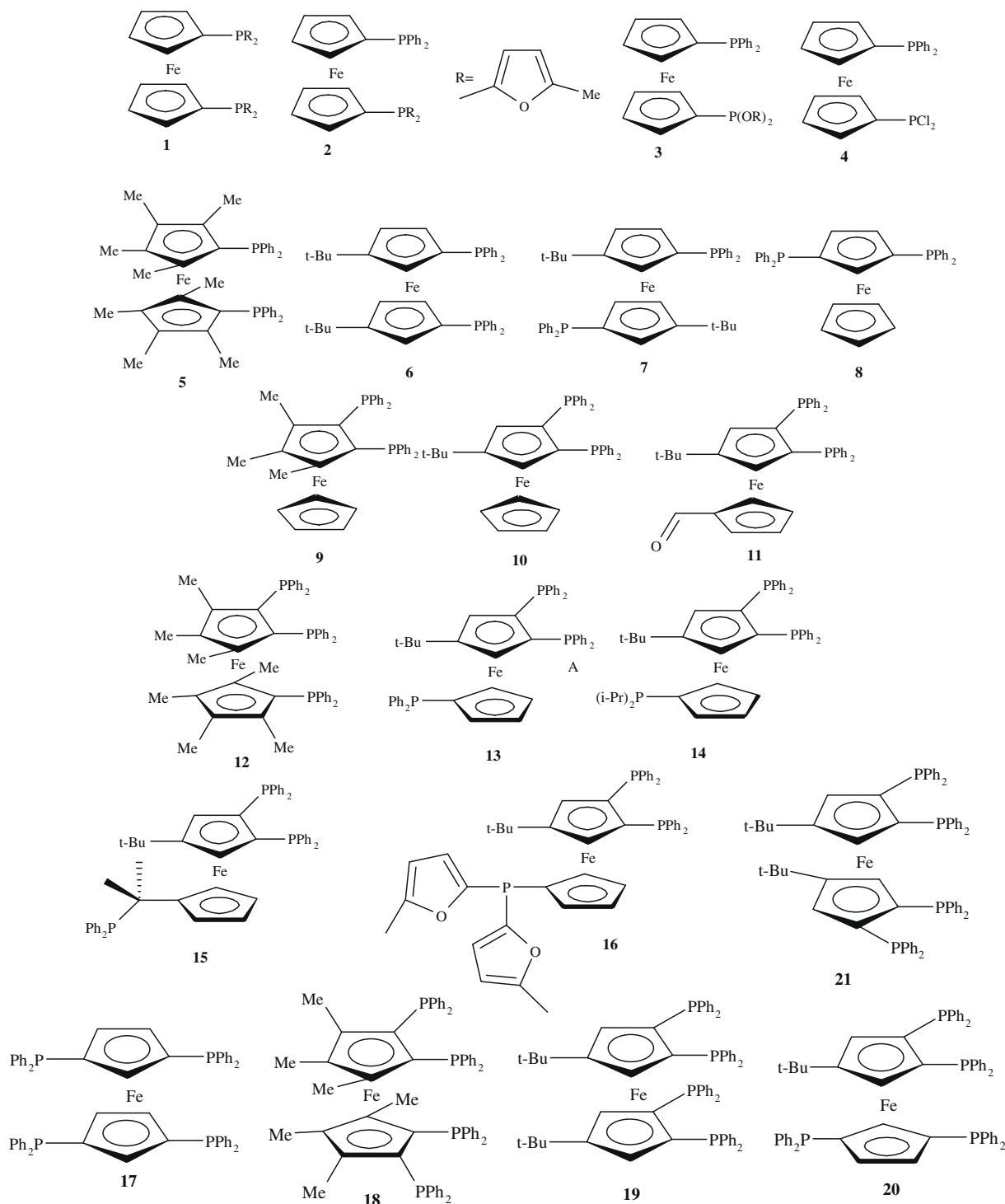
Scheme 5. Cyclic phosphines.

complexes are capable of undergoing multiple and reversible electron-transfer processes. As a result, the central metal ion: iron, cobalt, rhodium, iridium, nickel often accedes to unusual oxidation states. In some cases, these complexes display electron addition/removal processes able to trigger significant molecular rearrangements of the original framework [10].

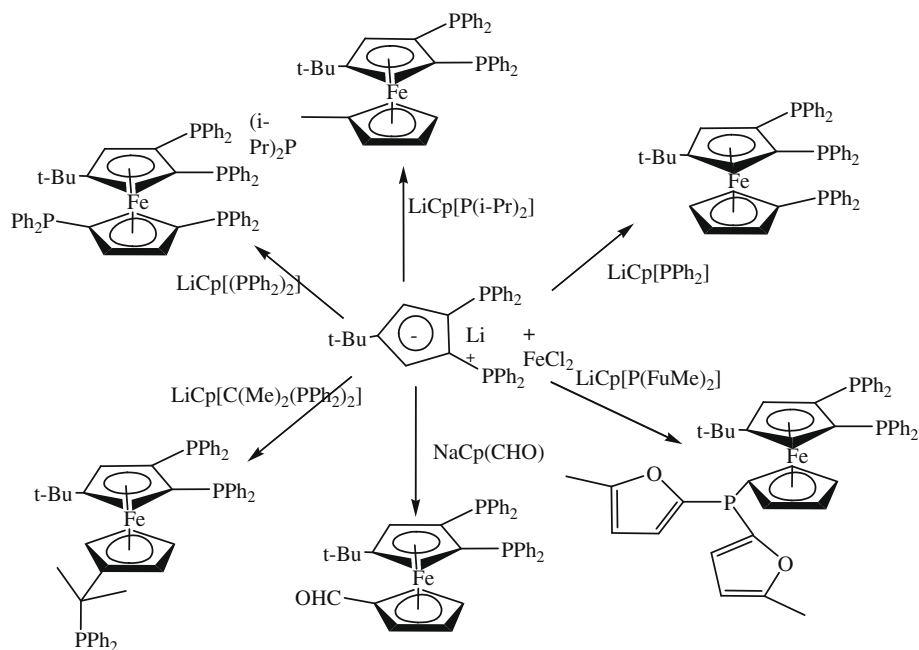
The tripodal tetraphosphines,  $\text{NP}_3$ , TPm and QP display one central phosphorus atom and three peripheral (or terminal) phosphorus atoms. Among these branched polyphosphines the most commonly used as ligand are:  $\text{PP}_3$ ,  $[\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PMe}_2)_3]$ :tris[3-

(dimethylphosphino)propyl] phosphine (TPm) and  $[\text{P}(o\text{-C}_6\text{H}_4\text{PPh}_2)_3]$ :tris[o-(diphenylphosphino)phenyl]phosphine (QP). The flexibility of these podand ligands provides tetradentate coordination in the majority of complexes.

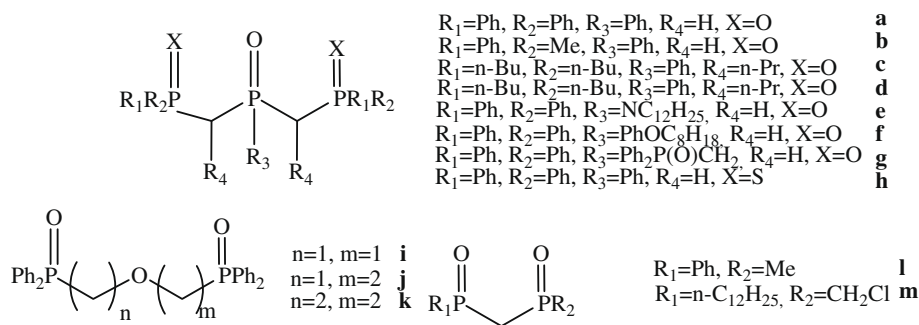
Bianchini et al. [11] developed the solid-state chemistry of Group VIII metal complexes stabilized by tripodal polyphosphines such as  $\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)$ ,  $(\text{NP}_3)$  and  $\text{MeC}(\text{CH}_2\text{PPh}_2)$ , (Me-triphos). Marchi et al. used the following ligands: bis(diphenylphosphino)ethyl propylamine, 1,8-bis(diphenylphosphino)-3,6-dioxaoctane in order to synthesize and characterize nitrido-technetium(V)



**Scheme 6.** Structure of different ferrocenyl polyphosphines.



Scheme 7. The synthesis of di, tri and tetra ferrocenyl phosphines.



Scheme 8. Structure of polyphosphine oxides.

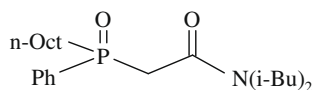
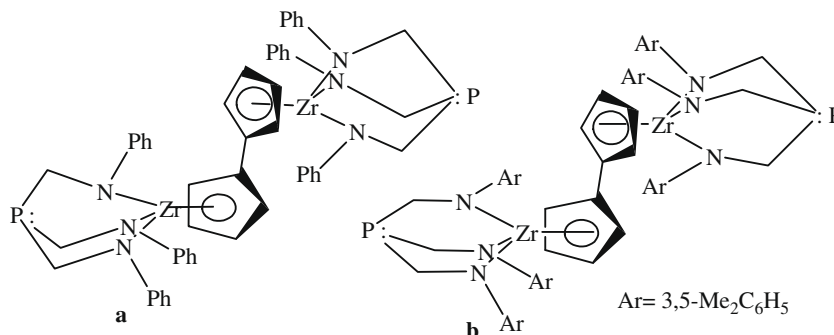


Fig. 4. Octylphenyl(*N,N*-diisobutylcarbamoylmethyl) phosphine.

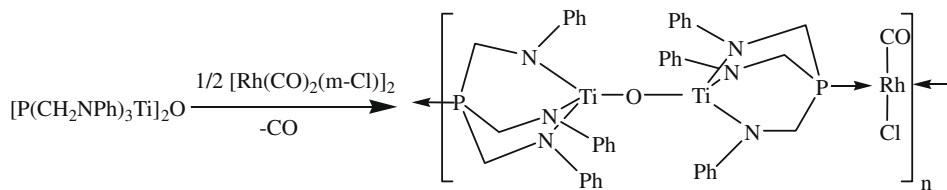
and -rhenium(V) complexes of general formula  $[MCl_2 L]$  [ $M = Tc$  or  $Re$ ] [12].

Using tripodal polyphosphines (Fig. 1), it was found that a variety of homogeneous reactions are catalyzed in a selective way [13].

Bianchini et al. reported in 1995 an important result in the field of tripodal polyphosphine chemistry [14]. The modification of the



Scheme 9. Zirconium complexes.



Scheme 10. Titanium bridged binuclear complex polymer.

phosphine ligand Me-triphos, with the aim to make its metal complexes exclusively soluble in light alcohols and water has led to the new ligand sulphos (Fig. 2). Sulphos have a hydrophilic tail leading the triphos type ligands to their further use in liquid biphasic catalysis.

## 2.2. Linear polyphosphines

A large number of linear triphosphines are known. They lead to various modes of coordination depending on:

- the substituents present on the phosphorus atoms,
- the other ligands bonded to the metal,
- the backbone length of the phosphine.

The most commonly used linear triphosphines were:  $[(\text{Ph}_2\text{PCH}_2)_2\text{PPh}]$  bis[(diphenylphosphino) methyl]phenylphosphine (dpmp),  $[(\text{Ph}_2\text{PCH}_2\text{CH}_2)_2\text{PPh}]$ , bis[2-(diphenylphosphino)ethyl]phenylphosphine (etp) and  $[(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2)_2\text{PPh}]$  bis[3-(diphenylphosphino) propyl]phenylphosphine (tpp). 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 angle formed by the phosphorus atoms with the metal, tetrahedral,

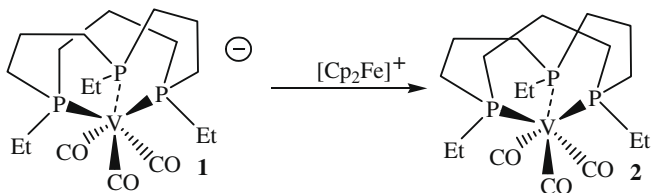
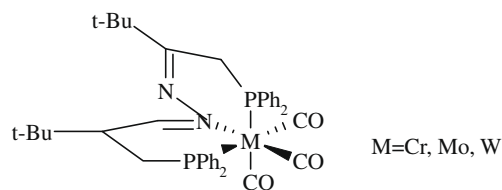
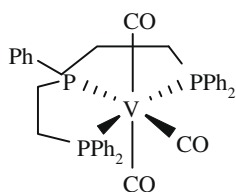
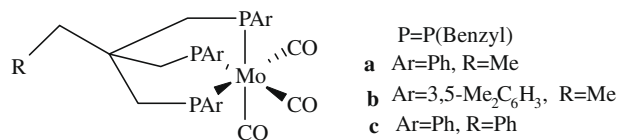
Scheme 11. The complex of *fac*- $[(12\text{ane})\text{P}_3\text{Et}_3]\text{V}(\text{CO})_3$  with  $[\text{Cp}_2\text{Fe}]^+$ .Fig. 7. The complexes  $[\text{M}(\text{CO})_3(\text{N},\text{P},\text{P}-(\text{PPh}_2\text{CH}_2\text{C}-(t\text{-Bu})-\text{N}-\text{N}-\text{C}-(t\text{-Bu})\text{CH}_2\text{PPh}_2)]$ .Fig. 5. *Mer* vanadium carbonyl complex.

Fig. 8. Mo complexes.

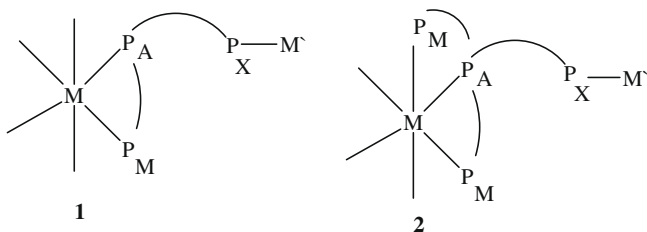
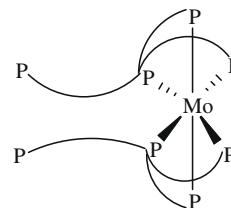
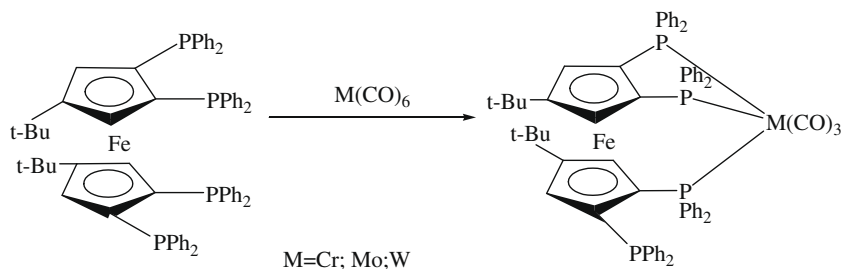


Fig. 6. Group VIB metal carbonyl complexes.

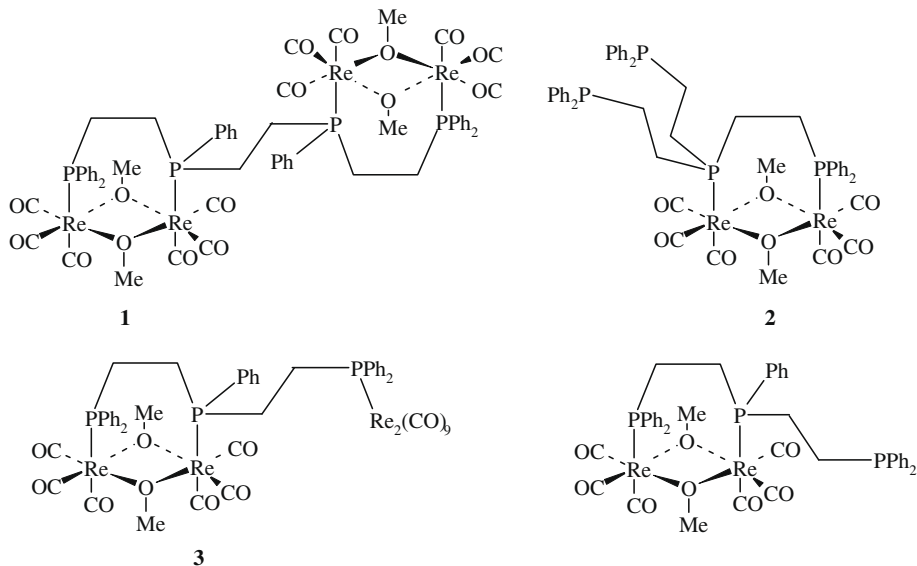
Fig. 9.  $\text{Mo}(\text{PP}_3)_2$  complex.

**Table 1**  
The  $^{31}\text{P}$  NMR data of metal carbonyl complexes.

Nr. crt.	Compound	$^{31}\text{P}$ NMR ( $\text{CDCl}_3$ , $\delta$ (ppm))
<b>1a</b>	$\text{Cr}(\text{CO})_4(\text{Pf-Pf-Pf})\text{Mo}(\text{CO})_5$	80.1 ( $\text{P}_A$ , dd, $^2J_{\text{XA}} = 34.2$ Hz, $^2J_{\text{MA}} = 4.4$ Hz), 79.2 ( $\text{P}_M$ , d, $^2J_{\text{AM}} = 4.6$ Hz), 30.9 ( $\text{P}_X$ , d, $^2J_{\text{AX}} = 37.0$ Hz)
<b>1b</b>	$\text{Cr}(\text{CO})_4(\text{Pf-Pf-Pf})\text{W}(\text{CO})_5$	79.7 ( $\text{P}_A$ , dd, $^2J_{\text{XA}} = 34.9$ Hz, $^2J_{\text{MA}} = 5$ Hz), 78.9 ( $\text{P}_M$ , d, $^2J_{\text{AM}} = 5.1$ Hz), 12.4 ( $\text{P}_X$ , d, $^2J_{\text{AX}} = 33.7$ Hz)
<b>1c</b>	$\text{Mo}(\text{CO})_4(\text{Pf-Pf-Pf})\text{Cr}(\text{CO})_5$	56.6 ( $\text{P}_A$ , dd, $^2J_{\text{XA}} = 34.7$ Hz, $^2J_{\text{MA}} = 6.4$ Hz), 55 ( $\text{P}_M$ , d, $^2J_{\text{AM}} = 5.7$ Hz), 49.7 ( $\text{P}_X$ , d, $^2J_{\text{AX}} = 33.1$ Hz)
<b>1d</b>	$\text{Mo}(\text{CO})_4(\text{Pf-Pf-Pf})\text{W}(\text{CO})_5$	56.6 ( $\text{P}_A$ , dd, $^2J_{\text{XA}} = 38.1$ Hz, $^2J_{\text{MA}} = 6.4$ Hz), 55.3 ( $\text{P}_M$ , d, $^2J_{\text{AM}} = 4.9$ Hz), 12.5 ( $\text{P}_X$ , d, $^2J_{\text{AX}} = 37.3$ Hz)
<b>2a</b>	$\text{Mo}(\text{CO})_3(\text{P-Pf}_3)\text{W}(\text{CO})_5$	87.3 ( $\text{P}_A$ , dd, $^2J_{\text{XA}} = 35.9$ Hz, $^2J_{\text{MA}} = 6.2$ Hz), 56.5 ( $\text{P}_M$ , d, $^2J_{\text{AM}} = 6.9$ Hz), 11.5 ( $\text{P}_X$ , d, $^2J_{\text{AX}} = 33.1$ Hz)
<b>2b</b>	$\text{W}(\text{CO})_3(\text{P-Pf}_3)\text{Mo}(\text{CO})_5$	75.8 ( $\text{P}_A$ , dd, $^2J_{\text{XA}} = 35.6$ Hz, $^2J_{\text{MA}} = 5.3$ Hz), 41.4 ( $\text{P}_M$ , d, $^2J_{\text{AM}} = 5.7$ Hz), 29.7 ( $\text{P}_X$ , d, $^2J_{\text{AX}} = 37.7$ Hz)



Scheme 12. 1,1',2-Triligate complexes of Cr; Mo; W.



Scheme 13. Re complexes.

trigonal–bipyramidal, square–pyramidal or octahedral geometries were identified. The phosphine tris[2-(diphenylphosphino)ethyl]phosphine (Fig. 3) prepared by King and co-workers was the first linear tetratertiaryphosphine obtained [6,7,9]. The linear tetraphosphine hptpd is especially interesting since it can exist in three stereoisomeric forms (*d*, *l* and *meso*).

### 2.3. Cyclic and macrocyclic polyphosphine ligands

McFarlane discovered [15,16] that the reaction between sodium diphenylphosphide and the appropriate polyfluorobenzene  $\text{C}_6\text{H}_{6-n}\text{F}_n$  in refluxing liquid ammonia provides a convenient route to the polykis(diphenylphosphino)benzenes,  $(\text{Ph}_2\text{P})_n\text{C}_6\text{H}_{6-n}$  [ $n = 2-4$ ], compounds **a** to **g** (Scheme 1). These polyphosphines have considerable potential as multi- and ambi-dentate ligands with a rigid skeleton that may facilitate or inhibit chelation to a metal center or bridging of several metal centers.

Hundred and eleven derivatives of the polykis(diphenylphosphino)benzenes,  $(\text{Ph}_2\text{P})_n\text{C}_6\text{H}_{6-n}$  [ $n = 2-4$ ], obtained by oxidation or reaction with sulfur, selenium, iodomethane,  $\text{M}(\text{CO})_6$  [ $M = \text{Cr}, \text{Mo}, \text{W}$ ],  $[\text{codRh}-\mu\text{-Cl}]_2$ , or  $(\text{PhCN})_2\text{MCl}_2$  [ $M = \text{Pd}, \text{Pt}$ ], were reported together with their  $^{31}\text{P}$  NMR spectra [17].

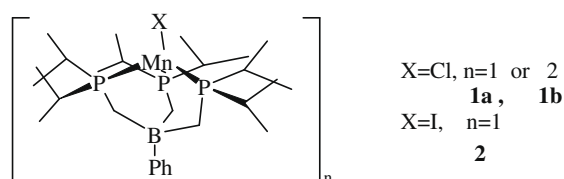
Metal complexes with chelating polyphosphine ligands usually have more predictable geometries and better control of the processes at the metal centers. Tetrakis(phosphino)benzenes **d–e** (Scheme 2) have been shown to be effective binucleating ligands. Some of these compounds have displayed attractive electrical and optical properties. A different synthetic route to similar tetra-

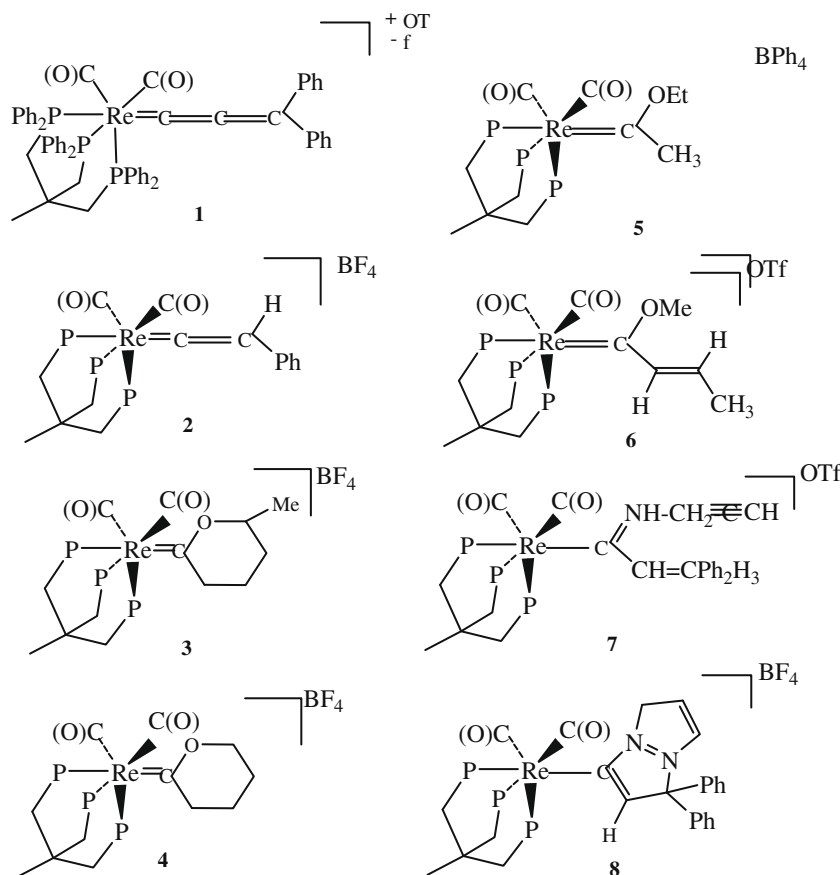
kis(phosphino)benzenes of the general formula 1,4-( $\text{PPh}_2$ )<sub>2</sub>-2,5-( $\text{PR}_2$ )<sub>2</sub>- $\text{C}_6\text{F}_2$  ligands **a–c** was also developed [18].

*Cis*, *trans*, *cis*-1,2,3,4-tetrakis(diphenylphosphino) cyclobutane (dppcb) is a new tetradentate phosphine formed in situ. A new tetraphosphine *cis*, *cis*, *cis*-1,2,3,4-tetrakis(diphenylphosphino)methyl)cyclopentane (tedicyp) with interesting catalytic applications was reported [19]. Also studies on cyclocarba- and cyclodicarba-tetraphosphines were performed [20,21] (Scheme 3).

The coordination behavior of macrocyclic ligands was studied by Mangani et al. [22] and it was reported that the synthesis and the complex formation of macrocycles **a–e** (Scheme 4) diastereomers of [18]-aneP<sub>4</sub>E<sub>2</sub>, which contain four phosphane groups and two different donor atoms ( $E = \text{O}, \text{S}, \text{N-Pr}$ ).

Facile reactions of polyphosphines (di, tetra, and penta species) were exploited to prepare a series of new organosubstituted diphosphinophosphonium and cyclotetraphosphinophosphonium cations **a–c** or hexaphosphorus and pentaphosphorus alternatives **d** and **e** (Scheme 5) [23].

Scheme 14. [PhBPi-Pr<sub>3</sub>]MnCl (1) and [PhBPi-Pr<sub>3</sub>]-MnI (2) complexes.



Scheme 15. Other Re complexes.

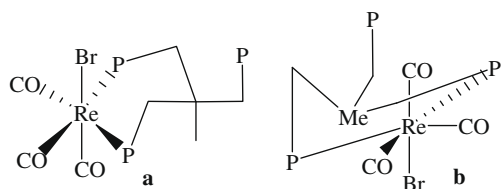


Fig. 10. Biligate Re complexes.

#### 2.4. Ferrocenyl polyphosphines

The creation of ferrocenyl phosphines [24] are of interest, regarding their present application or further investigations. The ferrocenyl backbone, due to its particular sandwich structure, displays a number of different conformations in the solid-state as in solution. Di-, tri- and tetradentate ferrocenyl polyphosphines involved in transition metal complexes with Cr, Mo, W, Rh, Ni, Pd, Pt and Cu are presented in Scheme 6.

It was established that the triphosphine **11**, incorporates an electron-donating substituent,  $-i\text{-Pr}$  group, is one of the most

efficient catalytic auxiliary reported to date in the Heck–Sonogashira alkylation reaction.

### 3. Basic routes for synthesis of polyphosphines

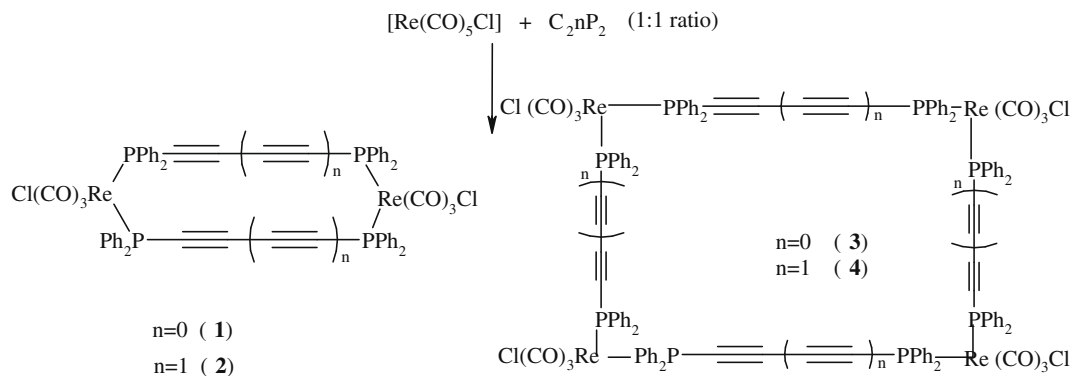
Ligand chemistry remains a pivotal science naturally connecting modern organic, inorganic, organometallic and coordination chemistry through an array of valuable applications, mainly catalysis. Multidentate ligands represent a fascinating class of compounds that offer a variety of coordination modes, for which new structures are developed each year. Triphos is prepared by the reaction of  $\text{Ph}_2\text{PNa}$  and  $\text{CH}_3\text{C}(\text{CH}_2\text{Cl})_3$ .

The required sodium diphenylphosphide is conveniently obtained by cleaving triphenylphosphine with sodium in liquid ammonia, treating it with water, and then extracting it with ether [1]. The traditional methods of polyphosphine synthesis have been documented by Chatt [25]. Some of the first polydentate phosphines were reported in 1962 by Heverston and co-workers, using metathesis reactions with alkali metal phosphides and alkali halides [1]. The most dramatic advance in synthesis was made by the work of King et al. [6,7] using two methods: base-catalyzed

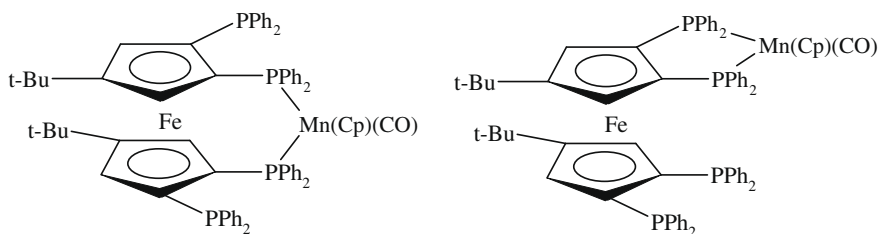
**Table 2**  
The  $^{31}\text{P}$  NMR data for complexes 1–6.

Compound	$^{31}\text{P}$ NMR (202 MHz, $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$ , 25 °C)	$^{31}\text{P}$ NMR (202 MHz, $\text{CD}_3\text{CN}$ , 25 °C)
<b>1</b>	$[\{\text{Re}(\text{CO})_3\text{Cl}(\text{C}_2\text{P}_2)\}_2]$	$\delta = -9.0$ (s)
<b>3</b>	$[\{\text{Re}(\text{CO})_3\text{Cl}(\text{C}_2\text{P}_2)\}_4]$	$\delta = -14.5$ (s)
<b>4</b>	$[\{\text{Re}(\text{CO})_3\text{Cl}(\text{C}_4\text{P}_2)\}_4]$	$\delta = -15.6$ (s)
<b>6</b>	$[\{\text{Re}(\text{CO})_3\text{Cl}\}_2\{\text{Os}(\text{bpy})_2\}_2(\text{C}_2\text{P}_2)_4](\text{PF}_6)_4]$	$\delta = -8.3$ (s, Re–P), $-9.1$ (s, Os–P)





Scheme 16. The way for synthesis of metallocyclic species.



Scheme 17. Ferrocenyl phosphine-Mn complexes.

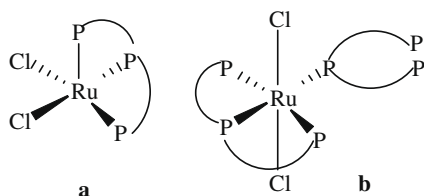
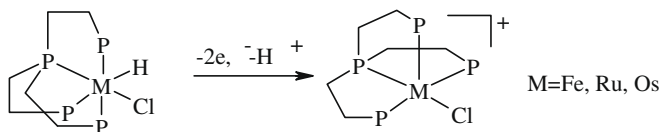


Fig. 11. Geometry of Ru compounds.

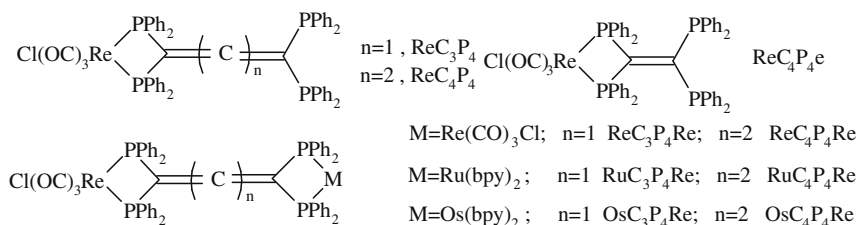
Scheme 18. The conversion of  $[(\text{PP}_3)\text{M}(\text{H})\text{Cl}]$  into  $[(\text{PP}_3)\text{MCl}]^+$ .

and the free radical-catalyzed addition of P-H bonds across the double bond of vinyl phosphine. Polyphosphine-metal complexes are thermodynamically more stable than comparable monophosphine analogs leading to the isolation and characterization of many

reactive intermediates. Brown et al. [26] have summarized the important aspects of phosphine ligand, steric effects for monodentate compounds of phosphorus. Work with polyphosphines will greatly enhance the directions of this category of compounds in synthesis. The stereochemistry of many polydentate complexes can be accurately described in an elegant series of studies by Kepert [27]. A valuable rising is the concept of preorganization and it was introduced by Cram et al. [28]. According to this concept the stereochemical arrangement of the free ligand can be synthetically prearranged by a knowledge of the donor-acceptor complex. The synthesis of some di, tri and tetra ferrocenyl phosphines are presented in Scheme 7 [29]. Three adjacent positions can be blocked on the ring by employing a trimethylcyclopentadienyl lithium salt. On an unsubstituted-Cp cyclopentadienyl ring, 1,3-disubstitution is obtained upon lithiation and consecutive quenching reactions.

#### 4. Complexes

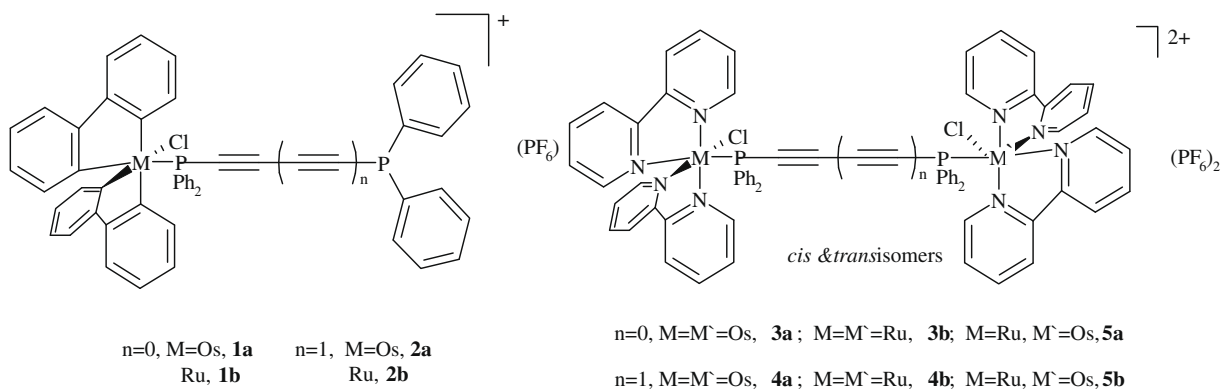
By a purposeful variation of the polyphosphine ligand, metal, coligand and reaction conditions, a great variety of organometallic and organic products can be stoichiometrically and catalytically synthesized in a highly selective manner. The use of polyphosphine ligands allows the isolation and characterization of many intermediate species not normally seen in catalysis cycles.

Scheme 19.  $\text{Re}^I$ ,  $\text{Ru}^{II}$ , and  $\text{Os}^{II}$  complexes that contain rigid polyphosphine/cumulene spacers.

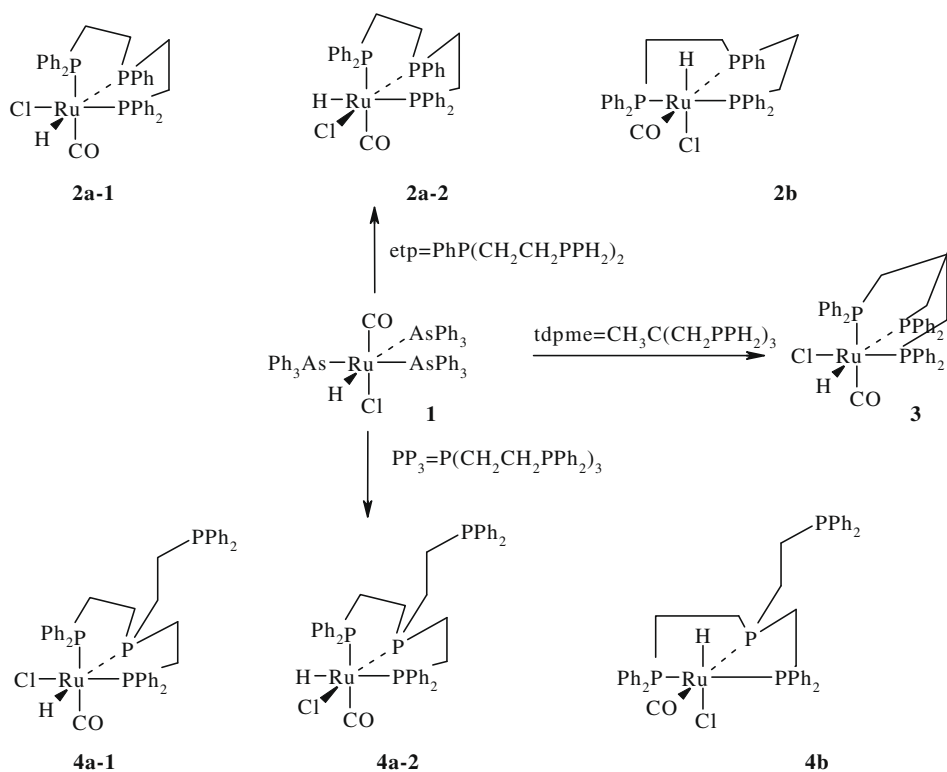
## 4.1. Group IIIB – Sc, Y, La, Ac

The nuclear industry produces radioactive liquid wastes with high level radioactivity. The main components of wastes are so-

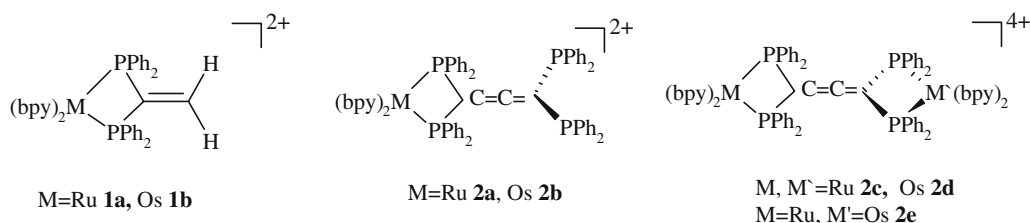
dium nitrate and nitric acid, they contain also radioactive elements such as actinides and fission products. The association of supported liquid membrane (SLM) and specific chelating agents could be one of the most powerful separation processes. A characteristic prop-



**Scheme 20.** Structure of  $[\text{Cl}(\text{bpy})_2\text{M}(\text{Ph}_2\text{PC}=\text{CH})](\text{PF}_6)$  ( $\text{M} = \text{Ru}^{\text{II}}, \text{Os}^{\text{II}}$ ).



**Scheme 21.** Synthesis of ruthenium (II) complexes.



**Scheme 22.** Monometallic and homo- and hetero-bimetallic  $\text{Ru}^{\text{II}}$  and  $\text{Os}^{\text{II}}$  complexes.

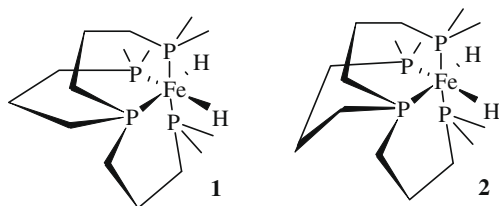


Fig. 12. The iron dibhydride  $\text{FeH}_2(\text{PP}_3)$ .

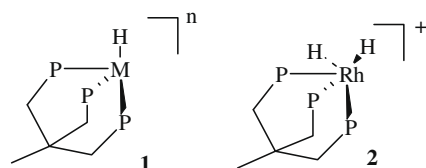


Fig. 13. Structure of  $[\text{Rh}(\text{H})_2(\text{triphos})]^+$  and  $[\text{RuH}(\text{triphos})]^+$  fragments.

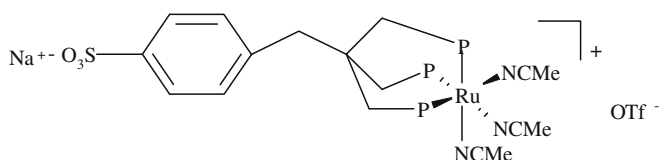


Fig. 14. The ruthenium complex  $[(\text{O}_3\text{S}(\text{C}_6\text{H}_4)\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3\text{Ru}(\text{NCMe})_3][\text{O}_3\text{SCF}_3]$ .

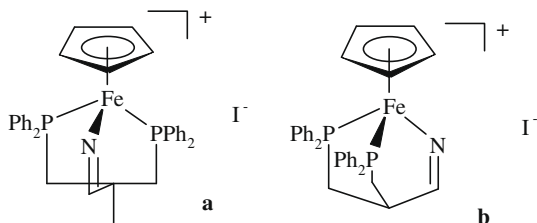


Fig. 15. Tripodal mixed nitrogen/phosphorus iron complexes.

erty of organic phosphoryl compounds is their ability to form complexes with metal ions, they are especially efficient for the complexation of hard cations.

Two major families of compounds have been evaluated in extraction. The first one is constituted by polyphosphine oxides with PCP linkage (compounds **a–k**, Scheme 8). The second one is represented by diphosphine dioxides with various ether bridges **l** and **m**.

Polydentate polyphosphine with (O)PCP(O) linkage proved their remarkable ability for the extraction of minor actinides and con-

firm their excellent position for the retreatment of nuclear wastes. This family is more efficient in extraction process than the reference (Fig. 4), octylphenyl(*N,N*-diisobutylcarbamoylmethyl) phosphine oxide for the extraction of actinides.

Triphosphine trioxides are the best compromise between high extraction efficacy and good actinide/lanthanide selectivity. In transport experiments by SLM, the high permeability of hydrophobic triphosphine trioxides was demonstrated for all the actinides [30].

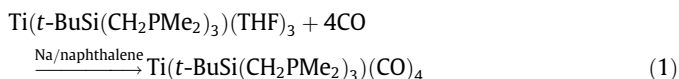
#### 4.2. Group IVB – Ti, Zr, Hf

Building compound using the diamagnetic early transition metals, zirconium (Scheme 9) and titanium with the goal of introducing redox active and paramagnetic metal-bridge fragments in the future were prepared [31].

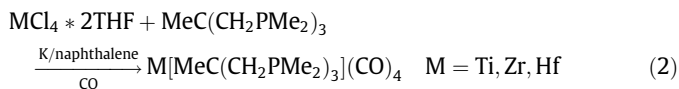
The bridged binuclear complexes should provide a facile route to polymeric materials that contain transition metals along the main polymer chain (Scheme 10).

The design of divergent metal-containing building blocks provides a facile route to linear rigid metal-containing polymers. Future usage of these building blocks in the assembly of higher-dimensional networks with functional physical properties has to be investigated.

A complex of titanium (Reaction (1)) with *t*-BuSi(CH<sub>2</sub>PMe<sub>2</sub>)<sub>3</sub> (trimpis) can be readily synthesized applying reducing methods, [32].



Other complexes of the titanium (Reaction (2)) were made in a similar fashion using  $[\text{MeC}(\text{CH}_2\text{PMe}_2)_3]$  as the ligand, [33].



#### 4.3. Group VB – V, Nb, Ta

Vanadium carbonyls stabilized by phosphine donors have long been known. Larger chelate ring sizes have been shown to decrease stability and rigid chelating ligands enhance stability. The complex [34] of *fac*-{[(12[ane]P<sub>3</sub>Et<sub>3</sub>)V(CO)<sub>3</sub>][Et<sub>4</sub>N]} was prepared (Scheme 11) by photolysis of solutions of [Et<sub>4</sub>N][V(CO)<sub>6</sub>].

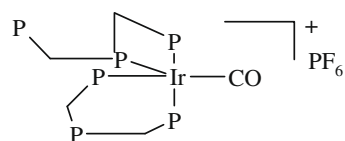


Fig. 17. The structure of Iridium complex  $[\text{Ir}(\text{dmp})_2\text{CO}]^+ \text{PF}_6^-$ .

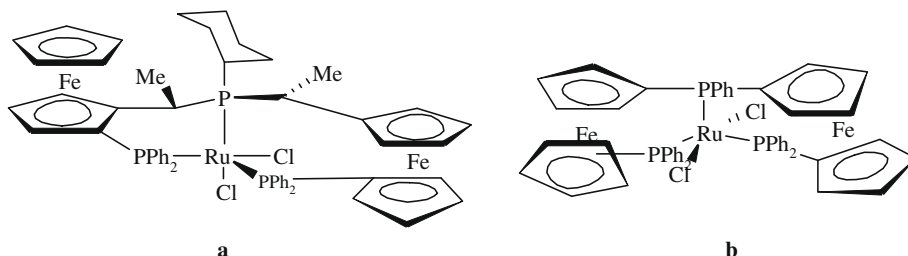


Fig. 16. Ru-Pigiphos complexes.

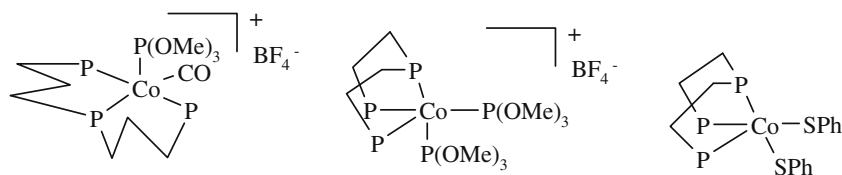
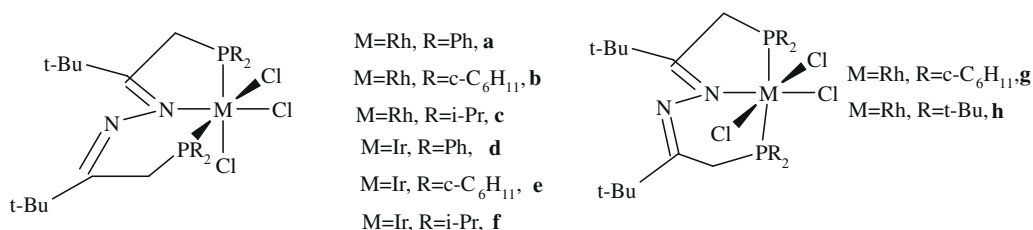


Fig. 18. Thiolate Co<sup>II</sup> complexes [Co(etp)(SPh)<sub>2</sub>].

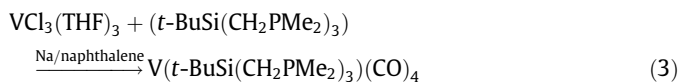


Scheme 23. Rhodium(III) and iridium(III) octahedral complexes.

The compound **1** can be oxidized to the V(0) derivative, *fac*-[12[ane]P<sub>3</sub>Et<sub>3</sub>]-V(CO)<sub>3</sub> **2** by [Cp<sub>2</sub>Fe][PF<sub>6</sub>] in good yield.

Carbonyl complex substitution patterns could be observed especially under photolytic conditions, when vanadium carbonyls were used as starting materials. The linear phosphine (etp) gave a *mer* vanadium carbonyl complex (Fig. 5).

Different approaches to vanadium complexes for the purpose of developing molecular precursors for the metalorganic chemical vapour deposition (MOCVD) have been used (Reaction (3)) [32].



#### 4.4. Group VIB – Cr, Mo, W

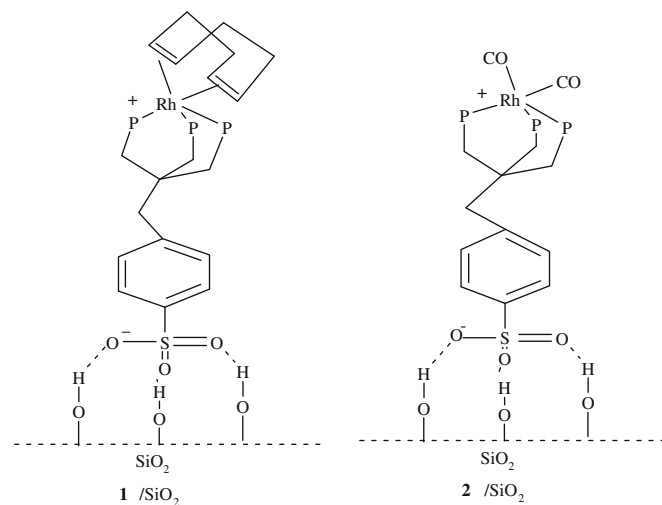
The mixed Group VIB metal carbonyl complexes, [M(CO)<sub>4</sub>(Pf-Pf)M'(CO)<sub>5</sub>] (M = Cr, M' = Mo, W; M = Mo, M' = Cr, W; Pf-Pf = PhP(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>) and [M(CO)<sub>3</sub>(P-Pf<sub>3</sub>)M'(CO)<sub>5</sub>] (M = Mo, M' = W, M = W, M' = Mo; P-Pf = P(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>) were obtained from [M(CO)<sub>4</sub>(Pf-Pf-Pf)] and M'(CO)<sub>5</sub>(CH<sub>3</sub>CN)] and from [M(CO)<sub>3</sub>(P-Pf<sub>3</sub>)] and [M'(CO)<sub>5</sub>(CH<sub>3</sub>CN)], respectively (Fig. 6).

The chemical shifts of phosphorus atoms (Table 1) P<sub>x</sub> are at ~50 ppm (Cr–P), ~30 ppm (Mo–P) and ~12 ppm (W–P) ppm, respectively. The coupling constant <sup>2</sup>J<sub>pp</sub> is about ~35 Hz when the two phosphorus atoms are coordinated to different metals. The relatively small value of <sup>2</sup>J<sub>pp</sub> for phosphorus atoms coordinated to the same metal (<sup>2</sup>J<sub>AM</sub>, 4.6–6.9 Hz; <sup>2</sup>J<sub>MA</sub>, 4.1–6.4 Hz) is due to the chelated ring effect [35].

Azine CH<sub>2</sub>PPh<sub>2</sub> was synthesized and reacted with Group VI B carbonyl metals. The complexes [M(CO)<sub>3</sub>{N,P,P-(PPh<sub>2</sub>CH<sub>2</sub>C-(t-Bu)-N-N-C(t-Bu)CH<sub>2</sub>PPh<sub>2</sub>)}] (with M = Cr, Mo, W, were obtained (Fig. 7), and the X-ray crystal structure of the molybdenum compound was reported [36].

The zerovalent chromium complex [Cr(tdmpe)<sub>2</sub>], [where tdmpe is 1,1,1-tris(diphenylphosphinomethyl)ethane] is the first example of a structurally characterized hexakis(trialkylphosphine)-coordinated Cr(0) compound. Comparing the coordination geometry around the Cr atom, [CrCl<sub>2</sub>(tdmpe)<sub>2</sub>] shown an octahedral with trans chlorine atoms, while the molecular geometry of [Cr(tdmpe)<sub>2</sub>] is best described as a trigonal antiprism due to the two triligate tripodal ligands which severely constrain the angles of the molecule [37].

X-ray analyses of the three compounds (Fig. 8) of type [RCH<sub>2</sub>C(CH<sub>2</sub>P(Ar))<sub>3</sub>Mo(CO)<sub>3</sub>], were reported and indicate closely similar octahedral structures [38].



Scheme 24. Mononuclear zwitterionic Rh(I) complexes.

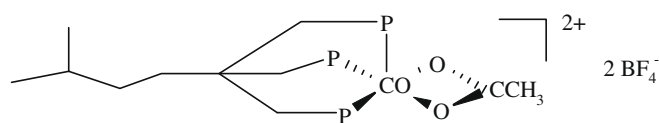


Fig. 19. Tripodal cobalt complex.

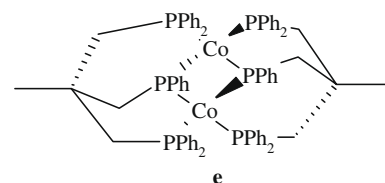


Fig. 20. Structure of [Co<sub>2</sub>{CH<sub>3</sub>C(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>PPh<sub>2</sub>}]<sub>2</sub>.

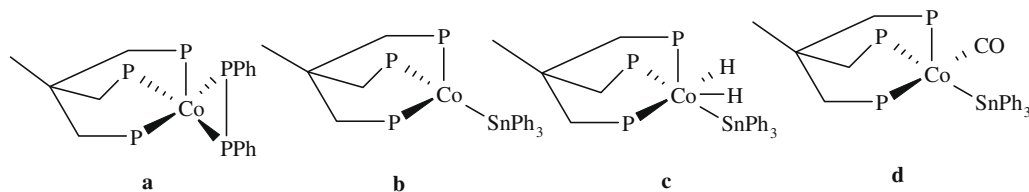


Fig. 21. Other Co complexes.

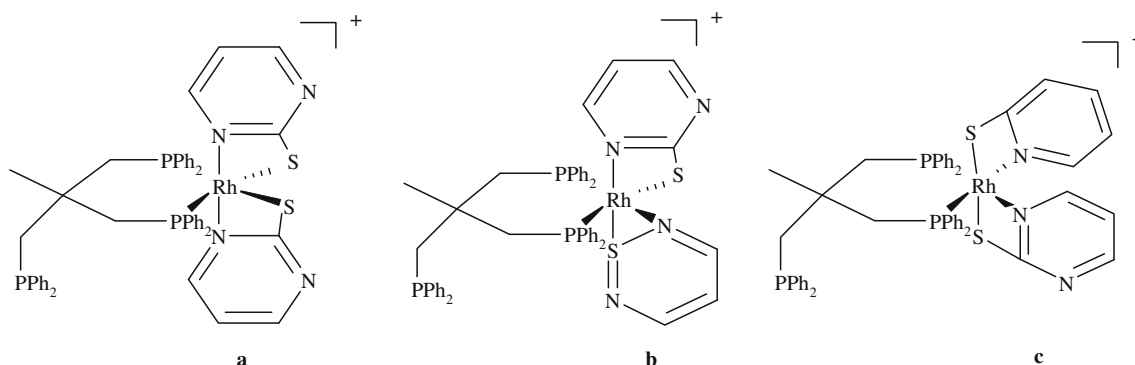


Fig. 22. Structure of Rh complexes.

Also the complex  $\text{Mo}(\text{PP}_3)_2$  was synthesized [39] by reaction of  $\text{trans}[\text{Mo}(\text{N}_2)_2(\text{PPh}_2\text{Me})_4]$  with one molar equivalent of  $\text{PP}_3$  (Fig. 9).

Results with Group VIIB metals have shown a 1,1',2-triligate coordination at the metal center for the carbonyl complexes  $[\text{M}(\text{CO})_3\mathbf{21}]$  ( $\text{M} = \text{Mo}, \text{Cr}, \text{W}$ ) (Scheme 12). The reactions occur despite the strong geometric constraints undergone by the different moieties in the resulting complexes [5].

#### 4.5. Group VIIB – Mn, Tc, Re

A high-spin five-coordinated manganese(II) complex  $[\text{Mn}(\text{tdpea})\text{I}]\text{BPh}_4 \cdot 2\text{CH}_2\text{Cl}_2$  with the tripod ligand  $\text{tdpea} = \text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$  was synthesized [40]. Marchini and co-workers synthesized and characterized nitrido-technetium(V) and -rhenium(V) complexes with formula  $[\text{TcNCl}_2\text{L}]$  [ $\text{M} = \text{Tc}$  or  $\text{Re}$ ] and  $\text{L} = \text{bis}(\text{diphenyl-1-phosphinoethyl})\text{propylamine}$ , 1,8-bis(diphenylphosphino)-3,6-dioxaoctane or 1,1,1-tris(diphenylphosphino)methyl)ethane [12]. These complexes, as well as the rhenium analogues, were also obtained starting from  $[\text{MnCl}(\text{PPh}_2)_3]$  ( $\text{M} = \text{Tc}$  or  $\text{Re}$ ) by substitution of the two phosphine groups [41].

It was [9] reported (Scheme 13) the formation of the complexes (*d:l*- and *meso*- $[\text{Re}_2(\mu\text{-OMe})_2(\text{CO})_6]_2$ - $(\mu, \eta^2\text{-hptpd})$ ) (**1**),  $[\text{Re}_2(\mu\text{-OMe})_2(\text{CO})_6]_2$ - $(\mu, \mu', \eta^2\text{-tdppep})$ ) (**2**),  $[\text{Re}_2(\mu\text{-OMe})_2(\text{CO})_6]_2$ - $(\mu, \mu', \eta^3\text{-triphos})$ - $[\text{Re}_2(\text{CO})_9]$ ) (**3**) and  $[\text{Re}_2(\mu\text{-OMe})_2(\text{CO})_6]_2$ - $(\mu, \eta^2\text{-triphos})$ ) (**4**) in the reactions of the respective polyphosphines with mixtures of  $\text{Re}_2(\text{CO})_{10}$ ,  $\text{Me}_3\text{NO}$  and  $\text{MeOH}$ .

Variable-temperature  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra of *d:l*-**1** compound were also performed. Rhenium polyhydrides complexes exhibiting high coordination numbers such as  $[\text{Re}(\text{tdpme})\text{H}_5]$ ,  $[\text{Re}(\text{tdpme})\text{H}_7]$ ,  $[\text{Re}(\text{tdpme})(\text{PPh}_3)_3]$  and  $[\text{Re}(\text{tdpme})(\text{CO})\text{H}_3]$  have also been identified by NMR [42].

By mixing the thallium reagent  $[\text{PhBPI-Pr}_3]\text{Tl}$  with  $\text{MnX}_2$  (where  $\text{X} = \text{Cl}$  or  $\text{I}$ ), [43] Mn(II) halides  $[\text{PhBPI-Pr}_3]\text{MnCl}$  (**1**) and  $[\text{PhBPI-Pr}_3]\text{MnI}$  (**2**) were synthesized (Scheme 14).

Barbaro et al. reported results obtained on studying the reactivity of the disubstituted allenylidene  $[\text{Re}(\text{C}=\text{C}=\text{CPh}_2)(\text{CO})_2$  (triphos)] $\text{OTf}$  ( $\text{OTf} = ^-\text{OSO}_2\text{CF}_3$ ) toward thiols and amines [44]. Other

complexes **2–8** (Scheme 15) were synthesized and analyzed by X-ray and NMR spectroscopy [45–47].

Gibson et al. [48] have synthesized new rhenium carbonyl complexes showing a biligate coordination of phosphine. The six membered metallacyclic ring  $\text{ReP}_2\text{C}_3$  adopts a chair conformation (Fig. 10).

New metalocyclic species that contain ditopic phosphane spacers with *sp* carbon chains and various photo- and redoxactive metal-based moieties, with  $\text{Re}^{\text{I}}$  and  $\text{Os}^{\text{II}}$  centers, including the dimeric  $[\{\text{Re}(\text{CO})_3\text{Cl}(\text{C}_{2n}\text{P}_2)\}_2]$  ( $n = 1$ , **1**;  $n = 2$ , **2**), tetrameric  $[\{\text{Re}(\text{CO})_3\text{Cl}(\text{C}_{2n}\text{P}_2)\}_4]$  ( $n = 1$ , **3**;  $n = 2$ , **4**), and the mixed-metal species  $[\{\text{Re}(\text{CO})_3\text{Cl}\}_2\{\text{Os}(\text{bpy})_2\}_2(\text{C}_2\text{P}_2)_4](\text{PF}_6)_4$  (**6**) were synthesized and characterized [49].

One molecular precursor,  $[\text{Os}(\text{bpy})_2(\text{C}_2\text{P}_2)_2](\text{PF}_6)_2$  was also prepared and  $^{31}\text{P}$  NMR data are presented in Table 2.

The complexes were performed in THF/toluene 4:1 mixture at reflux for 2 days. The way of synthesis is presented in Scheme 16.

A bimetallic product with two terminal  $\text{Os}^{\text{II}}$  centers was found to be the favored product, which has a  $^{31}\text{P}$  NMR singlet at approximately  $\delta = 30$  ppm. The  $^{31}\text{P}$  NMR study reveals that these complexes with ditopic phosphanes are stable in air, and no oxidized species are observed.

The reactivity of the tetraphosphine ferrocenyl ligand under irradiation with the manganese precursor  $[\text{MnCp}(\text{CO})_3]$  was also studied (Scheme 17) [50].

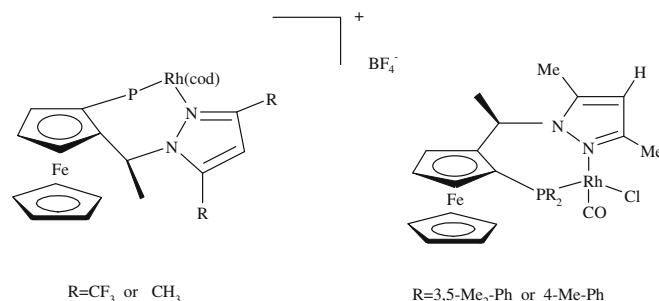
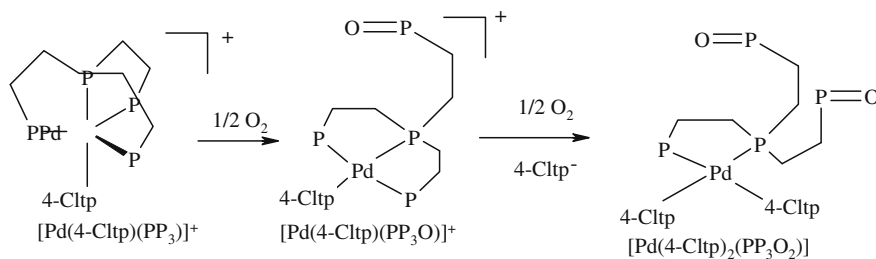
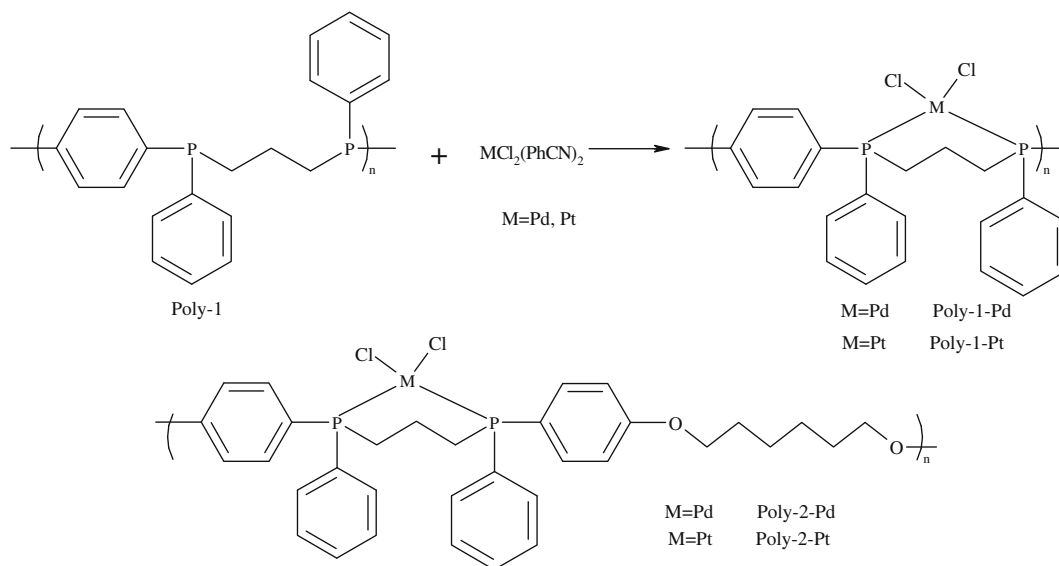
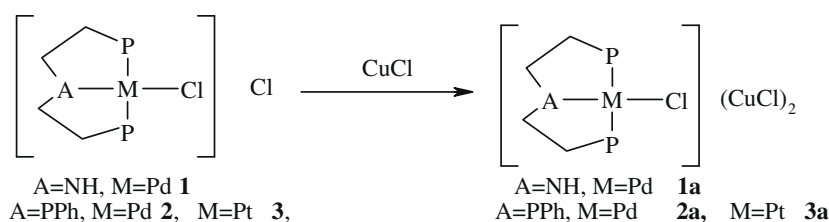


Fig. 23. Mixed ferrocenyl phosphino-Rh complexes.

Scheme 25. The synthesis of  $[\text{Pd}(4\text{-Cltp})_2(\text{pp}_3\text{O}_2)]^+$ .

Scheme 26. Polymer–metal complexes with high metal contents.



Scheme 27. Tripodal phosphine–Cu complexes.

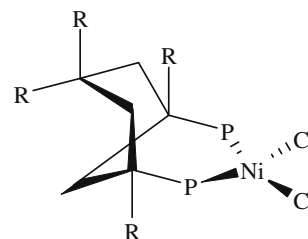
#### 4.6. Group VIII B – Fe, Ru, Os

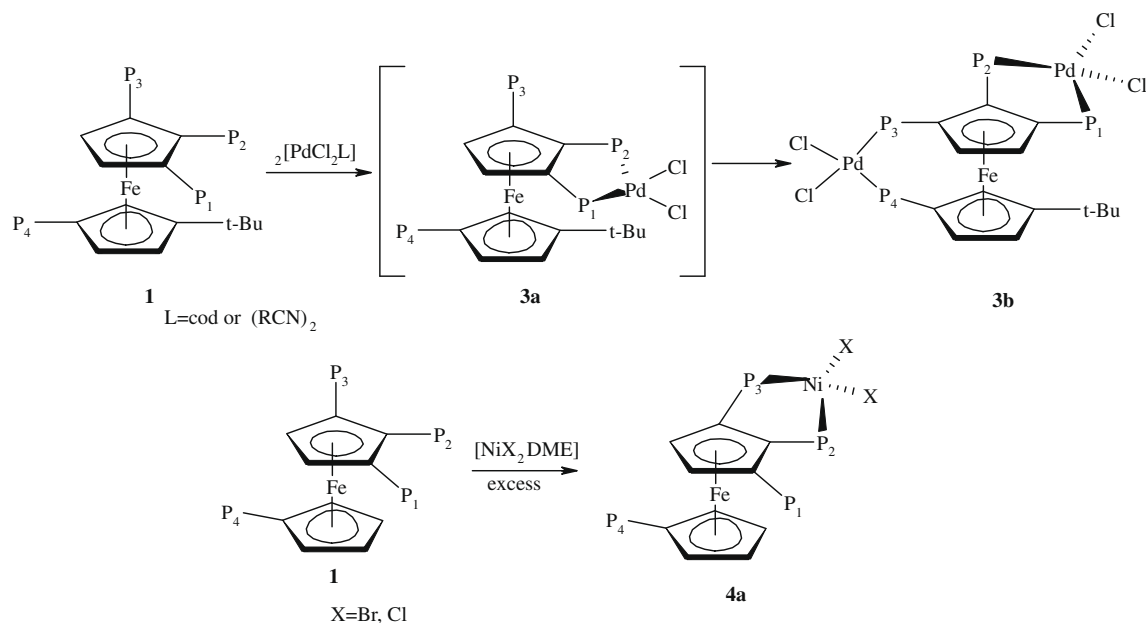
Depending on ligand used, the ruthenium complexes adopt *fac* or *mer* coordinations. *Fac*-coordination has been found for ttp in the five-coordinate  $\text{RuCl}_2(\text{ttp})$  [51], having a geometry intermediate between square-pyramidal and trigonal-bipyramidal **a** (Fig. 11). *Mer*-ruthenium/etp compound was obtained by change the metal:ligand ratio of starting products;  $\text{RuCl}_2(\text{etp})_2$  has been obtained from  $\text{RuCl}_2(\text{PPh}_3)_2$  reacted with 2 equiv. of etp.**b** [52].

The conversion of  $[(\text{PP}_3)\text{M}(\text{H})\text{Cl}]$  into  $[(\text{PP}_3)\text{MCl}]^+$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ), is outlined in Scheme 18 [10].

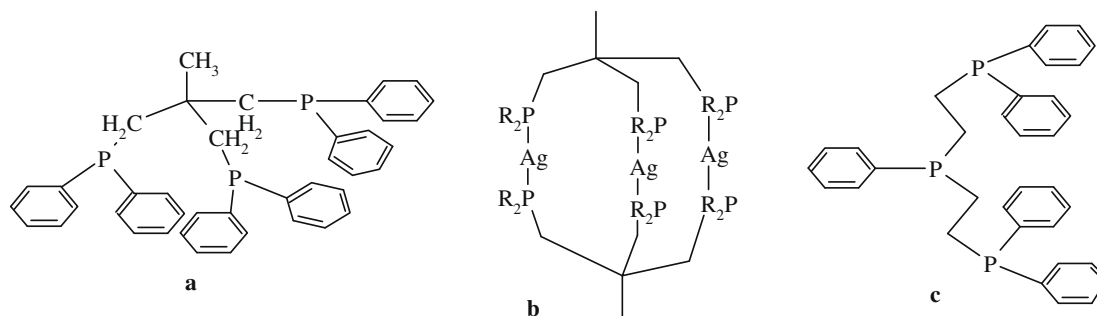
The synthesis of a series of  $\text{Re}^{\text{I}}, \text{Ru}^{\text{II}},$  and  $\text{Os}^{\text{II}}$  complexes that contain rigid polyphosphine/cumulene spacers was also reported. The polyphosphine spacers, namely, 1,1',3,3'-tetrakis(diphenylphosphino) allene ( $\text{C}_3\text{P}_4$ ) and 1,1',4,4'-tetrakis(diphenylphosphino) cumulene ( $\text{C}_4\text{P}_4$ ), are used to link together the metal centers (Scheme 19). The  $^{31}\text{P}$  NMR data were also reported [53].

Complexes by reactions of the spacers  $\text{Ph}_2\text{PC}=\text{CPh}_2$  ( $\text{C}_2\text{P}_2$ ) and  $\text{Ph}_2\text{PC}=\text{CC}=\text{CPh}_2$  ( $\text{C}_4\text{P}_2$ ) with *cis*- $\text{M}(\text{bpy})_2\text{Cl}_2$  or by coupling reaction between two  $[\text{Cl}(\text{bpy})_2\text{M}(\text{Ph}_2\text{PC}=\text{CH})](\text{PF}_6)$  ( $\text{M} = \text{Ru}^{\text{II}}, \text{Os}^{\text{II}}$ ) molecules (Scheme 20) were obtained [54]. All the synthesized compounds were analyzed by  $^{31}\text{P}$  NMR.

Fig. 24. Structure of biligate  $\text{NiCl}_2$  complex.



**Scheme 28.** Synthesis of palladium(II) and nickel(II) halide-ferrocenyl polyphosphines complexes.



**Fig. 25.** Structure of Me-triphos and Ph-triphos Cu complexes.

A series of ruthenium (II) complexes of polyphosphine ligands (**Scheme 21**),  $\text{RuHCl}(\text{CO})(\text{etp})$  (**2**),  $\text{RuHCl}(\text{CO})(\text{tdpme})$  (**3**) and  $\text{RuHCl}(\text{PP}_3)$  (**4**) [tdpme =  $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ ] have been prepared from  $\text{RuHCl}(\text{CO})(\text{AsPh}_3)_3$  (**1**) through typical substitution reactions [55].

Monometallic and homo- and hetero-bimetallic  $\text{Ru}^{\text{II}}$  and  $\text{Os}^{\text{II}}$  complexes [56] with the polyphosphines 1,1'-bis(diphenylphosphino)ethene (bpe) and 1,1',3,3'-tetrakis(diphenylphosphino)allene (tppa) have been prepared and characterized by  $^{31}\text{P}$  NMR spectroscopy (**Scheme 22**).

For the preparation of monometallic complexes **1a**, **1b**, **2a** or **2b** higher ligand-to-metal ratio (2,2–3:1) was used.

The iron dihydride  $\text{FeH}_2(\text{PP}_3)$  [57], with the terminal coordinated phosphine groups undergoes intramolecular exchange in addition to the iron-bound hydrides (**Fig. 12**).

The phosphorus atoms of the tetradentate ligand occupy four sites of a pseudo-octahedral coordination sphere, where two terminal phosphine ligands occupy axial positions with the apical phosphine and the remaining terminal phosphine occupying equatorial locations.

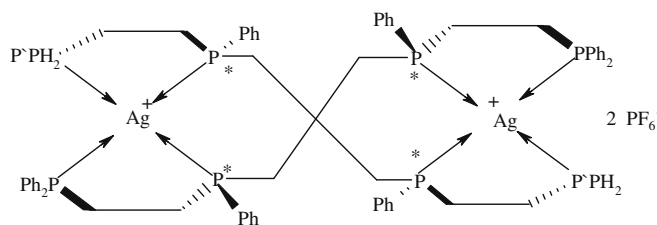
The rhodium(III) and ruthenium (II) fragments  $[\text{Rh}(\text{H})_2(\text{triphos})]^+$  and  $[\text{RuH}(\text{triphos})]^+$  are efficient catalysts for quinoline hydrogenation to 1,2,3,4-tetrahydroquinoline ( $\text{M} = \text{Ru}$  and  $n = +1$ ) compound **1** and compound **2** (**Fig. 13**) [54].

Using tripodal complex ligand an iron complex  $[\{(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3\} \text{Fe}(\text{NCMe})_3][\text{BF}_4]_2$ , which displays an octa-

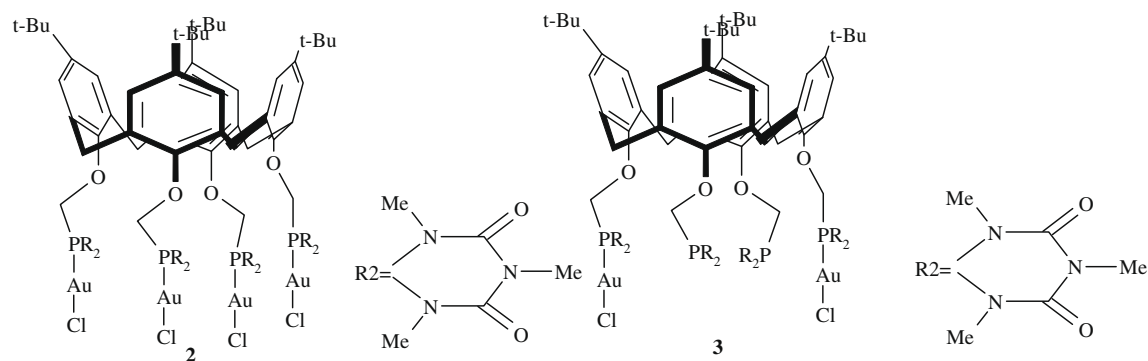
hedral geometry at the metal center, and the cobalt complex a five-coordinate distorted square-pyramidal geometry was synthesized and analyzed [58]. The chiral tripodal ligand with three different donor groups [59],  $\text{L} = \text{CH}_3\text{C}(\text{CH}_2\text{PR}_2)(\text{CH}_2\text{PR}'_2)(\text{CH}_2\text{PR}''_2)$ , with  $\text{R} = 2\text{-tolyl}$ ,  $\text{R}' = 4\text{-tolyl}$ ,  $\text{R}'' = \text{Ph}$  was used to obtain the complexes  $[(\text{L})\text{Fe}(\text{NCMe})_3][\text{BF}_4]_2$ .

The ruthenium complex  $[(\text{O}_3\text{S}(\text{C}_6\text{H}_4)\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3\text{Ru}(\text{NCMe})_3][\text{O}_3\text{SCF}_3]$  (**Fig. 14**) immobilized on silica via hydrogen bonding between the silanol groups of the support and the  $\text{SO}_3$  groups from the sulphos ligand and the triflate counteranion was also obtained [60].

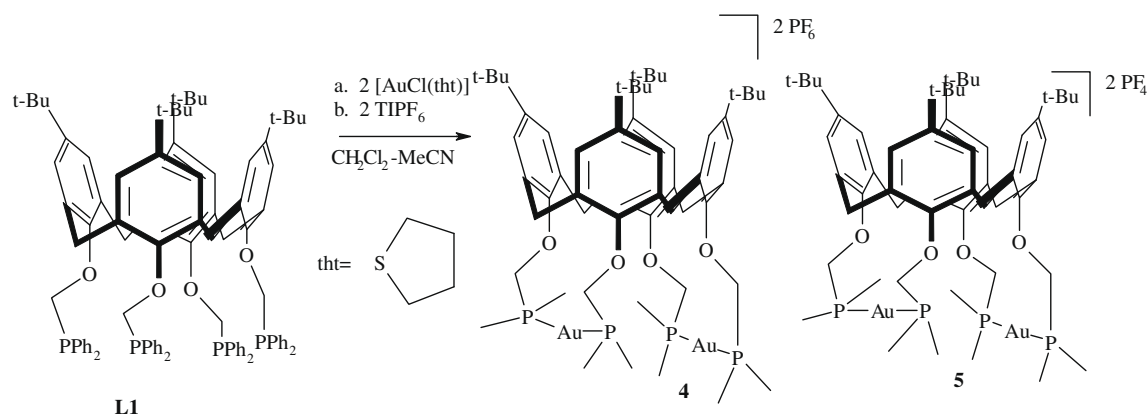
Using a tripodal mixed nitrogen/phosphorus ligands, Liu et al. [61] reported photochemical substitution reactions of  $[\text{Fe}(\text{CO})_2\text{Cp}]\text{I}$  with the amino-phosphines  $\text{CH}_3\text{C}(\text{CH}_2\text{NH}_2)(\text{CH}_2\text{PPh}_2)_2$  and  $\text{HC}(\text{CH}_2\text{NH}_2)(\text{CH}_2\text{PPh}_2)(\text{PPh}_2)$  (**Fig. 15**).



**Fig. 26.** (R,R,R,R)- $[\text{Ag}_2(\text{hptpd})_2][\text{PF}_6]_2$  complex.



Scheme 29. Au-complexes.



Scheme 30. Synthesis of Au-complexes.

Barbaro et al. [62] described the complex  $[\text{RuCl}_2(\text{Pigiphos})]$  formed from the reaction of Pigiphos [bis((*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl)cyclohexylphosphine] and  $[\text{RuCl}_2(\text{PPh}_3)_3]$  in toluene.

The synthesis of the bis-1-(1'-diphenylphosphinoferrocenyl)phenylphosphine, called triphosfer, was reported [63]. Triphosfer reacts with  $[\text{RuCl}_2(\text{PPh}_3)_3]$  to give the complex  $[\text{RuCl}_2(\text{triphosfer})]$  (Fig. 16b).

#### 4.7. Group IXB – Co, Rh, Ir

Iridium complex  $[\text{Ir}(\text{dpmp})_2\text{CO}]^+$  have the possibility to stabilize dinuclear and trinuclear mixed species in a controlled way (Fig. 17) through further chelate ring opening of the metal complexes [64].

Wei et al. [65] reported the thiolate  $\text{Co}^{\text{II}}$  complex  $[\text{Co}(\text{etp})(\text{SPh})_2]$  as being a five-coordinate compound (Fig. 18) with a *fac*-configuration of the triphosphine, the geometry around cobalt being intermediate between square-pyramidal and trigonal-bipyramidal.

Rhodium(III) and iridium(III) octahedral complexes of general formula  $[\text{MCl}_3\{\text{R}_2\text{PCH}_2\text{C}(t\text{-Bu})=\text{NN}=\text{C}(t\text{-Bu})\text{CH}_2\text{PR}_2\}]$  (M = Rh, Ir; R = Ph, *c*-C<sub>6</sub>H<sub>11</sub>, *i*-Pr, *t*-Bu;) were prepared (Scheme 23) [66].

It was shown that the two mononuclear zwitterionic Rh(I) complexes (sulfos)Rh(cod) (**1**) and (sulfos)-Rh(CO)<sub>2</sub> (**2**) [sulfos] =  $-\text{O}_3\text{S}(\text{C}_6\text{H}_4)\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3$ ; cod = cycloocta-1,5-diene] (Scheme 24) are effective catalysts for the hydrogenation of styrene to ethylbenzene and for the hydroformylation of 1-hexene to either C<sub>7</sub> aldehydes or C<sub>7</sub> alcohols in MeOH water-hydrocarbon mixtures. Both **1** and **2** can be grafted onto a high surface area silica with an immobilization procedure based *uniquely* on the capability of the sulfonate tail of sulfos to link the silanol groups of the support

via hydrogen bonding. The catalytic active sites are isolated Rh atoms, as in homogeneous phase [67].

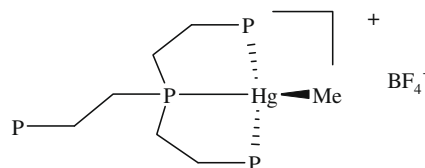
Using tripodal complex ligand (Fig. 19) a cobalt complex was synthesized and analyzed  $[\{(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{C}(\text{CH}_2\text{PPh}_2)_3\}\text{Co}\{\text{O}(\text{O})\text{CCH}_3\}]\text{BF}_4$  [62].

The following species [68],  $[(\text{tdpme})\text{Co}(\eta^2\text{-PhP}=\text{PPh})]$  (**a**) from PhPH<sub>2</sub> or PhPHNa,  $[(\text{tdpme})\text{Co}(\text{SnPh}_3)]$  (**b**) from Ph<sub>3</sub>SnH,  $[(\text{tdpme})\text{Co}(\text{H})_2(\text{SnPh}_3)]$  (**c**) from addition of H<sub>2</sub> to  $[(\text{tdpme})\text{Co}(\text{SnPh}_3)]$ ,  $[(\text{tdpme})\text{Co}(\text{CO})(\text{SnPh}_3)]$  (**d**) from addition of CO to  $[(\text{tdpme})\text{Co}(\text{SnPh}_3)]$ , and  $[\text{Co}_2\{\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_2\text{-CH}_2\text{PPh}_2\}]$  (Fig. 20) were

Table 3

The <sup>31</sup>P NMR data of the gold and silver complexes with calix[4]arene matrix.

Nr crt.	Compound	<sup>31</sup> P { <sup>1</sup> H} NMR (81 MHz, 293 K, CDCl <sub>3</sub> or CD <sub>2</sub> Cl <sub>2</sub> )
1	$[(\text{AuCl})_4\text{L}^1]$	$\delta = 22.7$ (s)
2	$[(\text{AuCl})_4\text{L}^2]$	$\delta = 101.6$ (s)
4	$[\text{Au}_2\text{L}^1][\text{PF}_6]_2$	$\delta = 40.6$ (br s)
5	$[\text{Ag}_2\text{L}^1][\text{BF}_6]_2$	$\delta = 4.6$ [dd, $J(^{107}\text{Ag}-\text{P}) = 509$ Hz, $J(^{109}\text{Ag}-\text{P}) = 585$ Hz, PPh <sub>2</sub> ]

Fig. 27.  $[\text{Hg}(\text{Me})(\text{PP}_3)]\text{BF}_4$  complex.



obtained and characterized in the solid-state by crystallographic studies (Fig. 21).

Brandt and Sheldrick [69] synthesized the following isomeric products (Fig. 22).

A series of diphosphinoazine rhodium amido carbonyl complexes  $[\{R_2PCH=C(t-Bu)-NN=C(t-Bu)CH_2PR_2\}Rh(CO)]$  ( $R = Ph, i-Pr, c-C_6H_{11}, t-Bu$ ) was prepared by deprotonation of cationic diphosphinoazine rhodium amino carbonyl complexes [70].

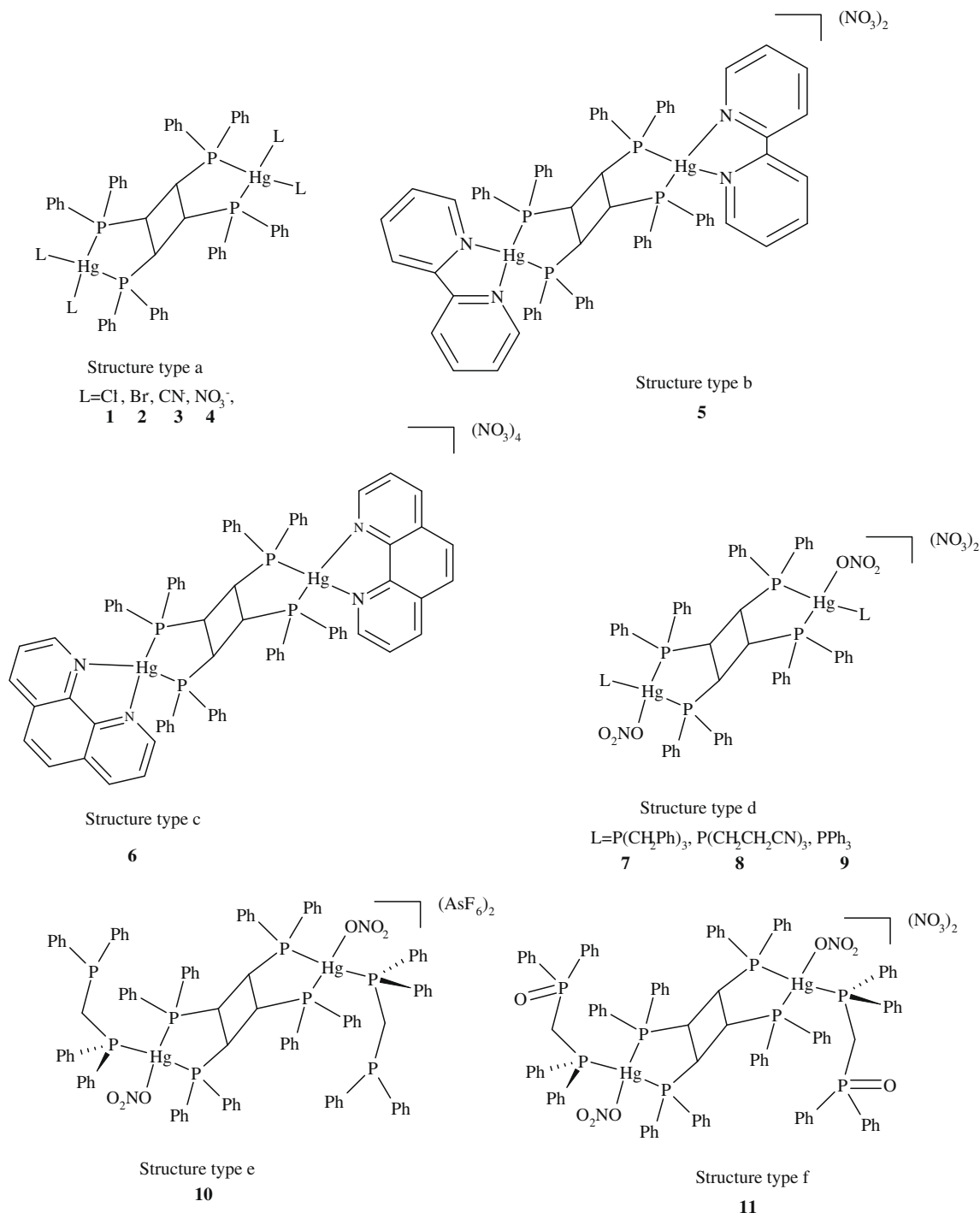
Mixed ferrocenyl ligands [71] with one phosphorus and two nitrogen donor atoms (Fig. 23) were obtained.

#### 4.8. Group XB – Ni, Pd, Pt

Platinum(II) complexes of  $CF_3PPH$  and  $CF_3tpp$  were synthesized and the spectral properties of these complexes are compared to known platinum(II) complexes [72].

The stepwise oxidation (Scheme 25) of five-coordinate trigonal-bipyramidal  $[Pd(4-Cltp)(PP_3)]^+$  to give square-planar  $[Pd(4-Cltp)-(pp_3O)]^+$  and  $[Pd(4-Cltp)_2(pp_3O_2)]$  was reported [73].

Oxidation of **Poly-1** to yield polyphosphine oxide (**Poly-1-O**) was examined (Scheme 26). Treatment of the polyphosphines with



Scheme 31. Structure of different Hg complexes.

Pd(II) and Pt(II) yielded corresponding polymer–metal complexes with high metal contents.

To explore the metal-coordination properties of the polymers, they were reacted with PdCl<sub>2</sub>(PhCN)<sub>2</sub> and PtCl<sub>2</sub>(PhCN)<sub>2</sub> leading to Poly-2-Pd and Poly-2-Pt [74].

Fernandez et al. [75] was interested in using precursors containing linear or tripodal polyphosphines such as [M(L)Cl]Cl (M = Pd, Pt; L = PNHP = bis[2-(diphenylphosphino) ethyl]amine, P<sub>3</sub>, NP<sub>3</sub>, PP<sub>3</sub>), for reactions with CuCl (Scheme 27).

A biligate coordination for phosphine was observed for NiCl<sub>2</sub> complex, a square-planar arrangement around the metal being preferred (Fig. 24). The X-ray diffraction analysis showed for the complex the chlorine atoms in a *cis*-configuration; the cyclohexane backbone displays a boat conformation [76].

Palladium(II) and nickel(II) halide complexes of the ferrocenyl polyphosphines (Scheme 28) were synthesized and characterized by multinuclear NMR [77].

Also from the NMR analysis of several nickel and palladium halide complexes of a constrained ferrocenyl tetraphosphine, the existence in solution phase of unique <sup>31</sup>P–<sup>31</sup>P “through-space” nuclear spin–spin coupling constants (JPP) had been evidenced [78].

#### 4.9. Group XIB – Cu, Ag, Au

Effendy et al. [79] reported the synthesis and spectroscopic characterization of new series of derivatives of Me-triphos and Ph-triphos (bis(2-diphenylphosphinoethyl) phenylphosphine) with silver salts (Fig. 25). The <sup>31</sup>P NMR data of silver complexes were reported.

When reacted with silver perchlorate and an excess of NaPF<sub>6</sub>, optically pure (S,S)-hexaphenyl-1,4,7,10-tetraphosphadecane, Ph<sub>2</sub>P-(CH<sub>2</sub>)<sub>2</sub>-PPh(CH<sub>2</sub>)<sub>2</sub>-PPh(CH<sub>2</sub>)<sub>2</sub>-PPh<sub>2</sub> (hptpd) spontaneously self-assembles into a dimeric helical silver complex: (R,R,R,R)-[Ag<sub>2</sub>(hptpd)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (Fig. 26). The X-ray structure has revealed both double helix and side-by-side helix conformers of the disilver cations in the unit cell. 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 [80].

The calix[4]arene matrix [81] is a macrocyclic building block that possesses a remarkable structural versatility and may undergo controlled multiple functionalisation. It has become a widely employed tool for engineering of highly sophisticated molecular and supramolecular systems. It was reported the synthesis and properties of multimetal species. In order to investigate its multiple binding properties towards gold centers, **L2** was allowed to react with 4 equiv. of [AuCl(tht)] (tht = tetrahydrothiophene) in order to obtain Au-complexes **3** (Scheme 29).

The complex **4** (Scheme 30) was formed as the sole product when **L1** was treated with an excess of [Au(tht)-(MeCN)]<sup>+</sup>. The <sup>31</sup>P NMR of the compounds **1–5** are presented in the Table 3.

#### 4.10. Group XIIB – Zn, Cd, Hg

Investigation of the coordination chemistry of Hg<sup>II</sup> is complicated by its tolerance for many different coordination numbers and coordination geometries. Polydentate donor ligands restrict the number of accessible structures. Only recently, it has been shown that the bidentate diphosphine Ph<sub>2</sub>PNHPPH<sub>2</sub> (dppam) strongly favors a face-to-face coordination of Hg<sup>II</sup> [82]. The use of chelating agents for the coordination of Hg<sup>II</sup> is important, since the initial step of the Hg–C bond cleavage process is the induction of higher coordination numbers by nature's mercury detoxification catalysts. The X-ray structure of the mercury complex [Hg(Me)(PP<sub>3</sub>)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, which displays a tricoordinated tetraphosphine PP<sub>3</sub>, was reported by Cecconi et al. [83] (Fig. 27).

Oberhauser et al. [84] prepared several novel complexes of Hg<sup>II</sup> with tetradentate phosphine *cis,trans,cis*-1,2,3,4-tetrakis(diphenylphosphino) cyclobutane (dppcb). There is wide interest [85,86] in complexes containing the core HgL<sub>2</sub>P<sub>2</sub> (P = triorganophosphine, L = anionic ligand) comparable to one half of [Hg<sub>2</sub>L<sub>4</sub>(dppcb)].

The complexes **1–11** (Scheme 31) illustrate the tendency that polydentate donor ligands often geometrically and entropically restrict the number of accessible structures for Hg<sup>II</sup>. Especially, the X-ray structures of **1–3**, **10**, and **11** indicate the preference of Hg<sup>II</sup> for tetrahedral and trigonal pyramidal coordinations in compounds containing dppcb.

### 5. Summary

A great potential in homogeneous catalytic reactions is shown by *hybrid* polydentate ligands, namely those containing different donor atoms. In fact, the *hybrid* ligands, particularly those with phosphorus and nitrogen donors, can provide free coordination sites at the metal during catalysis cycles by the alternative decoordination of either donor, depending on the electronic requirements of the metal–reactant assembly. Finally, it is worth mentioning that the use of tripodal polydentate ligands quite often allows the isolation and characterization of many intermediate species not normally observable in catalytic cycles where monodentate ligands are employed.

The powerful and rather cost and resources-saving aspect of the chemistry of metal/ferrocenylphosphines should provide in the future numerous fundamental and applied advances, at least equivalent to the progress accomplished for the last 50 years.

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