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PHOSPHAALKENES, PHOSPHOLYLS AND PHOSPHININES LIGANDS: NEW TOOLS IN COORDINATION CHEMISTRY AND CATALYSIS

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Abstract

This review covers recent achievements in the area of low coordinate phosphorus ligands featuring P=C double bonds such as phosphaalkenes, phospholide-based complexes and phosphinines. For each class of ligands, the most significant developments are presented and discussed. Particular attention has been paid to the use of these new systems as ligands in homogeneous catalysis.

1. Introduction

The development of the chemistry of heavier main group elements in the beginning of the 70s has profoundly marked several areas of chemistry. Undoubtedly, the discovery of low coordinate species featuring multiple bonding between these elements and others such as carbon and nitrogen will probably remain one of the most significant landmark in this history. However, though many impressive synthetic and theoretical developments were achieved,

only a few practical applications of this chemistry appeared during this pioneering period. Phosphorus has been probably (with silicon) one the most studied elements and, more than 30 years later, it is not really surprising to see the first implications of these discoveries slowly emerging in different areas. The field has now reached an impressive maturity and, as will be seen throughout this review, applications can now seriously be envisionned.

As written by one of its most prominent contributor, phosphorus can actually be regarded as multi-faceted element which can mimic either carbon or silicon or nitrogen depending on its coordinated state [1]. First, it is highly important, even for phosphorus chemists accustomed to the use of phosphorus derivatives in their usual oxidation state, mainly $\lambda^3\sigma^3$ (trivalent phosphorus atom with the coordination number 3) and $\lambda^5\sigma^4$ (pentavalent phosphorus atom with the coordination number 4) to figure out that these analogies, which are not evident at first glance, mainly result from the well-known difficulty of heavier main group elements to achieve sp^2 ($\lambda^3\sigma^2$) and sp ($\lambda^3\sigma^2$) hybridization. Therefore, as it will be underlined on many occasions throughout this review, the chemistry and electronic properties of low coordinate phosphorus species featuring a P=C double bond rarely compare with that of classical trivalent compounds (phosphines) (Figure 1).

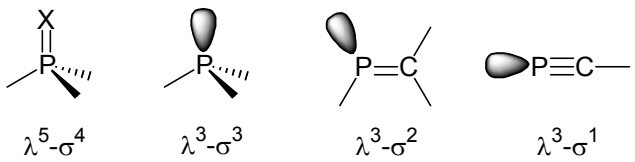


Figure 1: Some coordination states of phosphorus

The main objective of this review is not to present a full coverage of the use of all low-coordinate phosphorus derivatives in coordination chemistry but rather to emphasize the most recent and promising achievements that are expected to lead to interesting and rewarding applications in a near future. Though compounds incorporating a triple bond (phosphaalkyne) are fascinating species, their use in coordination chemistry will not be presented. A very extensive series of reviews on the chemistry of phosphaalkynes is available [2]. In this review, attention will be exclusively paid to the use of acyclic and cyclic derivatives incorporating a P=C double bond.

As a prerequisite, a discussion about the electronic structure of these P=C based ligands is needed to clarify some points. Thus, $\lambda^3\sigma^1$-phosphorus derivatives are often compared to their C=C carbon counterpart since phosphorus is isoelectronic of the C-H fragment. This analogy does not simply rely on this simple electronic equivalency and,

actually, some striking parallels can be drawn between the chemistry of the two systems. The fact that phosphorus is reluctant to give sp and sp^2 hybridization has been widely discussed and it is now well established that the weak overlap between 3s and 3p atomic orbitals on the element is mainly responsible for this situation (large difference in spatial distribution of AOs) [3]. This very specific electronic situation is supported by experimental observations. Thus in phosphaalkenes (P analogs of alkenes), the angle formed by the substituent at phosphorus and the carbon atom (about 100° depending on the substitution scheme at the carbon and phosphorus atoms) is significantly reduced compared to classical sp^2 classical C and N based systems (around 120°). Another important consequence of this weaker hybridization concerns the spatial distribution of lone pair n_p at phosphorus. Theoretical calculations (Natural Bond Analysis carried out on geometries optimized at the B3PW91/6-311++G(3df,2p) level of theory) clearly demonstrate that the orbital which describes this lone pair (for example in $HP{=}CH_2$) is not the highest in energy and features a very important 3s character (66% of the 3s OA and 34% of the 3p OA) [4]. At the opposite, in imines ($HN{=}CH_2$), the HOMO describes the lone pair at nitrogen and features a reverse orbital distribution (39% of the 2s OA and 61% of the 2p OA) (see figure 2). Note that the small energetic difference between the π and the n_p OM in $HPCH_2$ has already been suggested by UV photoelectron spectroscopy (-10.3 eV for the π bond and -10.7 eV for the n_p orbital)[5]. These data are not specific of phosphaalkenes and other low coordinate phosphorus ligands display similar properties. Thus, in phosphinines [6] and phospholide anions [7], which are the respective analogs of pyridines and pyrrolyl anions, the lone pair at phosphorus also lies at lower energy than the first molecular orbital which describe the π-system. Also, in phosphinine (61% of the 3s OA and 39% of the 3p OA) and pyridine (29% of the 2s OA and 71% of the 2p OA) the difference between the respective participation of the ns and np OAs in the lone pairs at the heteroatom is similar to that calculated in the case of $HPCH_2$ and $HNCH_2$ (Scheme 2). Another important consequence of this weaker hybridization concerns the basicity of the lone pair which is, as expected, very low in low coordinate phosphorus derivatives [8]. Accurate values of gas-phase proton affinities were obtained from ion-cyclotron resonance techniques: 219.4 $kcal.mol^{-1}$ for C_5H_5N and 195.8 $kcal.mol^{-1}$ for C_5H_5P [9].

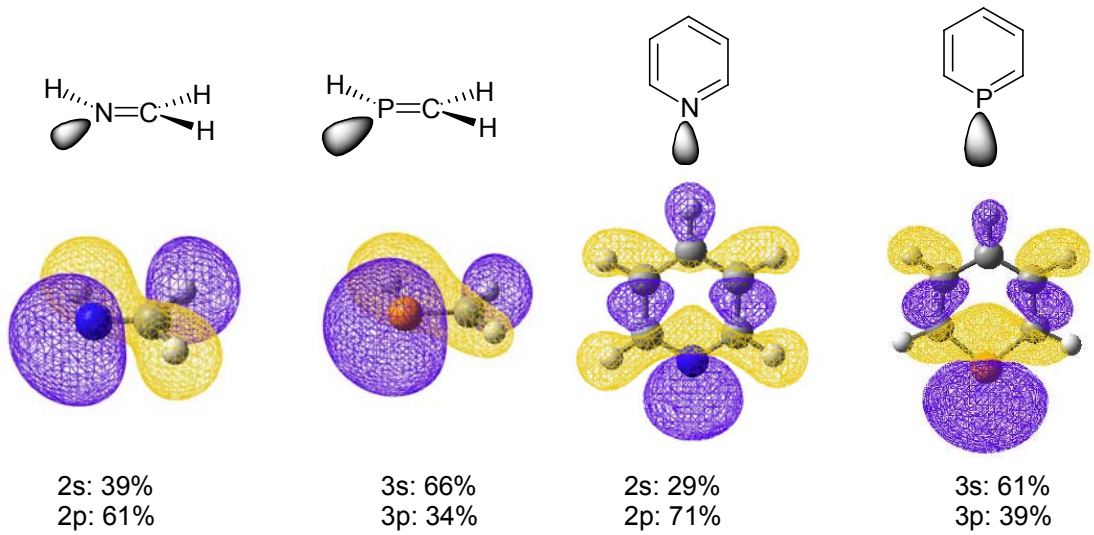


Figure 2: Molecular orbitals describing the lone pairs in $HP{=}CH_2$, $HNCH_2$, pyridine (C_5H_5N) and phosphinine (C_5H_5P) with relative percentage of ns and np contributions.

The difference of electronegativity is a second major effect that helps to rationalize difference observed in the respective reactivities of C=C, N=C and P=C based systems. Phosphorus (2.1) being more electropositive than carbon (2.5) and nitrogen (-3.0) according to the Pauling scale, the σ- P-C system is strongly polarized [10]. However, as attested by UV absorption and circular dichroism experiments made by Michl et al on phosphinines, the π-electronegativity of phosphorus appears to be more important than that of carbon [11]. Therefore, in such systems, phosphorus is expected to act as a σ-electron acceptor but as a π-electron donor. This very specific electronic balance makes the π-system apolar and explains why in some cases the reactivity of these low coordinate phosphorus compounds closely mimics that of their carbon derivatives. However, in P=C based systems the phosphorus atom still bears a significant positive charge. Thus, NBO calculations on $HP{=}CH_2$ (B3PW91/6-311++G(3df,2p)) reveal that a positive charge of resides at phosphorus (+0.42 e) [12]. Quite logically, in imines the situation is reversed and the nitrogen atom of $HN{=}CH_2$ bears a substantial negative charge (-0.59 e). Though interesting parallels can be established, the energy of the P=C bond strength (45 kcal/mol in $HP{=}CH_2$) remains weaker than that of olefinic systems (65 kcal/mol for $CH_2{=}CH_2$) [13]. As a consequence, most of these low coordinate derivatives only exist as isolable species when a significant kinetic stabilization, which prevents the oligomerization process, is provided. Usually, this can be achieved by encumbering either the phosphorus atom or the carbon atom. Molecules such as the Mes*PCH_2 phosphaalkene (Mes* = 2,4,6-tris-*t*-butyl-benzene) are highly resistant towards hydrolysis and oligomerization and can be isolated through classical chromatographic

purification. Another important way to stabilize the P=C systems obviously consists in incorporating the bond in a delocalized system to provide a thermodynamic stabilization. Historically, the phosphamethyne cyanine cation **1** was the first compound featuring a delocalized P=C bond system to be successfully isolated [14]. The aromaticity of group 15 heterocycles has been the subject of many debates but, henceforth, significant theoretical (homodesmic reactions and magnetic criteria) and structural arguments have been provided to emphasize the remarkable conjugative ability of the P=C system [15]. Thus, the aromaticity of phosphinines has been estimated to be approximately 88% of that of benzene [16] and phospholide anions are nearly as aromatic as their carbon counterparts, the ubiquitous cyclopentadienyl ligands (Figure 3) [17].

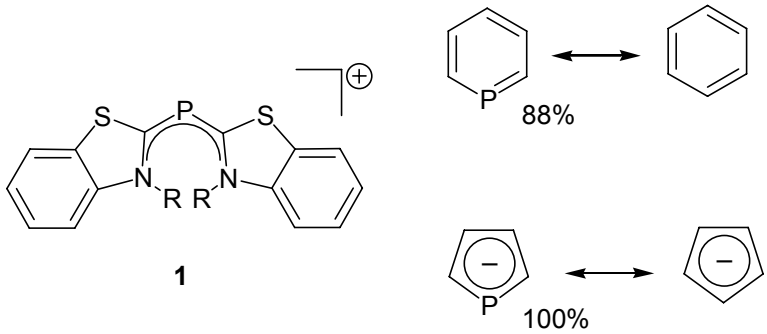


Figure 3: The phosphacyanomethine cation and the aromaticity of phospholyl anions and phosphinines.

Considering all these data, it is quite clear that the coordination chemistry of these P=C based systems is expected to be remarkably different from that of classical C, N and other P based ligands. Thus, if one considers coordination through the phosphorus atom lone pair (η^1-coordination), these derivatives are known to act as weaker σ-donor than most of classical sp^3 hybridized phosphines featuring three P-C bonds and imines. However, the electropositive character as well as the weakest hybridization of phosphorus makes the π*-system of these systems low in energy, thus yielding a significant π-accepting capacity. Noteworthy, a striking analogy that will be further discussed in the case of the cooordination chemistry of phosphinines, exists between P=C based ligands and the carbonyl ligand. Indeed, unlike to imines, the π*orbital is mainly developed on the element which is directly bound to the metal in both systems (on P in P=C systems and on C in CO) as depicted in figure 4.

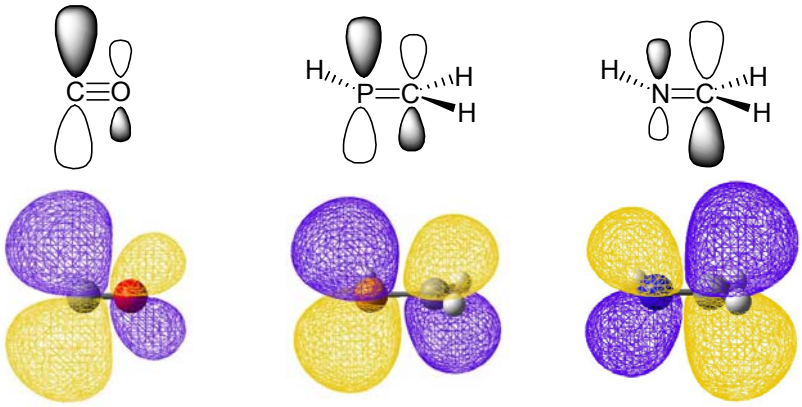


Figure 4: A comparison between the LUMOs of CO, $HPCH_2$ and $HNCH_2$ illustrating the π-accepting capacity of low-coordinate based phosphorus ligands.

Interestingly, all these low coordinated phosphorus ligands can accommodate various bonding modes and combination of bonding modes due to the presence of the phosphorus atom lone pair and a reactive π and π*-system. Indeed, one of the most important analogy with anionic and neutral carbon-based ligands resides in the fact that η^2, η^3, η^4, η^5 and η^6 coordination modes are also usually encountered with these derivatives. As will be seen later, this remarkable ability to yield π-complexes is at the origin of very important synthetic developments in coordination chemistry and applications in homogeneous catalysis. Some of the most usually encountered bonding modes are presented in the following scheme (Figure 5).

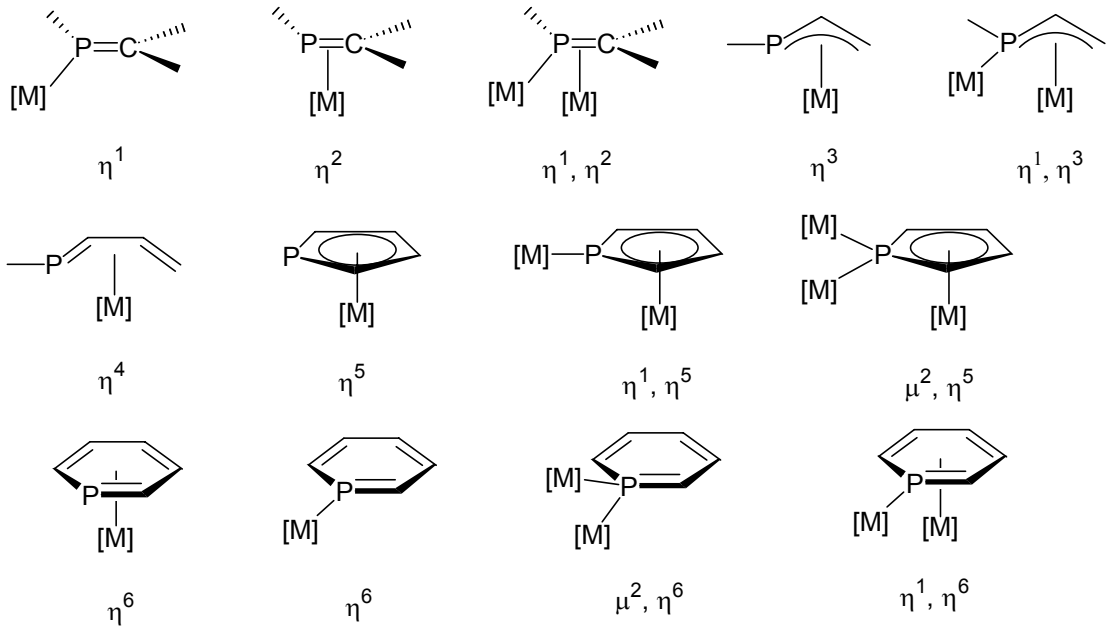
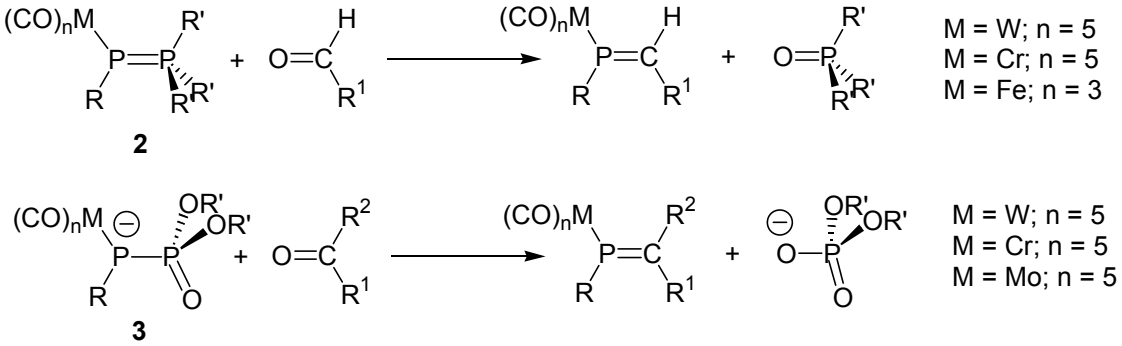


Figure 5: Some bonding modes of low coordinate phosphorus based ligands.

2. Ligands syntheses and Coordination Chemistry

2.1 Phosphaalkenes and their complexes

As previously explained, weakly substituted phosphaalkenes are usually highly unstable and a significant steric protection is needed to ensure a sufficient kinetic stability [18]. Phosphaalkene complexes are accessible via two routes, the most evident one consisting in coordinating a metal fragment at the phosphorus atom lone pair. A second approach, known as the Phospha-Wittig reaction, affords metal carbonyl derivatives of phosphaalkene with group 6 and 8 metals in a straightforward way (Scheme 1). This method, which is directly derived from the classical Wittig (reagent **2**) and Wittig-Horner (reagent **3**) reactions allows an easy access to a wide range of complexes of poorly substituted derivatives that could not be obtained following classical routes [19]. Note that this approach was extended to the synthesis of uncomplexed phosphaalkenes provided that a bulky group is present at the phosphorus atom [20]. A mettalaphospha-Wittig reaction has also been developed by Stephan et al. [21].



Scheme 1: The Phospha-Wittig and The Phospha-Wittig-Horner approaches toward phosphaalkene complexes.

A series of interesting kinetically protected mono bi- and tridentate ligands were reported by the groups of Geoffroy [22] and Yoshifuji [23] following the Phospha-Petersen route that involves the reaction of a silylated anion of the type RPHSi(*t*-Bu)Me_2 with an aldehyde. Some Pd(II) complexes were prepared and structurally characterized. In such systems, the presence of the bulky substituent Mes* proved to be essential to prevent oligomerization of the phosphaalkene. Interestingly, with C-arylated phosphaalkene an insertion an orthometallation takes place with the concomitant release of HCl and the ligand behaves as a classical "pincer" such as in dimer **4** (Figure 6). Importantly, 1,3 bis and 1,2,4,5-tetrakis(2-phosphaethenyl) benzene derivatives exhibited the same reactivity allowing the

synthesis of dimetallic complexes **5-7**. These complexes were electrochemically reduced between -0.92 and - 1.29 V (*vs* SCE), and the resulting paramagnetic Pd(I) and Pt(I) species were studied by ESR in liquid and frozen solutions. This reduction process was shown to be a ligand-centered process and it was shown that an appreciable part of the unpaired electron is localized on each of the phosphaalkene carbon atoms (20%) and phosphorus atoms (5%) [24]. The group of Geoffroy extended this approach to the synthesis of biphenyl derivatives such as **8** [25]. Palladium complexes of a 1,2-bis(2-phosphaethenyl) benzene such as **9** were also investigated and proved to be more reactive than 1,3-bis(2-phosphaethenyl) derivatives. In the presence of alcohol such as MeOH complex **10** which results from the methanolysis of one P=C bond is formed (Figure 6) [26].

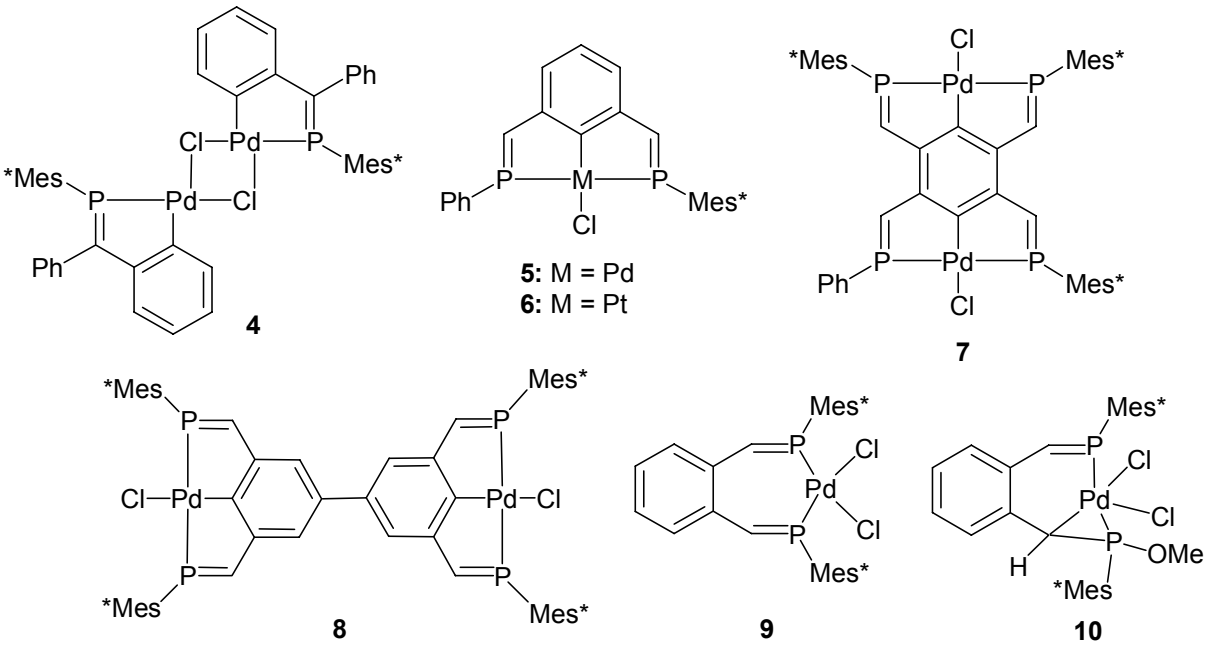
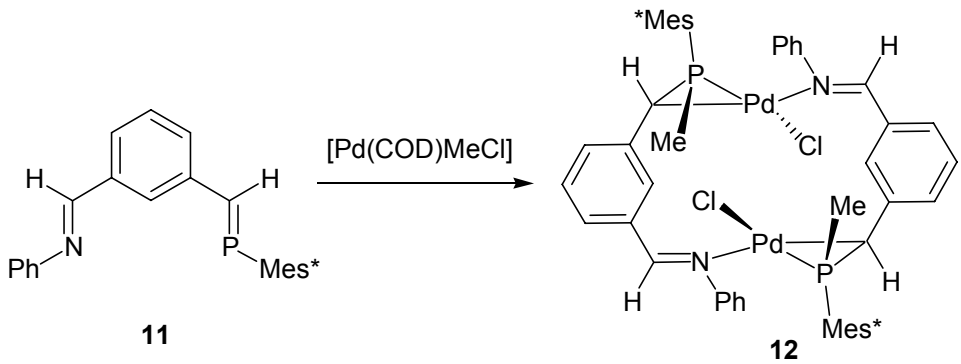


Figure 6: Some chelate and pincer ligands featuring phosphaalkene as ligands.

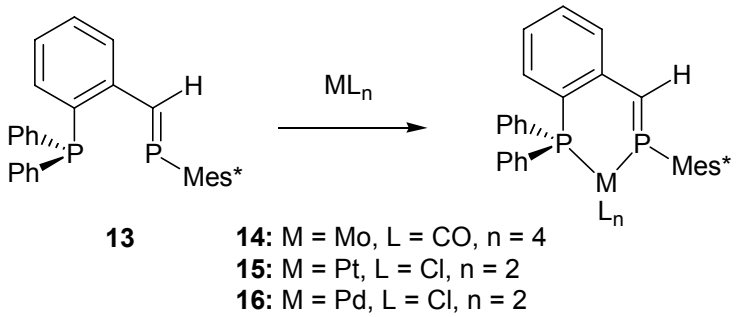
A similar strategy has been applied to the synthesis of an interesting mixed bidentate P-N ligand **11** featuring a phosphaalkene moiety and an imine ligand. Reaction of this ligand with [Pd(COD)MeCl] resulted into the formation of the bimetallic macrocyclic derivative **12**. In this transformation the structure of the phosphaalkene was not preserved and an insertion of the P=C bond into the Pd-Me bond has taken place presumably after classical η^1-coordination of the phosphorus atom lone pair (Scheme 2) [27]. Interestingly, one can note that this mechanism is analogous to the (1,1) insertion of carbonyls into a metal-alkyl bond thus underlying the close analogy between coordinated P=C and CO ligands. This reaction can also be viewed as the initial step of the well-known Heck reaction that allows the direct

functionalization of olefins. A similar reaction occurs when the imine moiety is replaced by a 2-pyridyl ligand.

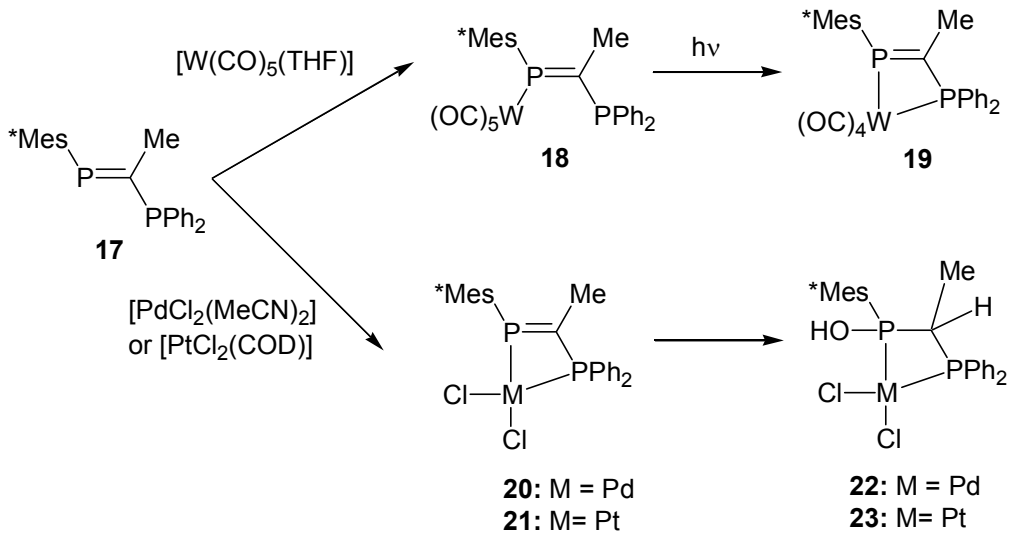


Scheme 2: Reaction of bidentate ligand N with [Pd(COD)MeCl]

Mixed bidentate ligands **13** featuring a classical diphenylphosphino group and a phosphalkene as ancillary ligand were reported by Stelzer et al. The corresponding molybdenum tetracarbonyl **14** as well as $PdCl_2$ and $PtCl_2$ chelate complexes **15** were readily synthesized and successfully characterized by X-ray crystallography (Scheme 3) [28]. Interestingly, a straightforward route to ligands such as **17** featuring the 1,3-diphosphapropene skeleton has also been recently developed by the group of Yoshifuji. Preliminary studies have showed that the systems can behave as mono and bidentate chelate ligands such as in the pentacarbonyltungsten complexes **18** and **19**. However, dichloride complexes of group 10 metals (M = Pd, Pt) such as **20** and **21** were found to be relatively sensitive towards moisture. Water readily reacts onto the P=C double bond to afford the corresponding hydroxy-phosphine complexes **22** and **23** (Scheme 4) [29, 30].

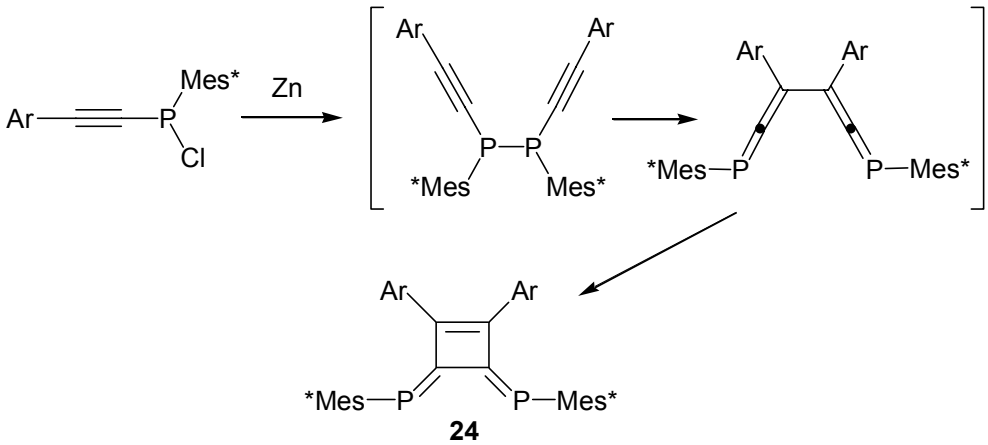


Scheme 3: Coordination chemistry of 1,3-diphposphapropenes with group 6 and group 10 metals.



Scheme 4: Coordination chemistry of ligand **17**.

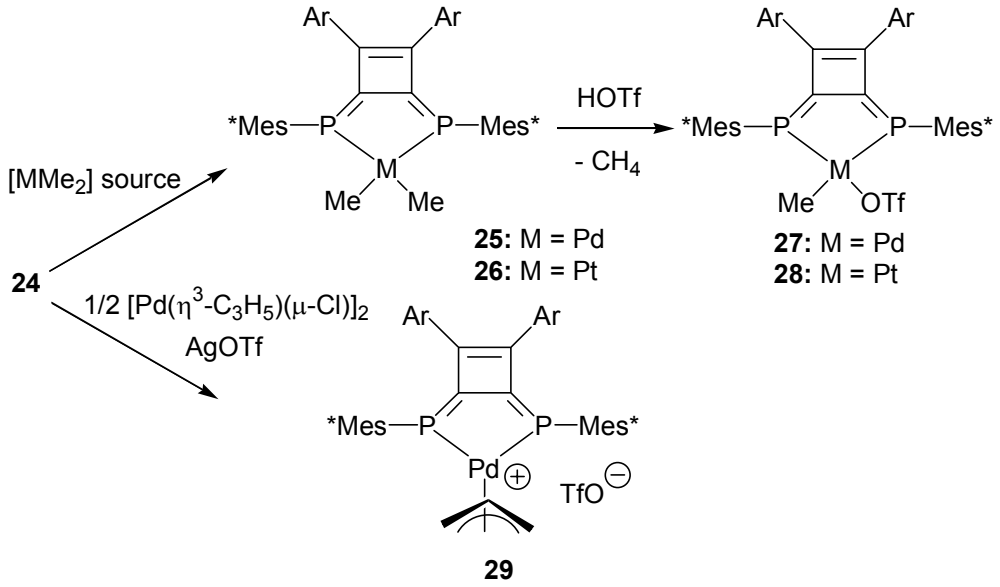
More recent studies focused on the synthesis and use in coordination chemistry and catalysis of phosphorus equivalents of 1,4-diazabutadiene ligands such as diphosphinidenecyclobutenes (DCPB) [31]. The group of Yoshifuji developed a convenient synthetic route based on the methodology developed by Appel. The key step of this procedure relies on a Phospha-Cope rearrangement that affords a (diphosphaallenyl) which spontaneously rearranges to yield the very stable compound **24** (Scheme 5). This procedure has also been extended to the synthesis of derivatives having ring-fused structures [32].



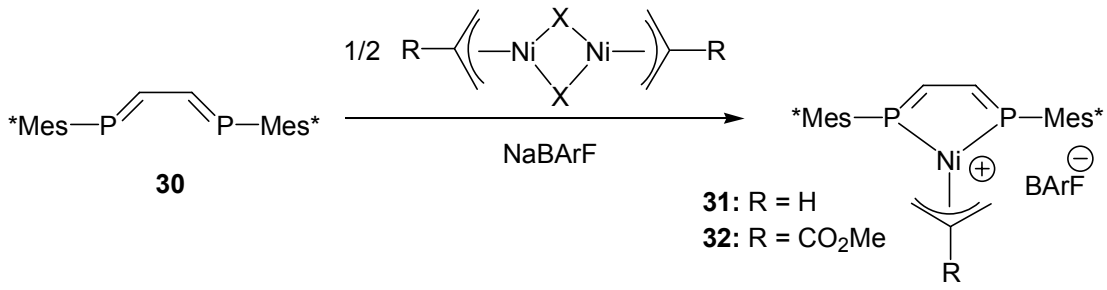
Scheme 5: Synthesis of diphosphinidenecyclobutene ligands

Various Pd(II) and Pt(II) derivatives of **24** were prepared according to classical procedures that involve displacement reactions of ligands with the $[MCl_2(MeCN)_2]$ [33], $[PtMe_2(SMe)_2]_2$ and $[PdMe_2(tmeda)]$ (tmeda = N,N,N',N'-tetramethylethylene diamine) precursors which function as a source of MCl_2 and MMe_2 fragments (M = Pd, Pt) respectively

[34, 35]. Reactions of these complexes **26** and **26** with trifluoromethane sulfonic acid yielded the expected cationic monomethyl derivatives **27** and **28** (Scheme 6). Cationic allyl palladium complexes such as **29** were also synthesized and characterized by X-ray crystal structure. As will be seen later all these palladium complexes showed an interesting catalytic activity in various processes. A view of one molecule of **29** is presented in figure 7. Less attention has been paid so far to cationic Ni(II) complexes. In 2003, Ionkin and Marshall from reported on the synthesis of a η^3-allyl(1,4-diphospha-(1,3)-butadiene) nickel complexes **31** and **32** which were tested in ethylene polymerization. The above mentioned complex were obtained by the reaction of the (E,E) stereoisomer of the 1,4-diphospha-1,3-butadiene **30** with the corresponding π-allylnickel halide dimers in the presence of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Scheme 7) [36].



Scheme 6: Synthesis of DCPB Pd and Pt(II) complexes.



Scheme 7: Synthesis of a 1;4-diphosphabutadiene Ni(allyl) cationic complex.

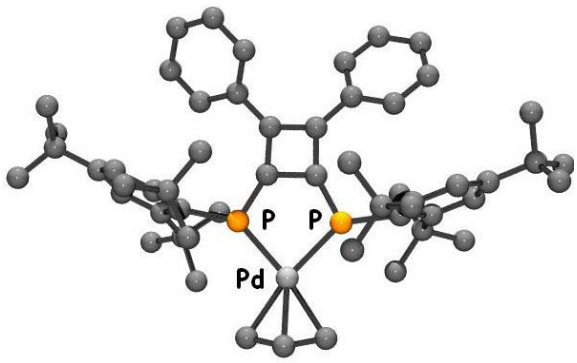


Figure 7: a view of one molecule of the 1,4-diphosphabutadiene Pd (allyl complex) **29**.

Heteroditopic ligand featuring a phosphaalkene and sulphur or nitrogen based ligand were also reported. An example is provided in the following scheme with the synthesis of Pd(II) neutral **33** and cationic complexes **34** of a mixed 2-methyl-3-thioxo-1,3-diphosphapropene ligand [37]. Brookhart and his group also reported on the synthesis of other mixed P-N, P-S systems [38]. Whereas mixed phosphaalkene-imine **35** ligands were prepared according to the elimination methodology developed by Bickelhaupt, the phosphaalkene-thioether **37** (R = Mes* or *t*-Bu) were obtained via the classical Phospha-Petersen route. It was shown that these ligands efficiently coordinate the cationic PdMe(MeCN) fragment as depicted in the following figure 8 to yield complexes **36** and **38**. As will be seen later, these complexes catalyze the oligomerization of ethylene with moderate to high rates but display higher stability compared to α-diimine-palladium related systems.

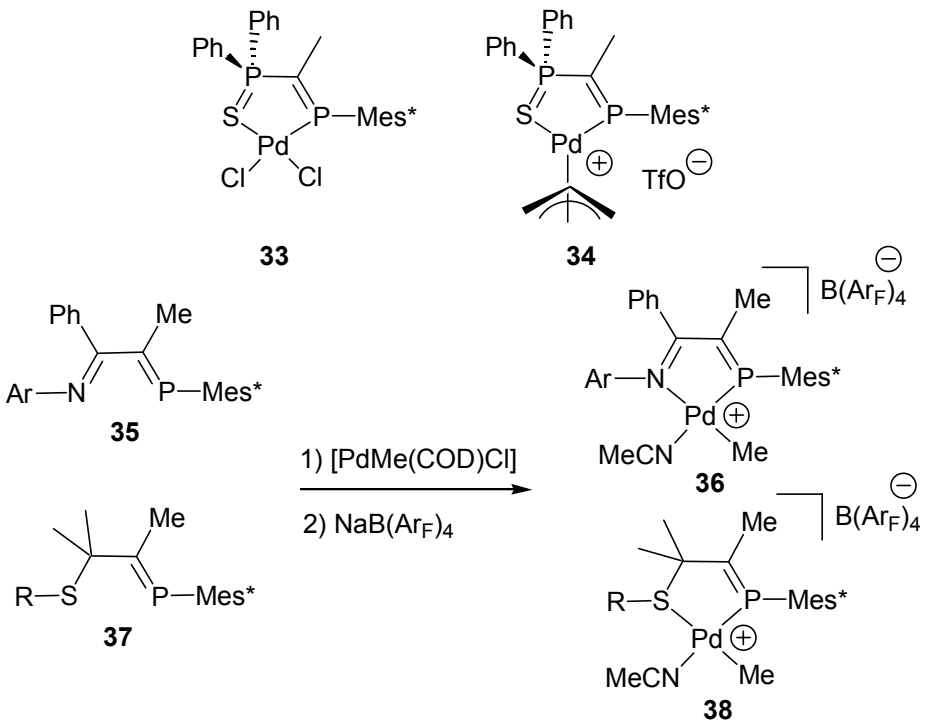
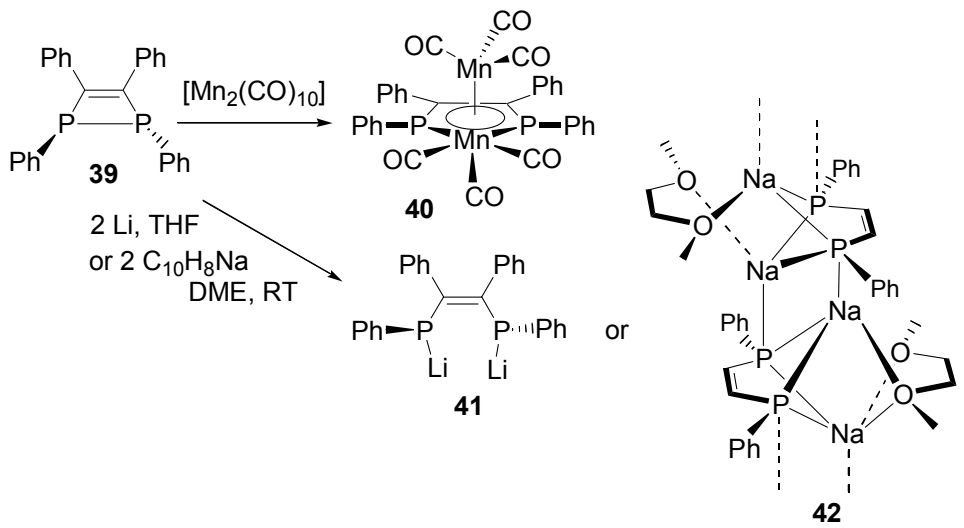


Figure 8: Mixed S,P and N,P based complexes featuring a phosphaalkene moiety.

Kinetically unstable phophabutadienes have also found application in the stabilization of other complexes. So far, studies were only limited to P-phenylsubstituted derivatives which do not exist under their free form but can be easily generated through their "masked form " the 1,2-dihydrophosphete ring **39** [39]. Two synthetic strategies have been devised to exploit the coordinating properties of these masked 1,4-diphosphabutadienes. The first one relies on the reactivity of the σ P-P bond. Indeed it was showed that some metal fragments can readily be inserted into this bond to yield a variety of structures. Though no mechanistic studies have been undertaken yet, these insertions are probably promoted in a first step by the coordination of one (or two) phosphorus atom lone pairs to the incoming fragment. For example, $[Mn_2(CO)_{10}]$ easily reacts with **39** to cleanly afford the bimetallic complex **40** [40]. In **40** the phosphabutadiene acts as a 8 electron donor. One may regard **40** as the coordination of a $[Mn(CO)_3]^+$ fragment onto the π-system of 1-tricarbonylmangana-2,5-diphospholene. Four electrons are given by the two phosphorus atom lone pairs and four additional electrons by the η^2-coordination of the two P=C bonds onto the $[Mn(CO)_3]^+$ fragment. As will be seen further, the same type of complex was also formed when a 2,2-biphosphinine is used as ligand. Metal complexes of group *10* metals were also studied in some details. Two synthetic routes were developed. Several $[Ni(L)_2]$ (L = phosphine or $(L)_2$ = diphosphine) fragments were inserted into the P-P bond of **39** to afford complexes in which the ligand behaves as a classical four-

electron donor [41]. Interestingly, a second route involving reaction of dianions of **41** has been employed. This second procedure relies on the dielectronic reduction of **39** that affords monomeric **41** and polymeric **42** dianions which can be regarded as the di-reduced form of the 1,2,3,4-tetraphenyl-1,4'diphosphabutadiene (Scheme 8) [42]. Reaction of these dianions with $[NiCl_2(L)_2]$ complexes yielded nickeladiphospholene complexes in which the ligand acts as a 2 electron-donor (1+1), the nickel atom being at the oxidation state +2 (distorted square planar geometry). Though in most cases only one form could be isolated, both forms were shown to equilibrate in some cases. The first route has been transposed to platinum complexes. The geometry of the [Pt(**39**)(dppe)] (dppe = $Ph_2PCH_2CH_2PPh_2$) complex was found to be intermediate between tetrahedral and square planar and a direct assessment of the oxidation state of the metal could not be precisely ascribed (Pt(0) complex in **43** and Pt(II) complex in **44**). The most important conclusion of this study was that a judicious choice of the phosphine co-ligands allows to finely tune the electronic delocalization within the metallacycle. Homoleptic complexes of group *10* metals were also prepared following the route that involves the reduction of the ligand as a prerequisite. Dianionic platinum complexes of these ligands were structurally characterized. However, examination of internal metric parameters within the diphosphametallacycle reveals that the platinum has the oxidation state +2 and that the complex cannot be considered as the coordination of two phosphabutadienes onto a dianionic Pt(2-) centre. In both complexes **45** and **46**, the two phosphorus atoms adopt a tetrahedral geometry. When cryptands are employed to encapsulate the Li cations, the complex adopts a square planar geometry as expected for a metal having the d^8 electronic configuration (Figure 9).



Scheme 8 : Reactivity of dihydrophosphete **N** towards $Mn_2(CO)_{10}$ and alkali.

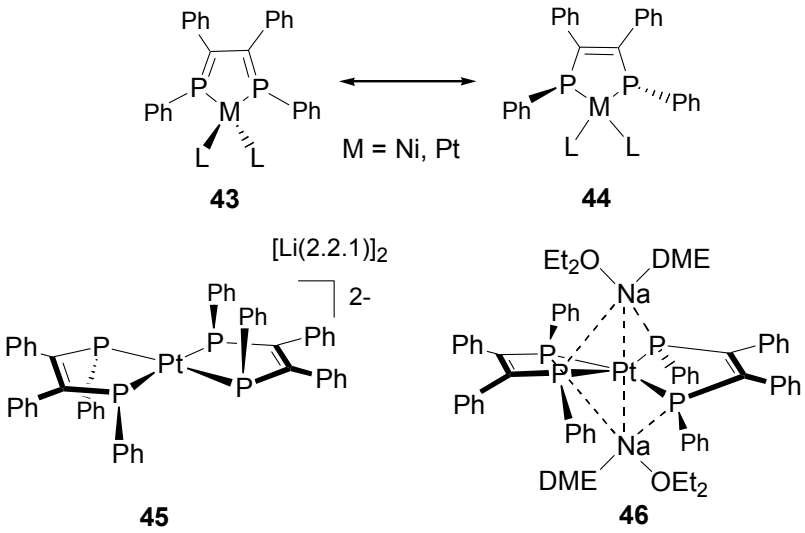
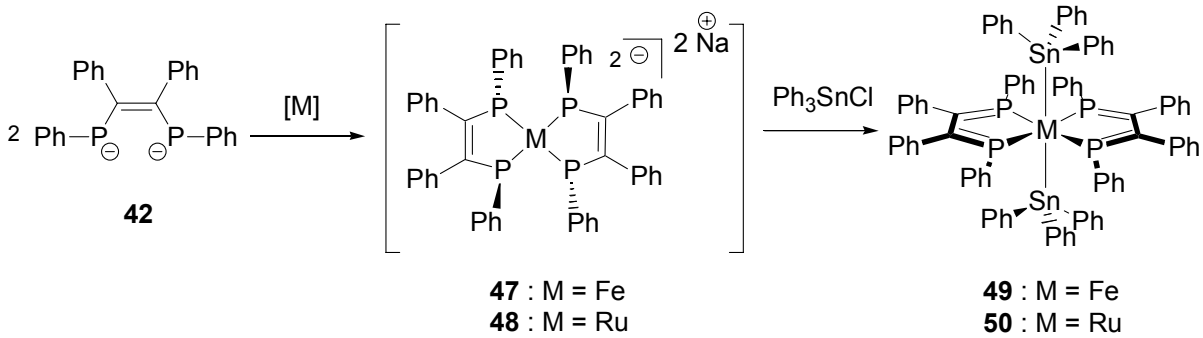


Figure 9 : Neutral and dianionic metalladiphospholene complexes of group 10 metals.

Similar results were obtained with Fe(II) and Ru(II) centres. As can be seen in the following scheme, reaction of dianion **42** in THF at low temperature with $[FeCl_2(THF)_{1.5}]$ and $[Ru(COD)Cl_2]_n$ afforded two dianionic complexes **47** and **48** of unknown structure. However treatment of these species with Ph_3SnCl yielded the two Fe(II) **49** and Ru(II) **50** complexes in which the ligands behaves as chelating 1,4-diphosphabutadienes, the two phosphorus atoms in each ligand adopting a trigonal planar geometry (Scheme 9).



Scheme 9: Fe and Ru Dianionic complexes of a 1,4-diphosphabutadiene.

Recently attention has been paid to the elaboration of polymers containing phosphabutadienes. In 2004, Yoshifuji et al. presented the first successful synthesis of 3,4-diphosphinidenecyclobutenes (DCPB)–based polymers **51** [43]. Other synthetic strategies allowing the synthesis of polymeric material such as **52** and **53** were also devised. The thiophene-base polymer **54** was obtained with 9% yield (M_n = 58 000, M_w/M_n = 7.8).

Importantly, reaction of the latter with the $[PdCl_2(PhCN)_2]$ precursor afforded an insoluble material. Elemental data suggest that the polymeric structure is in good agreement with the proposed formula featuring one $[PdCl_2]$ fragment for one DCPB ligand. Combustion data also confirmed the absence of nitrogen atom and therefore of free $[PdCl_2(PhCN)_2]$ (Figure 10) [44]. Though it comes out of the scope of this review, it must also be mentioned that phosphaalkenes were recently employed to prepare phosphine-based polymeric materials. Thus the $MesP{=}CPh_2$ phosphaalkene **55** (Mes = 2,4,6-trimethylphenyl) was polymerized between 150-200°C to yield the alternating polymethylenephosphine **56** ($M_w \approx 10^4$ $gmol^{-1}$) polymer using MeLi or VAZO as initiators (VAZO = azobis(cyclohexanecarbonitrile) [45]. The same compound was also employed in a radical promoted polymerization process with styrene using VAZO as initiator to produce the hybrid inorganic-organic copolymer **57** ($M_w \approx 10^4$ $gmol^{-1}$). For example co-polymerization of **55** (20%) with 80% of styrene affords a copolymer containing 2.16 wt% phosphorus which corresponds approximately to 9% incorporation of the phosphaalkene and 91 % of styrene [46]. Copolymer **57** was found to be soluble in common organic solvents, stable towards hydrolysis and slowly oxidizes in air (Scheme 10). Importantly, these two results open interesting perspectives in the chain-growth of polyolefins containing functional phosphorus moieties. Preliminary studies revealed that Pd(0) centres can be incorporated into copolymer **57**. The resulting material was evaluated as supported catalyst for the Suzuki coupling of phenylboronic acid with bromobenzene [47].

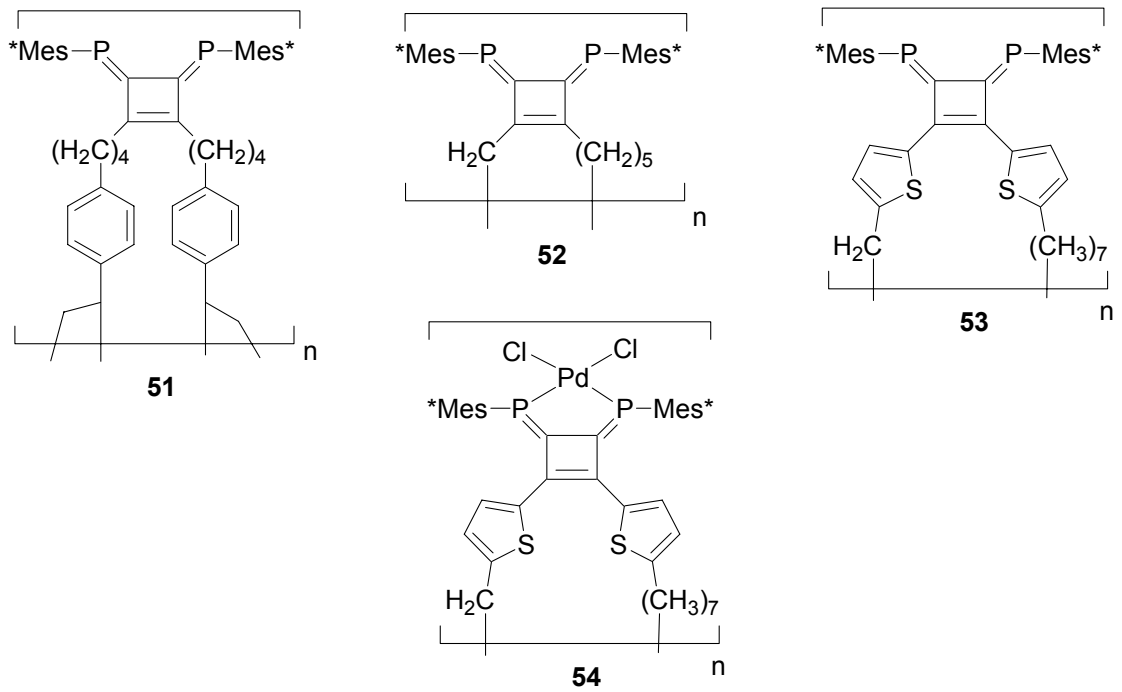
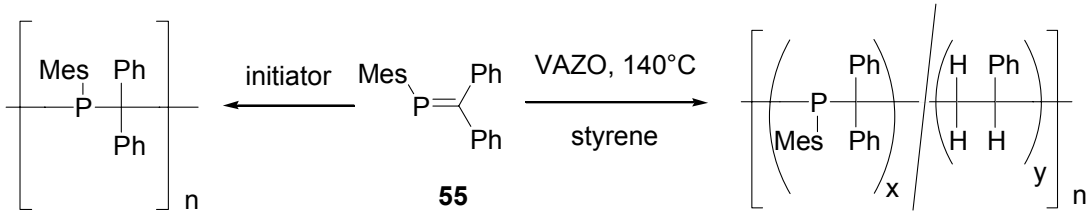


Figure 10: Phosphaalkene–based polymers incorporating the DCPB motif.



56 57

Scheme 10: Synthesis of phosphine-based polymers using MesP=CH_2 as precursor.

Other types of phosphaalkenes have also found applications in coordination chemistry. C-amino substituted phosphaalkene is an important class of compounds whose electronic properties markedly differ from classical-C substituted phosphaalkene. A review by Weber has recently summarized syntheses of these ligands and their complexes [48]. Due to the presence of a strong π-donor substituent (amino group), the polarity of the P=C double bond system is inversed and in such ligands, the C-N bond presents a siginificant double bond character and the rotation barrier of the P=C bond is significantly weakened. Theoretical calculations heve confirmed these experimental observations. NBO analysis carried out within the framework of DFT at the B3LYP/6-31G* level of theory have unambiguously showed that the positive charge at the phosphaalkene is significantly reduced in C-amino substituted species with regards to classical phosphaalkenes (figure 11) [49]. In disubstituted ligands which can formely be regarded as adducts between a stabilized diaminocarbene and a phosphinidene fragment, the charge at phosphorus is close to zero. Therefore, the resonance structure drawn in figure 11, which features two lone pairs at the phosphorus atom, can be employed to describe these species. Accordingly, their coordinating behaviour differs from that of phosphaalkenes. An illustrative example was provided with the reaction of the diaminophosphaalkene **58** with BH_3.THF which yields adduct **59** (Figure 12) [50]. Similarly, it was also showed that mononuclear $Cr(CO)_5$ complexes are dismutated into binuclear species such as **60** and the free ligand [51]. Dinuclear complexes such as **61** were also more conventionnaly prepared by reacting P-metallated species with transition metal fragments ($Ni(CO)_4$ in this case) [52]. Several studies were also devoted to the chemistry of cyclic species such as the diphosphirenium ligand **62**. In 1994, Bertrand and coll. showed that [$Pd(PPh_3)_2$] insert into the P-P bond to yield the interesting complex **63** [53]. The coordination chemistry of 1*H*-diphosphirenenes was also studied by the same group. Upon reaction of **64** with one equivalent [$W(CO)_5$(THF)] coordination does not take place through the lone pair of

sp^2-hybridized P atom but through that of the phosphino group [54]. However in the presene of two equivalents the two lone pairs were complexed. Moreover, it was also showed that reaction of $[Fe(CO)_9]$ led to a breaking of the P-P bond to afford the interesting dinuclear iron complex **65** [55].

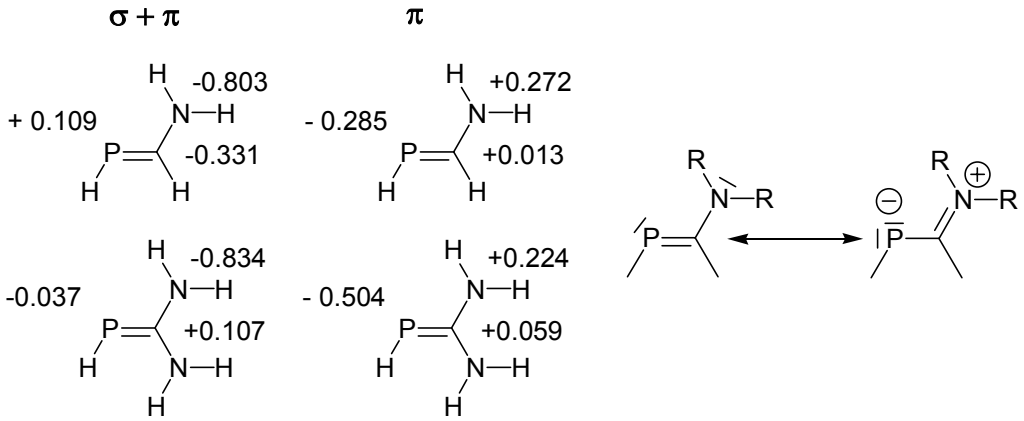


Figure 11: Phosphaalkenes with inverse electron density.

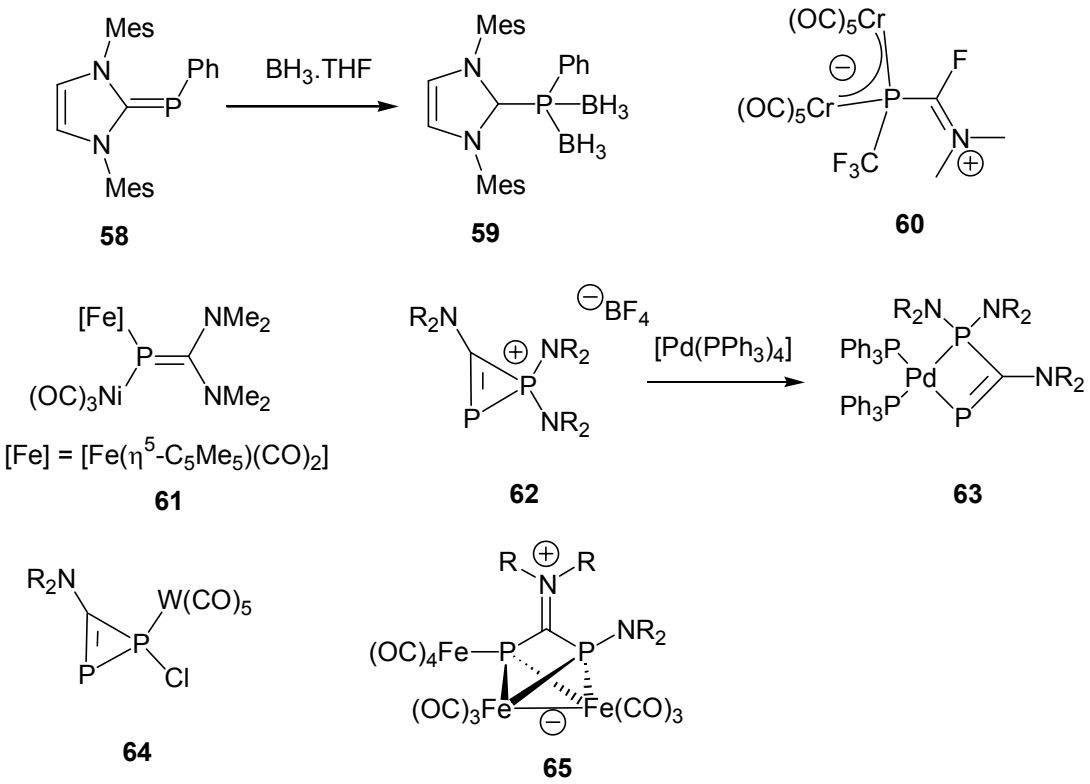


Figure 12: Some complexes of C-aminsusbtituted phosphaalkenes

2.2 *Phospholide ligands and their complexes*

Like their carbon counterparts, the ubiquitous cyclopentadienyls anions, phospholyls are probably the most widely studied and employed low coordinate-based phosphorus ligands

in coordination chemistry and catalysis. This is mainly due to their great availability and to their remarkable capacity to stabilize different alkali, main group elements, transition metals, actinides and lanthanides in very different oxidation states. Since the discovery of phosphacymantrenes [56] and phospha [57] and diphosphaferrocenes by Mathey et al. [58], the field has become so large that it would not be reasonable to propose a full coverage in a single sub-chapter. Furthermore, excellent and very complete reviews written by experts in the field have appeared over the last few years and readers can refer to it for further details [59]. Therefore, in this sub-chapter, only the most recent and most promising developments in the chemistry of monophospholyl ligands will be addressed. Under the generic name "monophospholyl", we only consider aromatic five membered rings featuring a single phosphorus atom and no other heteroatom. However it must be mentioned that the chemistry of polyphospholyl anions is still a very active field of investigation [60].

One of the most significant property of phospholyl ligands is their ability to act as both as a good π-donor and π-acceptor ligand. Though no theoretical calculations aimed at estimating the balance between the two effects one currently admits that phospholyl ligands are slightly less good π-donors than their carbon analogs but usually exhibit a greater π-accepting capacity (equivalent substitution scheme). On the basis of IR-Raman experiments it was proven that the phospholyl ring is an intrinsically poorer π-donor than the cyclopentadienyl ligand towards Mn in cymantrene complexes [61]. On the other hand the stronger π-accepting capacity of the phospholyl ligands is evident from electrochemical data recorded in a series of phosphaferrocenes. Indeed, it has been shown that the replacement of a CH fragment by an sp^2-phosphorus atom in ferrocenes is associated with an anodic oxidation potential shift of about 185 mV [62]. Importantly, this value was found to be nearly independent of the substitution pattern of the ring. Though the introduction of phosphorus is believed to destabilize the corresponding phosphaferricinium cations, phospha **66** [63] and diphosphaferricinium **67** [64] have been isolated and structurally characterized very recently (Figure 13). Examination of X-ray data clearly suggest that in both complex the oxidation takes place on a non-bonding centred metal-orbital that features no (or a very weak) participation of the ligand.

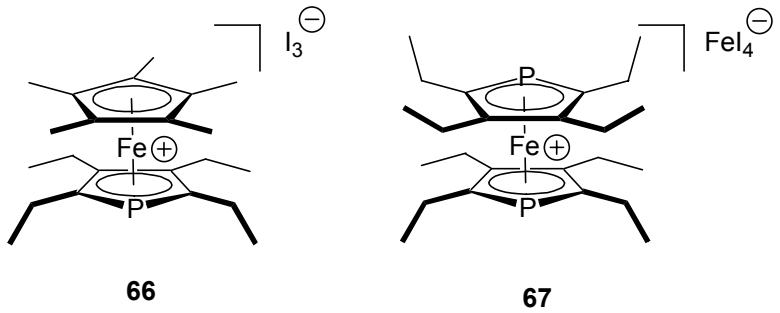
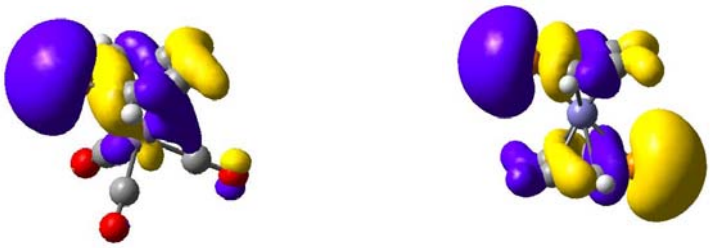


Figure 13: Phospha and diphosphaferricinium complexes.

Several synthetic approaches towards phospholyl anions were developed. The first one involves the cleavage of a P-R bond of a phosphole [65]. This two electron reductive process is driven by the aromaticity, phospholyl anions showing a strong aromatic character contrary to phospholes. In general R is a phenyl or an halogeno substituent (mainly Cl) [66] and reactions can be carried out with Li, Na or K [67]. A second route relying on the cleavage of P-P bonds or P-CH_2-CH_2-P [68] or P-alkyls bonds was also devised [69]. This approach allows for the synthesis of pure solutions of phospholyl anions since no R^- anions are produced. Transient 2*H*-phospholes formed through a 1,5-sigmatropic shift of the R group at phosphorus can also be employed as a very convenient source of phospholyls anions when the sigmtropic reaction is carried out in the presence of a base [70]. This new method has found many applications in the synthesis of 2-functional phospholyls and their transition metal complexes. Finally, a fourth method, which relies on the reaction of $MP(SiMe_3)_2$ (M = Ca, Sr) with diynes has been recently achieved [71].

Phospholyls can be regarded as ambivalent ligands that can coordinate elements and transition metals either trough their π-system (η^5-coordination) or through the phosphorus atom (η^1-coordination). However, it is now well established that the formation of η^1-complexes is strongly disfavoured by the presence of substituents at the α-positions at phosphorus as will be seen in further examples. Not only phospholyls but also their complexes π-complexes, which will be named as phosphametallocenes can act as efficient ligand through their phosphorus atom lone pair (under the generic name "phosphametallocene", structures involving η^5-phospholyl-metals units are considered including half-sandwich complexes). Like in other low coordinated phosphorus compound, the phosphorus atom lone pair of these phosphametallocene features a very important contribution of the 3s orbital at phosphorus and is therefore highly spherical. As will be seen later, this electronic feature accounts for chelate bonding modes observed in the coordination chemistry of these metallocenes. For example, theoretical calculations indicate that in

phosphacymatrenes and phosphaferrocenes the participation of the 3s orbital is about 68% and 67 % respectively (B3PW91/6-31+G* and LANL2DZ for Fe) (Figure 14) [72]. Recent calculations using the Charge Decomposition Analysis program (CDA) have also clearly demonstrated that phosphaferrocenes behave as modest σ-donor but good π-acceptor ligands [73]. This result was confirmed by experimental observations. Indeed, unlike classical tertiary phosphines, phosphaferrocenes do not bind efficiently boranes and no stable adducts are obtained upon reaction with reagents such as BH_3.THF [74]. However, Lewis adducts with electron deficient group 13 fragments, such as BF_3 [75] and BBr_3, [76] have been charcterized



$[Mn(C_4H_4P)(CO)_3]$ $[Fe(C_4H_4P)_2]$

Figure 14: Molecular orbitals describing the lone pair at phosphorus in $[Mn(C_4H_4P)(CO)_3]$ (HOMO-5) and $[Fe(C_4H_4P)_2]$ (HOMO-8) as given by theoretical calculations at the B3PW91/6-31+G*, LANL2DZ level of theory.

As previously explained, phospholyls ligands are sufficently good π-donor ligands to coordinate as much elements as cyclopentadienyl anions and not surprisingly it appears that an important part of the periodic table has already been explored.

Since the first structural characterization of a η^5-lithium phospholide complex $[Li(tmeda)(PC_4Me_4)]$ by Theopold et al. in 1989 (the corresponding K derivative was also reported), further studies focusing on the coordination of group 1 elements have been reported. A second important paper by Carmichael and Mathey deals with the chemistry of Na and K complexes of a 2,2'biphospholyl anion [77]. In this study it has been shown that the nature of the complex can be controlled by adjusting the metal stochiometry. Dimers **68** and **69** were characterized by X-ray crystal structure analysis (Figure 15). In 2002, Nief et al. reported on the synthesis of Rb and Cs derivatives of the tetramethylphospholyl anion [78]. Complexes **70** and **71** were prepared by reacting the corresponding 1,1'-biphosphole with strontium or caesium metals in THF [79]. Interestingly, as expected with large metal alkali as counter-anions, solvent–free complexes were obtained. This makes them suitable precursors in the chemistry of lanthanides and actinides where co-solvents are often prohibited.

Group 2 metal complexes (M = Ca, Sr, Ba) were also synthesized by Westerhausen following a route that involves the reaction of $[M(P(SiMe_3)_2)_2]$.n THF with diynes [80]. As can be seen, the reaction with the barium precursor led to the dimer **72** of an 3-enynyl substituted phospholyl. Another Ca(II) complex was also more conventionally prepared through the reaction of distilled calcium with a mixture a 1-chlorophosphole and cyclopentadienyl [81]. An X-ray crystallographic study reveals that the complex adopts a polymeric structure in the solid state.

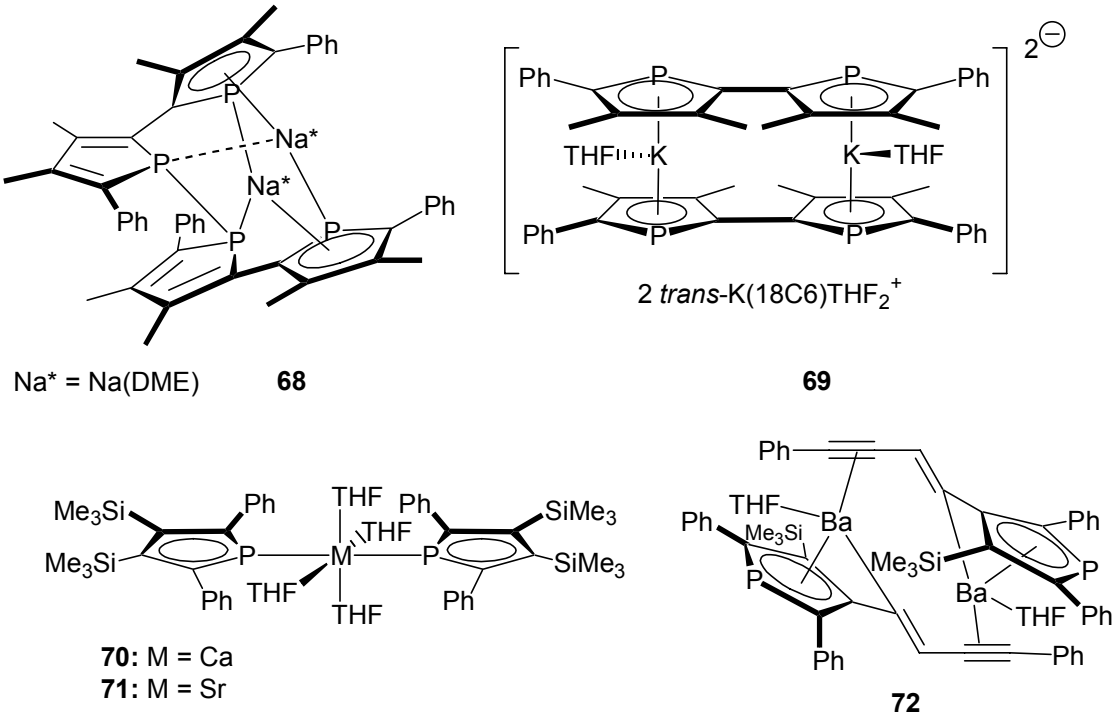


Figure 15: Group 1 and 2 phospholyl complexes.

Group 13 derivatives have also attracted a lot of attention in view of their potential use as single source of CVD precursors. Theopold et al. first reported on the synthesis of a bis η^1 complex **73** and the reaction of the of the solvent-free $[Li(PC_4Me_4]$ salt with InCl yielded an insoluble polymer formulated as $[(InP(C_4Me_4)]_n$ which decomposed to the corresponding 1,1'-biphosphole and indium metal upon sublimation or dissolution in THF [82]. More interestingly, a Ga(I) polymeric material **74** has been prepared by reaction metastable solutions of [GaBr] with the lithium salt of the 2,5-ditertiobutylphospholyl anion [83,84]. Like its cyclopentadienyl analog this η^5-gallium complex is isolobal of CO and was also characterized as it $Cr(CO)_5$ adduct **75**. Finally, group 4 complexes **76** (Sn) and **77** (Pb) have also been prepared by metathesis of $SnCl_2$ and $PbCl_2$ with different source of phospholide

anions. The presence of two *t*Bu groups at α position at phosphorus proved to be necessary to prevent the reductive elimination to yield the corresponding 1,1'-biphosphole, the coupling only occurring at 80°C in the case of the Pb derivative [85]. Indeed, when no bulky groups are present such as in the 3,4-dimethylphospholyl anion, a rapid precipitation of lead metal takes place. Phospholyl complexes fo group 13 elements are presented in the following figure 16.

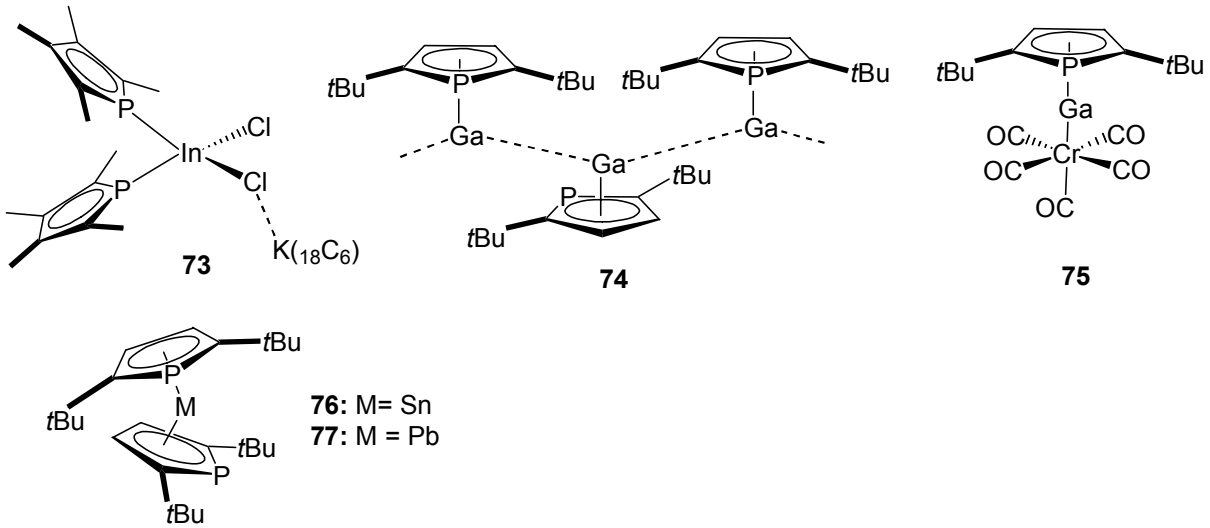


Figure 16: Some Phospholyl group 13 complexes

Most of phosphametallocene complexes were synthesized with transition metals. The field became so large over the last 20 years than a full coverage would not be reasonable in the scope of this review. Therefore, only the most significant achievements will be discussed especially when the considered complexes have found (or may find) applications either in the elaboration of materials or in catalysis. Quite logically, in view of the wide use of cyclopentadienyl ligands in the elaboration of olefin polymerization catalysts, early studies focused on the coordination chemistry of group 4 metals and some Ti and Zr phospholyl-based complexes were synthesized, characterized and tested at the industrial scale [86]. This point will be addressed later on. Recent studies focused on the synthesis of new diphospha-zirconocene **78** and hafnocene **79** complexes which were straightforwardly prepared by metathesis of Li or K phospholide salts with MCl_4 complexes (Figure 17) [87]. In the same study it was shown that the *rac* zirconocene complex equilibrates in solution to give a mixture the *meso* and *rac* complexes through the slippage of one phospholyl ligand. Accordingly, it was also demonstrated that the isomerization process is favoured by the presence of Lewis–basic species such as THF or PMe_3. The isomerization process of the zirconium complex **78** proceeds at significantly slower rate ($t_{1/2}$ [THF]) 30 min; $t_{1/2}$ [benzene]) 12 h) than that of the

Hafnium derivative **79** ($t_{1/2}$ in benzene << 10 min). Importantly, Nief et al. have showed that a $ZrCl_2$ derivative **80** of the tetramethylphospholyl ligand is a source of the diphosphazirconocene complex upon reduction with Mg [88]. This transient 14 electron complex reacts with CO, $Me_3SiCCSiMe_3$ and 2-butyne to afford the corresponding Zr(II) and Zr(IV) complexes which were fully characterized. More recently, Hollis et al. unambiguously demonstrated that a configurationally stable $Ti(CO)_2$ complex **81** could be prepared by using the 2-phenyl-3,4-dimethylphospholyl ligand [89]. Interestingly, it was shown that this Ti(II) complex exhibits a significant higher barrier to isomerization than its Ti(IV) analogue (dichloro derivative). Accordingly, DFT calculations have showed that, in the transition state of the isomerization process, a four-electron-two-orbital destabilizing interaction occurs between the lone pair at phosphorus of the slipping ligand with the non-bonding a_1 orbital at Ti. It must be mentioned that studies were not limited to analogues of sandwich complexes of group 4 metals and in 1998 Spence et al. reported on the synthesis and use of a bridged phospholyl-amido titanium catalyst **82**. The silyl substituted phospholyl anion was synthesized through a classical zirconocene-mediated route [90].

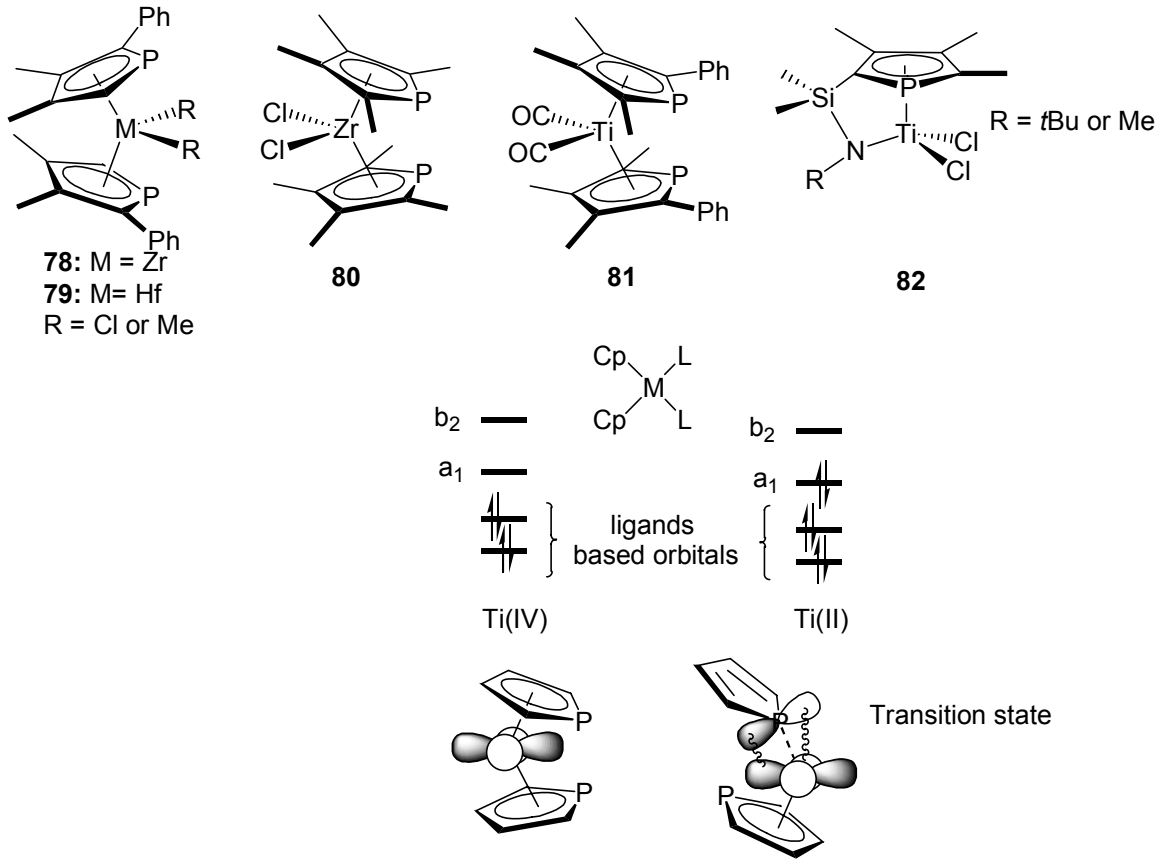


Figure 17: Some group 4 phospholyl complexes

The synthesis of paramagnetic complexes also attracted a lot of attention. Though phospha and diphosphaferrocenium cations were structurally characterized very recently, earlier studies in this area were made by Nixon et al. who employed the 3,5-di(*t*Bu)-1,2,4-trisphospholyl ligand to stabilize the corresponding chromocene complex [91]. Since this date, further spectacular complexes of general formula [MC_x*t*Bu_xP_{10-x}] (x = 4-6) with M = Sc, Ti, V were reported by Cloke et al. [92]. On the other hand the group of Zenneck also reported on the synthesis of Mn and Co complexes of the 3,5-di(*t*Bu)-1,2,4-trisphospholyl ligand [93]. However, recent studies by Carmichael and Mathey have shown that paramagnetic complexes can also be built from monophospholyl ligands such as the easily available 2,5-di(*t*Bu) phospholyl derivative [94]. The use of monophospholyl offers interesting advantages such as the possibility to finely ”tune” the electronic properties of the phosphorus atom through the incorporation of functional groups at the periphery of the ring. Furthermore, phospholyl derivatives and their cyclopentadienyl analogs bear a close analogy and it is therefore expected that modified materials or catalysts could be more rationally conceived. Additionally, the presence of a lone pair at phosphorus allows for the elaboration of sophisticated bimetallic complexes, edifices and materials than could not be assembled using classical cyclopentadienyl ligands and offers an additional possibility to modulate the electronic properties of the phosphametallocene through coordination.

A series of complexes is presented in the following figure 18. The octamethyl diphosphachromocene **83** was synthesized by Kölher et al. through the metathesis of the potassium phospholide salt with $CrCl_2$ and oxidized with with [Fc][BPh_4] to produce the red 17 VE chromocenium derivative **84**. This complex proved to be air and THF sensitive [95]. EPR data confirmed the structure proposed (I = 3/2) and ^{1}H NMR (variable temperature experiments) studies have unambiguously demonstrated the participation of the π-orbitals of the ligand (HOMO and HOMO-2) in determining the ligand spin density. Carmichael and Mathey reported on the synthesis of phosphametallocenium of group 9 metals **85-87** using the easily available 2,5-di(*t*Bu)phospholyl anion as ligand [96]. Reduction of the compound **85** with Mg in THF afforded the purple air-sensitive phosphacobaltocene **88** in a very good 75% yield [97]. Interestingly, though no direct comparison can be drawn because of a different substitution pattern, it must be mentioned that the phosphorus cation is much more easily reduced (-0.73 V *vs* SCE) than the [CoCpCp*] (-1.17 V *vs* SCE in DMF) complex confirming the greater π-accepting capacity of the phospholide ligand. NMR experiments have suggested that the SOMO involves an significant contribution of the π_s orbital that features a node at

phosphorus. Very recently, a second example of phosphacolbatocene was obtained using the 1,3-di(*t*-Bu) cyclopentadienyl as ligand [98]. Another significant breakthrough in this area was provided by the successful preparation of the olive green phospharhodocene **89** (Figure 18) [99]. Complex **89** was obtained through the chemical reduction of the corresponding phospharhodocinium salt by [$CoCp^*_2$] in pentane. Finally, the first example of the 20 VE paramagnetic phosphanickelocene **90** was prepared only recently. This deep green air-sensitive compound was obtained in yield up to 80% through the reaction of [Ni(acac)Cp*] with the lithium salt [$Li(THF)_2(PC_4tBu_2H_2)$] in THF at -78°C [100]. The formulation of **90** was confirmed by an X-ray crystal structure analysis and given the presence of two SOMOs, no ^{31}P NMR resonance could be detected between ± 3000 ppm. This complex was found to be soluble and stable in dry degassed pentane, toluene and dichloromethane and can be handled briefly in air in the solid state. Importantly it was shown that the steric bulk around phosphorus plays a determinant role in preventing the dimerization process. Thus, when the same experiments carried out with the less bulky 3,4-dimethylphospholyl, only led to the formation of dimer **92**. DFT calculations carried out on the parent diphosphanickelocene [$Ni(\eta^5\text{-}C_4H_4P)_2$] is unstable towards dimerization to yield the corresponding complex ([$Ni(\eta^5\text{-}C_4H_4P)(\mu^2\text{-}C_4H_4P)]_2$. An electrochemical study of **90** revealed that a one-electron oxidation process takes place at + 0.03 V *vs* SCE in THF. The corresponding phosphanickelocenium **91** was thus prepared through a chemical oxidation with $AgBF_4$ and structurally characterized. Though sterically protected, complex **91** is sensitive towards the attack of ligands at the nickel atom. Reaction with PMe_3 afforded complex **93** which results from the ring slippage of the phospholyl ligand (Figure 18).

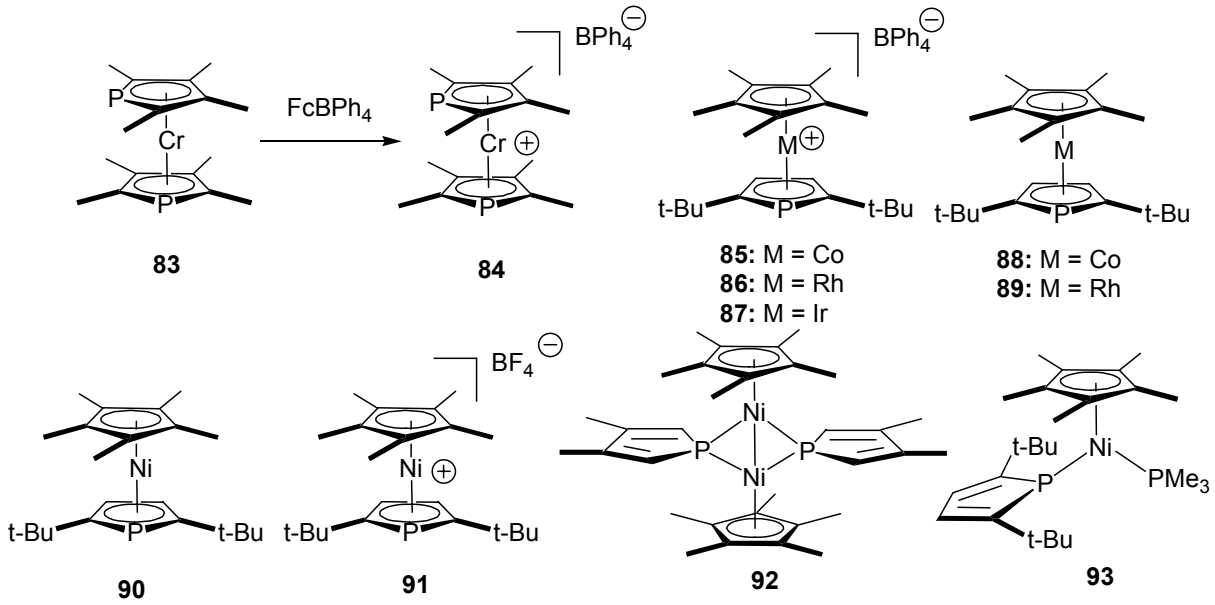


Figure 18: Some representative phospholyl complexes of transition metals.

Phosphacymantrenes and phosphaferrocenes, which were the first examples of phosphametallocenes, are probably the most easily available low-coordinated based phosphorus ligands and, therefore, they constitute a very important class of compounds. Furthermore, at least in the case of phosphaferrocene, important developments were recently achieved in homogeneous catalysis as will be seen further. Most efforts recently focused on the synthesis of new functionalized structures. Indeed, like in the ferrocene series, the phosphaferrocenyl backbone can be exploited to devise ligands possessing a planar chirality. The group of Ganter has shown that the formyl derivative **94** could be employed as a very convenient precursor for the synthesis of various enantiomerically pure ligands such as **96**, resolution of the two enantiomers of **96** being achieved through chromatographic separation of the corresponding aminals **95** (Figure 19) [101]. Other bidentate ligands were also prepared such as the bis(phosphaferrocenyl)ferrocene **97** and systems featuring side functional arms [102, 103]. Very efficient phosphaferrocene-based catalysts have been designed by the group of Fu in the Fe($\eta^5C_5Me_5$) series such as **98**, **99** [104] and the mixed phosphafarrerocene-oxazoline ligand **100** [105]. The resolution was carried out by chiral HPLC of the intermediate alcohol **98**. Another approach was elaborated by the group Hayashi for the synthesis of phosphanyl substituted phosphaferrocenes such as **101** through the use of an enantiomerically pure chiral phospholyl ligand (Figure 19) [106]. Palladium and platinum(II) dichloride complexes of these ligands were characterized in the same study. Quite recently this strategy was also exploited by Carmichael et al. in the synthesis of the first enantiomerically pure phospharuthenocene bidentate **102** featuring a diphenylphosphino

pendant group [107]. Note that the first example of phospharuthenocene was synthesized by the same group in 1994 [94]. Elegantly, the same group showed in 2004 that the use of esters such as **103** could be employed for the chiral resolution of phospharuthenocenes [108]. Very recently, the successful synthesis of the first 2-(2'-methoxynapht-1'-yl)-3,4-dimethylphospholyl anion allowed for the preparation of enantiomerically pure phosphaferro and phospharuthenocenes **104** and **105** (Figure 19). X-ray crystallography showed that the naphtyl group in both compounds adopt orientation which might be favourable for enantioselection but NMR studies have showed that in solution, the two compounds equilibrate (Figure 20). The energetic barrier to rotation was calculated on the basis of NMR experiments (72 $kJmol^{-1}$ for **104** and 79 $kJmol^{-1}$ for **104** respectively) [109].

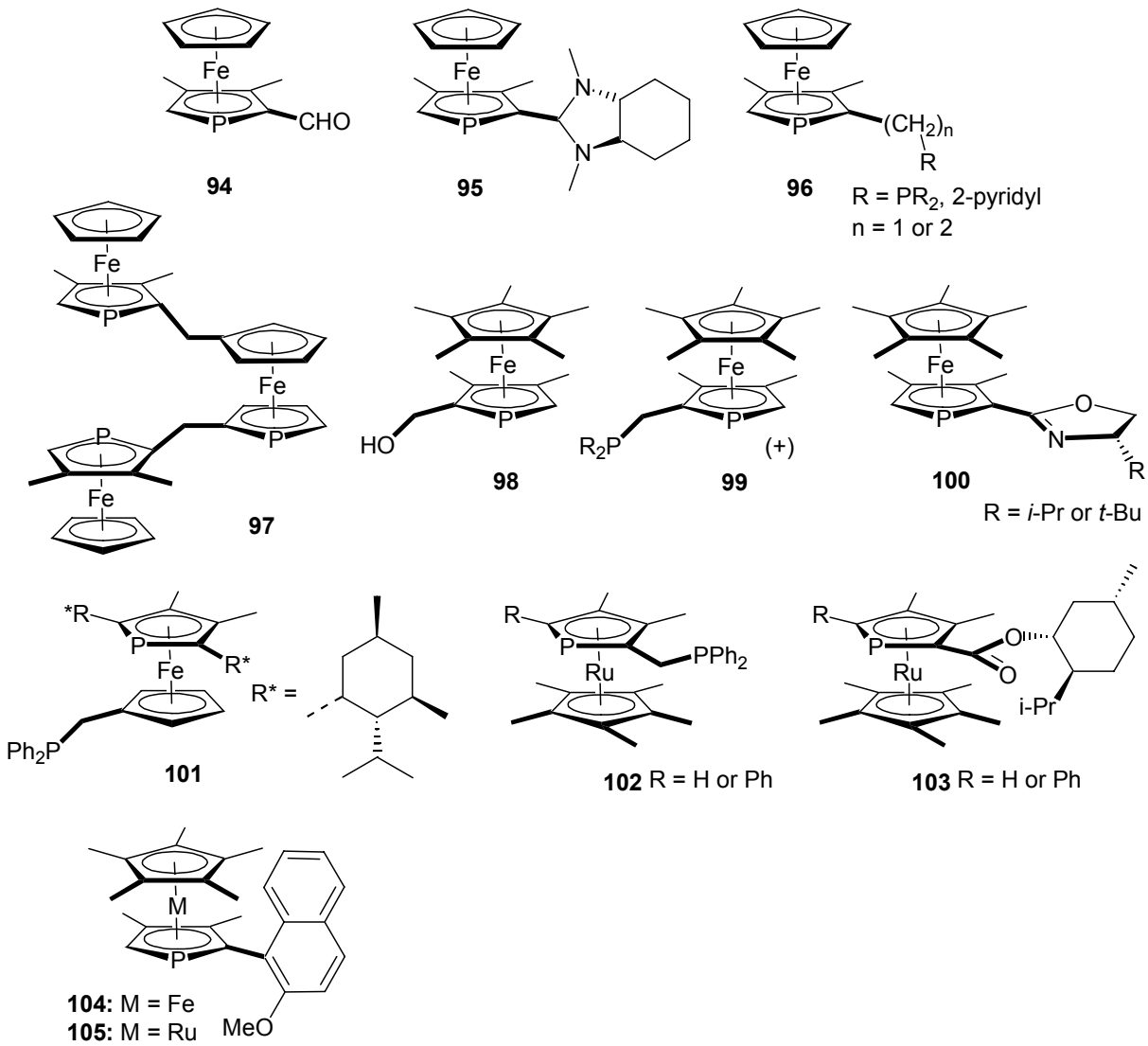


Figure 19: Some representative examples of chiral phosphaferrocenes.

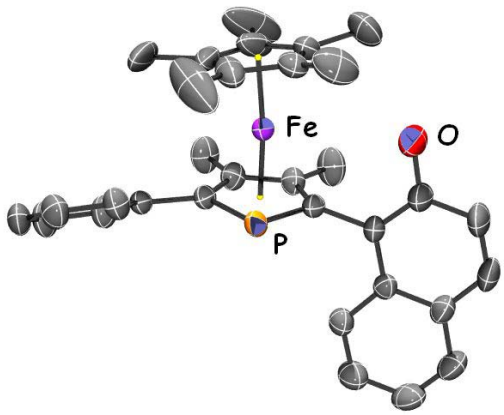
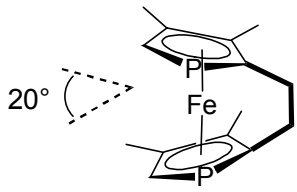


Figure 20: A view of one molecule of phosphaferrocene **104**.

Phosphaferrocenes were also incorporated in tridentate based ligands featuring two pendant phosphinines ligands [110]. Fewer efforts were achieved in the synthesis of chiral diphosphaferrocenes so far. In 1998, the group of Fu reported on the successful separation by chiral HPLC of the two enantiomers of the (2-phenyl-3,4-dimethyl)diphosphaferrocene [111]. The absolute configuration of the (-) enantiomer was established by X-ray crystal structure analysis. One cannot conclude this brief summary of the synthesis of new phosphaferrocenes without mentioning the synthesis of the first example of 1,1'-diphospha[2]ferrocenophane **106** by Mathey et al. which, as shown by X-ray crystallography, display a tilt angle of 20°(Figure 21) [112].



106

Figure 21: A 1,1'-diphospha[2]ferrocenophane.

Comparatively, less attention has been paid to the synthesis of 2-functional phosphacymantrene derivatives which also display a planar chirality. The group of Mathey reported on the successful preparation of the two *rac* and *meso* diastereomers of the bidentate ligand **108** which were assembled through a conventional McMurry mediated route from the corresponding 2-acetylphosphacymantrene **107**. The two diastereomers were structurally characterized (Figure 22). When the coupling was performed on the 2-benzoylphosphacymantrene, the *trans* olefin **109** was obtained as the major compound [113]. The same authors exploited the reactivity of a carbenium derivative **110** of a phosphacymantrene in the preparation of the bidentate ligand **111** which was recovered as a

mixture of diastereomers (Figure 22) [114]. One of these was structurally characterized. Note that phosphacymantrenes have also find an interesting application in the synthesis of phospholyl anions through a two-electron reductive process [115].

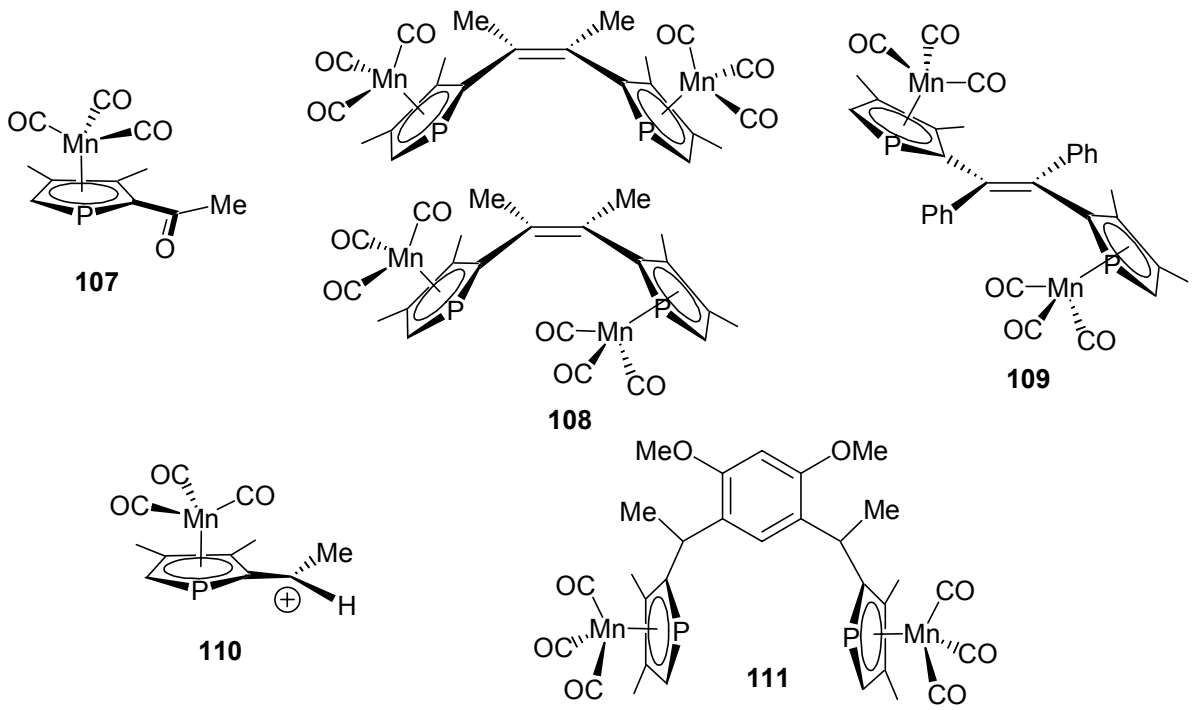


Figure 22: Some functionnal mono and bidentate phosphacycmantrene ligands.

Though the organic chemistry of phosphaferrocenes has been widely explored in view of their use as ligands, some aspects of their coordination chemistry remain relatively unclear. The $[RuH_2(\mu\text{-}H_2)(PCy_3)_2$(2-phenyl-3,4-dimethylphosphaferrocene)] **112** was structurally characterized and found to be fluxional on the NMR time scale at room temperature. The exchange between the dihydrogen ligand and the two hydrides was characaterized by a $\Delta G^{\ddagger}$ of 46.2 kJ.mol^{-1} at 263 K. Substitution of the H_2 ligand was easily achieved with ethylene and CO to yield the corresponding Ru(II) complexes (Figure 23) [116]. Also with ruthenium as metal, it is worth mentioning that Cp*RuCl derivatives of a 2-(2'-metyhylpyridyl)-3,4-dimethylphosphaferrocene **113** were also prepared by Ganter et al. from a classical ligand exchange reaction using the tetrameric $[\{RuCp^*Cl\}_4]$ complex (only one diastereomer of **113** is represented) [117]. A mixed anionic ligand featuring a phosphaferrocene moiety and cyclopentadienyl was also employed in the synthesis of the Ru(II) complex **114** in which the phosphaferrocene behaves as a pendant two electron donor ligand [118]. The first homoleptic complexes of these ligands were only synthesized in 1999. The cationic tetrakis(phosphaferrocene) Rh(I) complex **115** was obtained through a classical displacement

of ligand from $[Rh(COD)Cl]_2$ in the presence $AgBF_4$ as chloride abstractor [119]. A similar strategy in the case of iridium led to the pentacoordinated complex **116** in which the COD ligand proved to be firmly bound to iridium thus preventing the formation of the corresponding homoleptic complex. A RhCl **117** complex of the a mixed phosphaferrocene-phosphinine tridentate ligand was also assembled through a zirconocene mediated route.

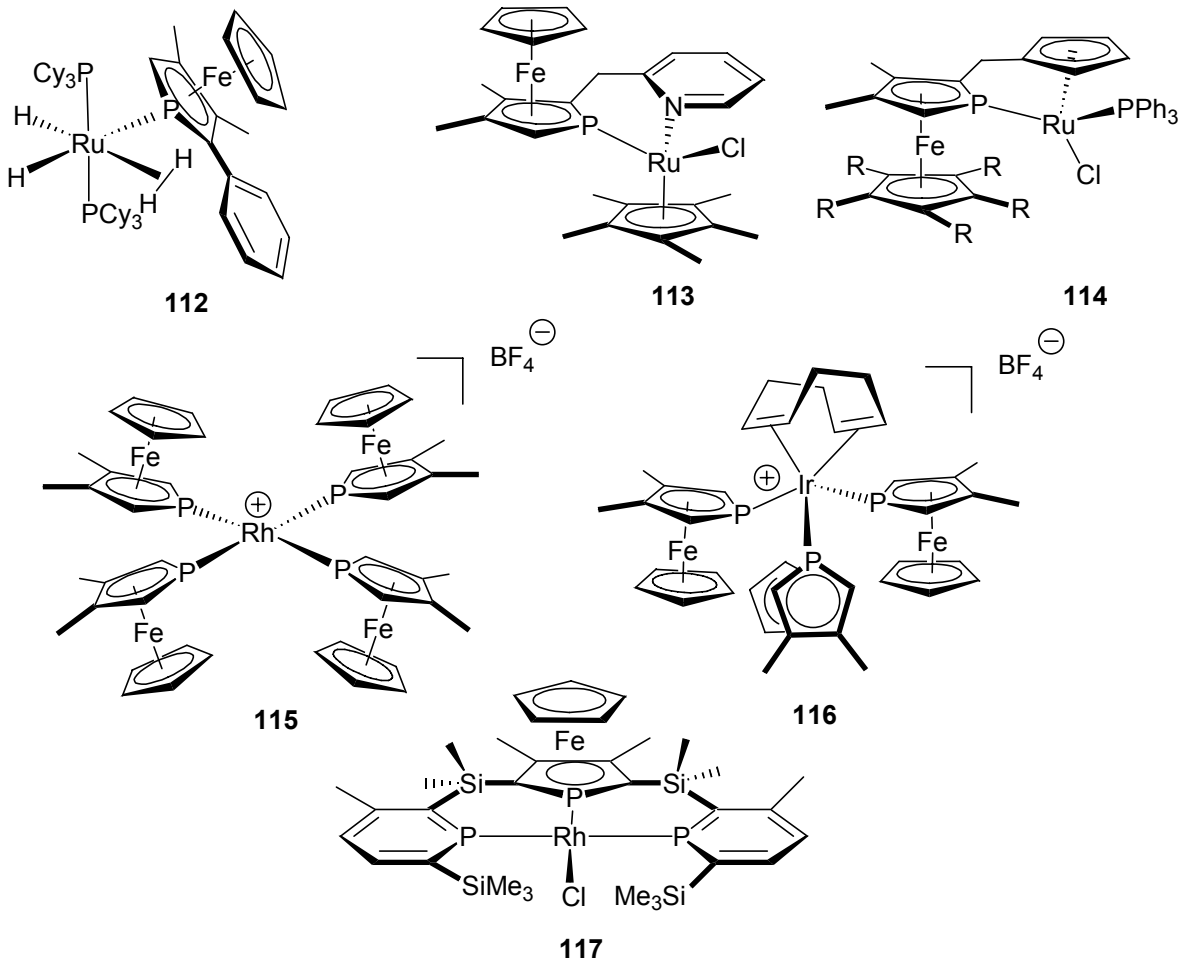


Figure 23: Group 8 and 9 phosphaferrocene complexes.

Though pioneering works had shown that phosphaferrocenes essentially behave as two-electron donor ligands, recent studies demonstrated that the central iron atom can also be involved in coordination of transition metal centers (Figure 24) and some of Pd(II) dimeric complexes such as **119** were formed by slow decomposition of $PdCl_2$ complexes **118** in dichloromethane or through their reaction with $[Pd(dba)_2]$ (Figure 24) [120]. In these complexes the phosphaferrocene behaves like ferrocenes in some cases as a four-electron donor, two electrons being given by the lone pair and two additional by a non-bonding orbital at iron.

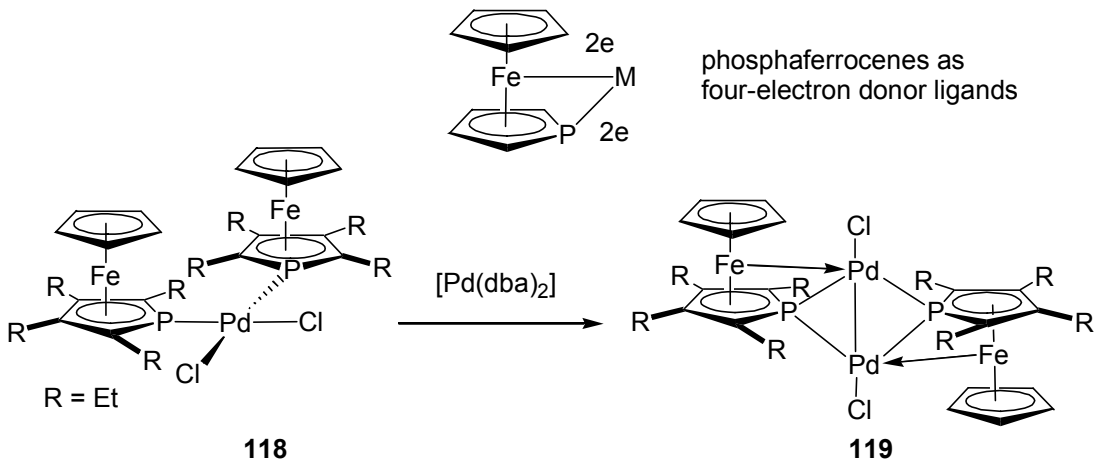


Figure 24: Phosphaferrocenes as four-electron donor ligands: application in the synthesis of dimetallic palladium(II) complexes.

Diphosphaferrocenes logically behave as four electron donor ligands but they tend to form polymeric materials when the metal fragment possesses two available vacant sites. Interestingly, it was shown that the issue of the reactions is strongly dependant upon the substitution scheme of the ligand. Thus, the presence of substituents at the α positions at phosphorus clearly forces the ligand to adopt a chelate bonding mode in most cases. Cowley et al. were the first to mention this quite unusual bonding mode which involves a side-on coordination of the two lone pair at phosphorus. Indeed, in 1993 during experiments aimed at studying the oxidation process of the octamethyldiphosphaferrocene, they isolated the cationic silver complex **120** (Figure 25) [121]. This unusual coordination mode can be encountered with many other metallic fragments. Thus, shortly after, the tetrahedral bis(diphosphaferrocene) Pd(0) complex **121** was isolated in good yield from the reaction of $[Pd(dba)_2]$ with the free ligand, the octaethyldiphosphaferrocene [122]. An X-ray crystal structure analysis revealed that the P-Pd bond makes an important angle with the main plane of the ligand (about 50°). The homoleptic copper(I) **122**, gold(I) **123** [73] and the cationic $GaCl_2^+$ **124** complexes were also prepared and structurally characterized (Figure 25) [123]. DFT calculations indicate that this particular bonding mode mainly results from the important sphericity of the phosphorus atom lone pair (important 3s character). A charge decomposition analysis (CDA) carried out on the $[Cu(dpf)_2]^+$ (dpf = $(PC_4H_4)_2Fe$) and the $[Cu(dpe)2]^+$ (dpe = $H_2PCH_2CH_2PH_2$) complexes reveals that σ-donation dominates. However, a similar study carried out on the homoleptic $[Ni(dpf)(CO)_2]$, $[Ni(dpe)_2(CO)_2]$ $[Ni(dmpe)_2(CO)_2]$ (with dmpe = $Me_2PCH_2CH_2PMe_2$) clearly demonstrates that the dmpe ligand behaves as the stronger σ-

donor ligand, the π-accepting capacity of the dpf ligand being similar to that of dpe. In the same study it was shown that several MOs account for this unusual chelate bonding mode: the orbitals which describe the lone pair at phosphorus and the π* of the phospholide ligand (mainly 3pz contribution at P) as well as the MO which describe the P-Fe bond participates significantly to the bonding. Two views of the HOMO-17 and HOMO-20 MOs of the calculated $[Cu(dpf)_2]^+$ complex are shown in the following figure. Importantly, the calculations also reveal that the participation of non-bonding orbitals at iron is weak.

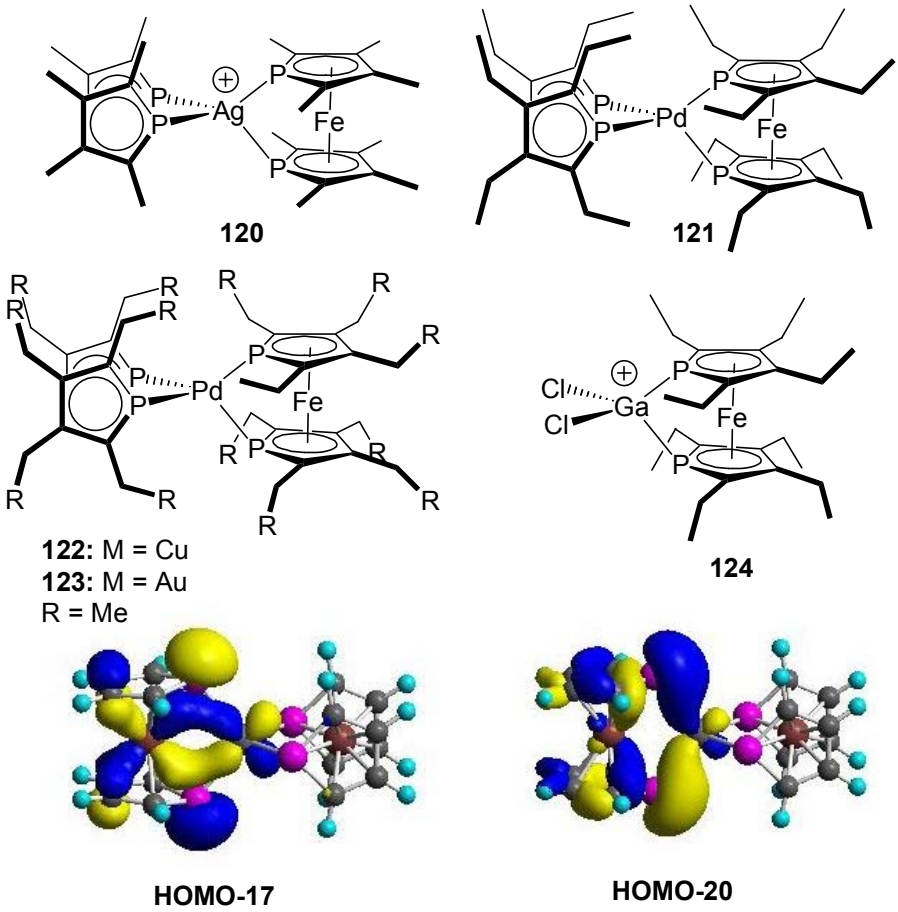


Figure 25: Diphosphaferrocenes as chelate ligands and two views of two important MOs (H-17 and H-20) that describe the P-M bonding in such complexes.

This bonding mode was also exploited in the synthesis of dicationic edifices incoporating four palladium atoms such as **125**. In each ligand one phospholyl unit behaves as two-electron donor (η^1-coordination) whereas the second bridges two palladium centres in a η^2-fashion. This complex was assembled through the reaction of the dinuclear complex **126** with $FeCl_2$ (Figure 26). A mechanism involving the transient formation of neutral bimetallic dichloride complex was tentatively proposed [120]. Complex **125** was also employed as a

source of the trimetallic complex **127** which features a central square planar zerovalent Pd atom. No calculations have been undertaken yet to see whether the central atom is surrounded by four or eight electrons. Nonetheless, examination of metric parameters strongly suggests that no direct Fe-Pd bonding is involved. Like in **126** it has been proposed that Fe-P bonds also participate to the stabilization of the central Pd atom (Figure 26) [124].

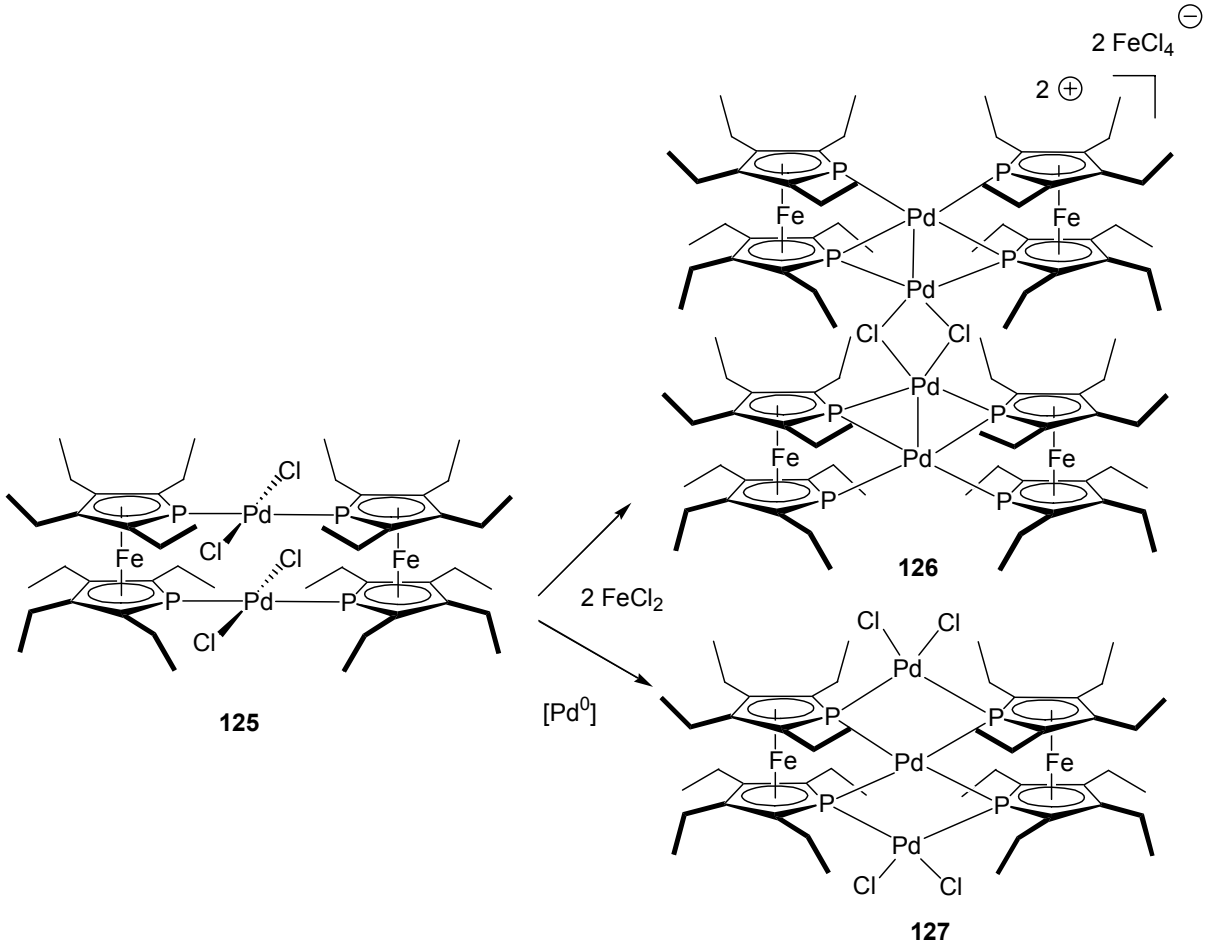


Figure 26: Phosphaferrocene palladium complexes.

In comparison to the chemistry of cyclopentadienyl ligands benzannelated phospholide ligands have not been extensively used so far in coordination chemistry and catalysis. However, Gudat et al. developed the chemistry of bis(phosphonio)isophosphindolide cations such as **128** [125]. The central phosphorus atoms of these ligands, which feature a formally negatively charged heteronaphthalenic 10-π electron system, exhibits ambiphilic properties similar to those of the phosphorus in phosphenium ions. While in complexes such as **129**, the bonding is identical to what observed in classical phosphenium cations derivatives in the bimetallic complex **130**, the bonding in the

Cu_2P unit was described in analogy to copper aryls as a dative two-electron, three center bond which probably involves σ and π donation from the ligand and significant M(d)→L(π*) back donation [126]. Electronic properties of these ligands seem to be relatively close to those of phosphinines. Thus it was shown that reaction with $HgCl_2$ affords complexes that formally result from a 1.1-oxidative addition at the diccordinate phosphorus center. In the presence of alcohols zwitterionic systems such as **131** are formed (Figure 27) [127]. The bis (phosphonio)benzophophospholide backbone was also employed to build phosphine fucntionalized systems which features two phosphorus centers with notably different electronic properties. Monocationic nickel and iron carbonyl derivatives of these ligands were characterized and spectroscopic data suggest that the central phosphorus atom exhibit electronic properties similar to that of phosphates [128]. Cationic and dicationic rhodium(I) such as **132** were also assembled and tested as catalysts in the hydroformylation process of olefins [129].

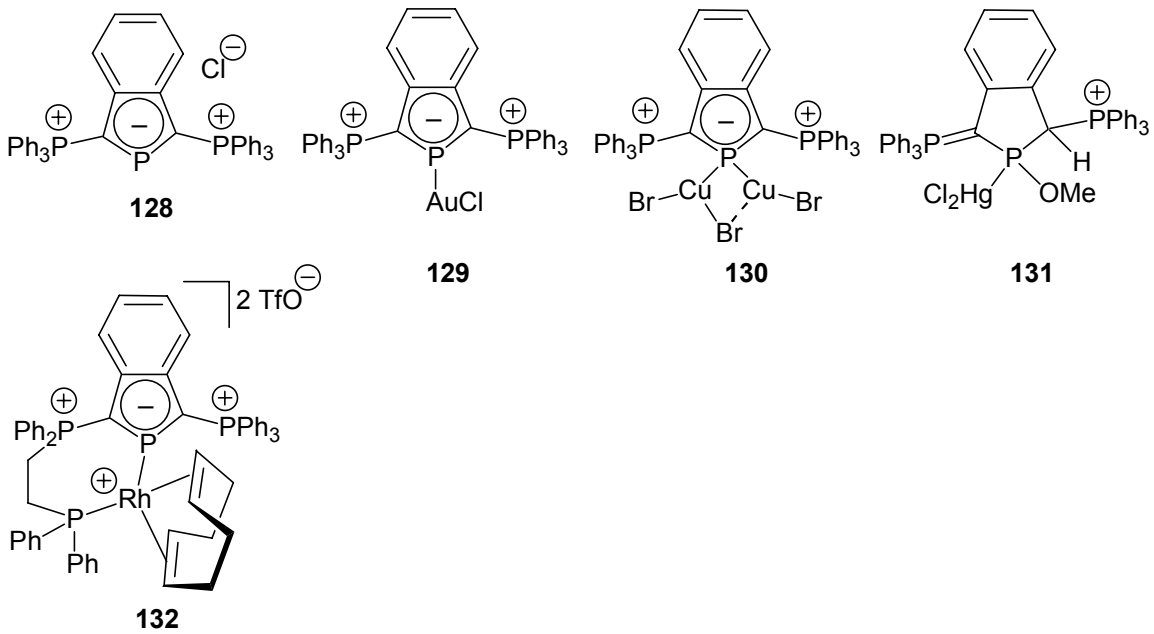
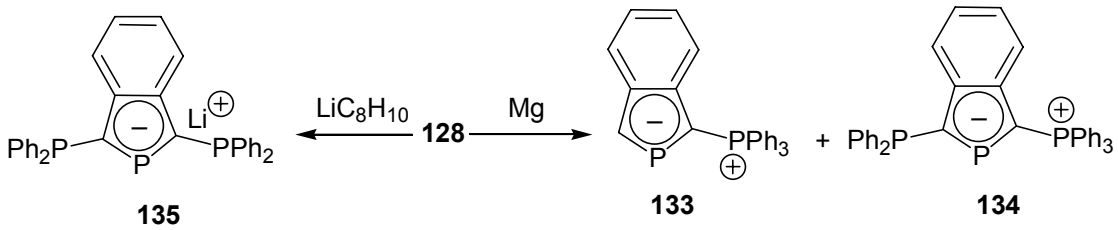


Fig 27: bis (phosphonio)benzophophospholide complexes.

Recently, new developments have emerged with the discovery of a reduction process of **128** that yields neutral phosphoniobenzophospholides **133** and **134** or anionic phosphanyl-benzophospholide **135** depending on the reducing agent employed (Scheme 11) [130]. Ligand **133** was reacted with a variety of metal fragments and σ and π complexes could be formed depending on the nature of the precursor. An illustrative example was given by the synthesis of chromium complexes **134** and **135** [131] and their group 7 analogues **136-137** and **138-139**

Bimetallic species were also synthesized and structurally characterized. In these complexes, the ligand acts as a four-electron donor and coordinates metal centres through its phosphorus atom lone pair (η^1-coordination) and through the unsubstituted P=C double bond (η^2-coordination). The ambident character of **133** was also nicely illustrated with the synthesis of the Cu(I) complex **140** [132] On the other hand ligand **134** has also found interesting applications in the synthesis of bimetallic complexes. Thus reaction with $[Mn_2(CO)_{10}]$ and $[MoCp(CO)_2]_2$ dimers afforded complexes **141** and **142** [133]. Note that the writing of **142** is arbitrary and a complete structural assignement proved unfeasible since no decision regarding the presence or the absence of a Mo-Mo bond could be made. Therefore **142** can also be written as a chelate complex featuring the coordination of the second $[MoCp(CO)_2]$ fragment onto the P=C double bond. Note that a Co(I) complex **143** mixed bis-phosphonio-benzophospholide featuring a pendant diphenylphosphino group was also synthesized and involves π-coordination of the P=C bond exclusively (Figure 28). This result is fully rational when one considers that the basicity of the diphenyl group is more important than that of the dicoordinate phosphorus atom [134]. A review on the chemistry of these zwitterionic phosplide derivatives recently appeared [135].



Scheme 11: Reduction process of a bis (phosphonio)benzophophospholide ligand.

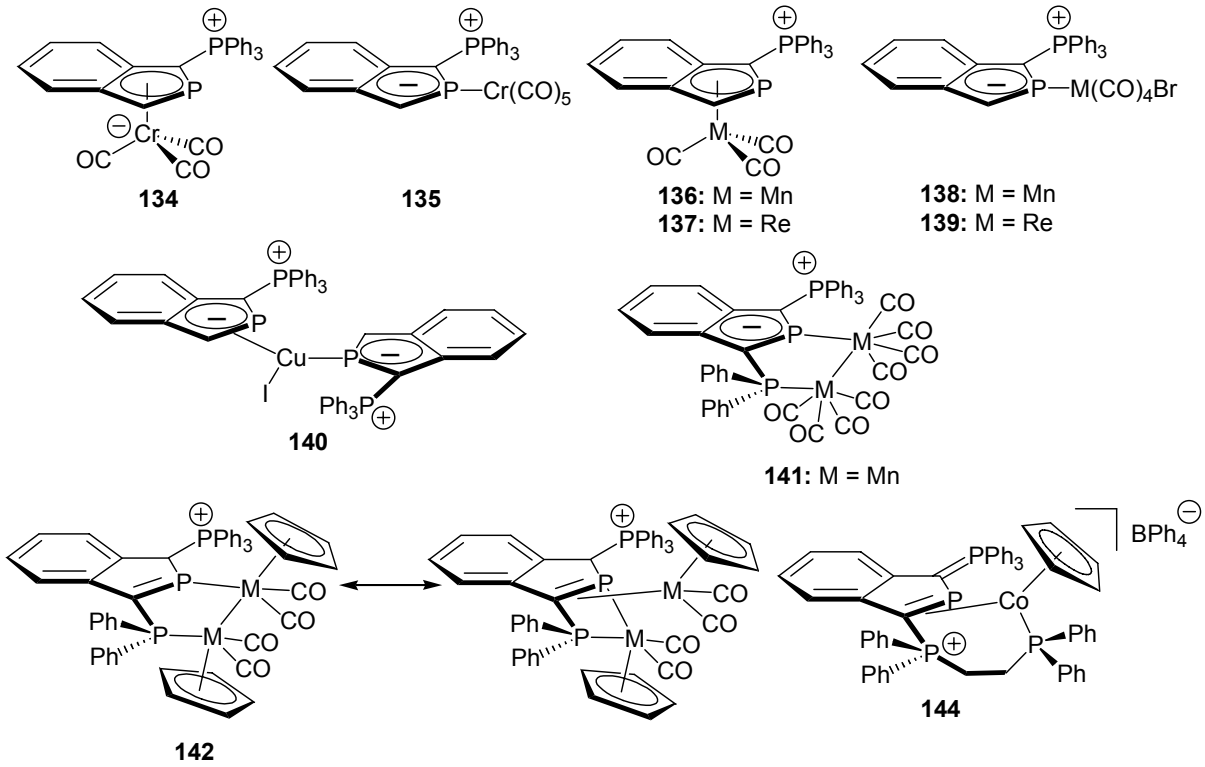


Figure 28: Phosphoniobenzophospholides and anionic phosphanyl-benzophospholide complexes.

Finally, to conclude this sub-chapter devoted to the chemistry of phospholide ligands, one must also mention their important implication in the chemistry of lanthanides and actinides. For further details, readers can refer to the two exhaustive reviews published by F. Nief in 1998 [136] and 2001 [137]. Cyclopentadienyl ligands and their derivatives are ubiquitous in the chemistry of group 3 metals and quite logically studies aimed at studying the replacement of a CH unit by an heteroatom such as phosphorus (N, P, AS, Sb) started very early. Like pyrrolyl anions, phospholyl can bind group 3 metals through the phosphorus atom (η^1) or through their π-system (η^5). The substitution scheme of the ring and especially the presence of functional groups at the α-position at phosphorus can be employed to control the outcome of the reaction. With poorly substituted ligands such as dmp **145** (3,4-dimethylphospholyl) η^1-coordination predominates, whereas with ligands such as Tmp **146**, Dpp **147** or Dtp **148**, η^5-coordination is more frequently encountered (Figure 29).

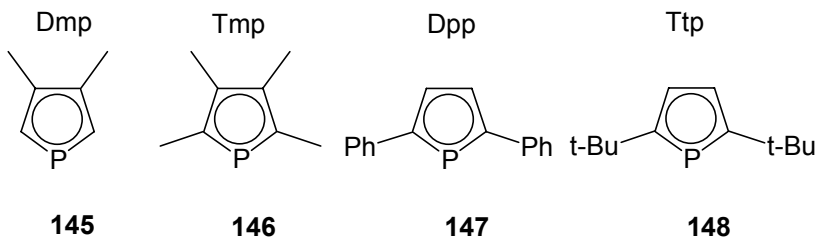


Figure 29: Some phospholyl ligands

A number of Ln(III) ate complexes such as $[(\eta^5\text{-Tmp})_2LnCl_2Li(S)_2]$ [138] (Ln = Y, Lu, S = solvent = Et_2O, DME) and $[(\eta^5\text{-Tmp})_2LnCl_2K]$ (Ln = Nd, Sm) have been prepared through the reaction of appropriate metal alkali phospholide with $LnCl_3$ [139]. Though the structure of the $[\{(\eta^5\text{-Tmp})(\mu{:}\eta^5,\eta^1\text{-Tmp})Sm(\mu^3\text{-Cl})_2K(Et_2O)\}_n]$ complex was found to be very similar to that of the $[\{(\eta^5\text{-Cp*})Ce(\mu^3\text{-Cl})_2K(THF)\}_n]$ complex synthesized by Evans [140], additional coordination occurs through the phosphorus atom lone pairs to yield a polymeric material. In 2002, Visseaux et al. reported on the successful preparation of a mixed cyclooctatetraenyl-phospholyl samarium and neodynium(III) complexes **149** and **150** using the 2,5-bis(trimethylsilyl)phospholyl ligand. Both complexes were obtained from the reaction of the corresponding phospholyl potassium salt with the $[(COT)LnCl(THF)_2]$ precursors (COT = cyclooctatetraene, Ln = Sm, Nd) (Figure 30) [141].

There are also some striking analogies between the chemistry of phospholyl anions with divalent lanthanide and that of Cp* derivatives. Complexes such as $[(\eta^5\text{-L})_2Ln(THF)_2]$ (Ln = Yb, Sm, L = Tmp, Dpp) were obtained through classical metathesis the corresponding phospholyl potassium salts with $[LnI_2(THF)_2]$ precursors [142]. A more straightforward approach which consists in inserting Yb or Sm (employed as powders) into the P-P bond of the easily affordable 1,1'-biphospholyl derivatives was also developed [143]. The X-ray crystal structure of complex **151** has been recorded [144]. Structures of unsolvated species are still unknown and but it is believed that they adopt a polymeric structure involving intermolecular Ln-P σ bonds as linkers. Interestingly, the presence of two available lone pairs in **151** allowed for the preparation of the heterobimetallic Yb/Ru complex such as **152** [145]. A similar strategy was also employed for the synthesis of dimeric complexes **153**, the two phosphorus precursors being the 1-R-tetramethylphospholes (E = Cl, SPh) (Figure 30) [146].

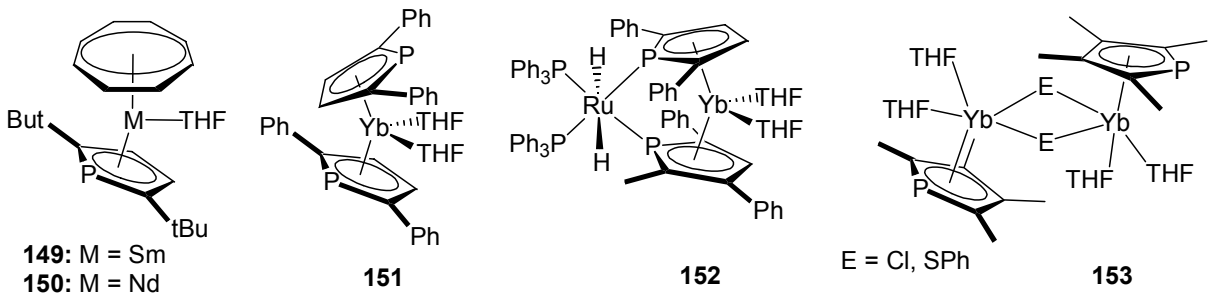


Figure 30: A series of representative Ln(III) complexes of phospholyl ligands.

Though the Tmp ligand **146** is sterically closer of the C_5Me_5H ligand than from Cp*, complexes analogs to the $[(\eta^5\text{-}C_5Me_4H)_3Ln]$ complexes (Ln = La, Sm, Tb) could not be prepared. A dimeric structure of general formula $[\{(\eta^5\text{-Tmp})Sm(\mu{:}\eta^5, \eta^1\text{-Tmp})_2(\mu\text{–}Cl)K(\eta^6\text{-toluene})\}_n]$ which formally results from the crystallization of the hypothetical $[(\eta^5\text{-}C_5Me_4H)_3Ln]$ complex with KCl was structurally characterized [147]. Under the same experimental conditions, reaction of the less sterically crowded Dmp ligand **145** yielded complex **154** in which each Sm atom can achieve a coordination number of 10 (Figure 31). The synthesis of mixed complexes featuring the Cp* ligand and different phospholyls was also reported. Formulation of these complexes proved to be extremely sensitive to the substitution scheme of the ring. Thus, reaction of the $[Cp^*_2Sm]$ complex with with the 1,1'-biphosphole Tmp-Tmp resulted in the formation of complex **155** in which coordination of the Tmp unit occurs in an η^1-fashion [148]. Note that in **155**, the coordination sphere of Sm is completed by an interaction with one of the methyl group of the Tmp ligand. Reaction with the Dmp-Dmp biphosphole afforded an unsymmetrical dimer in which one phospholyl ligand is η^5,η^1 bonded whereas the second one is only η^1-bonded to one Samarium atom. With Dtp, crowding of the phosphorus atom lone pair proved to be sufficient to allow for the synthesis of complex **156** (Figure 31) [149]. During the same study, the authors also reported on the successful synthesis of a homoleptic Tm(II) complex **157** (Figure 32). Reaction of this complex with azobenzene resulted in the formation of dark blue solutions from which complex **158** could be isolated and structurally characterized. A sulphur bridged complex **N** could also be obtained by reacting **159** with $Ph_3P{=}S$ which acts as a source of elemental sulphur. Note that a THF adduct of complex **157** was also structurally characterized [150].

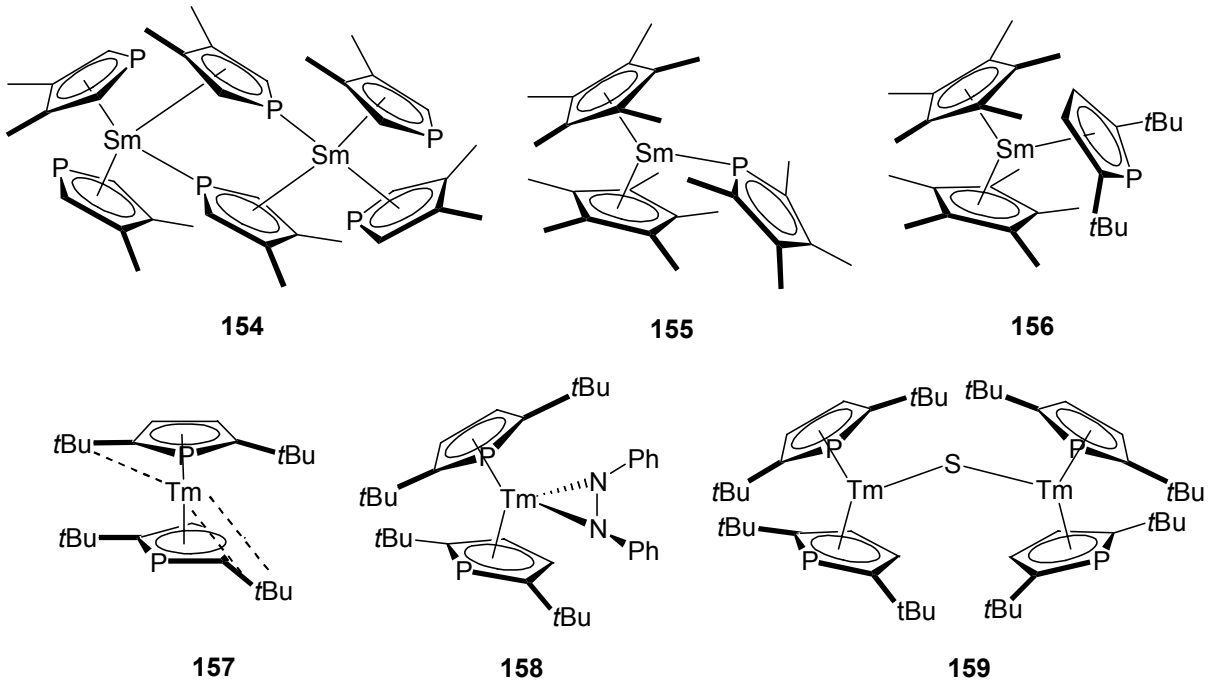


Figure 31: Some phospholyl-based Ln(II) complexes.

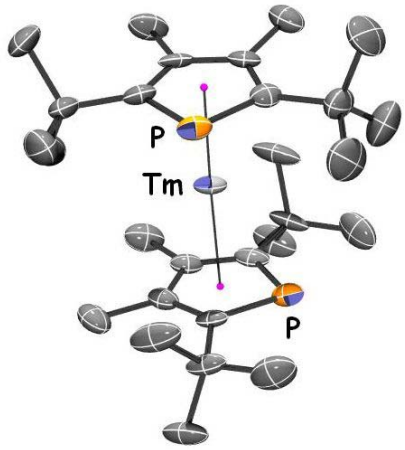


Figure 32: X-ray crystal structure of the [Tm(**N**)$_2$] complex.

Phosphorus analogs of indolyl **160** (DMPind = 2,3-dimethylphosphoindolyl) and carbazolyl (Pflu = phosphafluorenyl) **162** have also been employed in the coordination chemistry of Ln(II) species. It was shown that the introduction of a second aromatic unit in Pflu dramatically modifies the coordination behaviour. Thus, whereas η^5-coordination occurs in complex **161** [(η^5-DMPind)$_2$Sm(THF)$_2$], the Pflu ligand favors η^1-coordination a shown by the synthesis of the Sm complex **163** (Figure 33) [151]. An Yb complex having the same formula has also been characterized but the two phosphorus ligands are located in a *cis* fashion and display a bent coordination [152]. Though no calculations have been undertaken

to rationalize this preference, it has been convincingly proposed that the double annelation in Pflu may result in a significant weakening of the π-electron donating capacity.

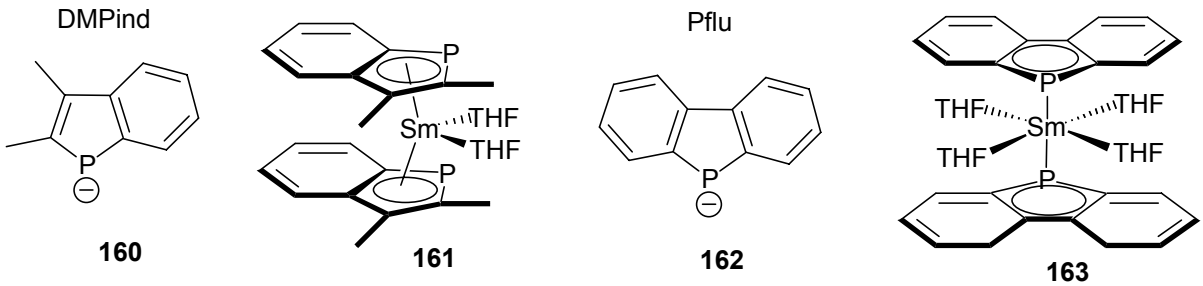


Figure 33: Phopshoindolyl and phosphafluorenyl Sm(II) complexes.

Phospholyls anions also proved to be excellent ligands of actinides. The easily available Tmp ligand has been extensively employed and there is a striking parallel with the chemistry of the Cp* ligand. Mono, and bis(phospholyl) complexes of U(IV) such as [(η^5-Tmp)$_2$UCl$_3$(DME)] **164** and [(η^5-Tmp)$_2$UCl$_2$] [153], [(η^5-Tmp)$_2$U(BH$_4$)$_2$] **165** [154], [(η^5-Tmp)$_2$U(BH$_4$)$_3$] [155] could be prepared through the reaction of the KTmp salt with [UCl$_4$] or [U(BH$_4$)$_4$] (Figure 34). Mixed Cp*-phospholyl complexes such as [(η^5-Tmp)(η^5-Cp*)U(BH$_4$)$_2$] could also be synthesized [156]. A striking analogy was noted between the coordination behaviour of the Tmp ligand and that of C$_5$Me$_4$H. Indeed, contrary to what observed in the Cp* series, tris(phospholyl) U(IV) complexes such as [(η^5-Tmp)$_3$UCl] **166** which is the phosphorus equivalent of [(η^5-C$_5$Me$_4$H)$_3$UCl], could be synthesized and characterized [157]. Finally, like in the chemistry of Ln(III), the availability of the lone pair at phosphorus in U(IV) complexes was established by the synthesis of U-Ni heterobimetallic species such as **167** and **168**. Note that in **168** the Tmp ligand adopts a μ^2-coordination mode (Figure 34) [158].

Some low-valent U(III) complexes were conventionally prepared either by the reduction of the corresponding U(IV) complexes or through the reaction of the KTmp salt with the U(III) precursor [(η^6-mesitylene)U(BH$_4$)$_3$]. The formulation of complexes was found to be particularly dependent on the experimental conditions used. Thus, neutral dimeric species such as **169** were exclusively obtained when reduction occurred in toluene with the concomitant precipitation of NaBH$_4$ [157] (Figure 34). Under classical conditions, ate complexes were obtained. Importantly, on the basis of electrochemical data, it was shown that the Tmp ligand behaves as a poorer electron donor that the Cp* ligand. Thus, one–electron reversible reduction of [U (η^5-Tmp)$_2$ (BH$_4$)$_2$] and [U (η^5-Tmp)(η^5-Cp*) (BH$_4$)$_2$] respectively

occur at -1.49 V and -1.66V, the [U (η^5-Cp*)$_2$ (BH_4)$_2$] complex is reduced at -1.83V (*vs.* Cp_2Fe/Cp_2Fe^+) [154].

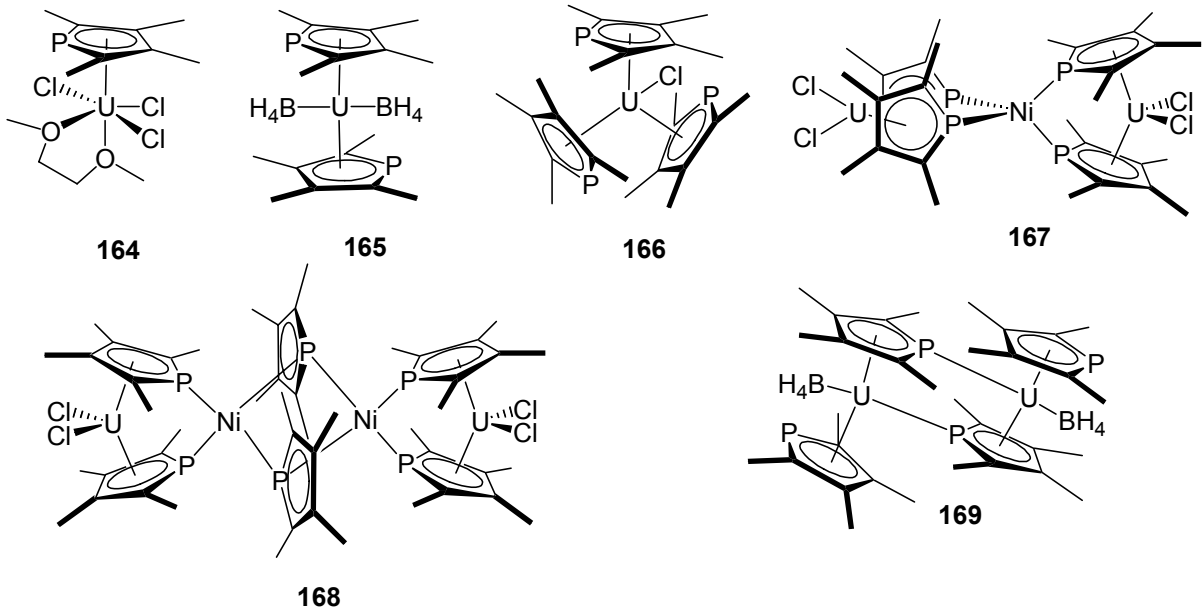


Figure 34: Some representative U(IV) and U(III) phospholyl complexes.

2.3 Phosphinines and their complexes

Phoshinines belong to a very important class of phosphorus heterocycles. Their discovery by Märkl in 1966 can really be considered as landmark in phosphorus chemistry [159]. Their successful synthesis unambiguously demonstrated that reactive P=C double bond systems could be thermodynamically stabilized by incorporation into an aromatic structure. Additionally their existence raised the problem of the extension of the concept of aromaticity to heavier main group elements. This problem had remained a field of controversy for a long time. Studies on the coordinating behaviour of these heterocycle started very early after their initial discovery and some classical complexes of metal carbonyls were first reported [160]. However the lack of efficient synthetic approaches towards functional derivatives really hampered their use as ligands in coordination chemistry and catalysis. Indeed, for along time the 2,4,6-tiphenyl substituted phosphinine remained the most easily accessible derivative. Considerable synthetic progresses have been made since this date and the development of new methods allowed for the synthesis of various functional derivatives. Among these, one can mention, ring expansion from phospholes [161], synthesis of 2-halogeno derivatives [162] and the use of diazaphosphinines [163] in the synthesis of tertrafunctional derivatives. In this sub chapter synthetic methods will only be detailed when necessary. For further details regarding

the synthetic approaches employed for the synthesis of polyfunctional compounds, readers will have to refer to specialized reviews [164].

As previously mentioned, the most significant electronic characteristic of phosphinines is their strong π-accepting capacity which makes them suitable ligands for the stabilization of electron-rich transition metal complexes. This was first evidenced by the work of Elschenbroich et al. who synthesized a series of homoleptic complexes of the parent phosphinine C_5H_5P. Historically, the tetrakis(phosphinine) Ni(0) **170** is the first example (Figure 35). This complex was easily produced by a classical displacement of ligand from the $[Ni(COD)_2]$ precursor in methycyclohexane at room temperature [165]. The geometry around Ni is tetrahedral, as expected for a d^{10} complex and Raman spectroscopy (ν Ni-P = 168 cm^{-1}) suggests that the Ni-P bond order is relatively important because of the strong π-back-bonding in the π* system of the ligand. Contrary to classical tetrakis(phosphine) Ni(0) complexes, **170** cannot be oxidized to yield a stable 17 VE species. Analogous homoleptic Ni(0) complexes featuring 2-halogenophosphinines as ligands were also prepared [166]. Note that chromium **171**, molybdenum **172**, tungsten **173** [167] and iron(0) **174** [168] complexes of C_5H_5P were also prepared and structurally characterized as well as the homoleptic Rh(I) complex **175** of the 2-methyl-3,6-diphenylphosphinine (Figure 35) [169]. The 17 VE $[V(\eta^6\text{-}C_5H_5P)_2]$ vanadium(0) complex **176** was also successfully synthesized through the metal atom-ligand condensation technique [170]. Contrary to what observed with groups *6-10* complexes coordination occurs through the π-system of the ring to yield the sandwich complex. Unlike its carbon counterpart, **176** was found to be very stable and can be exposed to air in solution without any apparent decomposition. Noteworthy, it was shown that the oxidation of **176** (to yield the 16 VE complex **177**) takes place at more anodic potential ($E_{1/2}$ = 0.18 V *vs* SCE) than that of its carbon analog the $[V(\eta^6\text{-}C_6H_6)_2]$ complex ($E_{1/2}$ = - 0.35 V *vs* SCE). Conversely, the reduction potential of **176** ($E_{1/2}$ = -1.99 V *vs* SCE), to form the 8 VE complex **178**, is cathodically shifted with respect to the benzene derivative ($E_{1/2}$ = -2.71 V *vs* SCE) (Figure 35). These data clearly show that phosphinines are as good π-donors as benzene derivatives but display a greater π-accepting capacity.

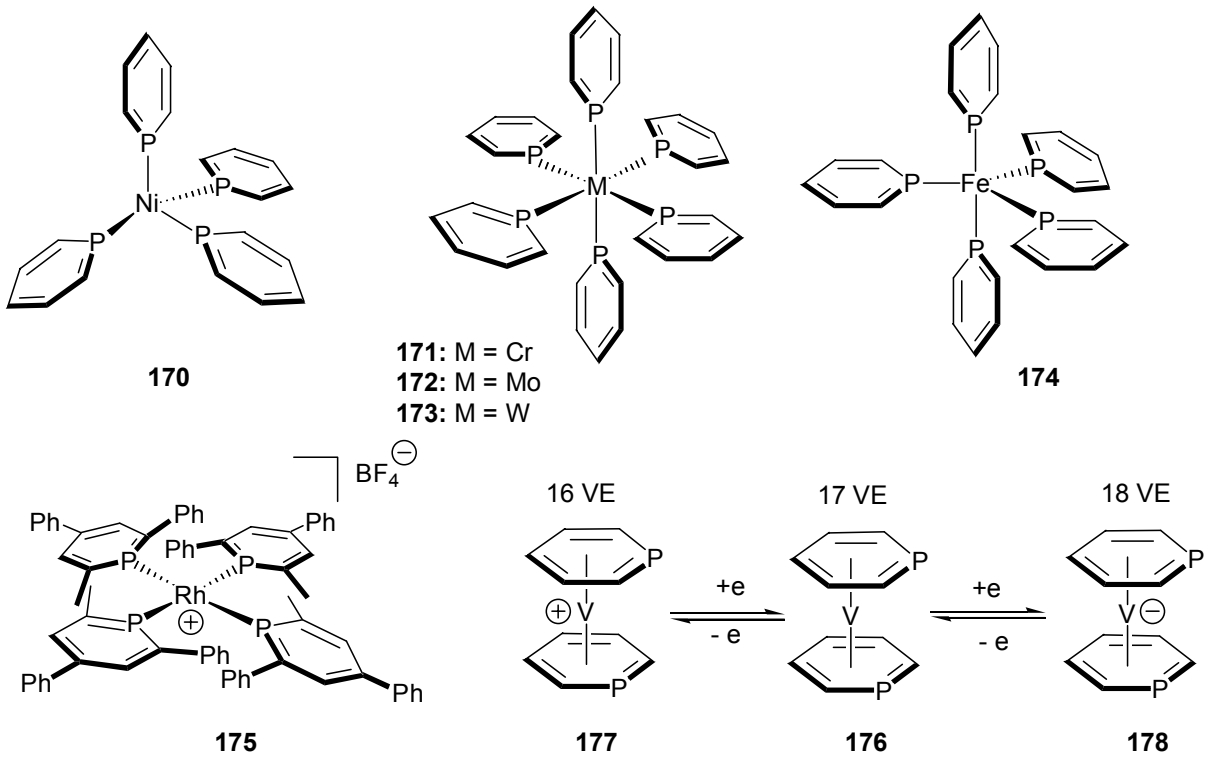


Figure 35: Some σ-homoleptic and π-complexes of phosphinines.

The tendency to form π complexes on going from the right to the left of the periodic table was confirmed by the preparation of the Ti complex **179** though here the presence of bulky groups at the periphery of the phosphorus atom probably prevents η^1-coordination [171]. However, like in the chemistry of phospholyl anions, the substitution scheme of the ring plays a determinant role on the outcome of the complexation. Thus, a sandwich chromium(0) complex of the bulky 2,4,6-tris(tertiobutyl) phosphinine **180** was synthesized through metal atom-ligand condensation at 77 K and structurally characterized (Figure 36) [171]. With iron, the introduction of only one trimethylsilyl group is necessary to favour the η^6-coordination mode. Complex **181** was obtained following two different techniques, either by reacting the free ligand with the $[Fe(COD)_2]$ precursor or by condensing the ligand and COD on iron metal atoms at low temperature [172]. Also with group 8 metals, η^6-ruthenium complexes of 2,6-bis(trimethylsilyl)phosphinines such as **182** were formed upon reacting the ligand with the $[Ru(\eta^5\text{-Cp*})(\eta^4\text{-}C_4H_{10})Cl]$ complex in the presence of $AgBF_4$ as chloride abstractor. During the same study it was showed that with poorly substituted phosphinines such as the 2-bromo-4,5-dimethylderivative (C_7H_8PBr), cationic classical η^1 complexes are formed $[Ru(\eta^5\text{-Cp*})(\eta^4\text{-}C_4H_{10})_3][BF_4]$ [173]. With group 9 metals, η^6-cationic complexes of the [M(COD)] (M = Rh, Ir) **183** and **184** were also obtained when a 2,6-

bis(trimethylsilyl)phosphinine is used as ligand. Interestingly η^1-coordination occurs when only one trimetylsilyl group is present to yield the cationic complex **185** [174]. Finally to complete this presentation of homoleptic complexes of phosphinines it must be noticed that cationic gold(I) complexes such as **186** were also reported (Figure 36) [175].

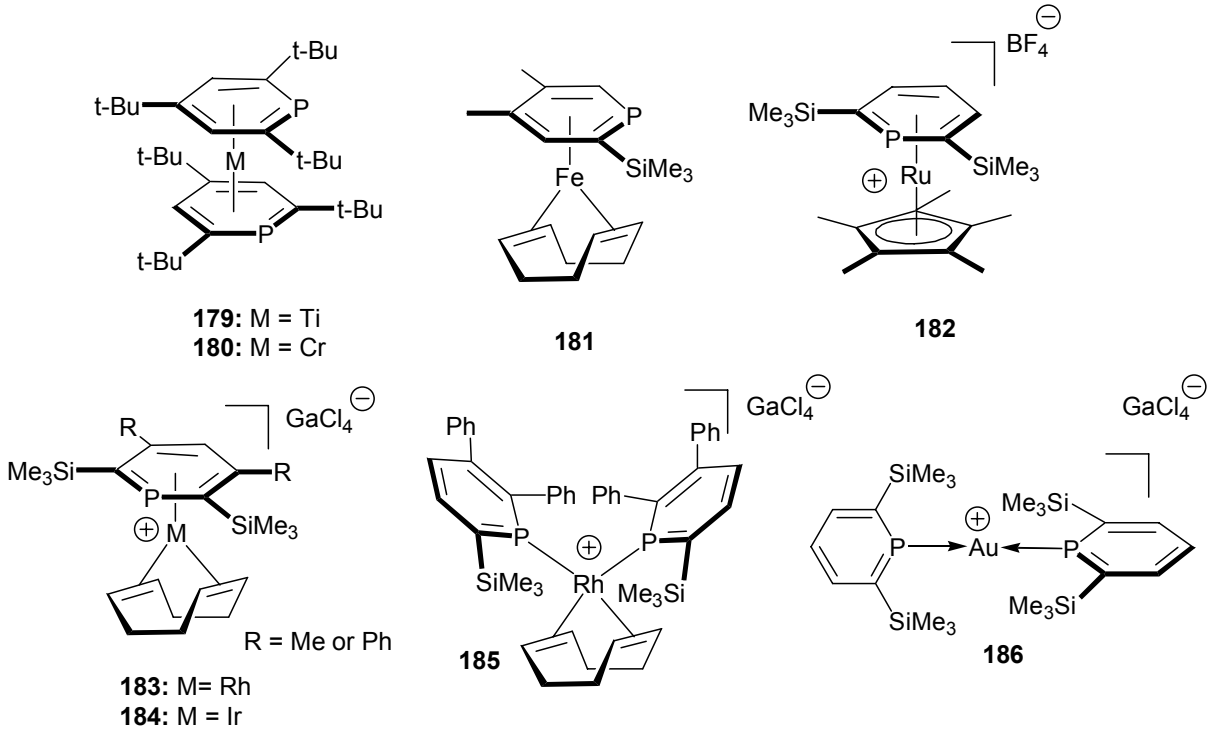


Figure 36 : σ and π-complexes of phosphinines.

Some other unusual bonding modes have been described for phosphinines. A first interesting example was provided with the synthesis of stable phosphabenzyne (2,3-dehydrophosphinines) zirconocene complexes. The methodology employed for their synthesis is similar to that used for the synthesis of classical η^2-benzyne zirconocene complexes and relies on a β-abstraction followed by the elimination of benzene or methane from the corresponding Zr(IV) derivatives. Whereas monomeric species such as **187** only involve coordination of the zirconocene fragment onto the pseudo triple-bond, dimeric complexes such as **188** were found to be very stable and were structurally characterized (Figure 37). In this dimer the coordination sphere of each zirconocene fragment is completed by the η^2-coordination of the pseudo triple bond and by that of phosphorus atom lone pair of the second phosphinine unit. These dimers function as a source of monomeric phosphabenzyne zirconocene complexes which proved to be reactive toward various substrates such as aldehydes, ketones, alkynes and sulfides. Examination of the X-ray data of **188** revealed that

the phosphabenzyne complex must be actually regarded as a metallacycle, like its carbon counterpart. Reaction of phosphinines with clusters also led to the discovery of surprising bonding modes. Thus, complexes **189** in which the ligand adopts a μ,η^2-coordination mode (2 electrons given by the lone pair at phosphorus and 2 electrons given by the P=C bond) results from the reaction of a 2-functional phosphinine with the $[Os_3H_2(CO)_{10}]$ cluster. The outcome of the reaction proved to be highly dependent on the amount of phosphinine used and the substitution scheme of the ring. The reaction with two equivalents of the 2-trimethylsilylphosphinine yields complex **190** in which the two ligands have lost their aromaticity and where involved in an intramolecular [4+2] cycloaddition (Figure 37) [176]. During an attempt to isolate a Pd(0) homoleptic complex from the reaction of the triphenylphosphinine ligand with $[Pd(OAc)_2]$ an unknown dimeric structure was formed but subsequent reaction with PMe_3 furnished the interesting triangulo Pd_3 cluster **191** in which each ligand adopts a μ^2 bonding mode. DFT calculations carried out at the B3LYP/6-31G(d,p) level of theory revealed a low bond order of the Pd-Pd bonds (0.11) and that coordination between the ligands and the Pd_3 core involve σ and π orbitals of the ligand. Some of these unusual bonding modes are prenseted in the following figure (Figure 37).

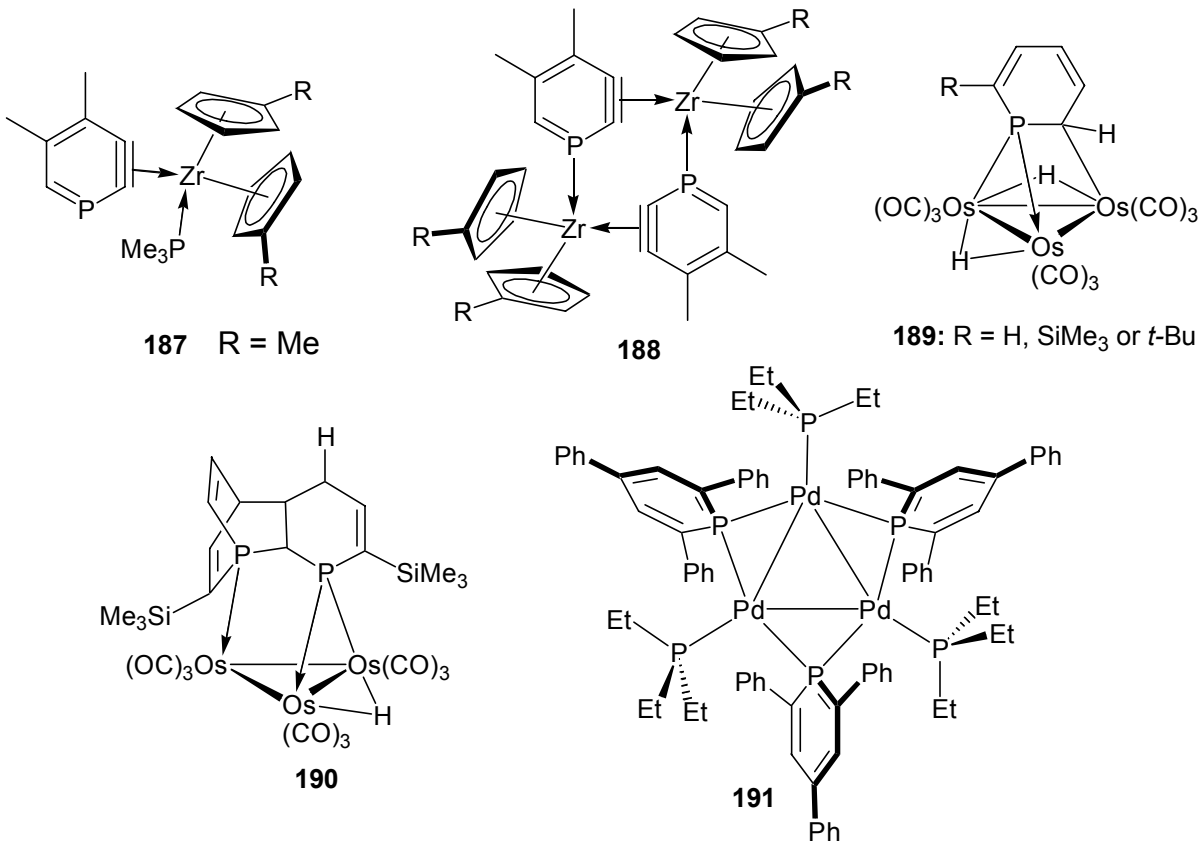


Figure 37: unsual bonding modes of phosphinnes.

Polydentate ligands featuring phosphinines have also found applications in coordination chemistry. Thus some complexes of 2-phosphinophosphinine were reported. Classical Mn(I) **192**, Fe(I) **193** and Mo(I) **195** dimers were obtained by reacting the ligands with the appropriate precursors, $[Mn_2(CO)_{10}]$, $[Fe(\eta^5\text{-}Cp)(CO)_2]_2$, and $[MoCp(CO)_2]$, respectively (Figure 38) [177]. Among molybdenum dimers, only the ones bearing the most electron withdrawing ligands (R = OEt or *p*-OC_6H_4-*t*-Bu) evolved to the reformation of the Mo-Mo triple bond **196** by loss of two molecules of CO upon heating. Interestingly, heating of a 2-(phospholyl)phosphinine with the $[FeCp(CO)_2]_2$ dimer led to the bidentate 2-(2'-phosphininyl) phosphaferrocene ligand **194**. Only one group 10 dimeric complex has been synthesized so far. Complex **197** was prepared following two different routes ($Ni(COD)_2$/CO or $NiBr_2$.DME/Zn/CO) and was structurally characterized. Contrary to the analogous dppm complex, the strong π-accepting ability of the phosphinine ligand allowed for the stabilization of a mixed anionic Ni(-1)-Ni(0) complex whose formation was evidenced by cyclic voltammetry. In the same study devoted to d^{10} complexes, the same ligand was employed in the preparation of the tetranuclear Cu(I) complex **198** in which the iodine ligand is μ^4-face bridged onto the Cu_4 core [178]. Only one example in which a 2-phosphinophosphinine behaves as chelate **199** has been reported by Märkl [179]. Some representative complexes of 2-phosphinophosphinne ligands are reported in the following figure (Figure 38).

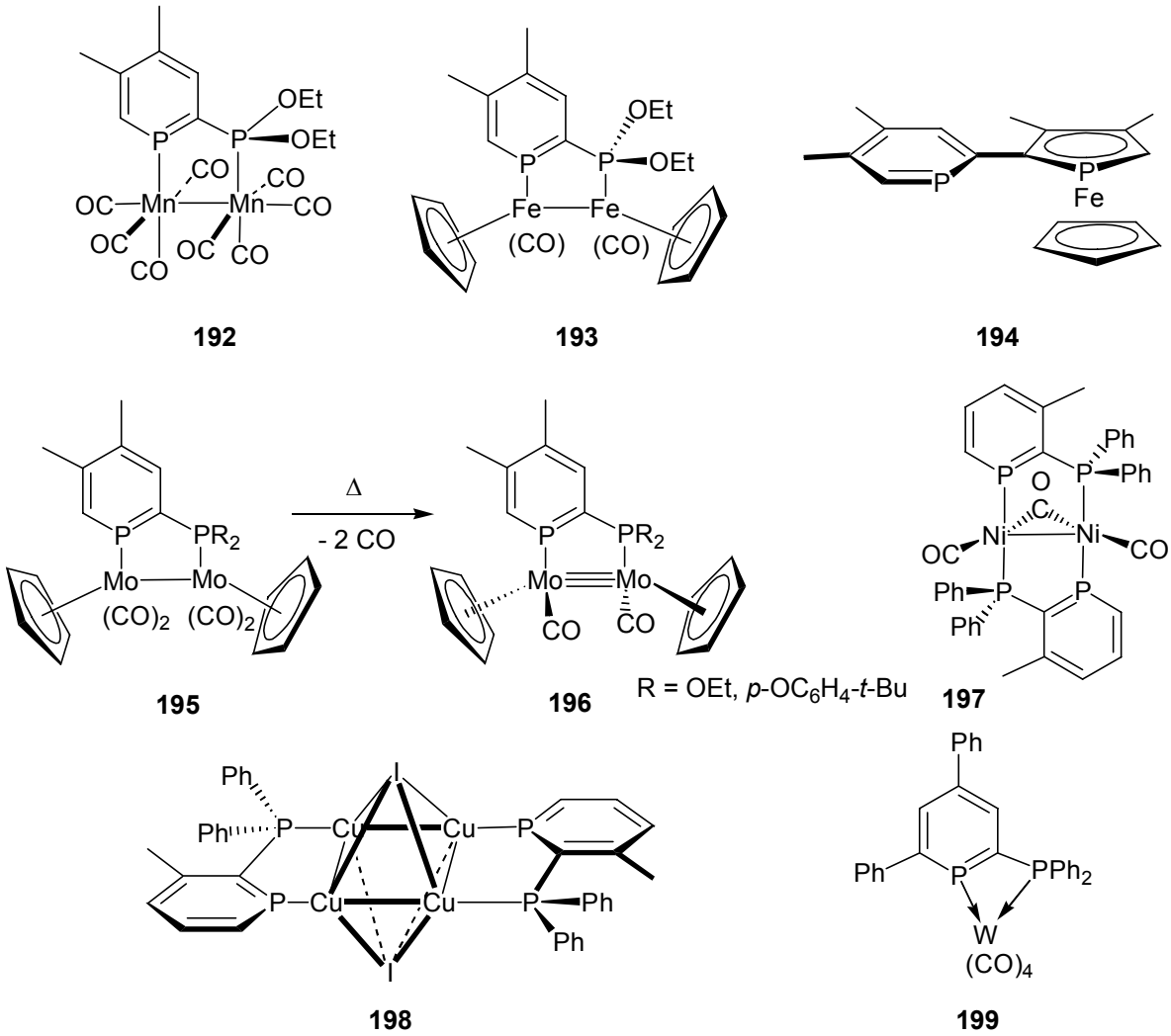


Figure 38: 2-phosphinphosphinine complexes.

Bipyridines and their derivatives such as functional oligopyridines are probably the most widely employed ligands in the coordination chemistry of nitrogen ligands. Their strong ability to coordinate various metal even in high oxidation state has been exploited in the elaboration of numerous supramolecular edifices and catalysts. An important electronic characteristic of these ligands resides in their aptitude to promote redox processes in transition metal complexes, one of the most illustrative example being provided by the $[Ru(bpy)_3]^{2+}$ cation which behaves as a powerful mediator in solar energy conversion schemes (photodecomposition of water, photovoltaic cells). Therefore, studies aimed at synthesizing phosphorus equivalents of these ligands started very early [180]. The first semi-equivalent of a bipyridine (NIPHOS) was synthesized by Mathey et al. in 1982 [181]. Some studies were devoted to the coordination chemistry of this interesting ligand but it rapidly became obvious that the coexistence of these two electronically different centres (P and N) was clearly incompatible. Indeed, phosphinine do not stand the presence of basic and nucleophilic

reagents whereas nitrogen ligands cannot be easily handled in acidic media (protonation of the lone pair). However some complexes of niphos were reported such as the [Cr(niphos)(CO)$_4$] complex **200** [182]. The group of Venanzi reported on the synthesis of interesting dimers **201** and **202** with group *9* metals. In these complexes, the phosphinine ligand adopts a μ^2-bonding mode (Figure 39) [183]. Some cationic Pd(II) and Pt(II) complexes such as **203** were also reported but they proved to be highly sensitive towards nucleophilic reagents. Thus, complex **203** readily reacts even with traces of water and alcohols to yield complex **204** in which addition of the nucleophile occurred onto the P=C double bond of the phosphinine (Figure 39). Though no theoretical calculations were carried out, one may propose that weak π-back bonding capacity of the [PtLCl] fragment strongly contributes in dearomatizing the ring [184].

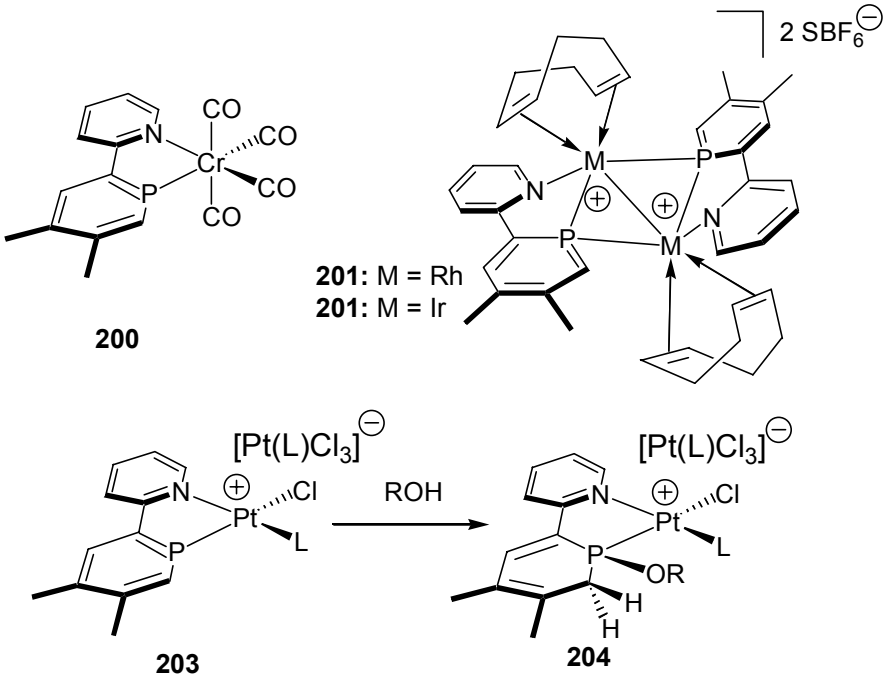


Figure 39: Complexes of NIPHOS.

The real analogues of 2,2'-bipyridines, the 2,2'-biphosphinines, were synthesized for the first time in 1991 [185]. Though the symmetry of the MO are similar, these ligands markedly differ from their nitrogen analogs. As can be seen on the view presented in figure 40, the symmetry of the π* LUMO is identical but the distribution of coefficients is different [186]. Thus, in biphosphinines the LUMO is mainly developed on the two phosphorus atom whereas in bipyridines, the most important coefficients are localized on the carbocyclic part of the molecule. Most significantly, it was shown by electrochemical measurements that the LUMO of the parent 2,2'-biphosphinine **205** lies at lower energy than that of 2,2'-bipyridine

(Scheme 12) [187]. The mono radical anion of the easily available 3,3',4,4'-tetramethyl-2,2'-biphosphinine **206** was structurally characterized as well as the dianion. Both structures are presented in Scheme 13. In the monoradical anion [**206**][Li(2.2.1)], the two rings are coplanar on good agreement with a complete delocalization of the odd electron. Accordingly, the internal C2-C2' bond distance between the two rings is significantly shortened (1.440(2) Å) with regards to the neutral ligand tmbp (1.490(2) Å). Two structures were obtained for the dianion **206**$^{2-}$. When the reduction was carried out with sodium metal in DME the polymeric structure [**206**][$Na_2(DME)_{1.5}]_n$ (DME = 1,2-dimethoxyethane) was formed. In good agreement with the shape of the LUMO the C2-C2' bond in **206** has acquired a significant double bond character (1.401(4) Å). In the second structure [**206**][$Li(2.2.1)]_2$ which is not shown in scheme 13, the two lithium cations were cryptated with (2.2.1) and the C2-C2' bond distance is also significantly shortened at 1.40(1) Å.

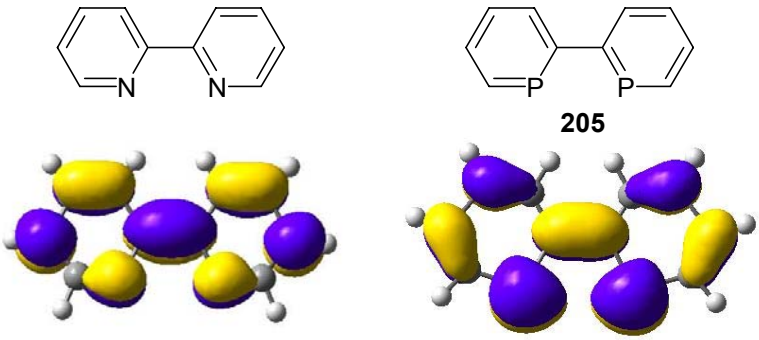
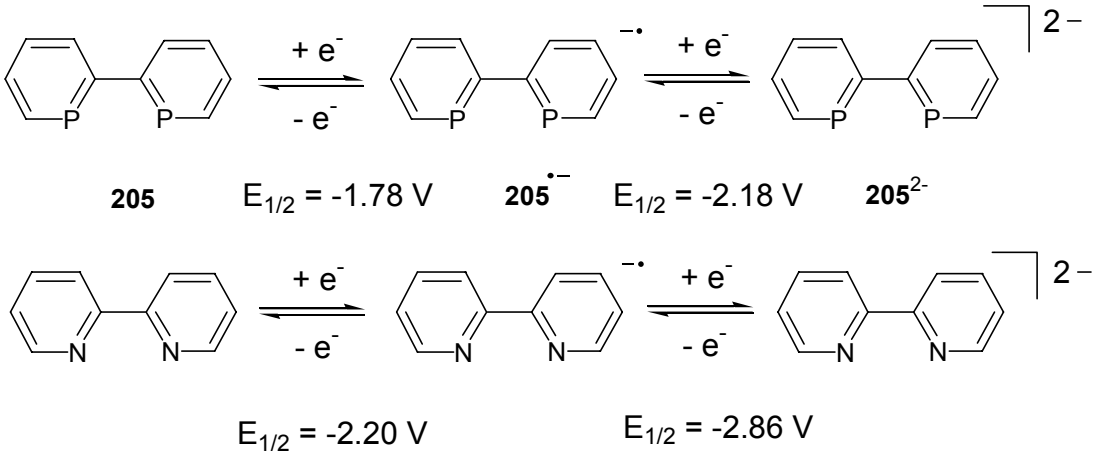
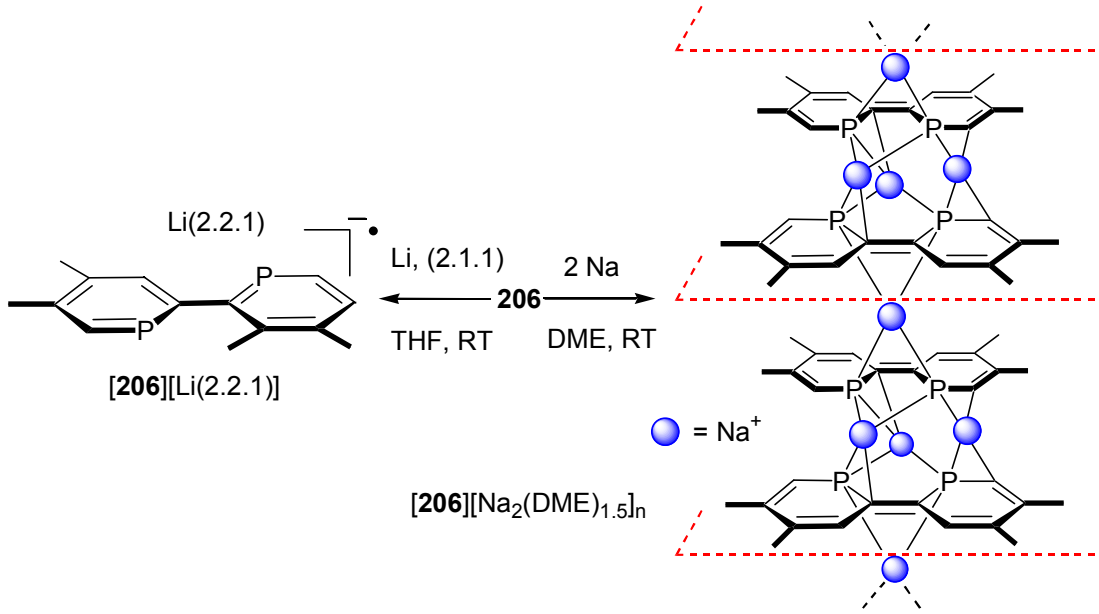


Figure 40: LUMO 2,2'-biphosphinines and 2,2'-bipyridine



Scheme 12: Electrochemical reduction of 2,2'-bipyrdine and 2,2'-biphosphinine.



Scheme 13: Reduction of the tmbp ligand into its corresponding mono radical anion and dianion radical (the DME molecules in the structure of the dianion have been omitted for clarity).

Many biphosphinine complexes were synthesized using the tmbp ligand. Like with the niphos ligand, it was observed that the electron-richness of the metallic fragment governs the stability of the complex. Thus, whereas complexes of electron rich metal fragments were found to be stable, coordination to electron deficient fragments resulted in a dearomatization of the phosphinine ring. A significant example was provided by the synthesis of the phosphorus analog of the ubiquitous dicationic $[Ru(bpy)_3]^{2+}$ complex. Complex **207** which was found to be highly reactive towards traces of moisture or nucleophilic reagents could not be isolated. However the replacement of two strong π-acceptor biphosphinine ligands by two strong σ-donor 2,2'-bipyridines led to the formation of a very stable and isolable complex **208** which was structurally characterized (Figure 41) [188]. This example clearly emphasizes the fact that contrary to 2,2'-bipyridines, 2,2'biphosphinines favour coordination of electron rich metal fragments. Not surprisingly, coordination of tmbp to the electron-rich $[Ru(\eta^5\text{-Cp*})Cl]$ fragment afforded complex **209** which proved to be not moisture sensitive [189]. An additional significant example was provided by the synthesis of the cationic platinum(II) complex **210**. Interestingly, the phosphinine ligand which is trans to the less electron-donating ligand (Cl) proved to be the most sensitive towards hydrolysis. Reaction with traces of water led to the formation of complex **211** that features a 1,2-dihydrophosphinine ligand *trans* to the Cl ligand (Figure 41).

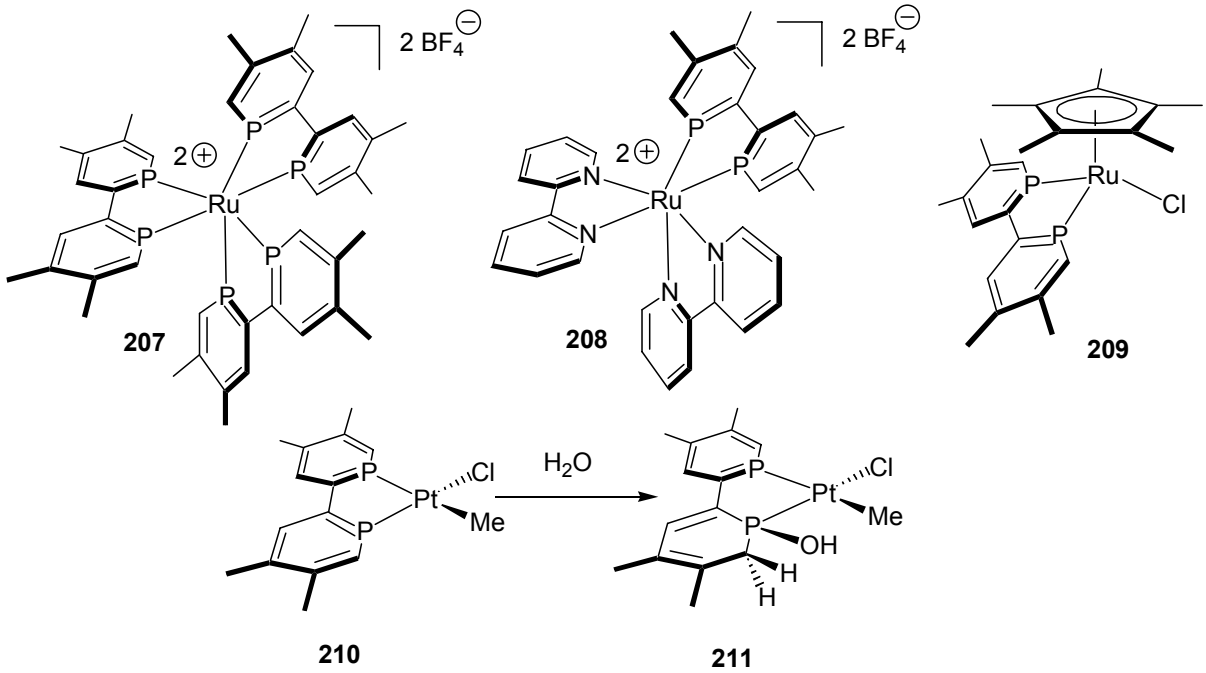


Figure 41: Reactivity of divalent biphsophinine complexes.

Not surprisingly then, the most significant results were obtained in the synthesis of highly electron-rich or electron excessive metal complexes. As will be seen with the following examples, contrary to classical tertiary phosphines and bipyridine ligands, 2,2'-biphosphinines efficiently stabilize many reduced complexes. Two synthetic approaches were devised. The first one which turns out to be the more conventional consists in reducing a preformed complex. However this approach is limited since many 2,2'-biphosphinines complexes of electron deficient metal centres are not stable. The second approach, which has been the more widely used, takes advantage of the easy reduction of the ligand. Monoradical anions or dianions of 2,2'-biphosphinine react with highly or moderately oxidized metal centres to yield the corresponding neutral or anionic complexes [190]. This second methodology was employed for the preparation of homoleptic dianionic complexes of group 4 metals by reacting the dianion of tmbp with MCl_4 complexes (M = Ti, Zr, Hf) complexes **212-214**. Though these complexes have the d^6 electronic configuration, they adopt a trigonal prismatic geometry. Similar geometries were observed with group 6 metals (M = Cr, Mo, W) **215-217**. Theoretical calculations performed on the $[W(tmbp)_3]$ complex have shown that the real oxidation state of the complex is not zero and that a significant part of the electron density is delocalized over the three ligands [191]. Group 7 anionic metal complexes were obtained through the reduction of the corresponding $[M(tmbp)(CO)_3X]$ (M = Mn, Re; X = Cl, Br) complexes which proved to be stable enough to serve as precursor. In the solid state, the

Mn(-1) complex **219** adopts a polymeric structure [192]. Note also that a dinuclear Mn(I) complex **218** (analogous to complex **40**) in which the biphosphinine ligand behaves as a 8 electron donor has also been prepared through the reaction of the ligand with $[Mn_2(CO)_{10}]$ and structurally characterized Some of these reduced complexes of group 4, 6 and 7 metals are shown in the following figure (Figure 42).

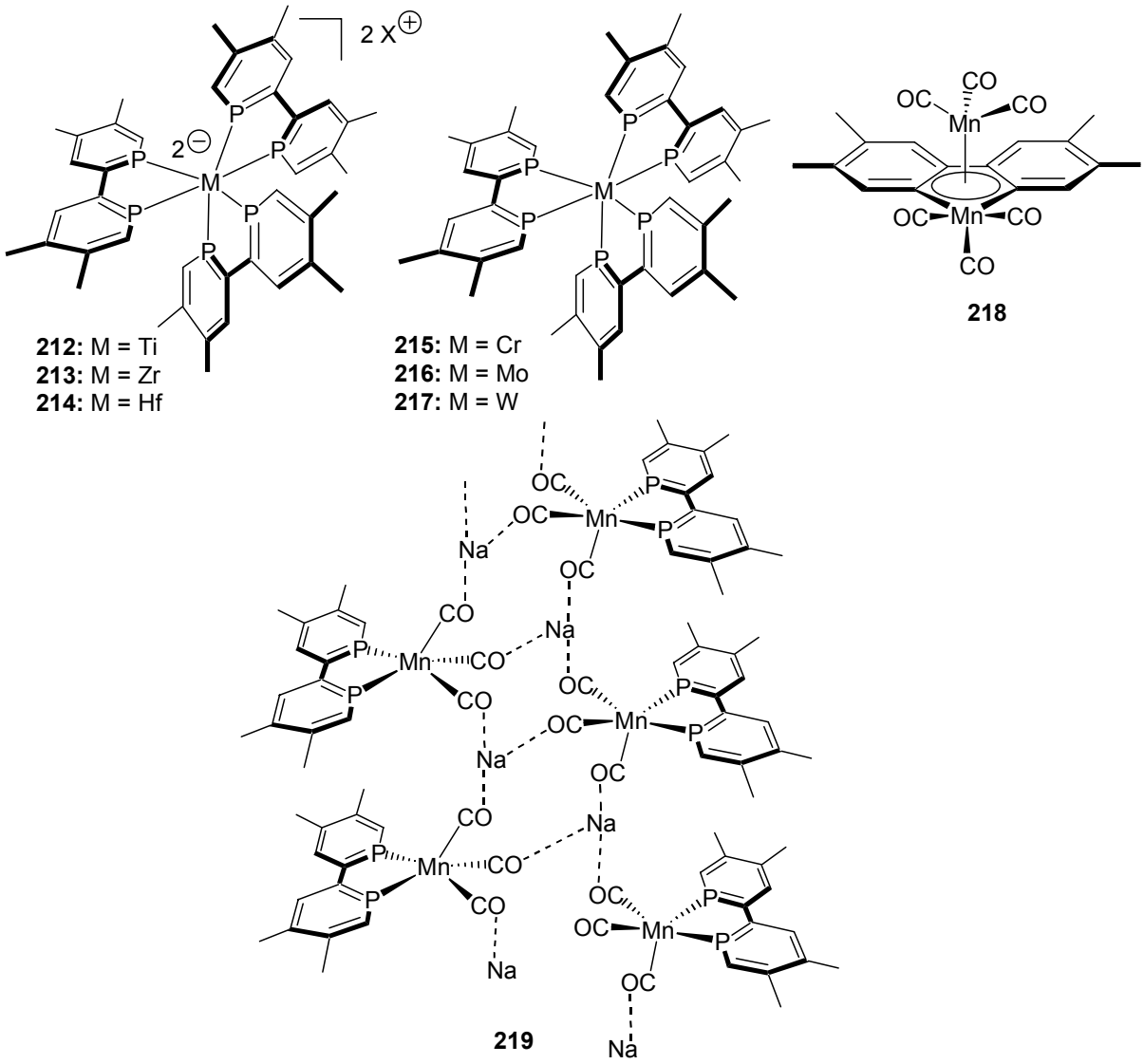


Figure 42: Biphosphinine reduced complexes of group 4,6,7 metals.

Interestingly, dianionic Fe(2-) and Ru(2-) complexes, analogues of the famous $[Fe(CO)4]^{2-}$ dianion were also prepared by the reaction of two equivalents of the dianion of tmbp (4,4',5,5'-tretamethyl-2,2'-biphosphinine) with the $[FeCl_2.(THF)_{1.5}]$ and $[Ru(Cl)_2(COD)]$ complexes (Figure 43) [193]. Noteworthy, a X-ray crystal structure analysis revealed that the Ru(2-) complex **220** adopts a square planar structure, two weak interactions

occurring with $[Li(THF)_3]$ cations which are located along the main axis. A view of one molecule of **220** is presented in figure 44. This particular geometry, which is usually not expected for a complex having a d^{10} electronic configuration, will be discussed further. Three other low valent ruthenium complexes were synthesized and structurally characterized; the zerovalent $[Ru(tmbp)(\eta^6\text{-}C_{10}H_{14})]$ complex **221**, dimer **223** which results from the monoelectronic oxidation of **223** and the anionic Ru(0) complex **222** obtained through the reduction of the corresponding chloride complex $[Ru(\eta^5\text{-}Cp^*)(tmbp)Cl]$ with two equivalents of sodium naphthalenide (Figure 43) [194]. Also with group 8 metals, reaction of tmbp with the cluster $[Os_3(CO)_{10}(MeCN)_2]$ afforded the trinuclear complex **224** which proved to be photostable unlike its bipyridine analogue [195]. The second synthetic approach relying on the use of biphosphinine dianions was also employed for the synthesis of homoleptic complexes of group *9* metals **225** (M = Co) and **226** (M = Rh) (Figure 42). These complexes have a d^{10} electronic configuration they adopt a tetrahedral geometry as expected. However, three conformations are present in the unit cell of the Rh complex, only differing by the interplane angle formed by the two biphosphinine ligands (59, 63, 87°). A similar phenomenon was observed in the X-ray crystal structure of **225** (78° and 83°). These observations clearly point out that the energetic barrier between the square planar and the tetrahedral geometries is probably very weak in the d^{10} biphosphinine complexes. Note that in both cases, complexes were structurally characterized when the sodium cations cannot interact with the anionic complex (crypted with one molecule of (2.2.2)) [196a]. Only one reduced group *10* biphosphinine complex was reported. The monoelectronic reduction of the $[Ni(tmbp)_2]$ [197] complex yields the 19 VE species **227** which was characterized by EPR spectroscopy (Figure 43). Combination of EPR measurements and DFT calculations reveal that the unpaired electron is mainly delocalized over the two ligands [198].

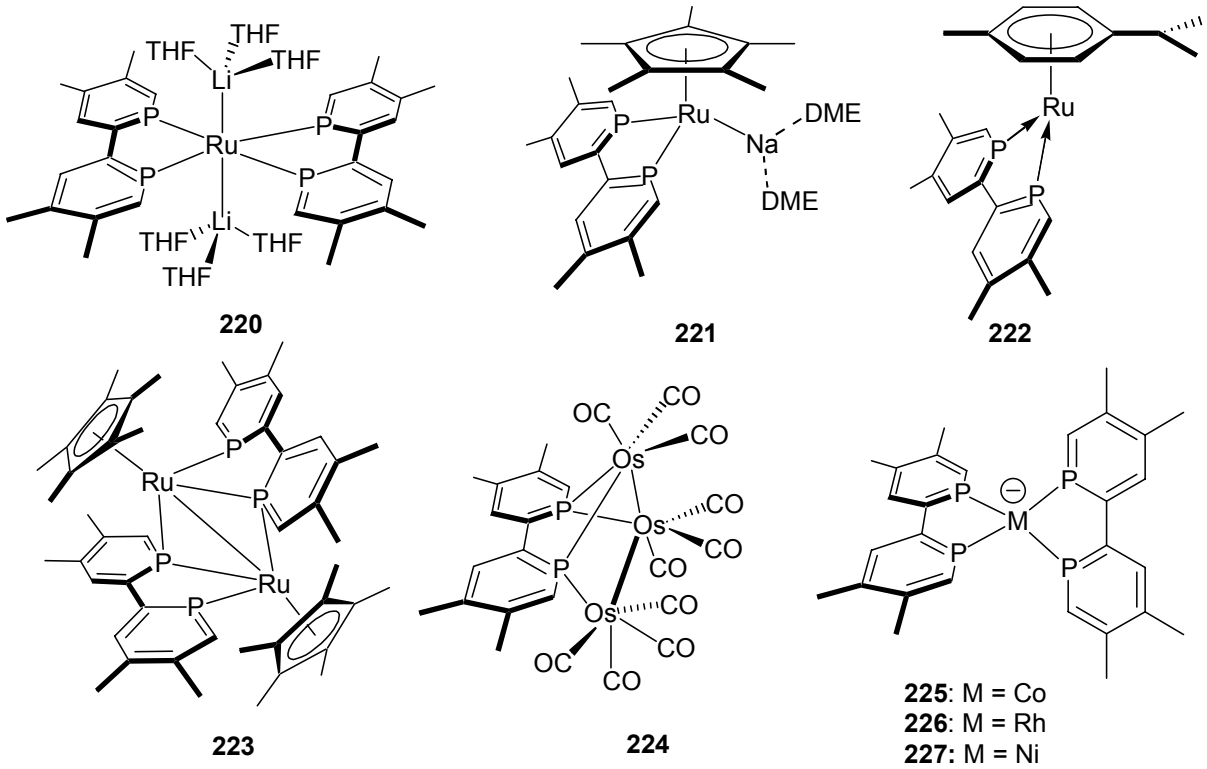


Figure 43: Biphosphinine reduced complexes of group 8,9,10 metals.

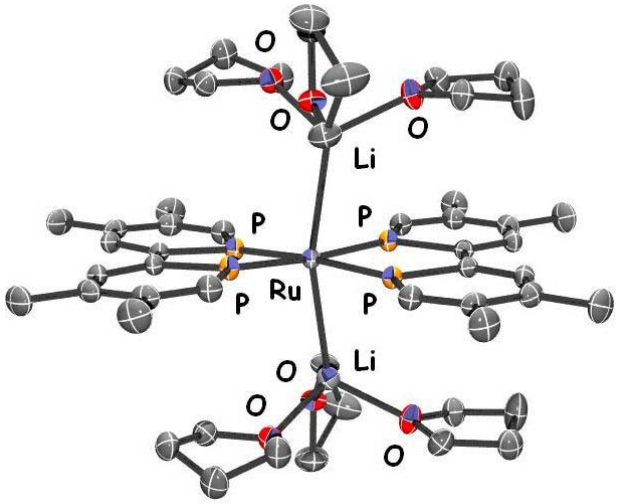


Figure 44: X-ray crystal structure of complex **220**.

The synthesis of these reduced complexes raised the problem of the assessment of the real oxidation state of the metal center. So far, this topic has not received so much attention but recent calculations by Jean et al. [196b] shed some light on some surprising geometrical features such as very particular structures of complexes having the d^{10} electronic configuration. The potential energy curves associated with the interconversion between square planar (SP) and tetrahedral (Td) conformations of the formal d^{10}-$[M(biphosphinine)_2]^q$

complexes (M = Ni, Pt, Co, Rh and Ru; q = charge) were studied by means of DFT calculations with the B3LYP functional. In good agreement with experimental data, complexes with M = Ni, Pt, Co and Rh were found to adopt a distorted tetrahedral conformation, the flatness of the computed potential energy curves accounting for the experimental characterization of several independent molecules and the fluxional behaviour observed in solution for M = Co and Rh. As expected for formal d^{10} complexes, the tetrahedral geometry was always found to be more stable than the square planar one. However, computed energy differences were found to be rather small (between 3.1 kcal mol^{-1} for M = Ru and 13.6 kcal mol^{-1} for M = Ni). Importantly, it was shown that the lower the d orbitals on the metal centre (Ni < Co < Pt < Rh < Ru) the less favoured the square planar conformation. Finally, these calculations revealed that for M = Ru, the slight preference for the tetrahedral geometry found in the calculated complex is not preserved in the presence of two counter cations (Na^+). This result is in perfect accord with the experimental data for the uncryptated complex **220**. In this complex, the HOMO is mainly described by the two π* orbitals on biphosphinines and the contribution of the metal is very small. To the extreme, this complex can be regarded as the coordination of two monoradical anions onto a Ru(0) d^8 center. On the contrary, in tetrahedral complexes, though the HOMO also features an important contribution of the π*orbitals of biphosphinine, the participation of the metal is more important and complexes are closer to real d^{10} species. The HOMO of $[Ru(biphosphinine)_2]^{2-}$ and $[Co(biphosphinine)_2]^-$ are presented in the following figure.

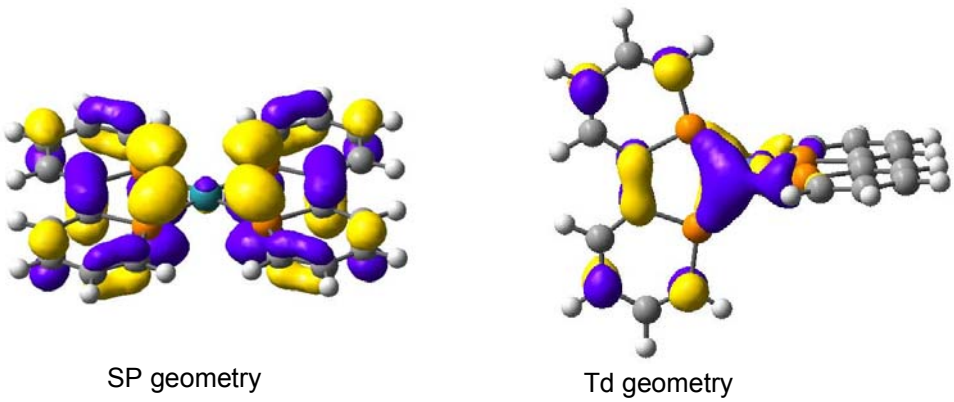
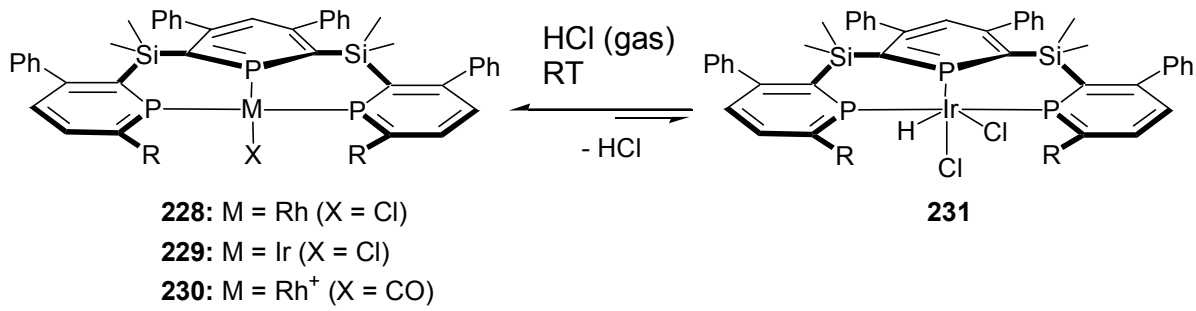


Figure 45: HOMOs of d^{10} biphosphinine complexes adopting either a square planar or a tetrahedral geometry.

Recent progresses in the elaboration of synthetic strategies toward functional phosphinines have provided an access to a wide range of sophisticated phosphinines-based ligands and edifices. Henceforth, new bi-and tridentate ligands are available and their

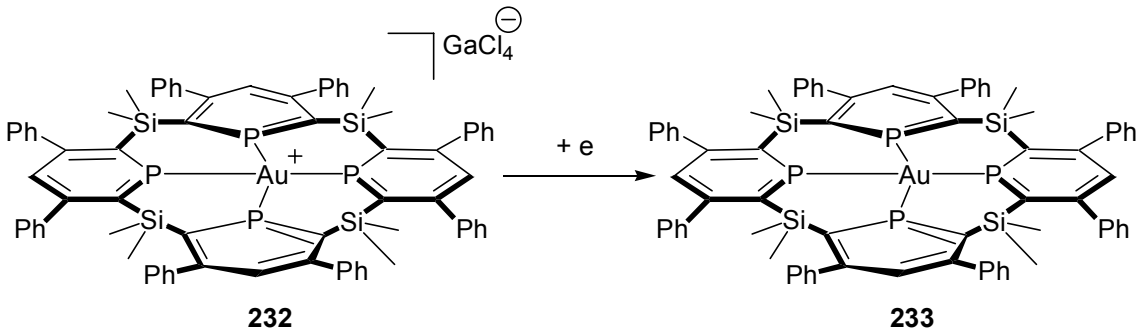
coordination chemistry has been explored. For example, Rh(I) **228** and Ir(I) **229** complexes of a tris(phosphinine) ligand were synthesized and some cationic derivatives of these complexes were prepared [199]. A value of (ν(CO) = 2035 cm^{-1}) for the cationic complex [Rh(tris(phosphinine))(CO)][BF_4] **230** compared to 2016 cm^{-1} in [Rh(COD)PhP($CH_2CH_2PPh_2$)$_2$][PF_6] clearly suggests a weaker π-back donation in the CO ligand in **230** . This observation is in good agreement with the strong π-accepting capacity of phosphinines which significantly enhances the Lewis acidity of the metal center. Another illustrative example was provided by the reaction of **229** with HCl. Indeed, unlike what is observed for classical Ir(I)HCl_2 complexes of tridentate tertiary phosphine ligands which are stable, the [Ir(tris(phosphinine))HCl_2] **231** complex was found in equilibrium with **229** at room temperature (Scheme 14) [199].



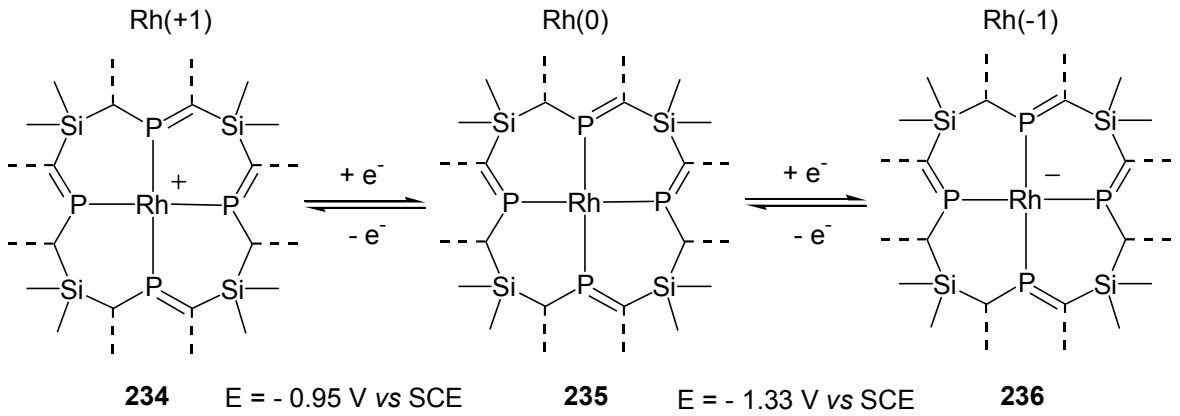
Scheme 14: Group 9 complexes of a tris(phosphinine) ligand.

The most significant developments were achieved with silacalix-[n]-phosphinines which are the first examples of macrocyclic structures featuring sp^2-hybridized phosphorus atoms [200]. The chemistry of Au(I) derivatives was investigated and complex **232** was structurally characterized. Contrary to what was observed with classical phosphine based Au(I) complexes, the two electron oxidation process does not yield a stable species and release of the ligand is observed. However, most importantly, reduction of complex **232** with sodium naphthalenide at low temperature yielded the corresponding Au(0) complex **233** which was identified by EPR spectroscopy. Accordingly to the electronic structure of **233**, the EPR signal appears as very characteristic a quartet of quintuplets, Au having a spin of 3/2. Complex **233** which proved to be stable up to 243 K is one of the rare example of stable monomeric Au(0) complexes (Scheme 15) [201]. Indeed, it is well known that zerovalent complexes such as [$Au(CO)_n$] (n = 1,2) were characterized in CO matrices at low temperatures and slowly decompose when the temperature rises 77K. Thus, macrocyclic

ligands such as silacalix-[4]-phosphinines can be regarded as phosphorus equivalents of a CO matrix. The same type of ligands was employed for the stabilization of Rh(I) and Rh(0) complexes. Complex **234** was conventionally prepared through the reaction of the free macrocycle with $[Rh(COD)_2][BF_4]$ precursors in dichloromethane at room temperature. Electrochemical measurements have shown that the cationic complex **234** can undergoes two successives monoelectronic reductions to yield the corresponding neutral 17 VE complex **235** and then an anionic 18 VE species **236** (Scheme 16). The electronic structure of the paramagnetic complex **235** was studied by EPR spectroscopy. DFT calculations suggest that the overall geometry around Rh is square planar and that the one-electron reduction only induces a small tetrahedral distortion. These calculations also indicate that the odd electron is mainly delocalized over the four phosphinine units only 10 % of the spin density residing on the metal. In the same study it was demonstrated that though the unpaired electron is mostly delocalized on the ligands in such systems, the replacement of two phosphinines by two thiophenes units tends to increase the rhodium spin density on rhodium (35%) [202]. One cannot close this paragraph devoted to the coordination chemistry of phosphinine-based macrocycles without mentioning the synthesis of cationic group 11 complexes **237-239** of an extended macrocycle [203] made of three phosphinine units and Me_2Si-O-$SiMe_2$ linkers and the tungsten carbonyl complex **240** of a silacalix-[3]-phosphinine. The synthesis and the X-ray crystals structure of two tungsten tricarbonyl complexes of tripodal ligands such as **241** were also reported (Figure 46) [204].



Scheme 15: Reduction of cationic silacalix-[4]-phosphinine Au(I) **232** into the corresponding Au(0) complex.



Scheme 16: Reversible reduction of a silacalix-[4]-phosphinine rhodium(I) complex.

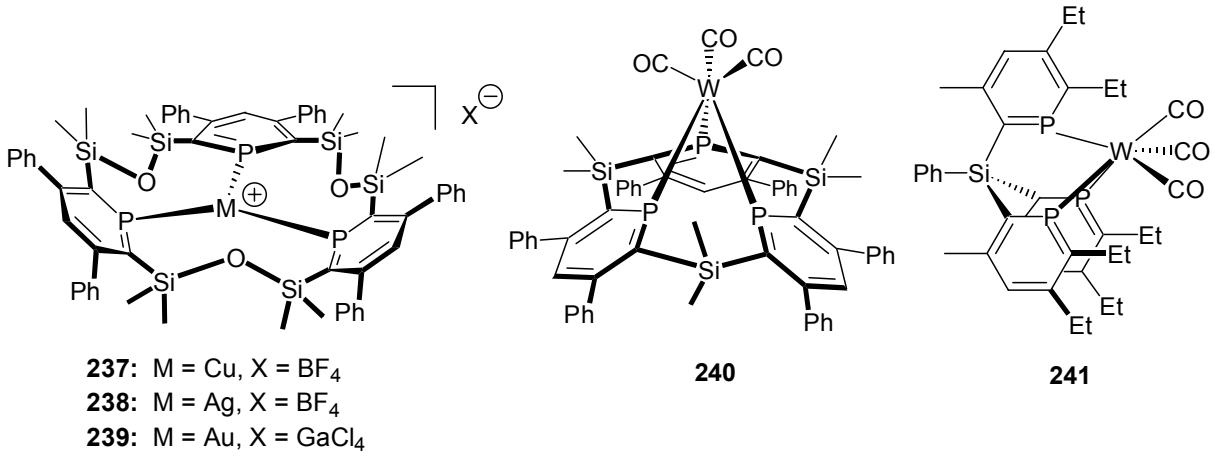
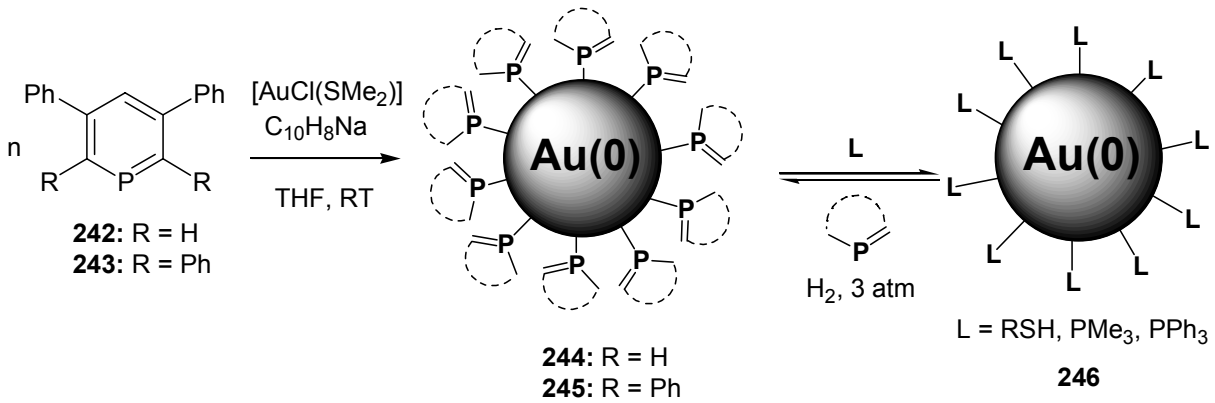


Figure 46: Tridentate and tripodal-based phosphinine complexes.

The remarkable ability of phosphinines, and in general of low-coordinate phosphorus compounds, to stabilize electron-rich metal centres opens interesting perspectives in nanosciences. Indeed, one may expect that their strong π-accepting capacity could be efficiently employed to assemble and modify electronic properties of metallic nanoparticles much more efficiently than classical phosphines do. So far, this area has not been thoroughly explored but a first report tends to validate this idea. In 2004, the first sp^2-based phosphorus stabilized nanoparticles, with gold as metal, were synthesized and characterized using phosphinines **242** and **243** as ligands. The synthethic procedure employed is straightforward and just relies on the reduction of the [AuCl(SMe_2)] precursor with sodium naphthalenide as a reducing agent in THF at low temperature [205]. Contrary to classical phosphines for which excess ligand is needed all these syntheses could be carried out in substochiometry (0.2 and 0.5 equiv.) allowing a good control of the particles sizes (Scheme 17). Gold NPs **244** and **245** (NP = nanoparticles) of 8.5 ± 2nm diameter were formed using a ratio ligand/precursor of 0.2.

Interestingly, it was observed that the grafting phosphinines at the surface of these Au NPs resulted in a significant shift of the plasmon band (from 520 nm for classical phosphines to 580 nm with phosphinines). It has been proposed that the red-shift observed mainly results from the strong electron-withdrawing capacity of phosphinine that reduces the electron density within the nanoparticles. A TEM image of these gold NPs is presented in figure 47. These nanoobjects were thought to be ideal candidates for detecting ligand exchange with phosphine and thiols followed through UV-visible spectroscopy. In order to make such a system suitable for detection, these Au NPs were immobilized in a matrix that preserves a good accessibility for the analyte to the detection center and good optical qualities. The one pot synthesis of mesoporous thin layers, functionalized with the gold nanoparticles, through evaporation induced self assembly (EISA) [206] was found to be the most convenient method. Indeed, narrow pore size distribution mesoporous silica thin films combine the advantages of sol-gel glasses (transparent, chemically inert, thermally and mechanically robust) with the porosity of their structure. These stabilized gold nanoparticules **246** were thus hosted in periodically organized mesoporous silica thin films and the resulting system proved to be remarkably efficient in the UV-visible detection of thiols and small phosphines such and PPh_3 and PMe_3 using 5ppm solutions (about 1000 equiv. compared to the phosphinine ligand). The powder obtained has a very large specific surface (1050 m^2g^{-1}) and a narrow pore size distribution (28 ± 1 Å). Importantly, reaction of these supported ligand substituted Au NPs with H_2 (3 atm) in the presence of the appropriate phosphinine ligand in excess allowed the regeneration of the initial sensor (Scheme 17) [207].



Scheme 17: Synthesis of phosphinine-based Au nanoparticles.

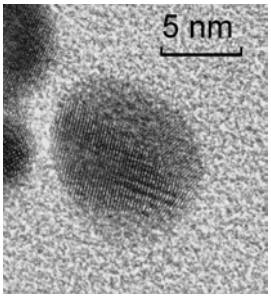
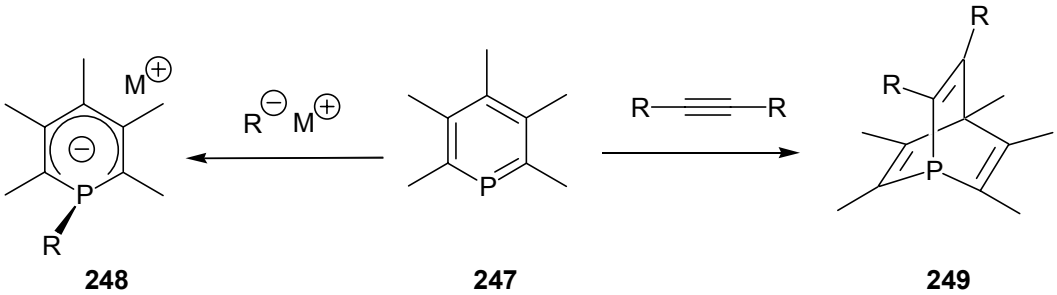


Figure 47: High resolution tranmsission electron microscopy of gold nanoparticles.

As previously seen, in some cases, coordination of the phosphinine ligand can significantly enhance the reactivity of the ring. Like 2*H*-phospholes which already proved to be a powerful source of new ligands upon reaction with different substrates, the phosphinine backbone can be easily modified to generate new structures. A recent review, written by Mathey, dealing with the applications of 2*H*-phospholes as synthetic intermediates in the elaboration of ligands recently appeared [208]. Phosphinine exhibit two interesting electronic peculiarities that can be exploited in the synthesis of new ligands and their complexes: the high electrophilicity of the phosphrus atom and the dienic character of the unsaturated system. Thus reaction of a phosphinine **247** affords phosphacyclohexadienyl anions **248**, which as will be seen further, have found important applications as ligands. On the other hand, the unsaturated system of phosphinines can be engaged as diene or as dienophile in Diels-Alder reactions to yield various bi and polycyclic structures [209]. For example, 1-phosphabarrelenes **249** result from the [4+2] cycloaddition of phosphinines with alkynes (Scheme 18). This reactivity which comes out of the scope of this review will only be discussed in the case of systems which have found applications in coordination chemistry and/or in the elaboration of catalysts.



Scheme 18: Reactivity of phosphinnes towards nucleophiles and alkynes.

A lot of attention has been paid to the reactivity of nucleophiles towards phosphinines. Pioneering studies by Ashe and Märkl had unambiguously showed that various nucleophiles add to the electrophilic phosphorus atom to yield the corresponding phosphacyclohexadienyl anions. These anions have found many applications in the synthesis of λ^5-phosphinines and dihydrophosphinines as well as in the elaboration of some π-complexes. Recently, structures of some lithium derivatives were studied by X-ray crystallography and their electronic properties investigated through DFT calculations [210]. When no cryptand is used, coordination of the lithium occurs through the π-system of the ring such as in complex **250**. In good agreement with this result, DFT calculations showed the negative charge to be mostly localized on the α-carbon atoms of these anions. An analysis of the charge distribution revealed that the electronic structure of these anions is closer to that of classical pentadienyl anions than to that of their analogs, the cyclohexadienyl anions. Interestingly a Natural Bond Orbital Analysis (NBO) and the analysis of Wyberg bond indices revealed that no delocalization takes place between the carbocyclic part of the ring and the phosphorus atom. The most important conclusion is that in such systems, the hydridization of the phosphorus atom lone pair is close to that of classical tertiary phosphines (Figure 48). However, in some cases coordination of the alkali at the phosphorus can occur to yield σ-complexes. Thus 2,6-bis(diphenylphosphinosulfide)-phosphinines such as **251** react with lithio compounds (for example *n*-butyllithium) to yield complexes **252** in which the lithium cation is encapsulated into the S-P-S pincer (Scheme 19). Note that in anion **252**, the coordination of the phosphorus atom is 3 and its oxidation number is 5 (σ^3-λ^5) suggesting an hypervalent character. This writing is an extreme form as encountered in classical Wittig ylids. It is important to note that no real double bonding occurs between the phosphorus atom and the two neighbouring ring carbon atoms and the conclusion of DFT calculations are not contradicted. This formalism was chosen for easiness in order not to handle charges in the writing of complexes. The writing of anion **252** featuring the delocalization of the charge on the pentadienyl skeleton could have been employed also.

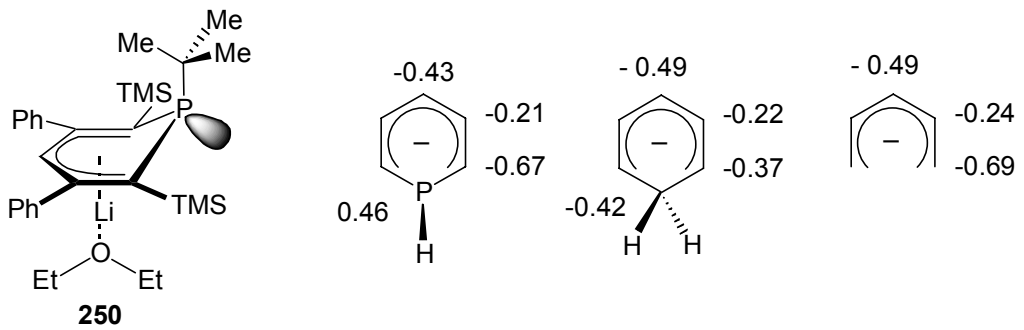
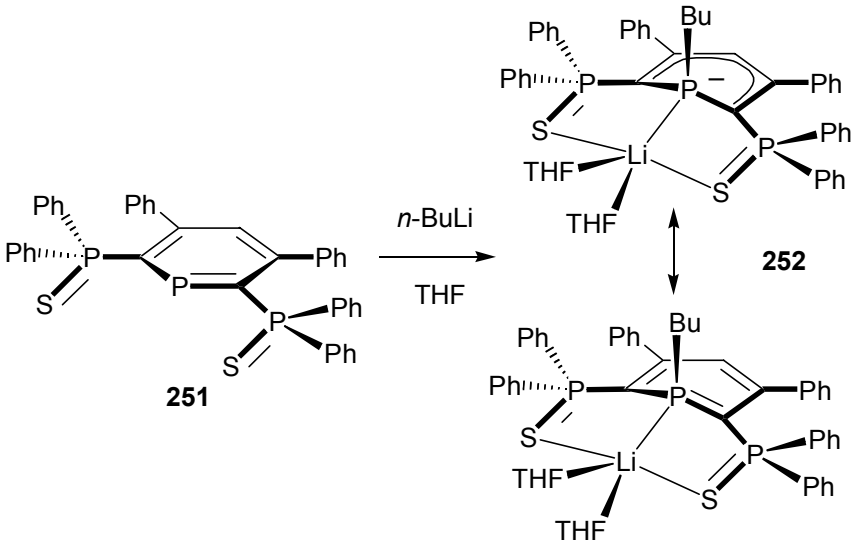


Figure 48: Phosphacyclohexadienyl anions.



Scheme 19: Reaction of phosphinine **251** with *n*-butyllithium.

The preference for η^1-coordination can be easily rationalized by considering a simple perturbation diagram of these phosphacyclohexadienyl anions MOs. In such systems, the HOMO is a π-orbital featuring important coefficient on the C_α and C_γ carbon atom and the HOMO-1 mainly describes the lone pair at phosphorus. Introduction of two ancillary groups possessing lone pairs results in a combination of these two orbitals with the in-phase combination of the two lone pairs. This combination features a four-electron repulsive interaction that strongly destabilizes the HOMO-1 (more important overlap). Therefore, in such tridentate S-P-S anionic ligands, the HOMO features an important contribution of the lone pair at phosphorus as well as a significant participation of the two lone pairs at the ligand thus favoring σ-coordination at phosphorus (Figure 49).

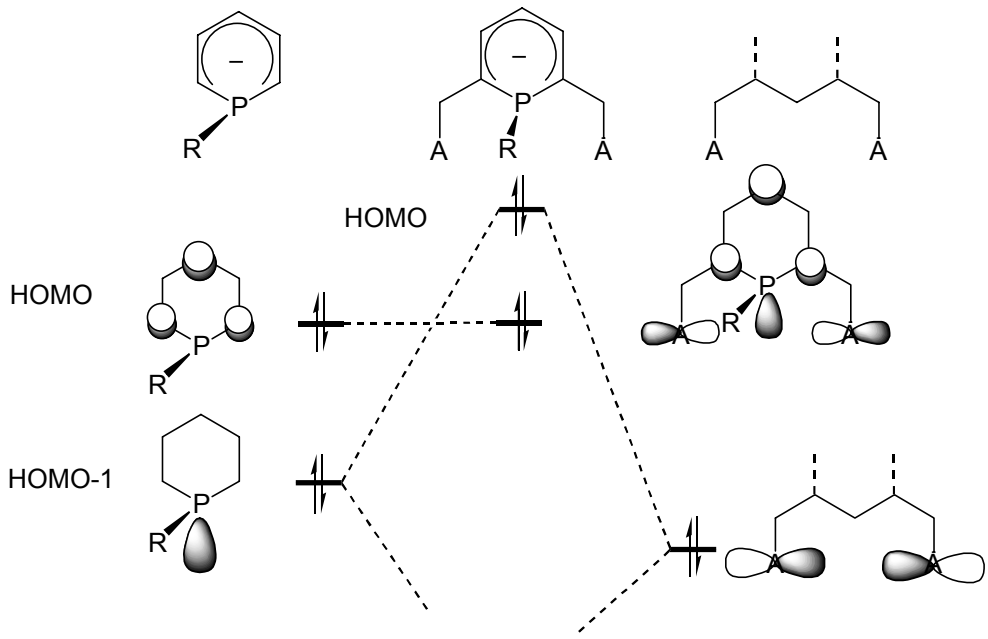
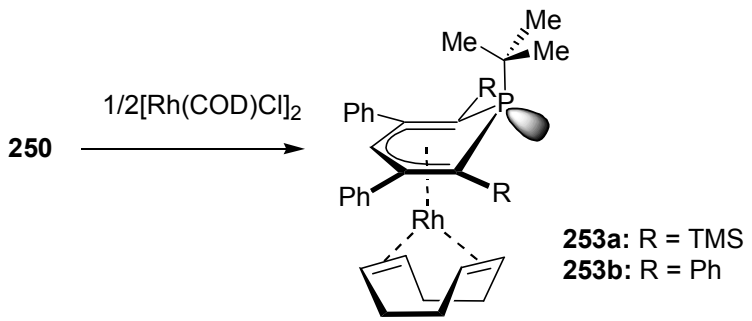
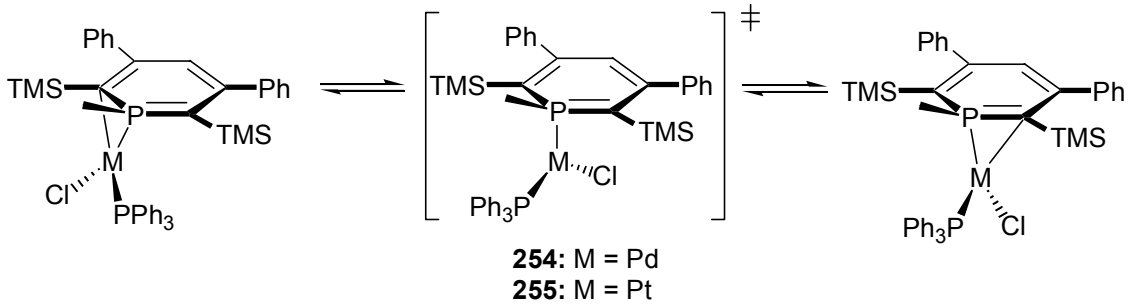


Figure 49: η^1 *vs* η^5-coordination in phosphacyclohexadienyl-based ligands.

Similar conclusions can be drawn upon examining the structure of phosphacyclohexadienyl complexes. When no susbtituents bearing lone pairs are present at the periphery of the phosphorus atom, η^5 coordination of the metal fragment occurs. Historically the first complexes to be reported by Märkl and Dimroth employed the (1-R-2,4,6-trisubstituted phosphinine) and iron metallic fragments [211]. Recently, Rh(I) complexes such as **253** were synthesized by reacting these anions with half an equivalent of the [Rh(COD)Cl] dimer (Scheme 20). Obviously the nature of the metal fragment also plays a significant role. Thus when this fragment bears two vacant coordination sites and is unwilling to be involved in π-coordination, η^2-coordination onto the P-C bond occurs. This was definitely established in the case of [$PdCl(PPh_3)$] fragments (M = Pd, Pt). Complexes **254** and **255** that are respectively formed from the reaction of anion **N** with [$MCl_2(PPh_3)_2$] complexes have been structurally characterized [212]. Interestingly, NMR experiments suggested that an equilibrium takes place between the two diastereomers in solution, the [$MCl(PPh_3)$] fragment rapidly exchanging from one P-C bond to the other one. Variable NMR experiments yielded ΔG values of 43.7 $kJ.mol^{-1}$ for **254** and 55.5 $kJ.mol^{-1}$ for **255**. These experimental results were ascertained through DFT calculations which were carried out using IMMOM (DFT-MM3, QM/MM hybrid method) (Scheme 21).



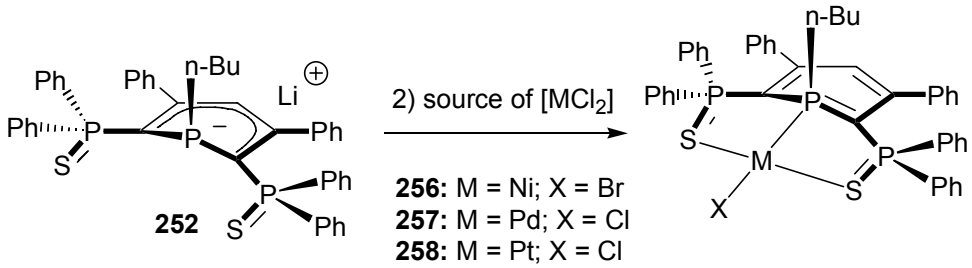
Scheme 20: Synthesis of η^5-Rh(I) complex **253**.



Scheme 21: η^2-(P-C)-coordination in phosphacyclohexadienyl ligands.

As expected, a different outcome is observed when the ring bears ancillary ligands at the peripheral positions at phosphorus. Like in the lithium complex **252**, the ligand acts a S-P-S pincer system that is able encapsulate different types of metal fragments. Initial experiments were carried out with group 10 metals and numerous complexes were synthesized (Scheme 22) [213]. Reaction of anion **252** with metal precursors such as [$NiBr_2$(DME)], [Pd(COD)Cl_2] and [Pt(COD)Cl_2] respectively yielded the corresponding complexes **256-258** which were structurally characterized. These neutral complexes were found to be particularly stable as well as their cationic derivatives resulting from the replacement of the halogen ligand at the metal. A CDA analysis reveals that the electronic balance between σ-donation and π-back donation is nearly equivalent to what observed in classical phosphine-based systems [214]. These results suggest that, at least, in these complexes, the central ligand behaves as a classical phosphine the charge being mainly delocalized over the carbocyclic part. Note that this bonding mode is not limited to tridentate ligands and the formation of σ-complexes also occurs when only one ancillary P=S ligand is present. Thus, very recently complexes featuring the heteroditopic P-S chelate ligand were synthesized such as ruthenium derivative **259** and the neutral Pd(allyl) derivative **260**. The chemistry of group 11 metals has also been recently explored and a series of Au(I) dimeric and monomeric complexes such as have been

synthesized. Whereas Au(I) complexes such as **261** adopt a T-shape geometry the overall geometry around the Cu(I) **262** is tetrahedral as expected (Figure 50).



Scheme 22: Synthesis of SPS-based group 10 and 11 complexes.

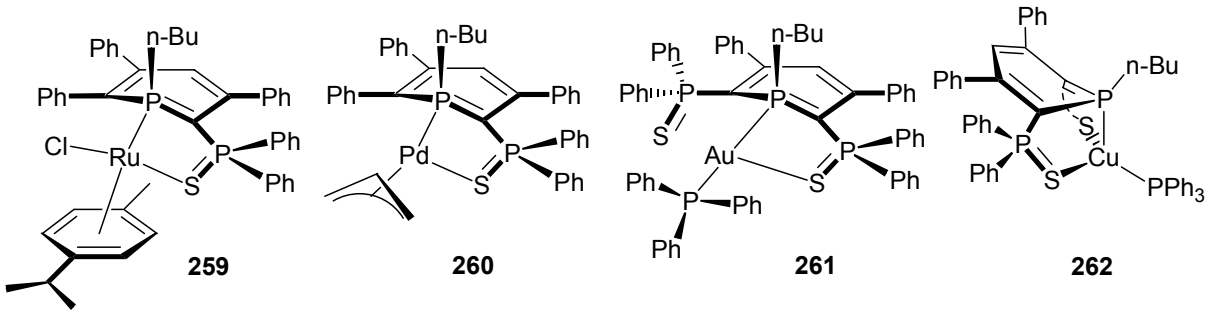
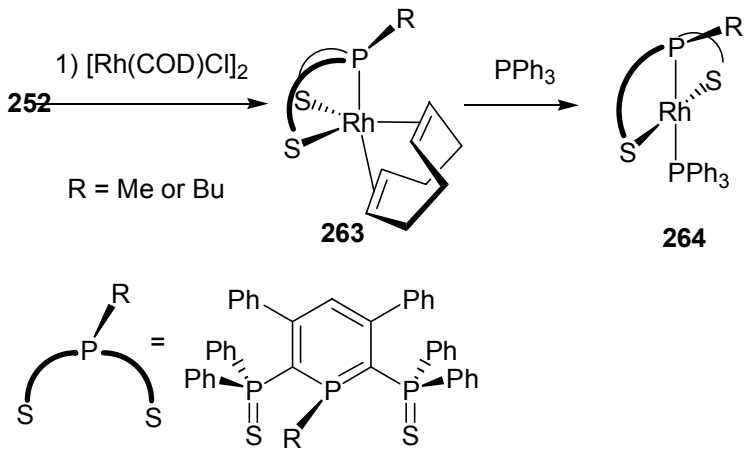


Figure 50: η^1-coordination complexes of mixed phosphinosulfide-phosphacyclohexadienyl ligands.

However most efforts focused on the chemistry of group *9* metals. Reaction of S-P-S anions such as **252** with Rh(I) precursors led to the formation of very reactive 16 VE tetracoordinated or very stable 18 VE pentacoordinated complexes (Scheme 23). Interestingly, it was found that these S-P-S ligands can accommodate two geometries: a square planar geometry as with group 10 metals (tetracoordinated complex **264**) but also a facial coordination as in the pentacoordinated complex **263**. The 16 VE complex **264** proved to be highly reactive towards various small molecules such as O_2, CO_2, CS_2, SO_2 which add onto the metal to yield the corresponding Rh(III) or Rh(I) complexes **265-269** at room temperature (Figure 51) [215]. Surprisingly, all these reactions regioselectively take place at the *syn* face of complex. Theoretical calculations were carried out within the DFT framework (B3PW91) to rationalize this surprising planar discrimination and it was found that four possible ways of additions can be considered but that the *syn* addition is favoured both by the low energetic barrier needed to form a distorted structure in the triplet state and the energy of the Rh-O bonds under formation [216]. Note that the same study was extended to the analogous Ir(III) complex which was structurally identified. Complex **264** also readily reacts with a source of Cl_2 (C_2Cl_6) to yield the expected Rh(III) **269** complex which was structurally

characterized (Figure 51). However reaction of **269** with an equivalent of the SPS anion **252** did not yield the expected homoleptic complex **270**. The most straighforward route to **270** was discovered by exploring the reactivity of anion **252** towards the $[RhCl_3(tht)_3]$ complex (tht = tetrahydrothiophene). Interestingly, complex **270** proved to be a convenient source of the stable 19 VE Rh(II) complex **271** upon reduction with Zn in THF at room temperature. Note that **N** can be regenerated upon exposition to the air in the presence of a source of the chloride couteranion. A combination of theoretical calculations and EPR spectroscopy revealed that the odd electron is mainly delocalized over the rhodium center and the two axial P=S ligands ((Figure 52).



Scheme 23: Synthesis of a S-P-S Rh(I) complex.

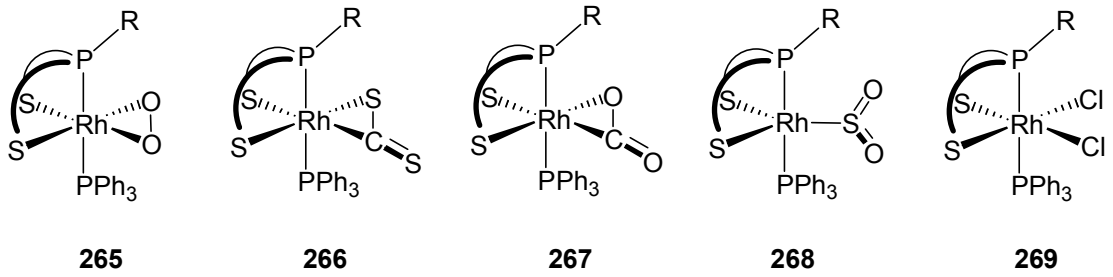


Figure 51: oxydation complexes of complex **264**.

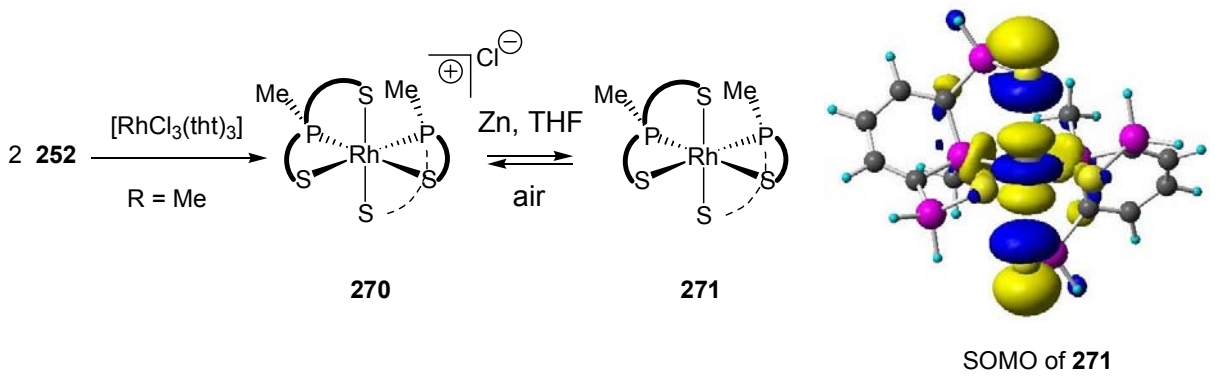
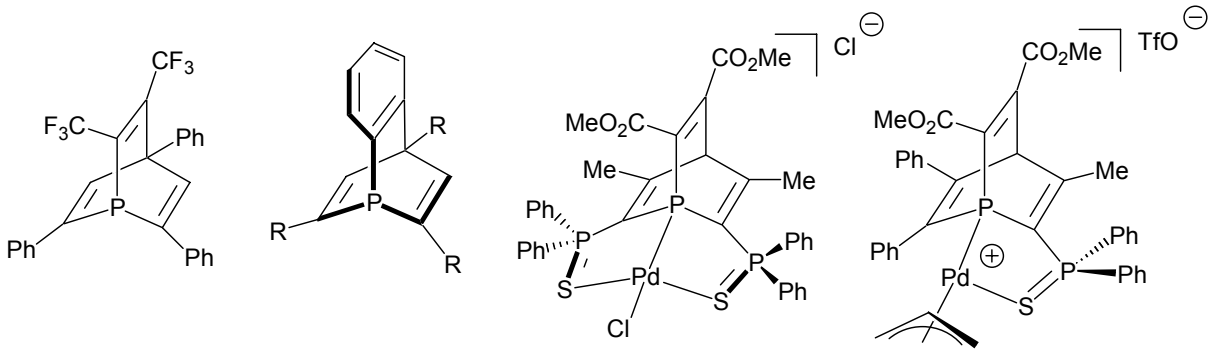


Figure 52: Synthesis of the paramagnetic 19 VE complex **271** and its SOMO as given by DFT calculations.

As explained above, the unsaturated system phosphinine can also be exploited in the synthesis of bicyclic ligands. In these transformations, the coordination state of the phosphorus atom raises to 3 and electronic properties of classical trivinylphosphines can be expected. Earlier studies in this area were achieved by Märkl and Bickelhaupt who employed phosphinines as a source of 1-phosphabarrelenes. In general phosphinines are not particularly reactive towards alkynes and [4+2] Diels-Ader reactions are only observed when the alkyne is substituted by strong electron-withdrawing substituents such as in **272** which results from the cycloaddition of the 2,4,6-triphenylderivative with hexafluorobutyne. One of the first published methods relies on the use of precursors of benzyne such as *o*-bromo-fluoro-benzene. However, in this case, some doubts remain about the mechanism involved. Contrary to what recently proposed in the recent synthesis of **273-275** [217], earlier studies had suggested that a two-steps process which relies on an initial nucleophilic substitution at phosphorus takes place in the initial step [218]. Importantly, Mathey and his group, as well as Märkl, employed phosphinine-sulfides and phosphinines tungsten pentacarbonyl complexes to synthesize a variety of bicyclic ligands featuring phosphabarrelenes sulfides and $W(CO)_5$ complexes. Though, some synthetic approaches towards phosphabarrelenes exist, the use of these ligands in coordination chemistry and catalysis is still limited. Recently, Breit et al. reported on a rhodium-based hydroformylation process that employs the 1-phosphabarrelene **273-275** as ligand. In 2005, in our group, phosphabarrelenes were incorporated in bidentate S-P and tridentate S-P-S structures when 2- and 2,6-bis(diphenylphosphinosulfide) substituted phosphinines were reacted with dimethylacetylene dicarboxylate [219]. A DFT study revealed that the presence of one or two electron withdrawing groups on the phosphinine as well on the ring thermodynamically favors the formation of a phosphabarrelenes. As will be seen further, cationic palladium(II) complexes of these ligands such as **276** and **277** have found promising applications in homogeneous catalysis (Figure 53).



272 **273:** R = Ph **276** **277**
274: R = i-Pr
275: R = 2,4-xylyl

Figure 53: Some phosphaberrelenes and their complexes.

3. Application in homogeneous catalysis.

As could be seen throughout the precedent chapter, the coordination chemistry of low coordinate phosphorus ligands slowly came to maturity and promising developments were achieved along the last decade. Quite logically, many groups have been interested over the last few years in evaluating the potential of such ligands and their respective transition metal complexes in homogeneous catalysis. However, in practice, only kinetically and/or thermodynamically stabilized systems can be efficiently employed and studies mainly focused on the use of stable phosphaalkenes, phosphametallocenes and their derivatives and to a less extent to phosphinines. All these developments will be presented in the following sub-chapters.

3.1 Phosphaalkenes

Non kinetically stabilized phosphaalkenes were found to be too reactive to be efficiently used as ligands and most studies logically focused on sterically protected molecules such a 1,2-disubstituted-3,4-diphosphinidenecyclobutenes. These studies were initiated by the group Yoshifuji who first investigated the use of some $PdCl_2$ derivatives in the coupling of *para*-bromo-nitrobenzene with trimethylsilylacetylene in the presence of CuI as additive and triethylamine as base [33]. These catalysts proved to be less performant than the classical $[PdCl_2(PPh_3)_2]$ complex and only low conversions were obtained. This failing can be easily rationalized when one considers that phosphaalkenes are poor σ-donor but strong π-acceptor ligands and that highly electron rich centres are needed to promote the initial additive oxidation step into the C-Br bond. More convincing results were obtained in the ethylene polymerisation process with complexes complexes such as **278-279** (Figure 54). The

most promising results were obtained with the 1,2-diaryl-3,4-diphosphinidene cyclobutene ligands DCPB-Y (Y stands for the functional group grafted at the *para* position of the aryl substituent) [220]. Similarly to diimine-Pd complexes, $PdMe_2$ complexes were found to be inactive but their corresponding cationic monomethyl complexes which were generated *in situ* by treatment with $H(OEt_2)_2BAr_4$ (Ar = $(CF_3)_2C_6H_3$) showed a good activity. The catalytic activity was found to be remarkably dependant on the substitution scheme of the cyclobutene ring and complex **278** yielded the most satisfying results. At 70°C in chlorobenzene (pressure of 10 kgf cm^{-2}), an activity of 123 $kgh^{-1}(molcat)^{-1}$) was obtained. Comparatively, these catalysts were found to be much more thermally stable than their nitrogen counterparts and no apparent decomposition was observed even when polymerisations were carried out at 100°C. Several cationic palladium complexes containg phosphinidine-imine and phosphinidine sulphide were also tested by the group of Brookhardt in the oligomerization/polymerisation of ethylene (26°C, 400 psi in CH_2Cl_2) [38]. These systems such as complex **281** showed a moderate to good activity and also proved to much more resistant than their nitrogen analogues. Even after 15 hours of reaction, complex **281** still displays a TON rate of 3000 TO/h (4300 h^{-1} after 3 hours). Analysis of the nature of the branching using ^{13}C NMR spectroscopy revealed that the polyethylene obtained using this catalyst is hyper branched with methyl to amyl branches identified and quantified (119 br.1000 C). As previously mentioned, only a little attention has been paid to cationic Ni(II) derivatives. Recently, the allylic **31** and **32** complexes were evaluated in the polymerization of ethylene. Like former systems polymers prepared were found to have a low degree of branching compared with α-diimine based catalysts but theses polymers present a good crystallinity. Like their (DCPD-Y) Pd complexes analogs, these nickel catalysts were found to remarkably stable under drastic conditions (up to 160°C) (Figure 54) [36]. Like their imines counterparts it was observed that upon increasing the temperature of polymerization (from 60 to 160°C), the productivity and molecular weight (M_w) have a tendency to decrease, but the degree of branching increases. In 2001, Ozawa and Yoshifuji showed that catalysts such as **29** could successfully be employed for the hydroamination of 1,3-dienes by primary amines (Scheme 24) [221]. A variety of dienes could be hydroaminated in good to excellent yields under mild conditions (RT) using 1-3 mol% of catalyst. Whereas the 1,4-addition is generally favoured, it was found that 1,2-addition to terminal vinyl group is preferred when one of the termini of the diene is substituted. Catalyst **29b** (R = OMe) was also effective in the catalyzed 1,2 addition of aniline to styrene but under harsher conditions (toluene 100°C).

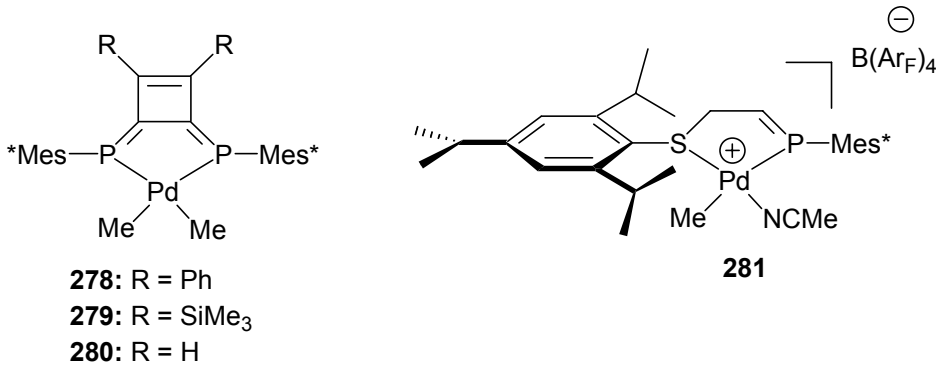
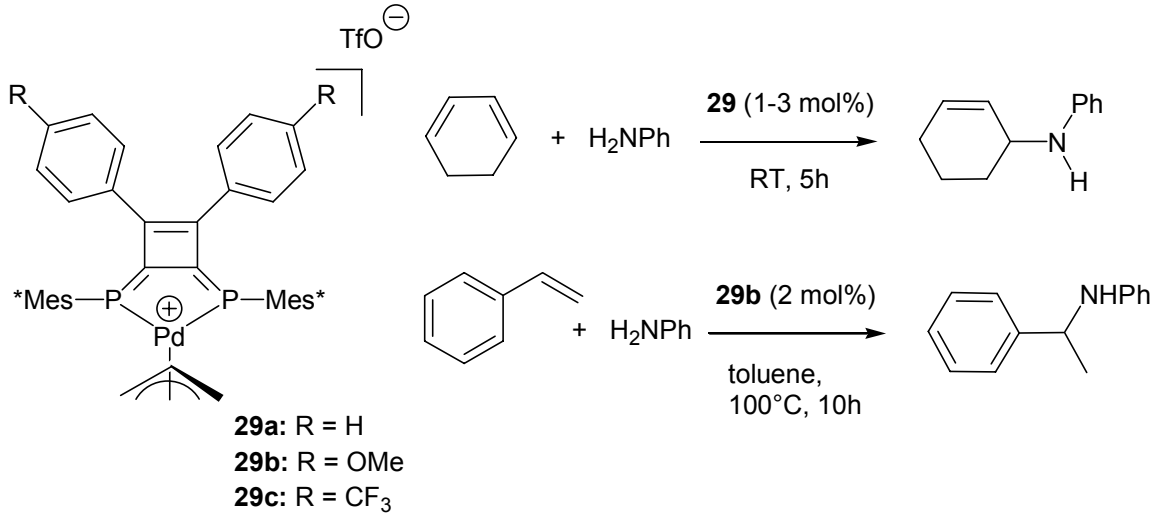


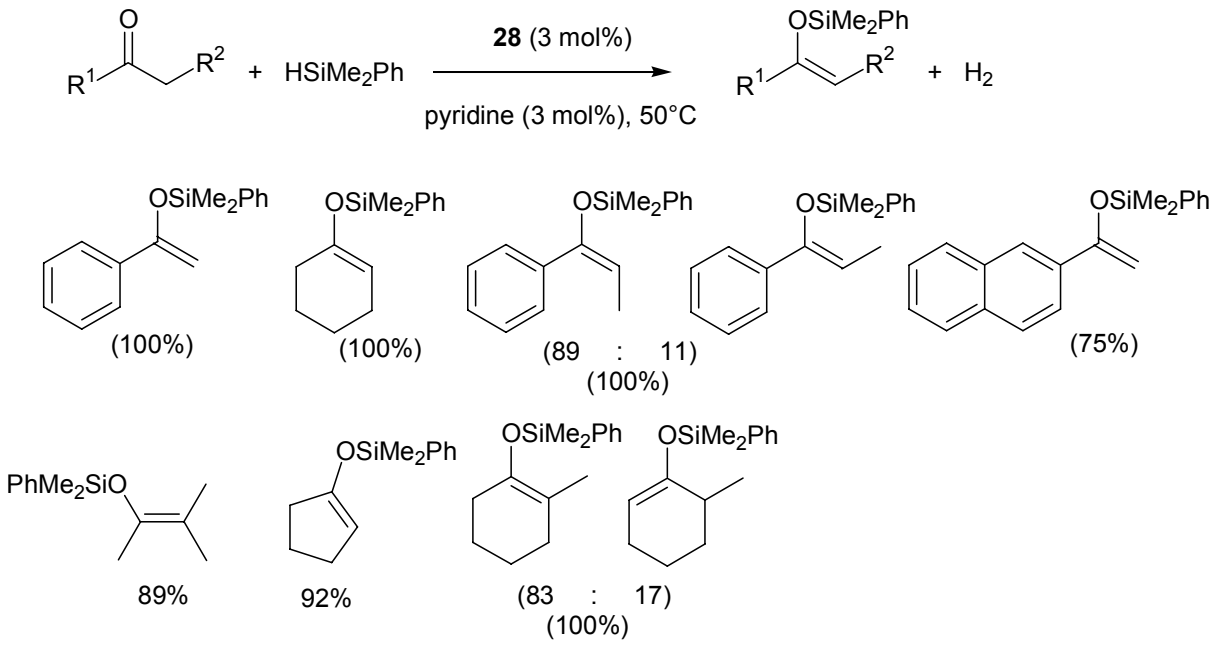
Figure 54: Ethylene polymerization catalysts



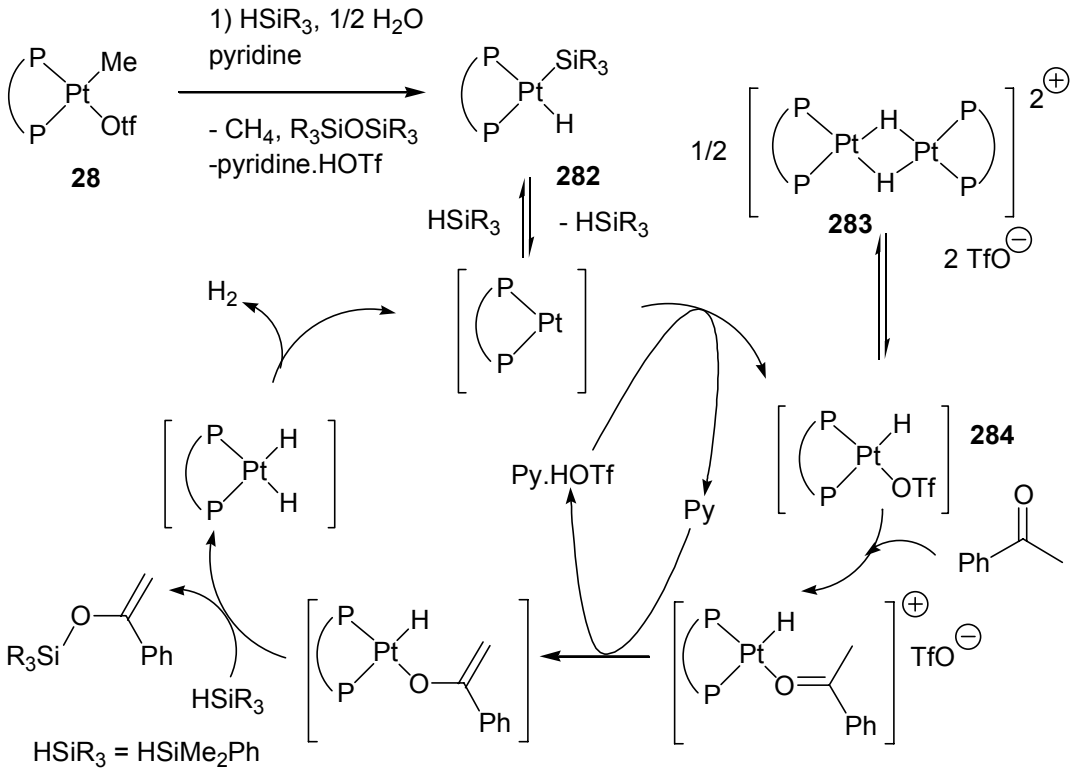
Scheme 24: hydroamination of 1,3-dienes by primary amines

Another important application of DCPB-Y ligands in catalysis deals with the dehydrogenative silylation of ketones [222]. Dialkyl and alkyl-aryl ketones readily react with $HSiMe_2Ph$ at 50°C in the presence of catalytic amounts of the cationic methylplatinum complex **28** (3 mol%) and pyridine (3 mol%) to yield the corresponding silyl enols ethers as dehydrogenative silylation products. Contrary to what usually observed with platinum-based catalysts no hydrosylilation compounds are formed (Scheme 25). The general scheme of this interesting transformation is presented in the following scheme as well as a series of examples. A sophisticated catalytic cycle which is depicted in scheme 26 was proposed. Several steps of this mechanism could be confirmed by stoichiometric reactions. Thus the formation of the hydrido complex **282** was confirmed by parallel experiments as well as the formation of the dimer **283** which is the resting state of the catalyst. Both complexes, which were synthesized independently, were shown to catalyze the transformation and complex **284**

reacts with acetophenone in the presence of $HSiMe_2Ph$ and pyridinium triflate to yield $CH_2=C(OSiMe_2Ph)Ph$ (Scheme 26).



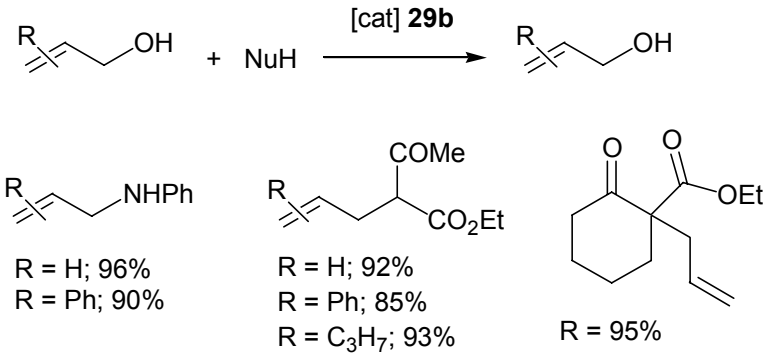
Scheme 25: Dehydrogenative sylilation of ketones catalyzed by DCPB-Pd complexes.



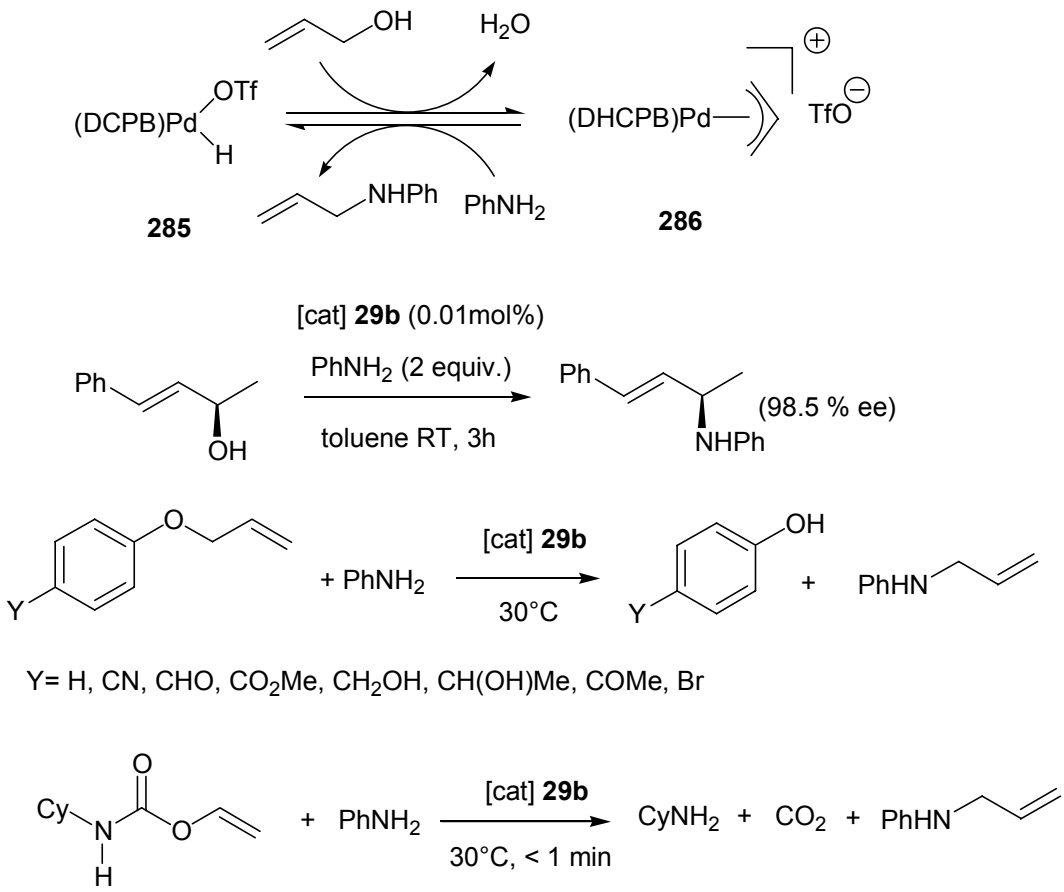
Scheme 26: A plausible catalytic cycle for the dehydrogenative sylilation of ketones catalyzed by DCPB-Pd complexes.

The catalytic conversion of allylic alcohols into N and C-allylation products is probably the most significant application of DCPB-Y ligands in homogeneous catalysis. In 2002, Ozawa and Yoshifuji reported on an interesting transformation that allows the direct functionalization of allylic alcohols. This transformation which is known as the "Tsuji-Trost" reaction is a reliable and widely used method that has found many applications in organic chemistry for the facile elaboration of C-C, C-N and C-O bonds. Due to the poor leaving ability of the OH group, this transformation requires as a prerequisite the introduction of a good leaving group onto the allylic moiety and typically, allylic carboxylates, carbonates, phosphates and related derivatives are widely employed. Therefore, the direct conversion of allylic alcohols into allylation products in a one reaction step is an economically rewarding process. Cationic allylic Pd(II) derivatives of DCPB-Y ligands efficiently catalyze this unusual transformation under mild conditions as depicted in the following scheme. The monoallylation of aniline was successfully performed with different substrates as well as the allylation of active methylene derivatives. Whereas the allylation of amines cleanly proceeded at room temperature within a few hours (2 to 12 hours) in the presence of $MgSO_4$ as water scavenger with low loading of catalyst (typically 0.1 mol%), the allylation of methylene derivatives required additional heating at 50°C. Representative examples of this catalytically promoted allylation process are presented in scheme 27 [223]. Importantly, it must be mentioned that DCPB-Y based catalyst proved to be much more active than allylic derivatives of dppf (bis-diphenylphosphino ferrocene) and diimine ligands. A convincing mechanism that relies on the transient formation of the hydridopalladium complex **285** has been proposed and already confirmed by stoichiometric parallel experiments (Scheme 28). The key step of this mechanism involves and equilibrium between **285** and the allyl complex **286** as depicted in the following scheme. It has also been proposed that the good catalytic activity of DCPB-Y complexes results from the strong π-accepting capacity of the ligand that tends increase the stabilization of the transition state of the attack of the amine at the opposite site of the allyl ligand. However no calculations have been undertaken yet to confirm this proposal. Importantly, it was also established that, like generally observed for palladium-catalyzed allylation reactions, the regio- and stereochemical courses are preserved. Thus, as shown in scheme 28, the optically alcohol was converted to the corresponding allylaniline with a nearly complete retention of configuration at carbon. An important extension of this reaction was reported in 2004 by Ozawa et al. with the deallylation of allyl ethers using complex **29b** as catalyst (Scheme 28). Thus numerous aliphatic ethers were easily deallylated in the presence

of aniline and 0.1 mo% of catalyst **29b**, all transformations proceeding at 50°C in toluene with substrates bearing vinyl, alkynyl, hydroxyl, acetoxy, silyloxy and acetal groups. Importantly, TBDMS, THF and MOM which are conventionally employed as protecting groups remained unchanged under catalytic conditions thus rending this process compatible with other protection methods of alcohols [224]. Deallylation of aromatic ethers could also be easily performed under milder conditions at 30°C. Allyloxy carbonyl groups which are known as versatile protecting groups for the hydroxy groups in carbohydrates, amino and imido groups in nucleoside bases and peptides were also successfully employed (Scheme 28). Complex **29b** showed a remarkable activity in this transformation which can be achieved within a minute whereas the same process lasts several hours using $[Pd(PPh_3)_4]$ (1 mol%) as catalyst in MeOH.



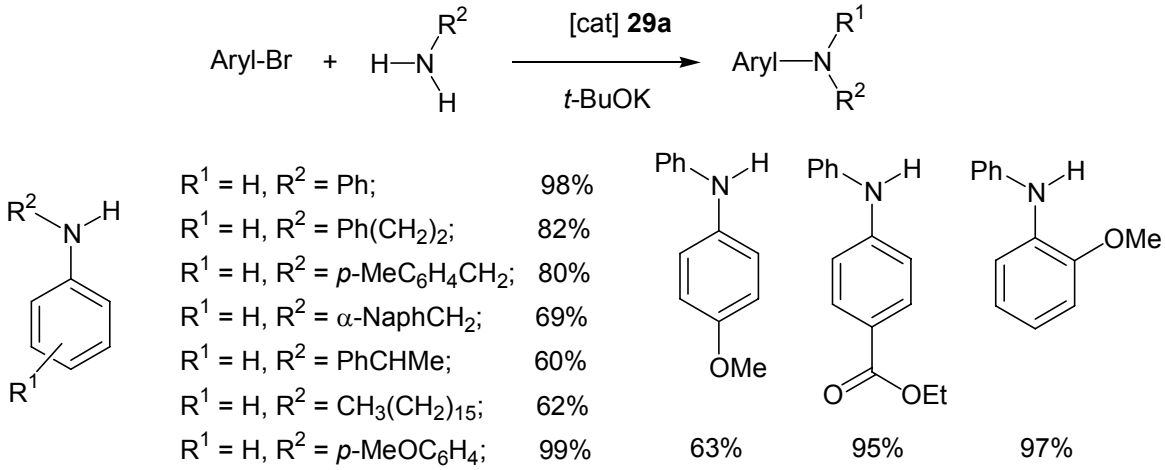
Scheme 27: Catalytic conversion of allylic alcohols into N- and C-allylation catalyzed by DCPB-based complexes.



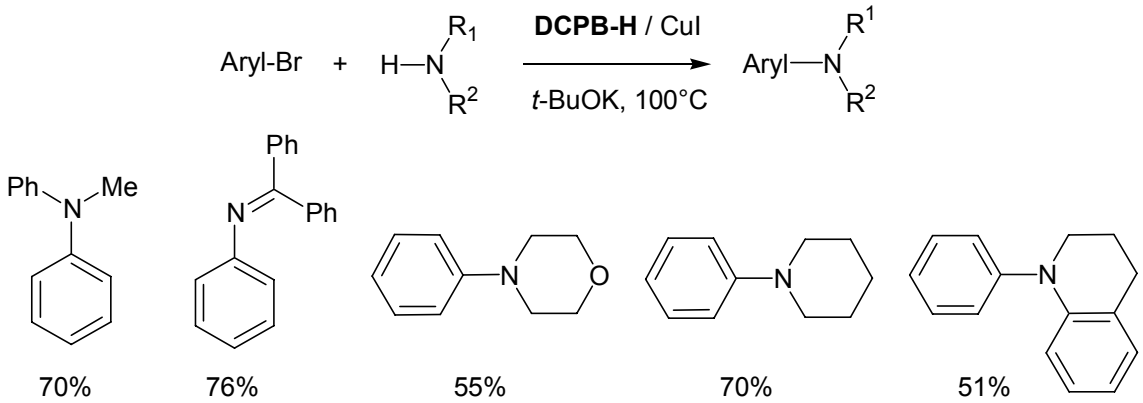
Scheme 28: Allylation of aniline catalyzed by DCPB-Y complexes.

In 2004, Yoshifuji et al. reported on the use of the cationic complex **29a** in catalyzed solvent free amination reactions of aryl bromides (Scheme 29). This reaction transformation takes place at room temperature in the presence of *t*-BuOK as a base and 2% of catalyst. Various functional arylbromo compounds and functional anilines could be converted into the corresponding diarylamines derivatives in fair to good yields [225]. Alkyl amines were also successfully grafted onto the benzene group using this procedure. Though more drastic conditions (100°C) were necessary to couple secondary amines with bromobenzene, reactions with morpholine and piperidine were carried out at room temperature. On the contrary, no coupling occurred with cyclohexylamine, urea, pivalolyl amide or *p*-nitroaniline. The same process was also examined with copper(I) complexes of DCPB-Y ligands by Yoshifuji and Ozawa in 2004 (Scheme 30). Secondary and primary amines were reacted with a variety of halogeno benzenes derivatives (X = I, Br, Cl) in the presence of t-BuOK in the absence of solvent at 100°C to afford the corresponding aminated compounds. All reactions proceeded with good to excellent yields using 2 mol% of CuI and 2 mol% of the DCPB-H ligand within 12 hours [226]. Though these catalyzed processes bear an important synthetic value it must be

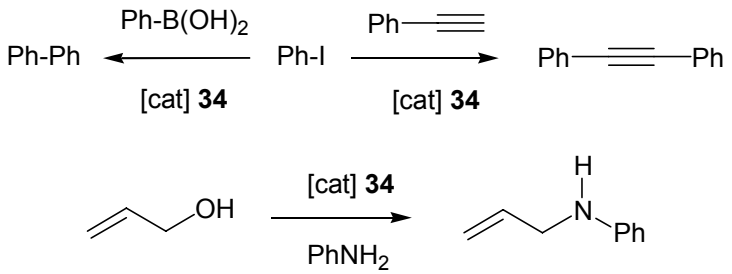
stresses out that in some cases, no metal is needed to promote such coupling [227]. Also with DCPB derivatives, one must mention that polymeric materials featuring DCPB ligands and thiophene units were also employed in the Sonogashira coupling between trimethylsilylacetylene and *p*-bromonitrobenzene. Importantly, this polymeric material which was found to be insoluble in DMF acts as an heterogeneous catalyst and its activity was found to be comparable with that of the corresponding monomeric complex. To conclude with this presentation on the reactivity of phosphaalkene complexes in catalysis, one must also mention that Pd(II) complexes of a bulky 2-methyl-3-thioxo-1,3-diphosphapropene were also employed in the Sonogashira and Suzuki coupling reactions of iodobenezenene with phenylacetylene and phenylboronic acid, respectively (Scheme 31). Like DCPB complexes, the cationic derivative **34** was also successfully employed in the allylation of allyl alcohol with aniline [228].



Scheme 29: Solvent free amination reactions of aryl bromides catalyzed by Pd(II) complexes of DCPB.



Scheme 30: Solvent free amination reactions of aryl bromides catalyzed by Cu(I) complexes of DCPB.



Scheme 31: Use of 2-methyl-3-thioxo-1,3-diphosphapropene palladium complex in the Sonogashira and Suzuki coupling reactions and the allylation of aniline.

3.2 Phospholide complexes and phosphametallocenes

Not surprisingly, phospholides complexes have been extensively used in homogeneous catalysis. As previously explained this mainly results from the close electronic analogy that exists between these anions and their carbon counterparts, cyclopentadienyls. Like cyclopentadienyls, phospholide complexes of early transition metals have found interesting applications in olefin polymerization processes. Indeed, on going from carbon to phosphorus derivatives one may expect a greater electrophilicity of the metal center which logically should induce a greater activity of the catalyst. Therefore titanocene and zirconocene based complexes have been widely employed as catalysts [86]. However, the presence of a phosphorus atom lone pair on the complex constitutes a major drawback since coordination of the co-catalyst (usually employed in large excess), such as [MeAlO]n (MAO), occurs partially blocking the activity of the catalyst. This effect has been well documented in the literature [86j, 86k]. Not surprisingly, the most efficient catalysts feature bulky groups at the periphery of the phosphorus atom (α-positions) to preclude coordination of the Lewis acid. Thus, complex **287** showed a good activity in the polymerization of propene in the presence of MAO (Figure 55). With 10 μmol of complex and 5 mmol of MAO at 45°C under 600 kPa, an activity of 170 kg of polypropylene per gram of Zr per hour and an M_n of 20 000 has been observed [87i]. Interestingly, it was shown that catalyst the titanium-based catalyst **82** + MAO can polymerize ethylene at 160°C much more efficiently than the unbridged mono(η^5-2,3,4,5-tetramethylphospholyl)titanium dichloride complex which shows a poor activity [90]. Catalytic performances of **82** compare with those of its carbon counterpart **288**. However it was concluded that the utility of this new catalyst is somewhat offset by the lower M_w PE obtained (50 .10^3 *vs* 126.10^3 for the cyclopentadienyl-based catalyst). In 2001, the group of Fu also reported on the catalytic activity of C_2-symmetric complexes **79**. Both species were found to efficiently catalyze the copolymerization of ethylene and hexane in the presence of MAO. With the dichloro complex **79a**, polymerization activities range from 5000 and 42 000

g PE mmol $Zr^{-1}h^{-1}$(100 psi $C_2H_4)^{-1}$ with a strong dependence on the Al/Zr ratio [87]. Under polymerization conditions at 75°C, a half-life time of 4 to 6 min was obtained. Analyses of the polymer produced revealed number average molecular weight (M_n) values between 40 000 and 94 000 with PDI (polydispersity indices) in the range 2.71-3.32. The dimethyl derivative **79b** also exhibited a high activity with an Al/Zr ratio of 1000. Activities in the range 38 000 to 41 000 g PE (mmol Zr)$^{-1}h^{-1}$(100 psi $C_2H_4)^{-1}$ were obtained but it was observed a decrease of the catalytic activity when the polymerization was carried out in the absence of 1-hexene comonomer (Figure 55). Numerous patents relating the use of group 4 phosphametallocene-based catalysts have been issued. Regarding polymerization of alkynes, it was shown that the Co(I) complex **289a** catalyzes the cyclotrimerization of EtC≡CEt to C_6Et_6 at 180°C whereas complex **289b** proved to be inactive (Scheme 32) [229]. Though no further investigations have been made it has been proposed that the presence of an available lone pair in **289b** favours clusters formation. Indeed a dimeric tetracobalt which features η^1,η^5-bonding modes of the 4-dimethylphospholyl ligand had previously been characterized [230].

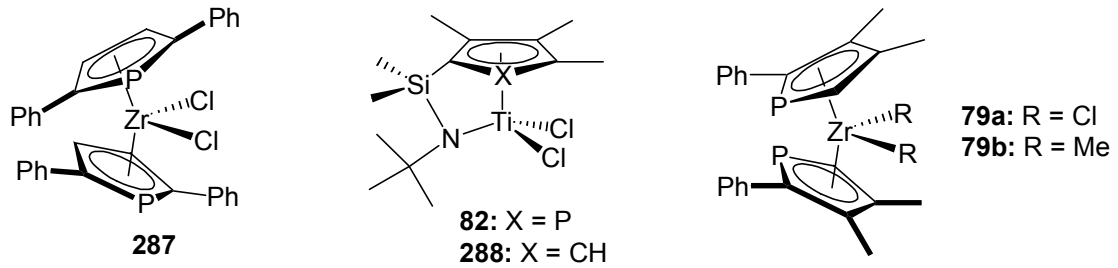
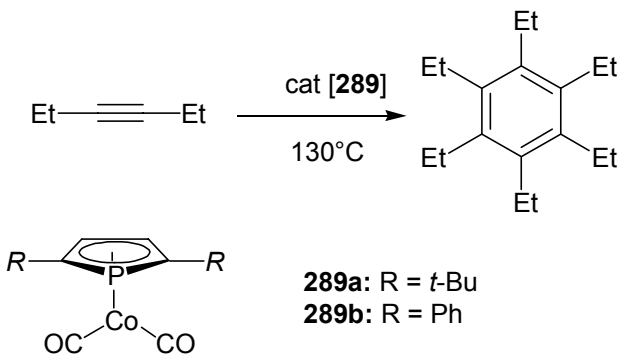


Figure 55: Phospholyl based group 4 catalysts.

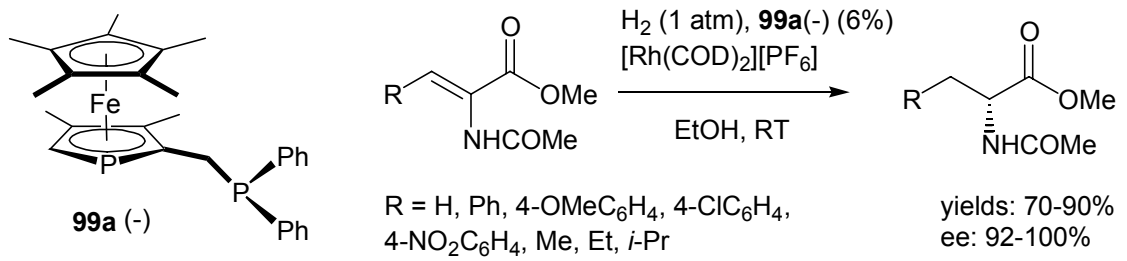


Scheme 32: Cylotrimerization of 3-hexyne by the phospholyl cobalt complex **289**.

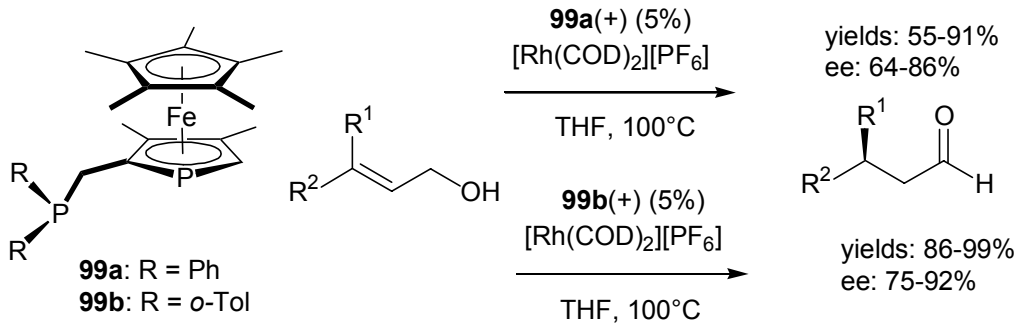
Undoubtedly, the most significant applications of low coordinate phosphorus ligands in catalysis were obtained with phospha and diphosphaferrocenes so far. As could be seen previously, these ligands, which combine a ferrocenyl backbone with unusual electronic

properties of a dicoordinate P atom, can accommodate many transition metal centres and oxidation states. Fu et al. were the first to report on the use as phosphaferrocenes after Ganter and his group showed that enantiomerically pure phosphaferrocenes could be prepared through the use of a chiral auxiliary. In 1998, the planar chiral bisphosphine **99a**(-) was successfully employed in the rhodium–catalyzed asymmetric hydrogenation of dehydroamino acids (Scheme 33) [231]. Under classical conditions at room temperature using 1 atm of H_2, several derivatives were reduced with a good to excellent enantioselectivity. A second significant application was reported in 2000 by the same group who showed that the [Rh(COD)(**99a**)(+))][PF_6] catalyst whose X-ray structure was recorded could performed the enantioselective isomerization of allylic alcohols to the corresponding aldehydes in THF at 100°C (Scheme 34). Importantly, this catalyst proved to be much more performant that the Rh^+/BINAP system which only yielded a best ee of 53%. With catalyst **99a**(+) ee obtained range from 64 to 86% with moderate to good conversion yields (55 to 91%). Later on, in a second report, it was shown that ligand **99b** and its air stable [Rh(COD)(**99b**)][BF_4] complex proved to be much more efficient in terms of conversion yields, scope and enantioselectivity. Furthermore, catalyst **99b** proved to be reusable. Some insights on the mechanism involved were gained on the basis of deuteration experiments. Thus, it was demonstrated that these asymmetric isomerizations proceed through an intramolecular 1,3-hydrogen migration pathway and that the catalyst preferentially activates one of the enantiotopic C1 hydrogen atoms [232]. The enantiopure phosphaferrocene-oxazoline ligands **100** have also found an interesting application in the palladium-catalyzed enantioselective allylic alkylation. As previously mentioned it was unambiguously shown that, contrary to classical phosphine oxazoline based-catalyst, the chirality of the nitrogen ligand is not decisive regarding the stereochemical course of the reaction comparatively to the planar chirality provided by the phosphaferrocenyl backbone [105]. In 2001, the group of Hayashi also designed bidentate ligand **101** which was successfully used in the asymmetric alkylation of rac-1,3-diphenyl-2-propenyl-2-propenyl acetate [106]. All reactions were also carried out at room temperature in the presence of BSA and KOAc in dichloromethane yielding excellent conversion yields and ee. Importantly it was observed that the ee is highly related to the amount of ligand used and an excess of ligand causes a significant loss of the enantioselectivity. This observation was rationalized by considering that, since the optical activity is provided by the ferrocenyl backbone, formation of the bis-phosphine complex **291** could be detrimental. Therefore the chelate complex **290** was thought to be the more active species (Figure 56). Note that the bis(phosphaferrocene)ferrocene ligand **97** was also used in the same transformation. Ganter

and his group showed that the palladium-catalyzed allylic alkylation proceeds with a conversion yield of 78% and an enentiomeric excess of 79% [102].



Scheme 33: Rhodium–catalyzed asymmetric hydrogenation of dehydroamino acids.



Scheme 34: Enantioselective isomerization of allylic alcohols to the corresponding aldehydes.

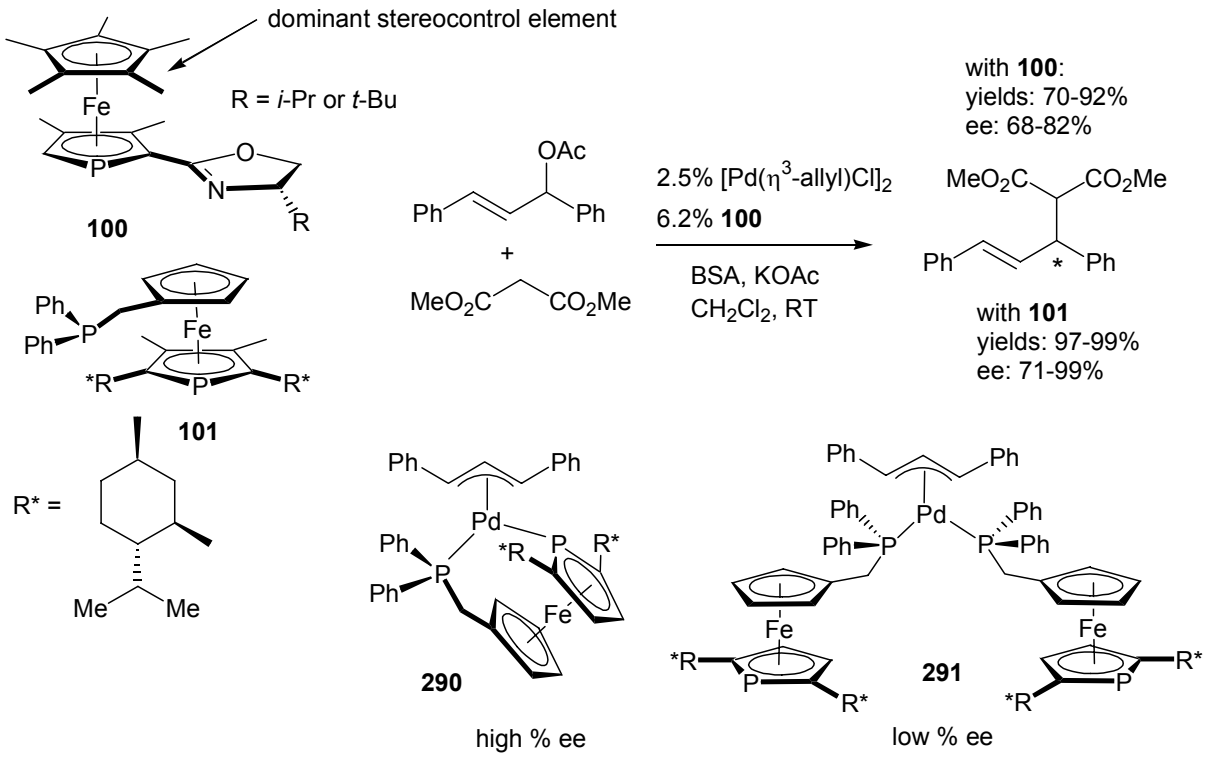
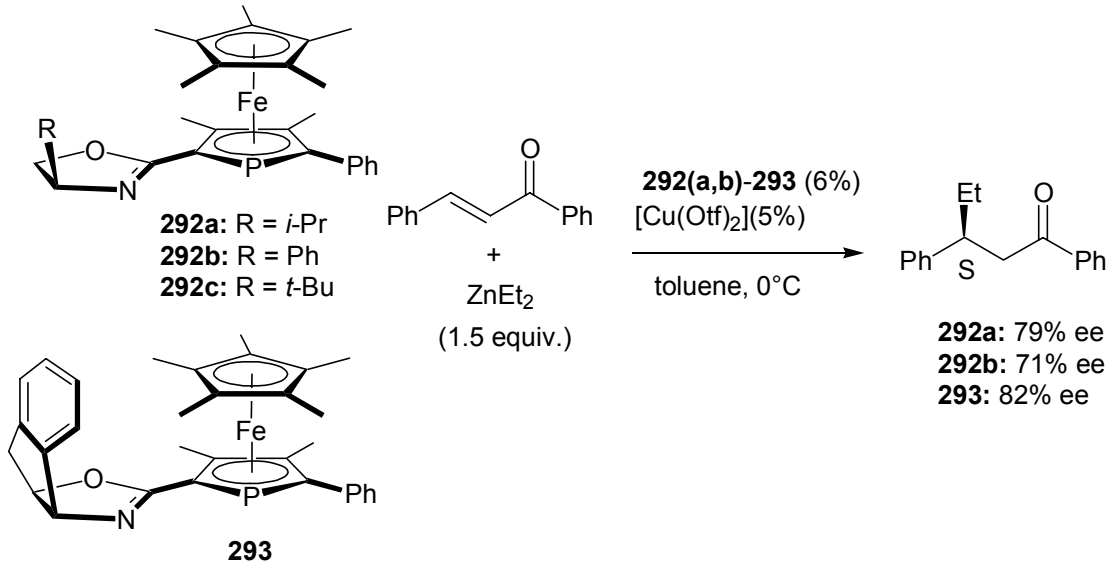
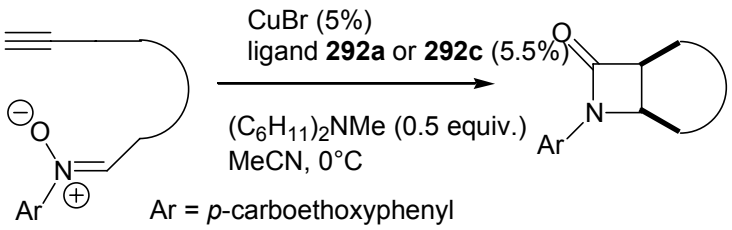


Figure 56: Alkylation of rac-1,3-diphenyl-2-propenyl-2-propenyl acetate

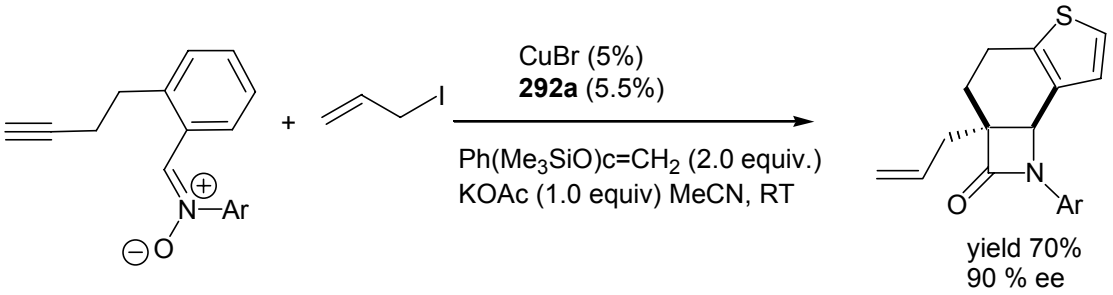
Copper(I) complexes of bidentate ligands incorporating a chiral phosphaferrocene moiety have also showed an interesting activity in three catalytic processes of synthetic relevance. First, a series of phosphaferocene-oxazoline ligand **292** and **293** was applied in the asymmetric conjugate addition of diethylzinc to acyclic enones to afford the corresponding ketones (Scheme 35) [233]. All transformations proceeded with good to excellent conversion yield and enantioselectivities. Contrary to what was previously observed in the palladium-catalyzed enantioselective allylic alkylation, the phosphaferroceneyl backbone did not proved to be the dominant stereocontrol element in these 1,4-additions. Structural variations of the ligands have showed that, though alteration of the phosphaferrocene ligand can provide useful enhancement of the enantiomeric excess, the central chirality of the oxazoline moiety is decisive. In 2003, ligands **292** and **293** were successfully employed in the Kinugasa reaction that allows the synthesis of β-lactams from the intramolecular cyclisation of alkyne-nitrone derivatives. It must be mentioned that these two ligands yielded better results in terms of yield and enenatioselectivities than bisoxazoline and bisazaferrocene derivatives (Scheme 36) [234]. In the same report, experimental conditions allowing the direct α-functionalization of the synthesized lactams were also found. Thus, in the presence of allyliodide alkyne-nitrone derivatives are converted into the allylic derivatives using **292a** as ligand. Finally, in 2004, the same authors reported on the use of similar copper catalysts in the enantioselective coupling of terminal alkyne with azomethine imines to produce five-membered nitrogen heterocycles. It was proposed that this transformation which involves a 1,3-dipolar addition of terminal alkynes relies on the transient formation of a copper acetylide. Here again, reactions proceeded with good conversion yields and very high ee (Scheme 37) [235].



Scheme 35: Copper catalyzed asymmetric conjugate addition of diethylzinc to acyclic enones catalyzed by Cu(I) phosphaferrocene complexes.



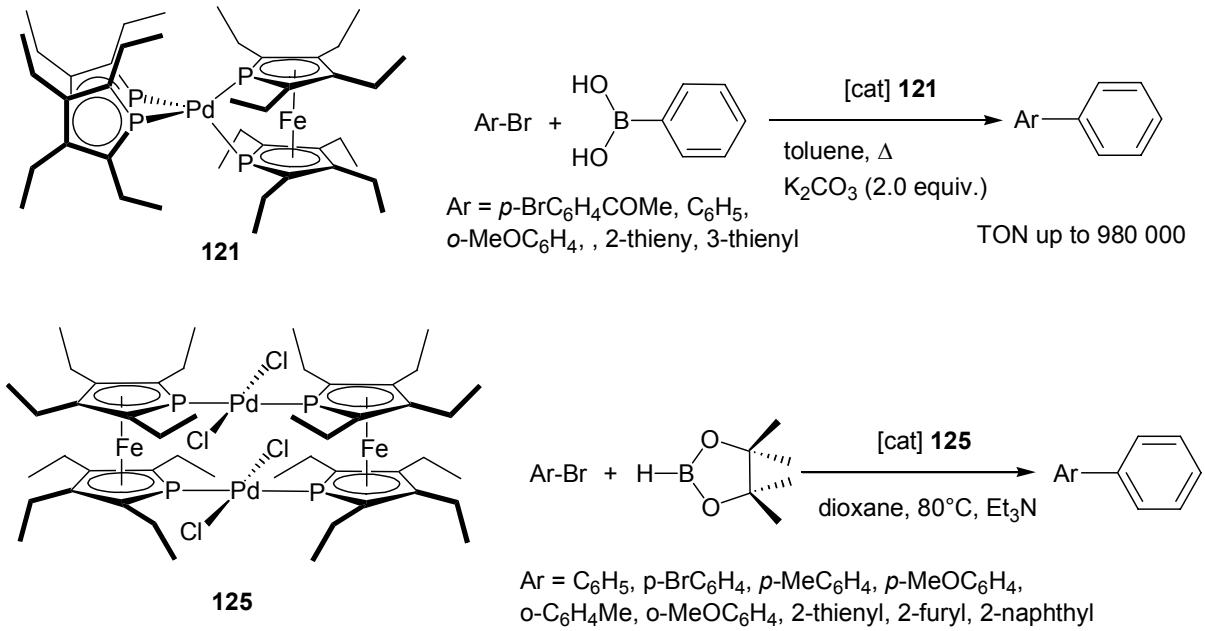
Scheme 36: The the Kinugasa reaction catalyzed by Cu(I) phosphaferrocene complexes.



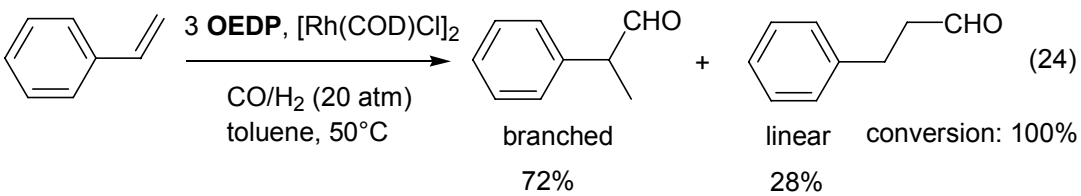
Scheme 37: Catalyzed enantioselective coupling of terminal alkyne with azomethine imines.

Comparatively, less attention has been paid to the use of diphosphaferrocenes as ligands for homogeneous catalysis. Two reports by our group dealt on their use in palladium cross coupling reactions allowing the formation of C-C and C-B bonds. The bis(octaethyldiphosphaferrocene)Pd(0) complex **121** was found to be an efficient catalyst for the palladium catalyzed Suzuki cross-coupling reaction that allows the synthesis of functional biphenyl from the reaction of bromoarenes with phenylboronic acid (Scheme 38) [122]. With 4-bromoacetophenone as substrate TON up to 980.10^3 were obtained. Though no mechanistic studies were undertaken to determine the nature of the active species, it is believed that 14 VE Pd(0) complexes are involved, the octaethyldiphosphaferrocene behaving as an hemilabile ligand because of its particular bonding mode that involves weak P-Pd bonds. The second report dealt with the use of dimer **125** in the Suzuki-Myaura coupling that furnishes an easy access to phenylboronic esters. Aryl iodides were thus efficiently coupled with pinacolborane in the presence of **125** and triethylamine as base (Scheme 38) [124]. Interestingly, high conversion yields were obtained in this process which was known to be difficult to catalyze (TON between 2600 and 2900). Reasonably, one can assume that the dimeric structure is not maintained during the catalytic cycle, **125** working as a source of a 14 VE complex. Additional experiments also showed that **125** efficiently catalyze the Suzuki cross-coupling

reactions and yield similar performances than those of the 18VE complex **121**. Note that octaethyldiphosphaferrocene (OEDP) was also tested in the hydroformylation of styrene and its activity compare with that of the 3,4-dimethyl and 3,4-diphenylphosphaferrocenes. The ratio between the linear and branched aldehydes was found to be dramatically dependant on the experimental conditions used. At 50°C, using a 3/1 ratio between OEDP and the rhodium precursor $[Rh(COD)Cl]_2$ and a ratio substrate/Rh of 475 under a pressue of 20 bar (CO/H_2), a complete conversion was obtained with a branched/linear ratio of 72/28 (Scheme 39). However, these performances can be estimated as relatively modest compared to the most efficient systems [236].



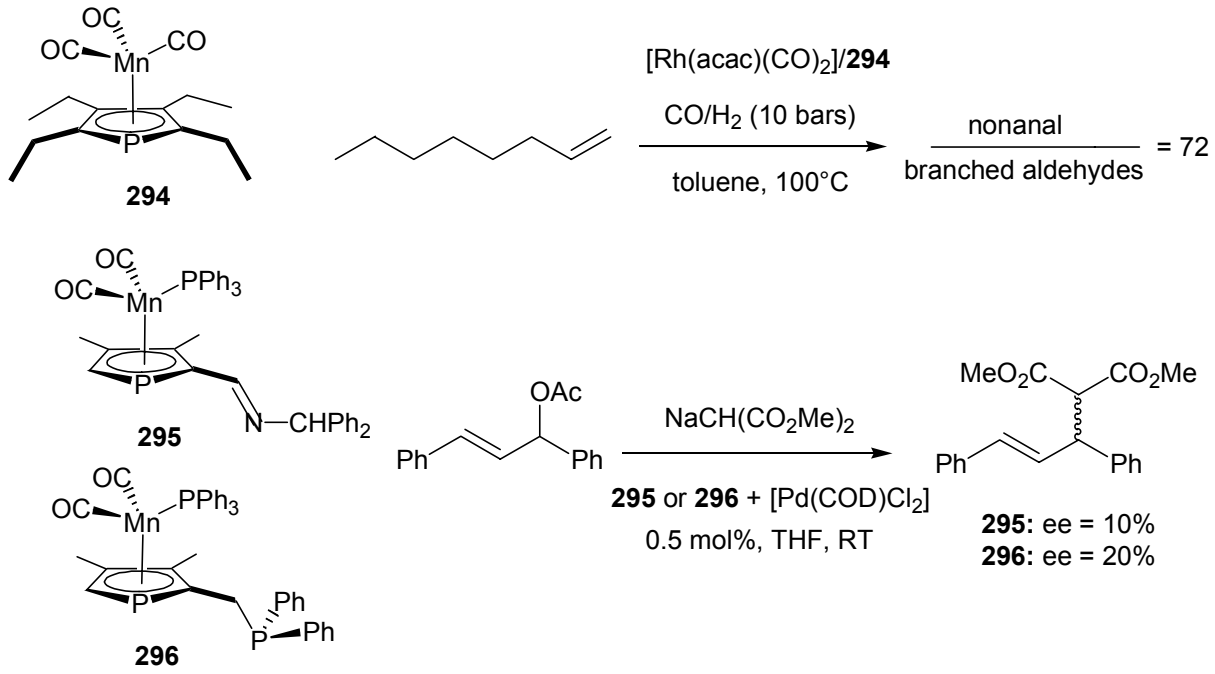
Scheme 38: Diphosphaferrocene Pd(0) and Pd(II) complexes in the Suzuki and Suzuki-Miyaura coupling reactions.



Scheme 39: Hyroformylation of styrene catalyzed by a diphosphaferocene Rh(I) complex.

Though they also display unique electronic and coordinative properties, phosphacymantrenes have not been the subject of intensive investigations so far comparatively to phospha and diphosphaferrocenes. Their activity in the hydroformylation of

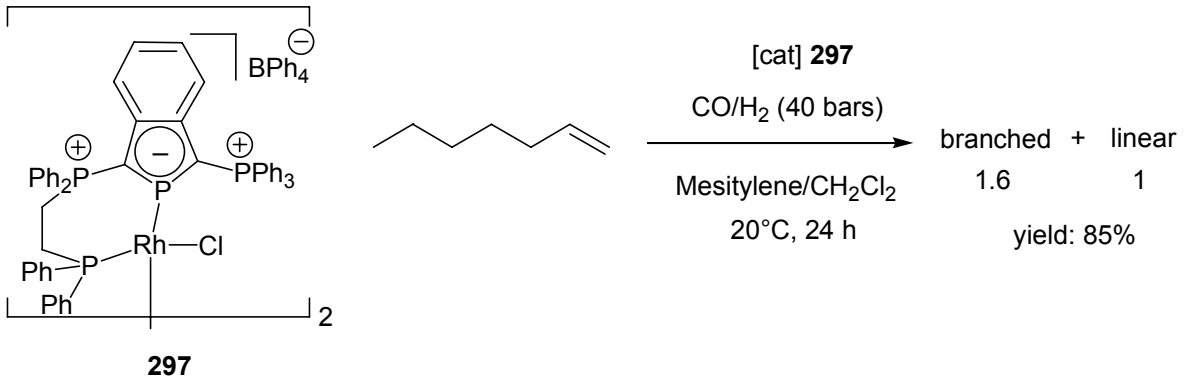
oct-1-ene has been evaluated with mono **294** and bidentate ligands such as **111** (Scheme 40). With ligand **294** using a Rh/ligand/octene ratio of 1:20:16667, the reaction takes place at 90°C under an initial pressure of 10 bars of CO/H_2. Under these conditions, in 4 hours, 100% of the starting material was consumed and a ratio of 73 was obtained between the linear nonanal and a mixture of aldehydes resulting from the hydroformylation of internal olefins which were formed through the isomerization of oct-1-ene. Under nearly similar conditions at 100°C in 2 hours, the combination of $[Rh(acac)(CO)_2]$ and bidentate ligand **211** yielded an almost complete conversion (98%) and a ratio of linear/branched aldehydes of 72 [237]. The first report dealing with the use of an enantiopure phosphacycmantrene was made only very recently by Mathey et al. The resolution of the $[Mn(\eta^5$-1-formyl-3,4-dimethylphospholyl)$(PPh_3)(CO)_3]$ complex was carried out by chromatography of the corresponding acetals and optically pure ligands **295** and **296** were prepared. Both ligands were tested in the nucleophilic allylic substitution with sodium malonate as incoming nucleophile and 1,3-diphenylallyl acetate as substrate. Though reaction rates turned out to be relatively important, the enantiomeric excesses were found to be relatively modest [238].



Scheme 40: Functional posphacymantrenes as ligands in homgeneous catalysis.

Only one report deals with the use of σ-complexes of phospholide. In 2001, Gudat et al. have used a rhodium(I) complexes of a bisphosphonio benzophospholide cation L such as **297**, to catalyze the hydroformylation of 1-hexene at 20°C under a CO/H_2 pressure of 40 bars

[129]. The dimeric species $[Rh(L)Cl]_2[BPh_4]_2$ proved to be three times as active as the monomeric $[Rh(L)(COD)]_2[OTf]_2$ complex and yielded 85% of the corresponding aldehydes (branched and linear) with a TON of 850 mol product.mol catalyst^{-1} after 24 h (Scheme 36). The activity of this catalysts was found to be superior to that of the $[Rh(acac)(CO)_2]/PPh_3$ system and compares with those of phosphinine-based catalysts as will be seen further. However, the regioselectivity towards the linear product (ratio of linear to branched aldehydes of 1.6:1) is dramatically inferior as compared to other catalysts [129].

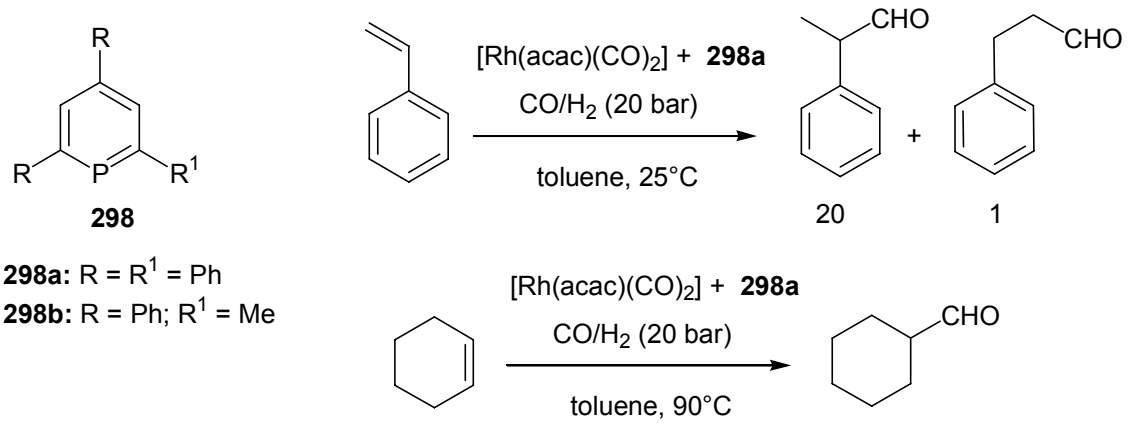


Scheme 41: A rhodium(I) complexes of a bisphosphonio benzophospholide cation in the hydroformylation of 1-hexene.

3.3 Phosphinines and their functional derivatives

With kinetically phosphaalkenes and phosphametallocene derivatives, phosphinines are the third type of low coordinate ligands that has been evaluated in catalysis. Indeed, at first glance, one may expect that the aromaticity of the ring would be enough to ensure a sufficient stability to the coordinated ligand in catalysts. However as could be seen in the section which covered the synthesis of coordination complexes, the stability of the phosphinine ligand was found to be dramatically dependant on the oxidation state of the metal and some reports have already established the enhanced reactivity of the P=C double bond in complexes having positive oxidation states. By definition, a prerequisite for the elaboration efficient catalyst is that ligands or parts of them (in the case of hemilabile systems), must be able to accommodate the different oxidation states involved in the catalytic cycle. In this regard one may expect that phosphinines are not well-tailored for the elaboration of powerful catalytic systems. Therefore it is not really surprising to see that only a few reports were devoted to applications of these ligands in catalysis. The most significant results were obtained by Breit et al. who showed that phosphinine rhodium(I) complexes could be considered as highly performant hydroformylation catalysts of olefins [239]. In the first two

reports, the hydroformylation of styrene was studied in depth and interesting performances were obtained with Rh(I) catalysts derived from the 2,4,6-trisubstituted ligands **298** [169a, 169b]. The reaction occurred under mild conditions in toluene at 25°C using the $[Rh(acac)(CO)_2]$ complex as precursor with a Rh:phosphinine:substrate ratio of 1:5:280 and a CO/H_2 (1:1) pressure of 20 bars. Under these conditions, using the triphenylderivative phosphinine **298a** as ligand, a yield of 30.8 % (TOF = 28.7 mol substate/mol catalysts.h^{-1}) was obtained. By comparison, under the same experimental conditions, the $[Rh(acac)(CO)_2]/PPh_3$ system proved to be by far less performant and yielded a conversion of 8% corresponding to a TOF of 7.5. Importantly, the regioselectivity was good and a 20:1 ratio in favour of the branched aldehyde was obtained. Note also that these catalysts could be reused at least two more times without significant loss of activity. Additionally, it was also shown that the use of phosphinines as ligands could also successfully address the difficult problem of the hydroformylation of internal olefins which is of crucial interest in both synthetic organic and industrial contexts. The rhodium(I)-based catalyst derived from ligand **298a** proved to be more performant than that derived from **298b** in the hydroformylation of cyclohexene which was chosen as model reaction. With **298a** as ligand, the conversion of cyclohexene into cyclohexylcarbaldehyde occurred at 90°C in toluene using a Rh:phosphinine:substrate ratio of 1:10:750 and an initial CO/H_2 pressure of 20 bar (Scheme 42). Under these conditions, a remarkable conversion yield of 28.6 % in 1 hour of reaction corresponding to a TOF of 214 substrate/mol catalysts.h^{-1} was obtained.

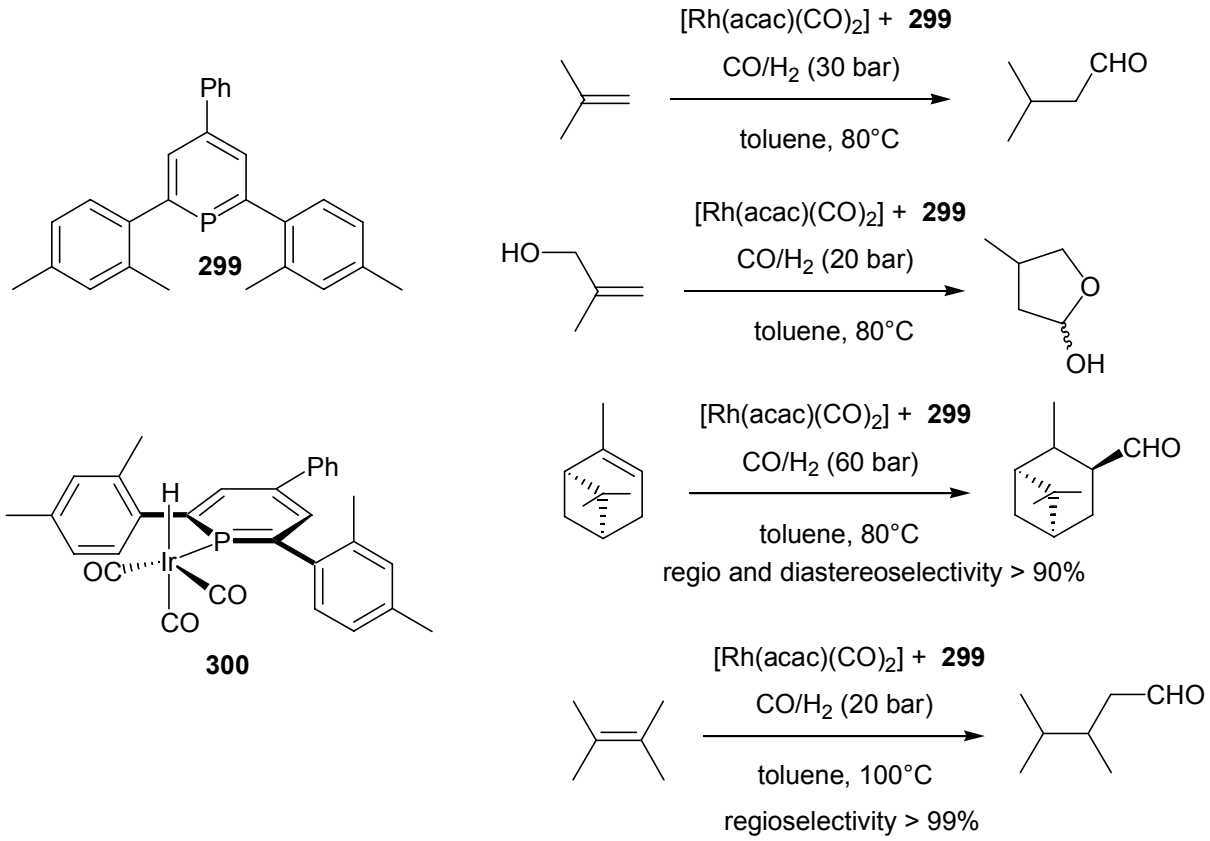


Scheme 42: Phosphinines-based Rh(I) catalysts in the hydroformylation of olefins.

In a third report [169c], in order to determine how steric effects can influence the course of the reaction, a series of functional phosphinines were evaluated under standardized conditions in the hydroformylation of oct-1-ene. The most satisfying results were obtained

with ligand **299** that features two xilyl groups at the α-positions at phosphorus. Turn over frequencies (TOF) up to 45370 h^{-1} were recorded when the reaction was carried out at 130°C with complete consumption of the starting material within 30 minutes. The same system was evaluated in the hydroformylation of internal olefins such as cyclohexene and oct-2-ene (E/Z mixture). In the case of cyclohexene at 90°C in toluene with a under a pressure of CO/H_2 (40 bar) and a Rh:**299**:substrate ratio of 1:20:4166 a TOF of 1959 h^{-1} was recorded. Comparatively, the commercial $[Rh(acac)(CO)_2]/PPh_3$ catalytic system only yields a TOF of 109 h^{-1} under the same experimental conditions. On the basis of kinetic experiment, it was found that the reaction is first-order with respect to the substrate indicating that the olefin coordination to the catalysts is the determining step of the catalytic cycle. With oct-2-ene, under 10 bar of pressure at 90°C, in 4 hours all the starting material was converted into aldehydes. Noteworthy, it was also observed that 24% of nonanal had been formed thus showing that the Rh/**299** based catalyst also isomerizes the olefin prior to hydroformylation. Comparatively, with the Rh/PPh_3 system under the same experimental conditions, 36 % of octenes are left unconsumed and only 5% of nonanal could be detected. Other di-susbtituted alkenes such as isobutene and methallyl alcohol were hydroformylated using the same catalytic system at 80 and 90°C respectively. A TOF of 3132 h^{-1} was obtained in the case of 2-methylpropene where the phosphinine based catalyst proved to be 100 times faster than the standard PPh_3-based catalyst. Similarly, but to a lesser extent, the phosphinine rhodium-based catalyst also proved to be more efficient than the PPh_3–based system: 2.5 faster with a TOF of 3291 h^{-1} (1317 h^{-1} for PPh_3) for the transformation of methallyl alcohol into the corresponding lactol. Trisubstituted alkenes such as the poorly reactive α-pinene were also hydroformylated by the same catalytic system whereas the Rh/PPh_3 system failed to provide any aldehyde product (Scheme 43). However more drastic conditions were necessary and the reaction was carried out using a CO/H_2 pressure of 60 bar at 80°C (TOF = 56 h^{-1}) and 20 equivalents of ligand **299** for one equivalent of the rhodium precursor. Remarkably, the hydroformylation of the tetramethylethylene could be carried out at 100°C under a CO/H_2 pressure of 60 bar yielding a good TOF of 118 h^{-1}. It is important to mention that, usually, hydroformylation of tetrasubstituted olefins exclusively occurs in low yields with cobalt-based systems under very drastic conditions. As noted previously in the hydroformylation of oct-2-ene, the phosphinine-based catalyst tends to favour isomerization and in this case the 3,4-dimethylpentanal was obtained as the exclusive reaction product. Some NMR experiments were carried out to determine the nature of the active species in such transformations. Thus reaction of the $[Rh(COD)_2][OTf]$ precursor with two equivalents of **299** under a pressure of CO/H_2 of 30 bar

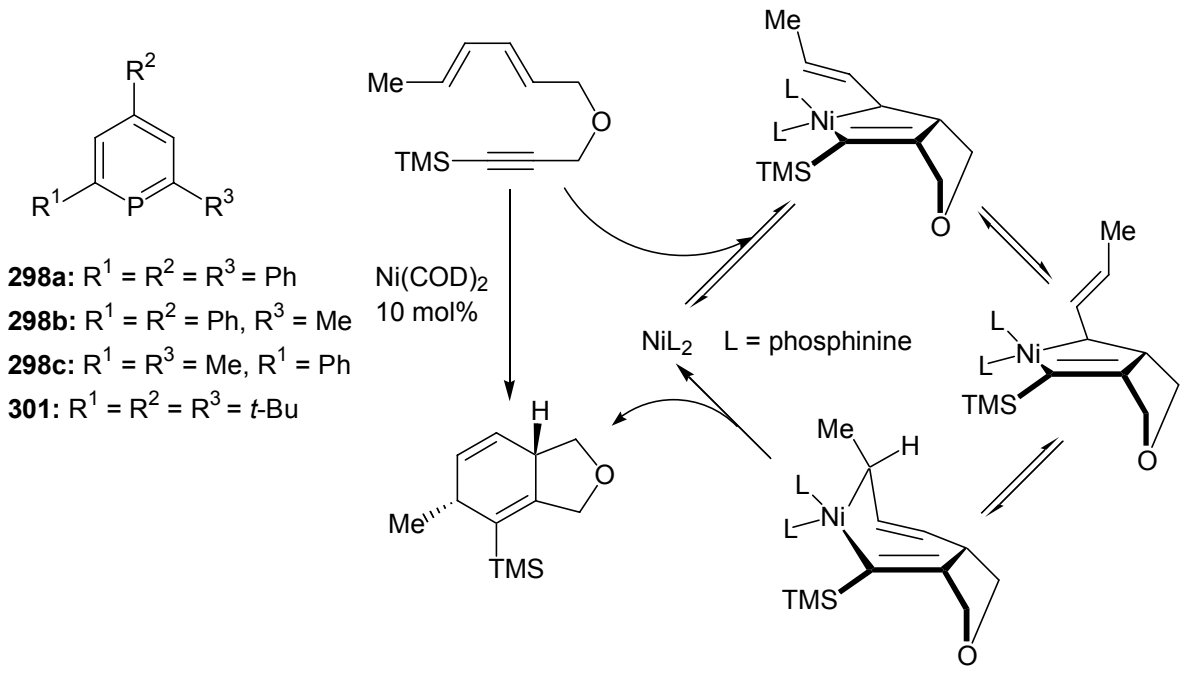
for 3 hours at 90°C yielded a complex that could not be definitely identified but which features a Rh-P bond. More significant results were obtained when iridium was used as metal (Scheme 43). Reaction of $[Ir(CO)_2(acac)]$ with **299** under the same experimental conditions yielded a species which was assumed to be the pentacoordinated hydrido-iridium complex **300** on the basis of ^1H and ^{31}P NMR data.



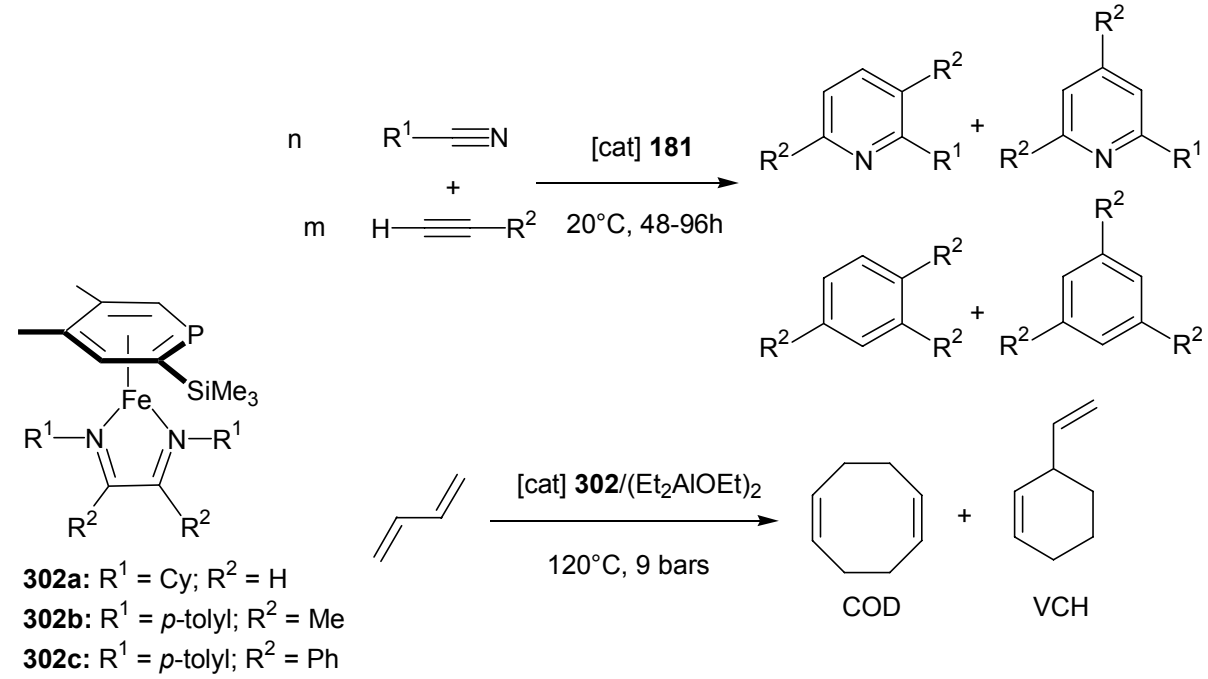
Scheme 43: Phosphinines-based Rh(I) catalysts in the hydroformylation of di-, tri- and tetra substituted olefins.

To complete this overview on the use of η^1-phosphinine complexes in catalysis, one must also mention that Ni(0) complexes of phosphinines **298 (a,b,c)** and **301** were also employed as catalyst in the intramolecular Wender's type [4+2] cycloaddition. The mechanism of this transformation is reported in scheme **44**. Indeed, due to their strong π-accepting capacity, phosphinines tend to favour reductive elimination, a step which is rate determining in this process. It was found that the rate of the reaction is strongly influenced by both electronic and steric properties of the ligand. Thus, the most interesting results in terms of reaction rate and conversion yields were obtained with the 2,4,6-triphenyl derivative which combines a significant steric bulk with a strong π-accepting capacity. Unfortunately, large amounts of the catalyst precursor $[Ni(COD)_2]$ (10 mol%) and ligand (20 mol%) were needed

to ensure a nearly complete conversion (92%) when the reaction was carried out in cyclohexane at 80°C. In the same study, Tolman's cone angle of the four ligands were also estimated (135° for **298a**, 123° for **298b**, 117° for **298c** and 128° for **301**) (Scheme 44) [240].[1] Apart from these two applications, no other reports deal with the use of η^1-complexes of phosphinines in catalysis. In some instances, η^6-complexes were shown to be more stable than the η^1-complexes but their use in catalytic processes have only been rarely reported. In fact the only report was made by Zenneck et al. who showed that η^6-Fe(0) complexes **181** of the 2-trimethylsilyl-4,5dimethylphosphinine could catalyze the cyclotrimerization of dimethylacetylene dicarboxylate and that of alkynes with nitriles to form pyridines [172a, 172b]. Interestingly, the activity of this complex was found to be superior to that of the [Fe(η^6-toluene)(COD)] complex. Reaction of methylpropargyl ether with butyronitrile in the presence catalytic amounts of complex **181** (ratio alkyne:nitrile:catalyst = 620:2720:1) at room temperature in toluene yielded a mixture of functional benzenes and pyridines. TON for the formation of pyridines reached 160 and those for the formation of benzenes 326 corresponding to a chemoselectivity of 0.49. However, catalytic performances recorded do not match with industrial requirements and do not compare with those of the ubiquitous cyclopentadienyl cobalt-based catalysts. The catalytic activity of related complexes **302** featuring a 1,4-diaza-1,3-diene (DAD) as co-ligand of iron was also compared to that of its carbon counterparts [Fe(η^6-toluene)(DAD)] complexes in the cyclodimerization of 1,3-butadiene [172c]. All experiments were carried using [$(Et_2AlOEt)_2$] as co-catalyst at 120°C under a pressure of 9 bar. Strong evidences for the [Fe(DAD)] fragments as the active species of this dimerization process were given by competitive experiments carried out with the corresponding Fe(COD) complexes. It was shown that the η^6-toluene-based systems act approximately ten times faster than the phosphinine complexes **302** and yield higher TON for the formation of COD (cyclooctadiene) and VCH (vinylcyclohexene). Thus, with the [Fe(η^6-toluene)((2,6-Me_2Ph)NCMe)$_2$)] complex TONs of 1479 and 130 were respectively obtained for the formation of COD and VCH (Scheme 45). Comparatively, complex **302b** which yielded the best results in the phosphinine series afforded COD and VCH with TONs of 94 and 54 only. From these different experiments it was proposed that the strong Fe-phosphinine interaction hampers the generation of the [Fe(DAD)] catalyst and that the catalytic activity follows the stability of these 12 VE intermediates [172c].



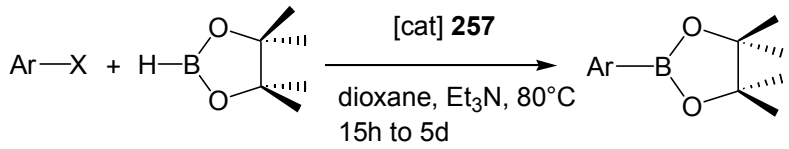
Scheme 44:Phosphinine Ni(0) complexes in the intramolecular Wender's type [4+2] cycloaddition.



Scheme 45: η^6-phosphinine Fe(0) complex in the cyclotrimerization of alkynes with nitriles to form pyridines.

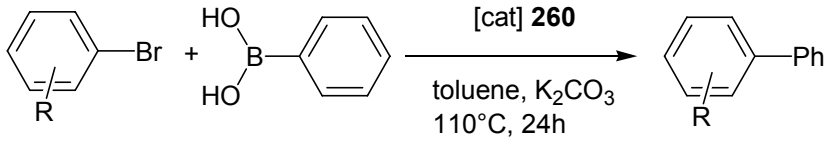
The reactivity of the P=C system of phosphinines upon coordination to metals having a positive oxidation state is a cumbersome problem which often precludes the systematic use of these ligands in catalysis. However, as could be seen in the chapter devoted to the coordination of these aromatic rings, electronic properties of phosphinines can be judiciously employed to generate new structures. Thus, upon reaction with nucleophiles phosphinines

afford phosphacyclohexadienyl anions which exhibit interesting coordinative properties. Recently, reactivity of these anions was re-investigated and some of these new ligands and their derived complexes have found interesting applications in some catalytic processes. σ^4, λ^5-phosphinine palladium complexes were the first to be evaluated as catalysts in 2002. It was shown that complex **257** efficiently catalyzes the cross-coupling reaction between pinacolborane and iodoarenes to afford the corresponding arylboronic esters (Miyaura reaction) (Scheme 46) [213b]. All couplings were performed in dioxane in the presence of triethylamine as base using low loadings of catalyst (about 1.10^{-4} mol%) and TON up to 10000 were obtained in the coupling reaction of iodobenzene and 4-iodotoluene. Additionally, the activity of N (0.05 mol%) was also tested in the classical Heck coupling reaction between methyl-acrylate and iodobenzene to afford the *trans*-cinnamate in a quantitative yield [213b]. Much more recently, the allyl-palladium complex **260** proved to be a very powerful catalyst for the Suzuki-Miyaura coupling of bromoarenes with phenylboronic acid when the reaction was carried out in toluene under reflux using K_2CO_3 as base (Scheme 46). The best TON were obtained when 4-bromoacetophenone was used as substrate (TON = 799 000). Importantly, this result demonstrates that sulphide ligands, which are often considered as poisons for catalysts, could be employed to our advantage without difficulties [241].[2] In the same report, a ruthenium-cymene complex **259** of the same ligand was employed in the transfer hydrogenation of ketones, all reactions being conducted in the presence of KOH as base in refluxing isopropanol (Scheme 46). However TON (ranging from 82 to 200) were found to be relatively modest with regards to those obtained with the most efficient systems such as Noyori's-based catalysts.



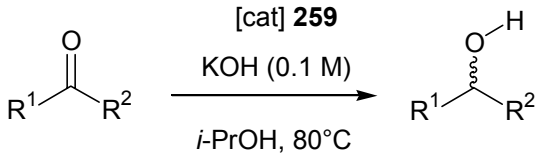
Ar = *p*-MeC_6H_4, o-MeC_6H_4, 2-thienyl
2-naphthyl, *p*-BrC_6H_4, *p*-$MeOC_6H_4$

TON from $5.1.10^3$ to 10000
yields from 45 to 96%



R = H, *p*-OMe, *p*-Me, *p*-COMe

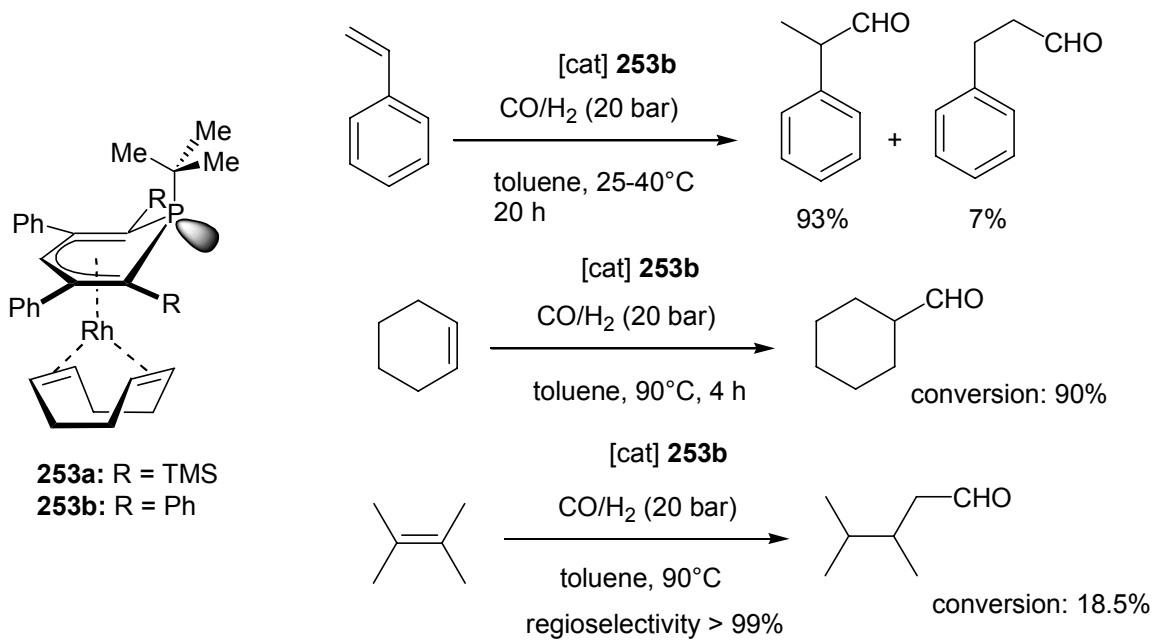
TON from 80.9 10^3 to 799 10^3
yields from 24.4 to 79.9 %



Scheme 46: SPS based Pd(II) and Ru(II) complex in catalysis.

As previously explained, phosphahexadienyl ligands can also serve as precursors of η^5-complexes. Though the catalytic potential of these complexes has not been thoroughly investigated so far, a preliminary result suggests that further interesting developments can be expected. In 2005, it was reported that rhodium(I) complexes **253a,b** display a very good activity in the hydroformylation process of olefins. Thus, good conversion yields and TON were obtained in the hydroformylation of styrene and cyclohexene under mild conditions using low-loading of catalyst. Thus, the tetraphenyl derivative **253b** catalyzed the transformation of styrene at 40°C using a CO/H_2 pressure of 20 bars and 0.5% of catalyst with a ratio between the branched and linear aldehydes of 93/7 (Scheme 47) [242]. This result can be compared with those obtained by Breit et al. with the phosphinines-rhodium based catalyst. Though better TON and regioselectivity were obtained with phosphinines one must take also into account that a fivefold excess of ligand was needed. The same catalyst was also tested in the hydroformylation of cyclohexene and 2,3-dimethylbut-2-ene. With cyclohexene, very good results were obtained and in 4h at 90°C using and initial pressure of 20 bar of CO/H_2, 62.2% of the starting material was converted into the corresponding cyclohexenecarboxaldehyde using a catalyst:substarte ratio of 1:4160 (TOF = $648.h^{-1}$). This performance can be compared with Breit's catalyst using 40 bar of pressure and a Rh:ligand

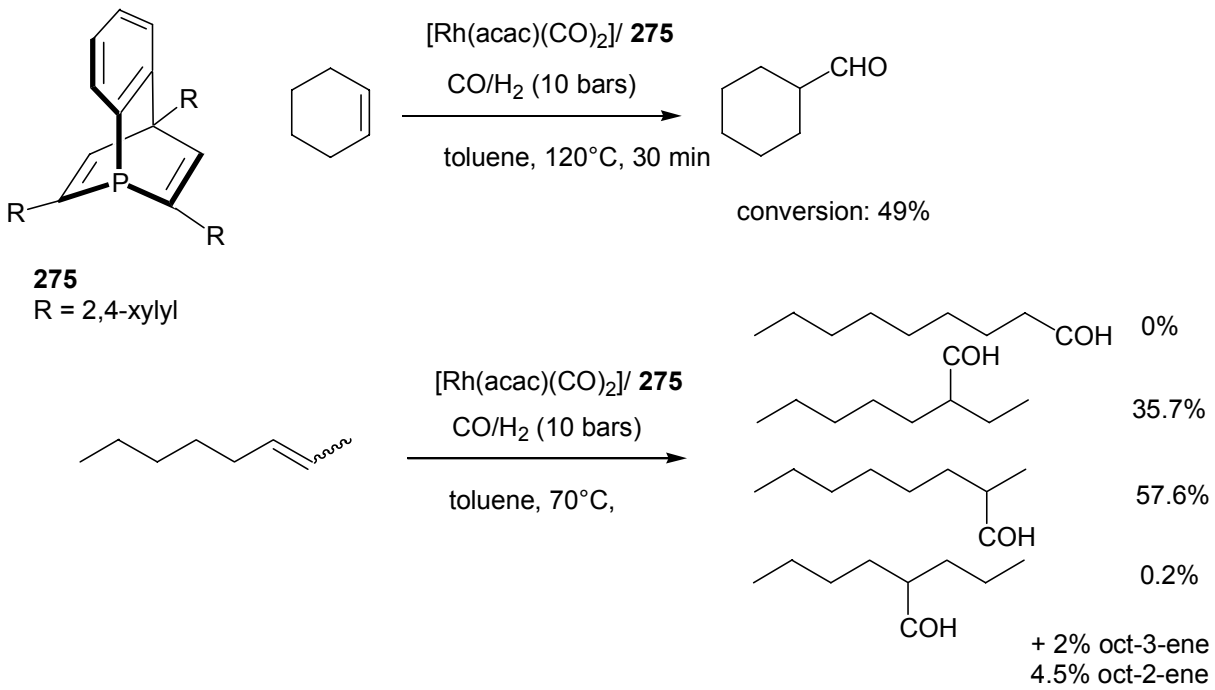
ratio of 1:20. Like phosphinine-based catalyst an isomerization takes place prior to the hydroformaylation in the case of 2,3-dimethylbut-2-ene and 3,4-dimethylpentanal was formed in a 18.5 % yield by only using an initial pressure of 20 bar with a **253b**:substrate ratio of 1:1000 at 90°C in toluene. This last result emphasizes the great potential of these new catalytic systems. No mechanistic investigations were undertaken so far to rationalize the mechanism of this hydroformylation process and on the basis of these results it remains difficult to propose whether the structure of the η^5-complex is maintained or if a η^1-coordinated species was formed (Scheme 47) [242].



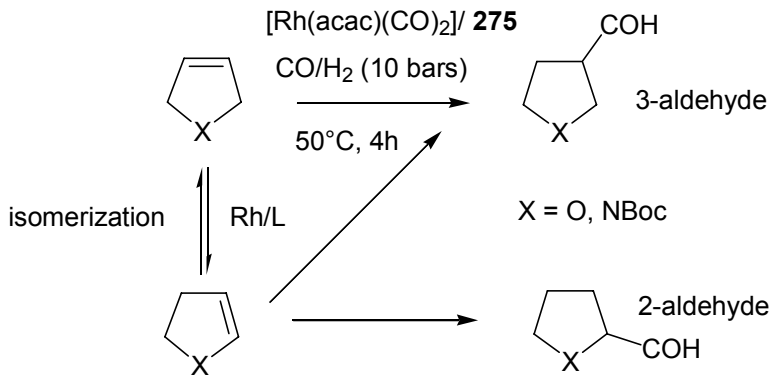
Scheme 47: Phosphacyclohexadienyl Rh(I) complexe in the hydroformylation process.

Another interesting possibility to circumvent the high reactivity of phosphinines is to exploit the presence of the weak HOMO-LUMO gap in [4+2] Diels-Alder reactions to form 1-phosphabarrelenes. Recently, these ligands have found two interesting applications in catalysis. The first report is due to group of Breit who investigated the use of 1-phosphabarrelenes-rhodium(I) complexes derived from ligands **273-275** in the hydroformylation of olefins [217]. Remarkably, these new rhodium-based catalysts showed a greater activity than that of the corresponding phosphinine complexes and the hydroformylation occurred 1000 times faster than the Rh/PPh_3 system which is one industrial system. Thus cyclohexene was converted in 30 min at 120°C into cyclohexylcarboxaldehyde in a 49% yield using two equivalents of ligand and a CO/H_2 pressure of 5 bar (TOF = 12231 mol substrate/mol catalyst h^{-1}) (Scheme 48). However, the most important advantage of these

new catalysts is their ability to achieve the hydroformylation of internal olefins without provoking isomerization toward the corresponding terminal alkene. A nice illustration was provided by the hydroformylation of oct-2-ene (E/Z = 77/23) which essentially yielded aldehydes resulting from the hydroformylation of the internal C=C double bond under relatively mild conditions for this type of substrate, using 10 bar of CO/H_2 at 120°C in toluene with a cyclohexene/ligand/Rh ratio of 4160:20:1. A similar observation was made with heterocyclic alkenes which are known to isomerize easily (Scheme 48). The hydroformylation of heteroatom substituted cyclopentenes such as 2,5-dihydrofuran and N-Boc-pyrroline was studied. In both cases, the transformation proceeded in good yields at 50°C in toluene using a CO/H_2 pressure of 10 bar (substate/ligand/Rh, 2011:20:1) and free of alkene isomerization, the 3-aldehyde being recovered as the major compound. Comparatively, the $P[O(2,4\text{-di-}t\text{BuC}_6H_3)]_3$ rhodium-based catalyst furnished a significant amount of the 2-aldehyde resulting from the hydroformylation of the isomerized 2,3-dihydro heterocyclopentenes (Scheme 49). In this case again complex derived from ligand **275** proved to be the most active [217].

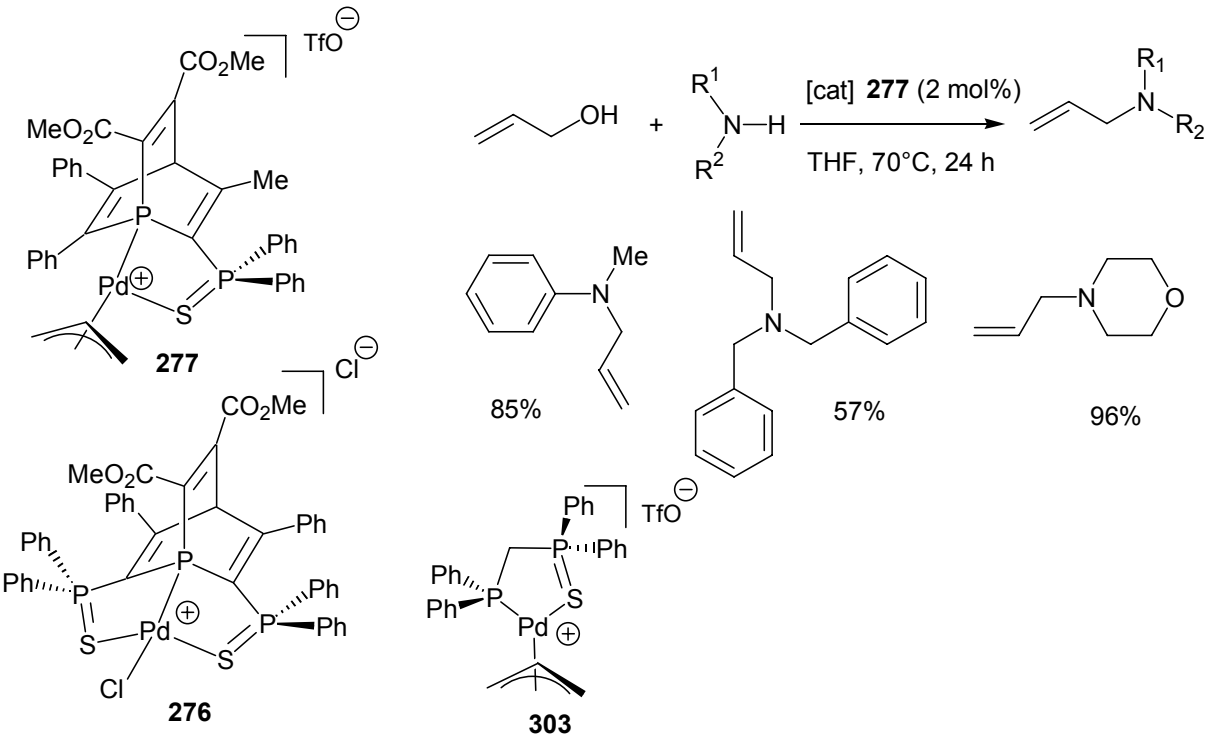


Scheme 48: Phosphaberrelene Rh(I) catalysts in the hydrofoamylation of hexene.



Scheme 49: Phosphaberrelene Rh(I) catalysts in the hydroformylation of the isomerized 2,3-dihydro heterocyclopentenes.

A second important application of 1-phosphabarrelenes was reported in 2005 by our group [219]. Complex **276** yielded interesting performances in the Suzuki-Myaura coupling to form biphenyl derivatives. For example, biphenyl can be produced in 2 hours with a 90% yield using 1.10^{-5} equiv of **N** (TON 90 000) as catalyst in toluene under reflux. A conversion of 70% was obtained using 10^{-7} equivalent of **276**, although a longer heating period was required (24 hours; TON = 7.10^{6}). Finally, a conversion of 95% was obtained using 10^{-5} equivalent of complex in 24h (TON 95 000). More importantly, the same catalyst has found an important application in a synthetically useful process: the allylation of secondary amines with allylic alcohols. Contrary to Yoshifuji's catalysts, reaction of allylalcohol with secondary amines did not stop after the monoallylation process and diallylamines were formed in large amounts. Logically, it was found that secondary amines react in THF at 70°C with allylalcohol to produce the corresponding allylamines in fair to good yields using 2% of catalyst **277**. Contrary to what observed with nickel complexes no additives such as Lewis acids were necessary to complete these transformations. Like with the DPB-based catalyst, the mechanism of this important transformation has not been elucidated so far. However, the electronic properties of the barrelene ligand probably play a very important role in the success of this transformation since classical tertiary phosphine do not catalyze the allylation. Complex **303**, which combines both a phosphine and a phosphinosulfide ligands, proved to be totally inactive under the same experimental conditions (Scheme 50) [219].



Scheme 50: A phosphabarrelene Pd(II) complex in the catalyzed allylation of secondary amines.

4. Conclusion

As can be seen, the chemistry of low coordinated phosphorus derivatives has now reached a significant maturity and these compounds are slowly emerging as a new class of phosphorus ligands endowed with very specific electronic properties. This mainly results from tremendous synthetic efforts that have been made to render these compounds available on relatively large scales. It is now obvious that their fields of application will be different but complementary from that of classical phosphines or their nitrogen counterparts. Though some overlap exists between the different areas, their strong π-accepting capacity offers interesting perspectives in coordination chemistry and catalysis. The synthesis of reduced complexes with phosphinines as ligands has amply demonstrated that, in most cases, these ligands can be regarded as genuine phosphorus equivalents of the carbonyl ligand. Many developments are expected in this area of coordination chemistry with the elaboration of tailored catalyst that are able to whistand highly reductive media contrary to classical phosphines-based systems. Another area of possible development concerns the modification of metal surfaces through coordination. In that respect, the recent synthesis of phosphinine-stabilized gold nanoparticles is a promising results and one can predict that many other interesting developments can be expected with the stabilization of nanoparticles or surfaces made of highly oxidizable

transition metal atoms (modification of catalytic, electronic or optical properties, elaboration of sensors, …….). Over the last few years impressive efforts have also been made to popularize the use of these ligands in homogeneous catalysis, and in this direction again, very significant results have been obtained. Though the potential of these ligands under industrial settings has still to be improved, it is quite clear that their electronic peculiarities could be wisely exploited in the elaboration of new catalytic transformations. Finally, another area that is likely to evoke a lot of interest in future is the derivatization of the most reactive compounds that cannot be directly employed as ligands in catalysis. Indeed, the various synthetic methods developed for their syntheses offer interesting approaches towards polyfunctional derivatives that can be easily converted into highly functionalized cyclic or acyclic phosphines derivatives through simple chemical transformations. In conclusion the field is now open for systematic investigations and there are still plenty of new problems and perspectives to be tackled. Only time will tell wether this will be sustained into the future.

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