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Transition metals in phosphinine chemistry

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Contents

Abstract

The implication of transition metals in phosphinine chemistry is reviewed. After a short theoretical introduction, three different topics are examined: syntheses in which phosphinines are formed using a metal-mediated approach, transformations of preformed phosphinines induced by metals, and phosphinines in coordination chemistry. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Phosphorus; Transition metal complexes; Phosphinines

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List of Abbreviations

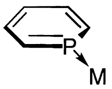
bpy,	2,2′-bipyridine
COD,	1,5-cyclooctadiene
COT,	cyclooctetraene
Cp,	cyclopentadienyl (η^5-C_5H_5)
CpMe,	methylcyclopentadienyl (η^5-C_5H_4Me)
Cp*,	pentamethylcyclopentadienyl (η^5-C_5Me_5)
Cp′,	ethyltetramethylcyclopentadienyl (η^5-C_5Me_4Et)
Cp″,	1,3-ditertiobutylcyclopentadienyl (η^5-$C_5H_3(^tBu)_2$-1,3)
dppe,	1,2-bis(diphenylphosphino)ethane
niphos,	2-(2′-pyridyl)-4,5-dimethyl-phosphinine
NBD,	2,5-norbornadiene
THF,	tetrahydrofuran
tmbp,	4,4′,5,5′-tetramethyl-2,2′-biphosphinine

1. Introduction

In the middle of the seventies, the chemistry of phosphorus and silicon, and that of their heavier analogues (As, Ge...), underwent a striking renewal with the discovery of low coordinated compounds. This breakthrough turned out to be quite remarkable since for a long time it was believed that $p\pi$–$p\pi$ multiple bonding could not occur for the heavier main group elements. Among all the elements concerned, phosphorus has probably been the most thoroughly studied because of its close analogy to carbon [1]. More than twenty years after these discoveries, it appears that phosphorus analogues of the better known sp and sp^2-hybridized carbon and nitrogen derivatives have been synthesized and studies are now slowly focusing on their exploitation in more applied projects. Certain general trends emerge from the reading of several recent detailed reviews. Hence, whereas highly reactive species such as diphosphenes (RP=PR) [2], phosphaalkenes ($R{-}P{=}CR_2$) [3] and phosphaalkynes (P≡CR) [4–7] appear to be inevitable precursors for the synthesis of functionalized phosphines, phosphorus heterocycles and various polyphosphorus cage compounds, aromatic derivatives which are more stable, should be principally used for their unique electronic and/or coordinating properties. This fact is particularly valid for phosphinines which should become one of the most important building-blocks in the elaboration of sophisticated sp^2 phosphorus-based ligands and planar delocalized edifices. Historically, phosphinines, which were first synthesized by Märkl in 1966 [8], are the first example of aromatic compounds incorporating phosphorus. Since this initial discovery, studies have focused on detailed investigations of their electronic properties, on the synthesis of functionalized derivatives and on their use as ligands in coordination chemistry. Only a few reviews have been devoted to these different topics [9–12]. As we will see later, some of the most important synthetic developments in phosphinine chemistry involve transition metals. In this review, three aspects are examined. First, we shall examine reactions in which the metal plays a key role in the formation of the phosphinine ring. Then, the second part will be devoted to metal-mediated transformations of preformed phosphinines and, finally, developments in coordination chemistry will be detailed in the third part. We will address these different points after introducing phosphinines with a short theoretical survey.

2. Theoretical survey

The question of aromaticity of phosphinines and other heterocycles of group XV has been thoroughly discussed [13,14]. A calculated structure of the parent compound C_5H_5P ($P–C_\alpha$ 1.73 Å, $C_\alpha–C_\beta$ 1.41 Å, $C_\beta–C_\gamma$ 1.38 Å, $<$CPC 101°), established by a combination of electron diffraction and microwave data, shows that the ring is planar and that C–C bond lengths are close to their "normal" value in benzene (1.395 Å) [15]. These data which are consistent with an aromatic structure have been confirmed by calculations (SCF/3–21 G*) which indicate that the resonance energy of phosphinine can be estimated at 88% of that of benzene [16] (see also Ref. [2]d for MP2/6–311 G(d) calculations). However, these values do not reflect the important electronic perturbation induced by the introduction of phosphorus. When compared to classical alkyl- or arylphosphanes and pyridine, it appears that the phosphorus atom lone pair has lost its nucleophilicity. Calculations showed that the pK_a difference between the pyridinium ($pK_a = 5$) and phosphininium ($pK_a = -10$) compares with that of NH_4/PH_4 ($\Delta pK_a = 16$) [17]. Mainly as a result of the lower electronegativity of phosphorus (2.2) (2.5 for C and 3.0 for N), a Mulliken population analysis shows that the heteroatom bears a positive charge whereas the carbons of the ring are negatively charged (P $+0.55$, C_α -0.54, C_β -0.22, C_γ -0.25) [18]. This distribution, which suggests an important electronic transfer from phosphorus to the carbocyclic system, seriously contrasts with that observed in pyridine in which the heteroatom is negatively charged. These data are in good agreement with MO calculations which reveal that the lone-pair orbital (n_P) is only the third occupied level in phosphinines whereas it describes the HOMO in pyridines [18–20]. Conversely, the σ-donor ability of phosphinines will be sharply reduced. Nevertheless, having a LUMO (mainly localised at P and C_γ) of lower energy [20], phosphinines will act as better π-acceptor ligands. Obviously, this particular electronic configuration confers a very unusual organic and coordination chemistry on phosphinines. Hence, in contrast to oxygen, sulfur and nitrogen aromatic heterocycles, strong bases and nucleophilic reagents will tend to react at the heteroatom which is positively charged. This reactivity, which can be exploited to synthesize 1,2-dihydrophosphinines [21], has considerably hampered the derivatization of phosphinines by precluding classical approaches based on proton abstraction and metal–halogen exchange reactions. This partially explains why "neutral" methods involving transition metals have attracted so much attention. Concerning coordination chemistry, it is clear that the formation of stable η^1-complexes (type I, 2e donor) will be favored with transition metals in low oxidation states. As these ligands are as good a π-donor and are better π-acceptors than benzene [20], η^6-complexes of various metal centers are also accessible (type II, 6e donor and type III, 8e donor). Furthermore, a number of other non-conventional modes are also known. Whereas types IV (μ-P, 2e donor) and V (μ^3, 4e donor) describe complexes in which the P lone pair binds a dimetallic unit, type VI (η^1-P, η^2 PC, 4e donor) demonstrates that one of the P=C double bonds can also act as an additional binding site. Finally, type VII (η^1-P, η^2-C_2C_3, 4e donor), which can be described as an η^1-P complex of a coordinated-2,3-phosphabenzyne, has also been recently discovered as we will see later.



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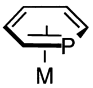

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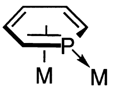

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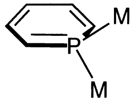

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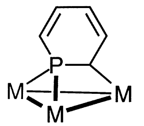

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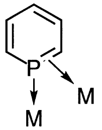

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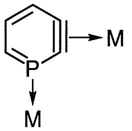


VII

3. Metal-mediated syntheses of phosphinines

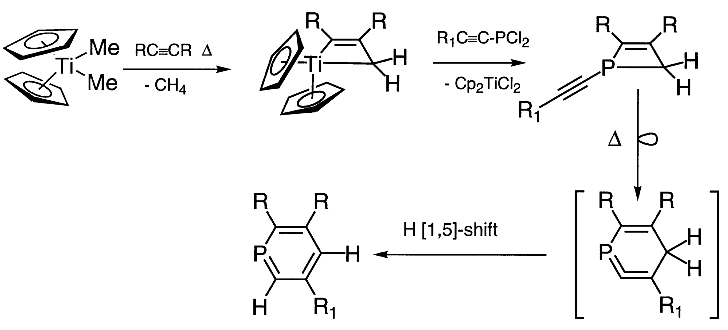
3.1. The use of Ti(IV) complexes

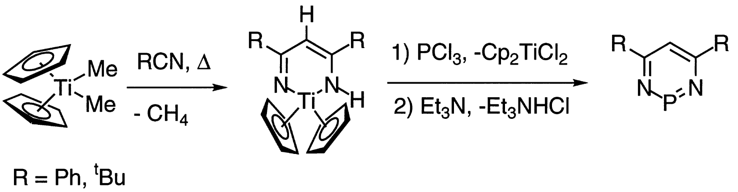
Titanacycles transfer reactions play an important role in the synthesis of many types of *group 15* heterocycles. Only two approaches, which both rely on the chemistry of the $Cp_2Ti{=}CH_2$ complex, are event to the synthesis of phosphinines. The first one, which was developed in 1996, involves the reaction of titanacyclobutene complexes with alkynyldichlorophosphines [22]. The thermal rearrangement of 1-alkynyl-dihydrophosphetes thus produced leads to 3,5,6-trisubstituted phosphinines via a two-step sequence which involves an intramolecular [4+2] cycloaddition reaction followed by a [1,5] hydrogen shift from C_4 to C_6.

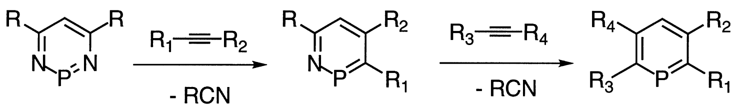
The second approach relies on the reactivity of Doxsee's 1,3,2-diazatitanacycles, which are readily formed from the reaction of Cp_2TiMe_2 with nitriles. Upon reaction with PCl_3 in the presence of Et_3N, 1,3,2-diazaphosphinines are formed via a N–Ti, N–P bond metathesis [23].

These highly reactive heterocycles proved to be very efficient precursors of 1,2-azaphosphinines and 2,3,5,6-tetrafunctional phosphinines upon reaction with functional alkynes via a thermally promoted [4+2] cycloaddition/cycloreversion sequence which involves an extrusion of nitrile [23,24].

This sequence has also been recently successfully extended to the preparation of functional arsinines [24].

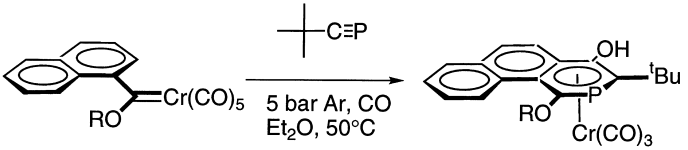






3.2. Annulation via carbene complexes

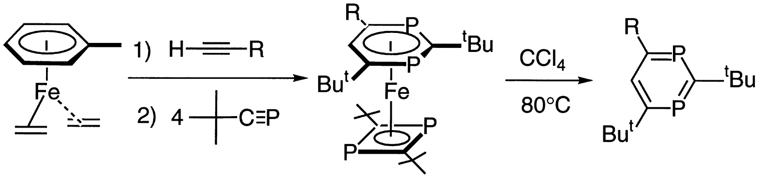
It is now well established that the chemistry of phosphaalkynes reveals close analogies with that of alkynes [4]. The reaction of *tert*-butylphosphaacetylene (^{t}BuC≡P) with pentacarbonyl chromium carbene complexes is one of the most spectacular examples which nicely illustrates that mimetism. Phosphorus equivalents of substituted hydroquinone π-Cr(CO)$_3$ complexes have thus been prepared under mild conditions via regioselective carbene annulation reactions [25,26]. It has also been shown that the Cr(CO)$_3$ fragment could easily be removed under CO pressure thus rendering this approach attractive for the preparation of 3-phosphaphenanthrene.



Evidence supporting the idea that similar steps in the mechanism are operative in the reaction of carbene complexes with alkynes and phosphaalkynes has been given by the reaction of tBuC≡P with vinylcarbene complexes [27].

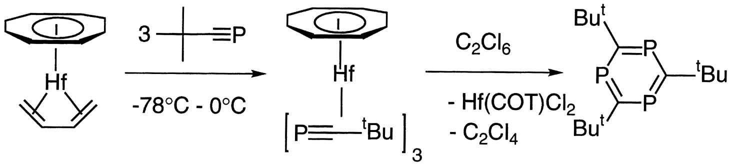
3.3. From phosphaalkynes to di and tri-phosphinines

In line with the preceding result, metal targeted cyclodi- and trimerization of *tert*-butylphosphaalkyne have also been the subject of numerous studies. In 1995, Zenneck *et al.* succeeded in the synthesis of the first 1,3-diphosphinine [28]. The reaction of the [Fe(η^2-ethylene)$_2$(η^6-toluene)] complex with four equivalents of ^{t}BuC≡P and one equivalent of alkyne yields a stable complex having a 2,4-di-*tert*-butyl-1,3-diphosphinine and a 2,4-di-*tert*-butyl-1,3-diphosphete as ligands. Decomplexation of the free ligand using CCl_4 as oxidant makes this approach attractive for preparative purposes.



R = H or $CH_2OC(O)CH_3$ .....

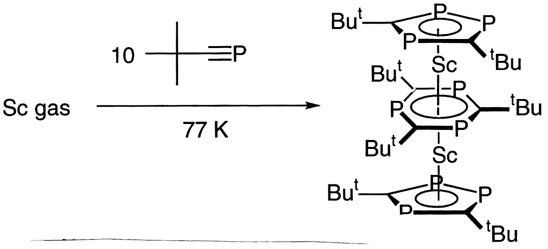
The synthesis of the first 1,3,5-tri-*tert*-butyl-1,3,5-triphosphinine proved to be more difficult to achieve. In 1987, the partial characterization of an η^6-molybdenum complex [Mo(η^6-$C_{15}H_{27}P_3$)(CO)$_2$(η^2-^{t}BuC≡P)], obtained from the reaction of ^{t}BuC≡P with [Mo(CO)$_3$(η^6-cycloheptatriene)], was reported [29]. Unfortunately, this result could not be confirmed by independent experiments. The first successful isolation, which was published by Binger *et al.* in 1995, involves the chemistry of hafnium(COT) complexes [30]. In the synthesis of 1,3-diphosphinines, the decomplexation of the free ligand was carried out using an oxidative process with C_2Cl_6.



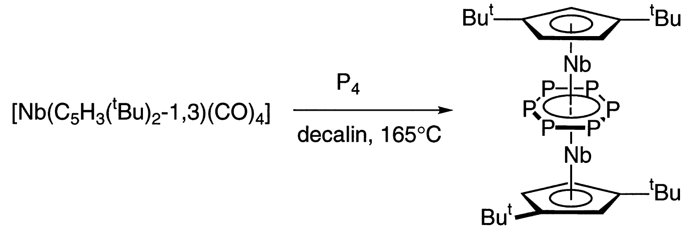
Finally, even more recently, Nixon's group has reported the synthesis of the first η^6-triphosphinine complex which was assembled in the coordination sphere of scandium [31]. Although obtained in very low yields (5–10% based on scandium), this unusual triple-decker sandwich complex, which presents a very low electron count (22 VE), has been characterized by X-ray diffraction study.

3.4. From P_4 to hexaphosphinine complexes

As seen above, the partial replacement of CH units in benzene by a isoelectronic P atom is a very appealing field of exploration. In the same way, a great deal of



effort has also been devoted to the synthesis of cyclo-P_6. Although it has never been proven that this latter might exist as a free ligand, a number of triple-decker sandwich complexes having a planar cyclo-P_6 unit as middle deck have been reported. In all cases, these complexes were directly prepared from the reaction of white phosphorus (P_4) with appropriate precursors: $[(Cp^*Mo)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_6)]$ [32], $[(Cp^*W)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_6)]$ and $[(Cp^*V)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_6)]$ [33], $[(Cp'Nb)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_6)]$ [34]. In the case of niobium, a Cp″ complex $[(Cp''Nb)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_6)]$ has also been prepared as shown below [35].



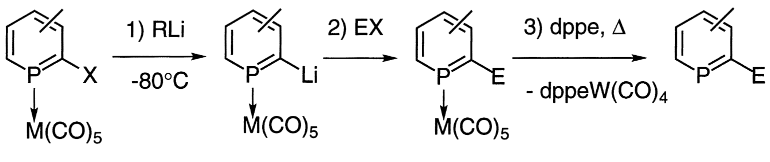
4. Metal-mediated transformations of phosphinines

4.1. Organometallic derivatives of P–M(CO)$_5$ complexes

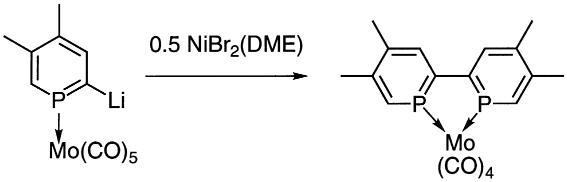
The complexation of the lone pair with $M(CO)_5$ (M = Cr, Mo, W) fragments has been used to partially overcome the problem of nucleophilic attack at the phosphorus atom. Whereas 2-chloro derivative P–$W(CO)_5$ complexes [36] undergo attack at phosphorus [37], a halogen to lithium exchange occurs at low temperature with 2-bromo- [38] and 2-iodophosphinines [39,40] using phenyl- and butyllithium, respectively. Trapping reactions with various electrophiles of the 2-lithio derivatives thus formed provide an easy access to 2-functional phosphinines after a subsequent decomplexation with dppe.

This approach turned out to be successful for the synthesis of the (tmbp) tetracarbonyl molybdenum complex by homocoupling of 2-lithiophosphinines with the $NiBr_2$.DME complex [41]. Although attractive, this method has no synthetic value since free tmbp cannot be released from the $Mo(CO)_4$ unit.

Complexation with $W(CO)_5$ has also been used to stabilize a 2-zinc derivative of a 4,5-dimethylphosphinine (2-ZnC_7H_8P) [42,43]. 2-Cupric and mercuric derivatives



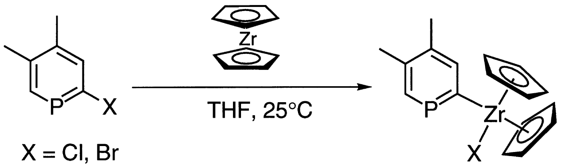
M = Mo or W
R = Ph (X = Br), Bu (X = I)
E = R_3Si, CO_2Et, PPh_2



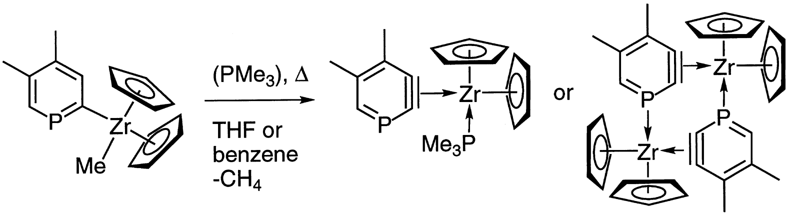
of this P–W$(CO)_5$ complex have thus been obtained by transmetallation with the corresponding salts. Additionally, the palladium-catalyzed cross-coupling reaction of (2-ZnC_7H_8P) with (2-IC_7H_8P)(W$(CO)_5$ affords the W$(CO)_4$(tmbp) complex [44].

4.2. Zirconium complexes

All the developments relying on the chemistry of cyclopentadienyl zirconium complexes involve the use of $ZrCp_2$(2-phosphininyl)X (X = Cl or Br) derivatives which are easily prepared by reacting zirconocene "Cp_2Zr" with 2-halogenophosphinines. Although no detailed mechanistic studies have been undertaken, this insertion, which apparently does not occur with other halogenated heterocycles, is thought to involve an initial coordination of the P lone pair at the Cp_2Zr fragment. An X-ray structure of the [$ZrCp_2(C_7H_8P)Cl$] complex has been reported [45].



As for classical C–zirconium(IV) complexes, the C_2–Zr bond reacts with various electrophiles such as D_2O, I_2, AgCl and BrCN to give 2-deutero, 2-iodo, 2-silver and 2-cyanophosphinines, respectively [45]. Another interesting feature of their chemistry concerns the substitution of the Zr–X bond with phenyl and methyllithium. As in arene chemistry, Zr–R (R = Me or Ph) derivatives thus formed undergo a thermally promoted β-elimination which leads to phosphabenzyne–zirconocene complexes. These can be isolated as PMe_3 [46] adducts or as dimers when the elimination is carried out without phosphine [47].



An X-ray crystal structure investigation of the dimer complex $[Zr(CpMe)_2(C_7H_7P)]_2$ (see Fig. 1) has recently revealed that the nature of the "pseudo" triple bond is comparable to that of benzyne–zirconocene complexes previously reported by Erker and Büchwald (1.361(2) Å in the dimer vs 1.364(8) Å in the benzyne complex).

The chemistry of these complexes closely parallels that of their carbon counterparts. Alkynes, aldehydes, ketones and nitriles regioselectively insert into the C_2–Zr bonds of the monomer or the dimer to give zirconacycles which can be subsequently converted into vinyl and alcohols derivatives respectively upon acidic hydrolysis [47].

An original 2-thiophosphinine has also been obtained from the thermal reaction of a dimer complex and, more directly, from its Zr–Me precursor with $Ph_3P{=}S$ which acts as a sulfur donor. Although no mechanistic studies have been undertaken yet, it seems therefore likely that this transformation involves the formation of a transient four-membered C_2SZrCp_2 zirconacycle as shown in the following equation [47].

Finally, quite recently, it has been demonstrated that $ZrCp_2$(2-phosphininyl)X complexes may also be used as a convenient source of $Ni^{(0)}$(2,2′-biphosphinines)(dppe) complexes upon reaction with $Ni(dppe)Cl_2$. This homocoupling reaction, which presumably proceeds via a C–Zr > C–Ni bond metathesis,

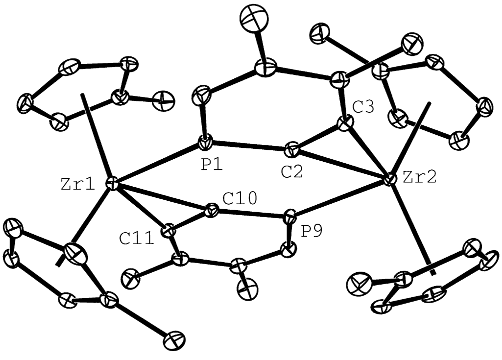
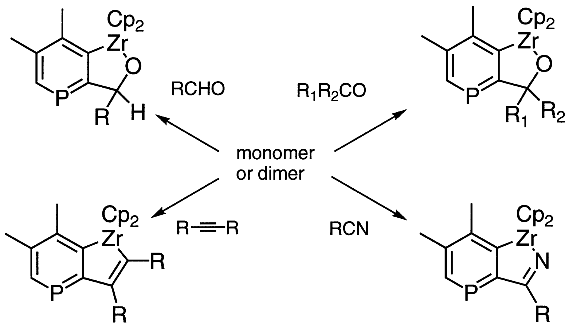
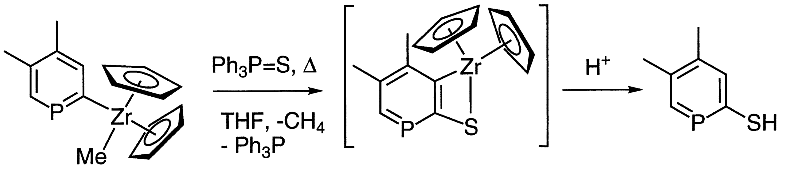
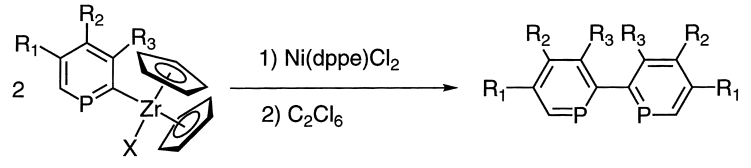


Fig. 1. X-ray crystal structure of $[Zr(CpHe)_2(C_7H_7P)]_2$





appears to be the best approach to 2,2′-biphosphinines, free ligands being obtained after oxidation of the $Ni^{(0)}$ complex with hexachloroethane [48].

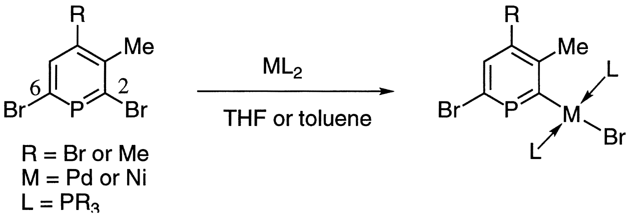


R_1, R_2, R_3 = H or Me

4.3. *Palladium and nickel catalyzed cross-coupling reactions*

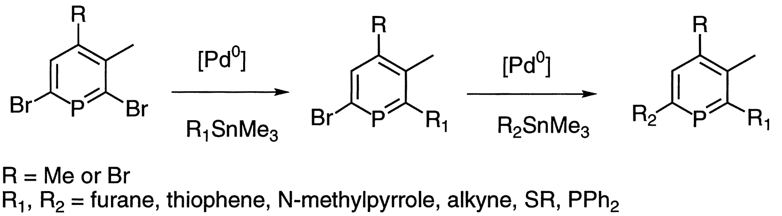
Palladium and nickel(0) complexes play a very important role in the synthesis of functional derivatives. In 1993, it has been shown that [PdL_2] (L = PPh_3, PFu_3 or L_2 = dppe) fragments insert into the C_2 and C_6–Br bonds of 2,6-di and 2,4,6-tribromophosphinines to give C–Pd(L_2)Br complexes [49,50]. Surprisingly, at 40 °C, with 3-methyl derivatives, this insertion exclusively takes place at the position (C_2) α to the methyl whereas the second C_6–Br bond remains unreactive. However, at higher temperatures (100 °C), a competition is observed between the insertion at C_2 and C_6. The X-ray crystal structure of the [$Pd(dppe)Br(C_5H_4PBr_2)$] complex has been recorded [51].

Semi-empirical calculations (AM1) have been undertaken to elucidate this surprising regioselectivity. Apparently, a destabilizing through-space interaction between the methyl group and the bromine activates the C_2–Br bond [51].



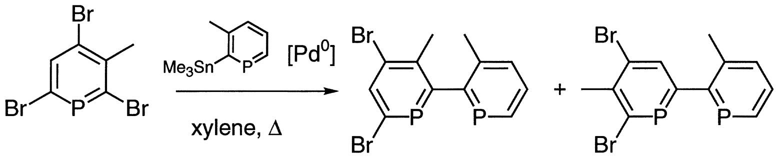
R = Br or Me
M = Pd or Ni
L = PR_3

The most striking development of this chemistry concerns the synthesis of 2,6-difunctional compounds via catalyzed cross-coupling reactions between these polybromophosphinines and heteroaryltin, alkynyltin, thioalkyltin, arylzinc and silylphosphine derivatives. A number of symmetrically and unsymmetrically disubstituted compounds, which could not be accessible using other known synthetic methodologies, have been prepared [49–51].

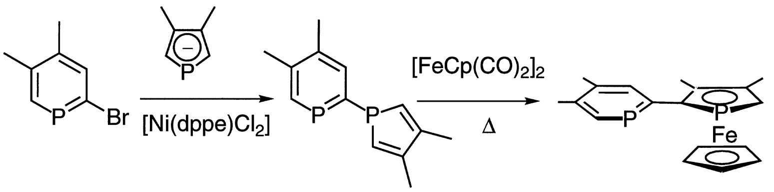


R = Me or Br
R_1, R_2 = furane, thiophene, N-methylpyrrole, alkyne, SR, PPh_2

Another interesting extension of these cross-coupling reactions concerns the synthesis of two 2,2′-dibromobiphosphinines which were obtained when a 2-trimethyltin-3-methylphosphinine was used as a partner. Unfortunately, due to drastic experimental conditions, no regioselectivity was observed and the two ligands were obtained in a 1:1 ratio [51].



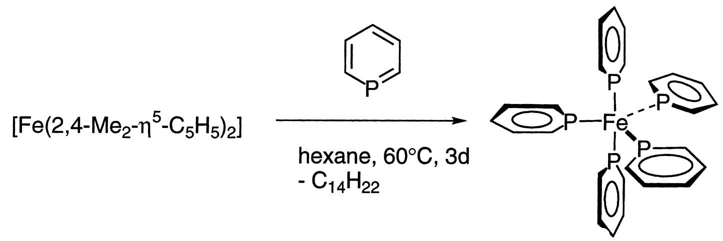
Finally, nickel(0) complexes have also been used to catalyze cross-coupling reactions between 2-bromo- or 2,6-dibromophosphinines and phospholide anions. The 2-(phospholyl)-phosphinines thus formed are very efficient precursors of various P–C–C–P chelate ligands having a phosphinine subunit [52]. An illustration of this chemistry is given in the following equation with the synthesis of a (2-phosphinyl)-phosphaferrocene complex [53].



5. Coordination chemistry

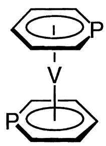
5.1. Monophosphinines

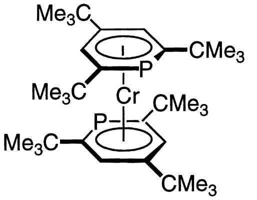
Coordination through the lone pair (η^1) is by far the most widespread mode of ligation. A number of complexes have been reported, mainly with the 2,4,6-triphenyl derivative (L) which for a long time remained the most easily available ligand: $LM(CO)_5$ complexes (M = Cr, Mo, W) [54–56]; LNi $(PR_3)_2$ [57]; L_3RhCl, L_2RuCl2 [58]; LAuI [59]; $LMn(CO)_2Cp$ [60]. More recently, Pd(II) [61] and Cu(I) [62] complexes of the 2-phenyl-4,5-dimethylphosphinine and various $W(CO)_5$ complexes of 2-functional phosphinines have also been prepared (see Section 4.1). Nevertheless, the existence of these complexes does not point out the exceptional ability of phosphinines to stabilize metal centers in low oxidation states. A nice illustration of this property was given by Elschenbroich *et al.* who investigated the synthesis of homoleptic complexes of the parent phosphinine (C_5H_5P) with zero-valent metals. Three complexes have been prepared and structurally characterized: $[Ni(\eta^1\text{-}C_5H_5P)_4]$ [63], $[Cr(\eta^1\text{-}C_5H_5P)_6]$ [64] and $[Fe(\eta^1\text{-}C_5H_5P)_5]$ [65]. The synthesis of the iron complex, which was prepared by analogy with that of $Fe(PF_3)_5$ from C_5H_5P and the bis(2,4-dimethyl-η^5-pentadienyl) iron, is presented in the following equation.

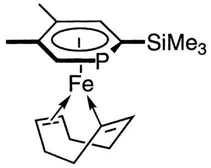


As mentioned above (see Section 3.2Section 3.3Section 3.4), in some instances, transition metals can promote the synthesis of η^6-complexes of mono and polyphosphinines. Commonly, as for other arene derivatives, they are also directly accessible from reactions of various metal fragments with preformed phosphinines. Initial studies mainly focused on carbonyl complexes of group VI (M = Mo, Cr, W), using 2,4,6-triphenylphosphinine [66,67] and 4-cyclohexylphosphinine which can act as an eight-electron donor ligand (η^1–η^6) because of its lack of steric hindrance at the α-positions [56]. Later, sandwich derivatives of manganese(I)

[Mn(η^6-phosphinine)Cp] (η^6 and mixed η^1–η^6) were also prepared by photochemical rearrangement of the corresponding η^1-complexes [60,68]. However, the most striking developments resulted from the use of MVS techniques (metal vapor synthesis) as demonstrated by the work of Elschenbroich *et al.* who first investigated the synthesis of vanadium [69] and chromium [70] sandwich complexes. Whereas early transition metals prefer the η^6-coordination, the η^1-mode predominates with late transition metals. Hence, in the case of chromium, the use of bulky groups at the phosphorus α-positions (C_2,C_6) proves to be necessary to avoid the formation of η^1-complexes. Another illustration of this behavior was given by Zenneck et al. who showed that an η^6-iron(COD) complex could be accessible with 2-trimethylsilylphosphinine as ligand [71,72]. Interestingly, this last complex shows a good activity in the catalyzed synthesis of functionalized pyridines from alkynes and nitriles.

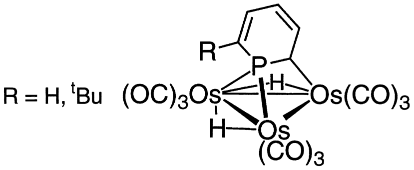






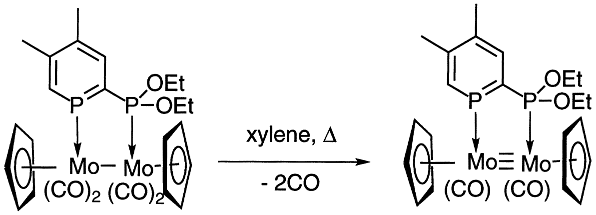
Quite recently, two other important advances in this area were made by Cloke *et al.* who reported the characterization of a titanium(0) $[\mathrm{Ti}(\eta^6\text{-}\mathrm{PC}_5\mathrm{H}_2^t\mathrm{Bu}_3\text{-}2,4,6)_2]$ [73] and of a holmium(0) $[\mathrm{Ho}(\eta^6\text{-}\mathrm{PC}_5\mathrm{H}_2^t\mathrm{Bu}_3\text{-}2,4,6)_2]$ [74] complex.

Finally, to conclude this presentation on ligating properties of monophosphinines, we mention the single report concerning interaction with clusters. In 1993, a $[\mathrm{Os}_3(\mu\text{-H})_2(\mu^3\text{-C}_5\mathrm{H}_4\mathrm{RP})(\mathrm{CO})_9]$ [75] complex containing a phosphinine which acts as a four-electron donor via its lone pair and one of its P=C π bonds was structurally characterized. In this structure, the ring does not adopt a planar geometry since the aromaticity is destroyed by the side-on coordination.



5.2. *2-Phosphinophosphinines*

There are relatively few examples of 2-phosphinophosphinine complexes. First investigations were made by Hugues et al. who synthesized a 2,3-bis (diphenylphosphino)phosphinine by reacting a 2*H*-phosphole with bis(diphenylphosphino)acetylene. Two complexes (PtCl_2 and NiCl_2) were synthesized [76]. However, the latter cannot really be considered as very representative since the lone pair of phosphinine is not involved in the coordination of the MCl_2 metal fragments. Later, classical $M(CO)_5$ [38,49,51] and $M(CO)_4$ [77] complexes of 2-diphenylphosphinophosphinines were also reported. Very recently, a straightforward synthetic approach to 2-dibromophosphinophosphinines has opened new perspectives in that field by allowing the preparation of several functional bidentate ligands having tunable basicities [78]. Some bridged dinuclear complexes of transition metals carbonyls have been reported: $[Fe_2(CO)_2Cp_2L]$, $[Mn_2(CO)_8L]$, $[Mo_2(CO)_4Cp_2L]$ [53], and more recently $[Ni_2(CO)_2(\mu\text{-}CO)(L)_2]$ [79] (L = 2-phosphinophosphinne). As outlined by the synthesis of the molybdenum dimer complex, the coordinating behavior of 2-phosphinophosphinines appears to be markedly different than that of their nitrogen counterparts, 2-phosphinopyridines, and to a lesser extent, than that of diphosphinomethane ligands. By analogy to the chemistry of $[Mo_2(CO)_6Cp_2]$, a triple-bonded molybdenum(I) complex has also been obtained by thermolysis of the corresponding single-bonded complex when the phosphino group is a phosphonite.

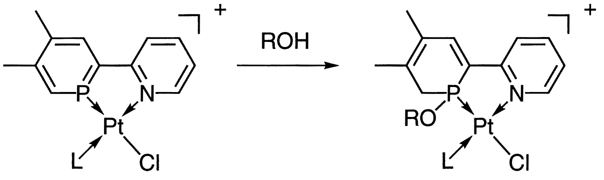


Studies have not been limited to the synthesis of carbonyl complexes of transition metals. Recently, a bipyramidal tetrameric Cu(I) complex of a 2-diphenylphosphino derivative (L) $[Cu_4L_2(\mu^2\text{-}I)_2(\mu^4\text{-}I)_2]$ having two μ^4-iodo ligands has also been structurally characterized [79].

5.3. 2-Pyridylphosphinines

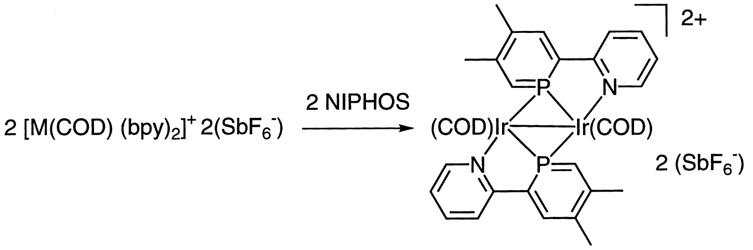
Studies on phosphorus analogues of 2,2′-bipyridines have attracted a lot of interest [80] owing to the important role played by the latter in the coordination chemistry of nitrogen. The first report in this area was made by Mathey *et al.* who in 1982 published the synthesis of a monophosphorus analog (niphos) [81]. Because of the strong difference of basicities between the two bonding sites, which precludes the use of basic and acidic media, the coordination chemistry of niphos proved to be difficult to master. However, some complexes have been reported. A first investigation demonstrated that complexation by zero-valent metal carbonyls (M = Cr, Mo, W) initially takes place at the strong π-acceptor phosphorus atom prior to chelate formation [82]. An X-ray structure analysis of the $Cr(CO)_4$ complex which shows that the ligand adopts a planar geometry has also been recorded. Later, Venanzi's group published more significant results with cationic Pd(II) and Pt(II) complexes which were prepared by reacting niphos with the corresponding

$[LMCl_2]_2$ ($L = PR_3$ or AsR_3) dimers [83]. Unfortunately, these complexes were found to be too reactive towards moisture for complete characterizations. Upon complexation, the aromaticity of the phosphinine unit is disrupted and protic reagents readily add at the external P=C formal double bond to give dihydrophosphinine complexes.



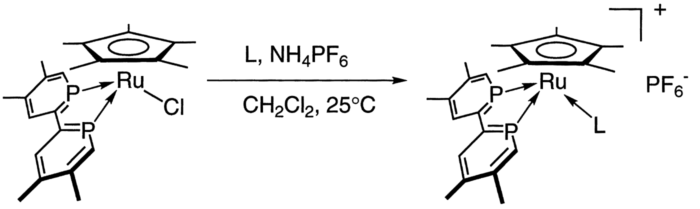
L = PPh_3, PMe_3, $AsMe_2Ph$...
R = H, alkyl, aryl

Finally, a very unusual bonding mode of phosphinine has been discovered by the same group during investigations on Rh(I) and Ir(I) complexes. Upon reaction with $[M_2Cl_2(DIEN)]$ (M = Ir or Rh; DIEN = COD or NBD) dimers, cationic complexes in which the two pyridines act as unidentate ligands and phosphinines as bridged ones (two-electron donor) are formed [84]. The X-ray crystal structure of the iridium complex has been reported.



5.4. *2,2′-Biphosphinines*

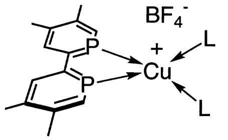
The first synthesis of a 2,2′-biphosphinine, the 4,4′,5,5′-tetramethyl derivative (tmbp), was successively achieved in 1991 by Mathey's group [85,86]. Since this first report, three other approaches which give access to other mono- and di-methyl substituted [87], to a dibromo- [51] and to the parent biphosphinine [48] (see Section 4.2) have also been reported. To date, all the studies have been conducted with the tmbp ligand which turns out to be the most easily available. An electrochemical study of this ligand revealed that, as expected, the LUMO of biphosphinines is significantly lower in energy than that of bipyridines. Hence, whereas the first monoelectronic reduction wave of tmbp occurs at −1.85 V (vs SCE in DMF), the corresponding wave for bpy lies at −2.20 V [41]. If we except the synthesis and structural characterization of a $Cr(CO)_4$ complex, early investigations mainly focused on ruthenium(II) and platinum(II) complexes. Whereas two Ru(II) complexes, *cis*-$[Ru(tmbp)Cl_2(dmso)_2]$ and *cis*-$[Ru(tmbp)_2Cl_2]$, prepared from the reaction of tmbp with $[\mathrm{RuCl_2(dmso)_4}]$, were stable enough in solution to be characterized [88], the coordination of tmbp to Pt(II) centers proved to be more problematic. In line with previous observations made on niphos complexes (see Section 5.3), an activation of one phosphinine subunit was also observed during the synthesis of a Pt(Cl)Me derivative. In the presence of traces of water, a selective addition occurs at the external P=C double bond of the phosphinine ring *trans* to the less electron-donating ligand (Cl) [89]. Although no theoretical study has been undertaken to rationalize this unexpected reactivity, it appears that the electron density available at the metal center plays a decisive role in providing (or not) sufficient π back-donation within the π* delocalized system of the ligand. Hence, whereas the dicationic $[\mathrm{Ru(tmbp)_3}]^{2+}$ complex was found too sensitive towards hydrolysis to be isolated, the more electron-rich $[\mathrm{Ru(bpy)_2(tmbp)}]^{2+}$ complex, accessible from the reaction of tmbp with $[\mathrm{Ru(bpy)_2(Me_2CO)_2}]^{2+}$, is stable [90]. Recently, another convincing illustration of this phenomenon was given by the synthesis of a very stable Cp* ruthenium(II) complex [Ru(tmbp)Cp*Cl] [91] which has been used as a precursor for the preparation of various cationic derivatives.



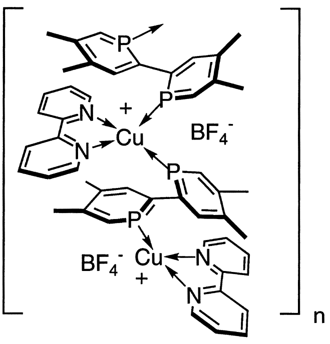
L = MeCN, $P(OMe)_3$, CNtBu, cyclooctene, pyridine, C_7H_8PBr

An electrochemical study also revealed that, due to a suitable balance between the electron-releasing capacity of the Cp* ligand and the strong π-accepting power of biphosphinine, stable (within the voltammetric time scale) $[\mathrm{Ru^{III}Cp^*(tmbp)Cl}]$ and $[\mathrm{Ru^0Cp^*(tmbp)}]^-$ complexes are formed upon oxidation and reduction, respectively. It has also been shown that cationic copper(I) complexes of tmbp $[\mathrm{Cu(tmbp)(L_2)}]^+$ are accessible using the precursor $[\mathrm{Cu(tmbp)(MeCN)_2}]^+$, which is obtained by ligand exchange from $[\mathrm{Cu(MeCN)_4}]^+[\mathrm{BF_4}]^-$ [92]. During the same study, a surprising polymeric helix resulting from a self-assembly process between tmbp, bpy and $[\mathrm{Cu(MeCN)_4}]^+[\mathrm{BF_4}]^-$ has also been structurally characterized. In this edifice, the tmbp acts as a linker between $\mathrm{Cu(bpy)}^+$ fragments whereas bpy acts as a chelate.

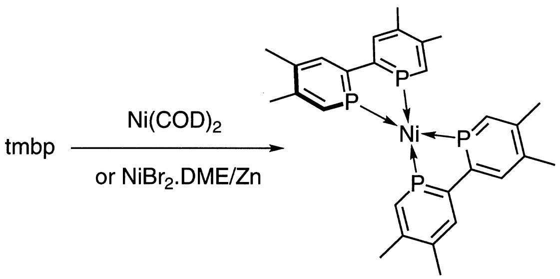
The most striking developments were obtained with zero-valent metal centers. In 1995, the homoleptic nickel complex $[\mathrm{Ni(tmbp)_2}]$ was been structurally characterized [93]. In contrast to its nitrogen counterpart $[\mathrm{Ni(bpy)_2}]$ synthesized by Bartak several years ago [94], this complex is stable towards air and moisture. However, the most illustrative comparison with the bipyridine complex came from an electrochemical study which revealed that, whereas $[\mathrm{Ni(bpy)_2}]$ decomposes upon reduction to Ni(0) and bpy anion radical, the $[\mathrm{Ni(tmbp)_2}]^{\cdot -}$ anion radical ($19e^-$) and $[\mathrm{Ni(tmbp)}]^{2-}$



L = dppe, PR$_3$, AsR$_3$, Et$_2$S, Py



(20e$^-$) dianion complexes could be electrogenerated. These results underline the exceptional ability of 2,2′-biphosphinines to stabilize low-valent highly reduced transition metal centers.



$$\mathrm{Ni(tmbp)_2} + e^- \rightleftharpoons [\mathrm{Ni(tmbp)_2}]^{-\bullet} \qquad E_1^0 = -1.64\ \mathrm{V}\ (\mathit{vs}\ \mathrm{SCE})$$

(stable in THF)

$$[\mathrm{Ni(tmbp)_2}]^{-\bullet} + e^- \rightleftharpoons [\mathrm{Ni(tmbp)_2}]^{2-} \qquad E_2^0 = -1.89\ \mathrm{V}\ (\mathit{vs}\ \mathrm{SCE})$$

(half life > 15 sec)

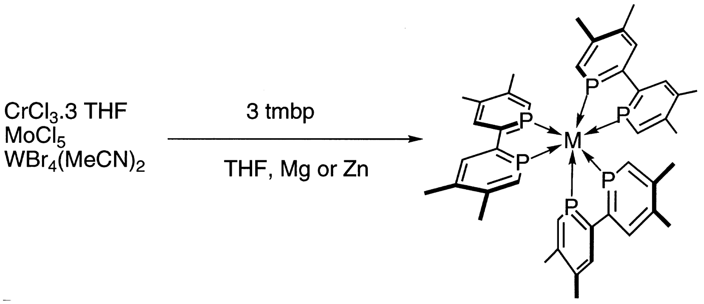
for comparison

$$\mathrm{Ni(bpy)_2} + e^- \longrightarrow [\mathrm{Ni(bpy)_2}]^{-\bullet} \qquad E_1^0 = -1.97\ \mathrm{V}\ (\mathit{vs}\ \mathrm{SCE})$$

(unstable in MeCN)

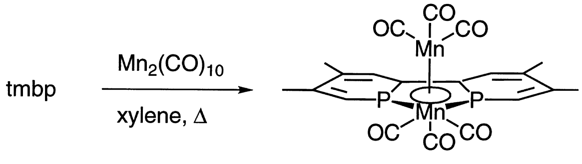
$$[\mathrm{Ni(bpy)_2}]^{-\bullet} + e^- \longrightarrow \mathrm{Ni(metal)} + 2\,\mathrm{bpy}^{-\bullet}$$

Recently, the preparation of these homoleptic complexes has been further extended to *group 6* metals. [M(tmbp)$_3$] (M = Cr, Mo, W) complexes have been synthesized using conventional reductive procedures of MCl_n salts by zinc or magnesium as depicted in the following scheme [95].



The X-ray crystal structure of the deep-purple tungsten complex revealed some interesting information. Surprisingly, the overall geometry is not octahedral but trigonal prismatic. Apparently, some electronic delocalization occurs within the WP_2C_2 metallacycle as indicated by short P–W (2.35–2.36 Å) separations and long internal P=C bond distances (1.742(3) Å). Additionally, in line with these data, the connection between the two phosphinine subunits is significantly shortened (1.442(7) vs 1.490(8) Å in the free ligand). The presence of a strong metal to ligand charge transfer absorption in the UV spectrum at 550 nm ($\epsilon = 4.38 \times 10^4$) confirms these observations.

Finally, classical halogeno-tricarbonyl-manganese and rhenium(I) complexes (*fac*-geometry) have also been synthesized by refluxing tmbp with the corresponding $M(CO)_5X$ (X=Cl or Br) salts [96]. However, a totally unexpected result was obtained by the thermal reaction of tmbp with $Mn_2(CO)_{10}$ which leads to a dimetallic complex having two $Mn(CO)_3$ units [97].



An X-ray crystal structure revealed that tmbp acts as an eight-electron donor towards the two metal fragments, four electrons being given by the two phosphorus lone pairs and four other by the two P=C bonds which bind in an η^2-fashion the second $Mn(CO)_3$ unit located above the plane of the five-membered ring. As in the Os_3 cluster presented before (see Section 5.1), the aromaticity of each phosphinine is destroyed by the side-on coordination.

6. Conclusion

As can be seen from the different results detailed above, the implication of transition metals in phosphinine chemistry is decisive. Although much work remains to be done, especially in devising synthetic methodologies allowing the derivatization of the ring, syntheses of sophisticated planar phosphorus edifices and ligands having tailored properties can now reasonably be expected. Interesting developments might also emerge in coordination chemistry with 2,2′-biphosphinines whose behavior markedly differs from that of classical phosphanes or bipyridines. The stabilization of highly reduced transition metal centers is an area where significant breakthroughs might be achieved. The study of the electronic, magnetic and optical properties of such complexes is still an unexplored and potentially very rewarding field of investigation. The use of phosphinines as ligands in homogeneous catalysis, in processes usually involving strong π-acceptor phosphanes, constitutes another exciting challenge. Obviously, in order to ensure a significant lifetime of the phosphinine ligands during the catalytic cycle, adequate steric and/or electronic protection of the reactive P=C ring bonds must be provided. In that respect, it has been demonstrated, quite recently, that α,α′-disubstituted phosphinines could be used as efficient ligands in the rhodium(I)-catalyzed hydroformylation of styrene [98]. This promising result should initiate a systematic investigation of this new class of ligands.

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