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THE CO/PC ANALOGY IN COORDINATION CHEMISTRY AND CATALYSIS

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Abstract

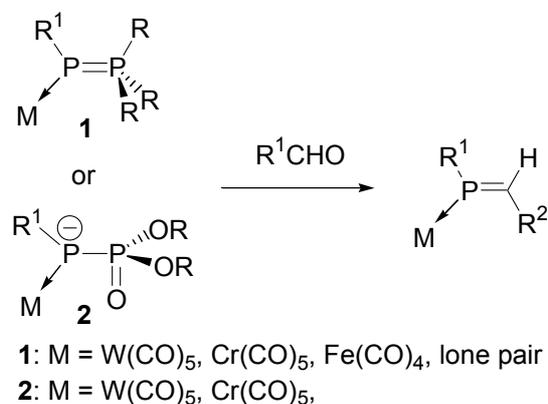
This short account summarizes recent results obtained in the coordination chemistry of phosphinines and emphasizes their analogy with CO ligands. Reduced complexes can be easily assembled through the reaction of reduced 2,2'-biphosphinine dianions with transition metal fragments. Theoretical calculations were performed to establish the oxidation state of the metal in these complexes. Though many reduced complexes are available, phosphinines proved to be too sensitive toward nucleophiles to be used as efficient ligands in most catalytic processes. However, the high electrophilicity of the phosphorus atom can be exploited to synthesize phosphacylohexadienyl anions which exhibit a surprising coordination chemistry. When phosphino sulfide groups are incorporated as ancillary tridentate anionic SPS ligands can be easily produced. These ligands can bind different transition metal fragments such as M-X (M = group 10 metal, X = halogen), Rh-L (L = 2 electron donor ligand), Cu-X and Au-X (X = halogen). Palladium(II) complexes proved to be active catalyst in the Miyaura cross-coupling reaction. Bidentate anionic PS ligands were also synthesized following a similar approach. Their Pd(II) (allyl) derivatives showed a very good activity in the Suzuki catalyzed cross-coupling process that allows the synthesis of biphenyl derivatives through the reaction of phenylboronic acid with bromoarenes.

Keywords: Reduction, Catalysis, Complexes, Phosphorus Heterocycles, Macrocycles.

I. Introduction

The “analogy” that exists between carbon and phosphorus in their low coordinated states slowly emerged as a significant field of investigation in the modern chemistry of main group elements.[1] Though, this analogy is limited, it clearly appears that molecules which feature doubly and triply bonded carbon-phosphorus systems behave as their carbon

counterparts in some organic transformations. Among numerous reactions, one of the most illustrative examples is given by the phospho-Wittig process that allows the formation of phosphoalkenes from the reaction phosphoranylidenephosphines **1** or their Horner-Emmons equivalents **2** with aldehydes (Scheme 1).[2]

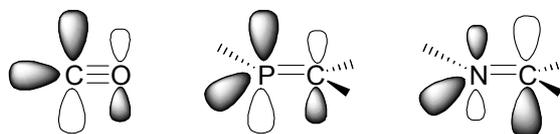


Scheme 1

The coordinative abilities of doubly or triply bonded systems also attracted a lot of attention since the discovery of the first phosphametalocene by Mathey and co-workers in 1975.[3] Since then, a considerable number of structures involving π -coordination of $P=C$ or $P\equiv C$ based systems have been reported and the domain rapidly expanded over the last ten years. Significant applications have also emerged especially in the area of homogeneous catalysis using complexes of aromatic phosphorus heterocycles such as phospholide anions.[4]

All these developments have found their origin in the complementary nature of carbon and phosphorus. Indeed, though at first sight phosphorus and carbon could be considered as very different elements with regards to their coordination states, both elements exhibit a remarkable combination of σ and π electronegativity. In fact, even if phosphorus is less electronegative than carbon, its π -electronegativity was shown to be more important than that of carbon especially when both elements are involved in a doubly or triply bonded system. This specific electronic situation implies that ligands incorporating $P=C$ systems present a close analogy with strong π -acceptor ligands such as carbonyl. Indeed, a simple molecular orbital diagram clearly shows that the LUMO of $P=C$ ligands is closer to that of CO than to that of classical $N=C$ based ligands. The main orbital coefficient is localized on the element which is directly bound to the metal. Obviously, $P=C$ systems exhibit a weaker π -accepting

capacity since they essentially behave as monodimensional π -acceptor ligands (CO being considered as a bi-dimensional acceptor ligand because of its two available orthogonal π^* -orbitals) (Scheme 2).

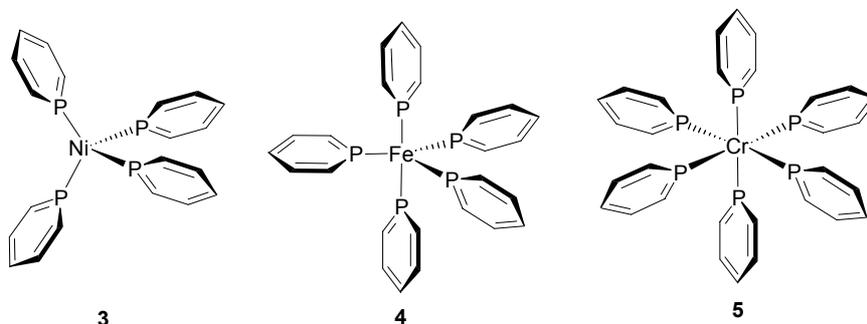


Scheme 2

II. Results and discussion

II.1) Reduced phosphinine transition metal complexes.

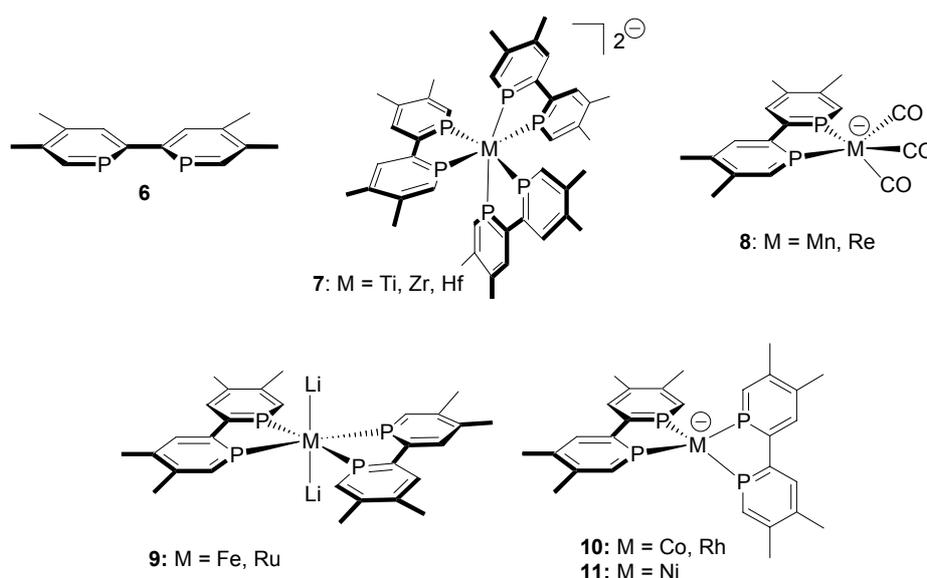
The analogy between P=C systems and the carbonyl ligand has been partially explored and exploited so far. Pioneering works were achieved by the group of C. Elschenbroich and our group over the last decade. The discovery of the first homoleptic phosphinine complexes **3-5** (Ni,[5] Fe,[6] Cr[7]) can really be considered as the starting point of this new facet of the “phosphorus-carbon analogy” (Scheme 3).



Scheme 3

Reasoning that the strong π -accepting capacity of ligand such as phosphinines could be employed to stabilize transition metal complexes in unusual negative oxidation states, we early launched a program aimed at developing the use of bi and polydentate ligands featuring phosphinines as binding sites.[8] One of the most famous ligand to be reported in this series was the 2,2'-biphosphinines **6** whose synthesis was achieved in 1991.[9] As expected from theoretical and electrochemical data, these bidentate ligands markedly differ from their nitrogen counterparts, the ubiquitous 2,2'-bipyridines. Whereas 2,2'-bipyridine are well adapted to the coordination of electron-deficient metal centers, 2,2'-biphosphinines clearly favor the coordination of very electron rich or electron excessive metal centers like CO.

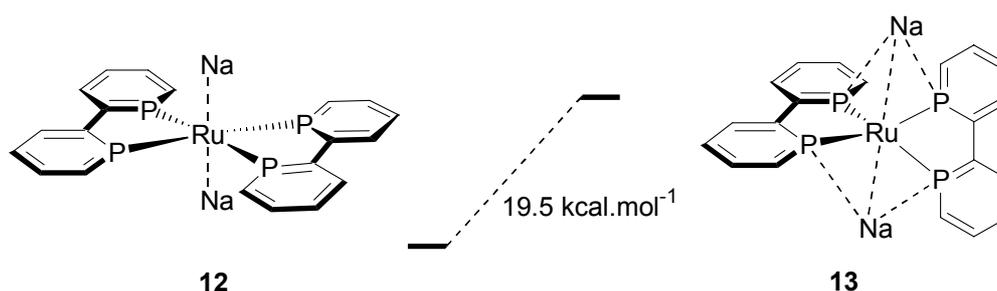
Definitive evidences were given by the synthesis of a series of negatively charged biphosphinine complexes of different metals: dianionic homoleptic complexes of group 4 metals **7** were synthesized,[10] monoanionic complexes of group 7 (M = Mn, Re) **8**,[11] dianionic complexes of group 8 (M = Fe, Ru) **9**,[12] monoanionic complexes of group 9 metals (M = Co, Rh) **10**,[13] and a 19 electron nickel(-1) complex **11** was characterized by EPR spectroscopy (Scheme 4).[14] These complexes were obtained using one of the two following methods : a first conventional method proceeds *via* reduction of preformed complexes with the appropriate number of electrons; a second approach relies on the prior synthesis of a mono radical anion of the biphosphinine or its dianion followed by complexation.[15] This last method, which had already proven to be very efficient in the coordination chemistry of sulfur and nitrogen ligands, could be extended to phosphorus and provided an access to a wide range of reduced complexes.



Scheme 4

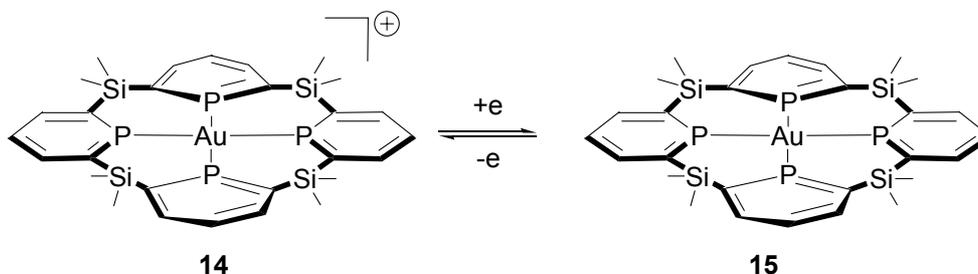
The existence of such reduced species obviously raises the question of the formal oxidation state of the metal. An interesting example was provided by the synthesis of formally d^{10} monoanionic (Co(-1), Rh(-1)) and dianionic (Ru(-2)) complexes with two biphosphinine ligands. Group 9 complexes adopt a distorted tetrahedral geometry in the solid state and group 8 complex adopts a square planar geometry. Recent theoretical studies [16] have shown that this particular situation is mainly due to the strong π -accepting properties of the biphosphinine ligands. It results in a small energy difference between the tetrahedral conformation (expected for a d^{10} - ML_4 complex) and the square planar conformation (expected for a d^8 - ML_4 complex).

In the absence of electrostatic interactions with the counter cation, a distorted tetrahedral geometry was actually found for the group 9 complexes. These calculations also revealed that the weak geometrical preference found for the tetrahedral conformation over the square planar one in the dianionic Ru(-2) complex (3 kcal.mol^{-1}) is reversed when interactions with cations occurred. In agreement with the experimental observation, calculations on the sodium complex actually show that the square planar complex **12** is more stable than its tetrahedral isomer **13**, the computed energy difference being equal to $19.5 \text{ kcal mol}^{-1}$ (Scheme 5).



Scheme 5

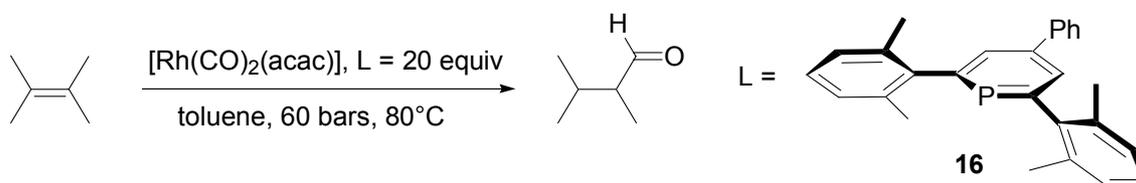
Studies were not limited to biphosphinines and macrocyclic derivatives have also found interesting applications in the stabilization of electron rich metal centers. Thus, it has been shown that a silacalix-[4]-macrocyclic could encapsulate a gold(I) center to afford complex **14**. Most interestingly, reduction of this complex provided a monomeric gold(0) **15** complex which proved to be stable up to 243 K. The fact that Au-CO decomposes at 70 K clearly suggests that phosphinine-based macrocycles can be considered as phosphorus equivalent of CO matrices.[17] Similarly, it has been showed that Rh(I) macrocyclic derivatives could be reversibly reduced to afford the corresponding Rh(0) and Rh(-1) complexes.[18]



Scheme 6

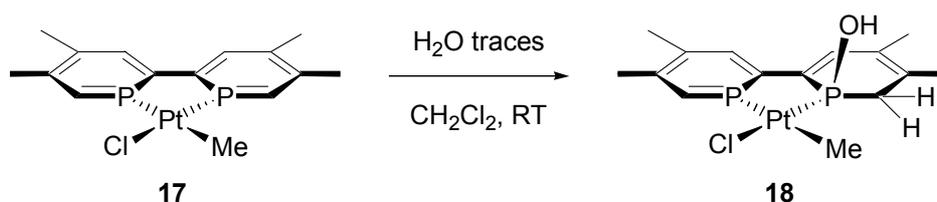
II.2) Phosphinines in homogeneous catalysis.

Homogeneous catalysis is another important field where phosphorus analogs of the carbonyl ligand may find interesting applications. Though low coordinated phosphorus ligands such as kinetically stabilized 1,4-phosphaabutadienes [19] and phosphoferrocenes already proved to be valuable systems,[20] only a little is known about the use of phosphinines. The most significant report was made by the group of Breit in collaboration with BASF in the hydroformylation of olefins process. Functional derivatives of the 2,4,6 triphenylphosphinines such as **16** exhibited an interesting activity in the hydroformylation of styrene and cyclohexene.[21] Most importantly, in more drastic conditions, they also exhibit a significant activity in the hydroformylation of tetramethylethylene to afford 2,3-dimethylbutanal through an isomerization process (Scheme 7)



Scheme 7

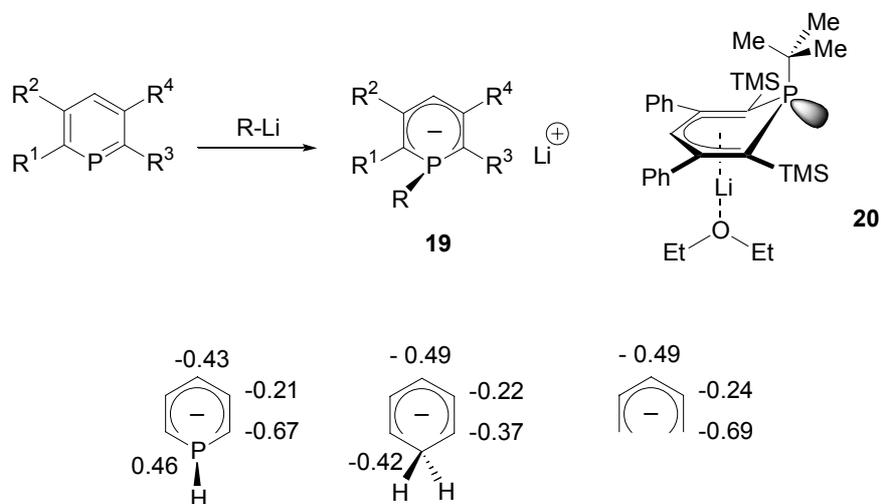
Unfortunately, if we exclude their use as π -ligands in the iron catalyzed cyclotrimerization of alkynes and nitriles to give pyridines,[22] phosphinines, once bound to a metal center, proved to be too sensitive toward nucleophilic attacks (like CO based analogous complexes) to be considered as potential ligands in metal-catalyzed processes involving nucleophilic reagents or bases. A representative example is provided by the hydrolysis of a [Pt(biphosphinine)ClMe] complex **17** which occurs when a dichloromethane solution of the complex is exposed to the presence of traces of water to afford compound **18** (Scheme 8). Interestingly the addition occurs onto the ring which is trans to the less electron donating ligand.[23]



Scheme 8

II.3) Phosphacyclohexadienyl anions and their related ligands.

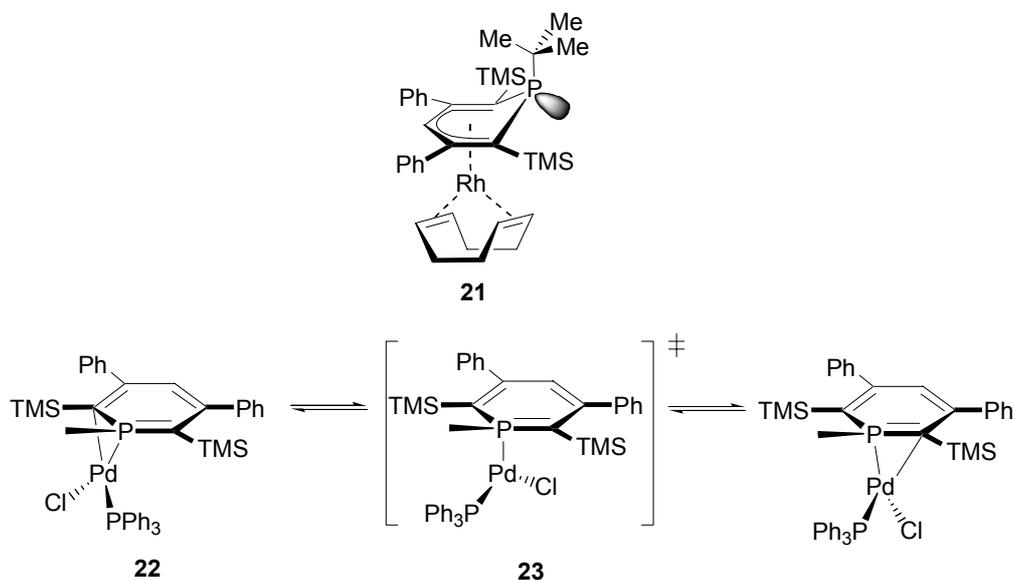
Exploiting the high electrophilicity of the phosphorus atom allowed us to circumvent this limitation. Thus phosphacyclohexadienyl anions **19** which are readily obtained through the reaction of nucleophiles with phosphinines exhibit a surprising reactivity towards metal fragments allowing the synthesis of unusual complexes. Four lithium complexes of these anions, such as complex **20**, were characterized by X-ray crystallography.[24] When no cryptand is used, coordination of the lithium occurs through the π -system of the ring. 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. In such systems, the hybridization of the phosphorus atom lone pair is close to that of classical tertiary phosphines (Scheme 9).[24]



Scheme 9

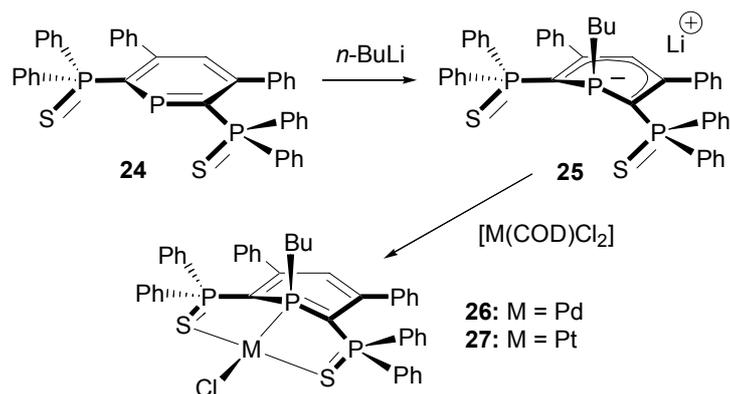
Reactions of these anions with transition metal precursors clearly depend on both the nature of the metal fragment and the substitution scheme of the ring. Whereas $[ML_nX]$ metal fragments react with anions to yield π -complexes such as the rhodium derivative **21**,[25] reaction with $[ML_nX_2]$ metal fragments (group 10 metals) yield η^2 -complexes such as **22** in which coordination occurs through the P-C bond (Scheme 10).[26] The solid state structure of **22** is not wholly retained in solution. Dynamic behavior of the $[M(PPh_3)Cl]$ ($M = Pd, Pt$)

fragment is apparent from the systematic changes observed in the variable temperature ^1H NMR data. DFT calculations on model complexes were performed to determine the structure of the transition state **23** in the case of the palladium complex. As can be seen in scheme 10, this transition state involves a η^1 -coordination of the $[\text{Pd}(\text{PPh}_3)\text{Cl}]$ fragment onto the phosphorus atom, the interconversion between the two enantiomeric complexes resulting from a simple rotation of the fragment (or the ligand) around the Pd-P bond axis in **23**. A good agreement was found between theoretical ($30.2 \text{ kJ}\cdot\text{mol}^{-1}$) experimental ($43.7 \text{ kJ}\cdot\text{mol}^{-1}$) ΔG^\ddagger values.[26]



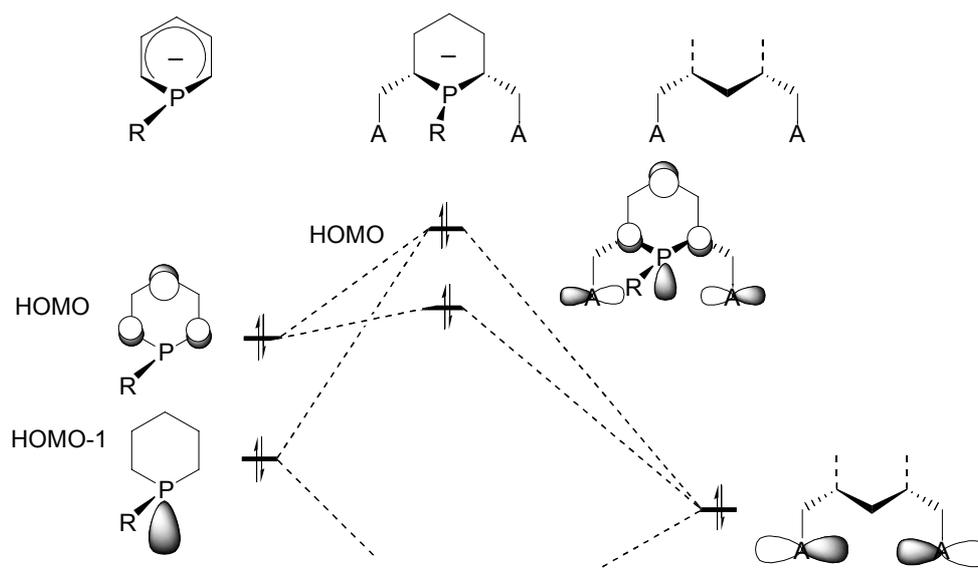
Scheme 10

Interestingly, the presence of ancillary peripheral ligands at the α -carbon atoms of the ring was found to be determinant in the synthesis of η^1 -P coordinated complexes. Thus, reaction of phosphinine **24** with n -BuLi afforded anion **25** which in turn was trapped with $[\text{M}(\text{COD})\text{Cl}_2]$ ($\text{M} = \text{Pd}, \text{Pt}$) to afford the corresponding complexes **26**, **27** in which the anion behaves as a tridentate ligand. These group 10 complexes were found to be remarkably resistant toward moisture and air oxidation (Scheme 11).[27-29]



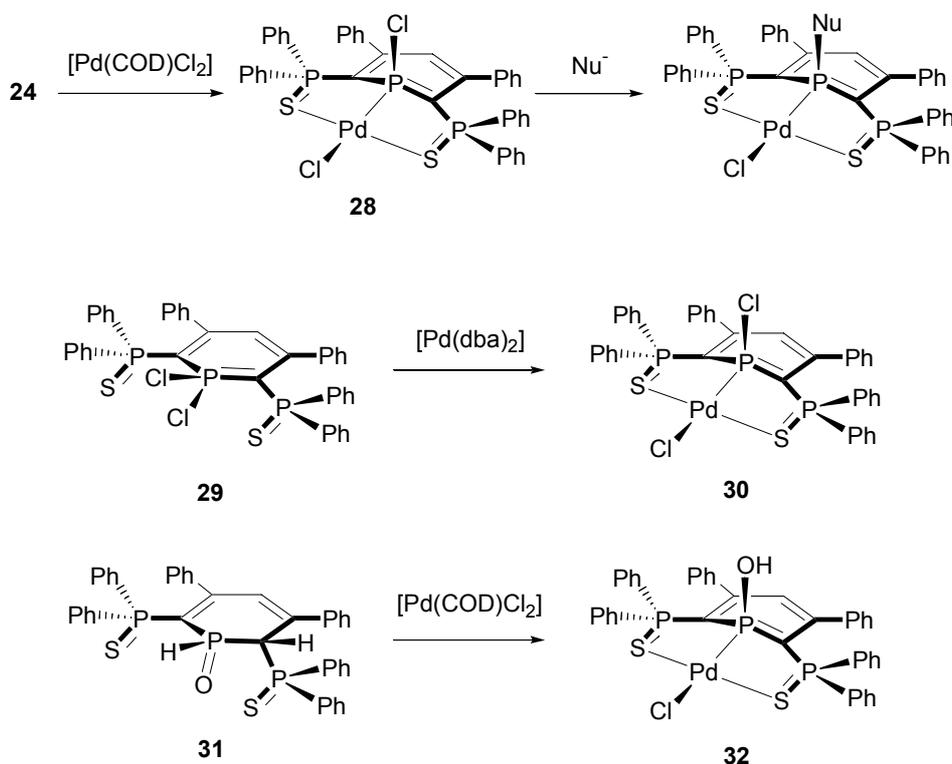
Scheme 11

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 result in a combination of these two orbitals with the in-phase combination of the two lone pairs. This results in a repulsive interaction that strongly destabilizes the HOMO-1 (more important overlap). Therefore, in such tridentate SPS 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 this favoring σ -coordination at phosphorus (Scheme 12).



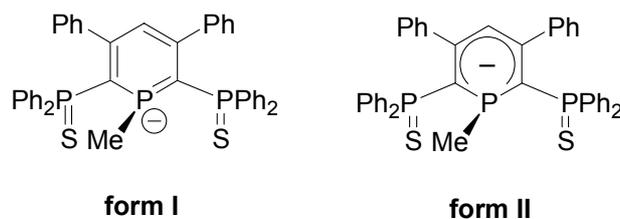
Scheme 12

Further studies showed that other synthetic strategies could be employed to synthesize group 10 square planar complexes. Thus, reaction of phosphinine **24** with $[\text{Pd}(\text{COD})\text{Cl}_2]$ affords the chloro-P chloropalladium complex **28** which can in turn be functionalized at phosphorus through nucleophilic substitution.[27] Another interesting method involves the oxidative addition of a P-Cl bond of a λ^5 -P-dichloro-phosphinine **29** onto a Pd(0) fragment to give complex **30**.[28] Most surprisingly, even P-oxide derivatives of 1,2-dihydrophosphinines such as **31** proved to be valuable precursors of tridentate SPS-based complexes such as **32** featuring a central P-OH group as ligand (Scheme 13).



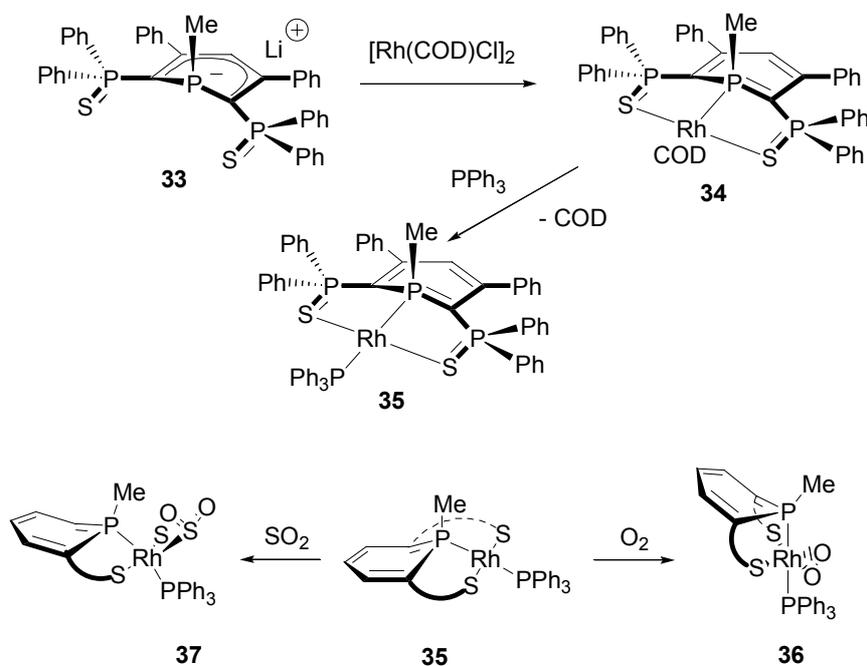
Scheme 13

All these σ -complexes can be regarded either as a λ^5 -metallated phosphinine (form I) or as a classical σ -complex of a phosphacyclohexadienyl anion (form II). Though both forms very likely contribute in the bonding, preliminary calculations suggest that form II is probably predominant (Scheme 14). DFT calculations and charge decomposition analysis (CDA) suggest that a delocalization takes place within the carbocyclic part of the ligand and that the central phosphorus atom behaves as a classical tertiary phosphorus atom.[28]



Scheme 14

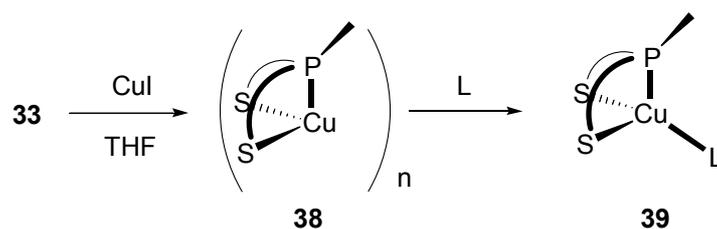
Other sigma complexes were prepared according to the same synthetic strategy. The most significant results were obtained in studying the chemistry of group 9 metals. Thus, reaction of anion **33** with the $[\text{Rh}(\text{COD})\text{Cl}]_2$ dimer yielded the very stable 18 electron complex **34** whose structure remains unknown. However, displacement of the COD ligand from **34** afforded the highly reactive square planar 16 electron complex **35** which was structurally characterized. Complex **35** proved to be highly reactive toward small molecules such as O_2 , CO_2 , CS_2 and SO_2 . Whereas reaction with O_2 , CO_2 and CS_2 yielded trigonal bipyramidal Rh(III) complexes in which the SPS ligand caps one face of the bipyramid such as in the $\eta^2\text{-O}_2$ complex **36**, reaction with SO_2 afforded a Rh(I) complex **37** which adopts a pyramidal geometry. Interestingly, in all cases, attack of the incoming ligand has taken place on the syn face of the complex (Scheme 15).[30] Calculations are currently underway in our laboratories to determine the origin of this facial discrimination.



Scheme 15

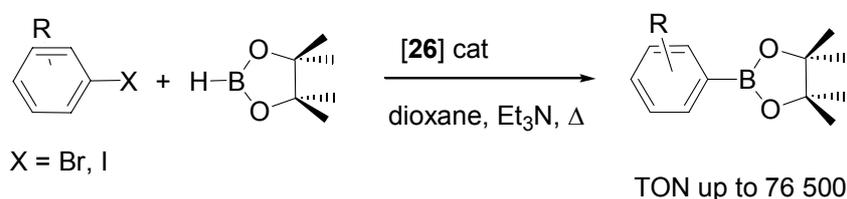
II.2) Mixed SP and SPS ligands and their complexes in catalysis.

The flexibility of the SPS ligand was also evidenced in a recent study dealing with the coordination chemistry of Cu(I) and Au(I) derivatives. An insoluble oligomeric copper complex **38** was obtained by reacting the anionic ligand **34** with CuI in THF at room temperature. Reaction of **38** with two electron-donor ligands such as 2,6-dimethylphenylisocyanide, *t*-butylisocyanide, PPh₃, P(OPh)₃ and pyridine afforded the expected tetrahedral Cu(I) complexes **39** in which the ligand caps three binding sites (Scheme 16).[31]



Scheme 16

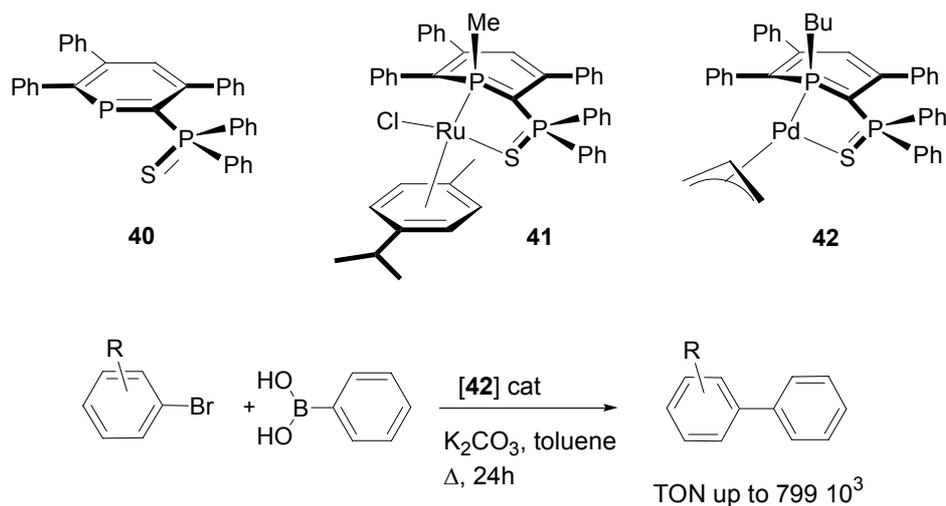
The catalytic activity of palladium (II) complexes of these SPS ligands was tested in different processes. In the Heck-coupling between methyl-acrylate and iodobenzene, methyl *trans*-cinnamate was produced in a quantitative yield with a TON of 10 000. A quite promising result was obtained in the Miyaura cross-coupling reaction which allows the formation of boronic esters from halogenoarenes and pinacolborane.[27] Whereas no reaction was observed with arylchlorides, catalyst **26** proved to be sufficiently reactive to convert iodo and bromo derivatives in dioxane at reflux in good yields. With aryl iodides TON up to 76 500 were recorded (Scheme 17).



Scheme 17

Importantly, we recently found that bidentate PS ligands could also be produced in a similar way by reacting alkyllithium derivatives with phosphinine **40**. Here again, coordination occurs through the phosphorus atom lone pair the sulfur ligand serving as a second binding site. Ru(II) cymene **41** and the Pd(II) allyl **42** complexes were easily produced

and characterized by X-ray crystallography. Though the ruthenium complex exhibited a moderate activity in the transfer hydrogenation of ketones using isopropanol as a proton source, complex **42** showed an interesting activity in the Suzuki coupling process that furnishes functional biphenyl derivatives through the reaction of phenylboronic acid with bromoarenes (TON up to 799 000 with 4-bromoacetophenone as substrate) (Scheme 18).



Scheme 18

In conclusion, it appears that, despite their high sensitivity which usually precludes their use as ligands in catalysis, phosphinines proved to be a valuable source of new heterocyclic ligands and complexes. Further studies will now focus on the systematic study of the binding properties of these new bidentate SP and tridentate SPS ligands in coordination chemistry and catalysis.

Acknowledgments: The authors thank the CNR and the Ecole Polytechnique for the financial support of this work.

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