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Complexes featuring tridentate iminophosphorane ligands:

Synthesis, reactivity, and catalysis

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Keywords: iminophosphorane, tridentate ligand, catalysis, polymerization, coupling reactions

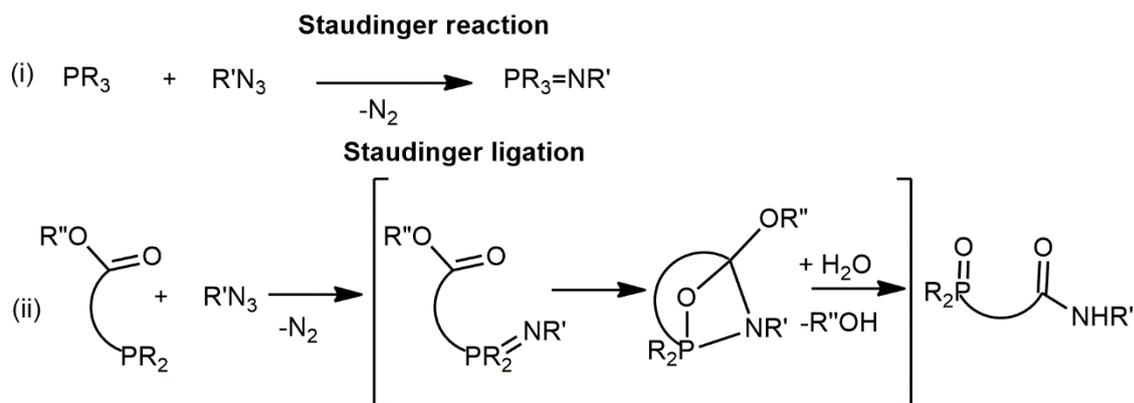
Highlights:

- (N,N,N) ligands are the more represented and especially bis(iminophosphorane) ones.
- Most complexes incorporate rare-earth elements, Pd^{II} or Ni^{II}
- Iminophosphorane can work cooperatively with the metal or a Lewis-acid additive
- Main catalytic applications concern polymerization and cross-coupling reactions
- A few examples of biomedical applications

Abstract: Even if iminophosphoranes ($R_3P=NR'$) were described more than a century ago they remain much less investigated in coordination chemistry than phosphine or N-heterocyclic based ligands, while they present like the latter a strong electron-donor ability. The variety of complexes supported by tridentate iminophosphorane ($P=N$) ligands is reviewed based on the nature of the coordination sites and their reactivity and/or catalytic applications are discussed.

1 Introduction

The chemistry of iminophosphoranes, the nitrogen analogues of phosphonium ylides, started with the seminal report of Staudinger concerning the oxidation of phosphine with azides (Scheme 1 (i)).^[1] These compounds of general formula $PR_3=NR'$ are known under different names: iminophosphoranes, phosphinimines or phosphazenes. They have found various applications in organic chemistry^[2, 3] and in catalysis because of their strong basicity.^[4] They are also intermediately formed in the Staudinger ligation, a very efficient and largely employed bioconjugation method (Scheme 1 (ii)).^[5, 6]



Scheme 1 : Staudinger reaction (i) and Staudinger ligation (ii)

For coordination chemistry, iminophosphoranes are strong σ and π donors because of the presence of 2 lone pairs at the N atom and do not exhibit accepting properties, they are therefore not reduced in presence of low valent metals. In this sense, the use of the ylene form is misleading since there is no π system in an iminophosphorane (Figure 1). The ylidic form accounts much better for the electronic properties of this group. The strong interaction between the P and N atoms resulting from negative hyperconjugation, i.e. delocalization of the N electron density in $\sigma^*(P-C)$ orbitals. This explains why the electron-donating properties of the iminophosphorane functions can be tuned via the N and P substituents, even if the latter is not directly involved in the coordination. Iminophosphoranes are hard donors^[7] and are therefore well-adapted to coordinate to electron deficient metal centers such as rare earth elements, early transition metals and highly oxidized centers while they are easily displaced on richer metals.^[8] Nevertheless, mixed ligands in which they are associated to softer coordinative functions can bind to a larger range of metals. Their association with phosphine was explored and the catalytic applications of their complexes have been reviewed some years ago.^[9] Because of the importance of pincer ligands in coordination chemistry,^[10, 11] we chose to focus on tridentate iminophosphorane ligands and the reactivity of their metal complexes. This review shows the different types of functional groups to which iminophosphoranes were associated and the range of metals that those mixed ligands can coordinate. The reactivity of the resulting complexes and their use in catalysis is also described. The ligands will be presented according to the nature of the coordinating atoms: starting with (N,N,N) ligands, then (N,N,P), followed by (N,N,C) ones, and to finish those incorporating chalcogen atoms. Because they have already been the subject of previous reviews the chemistry of bis(iminophosphoranyl)methanide and methanediide (NCN) complexes^[12-16] will not be discussed here.

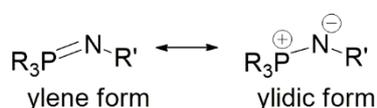


Figure 1 : Iminophosphorane limit forms

2 (N,N,N) Ligand

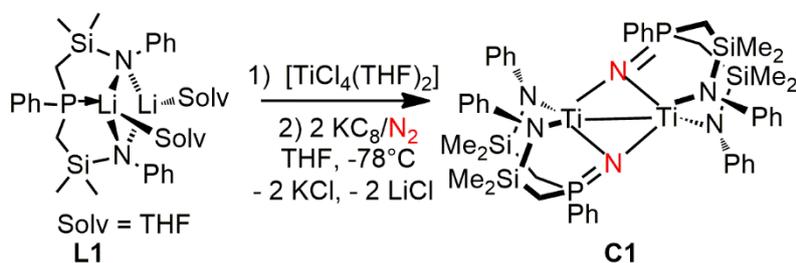
2.1 Mono(iminophosphorane) ligands

In tridentate (N,N,N) ligands featuring only one iminophosphorane function, the latter was associated to a N-heterocycle (pyridine, quinoline, pyrazole), an amine or amide function. We chose to present

the different structures developed following the type of ligand in the Green formalism^[17] in which L and X refer respectively to 2- and 1-electron donors. LX₂ ligands will be discussed first followed by L₂X and L₃.

2.1.1 LX₂ (N,N,N) ligands

To the best of our knowledge only one example of such ligands has been described. Fryzuk and coworkers reported a titanium complex featuring a bis(amido)-iminophosphorane ligand. The latter was formed in the coordination sphere of the metal upon activation of N₂. Indeed, coordination of **L1** to Ti^{IV} afforded diamidodiphosphine complex [(NPN)TiCl₂] evolving in presence of KC₈ (2 equiv.) under N₂ atmosphere in THF to form **C1**, a Ti^{III} dimer in which the initial central phosphine has been transformed into an iminophosphorane (Scheme 2).^[18]

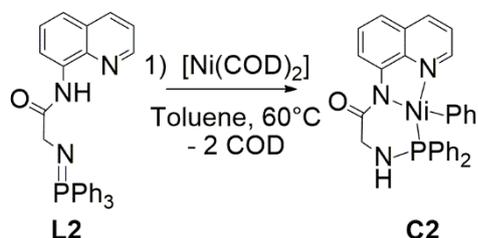


Scheme 2 : Formation of iminophosphorane upon reduction of a Ti complex under N₂

The activation of N₂ by well-defined complexes as well as the reactivity of nitride complexes represent an active area of research, and the formation of the iminophosphorane in the coordination sphere of a metal is not restricted to tridentate ligand supported metal centers. Examples of bidentate and tetradentate ligands were recently reported.^[19, 20]

2.1.2 L₂X (N,N,N) ligands

In the previous case the iminophosphorane moiety formed upon oxidation of the phosphine group and reduction of the metal. Upon studying the coordination of a tridentate amidoquinoline iminophosphorane ligand **L2** we observed the reverse i.e. the reduction of the phosphorus together with the oxidation of the metal center. Indeed, **L2** reacted with Ni⁰ to generate **C2** through a H transfer mediated by the metal and a phenyl migration leading to the formation of an aminophosphine (Scheme 3). Of note the reaction of **L2** with Ni^{II} precursors proceeded uneventfully.^[21]



Scheme 3 : Rearrangement upon coordination of a mono(iminophosphorane) (N,N,N) ligand to Ni

In 2011, Wang and coworkers synthesized mono(iminophosphorane) (N,N,N) Al and Zn alkyl complexes featuring a negatively charged N atom as X donor (Figure 2). They were tested for the ring opening polymerization (ROP) of ϵ -caprolactone and lactide.^[22] The reactions were conducted in toluene at 70°C and the alkyl complexes were activated by addition of benzyl alcohol. In those conditions, aluminum complexes **C3** (Figure 2) exhibited the higher activity with *ca.* 95 % conversion within minutes. They surpassed the Al **C4** complexes, which itself performed better than its Zn analogues (**C4**)

and the amido containing Zn **C3** complexes (Figure 2). For the *rac*-lactide ROP, the results were the opposite: the aluminum complexes were inactive while the zinc complexes gave atactic polylactide with *ca.* 95 % conversion at 70°C within 15 min.

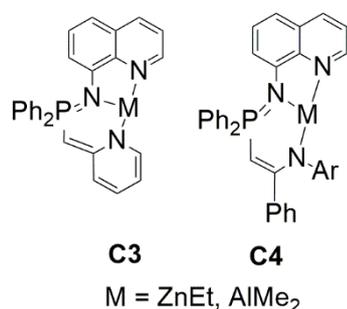
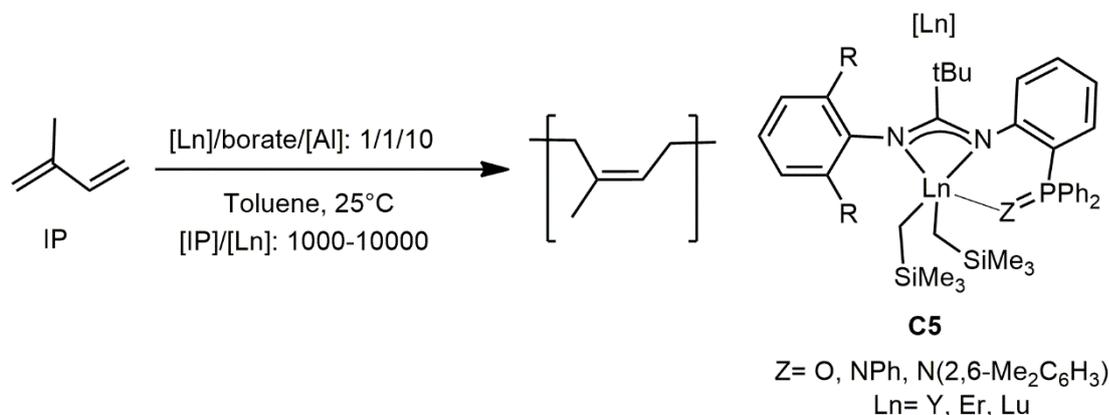


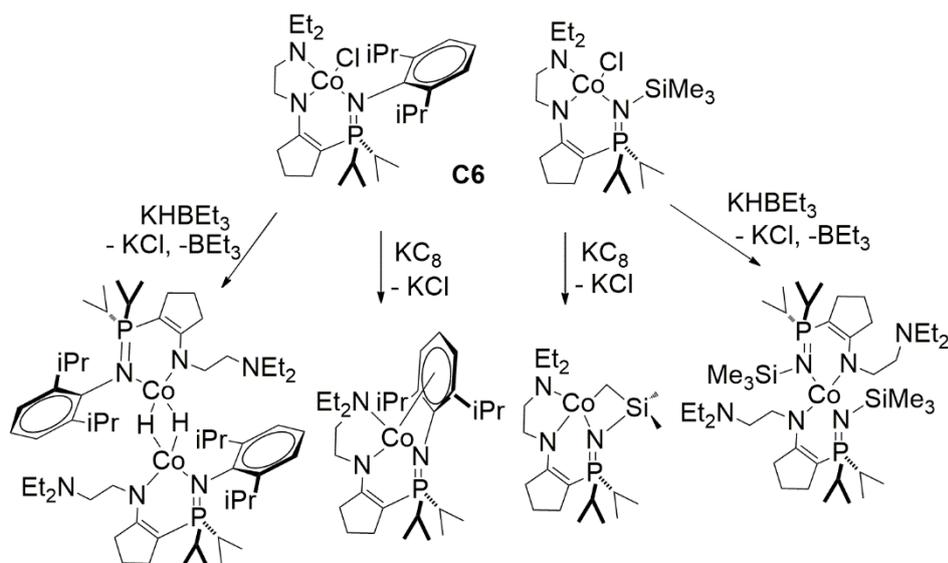
Figure 2 : (N,N,N) Zn and Al complexes tested for ϵ -caprolactone and *rac*-lactide

Rare earth metal complexes are generally better catalysts for polymerization processes because of their enhanced Lewis acid properties. Thus, Trifonov's group evaluated rare earth metal complexes (**C5**) featuring a tridentate ligand associating an amidinate moiety to a PO or a PN group for the stereospecific isoprene polymerization (Scheme 4).^[23] They established that bis(alkyl) complexes featuring a PO amidinate ligand were efficient and selective initiators for this polymerization with conversion of about 90 % at 25°C in toluene with 0.1 mol.% catalyst loading in presence of borate ([CPh₃][BF₄] or [PhNHMe₂][B(C₆F₅)₄]) and alkyl aluminum (AlⁱBu₃ or AlⁱBu₂H) as activators. High *cis*-selectivity was measured (up to 98.5 % of *cis*-1,4). The PN based complexes exhibited a lower conversion and a selectivity switched in favor of the *trans*-1,4. However with a bulkier group on the N=P moiety the *cis* selectivity could be restored.



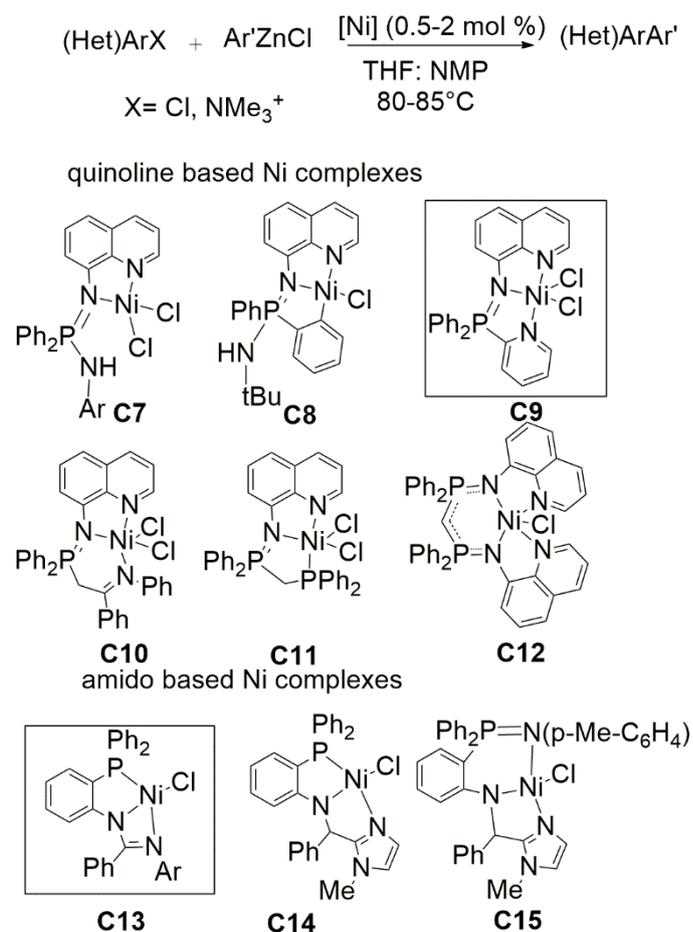
Scheme 4 : Polymerization of isoprene with rare-earth metal complexes

The electron richness of the iminophosphorane-based complexes should be an asset to catalyze reduction processes because of the improved hydridic character of the M-H in the active catalyst. In that context, Fryzuk's group investigated hydrosilylation reactions with Co^{II} complex featuring amine tethered enamido-iminophosphorane ligands (**C6**). The hydrosilylation of 1-hexene using PhSiH₃ with 0.005 mol.% catalyst led to a modest conversion after 24 h. Nevertheless, the versatility of this ligand system is evidenced by the diversity of Co^{II} complexes that was accessible (Scheme 5).^[24] The reduction of **C6** with KC₈ gave either a π -arene complex or a CH-activated complex depending on the substituent of the N of the iminophosphorane (aryl or TMS respectively). Similarly, **C6** reacted with KBHET₃ to yield either a dihydride bridged dimer or a homoleptic Co complex bearing 2 ligands in presence of respectively an aryl or a TMS substituent on the iminophosphorane.



Scheme 5 : Reactivity of Co^{II} complexes bearing an amine tethered enamido-iminophosphorane ligand

C-C coupling reactions are another class of catalytic processes for which mono(iminophosphorane) (N,N,N) metal complexes were employed. The group of Wang focused on nickel(II) complexes featuring a variety of N-based iminophosphorane ligands belonging either to the L₂X or L₃ family.

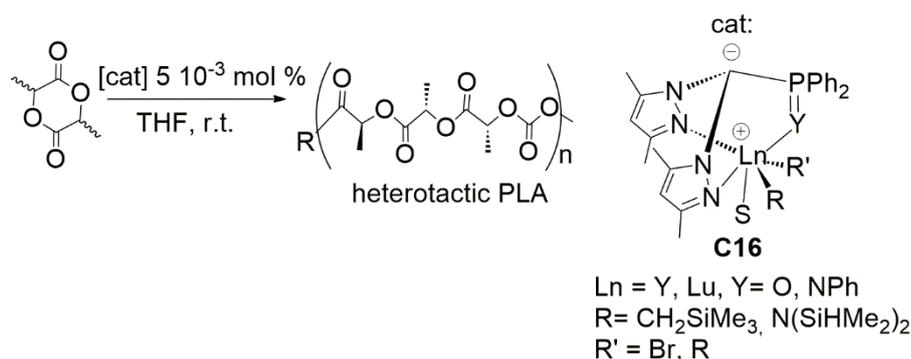


Scheme 6 : Ni complexes as catalysts for Negishi coupling

They compared a series of pincer quinoline based Ni complexes (**C7-C12**)^[25] for the cross-coupling of arylzinc and aryltrimethylammonium salts (Scheme 6). The reactions were conducted in a THF: NMP mixture at 80-85°C, 0.5 mol % of catalyst was used for the coupling with arylchloride and 2 mol.% with ammonium salts. They established that complexes with a tridentate ligand perform better than those with a bidentate or a tetradentate one. Among them, **C9** was the most efficient. This was ascribed to its better donor ability, nevertheless it performs better than **C8** that may be electron richer. Another series of Ni^{II} complexes featuring an amido based ligand (**C13-C15**) was evaluated for the Negishi coupling of aryl ammonium salts.^[26] In that case, **C13** was shown to be more efficient than **C14** or **C15**, but this observation was not rationalized.

2.1.3 L₃ (N,N,N) ligands

Other neutral L₃ ligands were developed by the group of Cui who synthesized bis(pyrazolyl)-iminophosphorane ligand and prepared their zwitterionic heteroscorpionate rare-earth metal complexes (**C16**, Scheme 7).^[27] Dialkyl Lu and Y complexes with either a phosphine oxide or an iminophosphorane coordinating group displayed high activity for the *rac*-lactide ROP at room temperature in THF (conversion of about 90 % within 15 min at 1:200 initiator:monomer ratio). Comparable performances were reported for phosphine oxide and iminophosphorane based initiators. Differences depending on the metal were found: yttrium-based catalysts exhibit higher reactivity while lutetium-based ones present a slightly better heteroselectivity. The selectivity can be further increased by employing initiators with a σ -halogen ligand.

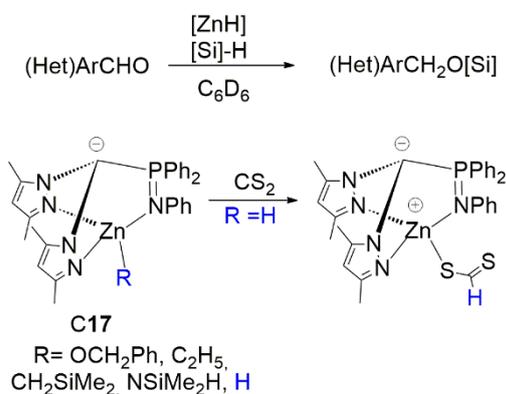


Scheme 7 : Lactide ROP with zwitterionic heteroscorpionate rare-earth metal initiators

Lately, zwitterionic Ca^{II} complexes featuring such an iminophosphorane scorpionate ligand with a phenyl or *o*-anisyl substituent on the N atom were synthesized and evaluated as initiators of the *rac*-lactide ROP.^[28] Depending on the substituent on the iminophosphorane N atom, a different coordination mode was observed: the complex with PPh₂=NPh exhibited a κ^3 -(N,N,N) coordination while those featuring the PPh₂=N(2-OMe-C₆H₄) moiety showed a κ^4 -(N,N,N,O) coordination. While at 25°C in THF both complexes lead to atactic poly lactides in a controlled manner. At low temperature (-78°C) the tacticity of the obtained polymer differs. The initiator with a P=NPh moiety forms a polymer with heterotactic sequences ($P_r = 0.84$) while the κ^4 -N,N,N,O complex led to isotactic poly lactides ($P_m = 0.78$). This was rationalized by the decrease of the swing rate of the side arm.

This ligand was also employed to prepare zinc complexes **C17**. Benzyloxy-, amido-, and alkyl-zinc complexes are able to catalyze the lactide polymerization. In THF at 30°C, better performances both in terms of activity and isoselection were reported for the benzyloxy complex.^[29] Moreover, it was transformed upon reaction with phenylsilane into a hydride complex and the latter was used to catalyze the hydrosilylation of benzaldehydes.^[30] Substituted benzaldehyde including 2-thiophene-

and 2-pyridyl-carboxaldehyde were reduced in C_6D_6 at $25^\circ C$ using either $PhSiH_3$ or Ph_2SiH_2 (Scheme 8). Of note, the reaction of the hydride complex with CS_2 afforded the insertion product.



Scheme 8 : Zwitterionic heteroscorpionate Zn-H complex: reactivity with CS_2 and hydrosilylation catalysis.

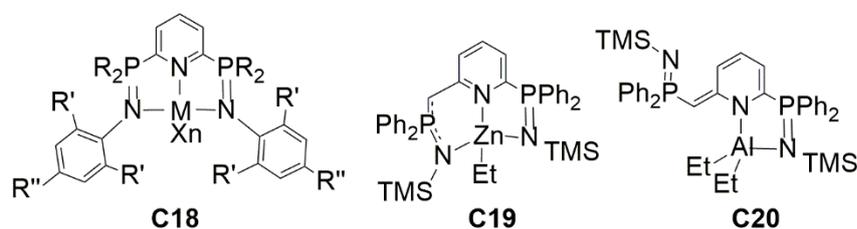
On the whole, mono(iminophosphorane) (N,N,N) metal complexes were investigated only in a dozen of reports focusing on a relatively short list of metals: rare-earth ones, Ti, Co, Ni, Zn, and Al with some applications in polymerization (of polar and non-polar monomers), cross-coupling reactions, and hydrosilylation reactions. In the following part, we will focus on bis(iminophosphorane) (N,N,N) ligands that were more studied but most papers only describe their coordination chemistry. Those ligands feature two lateral iminophosphoranes and differ by the nature of the central coordinating function that can be a N-heterocycle (pyridine or pyrrole anion), an amide or an amine.

2.2 Bis(iminophosphorane) ligand

2.2.1 With a central N-heterocycle

2.2.1.1 A central pyridine

A series of first row metal (V, Fe, Co, Ni) complexes featuring sterically hindered bis(iminophosphorane)pyridine L_3 ligands (Figure 3, **C18**) were synthesized, characterized, and evaluated for ethylene polymerization using MAO as the activator.^[31, 32] The V complexes were shown to give the higher molecular weight polymers.



$R = Ph, Cy, R' = Me, iPr, R'' = Me, H$

$M = Fe, Co, V \quad X = Cl, Br \quad n = 2, 3$

Figure 3 : (N,N,N) pyridine based initiators for polymerization reactions

Wang and coworkers developed a dissymmetric (N,N,N) pyridine based ligand where a CH_2 group is introduced in between the N-heterocycle and one of the P atoms. Tridentate coordination was

observed with Zn^{II} and bidentate one with Al^{III} (Figure 3, **C19**, **C20**). Those complexes were employed to catalyze the ROP of ϵ -caprolactone. The polymerization conducted at high temperature gave low conversion and was accompanied by intramolecular chain transfer.^[33] The coordination of this ligand to metalloids (Sn^{II} and Pb^{II}) and Yb^{II} was later reported.^[34]

For our part, we synthesized a more flexible bis(methyliminophosphoranyl)pyridine ligand and described its coordination to Cu^I and Cu^{II} (Figure 4), as well as low-valent f-elements (Yb^{II}, Tm^{II}, Sm^{II}, U^{III}). We evidenced the hemilability of the iminophosphorane with Cu^I, and the pincer coordination mode with Cu^{II}. **C21** was evaluated as a catalyst for cyclopropanation and [3+2] cycloaddition reactions.^[35] Hemilability was also observed with phosphaytterbocene complexes depending on the substitution pattern at the P atom.^[36] This phenomenon is accompanied by a η^5 (in **C23**) to η^1 switch for the phosphole ligand (in **C24**) that can be evidenced by a change of the $^1J_{Yb,P}$ constant. The coordination to iodide salts of low-valent f-elements (Ml_x, M=Yb, Tm, Sm, U, x=2,3) demonstrated the adaptability of this ligand allowing to observe the electron transfer from the metal to the ligand (either to the pyridine core or to an ancillary ketone).^[37]

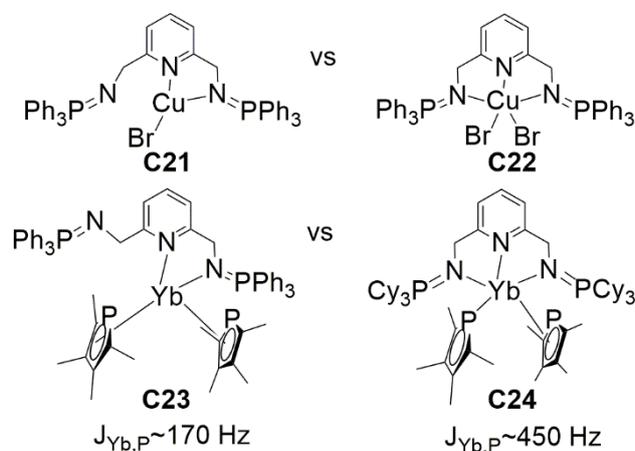
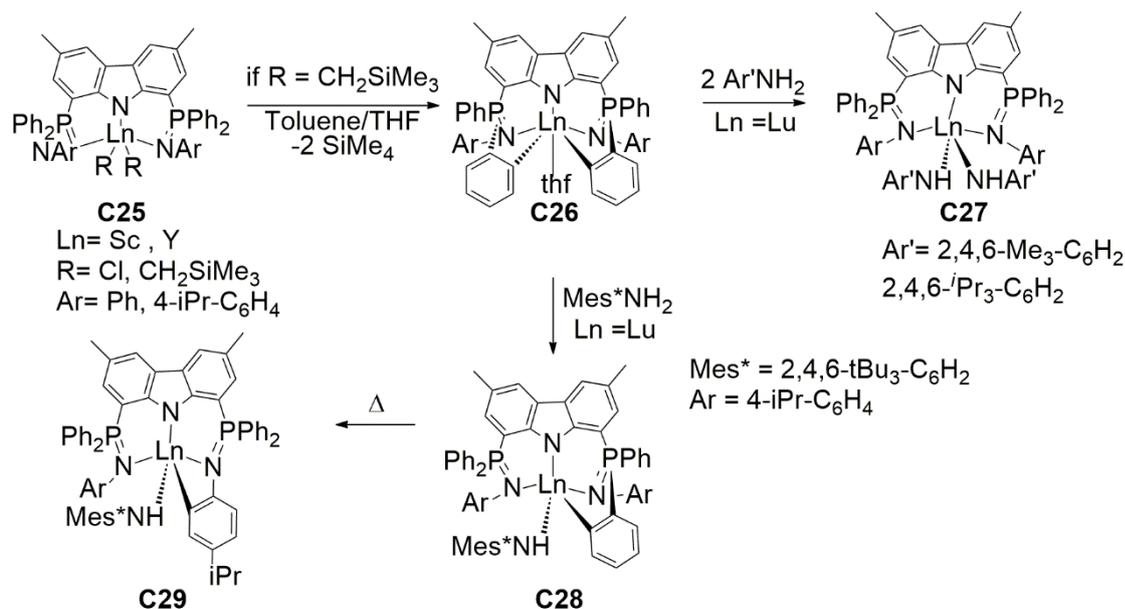


Figure 4 : Hemilability in bis(methyliminophosphoranyl)pyridine complexes

2.2.1.2 A central anionic pyrrole

Replacing the central pyridine by an anionic nitrogen donor led to a L₂X type ligand that is more appropriate to bind to rare earth metals. Thus, the group of Hayes investigated the coordination of monoanionic carbazole based ligand (**L3**, Figure 5) and isolated monomeric dichloro rare earth (Ln= Y, Sc) **C25** complexes by salt metathesis.^[38] Dialkyl complexes (Ln= Lu, Y) are not stable and evolve via an intramolecular metalative alkane elimination process involving the P-phenyl groups (Scheme 9).^[38, 39] Those ortho-metalated Lu (**C26**) complexes reacted with bulky anilines to give the bis(anilide) **C27** compounds resulting from metallacycle ring opening (Scheme 9).



Scheme 9 : Rare earth complexes featuring a bis(iminophosphorane)carbazole ligand

With the very bulky 2,4,6-tri-*tert*-butylaniline only one metallacycle opened to deliver the mono(anilide) **C28** complex which underwent a thermal rearrangement leading to the isolation of **C29** resulting from the metalation of the N-aryl substituent.^[40] These transformations occurred by direct metalation exchanges without the involvement of a transient imido complex.

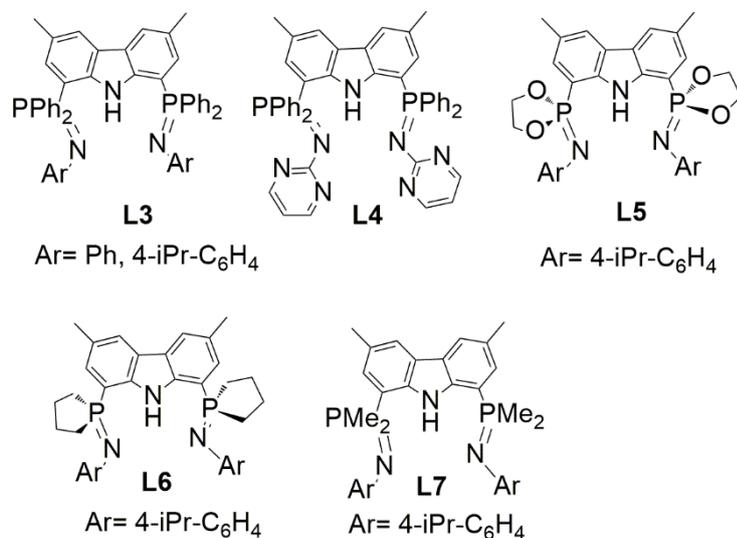
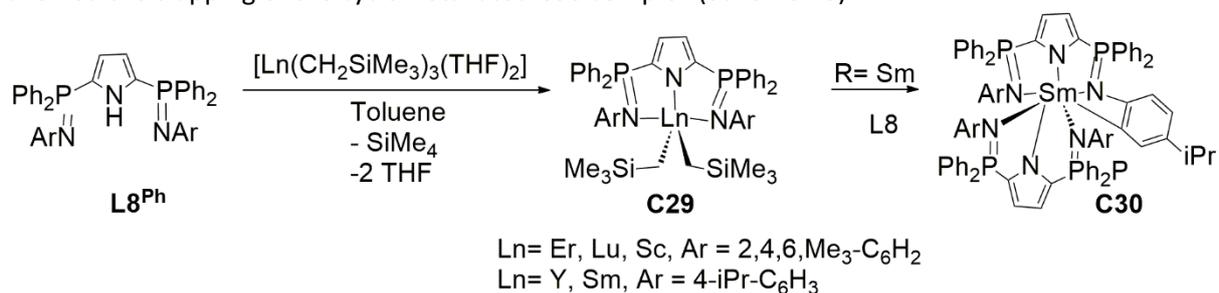


Figure 5 : Structures of carbazole based (N,N,N) ligands

In order to avoid the cyclometalative decomposition, the nature of the P and N substituents were changed (**Figure 5**). Introduction of pyrimidine at the N atoms (**L4**) suppressed the C-H activation process, but the migration of the 2 alkyls from the metal to the pyrimidine rings led to a dimer exhibiting dearomatized pyrimidine rings. The substituents on the P atoms were also modified in particular the introduction of phosphorus rings (**L5-L6**) was expected to constraint the geometry of the lutetium complexes and therefore disfavor the cyclometallation process. Indeed, no CH-activation was observed for dialkyl lutetium complexes featuring dioxaphospholane **L5** but they decomposed via the insertion of the dioxaphospholane rings into the Lu-alkyl bonds so that a bimetallic alkoxide complex was isolated.^[41] In the presence of diphospholane groups (**L6**), one of the N-aryl substituent is

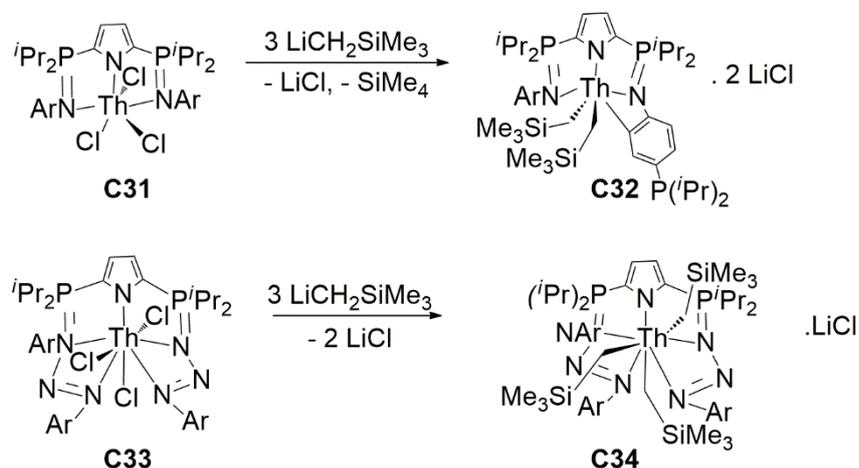
orthometallated while in the presence of a dimethylphosphino group (**L7**) CH-activation of the PMe_2 moieties was observed.^[42]

Keeping the idea of disfavoring CH-activation, Hayes and coworkers developed a pyrrole based bis(iminophosphorane) ligand (**L8^{Ph}**) which exhibits a larger bite angle that should prevent orthometalation. They isolated its dialkyl rare earth complexes **C29** ($\text{Ln} = \text{Lu}, \text{Sc}, \text{Er}$), that showed high thermal stability in solution (Scheme 10).^[43] Coordination of larger rare-earth elements was also investigated:^[44] the dialkyl yttrium complex was resistant to cyclometallation while its samarium congener was much more reactive. It underwent a rapid orthometallation of the N-aryl substituent and further evolved to give a dinuclear species. The addition of an additional equivalent of ligand allowed the trapping of the cyclometallated **C30** complex (Scheme 10).



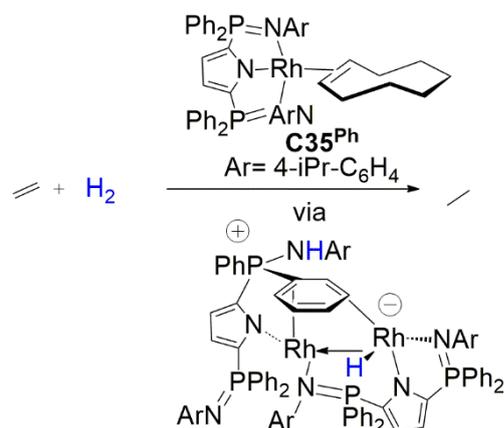
Scheme 10 : Dialkyl rare earth supported by a bis(iminophosphorane)pyrrole ligand

More recently the stability of trisalkyl thorium(IV) complexes supported by either a bis(iminophosphorane) ligand or its phosphazide congener was compared (Scheme 11). Cyclometallation of the N-aryl substituent was observed in **C32** but not in **C34**.^[45]



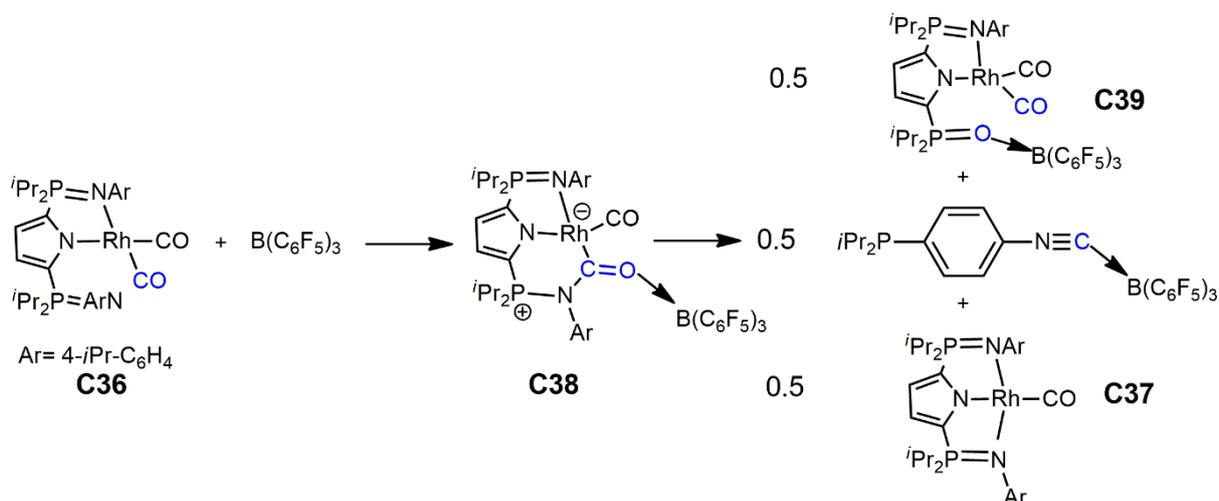
Scheme 11 : Thorium(IV) complexes supported by bis(iminophosphorane) or bis(phosphazide) ligands

The bis(iminophosphorane)pyrrole based ligand was also coordinated to transition metals. Rh^I complexes were shown to activate H_2 or CO , in both cases the iminophosphorane was shown to participate to the reaction. In **C35^{Ph}**, the cyclooctene can be substituted by olefins or diphenylacetylene. Under an H_2 atmosphere, hydrogenation takes place.^[46] The heterolytic cleavage of H_2 resulted in a bridging dirhodium hydride complex with a protonated iminophosphorane ligand evidencing its participation in the H_2 activation process (Scheme 12). In the presence of ethylene, the olefin complex was reformed, so that **C35^{Ph}** catalyzed the hydrogenation of ethylene under ambient conditions.



Scheme 12 : Hydrogenation with a (N,N,N) Rh complex involving cooperative H₂ activation

Following this work, the same group investigated the reactivity of the dicarbonyl complex **C36**. They hypothesized that the iminophosphorane present in the ligand structure may be able to activate CO in presence of a Lewis acid taking inspiration from FLP chemistry.^[47] In this case, the (N,N,N) ligand featured isopropyl groups in place of phenyls at the P atoms to exacerbate the electron density at the N atoms. Both [(ⁱPr₂NNN)Rh(CO)₂] with a κ²-N,N bonding motif and the mono carbonyl [(ⁱPr₂NNN)Rh(CO)] (**C37**) exhibiting a pincer coordination mode could be characterized. The reaction of **C36** with B(C₆F₅)₃ led to an iminophosphorane-borane stabilized metalated formamide complex. It decomposed at ambient temperature via an aza-Wittig reaction.

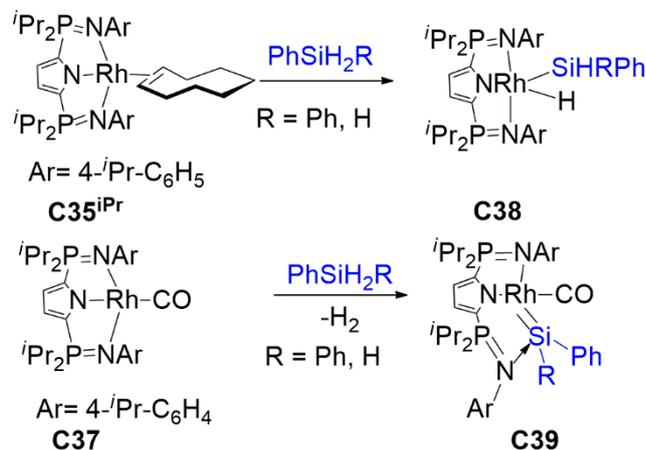


Scheme 13 : Activation and deoxygenation CO metathesis triggered by a (N,N,N) Rh complex

Three different products were isolated *in fine* a Rh dicarbonyl complex with a pending phosphine-oxide-borane group (**C39**), an isocyanide-borane adduct and the monocarbonyl complex **C37** (Scheme 13). In this rather rare example of CO deoxygenation, the ylidic iminophosphorane ligand worked cooperatively with the Lewis-acid to induce the observed transformation.

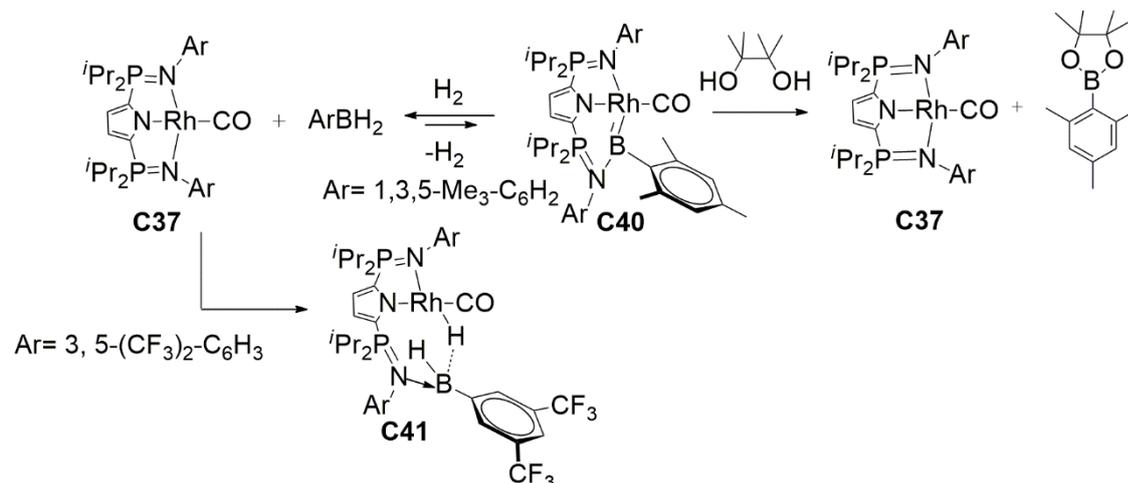
As the electron rich iminophosphorane proved efficient to stabilize electron deficient fragments it was also used to support Rh silylene complexes.^[48] [(ⁱPr₂NNN)Rh(CO)] (**C37**) and [(ⁱPr₂NNN)Rh(COE)] (**C35ⁱPr**) were reacted with silanes. While the olefin complex led to the Rh^{III} **C38** resulting from Si-H oxidative addition, **C37** led to the isolation and characterization of an iminophosphorane stabilized silylene complex (**C39**, Scheme 14). The proposed mechanism involves a Si-H oxidation, the deprotonation of

the Rh-H by the iminophosphorane, followed by the H-migration from Si to Rh, and finally the H₂ release reforming the iminophosphorane which stabilizes the electron-deficient silicon atom. In this example, the energy difference between the hard ylidic N donor ligand and the soft Rh^I metal center is important for the observed reactivity.



Scheme 14 : Rhodium silylene complex stabilized by bis(iminophosphorane) (N,N,N) ligand

Activation of borane with **C37** was then described (Scheme 15). Reaction with mesityl borane led to [(^{*i*}Pr₂NNN)Rh(CO)(BMe₃)] complex **C40** which was isolated in a poor yield because of the reversibility of the dehydrogenation process. Indeed, **C40** gave back the mono carbonyl complex under H₂. Upon addition of pinacol, the boronate derivative formed. With trifluoromethylene borane BH₂BAr (Ar = 3,5 (CF₃)₂-C₆H₃) the reaction stopped at the B-H agostic **C41** complex resulting from decoordination of one iminophosphorane arm.^[49]



Scheme 15 : Activation of B-H bond by a (N,N,N) Rh^I complex

The coordination chemistry of pyrrole based bis(iminophosphorane) ligands was extended to alkaline, earth-alkaline, and coinage metals. **L8**^{*i*Pr} ligands featuring bulky aryl substituents on the N atoms were coordinated to group 13 metals.^[50] Dichloride Ga and In complexes **C42** were isolated as well as neutral (**C43**) and cationic methyl aluminum (**C44**) compounds (Figure 6). Noteworthy with Al^{III}, the coordination mode depends on the steric hindrance, the mesityl **C43** exhibiting a pendant iminophosphorane group.

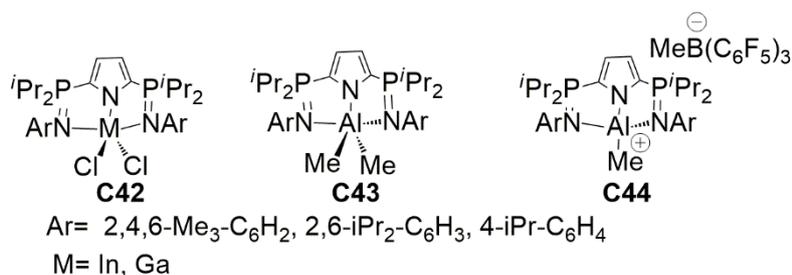
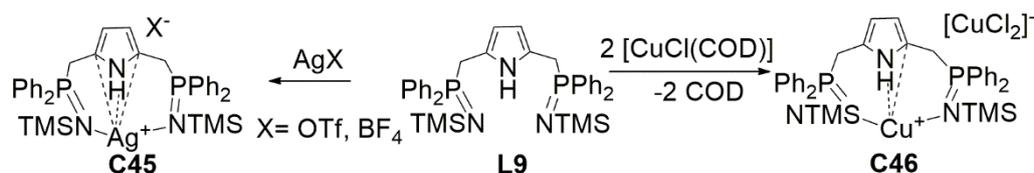


Figure 6 : Group 13 (N,N,N) metal complexes

The (N,N,N) **L9** ligand featuring a methylene spacer between the iminophosphorane functions and the pyrrole ring was also investigated. Its coordination to alkaline earth metals was described.^[51] A monomer, with κ^3 -(N,N,N) coordination was observed with Li while heavier congeners (Na, Cs) formed dimers. In those structures, each metal is coordinated in a bidentate fashion by one ligand (k^2 -(N,N) coordination involving the N pyrrole atom and one iminophosphorane) and η^5 to the pyrrole ring of the second ligand. In magnesium alkyl complexes bidentate (N,N) coordination was observed in the solid state. The coordination to Ag⁺ and Cu⁺ cations also led to monomers (Scheme 16) contrary to that of the bis(phosphine) analogue. In addition to the k^2 -(N,N) coordination, X-ray diffraction analysis and DFT studies suggest the existence of weak π -interaction between the metal and the pyrrole ring, which participate to the stabilization of those structures. η^2 -(C $_{\alpha}$ -N) interaction were evidenced in **C46** and η^3 -(C $_{\alpha}$ -N-C $_{\alpha'}$) in **C45**.^[52]



Scheme 16 : Cu^I and Ag^I complexes featuring a pyrrole based (N,N,N) ligand

2.2.2 With a central amide or amine ligand

Introducing an amide function in between 2 iminophosphorane is another way to develop L₂X type bis(iminophosphorane) (N,N,N) ligands. Three different ligand structures **L10-L13** were investigated and are shown below, the more flexible one (**L13**) was also studied in its amine version (Figure 7).

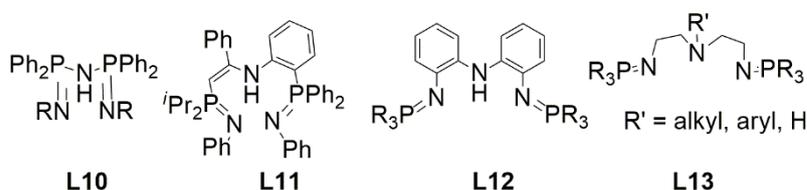


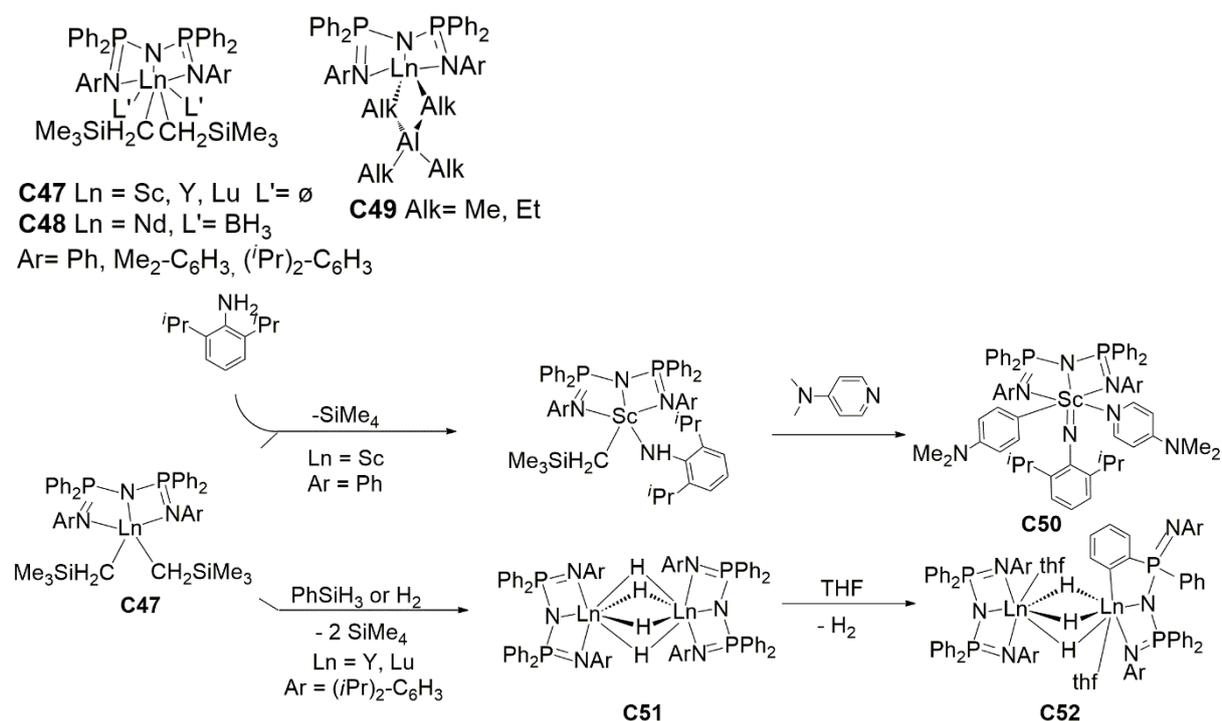
Figure 7 : Structure of (N,N,N) bis(iminophosphorane) ligands featuring a central amide or amine function

Acyclic phosphazene ligand [NH(PR₂=NTMS)₂] (Figure 7, **L10**) has been known since the 60's.^[53, 54] The structure of some of its alkaline, alkaline earth and aluminum complexes were described in the 90's,^[55, 56] while Sarsfield and coworkers compared the structure of [UO₂Cl{ η^3 -N(Ph₂P(NSiMe₃)₂)(THF)}] with that of this bis(iminophosphoranyl)methanide analogue.^[57]

The reactivity and catalytic ability of its rare earth complexes were investigated by the group of Cui. They used dialkyl [Ln(N(PR₂=NPh)₂)(CH₂SiMe₃)₂] (**C47**, Ln = Y, Sc, Lu) and its diborohydrido Nd **C48** congener [Ln(N(PR₂=Ph)₂)(BH₃)₂] for the (co)polymerization of dienes (Figure 8).^[58] These complexes in association with Al*i*Bu₃ and [CPh₃][B(C₆F₅)₄] are highly active for the polymerization of isoprene. The

stereoselectivity of the process depends on the metal center; *trans*-1,4 selectivity was observed with Lu and Sc and *cis* selectivity with the Y complex. **C48** in presence of MgBu₂ was an efficient and *trans*-selective initiator for the polymerizations of isoprene and butadiene. On the other hand, their copolymerization was best achieved with **C47** (Ln= Sc) in presence of Al_iBu₃ and [CPh₃][B(C₆F₅)₄]. More sterically hindered complexes featuring dimethyl- or di(isopropyl)-phenyl in place of phenyl at N were found totally inactive in polymerization. To understand this divergent behavior, Cui's group investigated the interaction between bulky rare earth complexes and AlMe₃ or AlEt₃. They isolated and characterized bimetallic Y-Al **C49** complexes which may resemble the active species operating in aluminum assisted Ziegler-Natta polymerizations processes (Figure 8).^[59]

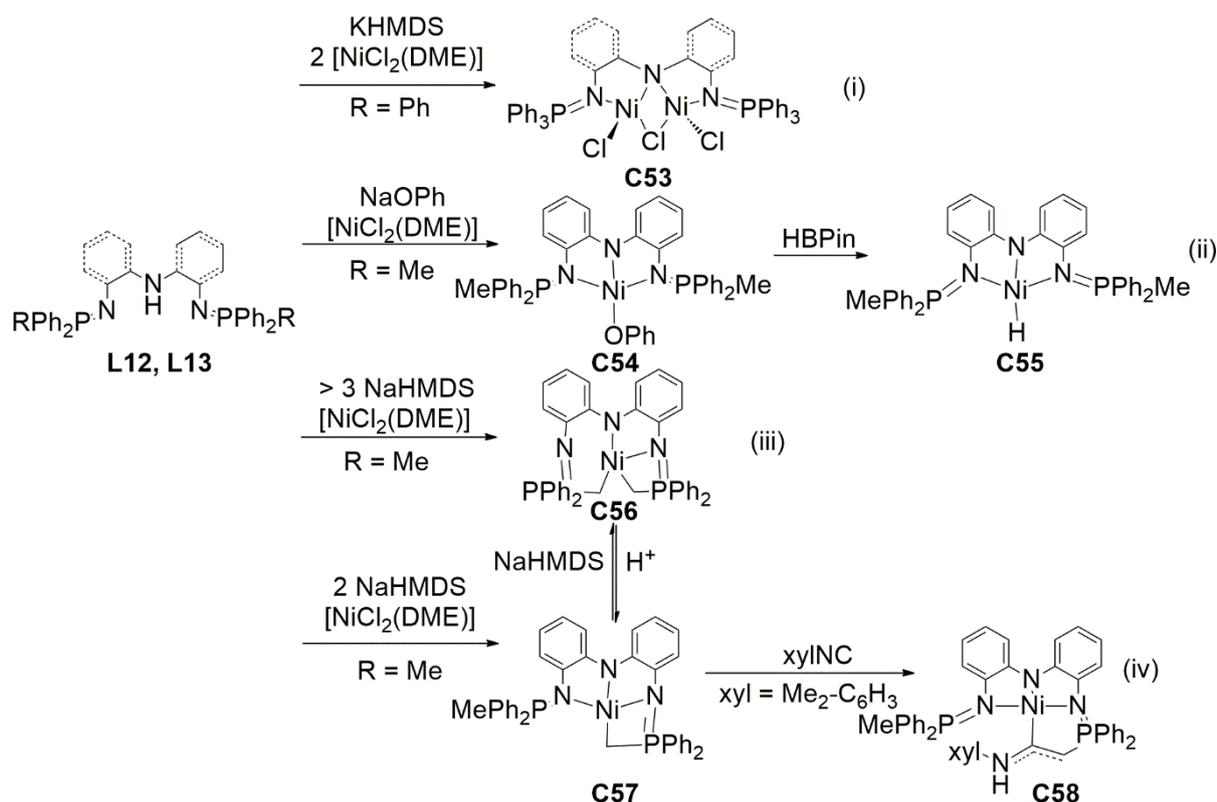
Figure 8 : (N(PR₂=NPh)₂) rare earth complexes



Moreover, **C47** was transformed into a terminal imido complex **C50**. The reaction involved the deprotonation of a mixed alkyl amido complex with dimethylaminopyridine (Scheme 17).^[60] The Y and Lu analogues did not evolve in the same manner and even the introduction of bulky aryl substituent in place of phenyl at P did not enable to isolate the terminal imido complex. However, **C47** complexes (Ln= Y, Lu) were shown to react with H₂ or silane to form dinuclear dihydro complexes (**C51**) with μ²-bridging hydrides (Scheme 17).^[61] The addition of THF induced the intramolecular activation of a sp² C-H from the P-Ph group via H₂ release yielding a phenyl-yttrium dimer **C52** with bridging hydrides.

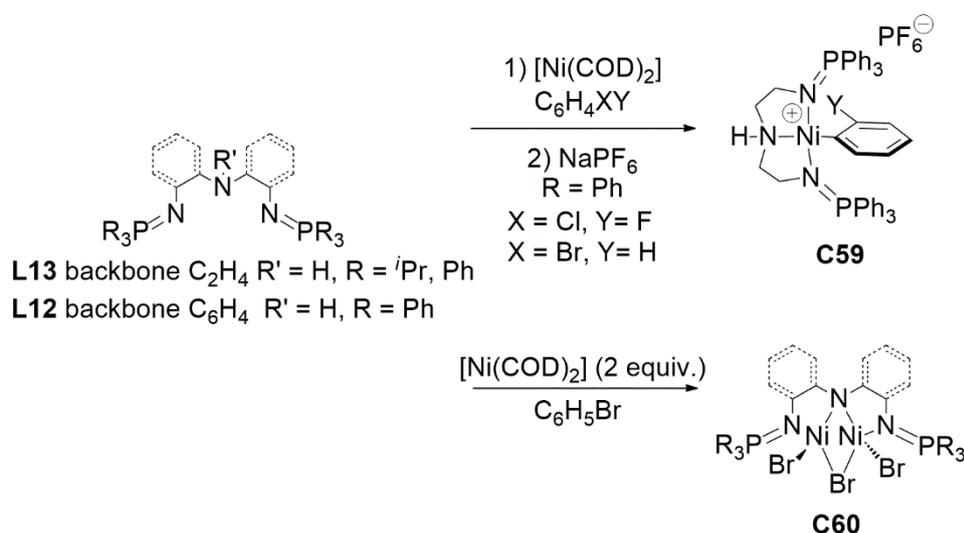
Scheme 17 Preparation of terminal imido scandium complex (top) and hydrido rare earth metal dimers

The other ligand structures presented in Figure 7 (**L11-13**) were coordinated to group 10 metals (Pd, Ni). The group of Wang investigated a series of amido based Ni complexes as catalysts for C-C coupling reactions. The Ni-Cl complex supported by the amido ligand **L11** was an efficient catalyst for the Kumada and Negishi coupling with aryl chlorides (see (N,N,P) ligand section for further details).^[62, 63]



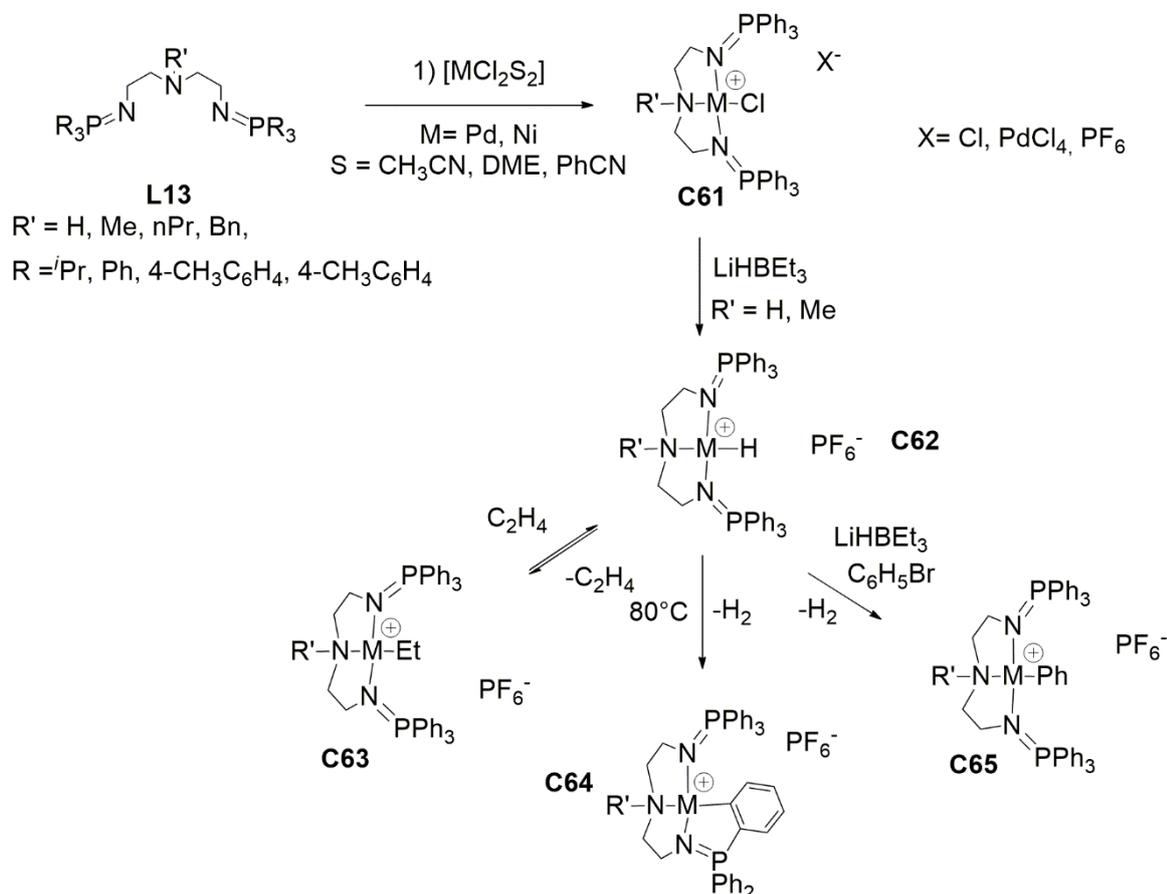
Scheme 18 : Nickel complexes supported by bis(iminophosphorane)-amido ligands

L12 and **L13** ligands led to Ni the dimer **C53** upon metalation with $[\text{NiCl}_2(\text{DME})]$ in presence of KHMDS (Scheme 18 (i)).^[64] The formation of a mononuclear Ni complex was not observed with only 1 equivalent while it was isolated later by another group using a slightly different ligand (NPPH₂Me instead of NPPH₃) and employing sodium phenoxide as a base. Complex **C54** yielded a hydride complex **C55** upon treatment with pinacolborane (Scheme 18 (ii)).^[65] The deprotonation of the methyl substituent on the P atom with excess $[\text{NaN}(\text{TMS})_2]$ resulted in the formation of a tricyclic dialkyl complex **C56** in which one iminophosphorane arm has been decoordinates (Scheme 18 (iii)). The use of only 2 equivalents of base allowed to retain both iminophosphorane coordination leading to a 4-membered Ni-metallacycle **C57**. The latter could be expanded by the insertion of isocyanide (**C58**, Scheme 18 (iv)).^[65]



Scheme 19 : Reactivity of (N,N,N) ligands with $[\text{Ni}(\text{COD})_2]$

Interestingly the reaction of those ligands with $[\text{Ni}(\text{COD})_2]$ led to different complexes.^[66] While the reaction of **L13** ($R = \text{Pr}, \text{Ph}$) with this Ni^0 precursor led to Ni metal, in presence of an aryl halide a mononuclear Ni-aryl species (**C59**) was isolated. The use of 2 equivalents of $[\text{Ni}(\text{COD})_2]$ with either **L12** or **L13** led to bimetallic Ni-amido **C60** complexes (Scheme 19).



Scheme 20 : Synthesis and reactivity of cationic Ni (N,N,N) complexes

The coordination of amino-bis(iminophosphorane) **L13** ligands with $[\text{MCl}_2\text{S}_2]$ precursor ($\text{M} = \text{Pd, Ni}$; $\text{S}_2 = (\text{CH}_3\text{CN})_2$ or DME) led to the corresponding cationic square planar complexes **C61** (Scheme 20).^[64, 67] Stephan's group further investigated the reactivity of those nickel complexes which formed cationic hydride Ni-H complexes **C61** upon reaction with LiEt_3BH .^[68] The latter, when heated, underwent an orthometallation accompanied by the release of H_2 giving **C64**. Reversible insertion of ethylene to form **C63** was also showed. On the other hand, reaction of $[(\text{N,N,N})\text{NiH}]$ complex with an hydride donor in bromobenzene led to the corresponding Ni-Ph complex **C65**.

A variety of (N,N,N) bis(iminophosphorane) ligand skeletons was investigated and found able to bind to a wide range of metals: f-element as well as early and late transition metals. Moreover, they proved able to stabilize different type of reactive complexes: hydride, silylene, or imido species for example. In some cases, the cooperative role of the iminophosphorane was evidenced. Nevertheless, only few of them were used in catalysis (olefin (co)polymerization, hydrogenation).

2.3 Tris(iminophosphorane) ligand

Example of tris(iminophosphorane) NNN ligands are rare. The group of Noels developed $\text{RC}(\text{CH}_2\text{NPR}_3)_3$ derivatives.^[69] Their Cu and Pd complexes **C66** were used for cyclopropanation^[70] and ethylene

oligomerization (Ni and Fe complexes were also evaluated) (Figure 9).^[71] Pd^{II} complexes exhibited the best activity for hexane production in the investigated series.

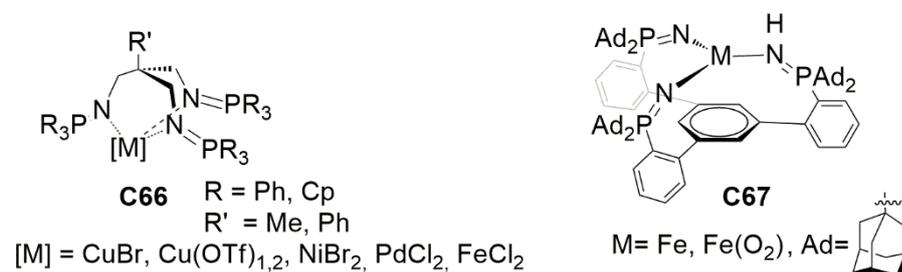


Figure 9. (N,N,N) complexes

Such ligand that combine three hard donors are particularly suitable to support highly oxidized metal centers, as shown lately by the group of Rittle which developed a sterically hindered rigid ligand platform. They reported the isolation of mononuclear Co^{III} complex supported by the tris(imidophosphorane) ligand^[72] as well as the isolation of a Fe^{II} complex **C67** stabilized by a (N,N,N) chelation, brought by 2 imidophosphorane and one iminophosphorane groups. Upon exposure to O₂, the latter led to the corresponding Fe^{III}-superoxo complex.^[73]

On the contrary, the introduction of a phosphine donor in combination with the iminophosphorane would facilitate the coordination to soft metals.

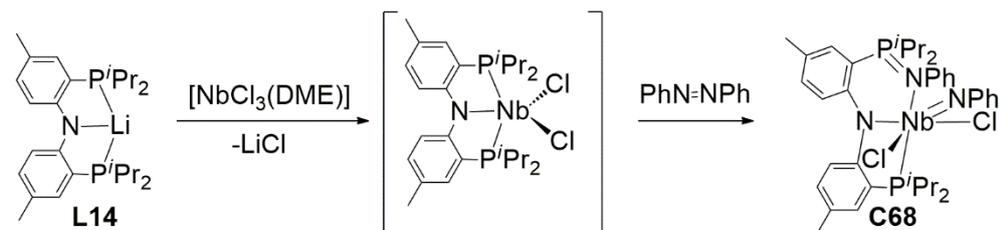
3 (N,N,P) Ligands

3.1 Mono(iminophosphorane) ligands

Mono(iminophosphorane) (N,N,P) ligands generally combine a phosphine and an iminophosphorane with either a N-based heterocycle (pyridine, quinoline, or pyrazolyl ring) or an amide group. The latter association is the most represented, and most often the P=N bond is formed within the coordination sphere of the metal via "N" insertion or transfer to the initial amido bis(phosphine) ligand.

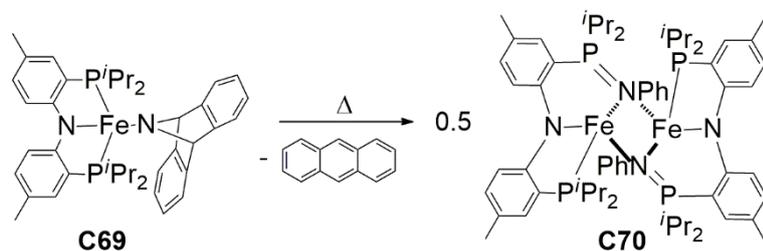
3.1.1 Amido-iminophosphorane-phosphine ligands

The group of Mindiola studied the reactivity of different metal complexes featuring a amido-bis(phosphine) ligand **L14**. In 2006, they described the ability of (P,N,P) Nb^{III} complexes to activate N₂.^[74] On their way to isolate the reactive [(P,N,P)NbCl₂] complex, they showed that it reacted with azobenzene to cleave the N=N bond via a metal-ligand cooperative 4-electron reduction which yielded the imido Nb complex **C68** containing an iminophosphorane (Scheme 21).



Scheme 21 : Isolation of (N,N,P) Nb imide complex

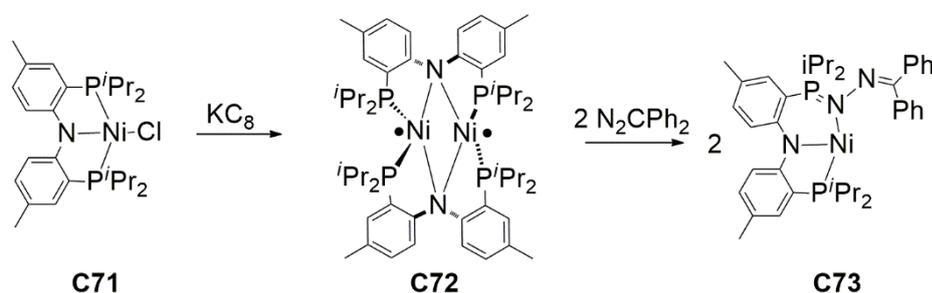
Comparable ligand oxidation was shown to occur within an amido iron(II) complex **C69** bearing the same ligand. Upon thermolysis at 70°C **C70** formed, in which the iminophosphoranes bridge the two metal entities (Scheme 22).^[75] The intermediacy of a Fe^{IV} nitride complex is proposed.



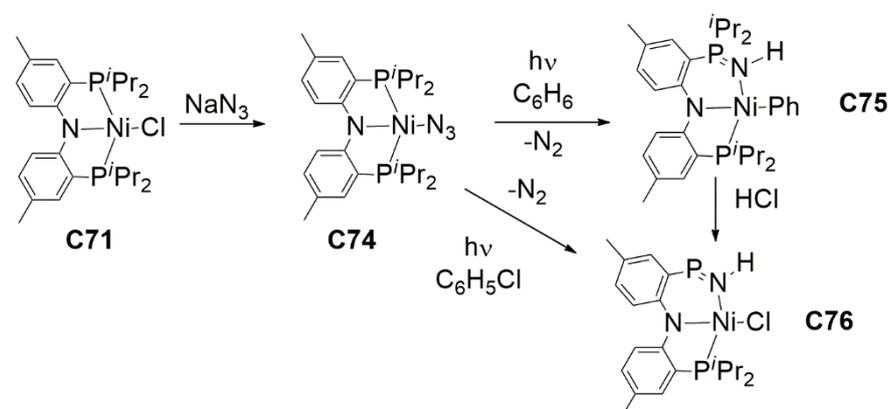
Scheme 22 : (N,N,P) Fe complex via a N-atom transfer from ferrous amido precursor

P=N bond formation within the coordination sphere of Ni was also described. Indeed, an original T-shaped (N,N,P) nickel complex **C73** was isolated upon reacting a (PNP)Ni^I dimer **C72** with 2 equivalents of diphenyldiazomethane (Scheme 23, (i)).^[76] One of the phosphine group was oxidized into a (phosphoranylidene)-hydrazone. Interestingly, the group of van der Vlugt investigated the reactivity of the nickel(II)-azido complex bearing the same (P,N,P) ligand **C74** (Scheme 23, (ii)).^[77] They showed that the irradiation in benzene led to the iminophosphorane [(N,N,P)NiPh] **C75** complex. DFT calculations are in agreement with the involvement of a Ni^{IV} nitrido derivative evolving via insertion of the nitridyl radical in the Ni-P bond giving an unsaturated imidophosphorane Ni^{II} complex, which is able to achieve the intermolecular C-H activation of the benzene solvent. When the irradiation was performed in chlorobenzene the [(N,N,P)NiCl] **C76** complex was isolated.

(i) Mendiola and Meyer, 2008



(ii) van der Vlugt, 2015



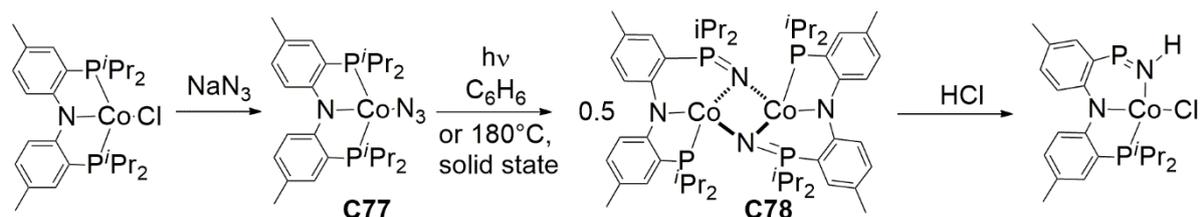
Scheme 23 : From (P,N,P) to (N,N,P) nickel complexes via N-transfer

The reactivity of the cobalt(II) congener is different.^[78] Indeed, activation of [(P,N,P)CoN₃] **C77** could be done photochemically or thermally. Insertion of the N of the transient cobalt nitrido complex gave a dimer in which the cobalt atoms are bridged by the anionic imidophosphorane group **C78** (Scheme

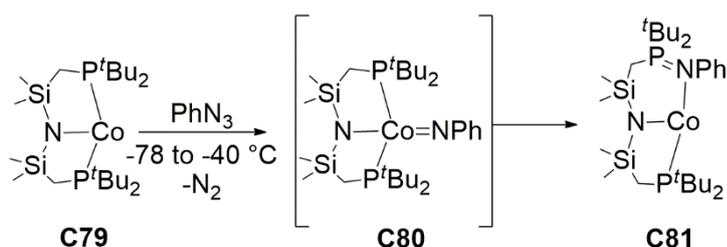
24, (i)). No activation of the solvent was observed. $[(N,N,P)CoCl]$ was obtained upon protonation of the dimer.

Some years before, the group of Caulton has explored the redox chemistry of **C79**, a $[(P,N,P)Co^I]$ complex supported by a different amido-bis(phosphine) ligand (Scheme 24, (ii)).^[79] Its reaction with phenylazide led also to the oxidation of one of the phosphine group to deliver a T-shaped Co^I complex featuring iminophosphorane (N,N,P) **C81**. Low-temperature NMR studies combined with DFT calculations suggested the involvement of a transient $Co(III)$ -imido intermediate **C80**. The obtained Co^I complex did not react under H_2 nor with an additional equivalent of phenyl azide.

(i) van der Vlugt, 2017



(ii) Caulton, 2008



Scheme 24 : Access to (N,N,P) Co complexes

As previously stated there are only few examples of mono(iminophosphorane) (N,N,P) ligand synthesis and coordination. Wang's group used one of those in the Negishi coupling of aryl ammonium salts but the presence of the iminophosphorane did not improve the catalytic performances (see section 2.1.2). The same group prepared a series of nickel complexes supported by amido pincer ligands either di(phosphine)-amido (**C82**), amido-phosphine-iminophosphorane (**C83-84**) or bis(iminophosphorane)-amido (**C85**) derivatives (Figure 10).

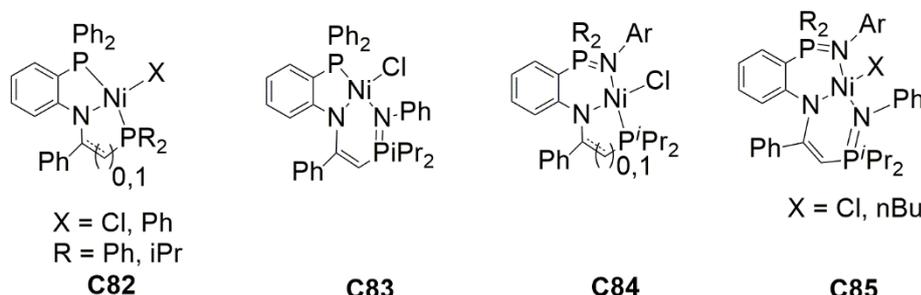
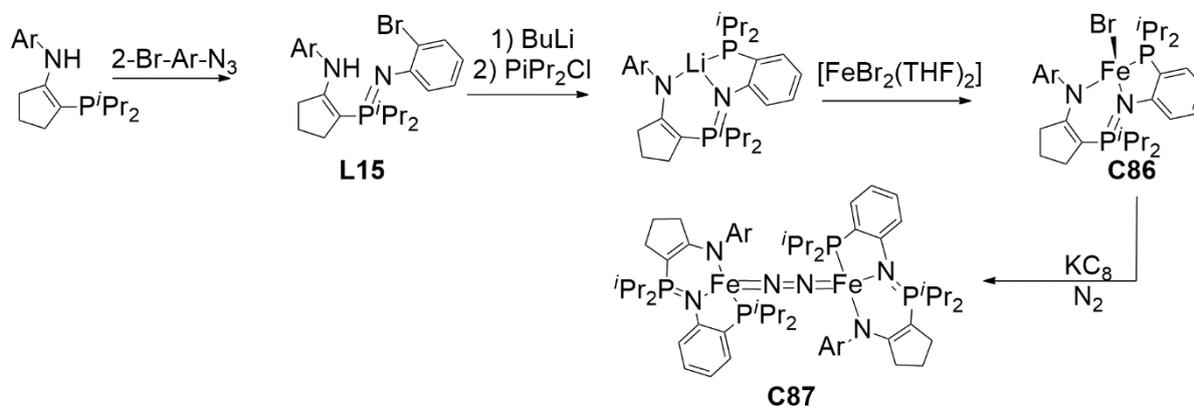


Figure 10 : Amido pincer ligands used as catalyst for C-C coupling reactions

C83-C85 complexes performed better than **C82** in the Kumada coupling of $p\text{-MeC}_6\text{H}_4\text{MgBr}$ and aryl chlorides.^[63, 80] The reactions were conducted in THF at room temperature with a catalyst loading between 2.0 and 4 mol.%. For **C84** they observed a different catalytic activity depending on the metallacycle size, this was not the case for the **C82** complexes. They also showed that amido **C83-C85** complexes are powerful catalysts for the Negishi reaction with aryl chlorides.^[62] The reactions were conducted at 70°C in a 1:1 mixture of THF and NMP at low catalyst loading (0.01 to 1 mol.%). As

commonly observed, the reactions were easier with electron-poor aryl halides and electron rich aryl zinc derivatives. Heterocyclic substrates were tolerated, while the coupling with 2-furyl zinc chloride was less efficient especially with unactivated aryl chlorides.

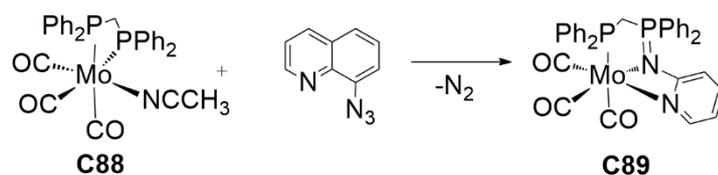


Scheme 25 : Activation of N₂ by an iron complex supported by an amido iminophosphorane (N,N,P) ligand

Another type of amido containing (N,N,P) ligand structure **L15** was developed by the group of Fryzuk (Scheme 25).^[81] The iminophosphorane functionality was chosen because of its excellent σ -donating ability in order to facilitate the activation of N₂. It was introduced by a Staudinger reaction on a cyclopentadienylidene phosphine amine derivative. Upon reduction of the iron(II) complex **C86** under N₂ atmosphere a dimer **C87** in which the iron centers are bridged by the dinitrogen molecule was formed. It was characterized as a high spin complex with a central (N=N)²⁻ moiety. They analyzed how the ligand participates to the activation process and showed that the backdonation from the iron $d\pi$ orbitals into N₂ π^* orbitals is responsible for the activation. The orientation of the metal $d\pi$ orbitals is governed by the large negative charge on the N of the iminophosphorane and the hyperconjugation with the phosphine group.

3.1.2 N-heterocycle-iminophosphorane-phosphine ligands

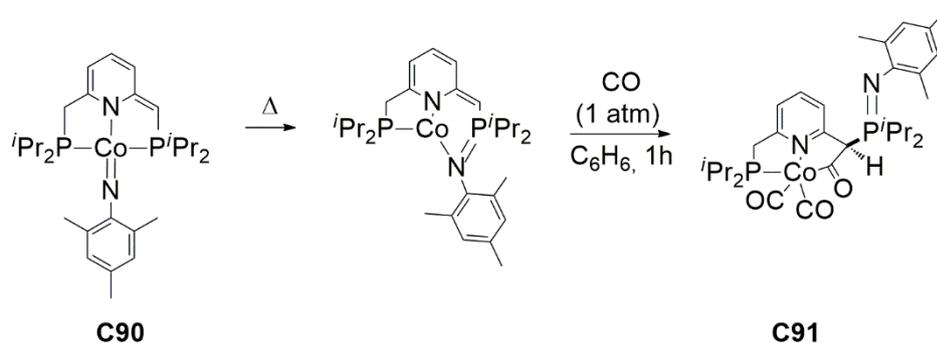
Examples of (N,N,P) mono(iminophosphorane) incorporating a N-heterocycle are rare. The first example of such complex **C89** was described by Bruce and coworkers who evidenced the formation of the iminophosphorane bond by reacting [Mo(CO)₃(PPh₃)(CH₃CN)₂] with 8-azidoquinoline.^[82, 83] They proposed the involvement of a transient nitrene complex and showed that it requires chelating azide derivative. The presence of two vacant coordination sites on the metal was also necessary. In the case of the bis(diphenylphosphine)methane complex **C88** (Scheme 26), the partial decooordination of the bis(phosphine) explained the conversion.



Scheme 26 : Staudinger reaction with the coordination of Mo⁰

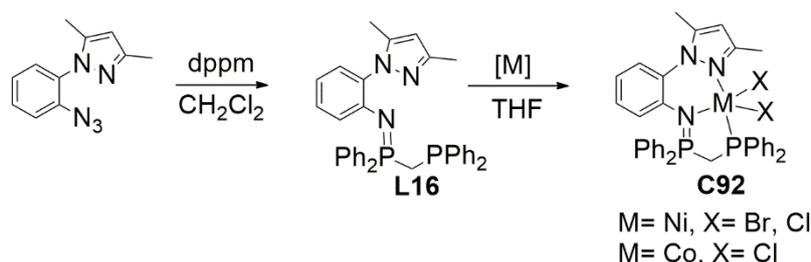
More recently, Chirik's group isolated a rare example of four-coordinate cobalt-imido complex **C90** stabilized by a dissymmetric (P,N,P) ligand (Scheme 27).^[84] Upon heating, N transfer occurred

selectively since the P-N bond formed exclusively on the deprotonated side. This selectivity was explained thanks to DFT calculations by a better thermodynamic stability of this complex compared to its isomer. Addition of CO led to a diamagnetic acyl complex **C91**.



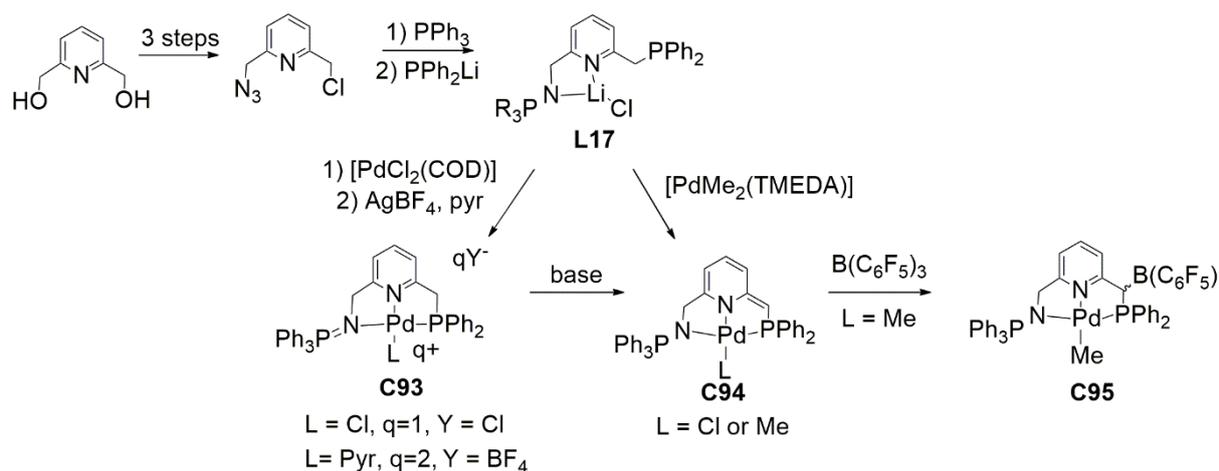
Scheme 27 : Access to Co (P,N,N) complex via N transfer

Dissymmetric (P,N,N) ligands were also directly synthesized. The group of Wang prepared a tridentate phosphine-iminophosphorane-pyrazol ligand **L16** and its cobalt and nickel complexes **C92** (Scheme 28).^[85] Ni **C92** complexes catalyzed the oligomerization of ethylene giving a mixture of C₄ and C₆ products with a productivity reaching 8.5 10⁶ g mol⁻¹ h⁻¹ at 40°C when activated by Et₂AlCl (Al/Ni ratio : 300/1). However, the cobalt **C92** complex required activation with MAO or MMAO and only the latter cocatalyst gave interesting productivity and selectivity.



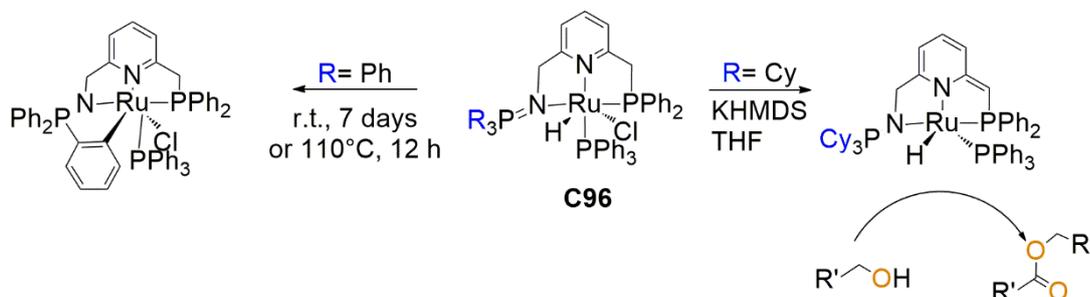
Scheme 28 : (N,N,P) Co and Ni complexes used for ethylene oligomerization

We described Ru(II) complexes featuring a comparable (N,N,P) ligand in which the imidazole is replaced by a NH₂ or NH group and studied their potential in catalytic transfer hydrogenation reactions.^[86, 87] Later we developed another (N,N,P) mono(iminophosphorane) ligand **L17** with a central pyridine scaffold. The synthesis involved the desymmetrization of the lutidine diol allowing access to 2-(azidomethyl)-6-(chloromethyl)pyridine, a key intermediate from which iminophosphorane and phosphine were introduced sequentially. The coordination of these ligands towards Pd^{II} and Ru^{II} was explored. Mono- and di-cationic pincer palladium **C93** complexes were isolated, as well as neutral **C94** resulting from the deprotonation at the benzylic position (Scheme 29). At this position reversible protonation was observed. In addition, C-B bond formation occurred upon reaction with B(C₆F₅)₃ leading to the zwitterionic complex **C95**.^[88]



Scheme 29 : Pyridine based (N,N,P) Pd complexes

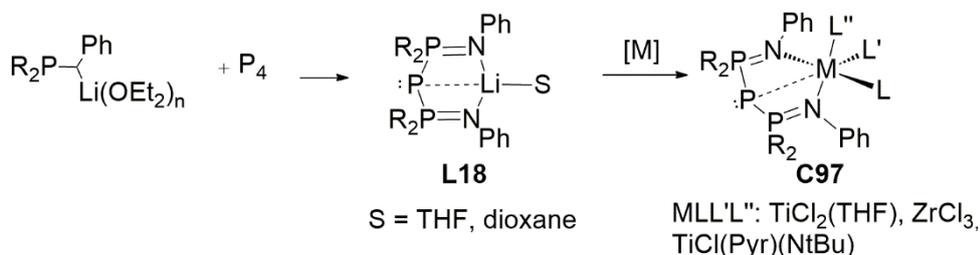
Ruthenium dichloride complexes were successfully synthesized and deprotonated however the stability of the monochloro hydride complexes **C96** depends on the N=P substituent. While cyclometallation was observed for the N=PPh₃ complex its cyclohexadienyl analogue did not evolve allowing the deprotonation of the benzylic position (Scheme 30).^[89] Therefore, this complex was used as a catalyst for the acceptorless dehydrogenation of alcohols and deliver esters in about 70 % yield after 24 h reaction at reflux.



Scheme 30 : Reactivity of (N,N,P) Ru complexes

3.2 Bis(iminosphosphorane) ligands

The only example of bisiminophosphorane (N,N,P) ligand we could find appeared recently. A. T. Normand *et al.* synthesized a series of group 4 and coinage metal complexes **C97** supported by a bis(iminophosphoranyl)phosphide (BIPP) **L18** ligand (Scheme 31).^[90] Reaction of lithium phosphinamido with excess P₄ led to BIPP lithium derivatives. Their reaction with Ti^{III}, Ti^{IV}, and Zr^{IV} gave monomeric metal complexes in which only electrostatic interaction between the central phosphorus and the metal was evidenced. This allowed further reactivity with coinage metal centers; heterobimetallic Ti-Au and Ti Cu^I complexes were isolated.



Scheme 31 : BIPP complexes

The authors conducted an important theoretical study on the nature of P-P bond in those complexes and concluded to a normal covalent bond and not a dative one.

The scarcity of bis(iminophosphorane) (N,N,P) complexes compared to their (N,N,N) congeners is surprising and would probably require further development.

There are more examples of ligand associating iminophosphorane and a C donor, those (N,N,C) ligands result either from a CH-metalation or incorporate a N-heterocyclic carbene.

4 (N,N,C) Ligands

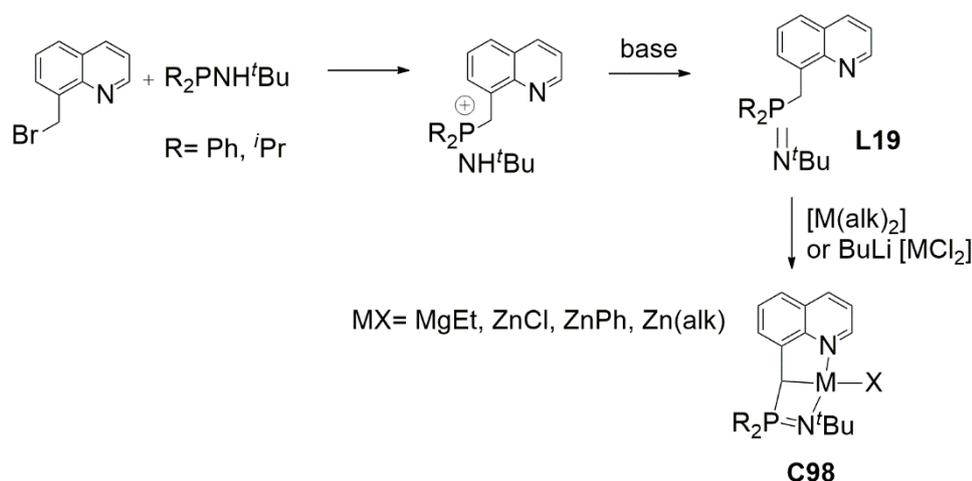
Different types of (N,N,C) iminophosphorane ligands were described, the majority of them containing only one P=N function

4.1 Mono(iminophosphorane) ligands

Mono(iminophosphorane) (N,N,C) ligands will be presented according to the nature of C-donor groups that can be an alkyl, an aryl or a NHC moiety.

4.1.1 Mono(iminophosphorane) ligand with an alkyl coordination site

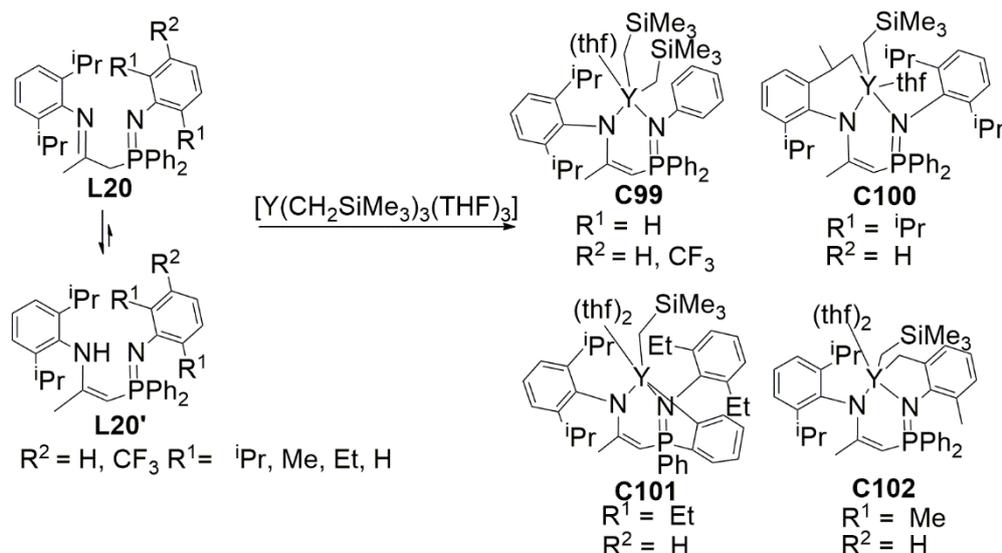
The group of Wang developed an original synthesis of a pincer NCN ligand with a central sp^3 C donor **L19**.^[91] The nucleophilic substitution of an aminophosphine on 8-bromomethylquinoline gave access to the aminophosphonium salt, the subsequent deprotonation led to the monoiminophosphorane ligand which was coordinated to Mg^{II} and Zn^{II} (Scheme 32).



Scheme 32 : (N,C,N) Zn and Mg complexes

C98 were evaluated as catalysts for the ring opening polymerization of ϵ -caprolactone. The alkyl magnesium complex allowed a total conversion of the monomer within minutes at $0^\circ C$ in toluene at a monomer:catalyst ratio of 100:1. Zinc complexes required the addition of excess benzyl alcohol to be active, and the polymerization was slower than with the Mg initiators. In the presence of the alcohol, the protonation at the benzylic position led to the active catalyst supported by the (N,N) ligand. The polymerization in presence of BnOH worked for both Mg and Zn initiators.

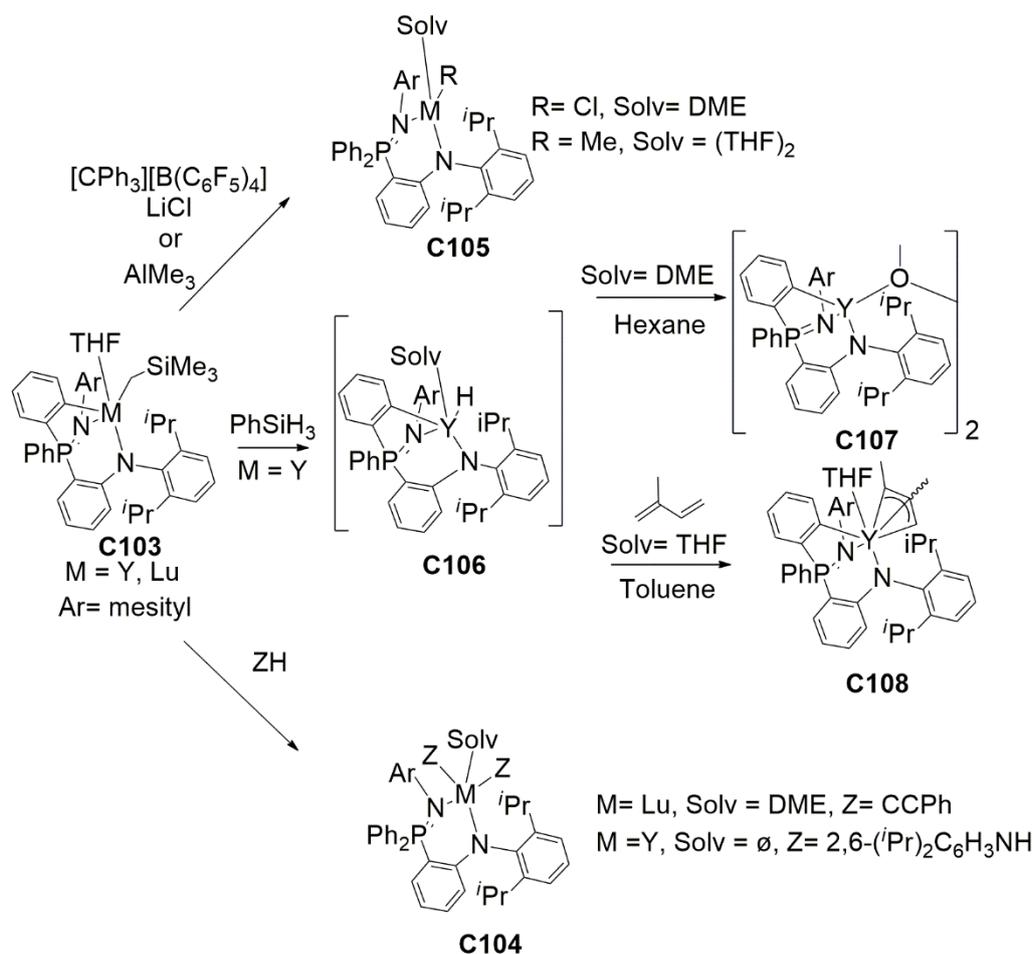
(N,N,C) yttrium complexes with a peripheral C-donor group were obtained thanks to CH-activation.^[92] Of note, **L20** exists under imine and/or amine forms depending on the nature of the substituents (Scheme 33). Nevertheless, upon reaction with the Y-alkyl precursor the imine isomer gradually transformed into the amine one so that only amino-iminophosphorane-alkyl complexes were isolated. The steric congestion was essential for the CH-activation to occur and determined also its locus. As shown in Scheme 33 both sp^3 - (**C100**, **C102**) or sp^2 -CH (**C101**) activations were observed. The activated position was dependent on the steric bulk of the aryl substituents at the iminophosphorane. All these complexes were able to polymerize polar monomers such as lactide, ϵ -caprolactone or methyl methacrylate.



Scheme 33 : Synthesis of (N,N,C) Y-alkyl complexes via CH-activation process

4.1.2 Mono(iminophosphorane) (N,N,C) ligand with an aryl coordination site

The same group further exploited the activation of sp²-CH bond by rare earth metals to synthesize anilido iminophosphorane rare earth complexes **C103** (M=Y, Lu) (Scheme 34).^[93] Both were shown to be excellent initiators for the lactide polymerization leading to atactic polylactides.

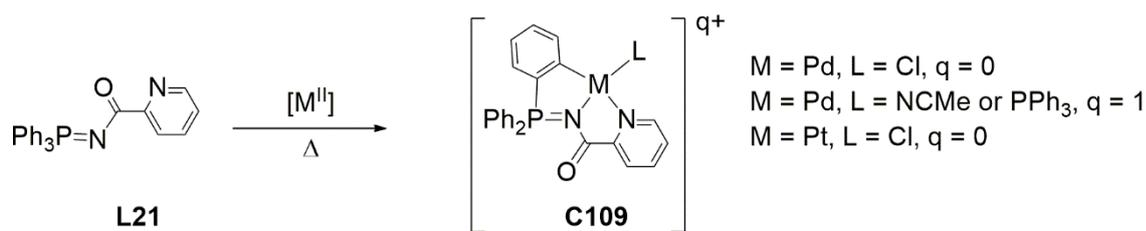


Scheme 34 : Reactivity of an anilido based (N,N,C) Y complex

The fate of the M-C bonds was also investigated, protonation occurred upon exposure of the Y complex to moisture leading to an hydroxo bridged dimer. The Y complex also reacted with 2 equivalents of an aniline derivative to form the bis(anilido) complex exhibiting a κ^2 -(N,N) ligand **C104**.^[93] Similarly the addition of phenylacetylene (2 equiv.) on the Lu complex led to the (N,N) bis acetylide complex.^[94] The Lu counterpart gave access to the chloride or methyl **C105** complex upon reaction with the trityl cation in presence of LiCl or AlMe₃ respectively.

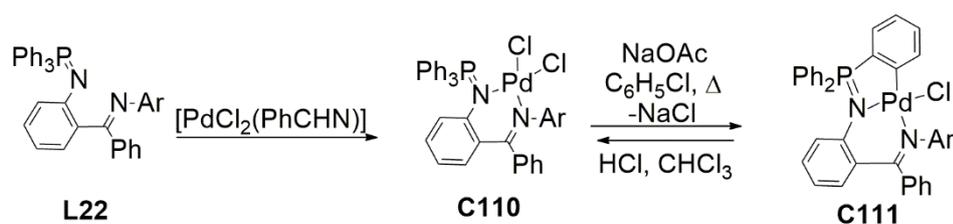
Furthermore, reaction of the Y-alkyl complex with phenylsilane led to a M-H **C106** intermediate that could not be trapped. It reacted further with DME to form a methoxy bridged dimer **C107** or with isoprene in toluene to give the η^3 -isopentene adduct **C 108** (Scheme 34).^[94]

Activation of sp² C-H was also achieved with late transition metals. Indeed Urriolabeitia reported in 2005 the orthometalation of an iminophosphorane-aniline **L21** derivative by Pd^{II} and Pt^{II} precursors leading to **C109** (N,N,C) metal complexes (Scheme 35).^[95, 96] The Pd complexes were employed as catalysts for the Mizoroki-Heck reaction between phenyl iodide and methyl acrylate. Moderate to good performances were observed and no major difference were found between bidentate and tridentate precatalysts. The active catalytic species were identified as Pd nanoparticles formed upon decomposition of the complex.^[96]



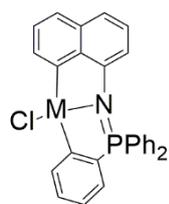
Scheme 35 : Synthesis of Pd and Pt (N,N,C) complexes

For the synthesis (N,N,C) Pd complexes featuring imine-iminophosphorane linkage, the group of Mehrkhodavandi proceeded in 2 steps: preparation of the (N,N) Pd dichloride **C110** complexes and then orthometallation by thermal activation (Scheme 36).^[97] They showed that the M-C bond can be selectively cleaved with a stoichiometric addition of acid.



Scheme 36 : Imine-based (N,N,C) Pd complexes

A quinoline based (N,N,C) Ni complex exhibiting a M-phenyl bond was investigated by Wang and coworkers as a catalyst for C-C coupling and was found less efficient than the (N,N,N) analogues (see Scheme 6).^[25]



M= Pd, Pt

C112

Figure 11 : (N,N,C) metal complexes tested as anticancer agent

Contel, Casini and coworkers also relied on cyclometallated quinoline based iminophosphorane ligands and developed Pt and Pd complexes (**C112**), which were tested as anticancer agents (Figure 11).^[98] The antiproliferative properties of the complexes were evaluated on 3 different types of cancer cell (ovarian, lung, and kidney); the selectivity was generally not pronounced for infected cells compared to non-tumorigenic ones except in the case of the ovarian cancer. No direct interaction with DNA could be evidenced implying a different mechanism for this anticancer activity than for *cis*-platin.

4.1.3 Mono(iminophosphorane) (N,N,C) ligand with an NHC donor

N-heterocyclic carbene (NHC ligand) is probably the most widely used C-based ligand in catalysis, its metal complexes have often shown improved performances compared to phosphine congeners.^[99, 100]

Therefore its σ -donating ligand were associated to those of the iminophosphorane to develop electron-rich tridentate ligands. The group of Wang studied the potential of mixed (NHC) iminophosphorane to propose Ni based catalysts for coupling reactions. Their structures are shown below (Figure 12).^[25, 101, 102] All are active catalysts for the coupling of aryl chlorides with aryl zinc or aryl Grignard reagents, nevertheless the best performances were observed with **C113** and **C115**, which exhibited similar activity.^[102] **C116** was the more sluggish catalyst because of the crowding around the metal center. The Negishi reactions were conducted in a NMP: THF mixture at 70°C with 0.05-0.2 mol.% catalyst. The Kumada reaction were preferentially achieved in THF at room temperature with 2-4 mol.% catalyst loading.

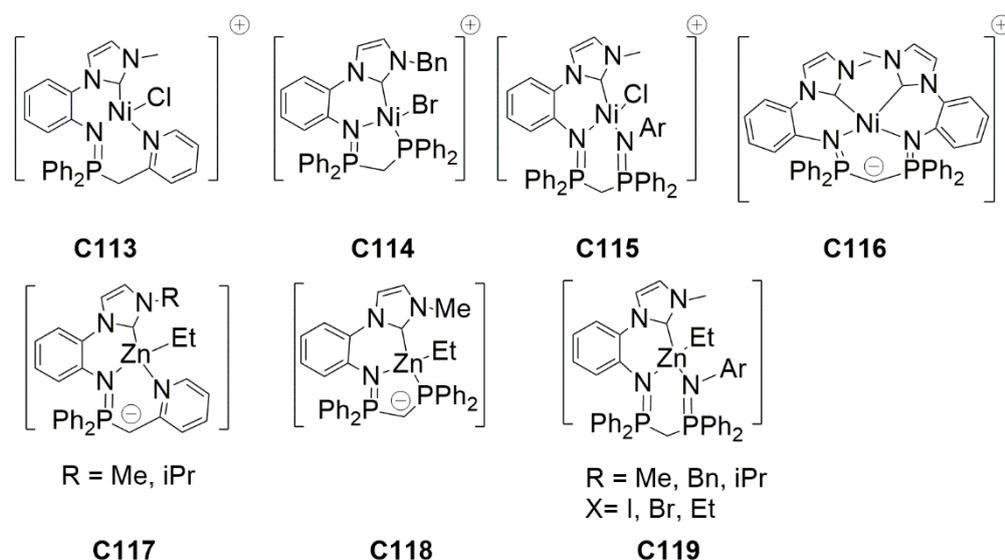
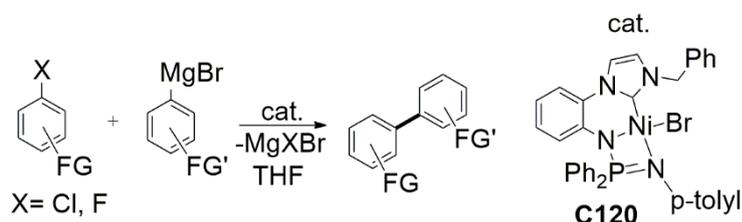


Figure 12 : Ni and Zn complexes supported by polydentate NHC-iminophosphorane ligands

These ligands were also coordinated to Zn^{II} and the obtained complexes (**C117-C119**) used as initiators for the polymerization of *rac*-lactide and ϵ -caprolactone upon activation with benzyl alcohol. **C117** and **C118** exhibit the best activities in the series. The polymerization of up to 1000 equivalents of lactide could be achieved within 24h at room temperature in toluene. The process was much slower with caprolactone.^[103] **C119** were inactive under the same conditions for both monomers.

The same group developed another pincer ligand featuring a phosphoramidate moiety an isolated based NNC Ni complex **C120** which was shown to catalyze the coupling of aryl Grignard reagents with either aryl chlorides and aryl fluorides (Scheme 37).^[101]

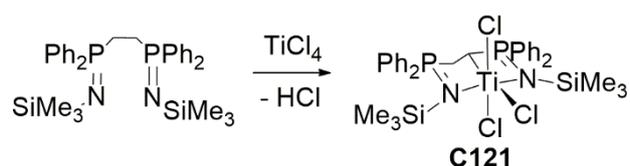
The reactions with aryl chlorides were performed in THF at room temperature with generally 2 mol.% catalyst. Reaction with fluoroaryl derivatives required higher temperature (70°C) and higher catalyst loading (2-10 mol.%). The iminophosphorane substituent influenced the catalytic performances, the best performances being obtained with a *p*-tolyl group at this position. The latter was an efficient catalyst for activated, unactivated, or deactivated chloro- and fluoro-aromatics.



Scheme 37 : Kumada coupling of aryl-chlorides and -fluorides with a (N,N,C) iminophosphorane based Ni catalyst

4.2 Bis(iminophosphorane) ligands

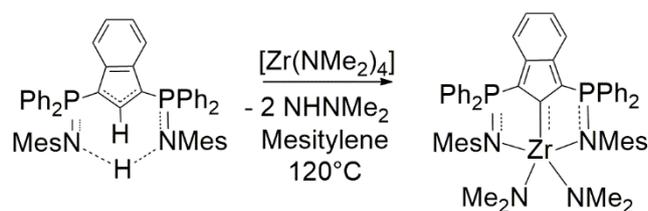
The most developed bis(iminophosphorane) (N,C,N) complexes are bis(iminophosphoranyl)methanide and -methanediide ligands prepared by deprotonation of the bis(iminophosphorane) precursor. They were already reviewed^[12-16] and will not be included in this report. Excluding those examples, bis(iminophosphorane) (N,C,N) ligand are quite rare. One of them was employed by the group of Wang to develop Ni and Zn based catalysts (Figure 12, **C115**, **C119**).^[102] In this NHC based (N,N,C) ligand the C-group is peripheral, it is not the case in other examples of bis(iminophosphorane) (N,C,N) ligands that were obtained by C-H activation after the coordination of the N atoms onto the metal. This synthetic method led to (N,C,N) ligand with a central C-donor group. Bochmann described the formation of a (N,C,N) TiCl₃ **C121** complex upon mixing TiCl₄ and (CH₂(CH₂PPh₂=NSiMe₃)₂)₂ via the release of HCl (Scheme 38).^[104] CH-activation also allowed the synthesis of pincer complexes with a central aryl chelated moiety.



Scheme 38 : Synthesis of a titanium (N,C,N) complexes

Thus, Bourissou and coworkers prepared in such a way indenyl pincer bis(iminophosphoranyl) and bis(thiophosphinoyl) complexes with [Zr(NMe₂)₄] as the metal precursor (Scheme 39).^[105] Harsher conditions were necessary for the metalation with the P=N based ligand than the P=S one. The analysis of the bonding in **C122** showed a strong σ -bond between the central carbon and the metal and a

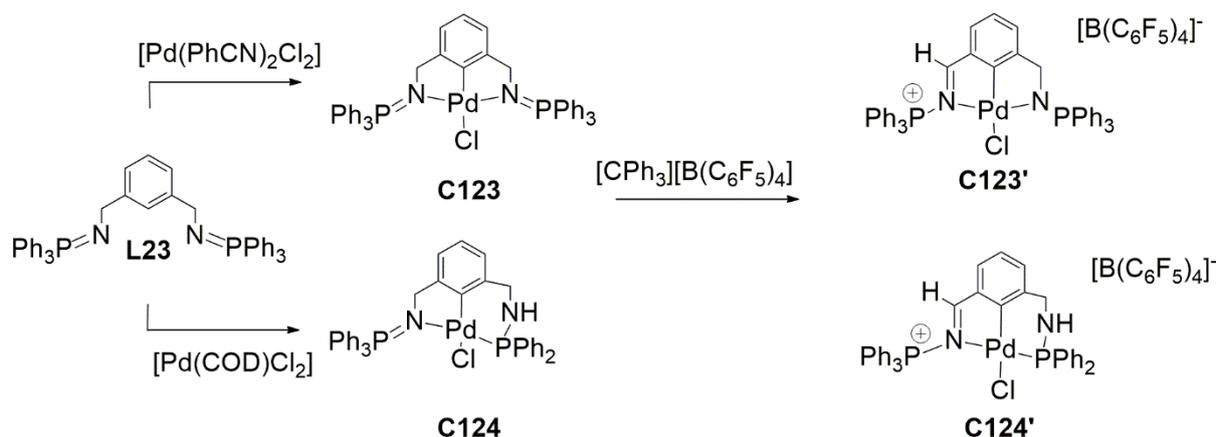
negligible π interaction, the central carbon keeping a partial negative charge after coordination. This bonding situation is very similar to that found in bis(iminophosphoranyl)methanediide systems.



C122

Scheme 39 : Synthesis of (N,C,N) indenylidene pincer complex

Stephan's group explored the cyclometallation of bis(iminophosphorane) **L23** ligand with Pd^{II} precursors (Scheme 40) and showed that the outcome of the reaction changed with the nature of the metal precursor.^[106] While reaction with [PdCl₂(PhCN)₂] led to the expected (N,C,N) Pd complex **C123**, reaction with [PdCl₂(COD)] led to an iminophosphorane-aminophosphine complex **C124**. The difference observed was tentatively explained by differences in the geometry of the Pd intermediate. The two Pd^{II} complexes lost hydride and not chloride anion upon reaction with [CPh₃][B(C₆F₅)₄]⁻ to yield monocationic Pd complexes.



Scheme 40 : Synthesis and reactivity of mono(iminophosphorane) (N,C,N) Pd complexes

A relatively small number of complexes featuring a tridentate iminophosphorane ligand structure associating 2 N donor groups and a C-based one was described. Except the NHC based ones they were mostly obtained by C-H activation. This process has been described with electron-poor metals (rare earth elements, Zr^{IV} or Ti^{IV}) as well as electron-rich ones (group 10 metals and Zn^{II}). The catalytic applications of (N,N,C) complexes focused on C-C coupling, and polymerization of polar monomers (lactide, caprolactone).

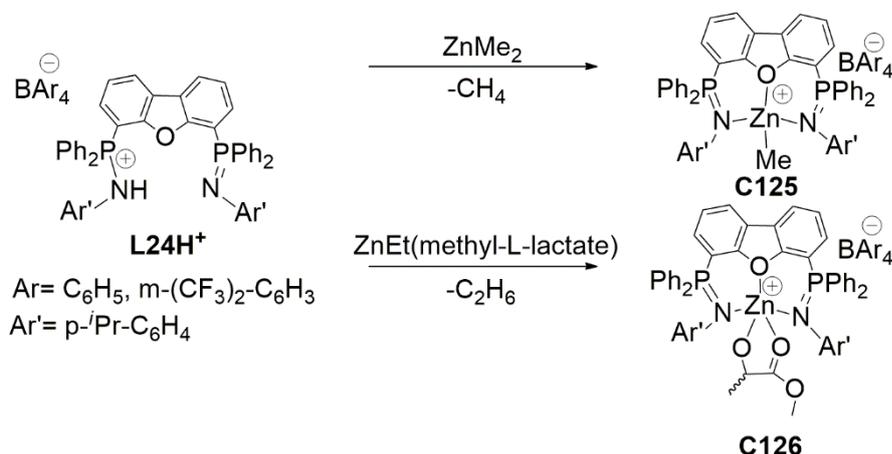
The next section deals with complexes supported by a tridentate ligand associating the iminophosphorane function to a chalcogen coordination group.

5 Chalcogen containing iminophosphorane tridentate ligands

5.1 (N, N, Ch) ligand

5.1.1 (N,N,O) ligands

Similarly to the carbazole skeleton, that was employed to develop anionic bis(iminophosphorane) (N,N,N) ligands (see section 2.1.2), dibenzofuran has served to develop a bis(iminophosphorane) (N,O,N) ligand.



Scheme 41 : Cationic zinc (N,O,N) complexes

Cationic zinc complexes **C125** were obtained via the reaction of ZnMe₂ precursor and the mono-protonated ligand **L24H⁺** (Scheme 41). These Zn-Me complexes were not active for lactide polymerization. However, the corresponding lactate complex **C126** synthesized by reaction of mono-protonated ligand and [ZnMe(methyl-L-lactate)] was a competent initiator. A conversion of 90 % in 50 min at 25°C in CH₂Cl₂ at a monomer: catalyst ratio of 200:1 was observed.^[107, 108] The polymer obtained was slightly heterotactic. Mechanistic investigations pointed towards a controlled coordination-insertion process.

The influence of the P and N iminophosphorane substituents on the polymerization activity was investigated. Higher activity was observed with a lower steric demand on the N atom, this was explained by a change in the binding mode: k³-(N,O,N) with of a phenyl on N vs k²-(N,N) with an ortho-tolyl group at this position, suggesting a beneficial effect of the O-coordination.^[109] Similarly, better activity was observed with initiators featuring only alkyl groups at P and N atoms.^[110] Such dibenzofuran (N,O,N) ligand was also prepared in a diastereomerically pure form, and its cationic zinc complexes are competent lactide polymerization catalysts.^[111] Nevertheless in all these polymerizations, the transesterification reactions limited the observed molecular weight. As expected a much lower activity in the ring opening polymerization of lactide ROP was reported by Wang and coworkers with a neutral zinc initiator bearing a pyrazolyl-iminophosphorane-enolate ligand (Figure 13, **C127**) upon activation by benzyl alcohol.^[112]

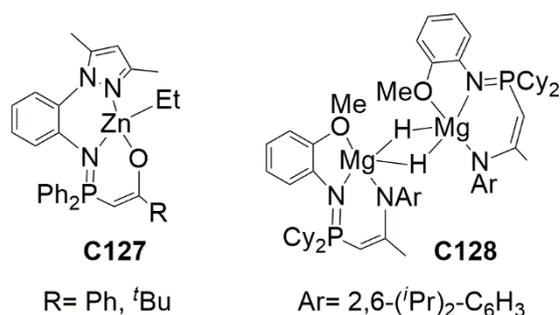
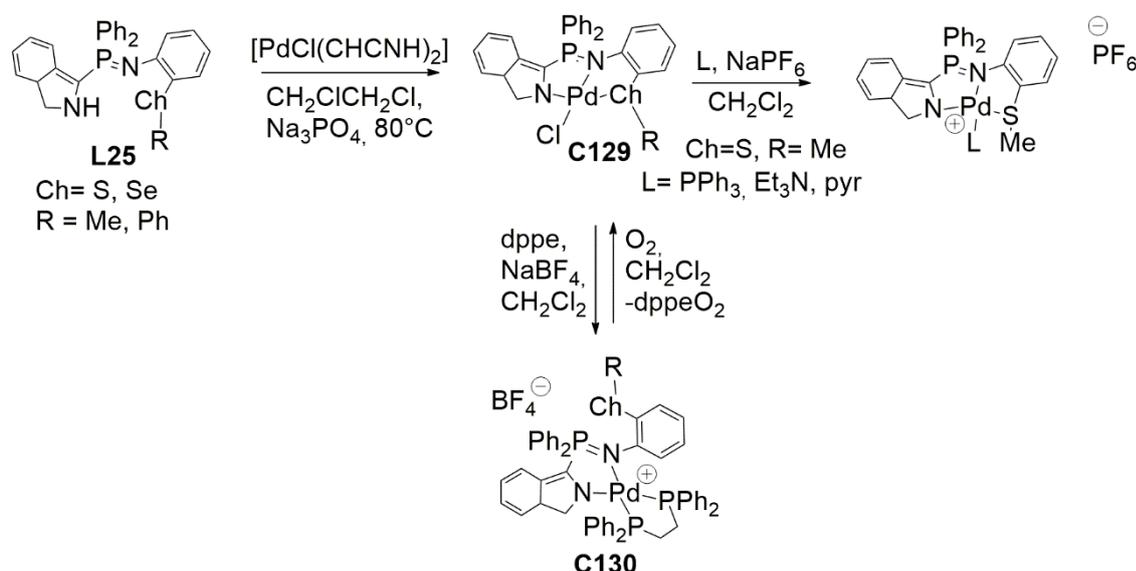


Figure 13 : (N,N,O) Zn and Mg complexes

Functionalized iminophosphorane amide ligands were employed to stabilize Mg-H dimers (Figure 13) that were used for the catalytic hydroboration of acetophenone. One example in that series exhibits (N,N,O) coordination (**C128**) but the latter is less reactive than its (N,N) congeners.^[113]

5.1.2 (N,N,S) or (N,N,Se) ligands

The group of Grevy synthesized a (N,N,S) and a (N,N,Se) **L25** ligand from 2-indolyldiphenyl phosphine thanks to a Staudinger reaction with an azide incorporating the thioether or selenoether function.^[114] Neutral pincer Pd^{II} complexes **C129** were isolated, no change of coordination occurred upon exchange with a monodentate ligand but a neutral κ^2 -(N,N) complex **C130** formed upon reaction with bis(diphenylphosphino)ethane evidencing the hemilabile coordination of the thio- or seleno-ether (Scheme 42). Oxidation of dppe restored the pincer coordination mode.



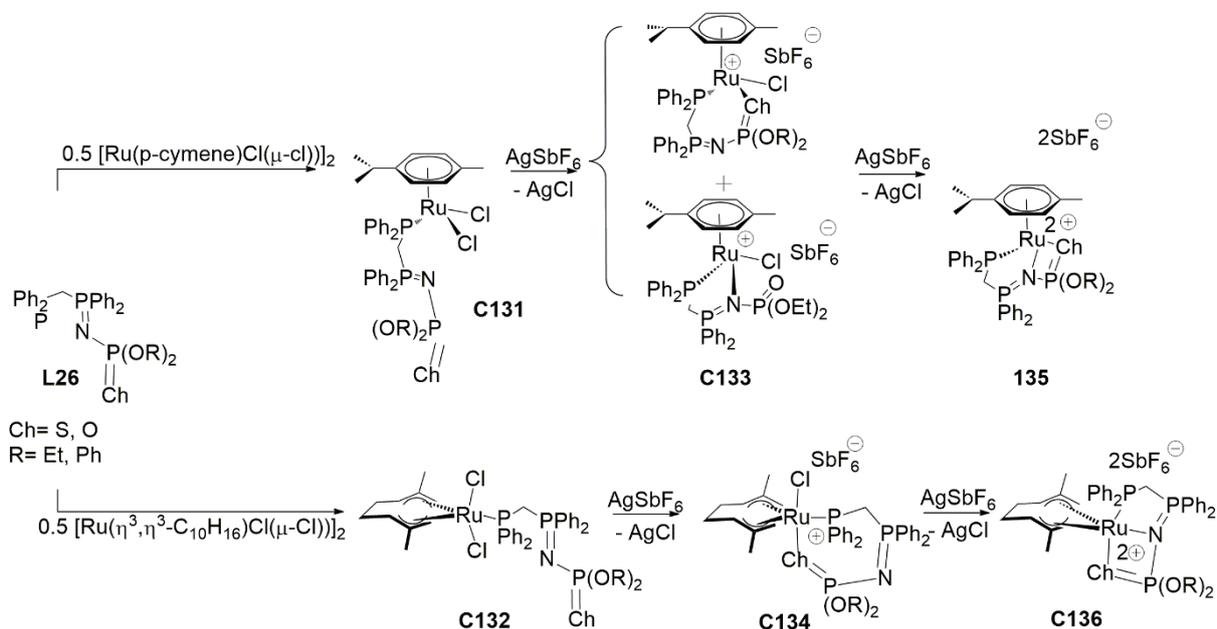
Scheme 42 : Pd^{II} complexes supported by a (N,N, Ch) ligand

5.2 (N, P, Ch) ligand

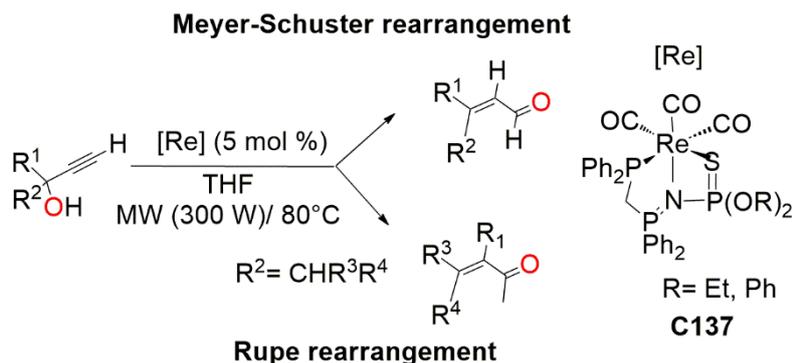
Very few ligands associate an iminophosphorane, a phosphine and a chalcogen chelating group. In general, the chalcogen, often a sulfur, comes from the (thio)phosphoryl substituent born by the N. Those ligands **L26** are prepared by monooxidation of bis(diphenylphosphino)methane with (thio)phosphoryl azides.^[115, 116] Their reaction with a Ru^{II} or Ru^{IV} chloro-bridged dimer led to neutral P-coordinated ruthenium dichloride complexes **C131** and **C132** respectively (Scheme 43). Sequential halogen abstraction induced the coordination of the P(O) or P(S) group and then that of the iminophosphorane leading respectively to mono- (**C133** and **C134**) and di-cationic complexes (**C135**

and **C136**). Note that a mixture of monocationic κ^2 -(P,N) and κ^2 -(P,O) **C133** complexes was obtained with P(O)(OEt)₂ substituent on the N, while only κ^2 -(P,O) compounds were observed with P(S)(OEt)₂ and P(O)(OPh)₂ substituents.

Scheme 43 : Stepwise coordination of (P,N,S) ligands to Ru^{II} and Ru^{IV} centers



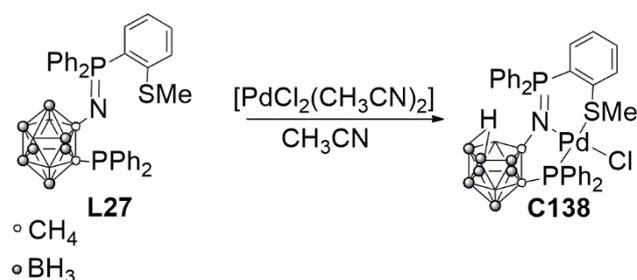
Moreover, the reactivity was slightly different between the P(O) and the P(S) series. In the phosphoryl P(O) series, the formation of the neutral κ^1 -P complexes **C131** was observed upon addition of excess sodium salt (NaX, X=Cl, Br, I, N₃, NCO) from either **C133** or **C135**.^[115] In the P(S) series, addition of excess sodium salt (NaX, X=Cl, Br, I, N₃) to the κ^3 -(P,N,S) complexes **C136** led to the monocationic κ^2 -(P,S) derivatives **C134** and not the neutral complex.^[116] Moreover, in the thiophosphoryl series, the addition of a neutral ligand (PPh₃, CH₃CN) suppressed the M-N bond, while it is maintained in presence of acetone contrary to what is observed in the P(O) series. Those complexes were used to catalyze the transfer hydrogenation of cyclohexanone by propan-2-ol. The reactions were conducted at 82°C with 0.4 mol.% catalyst in presence of NaOH (9.6 mol.%). Some common reactivity trends were observed; less sterically hindered (R=Et) complexes performed better than the phenyl ones, and the Ru^{IV} catalysts are more efficient than the Ru^{II} derivatives. Nevertheless, some differences were also noted. While for the phosphoryl complexes, cationic Ru^{II} and Ru^{IV} precatalysts **C133** and **C134** are more efficient than neutral ones **C131** and **C132**, in the thiophosphoryl series neutral Ru^{II} complexes performed better than cationic analogues. In each series the best performances were reported for the monocationic κ^2 -(P,X) complexes (**C133** and **C134**, X= O, S) with the thiophosphoryl supported one exhibiting the highest TOF. Thus, the hemilability of the P(X) group seems to not be the dominant factor for those catalysts since P(O) group was more labile than the P(S) one. NMR monitoring of a catalytic run indeed suggested a κ^2 -(P,S) complex formed by release of the bis(allyl) ligand. Hydrogenation of other dialkyl ketone and substituted acetophenone derivatives was achieved with the Ru^{IV} κ^2 -(P,S) **C134** complex. A rate-determining hydride-transfer step was suggested because of the lower reactivity observed with sterically hindered and electron rich aryl derivatives.



Some years later, the (P,N,S) ligand was used to synthesize the Re^I complexes **C137**, that were employed to catalyze the rearrangement of propargylic alcohols into α,β carbonyl compounds (Scheme 44).^[117]

Depending on the nature of the substrate, enals or enones were formed. The reactions were conducted with a catalyst loading of 5 mol.% in THF under microwave at 80°C and led to better performances for the phenyl complex (R= Ph). Interestingly, these two isomerization processes were also achieved in ionic liquid allowing the recycling of the catalyst. The use of 1-butylmethylimidazolium [BMILM][PF₆] as solvent gave the best results. For the Meyer Schuster isomerization 10 cycles could be done, but with an increased reaction time at each cycle. For the Rupe rearrangement a loss of reactivity was also observed; the reaction has to be conducted at higher temperature (130 vs 80°C) and only 4 cycles could be performed.

The group of Sousa-Pedrares described an original tridentate PNS ligand **L27** based on a carborane moiety containing a thioether group.^[118] Its coordination to Pd^{II} led to the complex **C138** (Scheme 45) resulting from partial deboronation. The presence of the thioether function increased the sensitivity of the carborane cage towards a nucleophilic attack by the solvent as no deboronation was observed with the bidentate (P,N) ligand in acetonitrile.



Scheme 45 : Coordination of carborane-based (P,N,S) ligand to Pd^{II}

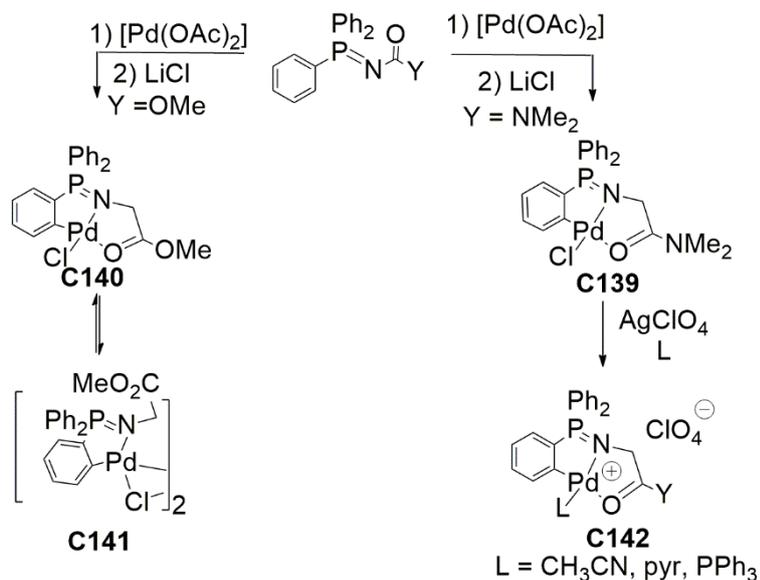
5.3 (N, C, Ch) Ligand

5.3.1 (O,N,C) ligands

Only (O,N,C) palladium complexes, with a peripheral C-based coordinating group, were described, they were formed by orthopalladation in (N,O) palladium complexes.

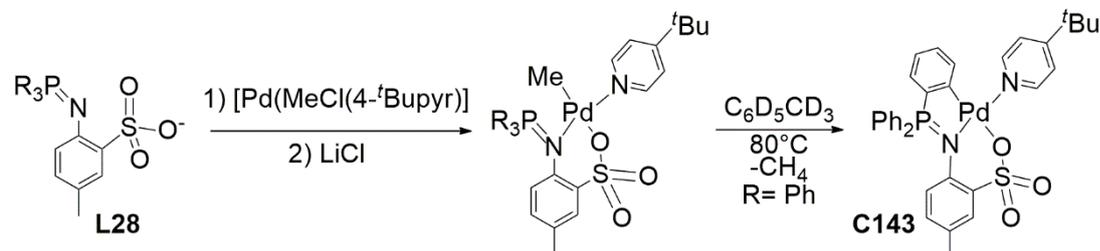
The orthopalladation of carbonyl containing iminophosphorane ligand led to different types of complexes depending on the nature of the carbonyl function.^[95] While the amide based ligand led to a mononuclear pincer complex **C139** upon reaction with [Pd(OAc)₂], the coordination of the ester group is weaker since variable temperature and DOESY NMR evidenced an equilibrium between a monomer

and a dimer (**C139** and **C140** respectively, Scheme 46). Nevertheless, both these (ONC) ligands exhibit a pincer coordination on a cationic Pd^{II} center (**C142**).



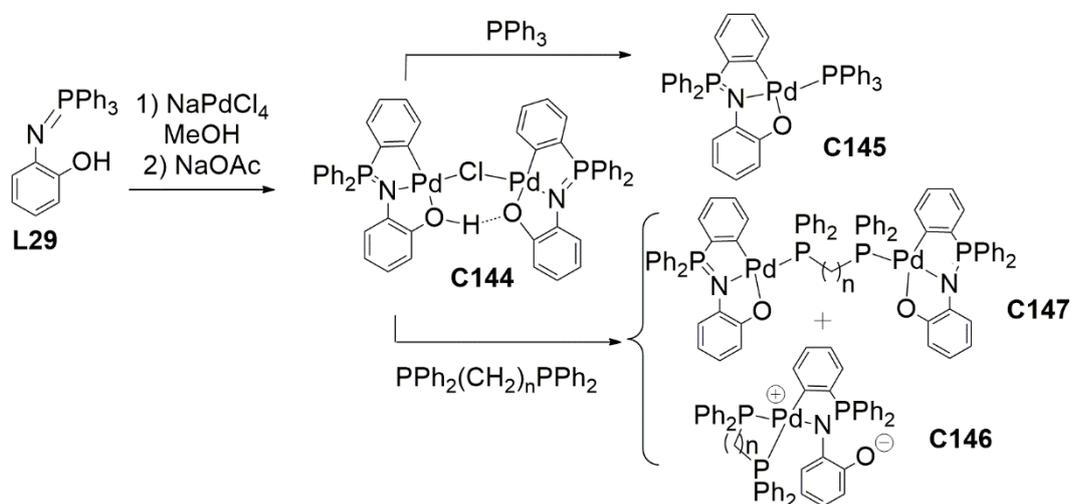
Scheme 46 : Neutral and cationic (N,C,O) palladium complexes

Burns and coworkers reported the coordination of iminophosphorane-arenesulfonate **L28** ligands to Pd^{II} and the thermally induced sp²-CH activation (Scheme 47).^[119] The formed orthopallated pincer complex **C143** did not evolve under an ethylene atmosphere. Note that no metalation occurred, as expected, with the PⁿBu₃=N derivative possessing sp³-CH bonds.



Scheme 47 : Orthometallation in an iminophosphorane (N,O) Pd complex

Moreover, palladation of **L29** derived from 2-aminophenol led to an original dimer **C144** exhibiting a bridging chloride and a bridging hydrogen (Scheme 48).^[120]



only the thiol bound the metal. This was explained by the deactivating effect of the ortho-carborane since pincer (S,N,C) coordination on Pd^{II} was shown for the phenyl based ligand **L31** (Figure 15).

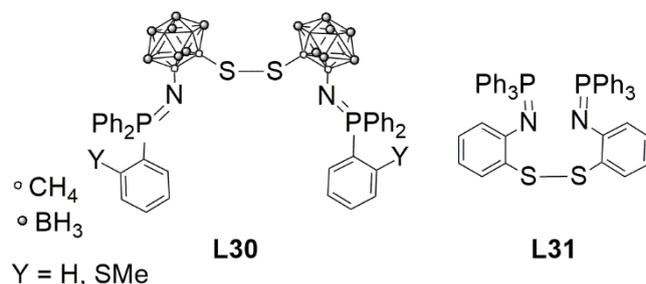


Figure 15 : Carborane or phenyl based sulfur containing iminophosphorane ligand

The tridentate chalcogen containing iminophosphorane ligands depicted in this section were coordinated to a very narrow range of metals (Re^I, Ru^{IV}, Ru^{II}, Pd^{II}, Pt^{II}, Zn^{II}). Some have found applications in catalysis for lactide polymerization, C-C coupling reactions, or transfer-hydrogenations while some others were shown to have anticancer properties.

6 Conclusion

This review shows approximately 60 different tridentate ligands that contains at least one iminophosphorane function. This seems to remain very limited in comparison with the diversity of the amine or amide analogues considering that their chemistry is more than one century old. The sensitivity of iminophosphorane to moisture may be an explanation however it highly depends on the ligand structure. It increases with the basicity of the nitrogen atom and the electrophilicity of the phosphorus therefore decreasing either the electron density on N or the electron deficiency on P can be helpful as well as the introduction of a steric protection. In addition, iminophosphoranes can be generated *in situ* from their corresponding acid and once incorporated in a complex, this sensitivity almost disappears. In that sense, it is not so different from the synthesis of NHC complexes, since the free carbene is rarely employed. The under representation of iminophosphorane in coordination chemistry cannot, in our opinion, be explained by a peculiar synthetic difficulty, it may not have entered the classical toolbox of coordination chemists yet. In terms of ligand structures, tridentate iminophosphorane ligands are dominated by (N,N,N) structures and more specifically those incorporating 2 iminophosphorane groups. Moreover, many of the structures presented in this review were only employed with a very limited number of metals. It is noteworthy that the coordination of those iminophosphorane tridentate ligands to rare earth metals was particularly studied. The strong electron-donating ability of iminophosphoranes is indeed well-adapted to stabilize those electron-deficient metal centers. In addition, Pd^{II} complexes are particularly well-represented, probably because the diamagnetism of those complexes facilitates their characterization by NMR spectroscopy. However, the electronic properties of iminophosphoranes make them suitable to bind to small cations like those from the first row of the periodic table and may be useful to offer alternatives to expensive and noble metal catalysts. Examples of nickel(II) complexes are the more numerous. The ability of the N=P function to work cooperatively with the metal or an additional Lewis acid to favor a specific reactivity is another asset. In terms of catalytic applications, metal complexes supported by tridentate iminophosphorane ligands were mainly employed for C-C coupling reactions and polymerization of olefins or polar monomers (lactide or caprolactone). There are fewer reports concerning their use in oligomerization, rearrangement reactions or reduction processes ((transfer) hydrogenation, hydrosilylation). For the latter reaction, the electron richness of iminophosphorane should impart a

high hydridic character to the involved M-H intermediate and led to enhanced reactivity. It is also noteworthy that a small number of complexes shown in this article were employed for biomedical applications. This is another application domain that iminophosphorane may conquer in the future. We hope that this article will help to stimulate the development of new P=N ligands and complexes since it remains a promising field of research.

7 Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

8 Acknowledgements

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