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Carbon-Phosphorus Ligands with Extreme Donating Character

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Abstract

Carbeniophosphines $[\text{R}_2\text{C}^+-\text{PR}_2]$ and phosphonium ylides $[\text{R}_3\text{P}^+-\text{CR}_2^-]$ are two complementary classes of carbon-phosphorus based ligands defined by their unique donor properties. Indeed, while carbeniophosphines are electron-poor P-ligands due to the positioning of a positive charge near the coordinating P-atom, phosphonium ylides are electron-rich C-ligands due to the presence of a negatively charged coordinating C-atom. Based on this knowledge, this account summarizes our recent contribution on these two classes of carbon-phosphorus ligands, and in particular the strategies developed to lower the donor character of carbeniophosphines and enhance that of phosphonium ylides. This led us to design, at both extremities of the donating scale, extremely electron-poor P-ligands exemplified by imidazoliophosphonites $[\text{R}_2\text{C}^+-\text{P}(\text{OR})_2]$ and dicarbeniophosphines $[(\text{R}_2\text{C}^+)_2-\text{PR}]$, and extremely electron-rich C-ligands illustrated by pincer architectures exhibiting several phosphonium ylide donor extremities. In the context of carbon-phosphorus analogy, the closely related cases of ligands where the C-atom of a NHC ligand is in close proximity of two positive charges, and that of a phosphonium ylide coordinated through its P-atom are also discussed. An overview of the synthetic methods, coordinating properties, general reactivity and electronic structure of all these C,P-based species is presented here.

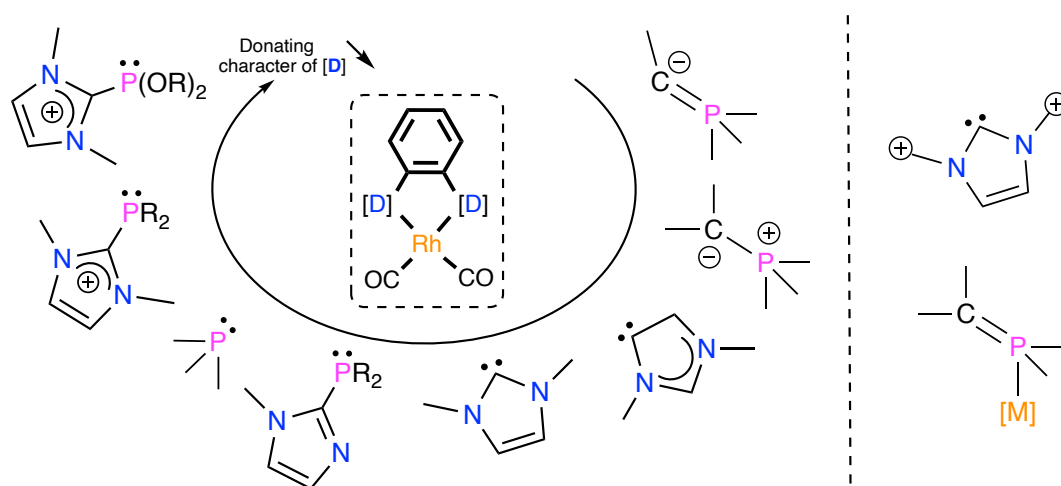
Keywords: Carbene, carbeniophosphine, phosphonium ylide, phosphine, positive charge, electronic donation, ligand.

I. Introduction

Beyond the diagonal analogy that exists between carbon and phosphorus in their low-coordinate states due in part to comparable electronegativity ($\chi_C = 2.5$ and $\chi_P = 2.2$) thus making C–P bonds weakly polar,^[1] carbon and phosphorus both play a fundamental role in coordination chemistry. Indeed, although this field of chemistry rather refers to the vertical analogy between phosphorus and nitrogen where phosphines act as softer and π -accepting $\sigma^3\lambda^3$ versions of amines, carbon ligands have become over the years essential just like phosphine ligands.^[2] Knowing that each coordinating element retains its own specificities, the main reason for the emergence of carbon ligands was mainly motivated by the desire to develop ligands with increased σ -donating character in order to improve the stability of the ligand-metal bond.^[3] However to achieve this goal, the best compromise between σ -donation and π -acceptation must be generally reached which justifies also the development of ligands with enhanced accepting properties as has been done earlier with phosphorus ligands. N-Heterocyclic carbenes (NHCs)^[4] and phosphines^[5] which fulfil these criteria to varying degrees are the most illustrious representatives of carbon and phosphorus ligand families having demonstrated on many occasions their huge potential in various domains of chemistry.^[6] Moreover, despite multiple variations of their structure carried out for decades, their current predominant role confirms that carbon and phosphorus elements still remain to this day coordinating atoms of choice for the design of new ligands. However, given the plethora of structure available, the development of new ligands can only be justified nowadays by the search for non-classical properties that can lead to novel reactivities and innovative applications.

Phosphonium ylides^[7] $[\text{R}_3\text{P}^+-\text{CR}_2^-]$ and carbeniophosphines^[8] $[\text{R}_2\text{C}^+-\text{PR}_2]$ also called α -cationic phosphines that can be regarded to some extent as extreme electronic variations of NHCs and phosphines respectively, obey these requirements. Their extreme character concerns the donating ability of the coordination site (C- vs P-atom) with respect to Lewis acidic centers that can be metallic or not in nature. Indeed, while phosphonium ylides are very electron-rich carbon ligands, even more than N-Heterocyclic carbenes as demonstrated by our group,^[9] carbeniophosphines are very electron-poor phosphorus ligands, quite comparable to phosphites.^[10] In the former neutral system, the ylidic bond is generally described as a strongly polarized P=C bond involving the resonance between two canonical limiting forms, i.e. the ionic ylide and the neutral ylène. However, a chemical description of this bond in terms of donor-acceptor interactions between $[\text{R}_3\text{P}:]$ and $[:\text{CR}_2]$ fragments with the contribution of two electron pairs has recently attracted some renewed interest from the community.^[11] On another side, carbeniophosphines can be regarded as donor \rightarrow acceptor

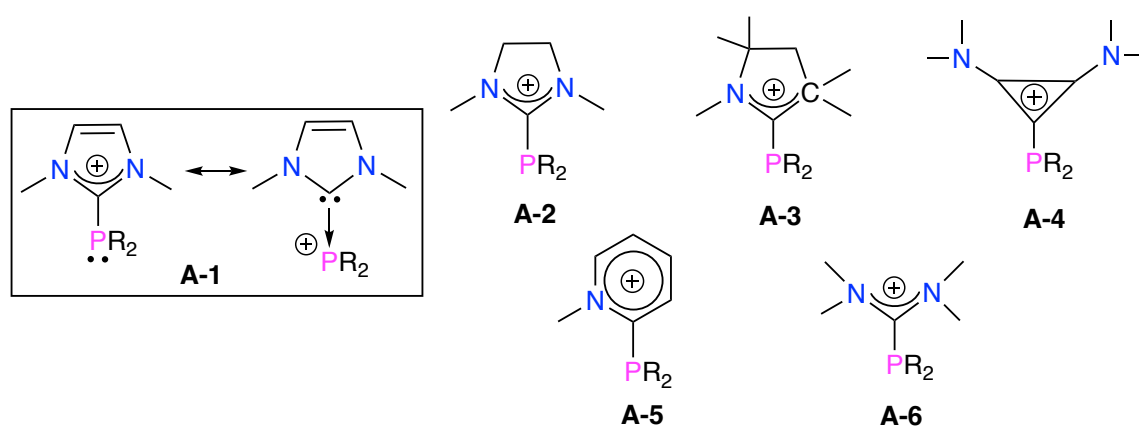
systems of carbene \rightarrow phosphonium type with a C \rightarrow P dative bond, the dative character of this bond being more or less pronounced depending on the nature of the two partners.^[12] According to these chemical descriptions, the structure of coordinated phosphonium ylides and carbeniophosphines can be formally rationalized by two related insertion processes, respectively that of a carbene $[:\text{CR}_2]$ into a phosphine \rightarrow metal bond and that of a phosphonium $[:\text{PR}_2^+]$ into a carbene \rightarrow metal bond, carbenes and phosphoniums being isolobal low-valent fragments.^[13] Based on the average of computed IR stretching frequencies of CO in a series of isostructural chelating RhCO_2 complexes featuring an *ortho*-phenylene bridge, we have more recently established an accurate ranking of the donating ability of main carbon-phosphorus ligands commonly used, ranging from very electron-rich anionic phosphonium ylides $[\text{R}_3\text{P}=\text{CR}^-]$ to very electron-poor cationic imidazoliophosphonites $[\text{R}_2\text{C}^+-\text{P}(\text{OR})_2]$, both located at the upper and lower limits of the donating ability scale (Scheme 1, left).^[14] Thus, interested for many years in the design of original ligands, this account reports selected examples on our contribution to the preparation of carbon-phosphorus ligands with unique electronic properties and summarizes their main characteristics going from fundamental aspects to applications. To our knowledge, this will be the first report where ligands with very distinct donating properties will be discussed together in a single article. In the context of C–P analogy involving ligands with peculiar electronic properties, cationic NHCs and complexes featuring unconventional P-metalated phosphonium ylides described recently in the group will be also tackled in this account (Scheme 1, right).



Scheme 1. Isostructural $\text{Rh}(\text{CO})_2$ complexes built from an *ortho*-phenylene bridge substituted by extremities (D) with different donating character, ranging from electron-rich carbon donors to electron-poor phosphorus donors (left).^[14] Representation of cationic NHCs and unconventional P-metalated phosphonium ylide complexes of interest (right).

II. Extremely Electron-Poor Phosphorus Systems

The main motivation to prepare cationic phosphines bearing a positive charge near the coordinating center is to access P-ligands with lower donor character than their neutral analogues. α -cationic phosphines are therefore positioned as complementary ligands to electron-poor phosph(in)ites and fluoroarylphosphines, the positive charge playing the role of electro-withdrawing alkoxy groups and fluorine atoms. Concerning the coordinating motif, the positive charge could be introduced by different organic fragments.^[8] Imidazolium-type **A-(1–2)**^[15] and related structures **A-3**,^[16] cyclopropenium **A-4**,^[17] pyridinium **A-5**,^[18] and amidiniums **A-6**^[19] were used for this purpose (Scheme 2). From a structural point of view, these cationic species exhibit a carbene–phosphenium character, the dative nature of the C–P bond determined by the difference between calculated homolytic and heterolytic dissociation energies, being more or less pronounced in function on the nature of carbene donor and phosphenium acceptor fragments.^[12] From IR ν_{CO} frequency values of RhCl(CO) complexes, α -cationic phosphines were shown to act as weaker donors than triarylphosphines^[20] and slightly stronger donors than trialkoxyphosphites.^[21] In the cationic series, cyclopropenium^[22] and imidazoliophosphines^[23] are the most and the least electron-donating ligands, respectively. It should be also noted that despite the presence of a positive charge conjugated to the P-center, carbeniophosphines are able to coordinate a large range of Lewis acids^[8] of metallic (Pd(II),^[12,24] Ni(II),^[25] Rh(I),^[26] Cu(I),^[27] Ag(I),^[28] Au(I)^[17]), and non-metallic nature (O, S).^[29] Regarding their applications, α -cationic phosphines were used in homogeneous biphasic catalytic transformations,^[8a] as well as ancillary ligands in π -acid type catalysis.^[30]



Scheme 2. Representation of known carbeniophosphines **A-(1–6)** with the two possible resonance forms in the case of **A-1**.^[8]

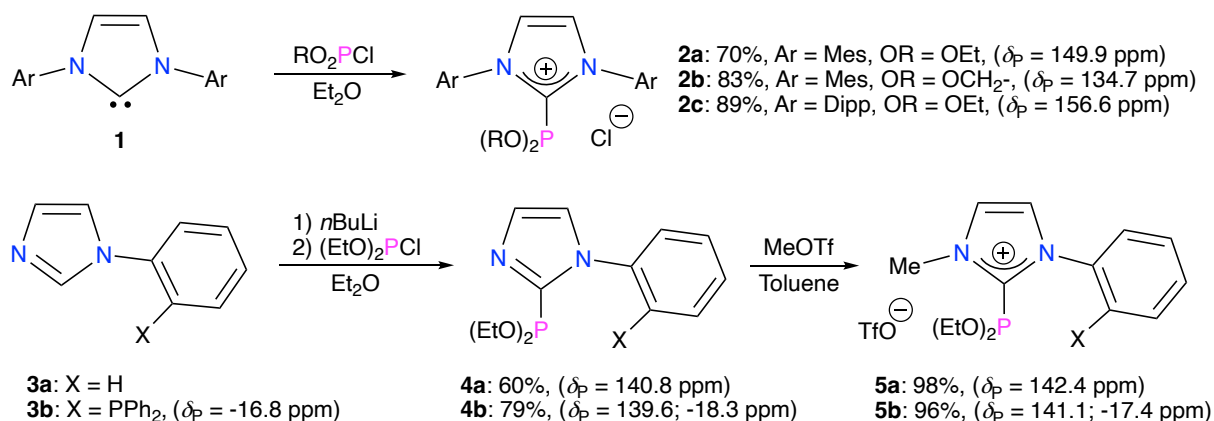
After these significant advances in the domain of electron-poor ligands, with the objective of further lowering the donating character of α -cationic phosphines, two distinct and complementary approaches were considered by our group:

1) Introduction of electron-withdrawing ($-I$ effect) alkoxy substituents at the P-center to access α -carbeniophosphonites (case of imidazoliophosphonites $[\text{N}_2\text{C}^+-\text{P}(\text{OR})_2]$).

2) Introduction of a second cationic fragment at the P-center to access α -dicarbeniophosphines (cases of diimidazolio- and dicyclopropeniophosphines $[(\text{R}_2\text{C}^+)_2-\text{PR}]$).

II. 1 Imidazoliophosphonites

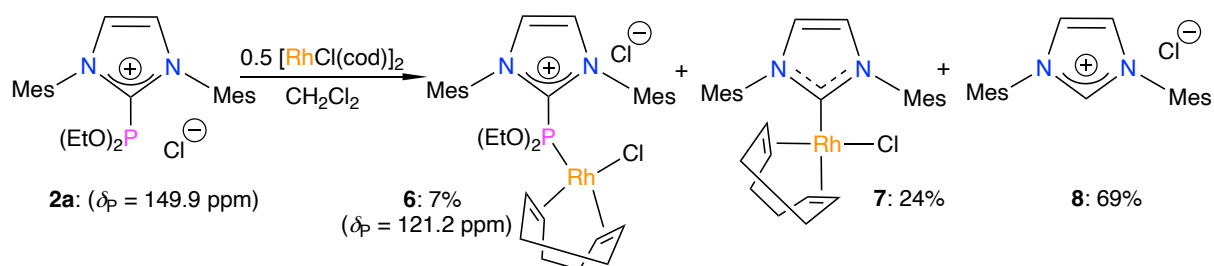
The preparation of imidazoliophosphonites which were unknown before this report was envisaged by two different strategies.^[31] The most direct method consists in adding chlorodialkylphosphites to stable free NHCs (IMes and IPr carbenes **1**) obtained by deprotonation of related imidazolium salts. This strategy allows the isolation of targeted cationic phosphonites **2a-c** in 70-89% yield (Scheme 3, up). The second method requires two steps from the more readily available N-aryl substituted 1*H*-imidazoles **3a,b**. After deprotonation of the CN_2 position of **3a,b** by *n*BuLi and subsequent addition of chlorodiethylphosphite, selective N-methylation of the neutral imidazolophosphonite intermediates **4a,b** with MeOTf led to their cationic analogues **5a,b** in quasi-quantitative yield.



Scheme 3. Two complementary approaches for the synthesis of imidazoliophosphonites.^[31]

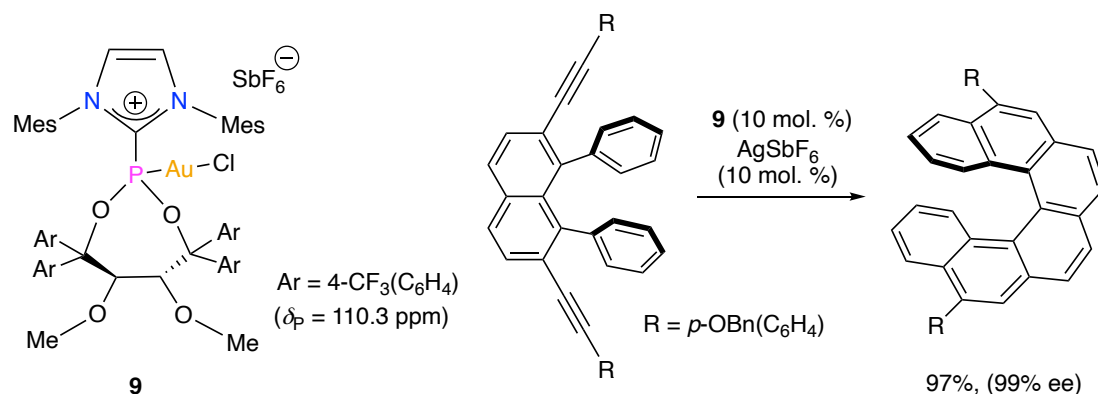
Despite some decomposition was observed over time ($t_{1/2} \sim 10\text{--}20$ h, 20°C, CH₂Cl₂) by hydrolytic cleavage of the $\text{N}_2\text{C}^+-\text{P}$ bond to form corresponding imidazolium salt and phosphine oxide products, we were able to achieve the coordination of these cationic P-species with a Lewis acidic Rh^I center. This reactivity was illustrated with the formation of

Rh^I complex **6** obtained from the reaction of imidazoliophosphonite **2a** with [RhCl(cod)]₂ complex (Scheme 4). However, this cationic complex **6** was obtained in poor yield along with NHC Rh(cod)Cl complex **7** and imidazolium salt **8** isolated in 24% and 69% yield, respectively. Anyway, the present reactivity demonstrates that imidazoliophosphonite **2a** retains some P-coordinating ability towards a metallic Lewis acid such as a neutral Rh^I center.



Scheme 4. Behavior of imidazoliophosphonite **2a** in the presence of [Rh(cod)Cl]₂ complex.^[31]

The formation of NHC complex **7** evidences the lability of the N₂C⁺–P bond as already observed in imidazoliophosphines and related Pd^{II} complexes.^[12] In fact, just like imidazoliophosphines, imidazoliophosphonites are better described as donor-acceptor adducts of NHC-dioxyphosphenium type with the existence of a dative N₂C⁺–P bond as confirmed by DFT calculations which found the heterolytic dissociation more favorable than the homolytic one. Another fundamental aspect concerns the frontier molecular orbitals (FMOs) of these cationic P-species, where the substitution of a phenyl ring by an ethoxy group results in the decrease of LUMO (mainly NHC–P bond) and HOMO (mainly P-lone pair) energies. Imidazoliophosphonites [N₂C⁺–P(OR)₂] act definitively as very electron-poor phosphorus ligands, being less σ -donating and more π -accepting than imidazoliophosphines [N₂C⁺–PR₂].^[31] While these cationic P-species prepared in the group proved to be too unstable to be used as ligands for applications in catalysis, Alcarazo et al. demonstrated that imidazoliophosphonites can be strongly stabilized by increasing the bulkiness at the P-atom and therefore considered in catalysis.^[32] As relevant example, we can cite the highly enantioselective preparation of substituted [6]-carbohelicenes via sequential Au-catalyzed hydroarylation of alkynes, thanks to the use of sterically hindered α -cationic chiral phosphonites derived from TADDOL (Scheme 5).^[32a]

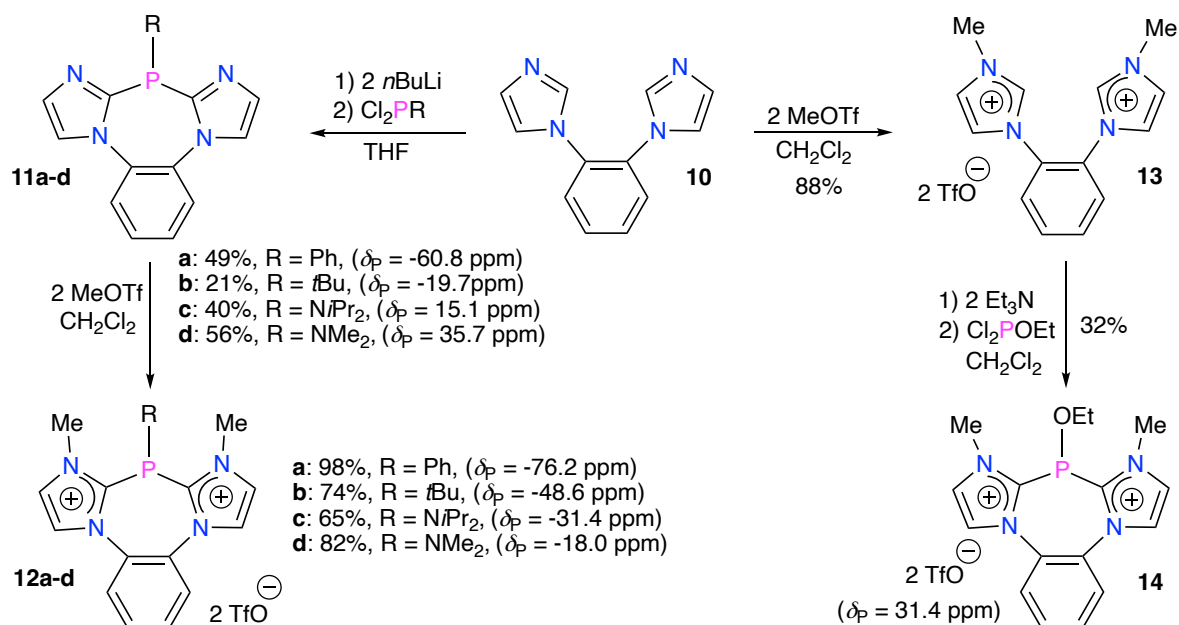


Scheme 5. Preparation of [6]-carbohelicenes catalyzed by chiral imidazoliophosphonite Au^I complex **9**.^[32a]

II. 2 Dicarbeniophosphines

a-Diimidazoliophosphines

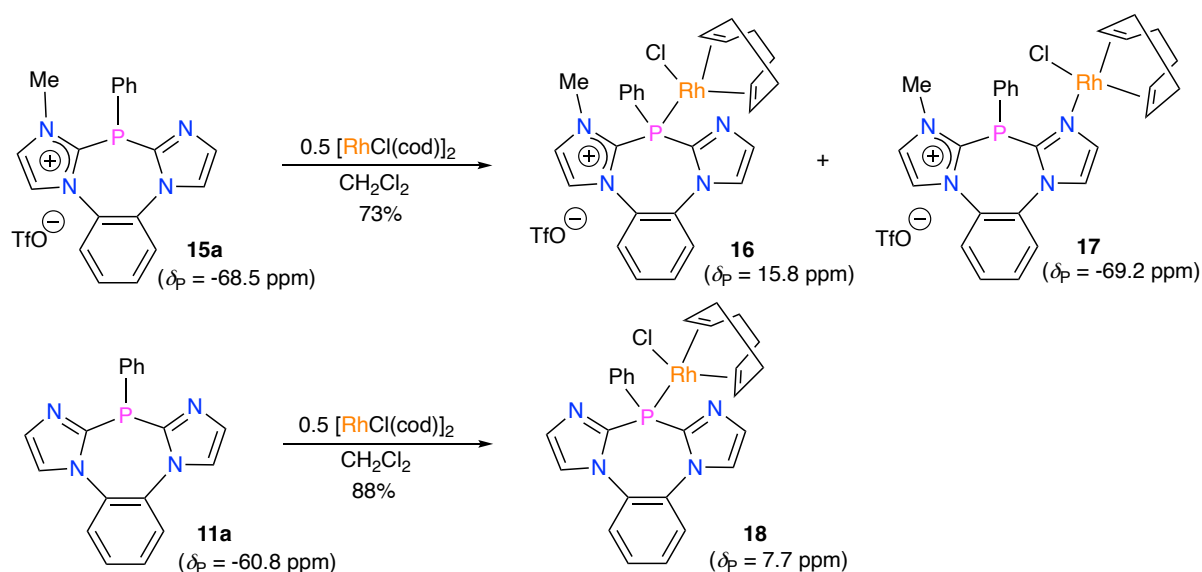
A general method was developed in the group to prepare P-substituted cyclic diimidazoliophosphines from the readily available 1,2-di(*N*-imidazolyl)benzene **10**.^[31] Indeed, double deprotonation of **10** with two equiv. of *n*BuLi followed by the addition of RPCl₂ enabled the formation of neutral diimidazolophosphines **11a-d** with moderate yield (21–56%), the P–R substituent possibly being a phenyl,^[31] a *t*Butyl^[33] or an amino group.^[34] Then, we were pleased to isolate by selective N-methylation of the two imidazole rings of **11a-d** the targeted cyclic dicationic diimidazoliophosphines **12a-d**. The yield was shown to be dependent of the nature of the P–R substituent, ranging from 65% yield with R = *Ni*Pr₂ to 98% with R = Ph (Scheme 6, left). Remarkably, from the same precursor **10** but by using a different approach, we were able to form the very electron-poor ethyl diimidazoliophosphonite **14** in 28% overall yield (Scheme 6, right). More precisely, after formation of the bis-imidazolium salt **13** by dual N-methylation of **10**, the introduction of the P-fragment was achieved by addition of dichloro(ethyl)phosphite in the presence of Et₃N.^[35] It's worth mentioning that only two acyclic diimidazoliophosphines obtained from the reaction between 1,3-dimethylimidazolium-2-carboxylate and dichlorophosphines were described before our contribution.^[36] However, no coordination chemistry of these dicationic P-species was mentioned in this article, which motivated us all the more to study that of our ligands.



Scheme 6. Preparation of diimidazoliophosphines **12a-d** and diimidazoliophosphonite **14** in a two-step procedure from 1,2-di(*N*-imidazolyl)benzene **10**.^[31,33-34]

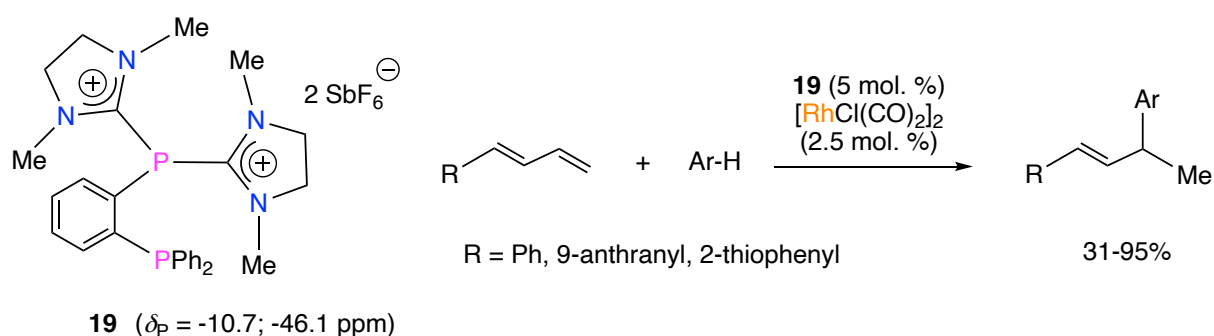
The presence of two cationic fragments at the P-center proved to be more effective in decreasing the donor character than the introduction of alkoxy substituents.^[31] Indeed, while imidazoliophosphonite **2a** was able to coordinate a Rh^I center, in the same conditions diimidazoliophosphine **12a** did not lead to any complexation. This absence of reactivity was also evidenced with other metallic centers (Pd^{II}, Cu^I, Cu^{II}) and oxidating agents (H₂O₂, S₈). These results suggest that diimidazoliophosphine **12a** is beyond the coordination limit with at least the tested Lewis acids. Interestingly, the mono cationic imidazolo-imidazoliophosphine **15a** obtained by mono *N*-methylation of **10** was found to maintain some coordinating ability towards [RhCl(cod)]₂ complex. However, it was observed the formation of two Rh complexes in a 1/1 ratio, complex **16** showing the coordination of the P-atom and complex **17** exhibiting the coordination of the *sp*² N-atom of an imidazole ring (Scheme 7). The concomitant existence of complexes **16** and **17** indicates that the presence of only one cationic charge makes it possible on the one hand to restore coordinating properties but also demonstrates that the mono cationic phosphine **15a** is located at the P-coordination limit towards a neutral Rh^I center. This is also in agreement with DFT calculations which found that the two isomers are very close in energy, the N-coordinated complex **17** being more stable than the P-coordinated complex **16** by only 1.76 kcalmol⁻¹. The critical role of the positive charge in **15a** was confirmed by the formation of a single complex, namely the P-coordinated complex **18** from the reaction between the neutral phosphine **11a** and [RhCl(cod)]₂ complex (Scheme 7). As

expected, all attempts to coordinate the extremely electron-poor imidazoliophosphonite **14** were unsuccessful.^[31]



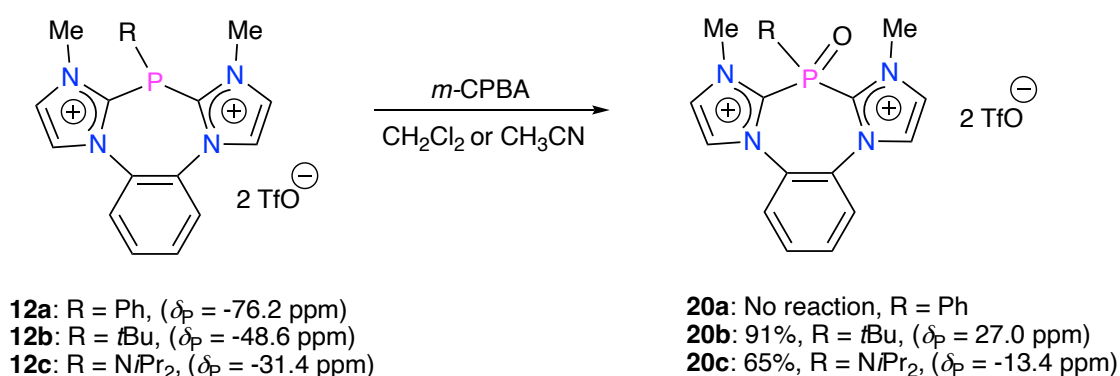
Scheme 7. Coordination issues of monocationic imidazolo-imidazoliophosphine **15a** and neutral imidazolophosphine **11a** with $[\text{RhCl}(\text{cod})_2]$ complex.^[31]

To restore the coordinating ability of the P-atom in α -dicationic phosphines, an elegant strategy was devised by Alcarazo et al. consisting in introducing an additional donor site.^[37] Thus, P,P-chelating ligands based on a dicationic 1,3-dimethyl-4,5-dihydroimidazoliophosphine and containing a $-\text{PPh}_2$ donor group were synthesized and one of these representatives **19** was evaluated in Rh^{I} catalyzed arylation of dienes. High activity was observed with electron-rich homo- and heteroarenes (Scheme 8).^[37a]



Scheme 8. Rh-catalyzed hydroarylation of dienes with α -dicationic chelating phosphine **19**.^[37a]

The same behavior was evidenced for the P-phenylated diimidazoliophosphine **12a** towards oxidation where the expected phosphine oxide could not be detected (Scheme 9).^[31] By contrast, analogues bearing more basic P-substituents such as *t*Bu and *Ni*Pr₂ substituents were found to undergo oxidation with *m*-CPBA affording stable dicationic phosphine oxides **20b,c** in 91% and 65% yield, respectively.^[31,33-34] The measurement of oxidation potential by cyclic voltammetry confirms the increasing electron deficiency of the P-atom going from the P-*tert*-butylated to the P-phenylated derivative ($E_{\text{P}}^{\text{OX}} = +2.83$ (**12a**), $+2.20$ (**12b**) V/SCE). This experimental method shows also that the introduction of cationic charges has a strong effect on the electronegativity of the oxidation site ($E_{\text{P}}^{\text{OX}} = +1.02$ (**11a**), $+1.32$ (**11b**) V/SCE).

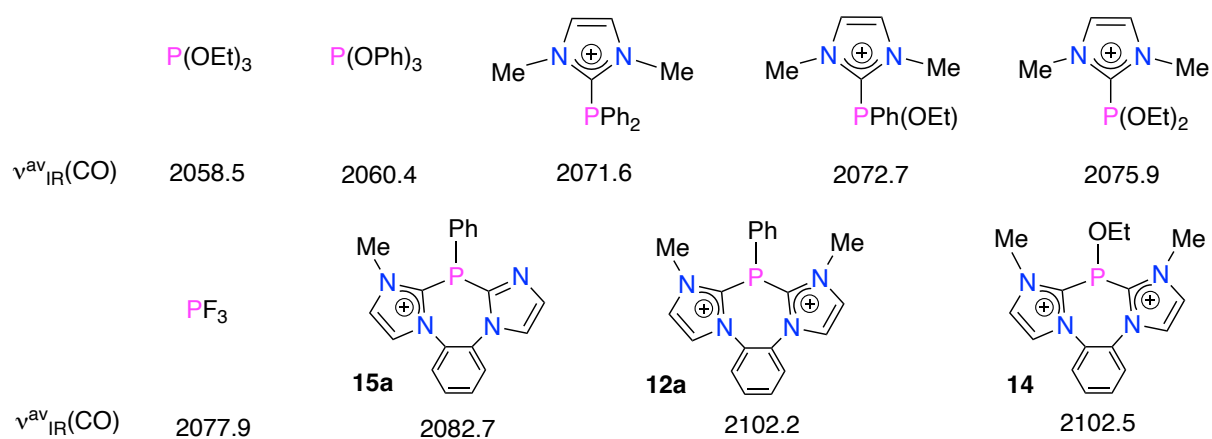


Scheme 9. Compared reactivity of P-substituted diimidazoliophosphines **12a-c** towards oxidation.^[31,33-34]

As in imidazoliophosphonites, the nature of the N₂C–P in diimidazoliophosphines was investigated by theoretical methods. Based on the [NHC–P(NHC)Ph]²⁺ model, the homolytic dissociation was calculated to be favored over the heterolytic dissociation indicating that the C–P bond in these dicationic systems exhibits a predominant covalent character.^[31] The difference observed with imidazoliophosphines and related systems was rationalized by the electrostatic strain of the released [(NHC)PPh]²⁺ fragment that results from a heterolytic dissociation. Concerning the FMOs, the same tendency was observed than in previous systems with the HOMOs (mainly P-lone pair) and LUMO (mainly NHC–P bond) being shifted deeper in energy when a cationic charge is introduced.

Based on experimental observations and DFT calculations of the IR ν_{CO} stretching frequencies of their [Rh(CO)₂Cl] complexes, the different electron-poor ligands were classified according to their donating character (Scheme 10).^[14,31] Thus, it was demonstrated that the introduction of an imidazolio fragment is more efficient than that of an ethoxy substituent in decreasing the donating ability of the P-atom. As expected, the dicationic

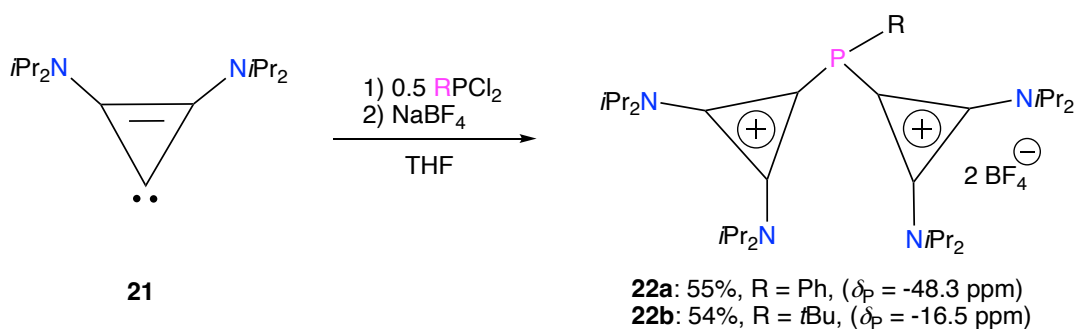
phosphinite **14** was also found to be the least electron-donating ligand of the series, combining the additional presence of two cationic fragments and an ethoxy substituent. Finally, towards a neutral Rh^I center, the mono cationic phosphine **15a** stands as the most electron-poor ligand of the carbeniophosphine family that preserve P-coordinating ability.



Scheme 10. Comparative scale of the electron-donating ability of electron-poor phosphorus ligands L based on the average of calculated IR ν_{CO} stretching frequencies (in cm^{-1}) in $[\text{Rh}(\text{L})(\text{CO})_2\text{Cl}]$ complexes.^[31]

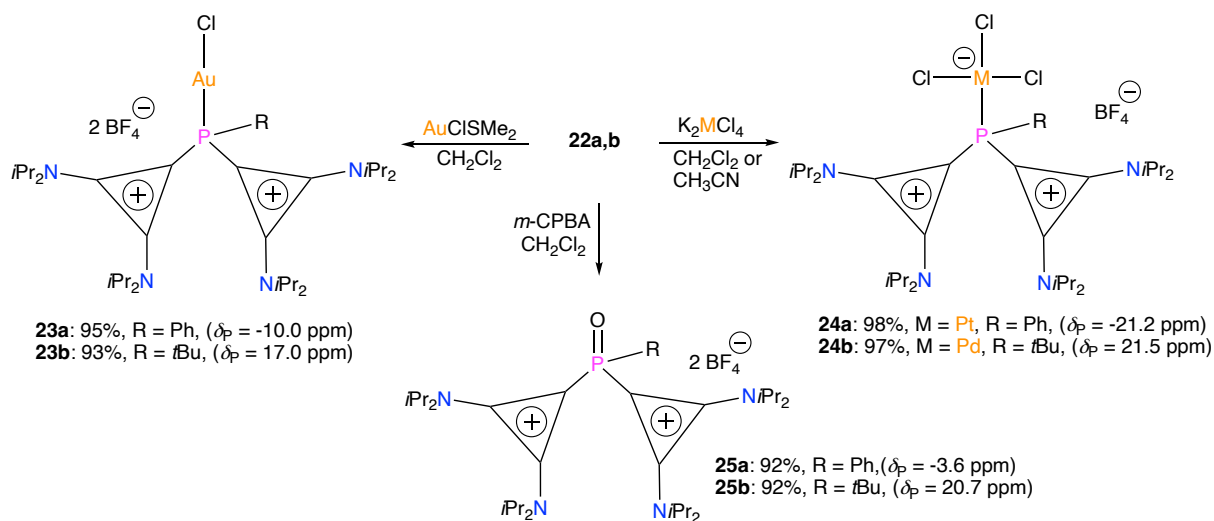
b- Dicyclopropeniophosphines

Since diimidazoliophosphines have shown their limit in term of coordinating properties, dicyclopropeniophosphines were then naturally targeted, cyclopropeniophosphines acting indeed as stronger donor than imidazoliophosphines.^[8] From a synthetic point of view, dicyclopropeniophosphines **22a,b** were prepared in one step by reacting phenyl or *tert*-butyl dichlorophosphines with the BAC carbene **21**^[38] obtained upon deprotonation of the corresponding bis(diisopropylamino) cyclopropenium salt (Scheme 11).^[39] The modest yields (54-55%) obtained for **22a,b** were explained by the competitive formation of P-chloro(cyclopropenio) phosphine adducts.



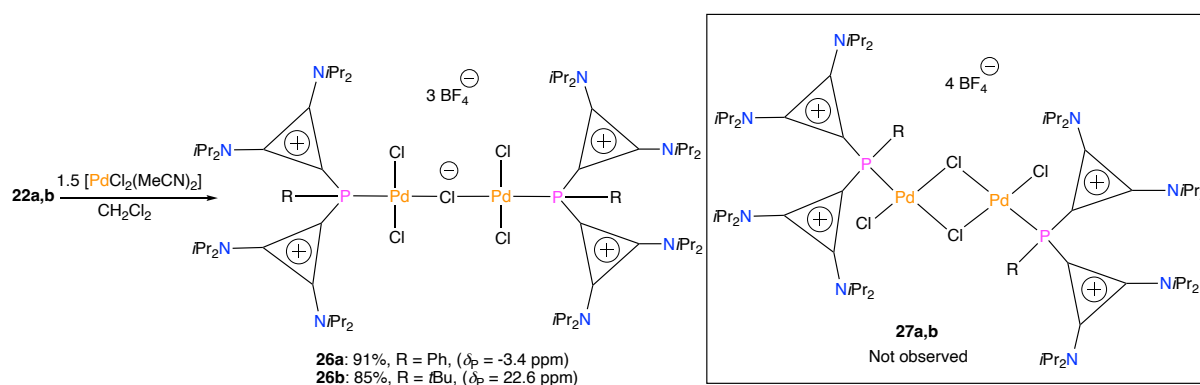
Scheme 11. Preparation method of dicyclopropeniophosphines **22a,b** from the BAC carbene **21**.^[39]

The P-substituent playing a critical role in the diimidazolio series, this parameter (Ph vs *t*Bu) was also evaluated here. In both cases, $\text{Au}^{\text{I}}\text{Cl}$ **23a,b** and $\text{M}^{\text{II}}\text{Cl}_3^-$ **24a,b** (M = Pt or Pd) complexes were obtained in excellent yield by reacting $(\text{Me}_2\text{S})\text{AuCl}$ and K_2MCl_4 metal precursors with dicationic phosphines **22a,b** (Scheme 12).^[29b-39] Both representatives **22a,b** undergo also P-oxidation with *m*-CPBA to give the corresponding dicationic phosphine oxides **25a,b** in 92% yield. These results, which contrast with the lack of reactivity observed with the P-phenylated diimidazoliophosphine **12a**, are in perfect agreement with the stronger donor character of BAC compared to NHC carbenes.^[38]



Scheme 12. Coordination of dicyclopropeniophosphines **22a,b** with metallic and non-metallic Lewis acids.^[29b-39]

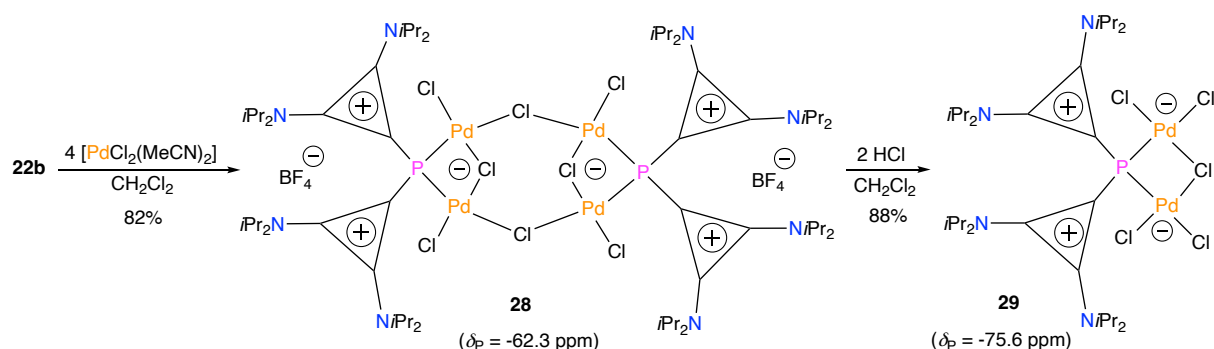
Unexpectedly, dinuclear Pd^{II} complexes **26a,b** were formed in good yield by reacting dicyclopropenylphosphines **22a,b** with [PdCl₂(MeCN)₂] complex (Scheme 13).^[39] Inspection of the solid-state structure of **26a** actually reveals the presence of a pentachlorinated structure featuring two Pd centers in a quasi-square planar environment with an intercalated dicoordinate chloride. This specific arrangement was rationalized by the existence of destabilizing electrostatic factors, the chloride bridge screening indeed the repulsion of the positive charges of the two phosphine ligands. At this stage, one can think that the observation of these unusual metallic structures was made to the detriment of more classical bridged μ -Cl-bridged dimeric structures of type **27a,b** typically observed with neutral phosphine ligands.



Scheme 13. Unusual coordination of dicyclopropenylphosphines **22a,b** with [PdCl₂(MeCN)₂] complex.^[39]

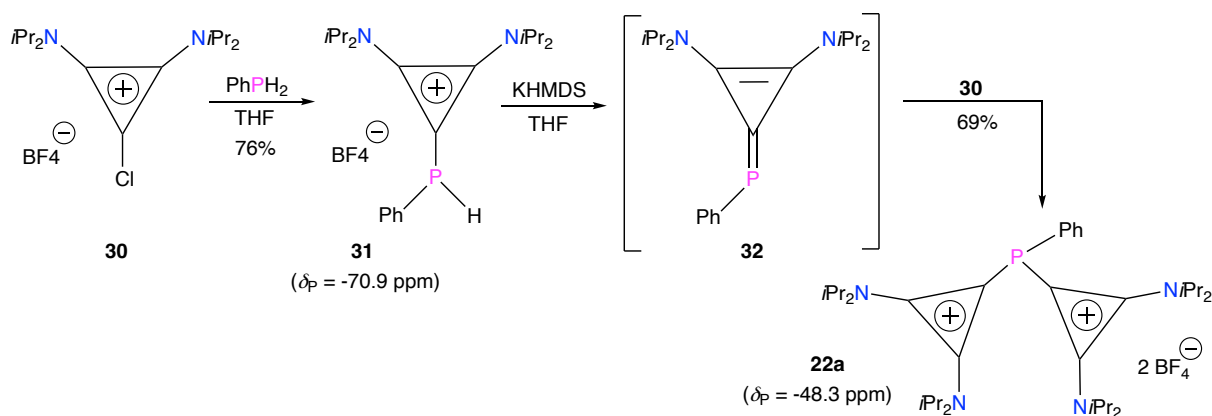
With an excess of [PdCl₂(MeCN)₂], the *P-tert*-butylated dicyclopropenylphosphine **22b** via the intermediate **26b** led to an unprecedented structure, namely the tetranuclear complex **28** based on a centrosymmetric Pd₄Cl₈²⁻ core behaving as a metallic bridge between two μ^2 - η^1 dicyclopropenylphosphido ligands (Scheme 14).^[39] The formation of the latter where each Pd atom in a quasi-square planar geometry exhibits a palladate character with a terminal Cl and two bridging Cl ligands results from the heterolytic cleavage of the P-*t*Bu bond. Another remarkable feature of this complex is the quasi-planarity of the eight-membered ring including four Pd atoms, two P atoms and Cl atoms. Here again, the formation of **28** was attributed to the best compromise found between steric and electrostatic factors as illustrated with the stability of Pd complex **26a** in the presence of an excess of [PdCl₂(MeCN)₂], the phenyl cation being indeed more reluctant to elimination than the *t*butyl cation. As other intriguing reactivity, one can note the dissociation of the tetranuclear Pd complex **28** towards

the dinuclear Pd complex **29** featuring a double zwitterionic dipalladate structure upon addition of HCl (Scheme 14). The specific arrangement of the PdCl₅ core involves the presence of one bridging Cl and four terminal Cl ligands with the absence of any Pd–Pd interaction as observed in its tetranuclear precursor **28**.^[39]



Scheme 14. Unusual coordination of dicyclopropenylphosphine **22b** in the presence of an excess of [PdCl₂(MeCN)₂] complex.^[39]

This part on dicyclopropenylphosphines must be placed in a broader context in which a huge contribution has been made by Alcarazo et al. In fact, the P-phenylated dicyclopropenylphosphine **22a** was for the first time synthesized by his group by the condensation of chlorocyclopropenium salt **30** with phenylphosphine.^[40] Then, it was shown that deprotonation of the resulting P-adduct **31** led to phosphalkene intermediate **32** which can react with a second equivalent of chlorocyclopropenium **30** (Scheme 15). This alternative method was reported to be valuable for other secondary phosphines. Based on TEP values, it was demonstrated that the donor character of dicyclopropenylphosphine **22a** is weaker than that of phosphites and comparable to that of PF₃ and P(CF₃)₃. As another striking fact, it was also mentioned that the corresponding AuCl complex can act as an effective π -acidic catalyst in hydroarylation reactions in particular for the preparation of hindered 4,5-disubstituted phenanthrenes.^[40]



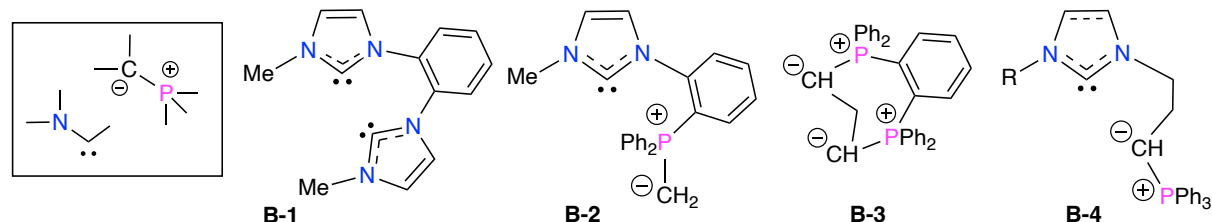
Scheme 15. Pioneer report of the preparation of dicyclopropeniophosphine **22a** by Alcarazo et al. following a different approach.^[40]

These different reports on dicarbeniophosphines $[(R_2C^+)_2-PR]$ show on the one hand that the chemistry of these cationic species is extremely rich with different coordination modes that can be governed by electrostatic interactions, and on the other hand that they have enabled progress, especially in the understanding of factors that influence the stability of ligand-metal bond. In this family, dicyclopropeniophosphines stand as more promising candidates than diimidazoliophosphines for catalytic purposes due to the stronger donor character of BAC compared to NHC carbenes with the effect of increasing the stability of ‘carbene–phosphenium’ interaction. In this race towards polycationic ligands, triscyclopropeniophosphines were also reported and found to facilitate the Pt-catalyzed hydroarylation of *ortho*-alkynylated biaryls.^[41]

III. Extremely Electron-Rich Carbon Systems

Aiming to develop ligands with extreme electronic properties, in complement to electron-poor (di)carbeniophosphines, we were also interested in the design of strongly donating carbon ligands.^[42] This part was initiated by the preparation of an isostructural series of $Rh(CO)_2$ complexes based on a rigid *o*-phenylene bridge and containing strongly σ -donating and weakening π -accepting NHC and/or phosphonium ylide donor extremities **B-(1–3)**.^[43] This tight association allowed us to demonstrate that phosphonium ylides behave as stronger donor than NHCs (Scheme 16).^[9] The initial synthesis developed in the imidazolyl-phenyl series was also successfully applied in the benzimidazolyl-naphthyl case allowing the formation of enantiomerically pure atropochiral palladate complexes.^[44] For catalytic purposes, a Pd(allyl) complex of ligand **B-2** was reported to be active in the 1,3-diphenylallylation of dimethyl malonate.^[45] Afterwards, other *C,C*-chelating NHC-phosphonium ylide systems were

prepared such as representative **B-4** where the two carbon donors are linked by a flexible C₃ propyl bridge.^[46] After this contribution, in order to make a decisive step towards even more strongly donating ligands, we focused our interest on the design of C,C,C-pincer systems, the electron density on the metal having to be significantly enhanced by the presence of three carbon donor extremities.^[47]

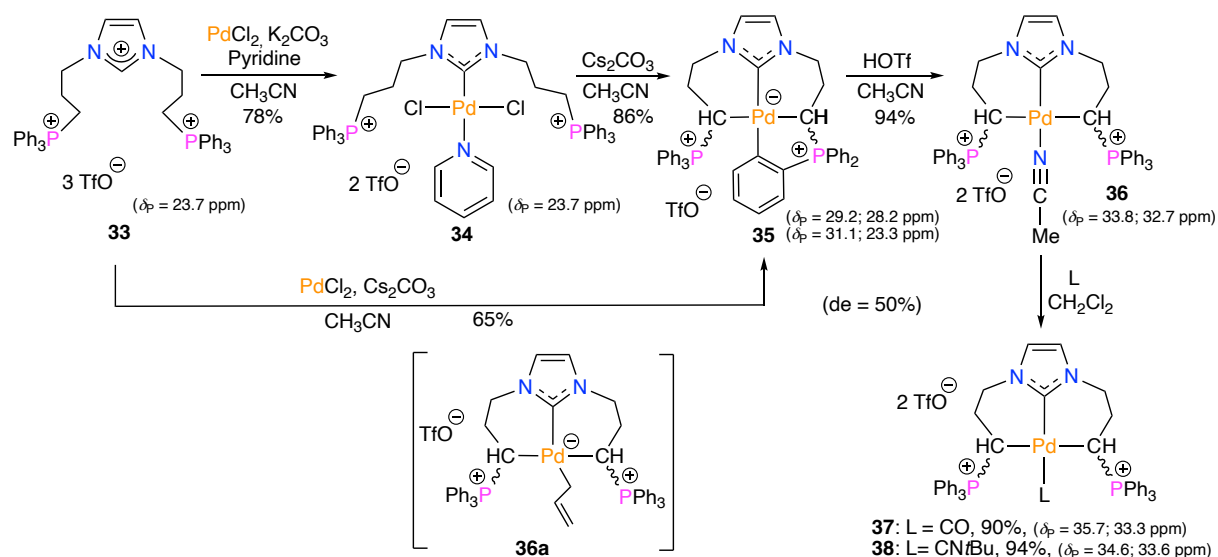


Scheme 16. C,C-chelating systems based on NHC and phosphonium ylide donor extremities **B-(1-4)**.^[42]

III. 1 NHC core-bis(triphenylphosphonium ylide) pincer complexes

A new category of pincer Pd^{II} complexes bearing a strongly donating C,C,C-NHC, diphosphonium bis(ylide) ligand was synthesized from the tricationic imidazolium salt **33** exhibiting two triphenylphosphonium side chains (Scheme 17).^[48] As developed in the bidentate NHC-ylide series,^[46] a sequential strategy was first considered to coordinate the imidazolium salt **33** obtained through the N-functionalization of 1*H*-imidazole by (3-bromopropyl)triphenylphosphonium bromide. Upon addition of PdCl₂ in the presence of the K₂CO₃/pyridine system in CH₃CN, the dicationic PdCl₂ complex **34** was first obtained in 78% yield. Then, in the presence of an excess of base, the *ortho*-metallated Pd complex **35** was isolated in 86% yield as a 75/25 mixture of two diastereomers. Noteworthy, the same complex **35** could be prepared in 65% yield in one step procedure upon deprotonation of salt **33** in the presence of PdCl₂ and an excess of Cs₂CO₃. Realizing that complex **35** could be formally considered as a constraint form of the targeted NHC core, bis(ylide) pincer complex where the coordination site *trans* to the NHC is neutralized by the *ortho*-metallation of one of the P⁺-phenyl moieties, the cleavage of this C_{ar}-bond was envisioned. For this purpose, complex **35** was reacted with a stoichiometric amount of HOTf in CH₃CN. Under these acidic conditions, the desired complex **36** featuring a central NHC and two peripheral phosphonium ylides was formed in 94% yield as a mixture of *meso*- and *dl*-diastereomers (*de* = 50%) standing as a rare representative of pincer complexes based on only carbon-based donor ends.^[48] The overall donor character of this pincer ligand was estimated by the measurement of ν_{CO} and ν_{CN}

stretching frequencies of Pd–CO and Pd–CN*t*Bu complexes **37–38** obtained by ligand exchange from **36**. Noteworthy, the IR ν_{CO} band of complex **37** was found to be at 2114 cm^{-1} in CH_2Cl_2 solution.^[48]



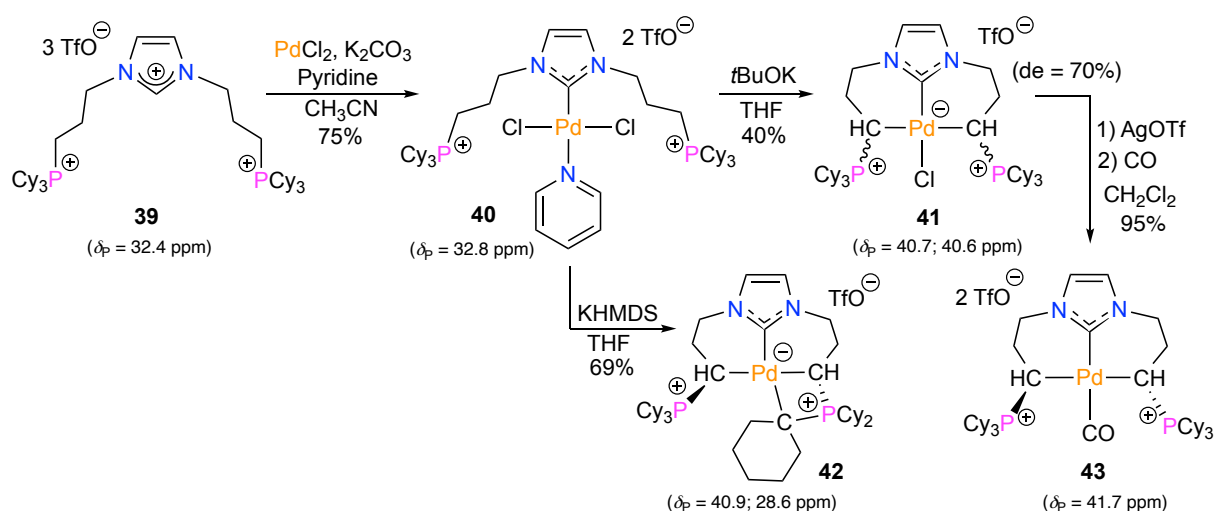
Scheme 17. Preparation of NHC core, diphosponium bis(ylide) Pd(II) pincer complexes **36–38** from the imidazolium salt **33** (in the PPh_3^+ series) and representation of the catalytic active η^1 -allyl-Pd pincer complex **36a**.^[48–49]

Based on this pioneering report, related NHC core, phosphonium ylide pincer Pd complexes featuring an NHC or a phenolate extremity were then considered in the group.^[49] In the Pd^{II}-catalyzed allylation of aldehydes with allyltributyltin, complex **36** was demonstrated to be the most effective in the series. The superiority of **36** was attributed to the stronger donating character of the *C,C,C*-NHC, bis(ylide) ligand which facilitate the nucleophilic attack of η^1 -allyl-Pd pincer complex **36a** proposed as catalytic intermediate on the aldehyde (Scheme 17).^[49]

III. 2 NHC core-bis(tricyclohexylphosphonium ylide) pincer complexes

After the preparation of NHC core, diphosponium bis(ylide) Pd^{II} pincer complexes **36–38**,^[48] we considered more recently the introduction of $^+\text{PCy}_3$ extremities which should lead to carbon-based pincer complexes with increased electron density at the metal center.^[50] Indeed, cyclohexyl groups characterized by strong inductive effect are expected to decrease the degree of positive charge on phosphorus atom and therefore enhance the donor ability of the *C*-ylidic extremities. The cyclohexyl substituents being *a priori* more resistant to C–H

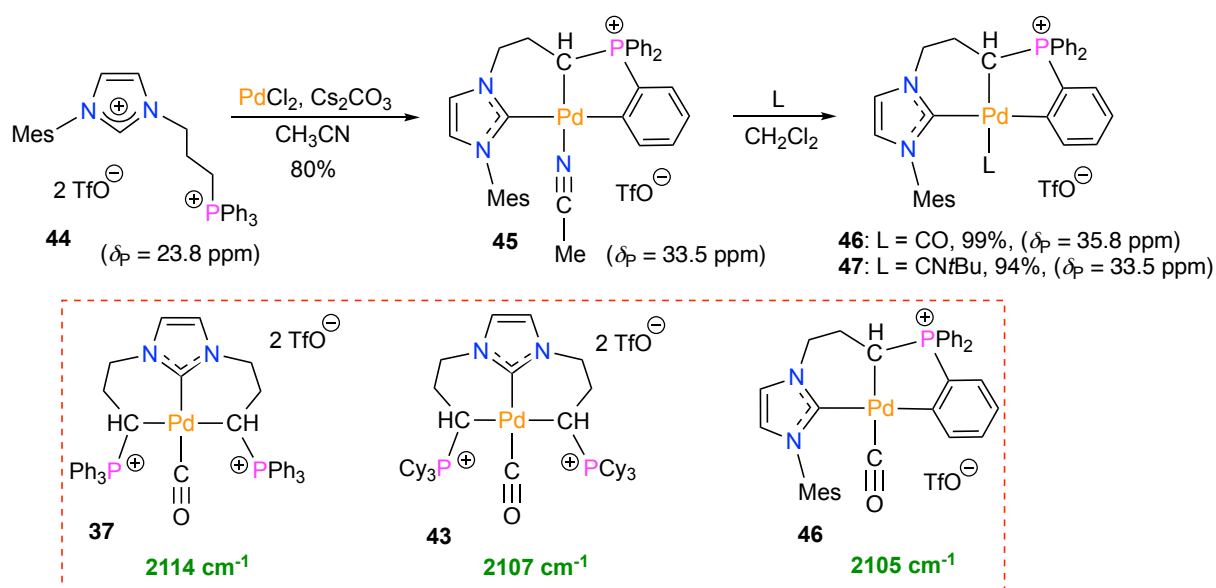
activation process, the preparation of such pincer complexes should be able to take place without the intermediate formation of *orthometalated* complexes. Similar to the $^+\text{PPh}_3$ series, the imidazolium salt **39** was thus treated with PdCl_2 in the presence of the K_2CO_3 /pyridine system in CH_3CN affording the dicationic NHC core $\text{PdCl}_2(\text{Py})$ complex **40** with two pending $^+\text{PCy}_3$ chains in 75% yield (Scheme 18). In the presence of *t*BuOK, complex **40** was then converted in THF to the pincer Pd complex **41** by C-coordination of the two lateral $^+\text{PCy}_3$ chains. This air-stable complex **41** isolated in 40% yield was obtained as a 85/15 mixture of two diastereomers. As anticipated, while no product resulting from $\text{C}(\text{sp}^3)\text{-H}$ activation was observed with *t*BuOK, the use of a stronger base (KHMDS or LDA) enabled the activation of a $\text{P}^+\text{-Cy}$ substituent yielding the novel cyclometalated palladate complex **42** as a unique diastereomer. To evaluate the donating character of the supporting ligand, we then turned to the preparation of a Pd-CO adduct. With this objective in mind, after treatment of the *trans* isomer of cationic pincer **41** with AgOTf in CH_2Cl_2 followed by CO gas bubbling, the targeted Pd-CO pincer complex **43** was formed in quasi-quantitative yield. Noteworthy, this complex was found to be too unstable to be isolated in a pure form being characterized by a $t_{1/2}$ of about 4 h. The corresponding IR ν_{CO} band was found at 2107 cm^{-1} in CH_2Cl_2 solution.^[50] The examination of experimental ν_{CO} frequency of related carbonyl Pd^{II} pincer complex **37** revealed that the substitution of $^+\text{PPh}_3$ groups by $^+\text{PCy}_3$ ones induces a shift to lower frequency of about 7 cm^{-1} demonstrating the greater electronic donation of the *C,C,C*-pincer ligand of **43** compared to that of **37** featuring $^+\text{PPh}_3$ ends.



Scheme 18. Preparation of NHC core, diphosponium bis(ylide) Pd(II) pincer complexes **41-43** from the imidazolium salt **39** (in the PCy_3^+ series).^[50]

III. 3 Phosphonium ylide core-NHC-aryl pincer complexes

Considering the *ortho*-metallation of P⁺-C₆H₅ substituents under basic conditions as evidenced in the NHC core pincer series (Scheme 17),^[48-49] one of the two N-donor arms in the N-phosphonio substituted imidazolium salt **33** was replaced by a more inert N-substituent, such as a mesityl group, the target being the preparation of a new pincer ligand bearing a central phosphonium ylide.^[51] Gratifyingly, the reaction of imidazolium salt **44** under *ortho*-metallation conditions, namely the addition of PdCl₂ in the presence of Cs₂CO₃ led selectively in one step to the cationic Pd^{II} complex **45** in 80% yield (Scheme 19). The formation of this C,C,C-NHC-ylide-aryl pincer results from a formal triple C–H bond activation of the dicationic precursor. The extreme donor character of such ligand enabled for the stabilization of Pd^{II}–CO **46** and Pd^{II}–CN*t*Bu **47** adducts. It's worth mentioning that **46** is stable at room temperature being one of the rare examples of Pd^{II}-CO complex characterized by X-ray diffraction analysis. The corresponding IR ν_{CO} band found at 2105 cm⁻¹ in CH₂Cl₂ indicates that the anionic NHC-ylide-aryl pincer of complex **46** is slightly more donating than the globally neutral pincer of **43** exhibiting two ⁺PCy₃ extremities. In fact, the introduction of the aryl moiety allows to compensate the presence of two phosphonium ylide donor ends.^[51]

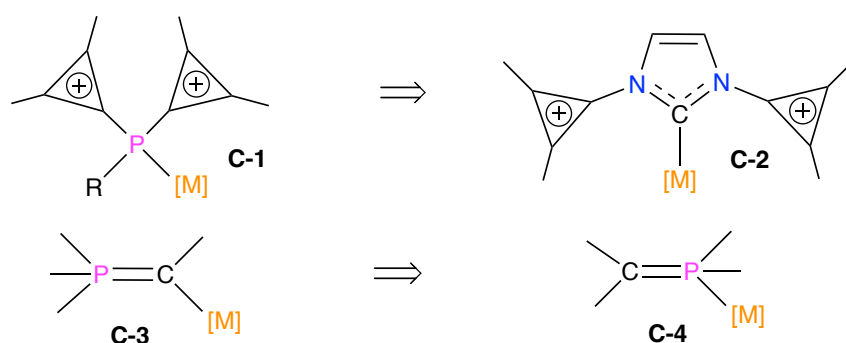


Scheme 19. Preparation of phosphonium ylide core Pd(II) pincer complexes **45-47** from the imidazolium salt **44**,^[51] and IR ν_{CO} frequency values of phosphonium ylide-based pincer Pd complexes **37**, **43** and **46**.^[48,50]

The extreme electronic properties of this pincer ligand featuring a central ylide were also confirmed on the basis of cyclic voltammetry and MOs analysis data.^[51]

IV. Closely related carbon-phosphorus systems

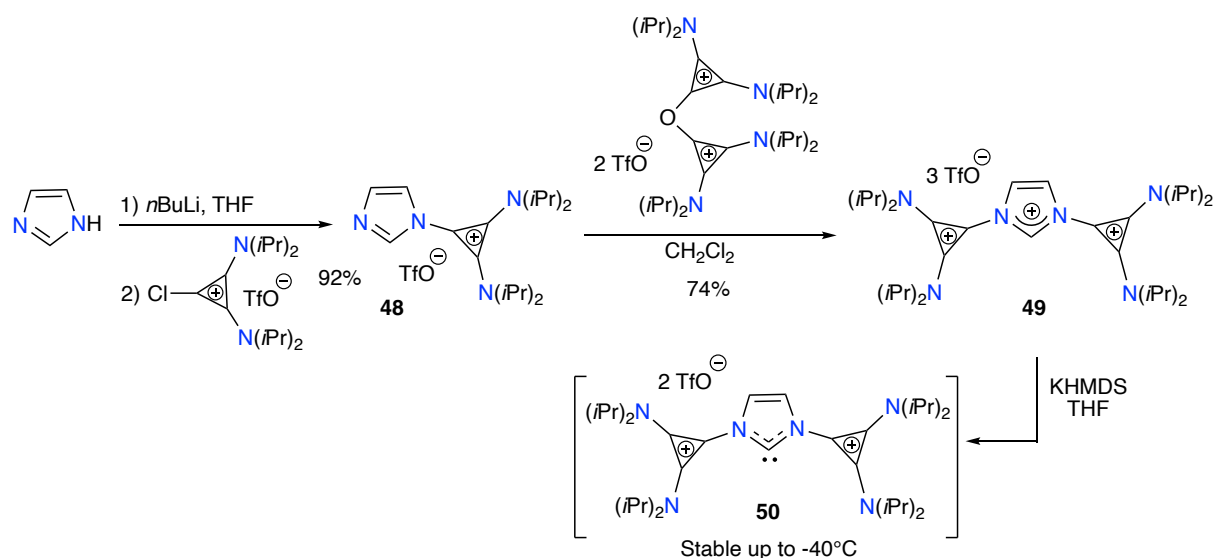
In the two first parts of this account, the chemistry of extremely electron-poor cationic phosphorus systems **C-1** on the one hand and extremely electron-rich neutral carbon systems **C-3** on the other hand was discussed. In the context of C–P analogy, we have recently targeted two new types of ligand systems where the coordinating roles between carbon and phosphorus elements would be formally reversed, i.e. carbon would become the coordinating atom in the close proximity of two cationic charges (**C-2**) and phosphorus the coordinating atom in an electron-rich phosphonium ylide structure (**C-4**) (Scheme 20).



Scheme 20. Analogy C–P between electron-poor dicationic cyclopropenio-substituted systems **C-(1–2)** and electron-rich neutral phosphonium ylide systems **C-(3–4)**.

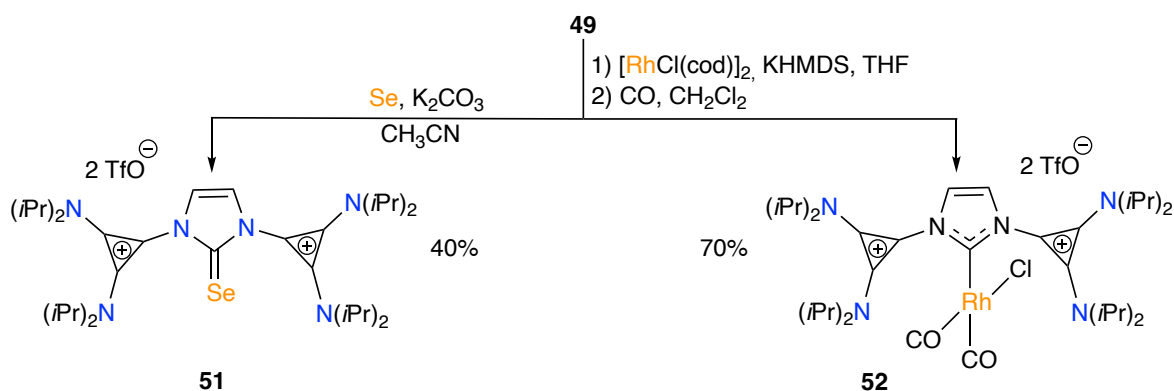
IV. 1 Bis(*N*-Cyclopropenio)-imidazol-2-ylidene

By analogy with dicyclopropenophosphines,^[39] we have recently targeted the preparation of dicationic NHC ligands based on two *N*-bis(diisopropylamino)cyclopropenio substituents.^[52] For this purpose, the imidazolium salt **49** was prepared in a two-step procedure from readily available 1*H*-imidazole. The *N*-cyclopropenio imidazole **48** was first isolated in 92% yield by reacting 1*H*-imidazole with *n*BuLi in THF followed by the addition of 1-chlorocyclopropenium triflate. Then, imidazole **48** was converted into the desired imidazolium salt **49** in 74% yield by using an “onio-substituent transfer” reagent.^[53] Upon deprotonation of salt **49** with an equivalent of KHMDS in THF, the dicationic free NHC **50** could be identified by ¹³C NMR spectroscopy but was found to be unstable, decomposing above –40°C into an unidentified mixture of products (Scheme 21).



Scheme 21. Preparation of the imidazolium salt **49** from 1*H*-imidazole with ^{13}C NMR identification of corresponding dicationic NHC **50**.^[52]

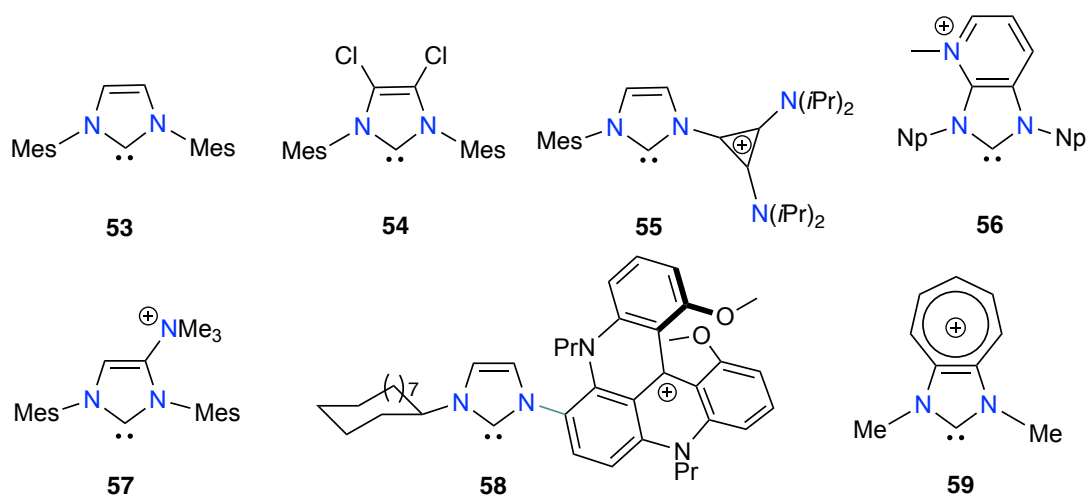
Generally, the electronic properties of a NHC refer to its σ -donation and π -acidity provided by the $^1J_{\text{CH}}$ coupling constant of the N_2CH carbon atom in imidazolium salt precursor and the ^{77}Se NMR chemical shift in $\text{NHC}=\text{Se}$ adduct, respectively. The overall electronic donation combining both effects is estimated from IR ν_{CO} stretching frequencies in corresponding NHC $\text{Rh}^{\text{I}}(\text{CO})_2$ complex. With this aim, the selenourea **51** was prepared in 40% yield by reacting the pre-ligand **49** with an excess of selenium in the presence of K_2CO_3 in CH_3CN , and the NHC $\text{Rh}^{\text{I}}\text{Cl}(\text{CO})_2$ complex **52** in 70% yield by treating **49** with 0.5 equiv. of $[\text{RhCl}(\text{cod})]_2$ in the presence of KHMDS in THF followed by bubbling CO through a CH_2Cl_2 solution (Scheme 22).^[52]



Scheme 22. Syntheses of the selenourea **51** and NHC Rh^{I} complex **52** from imidazolium salt **49**.^[52]

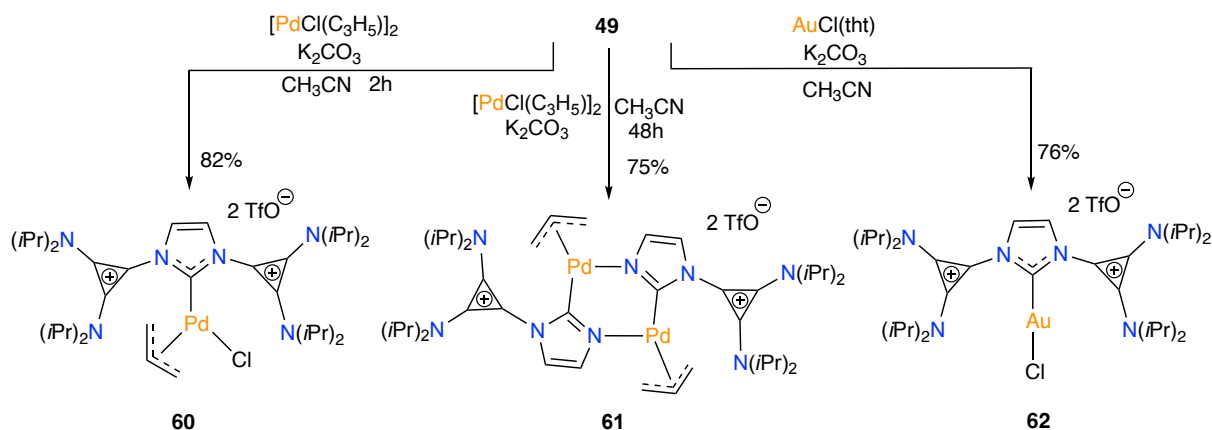
Electronic parameters of dicationic NHC **50** were then compared with other imidazol-2-ylidenes, in particular with cationic representatives bearing a positive charge near the carbene center. Firstly, the value of $^1J_{\text{CH}} = 232$ Hz for **49** superior that of mono (*N*-cyclopropenio) imidazolium salt (**55.H**)²⁺ ($^1J_{\text{CH}} = 229$ Hz) recently prepared in the group^[54] indicates that the introduction of a second positive charge lowers further the σ -donation of the carbene center. Then, $^1J_{\text{CH}}$ values of imidazolium salts based on neutral IMes **53** and IMes^{Cl₂} **54** of 225 and 232 Hz,^[55] and cationic NHC **57**,^[56] **58**^[57] and **59**^[58] of 231, 224, and 227 Hz demonstrates that **50** is one of the least σ -donating NHC known to date (Scheme 23). Concerning π -acidity, the ⁷⁷Se chemical shift of **50** ($\delta_{\text{Se}} = 197$ ppm) is strongly downfield shifted compared to NHC=Se adduct **55** ($\delta_{\text{Se}} = 112$ ppm). It was also evidenced that only cationic carbenes **56**^[59] and **59** ($\delta_{\text{Se}} = 245$ and 473 ppm)^[58] where the positive charge is delocalized through the π -system of the NHC present more π -acidic character. Finally, based on IR ν_{CO} stretching frequencies of Rh(CO)₂ complex **52** (2007 and 2094 cm⁻¹ in CH₂Cl₂), the calculated Tolman Electronic Parameter (TEP) value of 2061 cm⁻¹ shows that only planar cationic NHC **56** and **59** are characterized by a weaker overall donating character, and that the substitution of the neutral *N*-Mes group in IMes by a cyclopropenium moiety diminishes sequentially the overall electronic donation of the corresponding NHC (IMes: 2051 vs **55**: 2057 vs **50**: 2061 cm⁻¹). Thus, the introduction of a second cationic N-substituent significantly influences both σ -donation and π -accepting characters of the dicationic NHC **50**.^[52]

NHC	$^1J_{\text{CH}}$ (Hz) ^[a]	δ ⁷⁷ Se (ppm) ^[b]	TEP (cm ⁻¹) ^[c]
53	225	27	2051
54	232	114	2055
55	229	112	2057
56	-	245	2067
57	231	102	2056
58	224	65, 49	2055
59	227	473	2070
50	232	197	2061



Scheme 23. Electronic parameters $^1J_{\text{CH}}$ (Hz), δ_{sc} (ppm), and TEP (cm^{-1}) of selected imidazol-2-ylidenes **53-59**. ^[a] From imidazolium precursors. ^[b] From NHC=Se adducts. ^[c] From NHC Rh(CO)₂ complexes.^[52]

Despite the presence of two *N*-cationic substituents, NHC **50** presents a rich coordination chemistry (Scheme 24).^[52] For instance, treatment of imidazolium salt **49** with a neutral Pd^{II} center, such as [PdCl(π -allyl)]₂ complex in the presence of an excess of K₂CO₃ in CH₃CN was shown to afford two different Pd^{II} complexes depending on the reaction time. While in 2 hours the expected dicationic NHC Pd(allyl)Cl complex **60** was readily obtained in 82% yield, with a longer time a dimeric NHC Pd^{II} complex based on a central six-membered dipalladacycle featuring a *C,N*-chelating imidazolyl ligand was formed in 75% yield. The formation of dinuclear complex **61** was attributed to the cleavage of a N–C⁺ bond upon nucleophilic attack of a chloride anion or residual traces of H₂O.^[12] Imidazolium salt **49** was also able to coordinate Au^I metal centers as illustrated with the formation of dicationic NHC AuCl complex **62** isolated in good yield after treatment with AuCl(tht) and K₂CO₃ in CH₃CN. Noteworthy, steric constraint calculated using the SambVca web application^[60] concluded that NHC **50** is characterized by a steric pressure in between mono cyclopropenyl NHC **55** and larger IPr NHC. Concerning catalytic purposes, a moderate activity for Au^ICl complex **62** was observed in the intramolecular cyclization of *N*-(2-propyn-1-yl)benzamide and 2-ethynyl-2'-methyl-1,1'-biphenyl, which was rationalized by the fragility of dicationic NHC **50** as evidenced in the Pd case with the formation of dinuclear complex **61**.^[52]

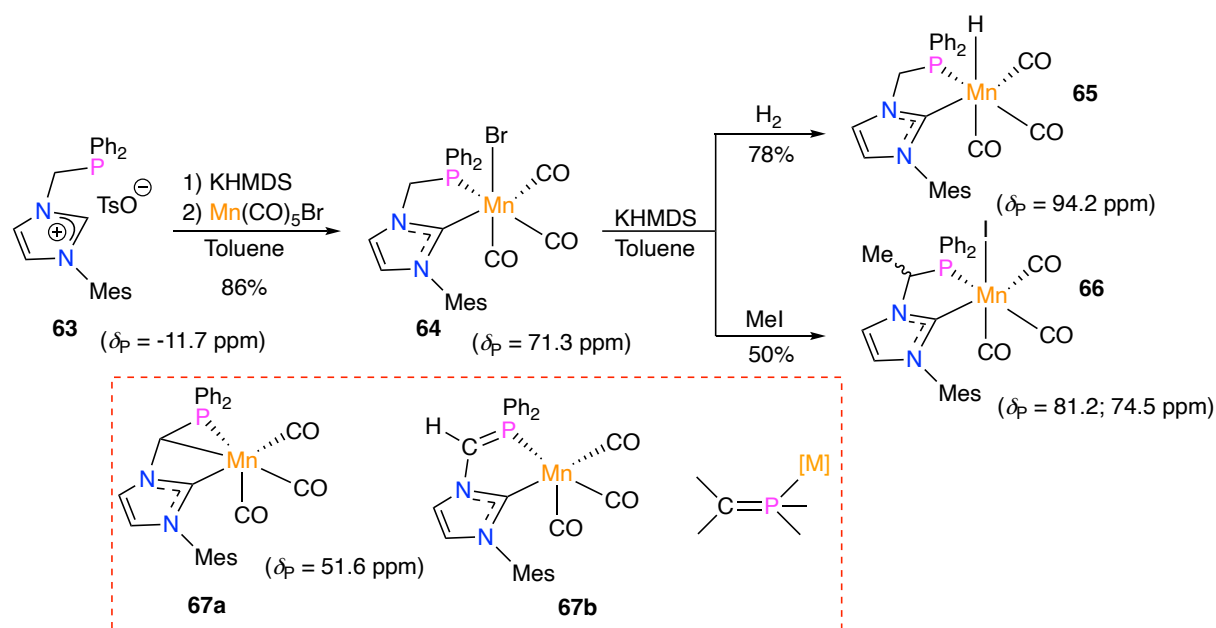


Scheme 24. Coordination issues of tricationic imidazolium salt **49** in Pd^{II} and Au^I series.^[52]

IV. 2 Non classical NHC-phosponium ylide complexes

Complementary to our research axis on all-carbon electron-rich NHC-ylide systems, we were also interested in other strongly donating ligands that associate an NHC moiety with a phosphine end. In this context, the phosphine imidazolium salt **63** was coordinated to a Mn^I center upon addition of [Mn(CO)₅Br] in the presence of KHMDS in toluene to form the NHC-phosphine Mn^I complex **64** in 86% yield as a single isomer (Scheme 25).^[61] With the aim of developing hydrogenation catalysts, **64** was reacted with KHMDS in toluene under H₂ atmosphere. Under these conditions, while the formation of the expected Mn^I hydride complex **65** was effectively observed, this reactivity questioned us about the location of the deprotonation site. To answer to this concern, the deprotonated intermediate was treated with an excess of methyl iodide leading to the new complex **66** in 50% yield as a mixture of two diastereomers. Inspection of the structure of **66** indicates that the methylation occurred at the carbon atom bridging NHC and phosphine donor moieties. All attempts to grow single crystals of the deprotonated species being unsuccessful, DFT calculations were undertaken at the BP86/def2-TZVP level. These calculations evidenced for the deprotonated complex the existence on five minima, the global minimum being attributed to the octahedral cyclometalated 18-e complex **67a** adopting a facial arrangement. However, four other minima were also calculated showing a square pyramidal 16-e geometry (2 *fac* and 2 *mer* isomers) arrangement based on an unusual chelating NHC-phosponium ylide ligand. Among them, the most stable NHC-ylide *fac*-complex **67b**, calculated to be only 7.5 kcal.mol⁻¹ higher in energy than **67a** is characterized by the presence of a classical ylidic P–C bond and a stronger P–Mn bond compared to NHC-phosphine Mn complexes **64-65** containing a typical dative P–Mn bond.^[61] To our knowledge, this mode of coordination for a phosphonium ylide has been rarely observed, and only two examples were experimentally reported, both in the iron case

with a monodentate phosphonium ylide^[62] and a more elaborated PNP pincer ligand.^[63] Noteworthy, the Mn^I complex **64** was found to act as one of the most efficient catalytic system for the hydrogenation of ketones. More precisely, a large variety of aryl(alkyl)ketones with different steric hindrance and functional groups was readily reduced with a maximum TON of 6200 in the case of acetophenone.^[64]



Scheme 25. Coordination behavior of the phosphine imidazolium salt **63** in presence of [Mn(CO)₅Br] complex.^[61]

Conclusion and perspectives

With a view to developing new ligands, carbon and phosphorus remain to this day essential coordinating elements. As illustrated in this account, they can lead to original structures characterizing by unique electronic properties located at the lower limit of the donating scale with imidazoliophosponite and dicarbeniophosphine ligands and at the upper limit with phosphonium ylide-based pincer ligands. Playing with both elements, complementary systems exemplified by an electron-poor dicationic NHC bearing two *N*-cyclopropenio substituents and electron-rich P-metallated phosphonium ylide complexes were prepared and successfully implemented in homogeneous catalytic processes. However, if the extreme electronic character presents several advantages such as that of allowing the stabilization of high-valent metal centers or the activation of strong bonds, it can have also certain disadvantages, namely inducing an increased reactivity and even an instability of the species concerned. As a possible prospect, the development of hybrid ligands featuring two electronically different

coordinating ends could bring novel advances in various domains of chemistry. For instance, they could benefit to all steps of a catalytic cycle to achieve better activity and selectivity or induce long-range ligand-metal-ligand charge-transfer (LMLCT) in photoactive systems. In such direction, chelating C,P-based ligands associating carbeniophosphine and phosphonium ylide donor extremities are promising candidates.

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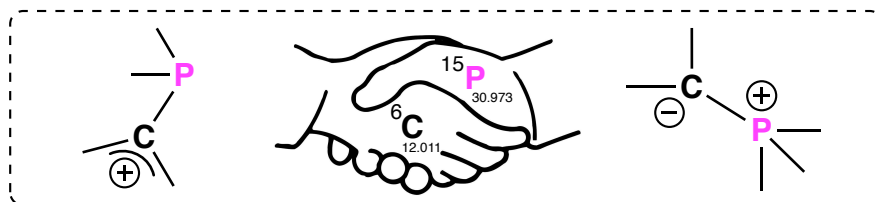
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Graphical Abstract



In coordination chemistry, *carbon and phosphorus* elements play a preponderant role being at the origin of the development of a large variety of ligands including *carbeniophosphines* and *phosponium ylides* located at both extremities of the donating ability scale.