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# Carbenes and phosphonium ylides: a fruitful association in coordination chemistry

Dmitry A. Valyaev<sup>a</sup> and Yves Canac<sup>\*a</sup>

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Among a plethora of  $\sigma$ -donor ligands available, carbon-centered ones have become essential, in particular with the emergence of N-heterocyclic carbenes (NHCs), positioning themselves as credible alternatives to traditional nitrogen- and phosphorus-based systems. Phosphonium ylides representing another class of neutral  $\eta^1$ -bonded carbon ligands have also been shown to act as effective Lewis bases. Considering the intrinsic features of the carbene and phosphonium ylide ligands, similar in terms of electronic properties, but different in terms of bonding mode, the design of hybrid systems combining these two types of carbon functionalities appeared to be a natural and exciting challenge. This Perspective comprehensively covers the chemistry of such ligand architectures from synthesis and fundamental aspects to catalytic applications.

## Introduction

Carbon, one of the most abundant elements in the universe, occurs mainly in nature in two well-defined allotropic forms, graphite and diamond. Other synthetic allotropic forms of carbon such as fullerenes<sup>1</sup> or nanotubes<sup>2</sup> are also known being the subject of intense research due to their remarkable physicochemical properties, which make them highly attractive as innovative materials.<sup>3</sup> Carbon is a fundamental constituent of living matter and obviously remains the principal building block in organic chemistry due to the participation of his four valence electrons in the formation of covalent  $\sigma$ - and/or  $\pi$ -bonds. By contrast, the role of carbon in coordination chemistry appears to be less preponderant,<sup>4</sup> since to act as a neutral coordinating element the carbon atom typically requires a lone pair of electrons to bind a Lewis acidic center that can be metallic in nature or not.

Neutral  $\eta^1$ -carbon ligands<sup>5</sup> such as carbon monoxide or isocyanides<sup>6</sup> correspond to this scenario, as do also singlet carbenes featuring two non-bonding electrons with antiparallel spin within the same molecular orbital. The first evidence for the possible use of singlet heteroatom-substituted carbenes as donor ligands was initially illustrated through the successive reports of metal complexes of these reactive divalent carbon species by Fischer,<sup>7</sup> Wanzlick<sup>8</sup> and Öfele<sup>9</sup> in the 60-70's. This pioneering work was followed a few years later by the isolation of the first stable singlet carbenes, namely a phosphino(silyl)-carbene and a cyclic diaminocarbene (NHC), respectively by the group of Bertrand<sup>10</sup> and Arduengo.<sup>11</sup> The strategy selected by these authors consisted of incorporating P- or N-heteroatoms to stabilize the electron-deficient carbon atom *via*  $\pi$ -donation in its empty *p* orbital thus restoring a formal 8-electron count at

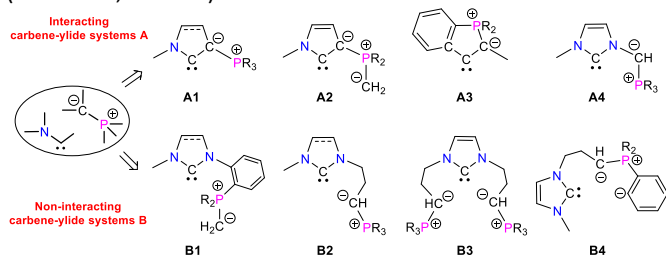
the coordinating center more in line with the octet rule. These two key reports were at the origin of the development of a large variety of carbenes and related carbon-based two-electron  $\sigma$ -donor ligands<sup>12</sup> possessing different steric and electronic properties, which have subsequently demonstrated their enormous potential not only in organic and organometallic catalysis, but also in the field of metal-based pharmaceuticals and functional materials.<sup>13</sup>

Like carbenes, phosphonium ylides fall into the category of neutral  $\eta^1$ -carbon ligands with a sole example of  $\eta^2$ -C=P coordination mode having been briefly mentioned in the literature.<sup>14</sup> Although phosphonium ylides are mainly described in their free state by the two canonical neutral ylene and ionic ylide structures,<sup>15</sup> the second form gives more account of their electronic structure evidencing the polar character of the P-C bond with a negatively charged carbon atom bearing an unshared pair of electrons next to a phosphonium moiety.<sup>16</sup> Discovered long before carbenes following the work of Michaelis<sup>17</sup> and Staudinger,<sup>18</sup> phosphonium ylides have not had the same dazzling success in coordination chemistry and homogeneous catalysis.<sup>19</sup> Their major role, which is still relevant today, was initially focused on organic synthesis with the selective formation of C=C bonds through the famous Wittig olefination of carbonyl compounds.<sup>20</sup> More generally, ylide-type species are now attracting a renewed interest from both fundamental<sup>21</sup> and practical points of view.<sup>22</sup> In coordination chemistry, the dipolar nature of phosphonium ylides – the most famous representatives of the family – enables them to form complexes with most of the metal elements.<sup>23</sup> It is worth mentioning that the first examples of transition metal complexes containing carbonyl-stabilized<sup>24</sup> and non-stabilized<sup>25</sup> ylide ligands were described in the 60-70's, followed by the huge contribution of Schmidbaur in the field.<sup>26</sup> In catalysis, the examples involving ylide ligands remain very limited<sup>27</sup> being thus opposite to a widespread use of carbenes. Part of the explanation can be found in the presence of a carbanionic  $sp^3$ -

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carbon atom, the source of the strong nucleophilicity of ylides, which can lead to highly reactive species, but to the detriment of their stability and the selectivity of processes.<sup>28</sup> To overcome these limitations, the chemistry of semi-stabilized and stabilized ylides, where the anionic charge is partially delocalized on C-ylidic substituents has been more developed.<sup>29</sup>

On the basis of common features, namely their strongly  $\sigma$ -donor and relatively weakly  $\pi$ -acceptor character, but also on their difference concerning the coordination mode (NHC:  $N^+=C^-$ ,  $2\bar{e}$  donor (Csp<sup>2</sup>, L type); ylide:  $P^+-C^-$ ,  $1\bar{e}$  donor (Csp<sup>3</sup>, X type),<sup>30</sup> soft NHCs and harder phosphonium ylides according to the HSAB theory<sup>31</sup> were associated over the two past decades in different arrangements.<sup>32</sup> These two carbon donors can either interact as in species of type **A**, where one fragment acts formally as the substituent of the other (Scheme 1, top), or simply occupy remote positions separated by an insulating linker to afford polydentate ligands of type **B**, where each carbon donor retains its own electronic and steric features (Scheme 1, bottom).



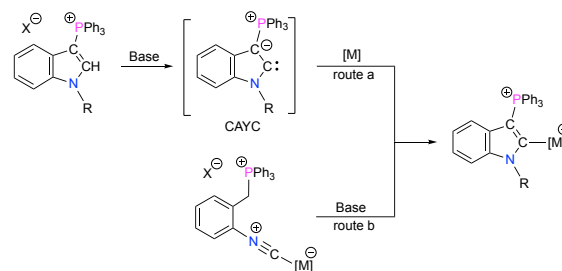
**Scheme 1.** Representation of known systems **A-B** associating carbene and phosphonium ylide functionalities with more or less pronounced interaction between them.

In this contribution, we will discuss how the subtle electronic differences between the two carbon moieties influence the stability of hybrid NHC-ylide systems **A-B** as well as the synthetic methods, fundamental aspects, and catalytic applications of these systems.

## Interacting carbene-ylide systems (type A)

### Cyclic amino(ylide) carbenes (CAYC) A1 and A2

On the basis of the preparation of an isostructural series of square-planar  $C,C$ -Rh(CO)<sub>2</sub> complexes, we demonstrated in 2008 that phosphonium ylides behave as stronger donor carbon ligands than NHCs.<sup>33</sup> In the meantime, amino(ylide)carbenes (CAYC), where one of the N-atoms of a NHC moiety is formally replaced by a Csp<sup>3</sup> ylidic carbon atom were targeted by the group of Kawashima<sup>34</sup> and Fürstner.<sup>35</sup> The main goal of these investigations was to take advantage of the lower electronegativity of carbon with respect to nitrogen and the pronounced  $\pi$ -donor ability of the phosphonium ylide to enhance the electron-donating properties of the carbene center while maintaining its overall neutral character.<sup>36</sup> Comparing to NHCs, higher HOMO and LUMO energy levels are indeed expected with CAYC ligands. To access metal complexes of these carbon species, two complementary synthetic approaches were developed, either by the deprotonation of a N-heterocyclic precursor bearing a triphenylphosphonium fragment (Scheme

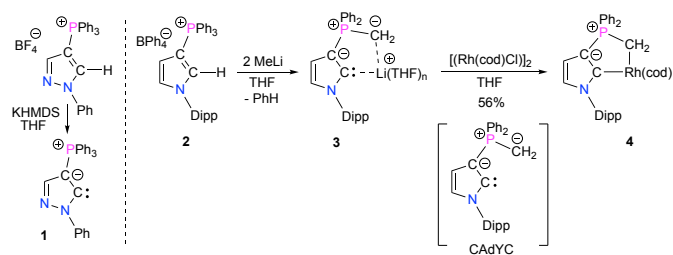


**Scheme 2.** Synthetic strategies devised to prepare metal complexes of CAYC ligands.<sup>34-38</sup>

2, route a) as illustrated by the reports of Kawashima<sup>34</sup> and Fürstner,<sup>35</sup> or by the base-assisted cyclisation of 1,2-phenylene triphenyl-phosphonio isocyanide complexes (Scheme 2, route b).<sup>37</sup> More recently, the latter strategy has also enabled the preparation of acyclic amino(ylide)carbene complexes.<sup>38</sup>

Free CAYC carbenes are generally too unstable to be isolated, however using the deprotonation route a representative **1** based on a pyrazolin-5-ylidene backbone was spectroscopically characterized and converted to the corresponding thioamide in the presence of sulfur thus confirming the real existence of this type of dicoordinate C(II) species (Scheme 3, left).<sup>35</sup> Targeting the isolation of a free CAYC carbene, Bertrand obtained an unexpected result using the deprotonation strategy from a heterocyclic precursor containing a pyrrole ring. It was found that the addition of two equiv. of MeLi to the phosphonium salt **2** gave after elimination of benzene the lithium adduct **3** which could be readily transmetalated by a Rh(I) fragment to afford the carbenic complex **4** (Scheme 3, right).<sup>39</sup> Although the metal center is not coordinated by the expected CAYC ligand, the structure of this Rh complex is unprecedented being described as a complex bearing a chelating anionic NHC-diylide ligand of LX type (CAdYC) where the ylide moiety plays a double role, one of the ylidic carbon atom stabilizing the electro-deficient carbene center while the other ylidic center coordinates with the metal.<sup>40</sup>

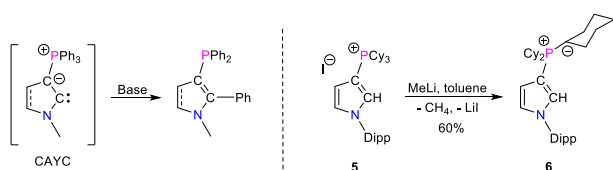
The initial expectation, namely the strong donor character of CAYC ligands was experimentally confirmed by measuring the IR stretching  $\nu_{CO}$  frequencies in a *cis*-[(CAYC)Rh(CO)<sub>2</sub>Cl] complex, which appeared to be at lower frequency ( $\langle\nu_{CO}\rangle$  2012 cm<sup>-1</sup>) than those of related NHC ligands ( $\langle\nu_{CO}\rangle$  2018-2039 cm<sup>-1</sup>).<sup>34</sup> From theoretical studies, it was deduced that the ylide center dramatically enhances the donating properties of CAYC



**Scheme 3.** Representation of the formation of the persistent CAYC carbene **1** (left)<sup>35</sup> and of the Rh(I) complex **4** featuring a chelating anionic CAdYC ligand (right).<sup>39</sup>

carbenes caused by an increase of the energy of the  $\sigma$ -symmetric lone-pair orbital at the carbene atom.<sup>41</sup> As might be expected, the introduction of two ylide functions near the carbene center was calculated to further increase the  $\sigma$ -donation, such a molecule could be an exciting challenge for years to come from an experimental point of view.<sup>42</sup> Desirous of taking advantage of these electronic properties, CAYC ligands were reported to be active in the Pd-catalyzed Buchwald-Hartwig amination<sup>34</sup> and in the Au-catalyzed cycloisomerization of eneallene and enyne derivatives,<sup>43</sup> a domain of applications which however remains to be developed.

The instability of these carbon-based species preventing their isolation is directly related to their extreme electronic properties, namely their strong nucleophilicity, which notably induces the 1,3-migration of a phenyl substituent of the phosphonium moiety to the neighboring carbenic position (Scheme 4, left).<sup>34</sup> The higher stability observed for CAYC **1** based on a pyrazolin-5-ylidene is justified by its lower basicity compared to (benz)imidazolin-2-ylidene analogues, which hinders the phenyl group migration. Anticipating that the formal 1,3-shift of the P<sup>+</sup>-substituent should be disfavored in the P<sup>+</sup>-trialkylated series compared to the P<sup>+</sup>-phenylated series due to a stronger P<sup>+</sup>-Csp<sup>3</sup> bond than a P<sup>+</sup>-Csp<sup>2</sup> bond, Gessner *et al.* recently prepared a CAYC precursor **5** bearing a tricyclohexylphosphonium group (Scheme 4, right).<sup>44</sup> If the transfer of the P<sup>+</sup>-substituent to the carbene was indeed avoided, the deprotonation of the cyclohexyl ring in  $\alpha$ -position of the P<sup>+</sup>-atom was observed leading instead to the selective formation of the phosphonium ylide **6** and not of the targeted CAYC carbene. Theoretical studies were then carried out in order to determine if proton shifts from the ylide substituents to the carbene center were thermodynamically favorable. These calculations showed that  $\alpha$ -deprotonated derivatives are more thermodynamically stable than the free carbene, as illustrated in the case of the P<sup>+</sup>-cyclohexyl group, where the  $\alpha$ -deprotonation is favored by approximately 14.3 kcal.mol<sup>-1</sup> and the activation energy for the H <sub>$\alpha$</sub>  shift from the cyclohexyl group to the carbene is low enough to be readily achievable at room temperature. It was also found that only  $\alpha$ -hydrogen free substituents might possibly allow for the effective stabilization of CAYC carbenes. However, in the case of the *tert*-butyl group while the H <sub>$\beta$</sub>  shift is kinetically less favored than the H <sub>$\alpha$</sub>  shift in the previous series, the  $\beta$ -deprotonated species remained thermodynamically favored over the free carbene and predicted to lead to the formation of isobutene and corresponding pyrrole. Based on this DFT study, it was concluded that the sterically hindered and  $\alpha$ -hydrogen free tris(adamantyl)phosphonium might be the ideal cationic



**Scheme 4.** 1,3-shift of a P<sup>+</sup>-Ph substituent in a CAYC carbene (left) and the formation of the phosphonium ylide **6** by deprotonation of the P<sup>+</sup>-Cy substituent of the phosphonium salt **5** (right).<sup>44</sup>

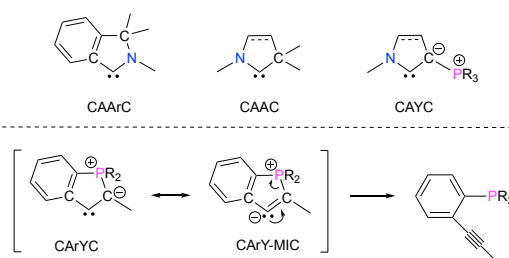
fragment to stabilize free CAYC carbenes, the energy barrier for intramolecular proton transfer and  $\beta$ -elimination being disfavored by about 11.2 kcal.mol<sup>-1</sup>.<sup>44</sup>

While the stabilization of carbenes by electron-rich ylide substituents in order to access strongly nucleophilic carbon species therefore remains a challenge to date, it was already successfully achieved with heavier group 14 carbene analogues such as silylenes,<sup>45</sup> germylenes,<sup>46</sup> and stannylens.<sup>47</sup> Clearly, the right choice of substituents especially on the cationic fragment should make possible the realization of this objective.

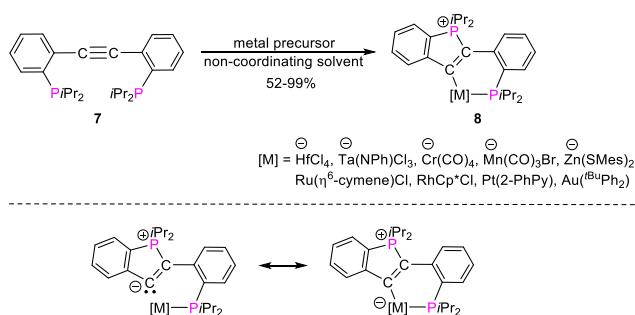
### Cyclic aryl(ylide) carbene (CArYC) A3

Inspired by the works on cyclic amino(aryl)carbenes (CAArC)<sup>48</sup> the aryl version of the famous cyclic amino(alkyl)carbenes (CAAC)<sup>49</sup> and related studies about CAYC ligands, Ballmann *et al.* focused recently on the preparation of a new type of cyclic carbene, namely the cyclic aryl(ylide)carbenes (CArYC), where the R<sub>2</sub>C-NR motif in CAArC ligand is formally replaced by a phosphonium ylide moiety R<sub>3</sub>P<sup>+</sup>-CR<sub>2</sub><sup>-</sup> (Scheme 5).<sup>50</sup> The difference with previous cyclic amino(ylide)carbenes concerns the relative position of the phosphonium ylide to the carbene which is now fully incorporated into the five membered ring. A few years ago, Bertrand predicted that the endocyclic nature of the ylide should make these carbenic species particularly unstable towards ring opening to form less constrained phosphino-alkyne derivatives,<sup>12a</sup> this rearrangement being based on the existence of a mesoionic resonance structure (CArYC-MIC) (Scheme 5).

Based on this reactivity and on previous studies with metal precursors featuring three available coordination sites,<sup>51</sup> Ballmann proposed that *i*Pr<sub>2</sub>-substituted 2,2'-diphosphinotolane **7** exhibiting two *cis*-positioned donor sites could be a precursor of choice to afford unprecedented CArYC metal complexes *via* the attack of one phosphine at the central alkyne moiety. From the reaction of diphosphine **7** with an element of each group of *d*-block characterizing by the presence of two accessible coordination sites, cationic or zwitterionic CArYC complexes of type **8** were thus isolated under mild conditions (Scheme 6, top). The cyclisation process involving the formation of a P-C bond was shown to be highly selective to afford  $\kappa^2(P,C)$ -chelating complexes with the exception of the yttrium case where only the carbon center is coordinated to the metal center. With the help of X-ray diffraction and DFT studies, the electronic structure of these carbene complexes was elucidated showing that the endocyclic ylidic P-C bond (1.81  $\pm$  0.03 Å) corresponds to a  $\sigma$ -P-C single bond while the adjacent



**Scheme 5.** Representation of CAArC, CAAC, CAYC carbenes (top), and CArYC vs. CArY-MIC carbenes with ring-opening of the latter form to phosphino-alkyne products.<sup>48-49</sup>



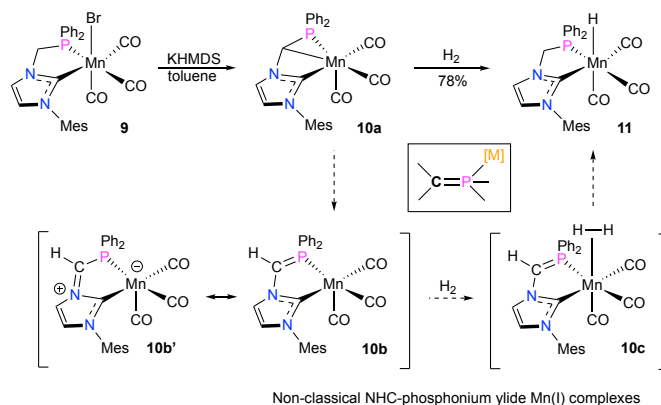
**Scheme 6.** General route to CAR-Y-MIC metal complexes **8** (top) and their possible resonance structures (bottom).<sup>50</sup>

C–C bond between the ylidic and the carbenic-type carbon atoms is consistent with a partially delocalized  $\pi\text{-C}=\text{C}$  double bond ( $1.37 \pm 0.02 \text{ \AA}$ ). The dative character of the  $\text{C} \rightarrow \text{M}$   $\sigma$ -bond was deduced from various QTAIM descriptors. All these data suggest that metal complexes **8** are better described as mesoionic carbene complexes (CAR-Y-MICs) with the existence of two main resonance forms, a non-bonding and a betaine-type structures (Scheme 6, bottom). The betaine structure accounts notably for  $\pi$ -backbonding interactions for  $d^1$  to  $d^9$  configured complexes. The P–C bond formation was demonstrated to be reversible through a series of molybdenum complexes provided that a *fac*-positioned open coordination site is available.<sup>50</sup>

This metal-templated synthetic route made thus it possible to prepare a wide variety of complexes of CAR-Y-Carbenes by overcoming their intrinsic instability in the free state and there is no doubt that these electron-rich carbene complexes will soon find applications, particularly in catalysis.

#### Acyclic (ylide)carbene **A4**

While in the two first cases, the ylide acts as a substituent of the carbene with the C-ylidic carbon atom being an integral part of the cyclic carbene structure, in the following system **A4** the two carbon units are adjacent to each other with the C-ylidic carbon atom directly attached to the N-atom of the carbene ring. This specific association between the two carbon units was achieved from the NHC-phosphine complex Mn(I) *fac*-[MnBr(CO)<sub>3</sub>( $\kappa^2\text{P,C-Ph}_2\text{PCH}_2\text{NHC}$ )] **9** prepared from corresponding phosphine imidazolium salt through the addition of KHMDS and Mn(CO)<sub>5</sub>Br. This Mn(I) complex **9** could be then selectively deprotonated with KHMDS at the carbon position located between the NHC and the phosphine fragments to afford an original 18-e NHC-phosphinomethanide Mn(I) complex **10a** capable to activate dihydrogen under very mild conditions to form the corresponding hydride product **11** (Scheme 7).<sup>52</sup> In fact, DFT calculations revealed that the preferred reaction mechanism involves the formation of the unsaturated 16-e Mn(I) complex **10b** based on an unconventional chelating NHC-phosphonium ylide ligand by the isomerization of the cyclometallated complex **10a** with an energy barrier of 15.7 kcal.mol<sup>-1</sup>. After coordination of H<sub>2</sub> and heterolytic cleavage of the H–H bond in the resulting NHC-ylide adduct **10c**, the hydride Mn(I) complex **11** is finally obtained. In complexes **10b-c**, the phosphonium ylide is coordinated to the metal center by its P-atom, a mode of coordination that has been rarely observed.<sup>53</sup>



Non-classical NHC-phosphonium ylide Mn(I) complexes

**Scheme 7.** Cooperative dihydrogen activation by the cyclometallated Mn(I) NHC-phosphinomethanide complex **10a** proceeding via the formation of complexes **10b-c** featuring an inverted NHC-phosphonium ylide ligand with P-metalloylide resonance structure.<sup>52</sup>

The interaction between the NHC and ylide moieties was evidenced by DFT studies showing that the 16-e NHC-ylide Mn(I) complex **10b** contains a small contribution of the zwitterionic 18-e resonance form **10b'**, where one of the N-atom of the NHC moiety is removed from the conjugation with the carbenic center, forming an iminium fragment and restoring the phosphine character to the P-atom. The calculated P–C bond lengths (1.717–1.741  $\text{\AA}$ ) in complexes **10b-c** are slightly shorter than the experimental values reported for more classical NHC-ylide ligands (1.750(7)–1.794(8)  $\text{\AA}$ ) consistent with some double bond character.<sup>33</sup> In addition according to ETS-NOCV study, P–Mn bonds in **10b-c** are significantly stronger than those in NHC-phosphine Mn(I) complexes **9** or **11** exhibiting a conventional P–Mn dative bond. Thanks to this new mode of metal-ligand cooperation involving the formal interplay between  $\lambda^5$ - and  $\lambda^3$ -P species, the Mn(I) complex **9** acts as one of the most efficient system for the hydrogenation of ketones (TON up to 6200).<sup>54</sup>

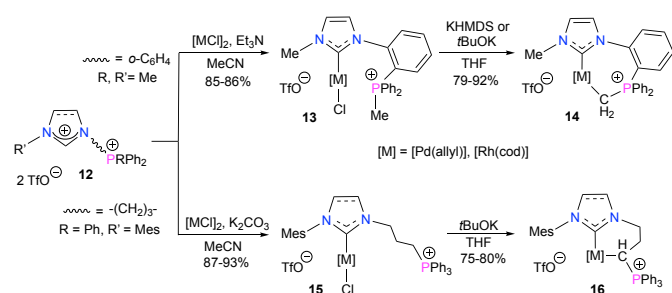
The implementation of the “R<sub>2</sub>PCH<sub>2</sub>” sequence in other transition metal complexes should allow the rapid development of cooperative systems, the ylide species obtained upon C–H deprotonation being able to activate inert bonds with potential applications in homogeneous catalysis.<sup>55</sup> It can also be predicted that the right choice of substituents on the two coordinating moieties could even render the ylide form more stable than the cyclometallated one.

#### Non-interacting carbene-ylide systems (type B)

In the following systems, the NHC and phosphonium ylide moieties are in remote position separated by an insulating link thus minimizing the electronic communication and the steric effects between them unlike previous associations of type **A**. Each carbon donor in such systems is therefore expected to act independently through a monodentate coordination mode.

##### C,C-chelating NHC-phosphonium ylide complexes **B1** and **B2**

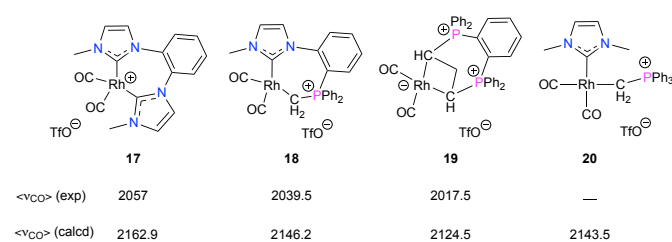
The phosphonium group can be attached to the N-atom of the heterocycle via a rigid aromatic *ortho*-phenylene bridge<sup>56</sup> or a more flexible propyl chain<sup>57</sup> (Scheme 8). From corresponding N-phosphonio-substituted imidazolium salts **12**, a slight difference in pK<sub>a</sub> values between the imidazolium and phosphonium



**Scheme 8.** Preparation of C,C-chelating NHC-phosphonium ylide complexes **14** and **16** from N-phosphonio-substituted NHC precursors **12** via a sequential deprotonation strategy.<sup>56-57</sup>

protons was shown to be beneficial for the development of a sequential strategy affording N-phosphonio NHC complexes **13** and **15** ([M] = Pd(II) or Rh(I)) by prior selective complexation of the carbene center. The pre-coordination of the NHC favored the anchorage of the proximal phosphonium ylidic position as illustrated with the formation of corresponding C,C-chelating NHC-phosphonium ylide complexes **14** and **16**. Noteworthy, the strategy developed in the achiral imidazolyl-phenyl case was transposed in the benzimidazolyl-naphthyl series leading to enantiomerically pure NHC-phosphonium ylide palladate complexes.<sup>58</sup> It should be also mentioned that all attempts to characterize an NHC-ylide ligand in its free state were unsuccessful. This synthetic approach is not restricted to bidentate systems since it has been applied more recently to the preparation of a Pd(II) complex of the C4 chelating bis(NHC), diphosphonium bis(ylide) ligand obtained as a single diastereoisomer of the *dl* form.<sup>59</sup> Concerning applications, a NHC-phosphonium ylide Pd(II) allyl complex of type **14** was reported to be an efficient pre-catalyst for the allylic substitution of 3-acetoxy-1,3-diphenylpropene suggesting that C,C-chelating NHC-ylide complexes deserve further study including in asymmetric catalysis.<sup>56a</sup>

In the *ortho*-phenylene series, the distant positioning of the two carbon fragments minimizing the steric effects between them was taken advantage of to assess their respective donor ability.<sup>33a</sup> The electronic properties of NHC and phosphonium ylide ligands were evaluated from IR spectra using average  $\langle \nu_{CO} \rangle$  stretching frequencies of an isostructural family of C,C-chelating Rh(CO)<sub>2</sub> complexes **17-19** containing two donor moieties of each kind (Scheme 9). From the low-frequency shift observed along the series ( $\langle \nu_{CO} \rangle$  2057, 2039.5 and 2017.5 cm<sup>-1</sup> for **17**, **18** and **19**, respectively), it was deduced that a phosphonium ylide is more donating than an NHC and that the



**Scheme 9.** Representation of Rh(CO)<sub>2</sub> complexes **17-20** based on NHC and phosphonium ylide donor extremities with corresponding experimental and calculated average  $\langle \nu_{CO} \rangle$  stretching frequencies (in cm<sup>-1</sup>).<sup>33a</sup>

two neutral carbon ligands behave in an independent way. The similarity of the calculated  $\langle \nu_{CO} \rangle$  frequencies between complex **18** (2146.2 cm<sup>-1</sup>) of a chelating NHC-phosphonium ylide ligand and its *cis*-analogue **20** (2143.5 cm<sup>-1</sup>) obtained after removal of the *ortho*-phenylene bridge confirms the absence of electronic communication and the minimization of steric interactions between the two carbon donors.

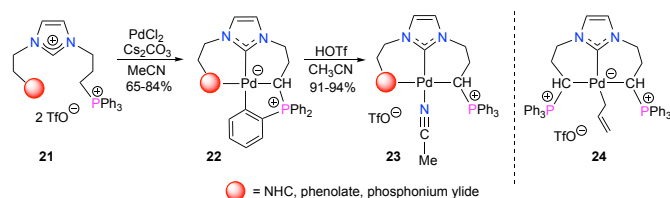
### NHC core phosphonium ylide-based pincer complexes B3

Inspired by the results obtained in the bidentate series, an isostructural family of NHC core, phosphonium ylide-based Pd(II) pincer complexes of type **23** was recently prepared where the third donor end can be either an NHC, a phenolate or a phosphonium ylide.<sup>60</sup> Although a sequential synthetic strategy can be also used here, the most convenient route involves the passage *via* the *ortho*-metallated Pd(II) complexes **22** obtained in one step upon deprotonation of the corresponding N-phosphonio substituted NHC precursors **21** in the presence of PdCl<sub>2</sub> and an excess of Cs<sub>2</sub>CO<sub>3</sub>, followed by acidic treatment to form the pincer Pd(II) complexes **23** of interest (Scheme 10, left).<sup>61</sup> The representative of LX<sub>2</sub>-type with two side phosphonium ylides was isolated as a mixture of *meso*- and *dl*-diastereomers (*de* = 50%) standing as a rare example of pincer complexes exhibiting only carbon-based donor extremities.<sup>62</sup> The overall donor character of the different pincer ligands was analyzed by comparison of the oxidation potentials,  $\nu_{CO}$  and  $\nu_{CN}$  stretching frequencies, as well as molecular orbitals in the related Pd-CN*t*Bu and Pd-CO complexes. These data led to the conclusion that NHC and phenolate ligands have a similar donor character being still inferior to that of the phosphonium ylide. This trend is in perfect line with previous studies conducted on C,C-chelating Rh(CO)<sub>2</sub> complexes based on NHC and phosphonium ylide extremities (Scheme 9). In the phosphonium ylide-based pincer series, the difference in donor ability was demonstrated to have a significant impact in the Pd-catalyzed allylation of aldehydes. In this transformation, the  $\eta^1$ -allyl-Pd pincer complex **24** (Scheme 10, right) with two phosphonium ylide ends proposed as catalytic intermediate on the basis of experimental and DFT data led indeed to better catalytic activity than related pincer complexes featuring only one ylide extremity.<sup>61</sup> Indeed, the strongly donating C,C,C-pincer ligand contributes to increase the electron density at the metal and therefore the nucleophilic character of the allyl moiety.

These results provide avenues for the design of carbon-based pincer complexes exhibiting ylides with different P-substituents and/or donor groups, which could make possible, for example, to further increase the electron density on the metal and/or to promote the release of an additional coordination site during a catalytic transformation.

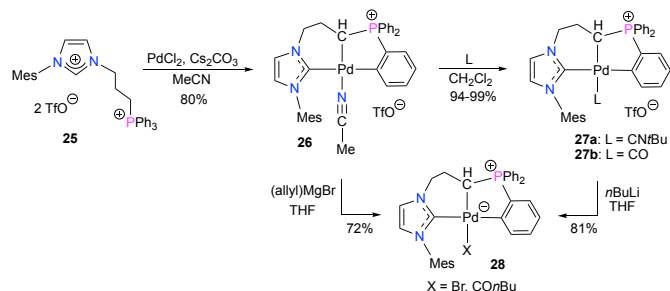
### Phosphonium ylide core NHC-aryl pincer complexes B4

Considering the possible *ortho*-metallation of one of the P<sup>+</sup>-C<sub>6</sub>H<sub>5</sub> substituents under basic conditions as observed in the NHC core pincer series (Scheme 10), one of the two N-donor arms in N-phosphonio substituted imidazolium salts was replaced by a N-spectator substituent, the target being the preparation of a new LX<sub>2</sub>-type pincer ligand based on a central phosphonium ylide bearing NHC and phenyl donor arms. The reaction of



**Scheme 10.** Preparation of NHC core phosphonium ylide-based pincer Pd(II) complexes **23** from N-phosphonio-substituted NHC precursors **21** via the *ortho*-metallated forms **22** (left) and the representation of the catalytic active  $\eta^1$ -allyl-Pd pincer complex **24** (right).<sup>60-62</sup>

imidazolium salt **25** bearing a mesityl group under *ortho*-metallation conditions, namely the addition of PdCl<sub>2</sub> in the presence of Cs<sub>2</sub>CO<sub>3</sub> led selectively in one step to the cationic Pd(II) complex **26** featuring the C,C,C-NHC-ylide-aryl pincer ligand (Scheme 11).<sup>63</sup> The formation of this complex results from a formal triple C–H bond activation of the cationic precursor. The overall donor character of this new phosphonium ylide core pincer ligand evaluated on the basis of  $\nu_{CO}$  and  $\nu_{CN}$  stretching frequencies of complexes **27** was found to be even higher than that of the C,C,C-NHC core, bis(phosphonium ylide) ligand of complex **23**. Remarkably, such an extreme donor character allowed for the stabilization at room temperature and the structural characterization of a Pd(II)–CO adduct **27b** standing as the first CO complex bearing an ylide ligand. The C–O bond distance of 1.117(4) Å in **27b** longer than in a related bis(NHC) complex (1.059(5) Å)<sup>64</sup> reflects the stronger  $\pi$ -backbonding in the former complex and the superior donor character of an ylide compared that of a NHC. X-ray diffraction and QTAIM analyses revealed also the existence of a weak attractive non-bonding interaction of about 1.7 kcal.mol<sup>-1</sup> between the C<sub>ipso</sub> carbon atom of the N-mesityl group and the carbonyl moiety, such interligand bonding being uncommon in square-planar metal complexes.<sup>65</sup> The unique electronic properties of the ylide core pincer backbone were also at the origin of the preparation of rare examples of zwitterionic phosphonium organopalladates **28** featuring bromide and acyl co-ligands obtained by the treatment of cationic pincer complexes **26** and **27b** with (allyl)MgBr and *n*BuLi, respectively.<sup>63</sup> The X nature of the *trans*-ylide coordinated ligand accounts for the transfer of the negative charge initially located at the C-ylidic extremity to the Pd atom with partial delocalization over the bromide and acyl co-ligands.



**Scheme 11.** Preparation of phosphonium ylide core NHC, aryl pincer Pd(II) complexes **26-28** from the N-phosphonio substituted NHC precursor **25**.<sup>63</sup>

The generalization of this straightforward approach to the preparation of other transition metal pincer complexes should be explored as well as their reactivity towards small molecules and catalytic activity in transformations requiring strongly donating complexes.

## Conclusions and perspectives

As mentioned in this review, carbon should not only be considered as a building block of organic molecules but also as a coordinating atom in the same way as nitrogen or phosphorus. In this direction, the association of two types of neutral  $\eta^1$ -carbon ligand namely the C-*sp*<sup>2</sup> hybridized carbenes and the C-*sp*<sup>3</sup> hybridized phosphonium ylides resulted in the development of original architectures with different complexity that can adopt mono-, bi-, tri- or tetradentate coordination modes. Regardless of the nature of the association, the two carbon donors transfer naturally their strong electronic density to the metal providing electron-rich complexes which catalysis can take advantage as evidenced by the efficiency of the Mn(I) complex of a non-conventional NHC-phosphonium ylide ligand for the hydrogenation of carbonyl compounds. However, while the combination of two strongly donating ligands enhance reactivity, it may also have a cost in terms of stability with the appearance of undesired transformations as illustrated with CAYC species. To overcome the possible instability of free carbon species, the generation of the reactive center in close proximity of the metal is undoubtedly an efficient method as exemplified with the straightforward synthesis of CAR<sub>Y</sub>C metal complexes. By taking advantage of a difference of acidity between the two carbon fragments, sequential coordination constitutes the optimal strategy for the preparation of heteroleptic non-interacting NHC-ylide systems. For catalytic purposes because the metal must satisfy different criteria for achieving the requested selectivity and activity over all the steps, the introduction of a less donating extremity to balance the highly electron-rich carbene and/or ylide moieties may constitute a possible alternative and deserves to be explored. As future directions, the association of phosphonium ylides with other types of carbenes such as CAACs which are better  $\sigma$ -donor and  $\pi$ -acceptor ligands compared to NHCs could be of interest. The activation of non-reactive chemical bonds and the stabilization of electropositive or high-valent metal centers in stoichiometric or catalytic transformations with these electron-rich systems represent also natural prospects. The association of soft NHC with harder ylides should obviously extend the scope of accessible metal centers and inevitably provide complexes with unique properties and reactivities. The implementation of strongly donating carbon ligands in photoactive systems is also a possible domain of interest, which could allow to design metal complexes with extended lifetime of the excited charge-transfer states *via* a destabilization of the metal-center energy states responsible for rapid deactivation. It's a safe bet that the reign of carbon ligands including carbenes and phosphonium ylides has only just begun which should benefit both fundamental and applied aspects of chemistry.

## Conflicts of interest

There are no conflicts to declare.

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