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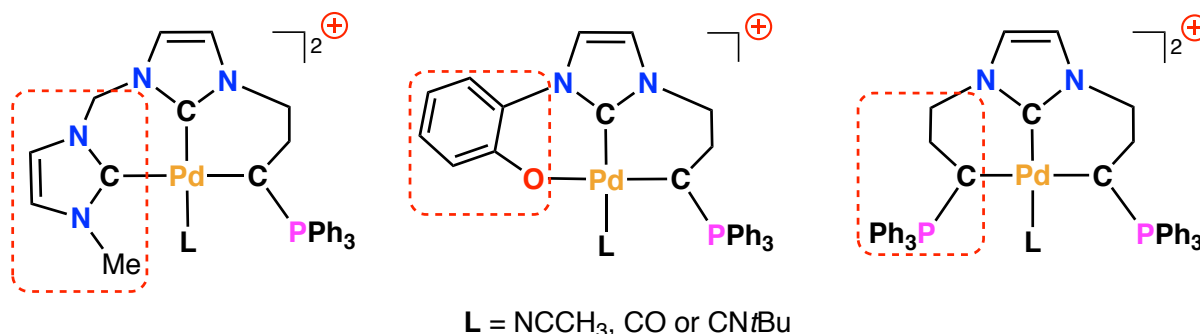
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# NHC Core Phosponium Ylide-Based Palladium(II) Pincer Complexes: The Second Ylide Extremity Makes the Difference

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## GRAPHICAL ABSTRACT:

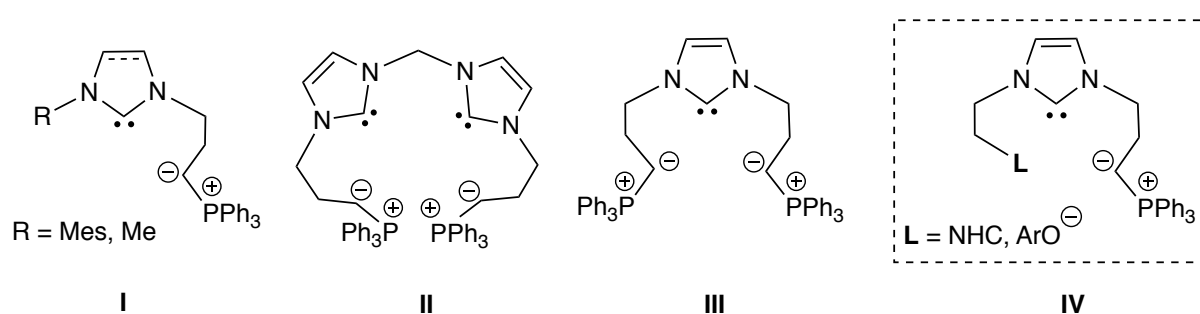


**ABSTRACT:** The coordinating properties of NHC (A), phenolate (B) and phosphonium ylide (C) moieties have been investigated systematically through the preparation of a family of NHC, phosphonium ylide-based pincer ligands where the third donor extremity can be either a NHC, a phenolate or a phosphonium ylide. The overall donor character of such ligands [NHC(A<sub>a</sub>B<sub>b</sub>C<sub>c</sub>)] ( $a + b + c = 2$ ) has been analyzed by comparison of the MOs (energy and shape), oxidation potentials ( $E_p^{ox}$ ), and IR  $\nu_{CO}$  and  $\nu_{CN}$  stretching frequencies of their isostructural pincer Pd(II) complexes [NHC(A<sub>a</sub>B<sub>b</sub>C<sub>c</sub>)PdL][OTf] (L = NCCH<sub>3</sub>, CO or CN*t*Bu). The three categories of pincer complexes based on phosphonium ylides were easily obtained by acidic treatment of their highly stable *ortho*-metallated Pd(II) precursors prepared in a single step from readily available N-phosponio-substituted imidazolium salts. Analysis of IR data indicated that NHC and phenolate ligands have a similar donor character but which remains lower than that of the phosphonium ylide. The impact on catalytic performance of the incorporation of a second strongly donating phosphonium ylide into the ligand architecture has been illustrated in the Pd-catalyzed allylation of aldehydes.

**Keywords:** Allylation, carbon ligand, NHC, palladium, phosphonium ylide, phenolate, pincer.

## 1. INTRODUCTION

The isolation of the first stable singlet carbenes<sup>1</sup> proved to be a trigger in the minds of chemists, leading in a short time to remarkable advances in various fields, such as organometallic chemistry, functional materials and homogeneous catalysis.<sup>2</sup> From there, considerable efforts have been provided to introduce structural diversity and carbene ligands have become unavoidable surpassing in some applications their illustrious predecessors based on group 15 elements.<sup>3</sup> Like carbenes, onium ylides and related species which are charge-neutral in their free state and act as strong  $\sigma$ -donors with weak  $\pi$ -acceptor ability,<sup>4</sup> have experienced a revival of interest confirming their potential as Lewis bases in main group<sup>5</sup> and coordination chemistry.<sup>6</sup> Phosphonium ylides, the most exemplified representatives of this family, differ in the hybridization state of the coordinating atom with respect to NHCs -  $Csp^3$ -type vs.  $Csp^2$ -type -, thus positioning themselves as a complementary class of carbon ligands. Based on the preparation of an isostructural series of Rh(I) dicarbonyl complexes, it was experimentally<sup>7</sup> and theoretically<sup>8</sup> demonstrated that phosphonium ylides behave as stronger donor ligands than NHCs. However, while NHCs promote a large number of transition-metal-catalyzed reactions,<sup>9</sup> the catalytic applications of phosphonium ylides remained in their infancy.<sup>10</sup> Following pioneering reports in the field aimed at developing catalytically activated ylide-based metal systems,<sup>11</sup> NHC and phosphonium ylide donor moieties were recently associated by a flexible  $C_3$ -propyl linker in the bi- (**I**),<sup>12</sup> tetradente (**II**),<sup>13</sup> and in the pincer series (**III**)<sup>14</sup> forming extremely electron-rich metal complexes, thanks to the design of a general synthetic strategy (Scheme 1).<sup>15</sup> As striking fact, the  $C,C,C$ -NHC, diphosphonium bis(ylide)ligand **III** of  $LX_2$ -type was shown to efficiently stabilize a Pd(II) carbonyl complex<sup>14</sup> whose examples of this type remain scarce due to easy Pd-CO dissociation.<sup>16</sup>



**Scheme 1.** Representation of recently reported chelating NHC, phosphonium ylide ligands **I–III**<sup>12–14</sup> and related targeted pincer systems of type **IV**.

These experimental advances encourage us to undertake a precise study on the electronic features of this type of carbon-based ligands and their pincer complexes in order to consider catalytic applications. The challenge is envisaged on the basis of the preparation of a test family of phosphonium ylide-based Pd(II) pincer complexes **IV** in which a globally neutral phosphonium ylide (1-e<sup>-</sup> donor (X-type)) of the symmetrical NHC, bis(phosphonium ylide) ligand **III** is strictly replaced either by a neutral NHC (2-e<sup>-</sup> donor (L-type)) or by an anionic phenolate (1-e<sup>-</sup> donor (X-type)) (Scheme 1).<sup>17</sup> The objective is to carry out this comparative study while preserving the overall architecture of the pincer complexes defined by the NHC core and the two fused six-membered palladacycles resulting from the coordination of the three donor ends. Furthermore, the meridional tridentate coordination mode of pincer ligands leaves generally an open coordination site,<sup>18</sup> which should be beneficial for the introduction of a carbonyl or an isocyanide co-ligand able to act as an electronic probe to evaluate the overall  $\sigma$ -donating vs.  $\pi$ -accepting properties of the targeted ligands.<sup>14,19</sup>

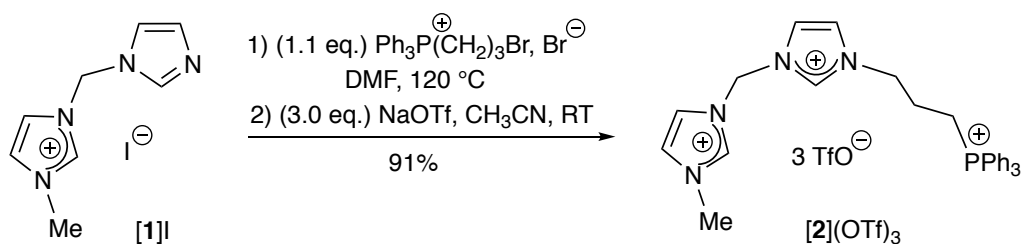
The present contribution addresses the preparation, the coordinating behavior towards Pd(II) centers, and the catalytic properties of NHC, phosphonium ylide-based pincer ligands of type **III–IV** (Scheme 1), providing thus a systematic comparison of three complementary coordinating functional groups (*ca.* phosphonium ylide, NHC and phenolate) of broad interest in organometallic chemistry and homogeneous catalysis.

## 2. RESULTS AND DISCUSSION

### 2.1 Synthesis and NMR characterization of NHC, phosphonium ylide-based pincer pre-ligands and their Pd(II) complexes

#### 2.1.1 Bis(NHC), phosphonium ylide series

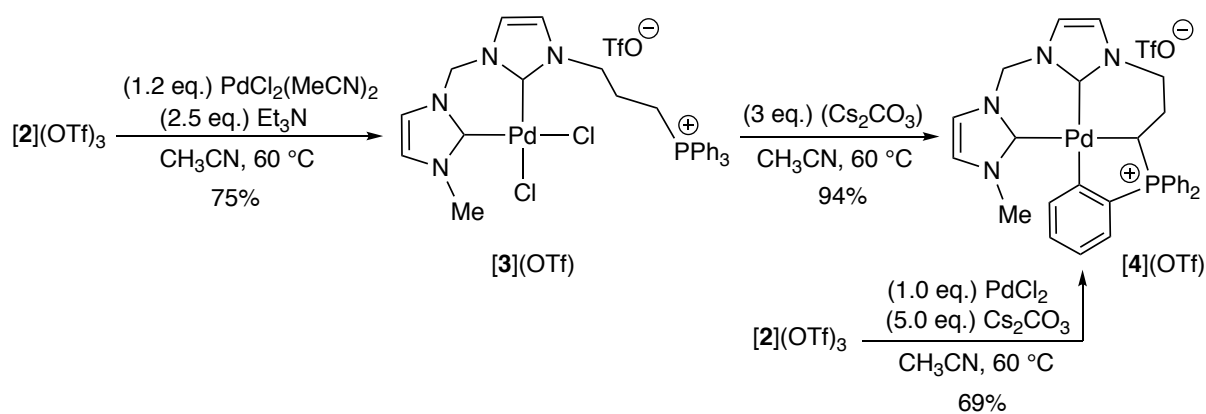
The first target was a palladium complex of the pincer ligand of type **IV** where the peripheral coordinating extremity L is a N-bonded N-methylimidazolylidene (Scheme 1, *right*). For this purpose, the N-phosphonio-substituted bis(imidazolium) salt **[2]**(OTf)<sub>3</sub> was readily prepared in 91% overall yield by treating 3-((1H-imidazol-1-yl)-methyl)-1-methyl-1H-imidazol-3-ium iodide **[1]**I<sup>20</sup> with 1.1 equiv. of (3-bromopropyl)triphenylphosphonium bromide in DMF at 120 °C followed by anion metathesis with NaOTf in CH<sub>3</sub>CN (Scheme 2).



**Scheme 2.** Preparation of  $N$ - $[(\text{CH}_2)_3\text{PPh}_3]^+$  substituted bis(imidazolium) salt  $[\mathbf{2}](\text{OTf})_3$  from  $[\mathbf{1}]\text{I}$ .

The  $^{31}\text{P}$  NMR spectrum of  $[\mathbf{2}](\text{OTf})_3$  displayed a single signal at  $\delta_{\text{P}}$  25.0 ppm in the normal range for phosphonium salts.<sup>21</sup> The two imidazolium protons of  $[\mathbf{2}](\text{OTf})_3$  were evidenced by the characteristic low field signals at  $\delta_{\text{H}}$  9.10 and 9.31 ppm in the  $^1\text{H}$  NMR spectrum. On the basis of recent results<sup>12-14</sup> where a difference in acidity between the H-atoms of imidazolium and alkyl phosphonium moieties was observed,<sup>22</sup> the complexation of  $[\mathbf{2}](\text{OTf})_3$  was envisioned through a sequential strategy. Treatment of pre-ligand  $[\mathbf{2}](\text{OTf})_3$  with a stoichiometric amount of  $[\text{PdCl}_2(\text{MeCN})_2]$  in the presence of  $\text{Et}_3\text{N}$  in  $\text{CH}_3\text{CN}$  cleanly afforded the  $N$ -phosphonio-bis(NHC)  $\text{PdCl}_2$  complex  $[\mathbf{3}](\text{OTf})$  in 75% yield (Scheme 3). The formation of complex  $[\mathbf{3}](\text{OTf})$  was clearly indicated by  $^1\text{H}$  NMR spectroscopy showing the disappearance of the C–H imidazolium signals of  $[\mathbf{2}](\text{OTf})_3$ . The unchanged environment of the phosphonium moieties in Pd complex  $[\mathbf{3}](\text{OTf})$  compared to  $[\mathbf{2}](\text{OTf})_3$  was demonstrated by the similarity of their  $^{31}\text{P}$  NMR chemical shifts ( $[\mathbf{2}](\text{OTf})_3$ :  $\delta_{\text{P}}$  25.0 ppm;  $[\mathbf{3}](\text{OTf})$ :  $\delta_{\text{P}}$  23.6 ppm). In the  $^{13}\text{C}$  NMR spectra, the  $\text{N}_2\text{C}$ –Pd carbon atoms of NHC complex  $[\mathbf{3}](\text{OTf})$  ( $\delta_{\text{C}}$  158.5 and 159.0 ppm) were typically found to be deshielded with respect to the  $\text{N}_2\text{CH}$  carbon atoms of precursor  $[\mathbf{2}](\text{OTf})_3$  ( $\delta_{\text{C}}$  138.6 and 138.8 ppm). The cationic character of Pd complex  $[\mathbf{3}](\text{OTf})$  was confirmed by ESI mass spectroscopy ( $\mathbf{3}^+$ :  $m/z$  642.9  $[\text{M} - \text{OTf}]^+$ ).

According to the conditions developed in the NHC, bis(ylide) series,<sup>14</sup> the  $\text{PdCl}_2$  complex  $[\mathbf{3}](\text{OTf})$  was treated with 3 equiv. of  $\text{Cs}_2\text{CO}_3$  in  $\text{CH}_3\text{CN}$  at 60 °C.<sup>23</sup> The present system allowed thus the selective formation of the *ortho*-metallated bis(NHC), phosphonium ylides Pd complex  $[\mathbf{4}](\text{OTf})$  in 94% yield. Gratifyingly, the latter could be obtained directly in 69% yield by reacting the dicationic salt  $[\mathbf{2}](\text{OTf})_3$  with  $\text{PdCl}_2$  in the presence of 5 equiv. of  $\text{Cs}_2\text{CO}_3$  in  $\text{CH}_3\text{CN}$  at 60 °C (Scheme 3). The *ortho*-metallated complex  $[\mathbf{4}](\text{OTf})$  available on a gram scale appeared to be highly stable in air both in the solid state and in solution, and insensitive to moisture.

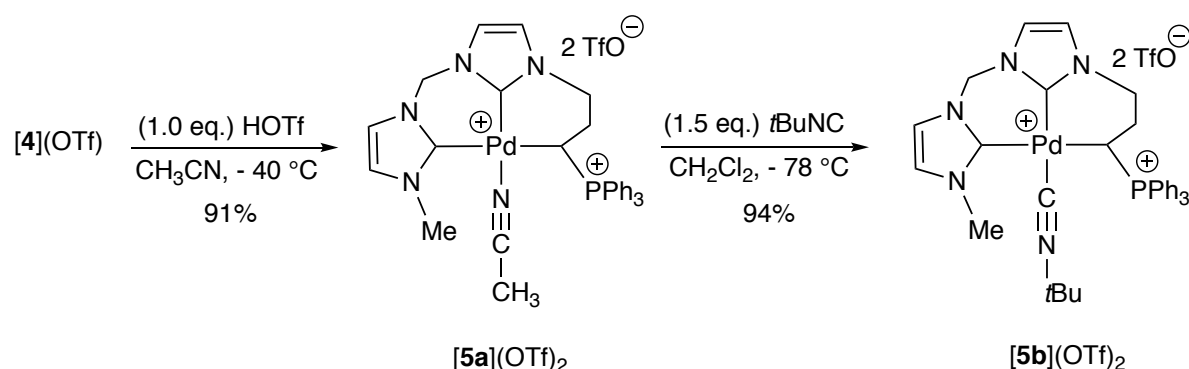


**Scheme 3.** Syntheses of N-phosphonio-bis(NHC) PdCl<sub>2</sub> complex **[3](OTf)** and bis(NHC), phosphonium ylide Pd(II) complex **[4](OTf)** from **[2](OTf)<sub>3</sub>**.

The structure of Pd complex **[4](OTf)** was first assigned on the basis of the <sup>31</sup>P NMR spectrum, which exhibited a deshielded singlet at  $\delta_{\text{P}}$  30.4 ppm compared to its N-phosphonio precursor (**[3](OTf)**:  $\delta_{\text{P}}$  23.6 ppm). The linkage of the CH ylide moiety was also apparent from the upfield shift of the corresponding <sup>13</sup>C{<sup>1</sup>H} NMR resonance ( $\delta_{\text{CH}}$  17.3 ppm (d, <sup>1</sup>J<sub>CP</sub> = 36.2 Hz). The <sup>13</sup>C NMR spectrum highlighted the presence of the characteristic strongly deshielded signal of the *ortho*-metallated carbon atom at  $\delta_{\text{C}}$  179.9 ppm (d, <sup>2</sup>J<sub>CP</sub> = 34.2 Hz) with the corresponding *ipso* quaternary carbon atom at  $\delta_{\text{C}}$  139.2 ppm (d, <sup>1</sup>J<sub>CP</sub> = 115.7 Hz). Noteworthy, the <sup>13</sup>C NMR signal of the carbenic carbon atoms of **[4](OTf)** underwent a significant shift upon coordination of the ylidic side arm (**[4](OTf)**:  $\delta_{\text{C}}$  177.7 and 178.8 ppm; **[3](OTf)**:  $\delta_{\text{C}}$  158.5 and 159.0 ppm). The cationic character of **[4](OTf)** was confirmed by ESI mass spectroscopy (**4**<sup>+</sup>: *m/z* 569.1 [M – OTf]<sup>+</sup>).

The Pd complex **[4](OTf)** can be considered as the “dormant form” of the bis(NHC), phosphonium ylide pincer complex where the coordination site *trans* to the central NHC donor, generally the most reactive position, is neutralized by the *ortho*-metallated carbon atom of a P<sup>+</sup>-phenyl ring. Based on this observation, complex **[4](OTf)** was treated by a stoichiometric amount of trifluoromethanesulfonic acid in CH<sub>3</sub>CN at –40 °C, leading after selective cleavage of the C<sub>ar</sub>–Pd bond to the Pd pincer complex **[5a](OTf)<sub>2</sub>** in 91% yield (Scheme 4). In the <sup>31</sup>P NMR spectrum, the complex **[5a](OTf)<sub>2</sub>** exhibited a single resonance at  $\delta_{\text{P}}$  33.9 ppm in agreement with a Pd coordinated ylide. The persistence of the Pd–CH bond was confirmed by <sup>13</sup>C NMR spectroscopy, showing a signal in the high-field region with correct multiplicity ( $\delta_{\text{CH}}$  9.9 ppm, (d, <sup>1</sup>J<sub>CP</sub> = 32.7 Hz)). The <sup>13</sup>C NMR signal of N<sub>2</sub>C centers of **[5a](OTf)<sub>2</sub>** ( $\delta_{\text{C}}$  158.1 and 168.6 ppm) were found in the typical range of carbenic carbon atoms. When recorded in CD<sub>2</sub>Cl<sub>2</sub>, the <sup>13</sup>C NMR spectrum showed the presence of a

coordinated  $\text{CH}_3\text{CN}$  molecule as indicated by the corresponding single resonance ( $\delta_{\text{C}}$  2.2 ppm).



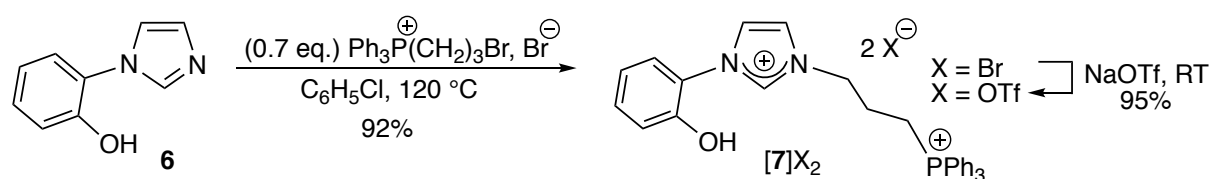
**Scheme 4.** Synthesis of the bis(NHC), phosphonium ylide Pd(II) pincer complex **[5a](OTf)<sub>2</sub>** from **[4](OTf)**, and exchange reaction at the Pd center of **[5a](OTf)<sub>2</sub>** with *t*-butyl isocyanide with formation of the pincer complex **[5b](OTf)<sub>2</sub>**.

To evaluate the overall donating properties of the bis(NHC) ligand of complex **[5a](OTf)<sub>2</sub>**, the substitution of the  $\text{CH}_3\text{CN}$  co-ligand by the stronger  $\sigma$ -donating *t*-butyl isocyanide able to act as a valuable IR probe was envisioned. The exchange reaction at the Pd atom was realized in  $\text{CH}_2\text{Cl}_2$  at  $-78\text{ }^\circ\text{C}$  affording the targeted isocyanide adduct **[5b](OTf)<sub>2</sub>** in 94% yield (Scheme 4). While the <sup>31</sup>P NMR spectrum remained almost unchanged ( $\delta_{\text{P}}$  35.0 ppm; **[5a](OTf)<sub>2</sub>**:  $\delta_{\text{P}}$  33.9 ppm), the coordination of the isocyanide was evidenced by the <sup>1</sup>H and <sup>13</sup>C NMR resonances of the *t*-Bu group at  $\delta_{\text{H}}$  1.06 ppm, and  $\delta_{\text{C}}$  29.5 and 59.7 ppm, respectively.<sup>24</sup> The  $\nu_{\text{C}\equiv\text{N}}$  IR band observed at  $2206\text{ cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$  confirmed the presence of the [Pd-C≡N-*t*Bu] sequence in complex **[5b](OTf)<sub>2</sub>**.<sup>25</sup> Having in mind the thermal stability of a Pd-CO complex of the bis(ylide) ligand (**[12c](OTf)<sub>2</sub>**, Table 1),<sup>14</sup> CO gas was bubbled through a solution of **[5a](OTf)<sub>2</sub>** in  $\text{CH}_2\text{Cl}_2$ . However whatever the experimental conditions used (CO pressure, T °C and reaction time), <sup>31</sup>P NMR monitoring indicated only the presence of **[5a](OTf)<sub>2</sub>**, the bis(NHC), ylide ligand being therefore not capable to stabilize a Pd-CO adduct, probably due to its insufficient donor character.

### 2.1.2 NHC, phenolate, phosphonium ylide series

Access to the third representative of the family based on a *C,C,O*- pincer ligand where the central NHC is N-substituted by a C-bonded phenolate and a C-bonded phosphonium ylide fragments, was envisioned from 1-(2-hydroxyphenyl)imidazole **6**.<sup>26</sup> Similar reactivity pattern to that observed previously could be obtained by reacting imidazole **6** with (3-bromopropyl)-

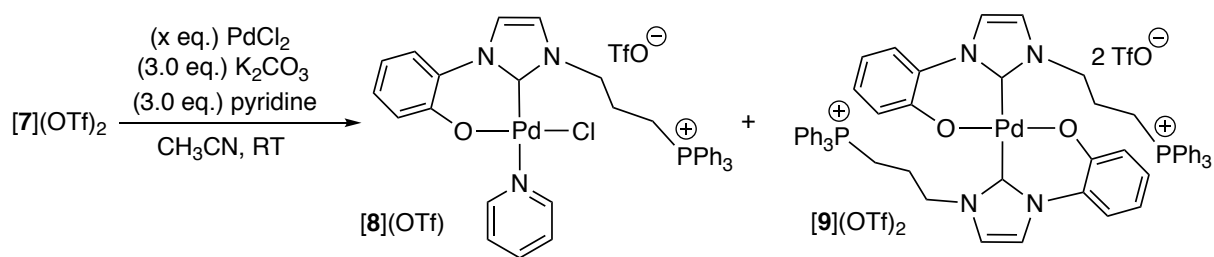
triphenylphosphonium bromide in C<sub>6</sub>H<sub>5</sub>Cl at 120 °C. The corresponding N-phosphonio substituted imidazolium salt [7]Br<sub>2</sub> was isolated in 92% yield (Scheme 5). By an anionic metathesis reaction carried out with NaOTf in CH<sub>2</sub>Cl<sub>2</sub>, the imidazolium [7]Br<sub>2</sub> was transformed into its triflate salt [7](OTf)<sub>2</sub> more soluble in conventional organic solvents with a yield of 95%. The presence of a singlet at  $\delta_p$  23.9–24.3 ppm in the <sup>31</sup>P NMR spectra for the pending phosphonium and a singlet at  $\delta_H$  9.2–9.9 ppm for the imidazolium core in the <sup>1</sup>H NMR spectra are in agreement with the dicationic character of salts [7]X<sub>2</sub> (X = Br, OTf).



**Scheme 5.** Preparation of *N*-[(CH<sub>2</sub>)<sub>3</sub>PPh<sub>3</sub>]<sup>+</sup> substituted imidazolium salts [7]X<sub>2</sub> (X = Br, OTf) from **6**.

Anticipating that [7](OTf)<sub>2</sub> should behave like an LX<sub>2</sub>-type ligand in the Green formalism,<sup>17</sup> its coordination was achieved by adding a stoichiometric amount of PdCl<sub>2</sub> in the presence of the K<sub>2</sub>CO<sub>3</sub>/pyridine system in CH<sub>3</sub>CN.<sup>27</sup> These specific conditions produce a 3/2 mixture of Pd(II) complexes [8](OTf) and [9](OTf)<sub>2</sub> in 85% overall yield differentiating by the ligand/metal ratio (Scheme 6). Their formation was clearly indicated by <sup>1</sup>H NMR spectroscopy which shown the disappearance of the characteristic imidazolium signal of precursor [7](OTf)<sub>2</sub>. In both cases, the absence of the <sup>1</sup>H NMR signal for the hydroxyl group suggests the concomitant O-coordination of the phenolate moiety. In [8](OTf), the linkage of the pyridine to the Pd center was clearly indicated by the presence of three <sup>1</sup>H NMR resonances at  $\delta_H$  8.86, 7.99 and 7.55 ppm in the aromatic region. Noteworthy, addition of 0.5 equiv. of PdCl<sub>2</sub> to [7](OTf)<sub>2</sub> in the presence of K<sub>2</sub>CO<sub>3</sub> resulted in the unique formation of the bis(NHC), bis(phenolate) Pd complex [9](OTf)<sub>2</sub>, isolated in 92% yield. Setting the ratio [7](OTf)<sub>2</sub>/Pd to 1/2 afforded a better selectivity ([8](OTf)/[9](OTf)<sub>2</sub>: 3/1, overall yield 85%). However to significantly improve the selectivity, more dilute conditions were needed leading with the initial stoichiometry ([7](OTf)<sub>2</sub>/Pd:1/1) to the complex [8](OTf) in a 75% yield with a ratio [8](OTf)/[9](OTf)<sub>2</sub> of 9/1 (Scheme 6).

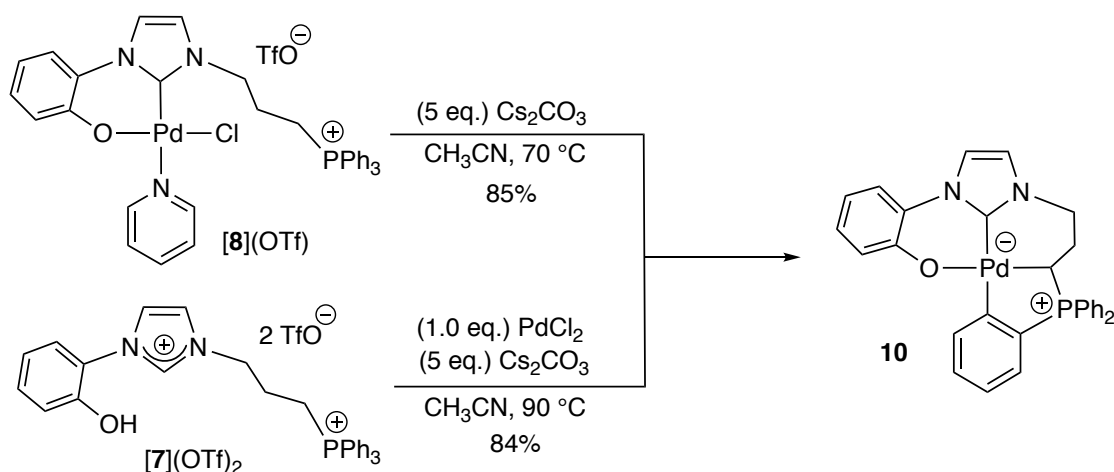




- a) PdCl<sub>2</sub> (1 eq.), [2.6 10<sup>-3</sup> M]: **[8](OTf)**/**[9](OTf)<sub>2</sub>**: 3/2, 85%  
 b) PdCl<sub>2</sub> (0.5 eq.): **[9](OTf)<sub>2</sub>**: 92%  
 c) PdCl<sub>2</sub> (2 eq.): **[8](OTf)**/**[9](OTf)<sub>2</sub>**: 3/1, 85%  
 d) PdCl<sub>2</sub> (1 eq.), [8.6 10<sup>-3</sup> M]: **[8](OTf)**/**[9](OTf)<sub>2</sub>**: 9/1; **[8](OTf)**: 75%

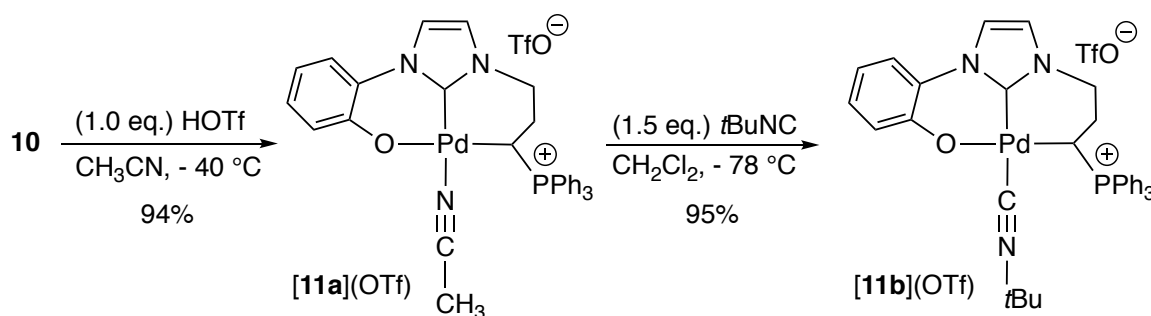
**Scheme 6.** Synthesis of N-phosponio-NHC, phenolate Pd(II) complex **[8](OTf)** and bis(N-phosponio-NHC, phenolate) Pd(II) complex **[9](OTf)<sub>2</sub>** from **[7](OTf)<sub>2</sub>**.

Thanks to the optimized conditions developed in the previous series, the complex **[8](OTf)** was readily converted in a 85% yield into its *ortho*-metallated form **10** upon addition of an excess of Cs<sub>2</sub>CO<sub>3</sub> in CH<sub>3</sub>CN at 70 °C (Scheme 7).<sup>23</sup> The *ortho*-metallated complex **10** could be also directly prepared from the pre-ligand **[7](OTf)<sub>2</sub>** in a 84% isolated yield following an one-pot strategy. The high stability observed with regard to air and moisture, as well as the possibility of preparing it on a gram scale make complex **10** a precursor of choice for the ensuing pincer. In the complex **10**, the coordination of the CH ylide moiety was unveiled by <sup>31</sup>P, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, especially on the basis on the high-field <sup>13</sup>C NMR doublet at δ<sub>CH</sub> 13.8 ppm with a <sup>1</sup>J<sub>CP</sub> coupling constant of 40.2 Hz. The *ortho*-metallated fragment is confirmed by the presence of corresponding strongly deshielded <sup>13</sup>C NMR signals at δ<sub>C</sub> 182.2 ppm (d, <sup>2</sup>J<sub>CP</sub> = 37.2 Hz) and δ<sub>C</sub> 137.1 ppm (d, <sup>1</sup>J<sub>CP</sub> = 119.7 Hz).



**Scheme 7.** Synthesis of the NHC, phenolate, phosphonium ylide Pd(II) complex **10** from N-phosponio-NHC, phenolate Pd(II) complex **[8](OTf)** or imidazolium salt **[7](OTf)<sub>2</sub>**.

To evaluate the donating properties of the *C,C,O*- pincer ligand of interest, the same sequential strategy as that developed in the bis(NHC) series was targeted. Thanks to two selective transformations, the pincer Pd-adducts **[11a]**(OTf) and **[11b]**(OTf) were formed in high yields from **10** by acidic cleavage of the *Csp*<sup>2</sup>-Pd bond of the phenylated ring followed by nucleophilic displacement of the incoming CH<sub>3</sub>CN co-ligand by *t*BuNC (Scheme 8). Upon exchange at the Pd(II) center (pyridine vs. CH<sub>3</sub>CN vs. *t*BuNC), the <sup>31</sup>P NMR chemical shifts remained essentially unchanged with the presence of a deshielded singlet (**10**: δ<sub>P</sub> = 33.8 ppm; **[11a]**(OTf): δ<sub>P</sub> = 29.0 ppm; **[11b]**(OTf): δ<sub>P</sub> = 31.8 ppm). In all cases, <sup>13</sup>C NMR spectra are characterized by the occurrence of a doublet at low field for the linked ylide moiety (**10**: δ<sub>CH</sub> = 13.8 ppm (<sup>1</sup>J<sub>CP</sub> = 40.2 Hz); **[11a]**(OTf): δ<sub>CH</sub> = 5.7 ppm (<sup>1</sup>J<sub>CP</sub> = 32.2 Hz); **[11b]**(OTf): δ<sub>CH</sub> = 3.3 ppm (<sup>1</sup>J<sub>CP</sub> = 32.7 Hz)). While in the complex **[11a]**(OTf), the presence of coordinated CH<sub>3</sub>CN was confirmed by the corresponding <sup>13</sup>C NMR resonance (δ<sub>C</sub> 2.2 ppm in CD<sub>2</sub>Cl<sub>2</sub>), in **[11b]**(OTf) the coordination of the isocyanide was evidenced by the typical IR ν<sub>CN</sub> band at 2207 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>. As in the bis(NHC), ylide series, no formation of Pd-CO adduct was observed when the complex **[11a]**(OTf) was treated with CO gas in CH<sub>2</sub>Cl<sub>2</sub>.

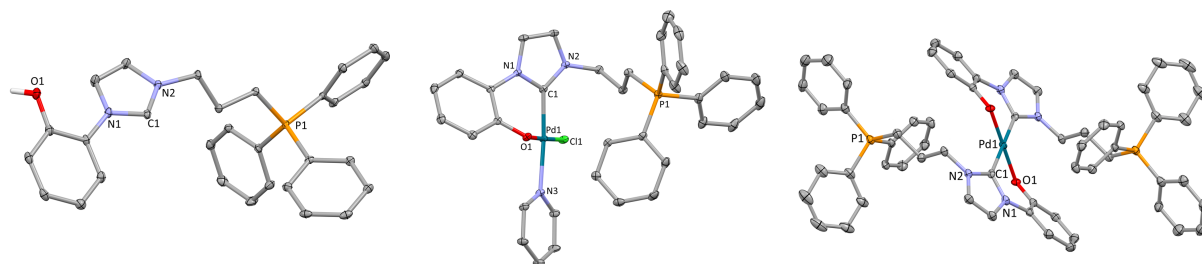


**Scheme 8.** Synthesis of NHC, phenolate, phosphonium ylide Pd(II) pincer complexes **[11a]**(OTf) and **[11b]**(OTf) from **10** by successive additions of HOTf and *t*BuNC.

## 2.2 Solid-state structural studies

Single crystal X-ray diffraction studies allowed us to establish the solid-state structures of the imidazolium salt **[7]**Br<sub>2</sub>, and of the corresponding Pd complexes **[8]**(OTf) and **[9]**(OTf)<sub>2</sub> (Figure 1).<sup>28</sup> In both complexes, the Pd(II) atom resides in a square-planar environment. However, while in the complex **[8]**(OTf), the position *trans* relative to the NHC is occupied by the pyridine, in the centro-symmetric complex **[9]**(OTf)<sub>2</sub>, the bidentate chelating *C,O*-ligand binds to the Pd atom in a *trans* fashion. Noteworthy, the N<sub>2</sub>C-Pd bond distances in **[9]**(OTf)<sub>2</sub> are slightly longer than in **[8]**(OTf) (**[8]**(OTf): C1-Pd1 = 1.965(3) Å; **[9]**(OTf)<sub>2</sub>: C1-Pd1 = 2.011(5) Å), a difference which may be tentatively attributed to the existence of

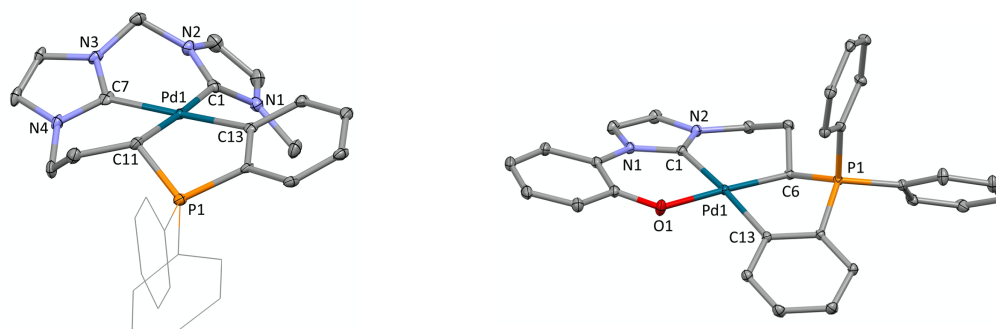
steric and electrostatic constraints between the facing cationic ligands in complex **[9](OTf)<sub>2</sub>**, the two triarylphosphoniums being on either side of the coordination Pd plane.



**Figure 1.** Perspective views of the cationic part of N-phosponio-imidazolium salt **[7]Br<sub>2</sub>** (*left*), N-phosponio-substituted NHC Pd complex **[8](OTf)** (*middle*), and bis(N-phosponio-substituted NHC) Pd complex **[9](OTf)<sub>2</sub>** (*right*) with thermal ellipsoids drawn at the 30% probability level. The H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **[7]Br<sub>2</sub>**: C1–N1 = 1.3394(18); C1–N2 = 1.3308(19); N1–C1–N2 = 108.47(13); **[8](OTf)**: C1–N1 = 1.359(3); C1–N2 = 1.344(3); C1–Pd1 = 1.965(3); O1–Pd1 = 2.0133(18); C11–Pd1 = 2.3162(6); N3–Pd1 = 2.127(2); N1–C1–N2 = 105.4(2); C1–Pd1–N3 = 172.79(10); O1–Pd1–C11 = 178.42(6); C1–Pd1–O1 = 84.21(9); C1–Pd1–C11 = 94.44(8); **[9](OTf)<sub>2</sub>**: C1–N1 = 1.361(7); C1–N2 = 1.353(7); C1–Pd1 = 2.011(5); O1–Pd1 = 2.001(3); N1–C1–N2 = 104.0(4); C1–Pd1–C1 = 179.994; O1–Pd1–O1 = 179.994; C1–Pd1–O1 = 93.92(17).

By marked contrast with the bis(ylide) series where single crystals of the *ortho*-metallated form could not be obtained,<sup>14</sup> the exact structure of related Pd complexes **[4](OTf)** and **10** was established by an X-ray diffraction analysis of single yellow crystals (Figure 2).<sup>28</sup> In complex **[4](OTf)**, the Pd(II) atom resides in a slightly distorted square-planar environment where the coordination plane is defined by four carbon donor extremities, namely the C1, C7, C11, and C13 atoms of the two NHCs, the phosphonium ylide and the *ortho*-phenylated moieties, respectively (Figure 2, *left*). The two *cis*-NHC fragments are positioned in respective *trans* position of the ylide and aryl groups with corresponding angles, which slightly deviate from ideal values (C1–Pd1–C11 = 173.95(18)°; C7–Pd1–C13 = 172.95(19)°). The NHC–Pd bond distances (C1–Pd1 = 2.018(2) Å; C7–Pd1 = 2.003(5) Å) fall within the range of related (NHC) Pd(II) complexes, being classically shorter than the ylide–Pd bond distance (C11–Pd1 = 2.112(5) Å) in agreement with their respective hybridization state (*Csp<sup>2</sup>* vs. *Csp<sup>3</sup>*).<sup>14</sup> The two fused six-membered palladacycles adopt a boat-like conformation with the sterically hindered tetrahedral phosphonium located in equatorial position while being an integral part of the *ortho*-metallated five-membered ring.

The *ortho*-metallated complex **10** presents a zwitterionic *C,C,C,O*-chelated structure, where the phosphonium positive charge is compensated by a palladate negative charge (figure 2, *right*). To accommodate a square planar geometry for the Pd(II) atom, the molecule is globally planar where only the phosphonium center and a CH<sub>2</sub> group of the propyl chain deviate from the planarity. The NHC core is located in *trans* position relative to the phenylated ring while the phenolate extremity is *trans* with respect to the ylide fragment (C1–Pd1–C13 = 172.71(4)°; C6–Pd1–O1 = 177.95(3)°). According to their respective hybridization state, the coordination bonds around the Pd center lie in the normal range for such donor groups (NHC: C1–Pd1 = 2.0107(10) Å; RC<sub>6</sub>H<sub>4</sub>O<sup>−</sup>: O1–Pd1 = 2.0411(8) Å; Ph<sub>3</sub>P<sup>+</sup>CHR<sup>−</sup>: C6–Pd1 = 2.0593(9) Å; RC<sub>6</sub>H<sub>4</sub><sup>−</sup>: C13–Pd1 = 2.0366(9) Å). The tau parameter ( $\tau_4$ ) which reflects the deviation from a square planar geometry was calculated in both cases.<sup>29</sup> The values found, respectively 0.091 and 0.065 in complexes [4](OTf) and **10**, close to 0, indicate a small deviation from a square planar geometry despite the presence of constrained structures.

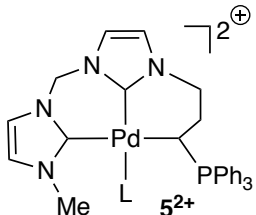
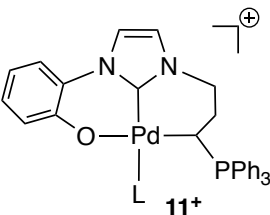
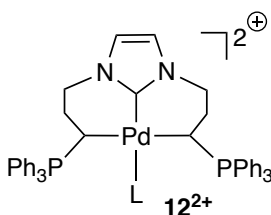


**Figure 2.** Perspective views of bis(NHC), phosphonium ylide Pd complex [4](OTf) (*left*), and NHC, phenolate, phosphonium ylide Pd complex **10** (*right*) with thermal ellipsoids drawn at the 30% probability level. The H atoms are omitted and phenyl rings are presented as wireframe for clarity in the case of [4](OTf). Selected bond lengths [Å] and angles [°]: [4](OTf): C1–N1 = 1.349(6); C1–N2 = 1.366(6); C7–N3 = 1.355(6); C7–N4 = 1.333(7); C1–Pd1 = 2.043(5); C7–Pd1 = 2.003(5); C11–Pd1 = 2.112(5); C13–Pd1 = 2.065(5); N1–C1–N2 = 103.0(4); N3–C7–N4 = 104.6(4); C1–Pd1–C11 = 173.95(18); C7–Pd1–C13 = 172.95(19); C1–Pd1–C7 = 85.75(19); C7–Pd1–C11 = 88.42(19); C11–Pd1–C13 = 85.71(18). **10**: C1–N1 = 1.3710(12); C1–N2 = 1.3522(13); P1–C6 = 1.7765(9); C1–Pd1 = 2.0107(10); O1–Pd1 = 2.0411(8); C6–Pd1 = 2.0593(9); C13–Pd1 = 2.0366(9); N1–C1–N2 = 104.85(8); C1–Pd1–C13 = 172.71(4); C6–Pd1–O1 = 177.95(3); C1–Pd1–O1 = 89.84(4); C6–Pd1–C13 = 87.77(4).

### 2.3 IR spectroscopy, cyclic voltammetry and theoretical studies of a series of Pd(II) pincer complexes.

The IR  $\nu_{\text{CN}}$  frequency values of Pd complexes **[5b]**(OTf)<sub>2</sub> ( $\nu_{\text{C}\equiv\text{N}}$  2206  $\text{cm}^{-1}$ ) and **[11b]**(OTf) ( $\nu_{\text{C}\equiv\text{N}}$  2207  $\text{cm}^{-1}$ ) indicate that the *C,C,C*-bis(NHC), phosphonium ylide and *C,C,O*-NHC, phenolate, phosphonium ylide ligands have a similar donor character. However, these values which occur at higher frequency than that of the Pd–CN*t*Bu complex of the bis(ylide), NHC ligand (**[12b]**(OTf)<sub>2</sub>:  $\nu_{\text{C}\equiv\text{N}}$  2194  $\text{cm}^{-1}$  in CH<sub>2</sub>Cl<sub>2</sub>)<sup>14</sup> suggest also that substitution of a NHC or a phenolate for a phosphonium ylide increase significantly the donor character of corresponding pincer ligands (Table 1). This trend is in line with previous studies conducted on an isoelectronic family of *C,C*-chelating [*o*-C<sub>6</sub>H<sub>4</sub>A<sub>a</sub>B<sub>b</sub>Rh(CO)<sub>2</sub>][OTf] complexes (A = NHC; B = Ph<sub>2</sub>P<sup>+</sup>CH<sub>2</sub><sup>-</sup>).<sup>7-8</sup>

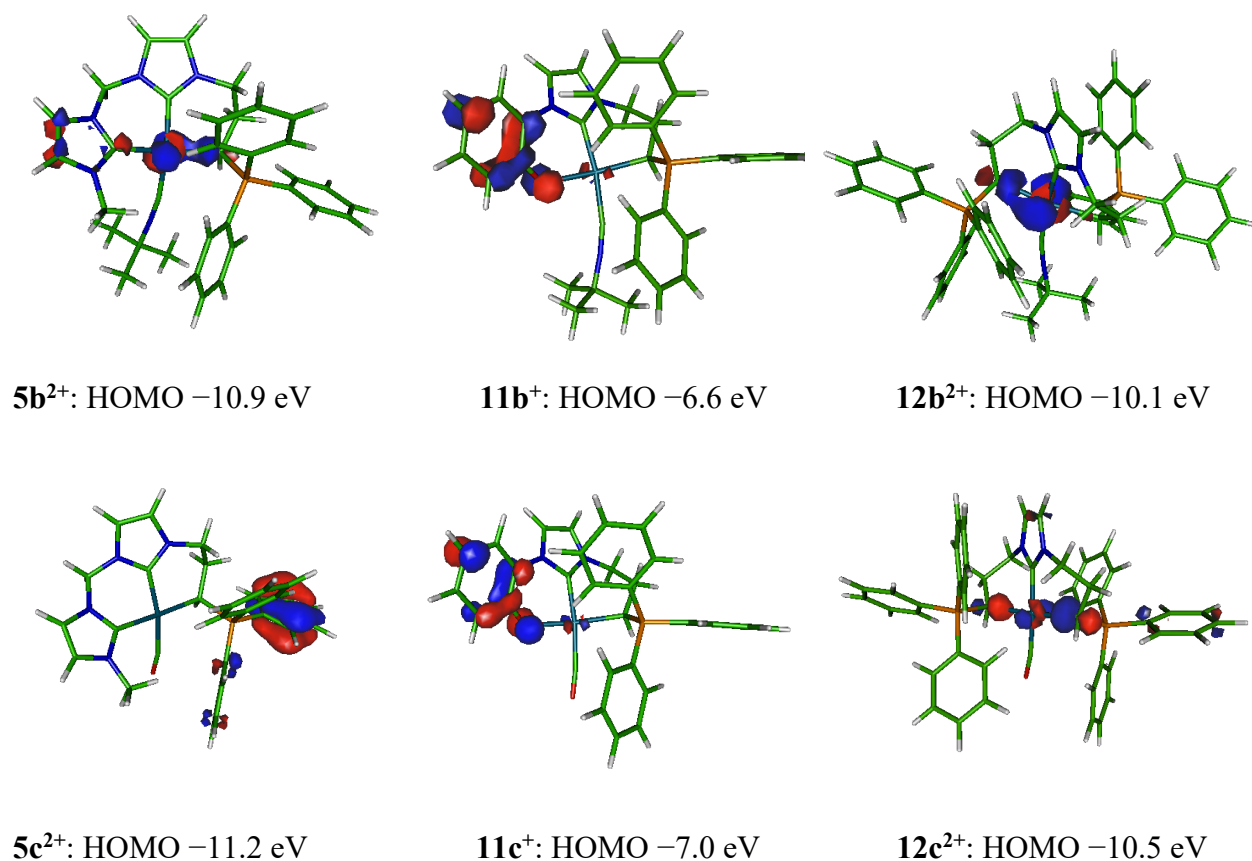
The IR  $\nu_{\text{CN}}$  and  $\nu_{\text{CO}}$  frequencies of cationic Pd complexes **5**<sup>2+</sup>, **11**<sup>+</sup> and **12**<sup>2+</sup> were calculated at the DFT level and compared with the experimental values.<sup>30</sup> A good agreement between experimental and calculated  $\nu_{\text{CN}}$  values was obtained with a constant gap of  $\Delta$  (calcd-exp)  $\approx$  8–9  $\text{cm}^{-1}$ . Both calculated  $\nu_{\text{CN}}$  and  $\nu_{\text{CO}}$  stretching frequencies confirm the strong donor character of phosphonium ylides as illustrated with the Pd–CO complex only observed experimentally in the case of the bis(ylide) ligand.<sup>14</sup> Along the two series, calculated values agree with the experimental trend, namely the highest donating properties of the pincer ligand in complex **12**<sup>2+</sup> and similar electron-donating properties for the ligands in complexes **5**<sup>2+</sup> and **11**<sup>+</sup>.

			
$\nu_{\text{CN}}$ (exp) <sup>a</sup>	<b>5b</b> <sup>2+</sup> : 2206	<b>11b</b> <sup>+</sup> : 2207	<b>12b</b> <sup>2+</sup> : 2194
$\nu_{\text{CN}}$ (calcd) <sup>b</sup>	<b>5b</b> <sup>2+</sup> : 2215	<b>11b</b> <sup>+</sup> : 2215	<b>12b</b> <sup>2+</sup> : 2207 2199 2203 (av.) <sup>c</sup>
$\Delta$ (calcd-exp)	9	8	9
$\nu_{\text{CO}}$ (exp) <sup>a</sup>	—	—	<b>12c</b> <sup>2+</sup> : 2114
$\nu_{\text{CO}}$ (calcd) <sup>b</sup>	<b>5c</b> <sup>2+</sup> : 2095	<b>11c</b> <sup>+</sup> : 2097	<b>12c</b> <sup>2+</sup> : 2076 2079 2077.5 (av.) <sup>c</sup>
$E_{\text{p}}^{\text{ox}}$ <sup>d</sup>	<b>5a</b> <sup>2+</sup> : 1.9 (1.5) <sup>e</sup>	<b>11a</b> <sup>+</sup> : 2.1 (1.8) <sup>e</sup>	<b>12a</b> <sup>2+</sup> : 1.6 (1.2) <sup>e</sup>

**Table 1.** Experimental and calculated IR  $\nu_{\text{CO}}$  and  $\nu_{\text{CN}}$  stretching frequencies ( $\text{cm}^{-1}$ ), and  $E_{\text{p}}^{\text{ox}}$  (V) for the cationic complexes **5**<sup>2+</sup>, **11**<sup>+</sup> and **12**<sup>2+</sup>.<sup>a</sup> IR frequency values measured in CH<sub>2</sub>Cl<sub>2</sub>.<sup>b</sup>

Calculations were performed at the PBE-D3/6-31G\*\*/LANL2DZ\*(Pd) level.<sup>c</sup> Complexes **12**<sup>2+</sup> exist as a mixture of *meso*- and *dl*-diastereoisomers.<sup>14 d</sup>  $E_{p}^{ox}$  values (V) are given with respect to SCE.<sup>e</sup> The values between brackets correspond to the  $E_{p}^{ox}$  (V) of related *ortho*-metallated forms.

The near-frontier orbitals of Pd pincer complexes **5**<sup>2+</sup>, **11**<sup>+</sup> and **12**<sup>2+</sup> were investigated in the isocyanide and carbonyl series.<sup>31</sup> The HOMOs of Pd–CN*t*Bu and Pd–CO adducts are depicted in Figure 3. In the isocyanide series, the HOMOs of carbon-based Pd complexes **5b**<sup>2+</sup> and **12b**<sup>2+</sup> involve a strong contribution of the orbitals of the Pd center and the carbon atom of the highly donating phosphonium ylide, accounting for the  $Csp^3$ –Pd  $\sigma$  bond (Figure 3, top). Consistently with the respective electron-richness of pincer ligands, the replacement of a NHC by a phosphonium ylide induces a shift of the HOMO towards higher energy (**5b**<sup>2+</sup>: –10.9 eV; **12b**<sup>2+</sup>: –10.1 eV). This variation is consistent with the formal charge at the palladium atom: +1 in **5b**<sup>2+</sup>, 0 in **12b**<sup>2+</sup>, the oxidation state of the metal (Pd(II)) and the overall charge of the complexes (+2) remaining the same. As the shape of HOMOs may be related to the ligand-metal interaction, the near-frontier MO energy levels of complexes **5b**<sup>2+</sup> and **12b**<sup>2+</sup> can be tentatively correlated with the electronic properties of corresponding C,C,C-pincer ligands following thus the same trend than IR  $\nu_{CN}$  and  $\nu_{CO}$  stretching frequencies. In contrast in complex **11b**<sup>+</sup>, the HOMO is strongly localized on the  $\pi$ -system and the oxygen atom lone pair of the phenolate donor with a negligible contribution of the Pd atom. The MOs exhibiting a significant contribution of the Pd and the ylide fragments are shifted much deeper in energy, as illustrated by the energies of HOMO–15 (–9.9 eV) and HOMO–16 (–10.0 eV). The MOs and in particular the HOMO (*ca.* –6.6 eV) lie significantly higher in energy compared to the carbon-based systems **5b**<sup>2+</sup> and **12b**<sup>2+</sup>. This difference can be assigned to the different overall charge [**11b**<sup>+</sup> (+1), **5b**<sup>2+</sup> and **12b**<sup>2+</sup> (+2)]. Since the HOMO does not properly account for the ligand-metal interaction in complex **11b**<sup>+</sup>, its energy cannot be directly related to the electronic properties of the ligand and therefore to the  $\nu_{CN}$  and  $\nu_{CO}$  frequency values. In terms of relative energy of HOMOs, the same general trend was found in the Pd–CO adducts (HOMO energy for **5c**<sup>2+</sup>: –11.2 eV; **11c**<sup>+</sup>: –7.0 eV; **12c**<sup>2+</sup>: –10.5 eV) (Figure 3, bottom). However, while the HOMOs remained mainly localized on the phenolate moiety and on the Pd and ylidic carbon atoms respectively in complexes **11c**<sup>+</sup> and **12c**<sup>2+</sup>, in the case of the bis(NHC) Pd complex **5c**<sup>2+</sup>, the HOMO is strongly localized on a P<sup>+</sup>-phenyl substituent on the way to the corresponding *ortho*-metallated form.



**Figure 3.** Representation of HOMOs of Pd complexes **5<sup>2+</sup>** (*left*), **11<sup>+</sup>** (*middle*) and **12<sup>2+</sup>** (*right*) with corresponding energy values (**b**: L = CN*t*Bu, *up*; **c**: L = CO, *down*). For complex **12<sup>2+</sup>**, only the HOMOs of the *dl*-isomer are represented. PBE-D3/6-31G\*\*/LANL2DZ\*(Pd) level of calculation.

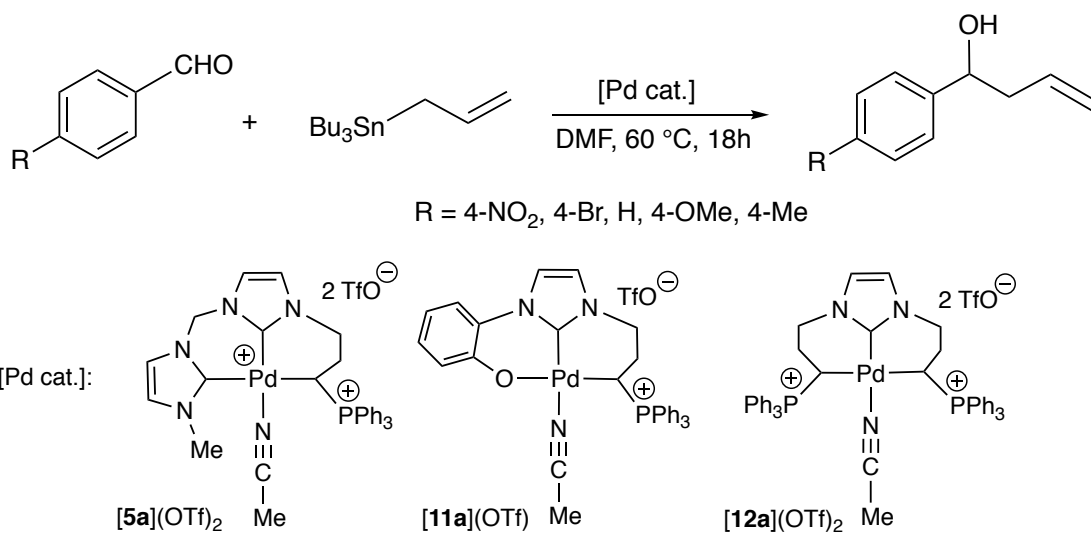
Considering that the oxidation potential ( $E_p^{\text{ox}}$ ) of a complex reflects generally the electronic properties of its ligand, the ylide-based Pd–NCCH<sub>3</sub> complexes [**5a**](OTf)<sub>2</sub>, [**11a**](OTf) and [**12a**](OTf)<sub>2</sub> and their corresponding *ortho*-metallated forms were investigated by cyclic voltammetry (Table 1). All oxidations were found to be irreversible with the  $E_p^{\text{ox}}$  values varying according to the donating character of the pincer ligand: the electron-rich bis(ylide) Pd complex [**12a**](OTf)<sub>2</sub> being indeed the most easily oxidized. Electrochemical measurements indicated also that going from the pincer complexes to their *ortho*-metallated forms results in a significant decrease of the  $E_p^{\text{ox}}$  values as expected since the latter complexes were formed by deprotonation of the former. The same relative variation observed for the  $E_p^{\text{ox}}$  values and the IR  $\nu_{\text{CO}}$  and  $\nu_{\text{CN}}$  stretching frequencies corroborate the assumption that the redox events are probably based on the Pd center.

## 2.4 Catalytic investigations

To evaluate the role of the structure of the pincer ligand on catalytic properties, the Pd-catalyzed allylation of aldehydes with allyltributyltin was selected. It was indeed reported that this transformation is efficiently catalyzed by pincer Pd(II) complexes bearing strongly  $\sigma$ -donating ligands,<sup>32</sup> which contribute to increase the electron density at the metal and therefore the nucleophilic character of the allyl fragment in a  $\eta^1$ -allyl-coordinated pincer complex identified as active catalytic intermediate.<sup>33</sup> The reactions were performed with various *p*-substituted aldehydes characterizing by different electronic requirement in the presence of catalytic amounts of the phosphonium ylide-based pincer Pd(II) complexes **[5a]**(OTf)<sub>2</sub>, **[11a]**(OTf) and **[12a]**(OTf)<sub>2</sub> in DMF at 60 °C for 18 hours (Table 2). Whatever the aldehyde, the bis(ylide) Pd complex **[12a]**(OTf)<sub>2</sub> complex showed the highest catalytic activity, the bis(NHC) complex **[5a]**(OTf)<sub>2</sub> being the least active. For example, benzaldehyde is converted in 81% after 18 h at 60 °C when **[12a]**(OTf)<sub>2</sub> is used as catalyst (5.0 mol %, entry 16), while in the same conditions, complexes **[5a]**(OTf)<sub>2</sub> and **[11a]**(OTf) produce the desired product in 30 and 58%, respectively (entries 14-15). With complex **[12a]**(OTf)<sub>2</sub>, the catalytic charge could be lowered to 1.0 mol % while keeping an acceptable yield (ca. 60%, entry 17). Homo-allylic alcohol products were obtained in higher yields with activated aldehydes, such as *p*-NO<sub>2</sub> and *p*-Br benzaldehydes. Gratifyingly, *p*-NO<sub>2</sub> benzaldehyde could be properly converted in the presence of 0.5 mol % of **[12a]**(OTf)<sub>2</sub> (80%, entry 6), being able to decrease the catalytic charge to 0.1 mol % (46%, entry 7). As expected, the electronically deactivated *p*-Me and *p*-MeO benzaldehydes were found to be less reactive, the bis(ylide) Pd complex **[12a]**(OTf)<sub>2</sub> allowing the formation of corresponding coupling products in 62 and 56% yield using a 5 mol % catalytic charge (entries 21 and 24).<sup>34</sup> The catalytic activity of complex **[12a]**(OTf)<sub>2</sub> is comparable to that reported with anionic [PCP] Pd(II) complexes,<sup>32-33</sup> but it appears to be higher than that observed with NHC Pd(II) complexes.<sup>35</sup>



**Table 2.** Catalytic allylation of aldehydes with phosphonium ylide-based pincer Pd complexes **[5a](OTf)<sub>2</sub>**, **[11a](OTf)**, and **[12a](OTf)<sub>2</sub>**.<sup>a</sup>



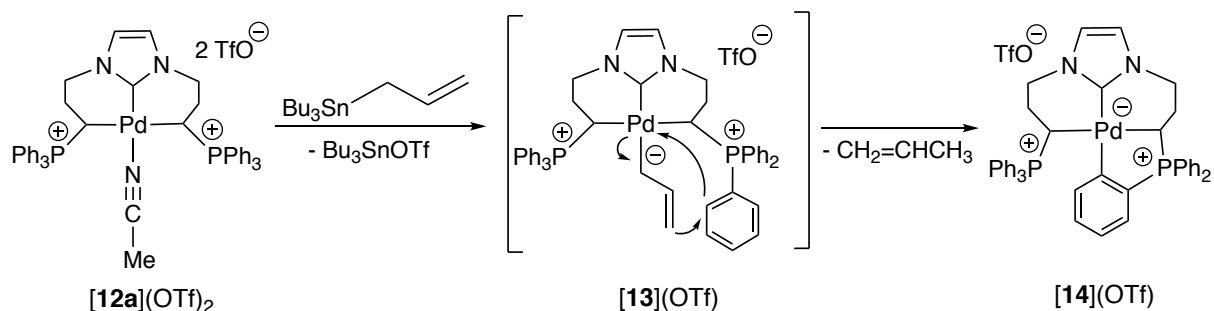
Entry	R	Complex	Cat. [%]	Conv. <sup>b</sup>
1	NO <sub>2</sub>	<b>[5a](OTf)<sub>2</sub></b>	5	50 (40)
2	NO <sub>2</sub>	<b>[11a](OTf)</b>	5	> 98 (92)
3	NO <sub>2</sub>	<b>[11a](OTf)</b>	1	78 (74)
4	NO <sub>2</sub>	<b>[12a](OTf)<sub>2</sub></b>	5	> 98 (97)
5	NO <sub>2</sub>	<b>[12a](OTf)<sub>2</sub></b>	1	86 (78)
6	NO <sub>2</sub>	<b>[12a](OTf)<sub>2</sub></b>	0.5	80 (70)
7	NO <sub>2</sub>	<b>[12a](OTf)<sub>2</sub></b>	0.1	46 (40)
8	NO <sub>2</sub>	-	-	11
9	Br	<b>[5a](OTf)<sub>2</sub></b>	5	35
10	Br	<b>[11a](OTf)</b>	5	66 (57)
11	Br	<b>[12a](OTf)<sub>2</sub></b>	5	91 (85)
12	Br	<b>[12a](OTf)<sub>2</sub></b>	1	34
13	Br	-	-	0
14	H	<b>[5a](OTf)<sub>2</sub></b>	5	30
15	H	<b>[11a](OTf)</b>	5	58 (42)
16	H	<b>[12a](OTf)<sub>2</sub></b>	5	81 (75)
17	H	<b>[12a](OTf)<sub>2</sub></b>	1	60 (54)
18	H	-	-	0
19	Me	<b>[5a](OTf)<sub>2</sub></b>	5	20

20	Me	[ <b>11a</b> ](OTf)	5	57 (45)
21	Me	[ <b>12a</b> ](OTf) <sub>2</sub>	5	62 (55)
22	MeO	[ <b>5a</b> ](OTf) <sub>2</sub>	5	10
23	MeO	[ <b>11a</b> ](OTf)	5	19
24	MeO	[ <b>12a</b> ](OTf) <sub>2</sub>	5	56 (45)

<sup>a</sup> All reactions were performed with 1.0 equiv. of aldehyde and 1.2 equiv. of allyltributyltin in DMF at 60 °C for 18 h. <sup>b</sup> Conversion determined by <sup>1</sup>H NMR, isolated yields in parenthesis.

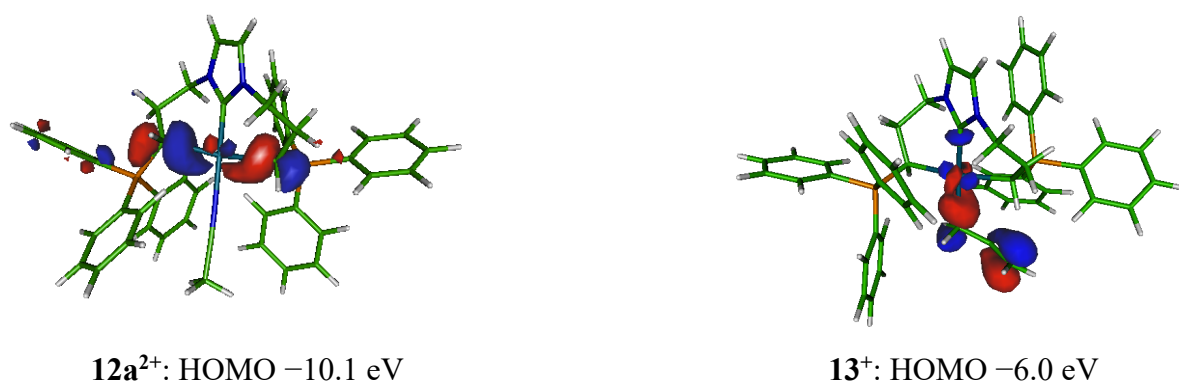
These results indicate that the ligand structure of pincer Pd complexes influence significantly the catalytic properties. The superiority of complex [**12a**](OTf)<sub>2</sub> can be attributed to the stronger donating properties of the *C,C,C*-NHC, bis(ylide) pincer ligand which would favor the nucleophilic attack of the  $\eta^1$ -allyl-pincer intermediate on the aldehyde. These findings are therefore in agreement with experimental and calculated IR  $\nu_{CO}$  and  $\nu_{CN}$  frequencies. With a similar donor character, the difference in activity observed between complexes [**5a**](OTf)<sub>2</sub> and [**11a**](OTf) also suggest that other factors may play a role and that a good balance in the catalytic system is generally required in order to benefit at all elementary steps.

To gain more insight on the catalytic mechanism, stoichiometric reactions were carried out from bis(ylide) complex [**12a**](OTf)<sub>2</sub>. The stability of [**12a**](OTf)<sub>2</sub> in DMF at 60 °C for 18 h was first confirmed by <sup>31</sup>P NMR monitoring. In the presence of a stoichiometric quantity of benzaldehyde in DMF at 60 °C for 18 h, the complex [**12a**](OTf)<sub>2</sub> was found to be unreactive. On the other hand, the addition on [**12a**](OTf)<sub>2</sub> of a stoichiometric amount of allyltributyltin in the same conditions led cleanly to the formation of the *ortho*-metallated complex [**14**](OTf) (Scheme 9).<sup>36</sup> This result is in favor of the formation of the  $\eta^1$ -allyl-Pd pincer complex [**13**](OTf), which in the absence of an electrophile, would stabilize by formation of the *ortho*-metallated product [**14**](OTf), the electron-rich allyl moiety playing here the role of an internal base. This reactivity is confirmed by the complete conversion of [**12a**](OTf)<sub>2</sub> into its *ortho*-metallated form [**14**](OTf) upon addition of KHMDS base in THF. In accordance with its high stability and the role of the  $\eta^1$ -allyl ligand in the Pd intermediate [**13**](OTf), the pre-catalyst [**12a**](OTf)<sub>2</sub> was recovered after catalysis by extraction with CH<sub>2</sub>Cl<sub>2</sub> in mixture with its *ortho*-metallated form [**14**](OTf).



**Scheme 9.** Proposed mechanism of formation of the *ortho*-metallated complex **[14](OTf)** from **[12a](OTf)<sub>2</sub>** in the presence of allyltributyltin.

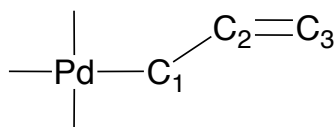
To further investigate the role of the strongly donating bis(ylide) pincer ligand in the  $\eta^1$ -allyl-Pd catalytic intermediate **13<sup>+</sup>**, DFT studies were undertaken at the PBE-D3/6-31G\*\*/LANL2DZ\*(Pd) level of calculation (Figure 4).<sup>31</sup> The difference in energy found between the OMs of **13<sup>+</sup>** and those of the pre-catalyst **12a<sup>2+</sup>** is consistent with the different overall charge [**13<sup>+</sup>** (+1) and **12a<sup>2+</sup>** (+2)], the MO levels of **13<sup>+</sup>** being indeed shifted up to higher energy compared to **12a<sup>2+</sup>** as illustrated with the relative HOMO energies (**12a<sup>2+</sup>**: -10.1 eV; **13<sup>+</sup>**: -6.0 eV). A close inspection indicates also a significant change in the nature of the HOMOs, namely that the HOMO initially localized on the two  $Csp^3$ -Pd bonds in **12a<sup>2+</sup>** is now strongly located on the  $\pi$ -system of the coordinated  $\eta^1$ -allyl fragment in **13<sup>+</sup>**, suggesting a preferential interaction of the allyl moiety with electrophiles.



**Figure 4.** Representation of the HOMOs of pre-catalyst **12a<sup>2+</sup>** and  $\eta^1$ -allyl-Pd pincer intermediate **13<sup>+</sup>** with corresponding energy values. In both cases, only the HOMOs of the *dl*-isomers are represented. PBE-D3/6-31G\*\*/LANL2DZ\*(Pd) level of calculation.

Based on these findings, the chemical reactivity of  $\mathbf{13}^+$  was further investigated using Fukui functions  $f$  condensed on Quantum Theory of Atoms in Molecules (QTAIM) or on Electron Localization Function (ELF) basins (Table 3). The largest  $f_{\text{ELF}}$  value (0.22) is obtained for the ELF valence basin of the allyl termini  $V(\text{C2,C3})$ , suggesting that it is the most sensitive bond to electrophilic attack. It is supported by  $f_{\text{QTAIM}}$  taking its maximum value for the C3 carbon atom ( $f_{\text{QTAIM}}(\text{C3}) = 0.29$ ), in agreement with the reactivity observed experimentally and with previous calculations performed on related models.<sup>33b</sup>

**Table 3.** Selected values of atomic QTAIM charges and Fukui functions  $f$  condensed on QTAIM and ELF basins for the  $\eta^1$ -allyl ligand in Pd complex  $\mathbf{13}^+$ . PBE-D3/6-31G\*\*/LANL2DZ\*(Pd) level of calculation.



	Pd	C1	C2	C3
Atomic charges (QTAIM)	-0.4	-0.3	-0.1	-0.2
$f_{\text{QTAIM}}$	0.16	0.25	0.08	0.29
$f_{\text{ELF}}$	C(Pd): 0.13	V(Pd, C1): 0.17	-	V(C2,C3): 0.22

### 3. CONCLUSION

An isostructural family of NHC core, phosphonium ylide-based Pd(II) pincer complexes where the third extremity can be modified was described according to two distinct synthetic pathways. While the difference in acidity between the cationic imidazolium and phosphonium moieties led to the development of a two-step method, the most direct route to the phosphonium ylide-based Pd(II) pincers involves the passage through the formation of *ortho*-metallated Pd complexes. Thanks to their high stability and availability, these *ortho*-metallated species serve as reservoirs for more reactive pincer complexes as illustrated with the formation of Pd–NCCH<sub>3</sub> adducts upon acidic treatment. Based on IR  $\nu_{\text{CO}}$  and  $\nu_{\text{CN}}$  frequencies,  $E_{\text{p}}^{\text{ox}}$  values and on the determination of MOs, a direct comparison between NHC (A), phenolate (B) and phosphonium ylide (C) moieties in related complexes [NHC(A<sub>a</sub>B<sub>b</sub>C<sub>c</sub>)PdL][OTf] ( $a + b + c = 2$ ; L = NCCH<sub>3</sub>, CN*t*Bu or CO) was undertaken, evidencing the stronger donor character of phosphonium ylides. This difference in donor

ability is valued for the first time in homogeneous catalysis for the Pd-catalyzed allylation of aldehydes. In this process, the intermediate formation of a  $\eta^1$ -allyl-Pd pincer complex was confirmed on the basis of experimental and theoretical studies. Other catalytic transformations are now targeted with these extremely electron-rich carbon-based pincer ligands. Future studies will also aim to extend this methodology to the preparation of pincer complexes featuring phosphonium ylide extremities with different P-substituents and/or other donor moieties such as amines and phosphines.

## EXPERIMENTAL SECTION

**General Remarks.** All manipulations were performed under an inert atmosphere of dry nitrogen by using standard vacuum line and Schlenk tube techniques. Glassware was dried at 120 °C in an oven for at least three hours. Dry and oxygen-free organic solvents (THF, Et<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, toluene, pentane) were obtained using a LabSolv (Innovative Technology) solvent purification system. Acetonitrile was dried and distilled over P<sub>2</sub>O<sub>5</sub> under argon. All other reagent-grade chemicals were purchased from commercial sources and used as received. Chromatographic purification was carried out on silica gel (SiO<sub>2</sub>, 63–200  $\mu$ m). <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectra were obtained on Bruker AV300, AV400 or NEO600 spectrometers. NMR chemical shifts  $\delta$  are in ppm, with positive values to high frequency relative to the tetramethylsilane reference for <sup>1</sup>H and <sup>13</sup>C and to 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P. If necessary, additional information on the carbon signal attribution was obtained using <sup>13</sup>C{<sup>1</sup>H, <sup>31</sup>P}, *J*-modulated spin-echo (JMOD) <sup>13</sup>C{<sup>1</sup>H}, <sup>1</sup>H–<sup>13</sup>C HMQC, and/or HMBC experiments. MS spectra (ESI mode) were performed by the mass spectrometry service of the “Institut de Chimie de Toulouse”. Elemental analyses were carried out by the elemental analysis service of the “LCC” using a Perkin Elmer 2400 series II analyzer. Voltammetric measurements were performed by the electrochemistry service of the “LCC”. 3-((1H-imidazol-1-yl)-methyl)-1-methyl-1H-imidazol-3-ium iodide [**1**]I<sup>20</sup> and 1-(2-hydroxyphenyl)imidazole **6**<sup>26</sup> were prepared according to previously described procedures.

NB: All compounds were found to be highly hygroscopic and difficult to weigh in air.

### Synthesis of pre-ligand [**2**](OTf)<sub>3</sub>

A solution of 3-((1H-imidazol-1-yl)-methyl)-1-methyl-1H-imidazol-3-ium iodide [**1**]I (1.04 g, 3.58 mmol) and 3-bromopropyl triphenylphosphonium bromide (1.84 g, 3.96 mmol) in DMF (70 mL) under nitrogen was stirred at 120 °C for 12 hours. After evaporation of the solvent under vacuum, the remaining solid was heated at 70 °C for 2 hours. The solid residue was dissolved in a minimum of CH<sub>3</sub>CN (10 mL), and after few minutes a solid precipitate

appeared. After filtration, the solid residue (2.45 g, 3.26 mmol) and sodium triflate (1.68 g, 9.78 mmol) were stirred in CH<sub>3</sub>CN (30 mL) at room temperature for 12 hours. The mixture was filtered through Celite, and the resulting solution was evaporated to dryness under reduced pressure. The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), and washed with water (20 mL). The aqueous phase was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL). The combined organic phases were dried over MgSO<sub>4</sub> and after evaporation of the solvent under vacuum, [2](OTf)<sub>3</sub> was obtained as a white powder (2.98 g, 91%). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>3</sub>CN, 25 °C): δ = 25.0 (s); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C) δ = 9.31 (s, 1H, N<sub>2</sub>CH), 9.10 (s, 1H, N<sub>2</sub>CH), 7.86–7.91 (m, 3H, H<sub>Ar</sub>), 7.70–7.77 (m, 14H, H<sub>Ar</sub>), 7.51 (t, *J*<sub>HH</sub> = 1.8 Hz, 1H, H<sub>Ar</sub>), 7.44 (t, *J*<sub>HH</sub> = 1.8 Hz, 1H, H<sub>Ar</sub>), 6.54 (s, 2H, NCH<sub>2</sub>N), 4.40 (t, *J*<sub>HH</sub> = 7.1 Hz, 2H, NCH<sub>2</sub>), 3.88 (s, 3H, NCH<sub>3</sub>), 3.30–3.37 (m, 2H, PCH<sub>2</sub>), 2.13–2.25 (m, 2H, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>CN, 25 °C): δ = 138.8 (s, N<sub>2</sub>CH), 138.6 (s, N<sub>2</sub>CH), 136.3 (d, *J*<sub>CP</sub> = 3.0 Hz, CH<sub>Ph</sub>), 134.8 (d, *J*<sub>CP</sub> = 10.1 Hz, CH<sub>Ph</sub>), 131.3 (d, *J*<sub>CP</sub> = 12.1 Hz, CH<sub>Ph</sub>), 125.7 (s, CH<sub>Im</sub>), 124.4 (s, CH<sub>Im</sub>), 123.6 (s, CH<sub>Im</sub>), 123.3 (s, CH<sub>Im</sub>), 121.5 (q, *J*<sub>CF</sub> = 320.9 Hz, CF<sub>3</sub>), 118.6 (d, *J*<sub>CP</sub> = 86.5 Hz, C<sub>Ph</sub>), 59.5 (s, NCH<sub>2</sub>N), 50.4 (d, *J*<sub>CP</sub> = 21.1 Hz, NCH<sub>2</sub>), 37.5 (s, NCH<sub>3</sub>), 23.6 (d, *J*<sub>CP</sub> = 2.0 Hz, CH<sub>2</sub>), 20.1 (d, *J*<sub>CP</sub> = 55.3 Hz, PCH<sub>2</sub>); MS (ES<sup>+</sup>): *m/z*: 765.1 [M – CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>; elemental analysis for C<sub>32</sub>H<sub>32</sub>F<sub>9</sub>N<sub>4</sub>O<sub>9</sub>PS<sub>3</sub>: calcd, C 42.02, H 3.53, N 6.12; found, C 41.87, H 3.36, N 6.01.

### Synthesis of complex [3](OTf)

[2](OTf)<sub>3</sub> (0.16 g, 0.17 mmol) and bis(acetonitrile)-palladium chloride (0.06 g, 0.22 mmol) were dissolved in dry CH<sub>3</sub>CN (12 mL). Triethylamine (60 μL, 0.43 mmol) was then added and the suspension was heated at 60 °C for 4 hours. After filtration over Celite, the solvent was removed under vacuum. The solid residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), the solution was washed several times with water and dried over MgSO<sub>4</sub>. After evaporation of the solvent, [3](OTf) was obtained as a yellow solid (0.10 g, 75%). Additional purification may be performed if necessary by passing the complex [3](OTf) over a small column of alumina (eluent CH<sub>2</sub>Cl<sub>2</sub>/EtOAc/CH<sub>3</sub>OH). <sup>31</sup>P{<sup>1</sup>H} NMR (121 MHz, CD<sub>3</sub>CN, 25 °C): δ = 23.6 (s); <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, 25 °C) δ = 7.83–7.89 (m, 3H, H<sub>Ar</sub>), 7.70–7.79 (m, 12H, H<sub>Ar</sub>), 7.34 (t, *J*<sub>HH</sub> = 2.2 Hz, 2H, H<sub>Ar</sub>), 7.04 (d, *J*<sub>HH</sub> = 2.0 Hz, 1H, H<sub>Ar</sub>), 6.97 (d, *J*<sub>HH</sub> = 2.0 Hz, 1H, H<sub>Ar</sub>), 6.23 (d, *J*<sub>HH</sub> = 13.1 Hz, 1H, NCH<sub>2</sub>N), 6.07 (d, *J*<sub>HH</sub> = 13.1 Hz, 1H, NCH<sub>2</sub>N), 4.77–4.87 (m, 1H, NCH<sub>2</sub>), 4.51–4.61 (m, 1H, NCH<sub>2</sub>), 3.80 (s, 3H, NCH<sub>3</sub>), 3.21–3.56 (m, 2H, PCH<sub>2</sub>), 2.14–2.35 (m, 2H, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>3</sub>CN, 25 °C): δ = 159.0 (s, N<sub>2</sub>C), 158.5 (s, N<sub>2</sub>C), 136.1 (d, *J*<sub>CP</sub> = 3.0 Hz, CH<sub>Ph</sub>), 134.7 (d, *J*<sub>CP</sub> = 10.6 Hz, CH<sub>Ph</sub>), 131.3 (d, *J*<sub>CP</sub> = 12.8 Hz, CH<sub>Ph</sub>), 123.8 (s, CH<sub>Im</sub>), 122.6 (s, CH<sub>Im</sub>), 122.5 (s, CH<sub>Im</sub>), 122.2 (s, CH<sub>Im</sub>), 121.6 (q, *J*<sub>CF</sub> = 320.8 Hz,

CF<sub>3</sub>), 119.0 (d,  $J_{CP}$  = 86.8 Hz, C<sub>Ph</sub>), 63.5 (s, NCH<sub>2</sub>N), 50.8 (d,  $J_{CP}$  = 21.1 Hz, NCH<sub>2</sub>), 38.8 (s, NCH<sub>3</sub>), 25.2 (d,  $J_{CP}$  = 3.0 Hz, CH<sub>2</sub>), 20.3 (d,  $J_{CP}$  = 54.4 Hz, PCH<sub>2</sub>); MS (ES<sup>+</sup>):  $m/z$ : 642.9 [M – CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>; elemental analysis for C<sub>30</sub>H<sub>30</sub>Cl<sub>2</sub>F<sub>3</sub>N<sub>4</sub>O<sub>3</sub>PPdS: calcd, C 45.50, H 3.82, N 7.07; found, C 45.81, H 3.81, N 6.74.

### Synthesis of complex [4](OTf)

1<sup>st</sup> method: Complex [3](OTf) (0.04 g, 0.051 mmol) and anhydrous Cs<sub>2</sub>CO<sub>3</sub> (0.05 g, 0.15 mmol) were dissolved in CH<sub>3</sub>CN (4 mL), and the suspension was stirred at 60 °C for 16 hours. After filtration over Celite, the solvent was evaporated under vacuum, affording complex [4](OTf) as a white solid (0.035 g, 94%). Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane at –20 °C gave pale yellow crystals suitable for X-ray diffraction.

2<sup>nd</sup> method: A mixture of [2](OTf)<sub>3</sub> (0.10 g, 0.11 mmol), PdCl<sub>2</sub> (0.02 g, 0.11 mmol), and anhydrous Cs<sub>2</sub>CO<sub>3</sub> (0.18 g, 0.55 mmol) was stirred at 60 °C in CH<sub>3</sub>CN (10 mL) for 12 hours. After filtration over Celite and evaporation of the solvent under vacuum, the crude residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and the solution was filtered over Celite. After evaporation of the solvent, the resulting solid was washed with Et<sub>2</sub>O (3 x 10 mL) affording [4](OTf) as a pale yellow powder (0.05 g, 69%).

<sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  = 30.4 (s); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C)  $\delta$  = 7.76–7.83 (m, 6H, H<sub>Ar</sub>), 7.67–7.70 (m, 2H, H<sub>Ar</sub>), 7.60–7.65 (m, 1H, H<sub>Ar</sub>), 7.48–7.51 (m, 2H, H<sub>Ar</sub>), 7.38 (d,  $J_{HH}$  = 1.9 Hz, 1H, H<sub>Ar</sub>), 7.21–7.25 (m, 1H, H<sub>Ar</sub>), 7.21 (d,  $J_{HH}$  = 1.9 Hz, 1H, H<sub>Ar</sub>), 7.13 (d,  $J_{HH}$  = 1.9 Hz, 1H, H<sub>Ar</sub>), 7.06–7.14 (m, 2H, H<sub>Ar</sub>), 6.98 (d,  $J_{HH}$  = 1.9 Hz, 1H, H<sub>Ar</sub>), 6.07 (d,  $J_{HH}$  = 13.0 Hz, 1H, NCH<sub>2</sub>N), 6.01 (d,  $J_{HH}$  = 13.0 Hz, 1H, NCH<sub>2</sub>N), 3.93 (td,  $J_{HH}$  = 3.7, 13.3 Hz, 1H, NCH<sub>2</sub>), 3.72 (s, 3H, NCH<sub>3</sub>), 3.02 (brt,  $J_{HH}$  = 11.7 Hz, 1H, NCH<sub>2</sub>), 2.64 (dd,  $J_{HH}$  = 2.6, 9.2 Hz, 1H, PCH), 2.41–2.46 (m, 1H, CH<sub>2</sub>), 2.05–2.26 (m, 1H, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>CN, 25 °C):  $\delta$  = 179.9 (d,  $J_{CP}$  = 34.2 Hz, C<sub>Ph</sub>), 178.8 (d,  $J_{CP}$  = 6.0 Hz, N<sub>2</sub>C), 177.7 (d,  $J_{CP}$  = 7.0 Hz, N<sub>2</sub>C), 142.6 (d,  $J_{CP}$  = 19.1 Hz, CH<sub>Ph</sub>), 139.2 (d,  $J_{CP}$  = 115.7 Hz, C<sub>Ph</sub>), 134.4 (d,  $J_{CP}$  = 9.0 Hz, CH<sub>Ph</sub>), 134.03 (d,  $J_{CP}$  = 2.0 Hz, CH<sub>Ph</sub>), 134.0 (d,  $J_{CP}$  = 9.0 Hz, CH<sub>Ph</sub>), 133.7 (d,  $J_{CP}$  = 3.0 Hz, CH<sub>Ph</sub>), 131.3 (d,  $J_{CP}$  = 20.1 Hz, CH<sub>Ph</sub>), 130.6 (d,  $J_{CP}$  = 10.1 Hz, CH<sub>Ph</sub>), 130.3 (d,  $J_{CP}$  = 3.0 Hz, CH<sub>Ph</sub>), 130.0 (d,  $J_{CP}$  = 12.1 Hz, CH<sub>Ph</sub>), 129.3 (d,  $J_{CP}$  = 87.5 Hz, C<sub>Ph</sub>), 127.5 (d,  $J_{CP}$  = 55.3 Hz, C<sub>Ph</sub>), 125.4 (d,  $J_{CP}$  = 7.0 Hz, CH<sub>Ph</sub>), 122.9 (s, CH<sub>Im</sub>), 122.7 (s, CH<sub>Im</sub>), 121.6 (q,  $J_{CF}$  = 320.8 Hz, CF<sub>3</sub>), 121.5 (s, CH<sub>Im</sub>), 120.4 (s, CH<sub>Im</sub>), 63.8 (s, NCH<sub>2</sub>N), 52.5 (d,  $J_{CP}$  = 3.0 Hz, NCH<sub>2</sub>), 39.5 (s, NCH<sub>3</sub>), 25.7 (d,  $J_{CP}$  = 3.0 Hz, CH<sub>2</sub>), 17.3 (d,  $J_{CP}$  = 36.2 Hz, PCH); MS (ES<sup>+</sup>):  $m/z$ : 569.1 [M – CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>; HRMS (ES<sup>+</sup>): calcd for C<sub>29</sub>H<sub>28</sub>N<sub>4</sub>PPd, 569.1097; found, 569.1100; elemental analysis for C<sub>30</sub>H<sub>28</sub>F<sub>3</sub>N<sub>4</sub>O<sub>3</sub>PPdS.0.5 H<sub>2</sub>O: calcd, C 49.49, H 4.01, N 7.70; found, C 49.43, H 3.91, N 7.22.

### Synthesis of complex [5a](OTf)<sub>2</sub>

TfOH (0.5 M in CH<sub>3</sub>CN, 0.14 mL, 0.067 mmol) was added at -40 °C to a solution of complex [4](OTf) (0.05 g, 0.069 mmol) in CH<sub>3</sub>CN (5 mL). The mixture was warmed to room temperature for 2 hours. After filtration over Celite, the solvent was removed under vacuum, and complex [5a](OTf)<sub>2</sub> was obtained as a pale yellow powder (0.06 g, 91%). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>3</sub>CN, 25 °C): δ = 33.9 (s); <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 25 °C) δ = 7.71–7.77 (m, 9H, H<sub>Ar</sub>), 7.57–7.61 (m, 6H, H<sub>Ar</sub>), 7.33 (d, *J*<sub>HH</sub> = 1.8 Hz, 1H, H<sub>Ar</sub>), 7.18 (d, *J*<sub>HH</sub> = 1.8 Hz, 1H, H<sub>Ar</sub>), 7.08 (d, *J*<sub>HH</sub> = 1.8 Hz, 1H, H<sub>Ar</sub>), 6.97 (d, *J*<sub>HH</sub> = 1.8 Hz, 1H, H<sub>Ar</sub>), 5.97 (d, *J*<sub>HH</sub> = 13.2 Hz, 1H, NCH<sub>2</sub>N), 5.65 (d, *J*<sub>HH</sub> = 13.2 Hz, 1H, NCH<sub>2</sub>N), 4.13–4.15 (m, 1H, NCH<sub>2</sub>), 3.82–3.87 (m, 1H, NCH<sub>2</sub>), 3.72 (s, 3H, NCH<sub>3</sub>), 3.44–3.49 (m, 1H, CH<sub>2</sub>), 2.45–2.57 (m, 1H, PCH), 1.90–1.95 (m, 1H, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125.8 MHz, CD<sub>3</sub>CN, 25 °C): δ = 168.6 (s, N<sub>2</sub>C), 158.1 (s, N<sub>2</sub>C), 134.8 (d, *J*<sub>CP</sub> = 8.8 Hz, CH<sub>Ph</sub>), 134.6 (d, *J*<sub>CP</sub> = 2.5 Hz, CH<sub>Ph</sub>), 130.5 (d, *J*<sub>CP</sub> = 11.3 Hz, CH<sub>Ph</sub>), 124.4 (d, *J*<sub>CP</sub> = 83.0 Hz, C<sub>Ph</sub>), 124.0 (s, CH<sub>Im</sub>), 122.6 (s, CH<sub>Im</sub>), 122.5 (s, CH<sub>Im</sub>), 122.2 (s, CH<sub>Im</sub>), 121.8 (q, *J*<sub>CF</sub> = 320.9 Hz, CF<sub>3</sub>), 63.1 (s, NCH<sub>2</sub>N), 52.6 (d, *J*<sub>CP</sub> = 12.6 Hz, NCH<sub>2</sub>), 38.7 (s, NCH<sub>3</sub>), 25.6 (s, CH<sub>2</sub>), 9.9 (d, *J*<sub>CP</sub> = 32.7 Hz, PCH); MS (ES<sup>+</sup>): *m/z*: 719.1 [M – CH<sub>3</sub>CN – CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>; HRMS (ES<sup>+</sup>): calcd for C<sub>30</sub>H<sub>29</sub>F<sub>3</sub>N<sub>4</sub>O<sub>3</sub>PPdS, 719.0696; found, 719.0709; elemental analysis for C<sub>33</sub>H<sub>32</sub>F<sub>6</sub>N<sub>5</sub>O<sub>6</sub>PPdS<sub>2</sub>·H<sub>2</sub>O: calcd, C 42.70, H 3.69, N 7.55; found, C 42.16, H 3.24, N 8.21.

### Synthesis of complex [5b](OTf)<sub>2</sub>

*t*-butyl isocyanide (9.32 μL, 0.082 mmol) was added at -78 °C to a solution of complex [5a](OTf)<sub>2</sub> (0.05 g, 0.055 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL). The mixture was warmed to room temperature for 4 hours. After filtration over Celite, the solvent was removed under vacuum, and complex [5b](OTf)<sub>2</sub> was obtained as a pale yellow powder (0.049 g, 94%). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 35.0 (s); <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) δ = 7.78–7.70 (m, 9H, H<sub>Ar</sub>), 7.66–7.61 (m, 6H, H<sub>Ar</sub>), 7.59 (d, *J*<sub>HH</sub> = 1.8 Hz, 1H, H<sub>Ar</sub>), 7.46 (d, *J*<sub>HH</sub> = 1.8 Hz, 1H, H<sub>Ar</sub>), 7.09 (d, *J*<sub>HH</sub> = 1.8 Hz, 1H, H<sub>Ar</sub>), 6.99 (d, *J*<sub>HH</sub> = 1.8 Hz, 1H, H<sub>Ar</sub>), 6.41 (d, *J*<sub>HH</sub> = 13.2 Hz, 1H, NCH<sub>2</sub>N), 5.80 (d, *J*<sub>HH</sub> = 13.2 Hz, 1H, NCH<sub>2</sub>N), 4.27–4.19 (m, 1H, NCH<sub>2</sub>), 4.07–4.01 (m, 1H, NCH<sub>2</sub>), 3.84 (s, 3H, NCH<sub>3</sub>), 3.44–3.34 (m, 1H, PCH), 2.53–2.35 (m, 2H, CH<sub>2</sub>), 1.06 (s, 9H, *t*Bu); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>CN, 25 °C)\*: δ = 167.5 (s, N<sub>2</sub>C), 163.1 (s, N<sub>2</sub>C), 134.6 (d, *J*<sub>CP</sub> = 2.5 Hz, CH<sub>Ph</sub>), 134.4 (d, *J*<sub>CP</sub> = 8.8 Hz, CH<sub>Ph</sub>), 130.4 (d, *J*<sub>CP</sub> = 11.3 Hz, CH<sub>Ph</sub>), 124.0 (d, *J*<sub>CP</sub> = 83.0 Hz, C<sub>Ph</sub>), 123.4 (s, CH<sub>Im</sub>), 123.2 (s, CH<sub>Im</sub>), 122.6 (s, CH<sub>Im</sub>), 121.7 (s, CH<sub>Im</sub>), 121.4 (q, *J*<sub>CF</sub> = 320.9 Hz, CF<sub>3</sub>), 62.9 (s, NCH<sub>2</sub>N), 59.7 (s, C(CH<sub>3</sub>)<sub>3</sub>), 51.5 (d, *J*<sub>CP</sub> = 12.6 Hz, NCH<sub>2</sub>), 39.2 (s, NCH<sub>3</sub>), 29.5 (s, CH<sub>3</sub>), 25.5 (s, CH<sub>2</sub>), 6.5 (d, *J*<sub>CP</sub> = 32.7 Hz, PCH); MS (ES<sup>+</sup>): *m/z*: 719.1 [M – *t*BuNC – CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>; HRMS (ES<sup>+</sup>): calcd for C<sub>30</sub>H<sub>29</sub>F<sub>3</sub>N<sub>4</sub>O<sub>3</sub>PPdS,



719.0696; found, 719.0711; elemental analysis for C<sub>36</sub>H<sub>38</sub>F<sub>6</sub>N<sub>5</sub>O<sub>6</sub>PPdS<sub>2</sub>. H<sub>2</sub>O: calcd, C 44.57, H 4.16, N 7.22; found, C 44.16, H 3.98, N 8.41. \* The <sup>13</sup>C NMR resonance of the CN quaternary carbon atom of coordinated *t*-BuNC was not observed.

### Synthesis of pre-ligand [7]Br<sub>2</sub>

1-(2-hydroxyphenyl)imidazole **6** (0.50 g, 3.12 mmol) and (3-bromo-propyl)-triphenylphosphonium bromide (0.96 g, 2.08 mmol) were heated at 120 °C in C<sub>6</sub>H<sub>5</sub>Cl (30 mL) for 15 hours. After evaporation of the solvent, the crude residue was washed with Et<sub>2</sub>O (3 x 80 mL) affording a white powder (1.19 g, 92%). Recrystallization from CH<sub>3</sub>CN at room temperature gave [7]Br<sub>2</sub> as colorless crystals suitable for X-ray diffraction. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>, 25 °C): δ = 24.3 (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 9.91 (s, 1H, N<sub>2</sub>CH), 8.29 (s, 1H, H<sub>Ar</sub>), 7.85–7.80 (m, 6H, H<sub>Ar</sub>), 7.77–7.72 (m, 3H, H<sub>Ar</sub>), 7.67–7.63 (m, 7H, H<sub>Ar</sub>), 7.53 (d, *J*<sub>HH</sub> = 8.2 Hz, 1H, H<sub>Ar</sub>), 7.37 (d, *J*<sub>HH</sub> = 7.9 Hz, 1H, H<sub>Ar</sub>), 7.31 (s, 1H, H<sub>Ar</sub>), 7.16 (t, *J*<sub>HH</sub> = 7.4 Hz, 1H, H<sub>Ar</sub>), 6.83 (d, *J*<sub>HH</sub> = 7.7 Hz, 1H, H<sub>Ar</sub>), 5.08 (m, 2H, NCH<sub>2</sub>), 3.93 (m, 2H, PCH<sub>2</sub>), 2.46 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 25 °C): δ = 150.3 (s, C<sub>Ph</sub>), 136.2 (s, N<sub>2</sub>CH), 135.3 (d, *J*<sub>CP</sub> = 3.0 Hz, CH<sub>Ph</sub>), 134.0 (d, *J*<sub>CP</sub> = 10.6 Hz, CH<sub>Ph</sub>), 131.3 (s, CH<sub>Ph</sub>), 130.7 (d, *J*<sub>CP</sub> = 12.8 Hz, CH<sub>Ph</sub>), 125.0 (s, CH<sub>Ph</sub>), 123.2 (s, CH<sub>Ph</sub>), 123.0 (s, CH<sub>Ph</sub>), 122.2 (s, C<sub>Ph</sub>), 120.6 (s, CH<sub>Im</sub>), 118.9 (s, CH<sub>Im</sub>), 117.6 (d, *J*<sub>CP</sub> = 86.8 Hz, C<sub>Ph</sub>), 49.0 (d, *J*<sub>CP</sub> = 21.1 Hz, NCH<sub>2</sub>), 24.9 (d, *J*<sub>CP</sub> = 3.0 Hz, CH<sub>2</sub>), 20.2 (d, *J*<sub>CP</sub> = 54.4 Hz, PCH<sub>2</sub>); MS (ES<sup>+</sup>): *m/z*: 543.1 [M – Br]<sup>+</sup>; HRMS (ES<sup>+</sup>): calcd for C<sub>30</sub>H<sub>29</sub>N<sub>2</sub>OPdBr, 543.1201; found, 543.1205; elemental analysis for C<sub>30</sub>H<sub>29</sub>Br<sub>2</sub>N<sub>2</sub>OP.H<sub>2</sub>O: calcd, C 56.09, H 4.86, N 4.36; found, C 56.0, H 4.66, N 4.72.

### Synthesis of pre-ligand [7](OTf)<sub>2</sub>

[7]Br<sub>2</sub> (0.97 g, 1.56 mmol) and sodium trifluoromethanesulfonate (0.67 g, 3.90 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (60 mL) and the solution was stirred at room temperature for 12 hours. After evaporation of the solvent, the crude residue was washed with water (30 mL). The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 30 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, [7](OTf)<sub>2</sub> was obtained as a white powder (1.19 g, 95%). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>, 25 °C): δ = 23.9 (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ = 9.20 (s, 1H, N<sub>2</sub>CH), 7.78–7.68 (m, 17H, H<sub>Ar</sub>), 7.41 (brs, 1H, H<sub>Ar</sub>), 7.27 (m, 1H, H<sub>Ar</sub>), 7.21–7.15 (m, 2H, H<sub>Ar</sub>), 6.83 (t, *J*<sub>HH</sub> = 7.7 Hz, 1H, H<sub>Ar</sub>), 4.66 (m, 2H, NCH<sub>2</sub>), 3.50 (m, 2H, PCH<sub>2</sub>), 2.30 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, 25 °C): δ = 151.2 (s, C<sub>Ph</sub>), 136.0 (s, N<sub>2</sub>CH), 135.4 (d, *J*<sub>CP</sub> = 3.0 Hz, CH<sub>Ph</sub>), 133.7 (d, *J*<sub>CP</sub> = 10.6 Hz, CH<sub>Ph</sub>), 131.6 (s, CH<sub>Ph</sub>), 130.7 (d, *J*<sub>CP</sub> = 12.8 Hz, CH<sub>Ph</sub>), 124.6 (s, CH<sub>Ph</sub>), 123.5 (s, CH<sub>Ph</sub>), 122.5 (s, CH<sub>Ph</sub>), 122.3 (s, C<sub>Ph</sub>), 120.6 (q, *J*<sub>CP</sub>

= 319.9 Hz, CF<sub>3</sub>), 119.9 (s, CH<sub>Im</sub>), 118.7 (s, CH<sub>Im</sub>), 117.4 (d,  $J_{CP}$  = 86.8 Hz, C<sub>Ph</sub>), 49.1 (d,  $J_{CP}$  = 21.1 Hz, NCH<sub>2</sub>), 24.4 (d,  $J_{CP}$  = 3.0 Hz, CH<sub>2</sub>), 19.6 (d,  $J_{CP}$  = 54.4 Hz, PCH<sub>2</sub>); MS (ES<sup>+</sup>):  $m/z$ : 613.2 [M - CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>; elemental analysis for C<sub>30</sub>H<sub>29</sub>F<sub>6</sub>N<sub>2</sub>O<sub>7</sub>PS<sub>2</sub>: calcd, C 50.40, H 3.83, N 3.67; found, C 51.08, H 3.72, N 3.94.

### Synthesis of complex [8](OTf)

A mixture of [7](OTf)<sub>2</sub> (0.20 g, 0.26 mmol), PdCl<sub>2</sub> (0.05 g, 0.26 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (0.11 g, 0.78 mmol), and pyridine (63.3 μL, 0.78 mmol) was stirred at room temperature in CH<sub>3</sub>CN (30 mL) for 12 hours. After filtration over Celite and evaporation of the solvent under vacuum, complexes [8](OTf) and [9](OTf)<sub>2</sub> were obtained as a pale yellow powder (ratio [8](OTf)/[9](OTf)<sub>2</sub>: 9/1). After recrystallization from CH<sub>3</sub>CN/Et<sub>2</sub>O at -20 °C, [8](OTf) was isolated in a pure form as pale yellow crystals suitable for X-ray diffraction (0.16 g, 75%). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>3</sub>CN, 25 °C): δ = 23.6 (s); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C) δ = 8.90–8.82 (m, 2H, H<sub>Py</sub>), 7.99 (tt,  $J_{HH}$  = 7.6, 1.7 Hz, 1H, H<sub>Py</sub>), 7.83–7.69 (m, 9H, H<sub>Ar</sub>), 7.66–7.60 (m, 7H, H<sub>Ar</sub>), 7.58–7.51 (m, 2H, H<sub>Py</sub>), 7.41 (d,  $J_{HH}$  = 8.2 Hz, 1H, H<sub>Ar</sub>), 7.31 (d,  $J_{HH}$  = 2.1 Hz, 1H, H<sub>Ar</sub>), 7.09 (t,  $J_{HH}$  = 7.4 Hz, 1H, H<sub>Ar</sub>), 7.00 (d,  $J_{HH}$  = 8.2 Hz, 1H, H<sub>Ar</sub>), 6.75 (t,  $J_{HH}$  = 7.7 Hz, 1H, H<sub>Ar</sub>), 4.77 (t,  $J_{HH}$  = 7.1 Hz, 2H, NCH<sub>2</sub>), 3.59–3.43 (m, 2H, PCH<sub>2</sub>), 2.55–2.38 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>CN, 25 °C): δ = 159.4 (s, N<sub>2</sub>C), 150.4 (s, CH<sub>Py</sub>), 148.6 (s, C<sub>Ph</sub>), 140.1 (s, CH<sub>Py</sub>), 136.1 (d,  $J_{CP}$  = 3.0 Hz, CH<sub>Ph</sub>), 134.7 (d,  $J_{CP}$  = 10.6 Hz, CH<sub>Ph</sub>), 132.0 (s, C<sub>Ph</sub>), 131.2 (d,  $J_{CP}$  = 12.8 Hz, CH<sub>Ph</sub>), 129.3 (s, CH<sub>Ph</sub>), 126.1 (s, CH<sub>Ph</sub>), 125.9 (s, CH<sub>Py</sub>), 121.3 (s, CH<sub>Ph</sub>), 120.8 (s, CH<sub>Ph</sub>), 120.7 (q,  $J_{CF}$  = 319.9 Hz, CF<sub>3</sub>), 120.3 (s, CH<sub>Im</sub>), 118.9 (d,  $J_{CP}$  = 86.8 Hz, C<sub>Ph</sub>), 117.0 (s, CH<sub>Im</sub>), 50.6 (d,  $J_{CP}$  = 21.1 Hz, NCH<sub>2</sub>), 25.4 (d,  $J_{CP}$  = 3.0 Hz, CH<sub>2</sub>), 20.4 (d,  $J_{CP}$  = 54.4 Hz, PCH<sub>2</sub>); MS (ES<sup>+</sup>):  $m/z$ : 684.1 [M - CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>; elemental analysis for C<sub>36</sub>H<sub>32</sub>ClF<sub>3</sub>N<sub>3</sub>O<sub>4</sub>PPdS.H<sub>2</sub>O: calcd, C 50.84, H 4.03, N 4.94; found, C 50.59, H 3.75, N 4.77.

### Synthesis of complex [9](OTf)<sub>2</sub>

A mixture of [7](OTf)<sub>2</sub> (0.10 g, 0.13 mmol), PdCl<sub>2</sub> (0.011 g, 0.065 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (0.054 g, 0.39 mmol) was stirred at room temperature in CH<sub>3</sub>CN (10 mL) for 12 hours. After filtration over Celite and evaporation of the solvent under vacuum, [9](OTf)<sub>2</sub> was obtained as a pale yellow powder (0.16 g, 92%). Recrystallization from CH<sub>3</sub>CN/Et<sub>2</sub>O at room temperature gave pale yellow crystals suitable for X-ray diffraction. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>3</sub>CN, 25 °C): δ = 23.4 (s); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 25 °C) δ = 7.79–7.71 (m, 6H, H<sub>Ar</sub>), 7.60–7.45 (m, 26H, H<sub>Ar</sub>), 7.33–7.29 (m, 4H, H<sub>Ar</sub>), 6.96 (t,  $J_{HH}$  = 7.4 Hz, 2H, H<sub>Ar</sub>), 6.86 (d,  $J_{HH}$  = 8.2 Hz, 2H, H<sub>Ar</sub>), 6.65 (t,  $J_{HH}$  = 7.7 Hz, 2H, H<sub>Ar</sub>), 4.82 (t,  $J_{HH}$  = 7.1 Hz, 4H, NCH<sub>2</sub>), 3.43–3.31 (m, 4H,

PCH<sub>2</sub>), 2.40–2.27 (m, 4H, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>CN, 25 °C): δ = 164.4 (s, N<sub>2</sub>C), 159.0 (s, C<sub>Ph</sub>), 136.0 (d, J<sub>CP</sub> = 3.0 Hz, CH<sub>Ph</sub>), 134.5 (d, J<sub>CP</sub> = 10.6 Hz, CH<sub>Ph</sub>), 131.2 (d, J<sub>CP</sub> = 12.8 Hz, CH<sub>Ph</sub>), 130.9 (s, C<sub>Ph</sub>), 128.6 (s, CH<sub>Ph</sub>), 125.3 (s, CH<sub>Ph</sub>), 121.7 (s, CH<sub>Ph</sub>), 121.4 (s, CH<sub>Ph</sub>), 118.5 (d, J<sub>CP</sub> = 86.8 Hz, C<sub>Ph</sub>), 118.3 (s, CH<sub>Im</sub>), 116.4 (s, CH<sub>Im</sub>), 49.0 (d, J<sub>CP</sub> = 21.1 Hz, NCH<sub>2</sub>), 25.6 (d, J<sub>CP</sub> = 3.0 Hz, CH<sub>2</sub>), 20.6 (d, J<sub>CP</sub> = 54.4 Hz, PCH<sub>2</sub>); MS (ES<sup>+</sup>): m/z: 1179.2 [M – CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>; HRMS (ES<sup>+</sup>): calcd for C<sub>61</sub>H<sub>54</sub>F<sub>3</sub>N<sub>4</sub>O<sub>5</sub>P<sub>2</sub>PdS, 1179.2297; found, 1179.2296.

### Synthesis of complex **10**

1<sup>st</sup> method: [**8**](OTf) (0.04 g, 0.048 mmol) and anhydrous Cs<sub>2</sub>CO<sub>3</sub> (0.078 g, 0.24 mmol) were dissolved in CH<sub>3</sub>CN (15 mL), and the suspension was stirred at 70 °C for 12 hours. After filtration over Celite, the solvent was evaporated under vacuum. The crude residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and the solution was filtered over Celite. After evaporation of the solvent, **10** was obtained as a pale yellow powder (0.023 g, 85%).

2<sup>nd</sup> method: A mixture of [**7**](OTf)<sub>2</sub> (0.30 g, 0.39 mmol), PdCl<sub>2</sub> (0.07 g, 0.39 mmol), and anhydrous Cs<sub>2</sub>CO<sub>3</sub> (0.63 g, 1.96 mmol) was stirred at 90 °C in CH<sub>3</sub>CN (30 mL) for 12 hours. After filtration over Celite and evaporation of the solvent under vacuum, the crude residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and the solution was filtered over Celite. After evaporation of the solvent, **10** was obtained as a pale yellow powder (0.19 g, 84%). Recrystallization from a saturated CH<sub>3</sub>CN solution at room temperature gave **10** as pale yellow crystals suitable for X-ray diffraction. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ = 33.8 (s); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C) δ = 8.27 (brd, J<sub>HH</sub> = 8.2 Hz, 1H, H<sub>Ar</sub>), 7.75–7.50 (m, 10H, H<sub>Ar</sub>), 7.45–7.35 (m, 4H, H<sub>Ar</sub>), 7.25 (brd, J<sub>HH</sub> = 8.2 Hz, 1H, H<sub>Ar</sub>), 7.08 (brt, J<sub>HH</sub> = 7.4 Hz, 1H, H<sub>Ar</sub>), 7.02 (brt, J<sub>HH</sub> = 7.4 Hz, 1H, H<sub>Ar</sub>), 6.94 (brs, 1H, H<sub>Ar</sub>), 6.44 (brt, J<sub>HH</sub> = 7.7 Hz, 1H, H<sub>Ar</sub>), 4.10–4.05 (m, 2H, NCH<sub>2</sub>), 3.21–3.14 (m, 1H, PCH), 2.25–2.19 (m, 1H, CH<sub>2</sub>), 2.00–1.89 (m, 1H, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CD<sub>3</sub>CN, 25 °C): δ = 182.2 (d, J<sub>CP</sub> = 37.2 Hz, C<sub>Ph-ortho</sub>), 176.2 (d, J<sub>CP</sub> = 7.0 Hz, C<sub>Ph</sub>), 160.3 (s, N<sub>2</sub>C), 150.7 (s, CH<sub>Ph</sub>), 137.1 (d, J<sub>CP</sub> = 119.7 Hz, C<sub>Ph-ipso</sub>), 136.3 (d, J<sub>CP</sub> = 19.1 Hz, CH<sub>Ph</sub>), 135.0 (d, J<sub>CP</sub> = 9.0 Hz, CH<sub>Ph</sub>), 134.4 (d, J<sub>CP</sub> = 10.1 Hz, CH<sub>Ph</sub>), 133.8 (d, J<sub>CP</sub> = 3.0 Hz, CH<sub>Ph</sub>), 133.7 (d, J<sub>CP</sub> = 8.0 Hz, CH<sub>Ph</sub>), 133.4 (d, J<sub>CP</sub> = 3.0 Hz, CH<sub>Ph</sub>), 131.4 (d, J<sub>CP</sub> = 13.1 Hz, CH<sub>Ph</sub>), 130.5 (d, J<sub>CP</sub> = 10.1 Hz, CH<sub>Ph</sub>), 130.1 (d, J<sub>CP</sub> = 3.0 Hz, CH<sub>Ph</sub>), 129.8 (d, J<sub>CP</sub> = 20.1 Hz, CH<sub>Ph</sub>), 129.7 (d, J<sub>CP</sub> = 11.1 Hz, CH<sub>Ph</sub>), 128.3 (s, C<sub>Ph</sub>), 127.7 (s, CH<sub>Ph</sub>), 127.4 (d, J<sub>CP</sub> = 85.5 Hz, C<sub>Ph</sub>), 127.0 (d, J<sub>CP</sub> = 54.3 Hz, C<sub>Ph</sub>), 125.5 (d, J<sub>CP</sub> = 10.1 Hz, CH<sub>Ph</sub>), 124.8 (brs, CH<sub>Ph</sub>), 124.2 (s, CH<sub>Ph</sub>), 122.4 (s, CH<sub>Ph</sub>), 122.1 (q, J<sub>CF</sub> = 319.9 Hz, CF<sub>3</sub>), 120.4 (s, CH<sub>Ph</sub>), 116.7 (s, CH<sub>Im</sub>), 112.8 (s, CH<sub>Im</sub>), 52.7 (d, J<sub>CP</sub> = 22.1 Hz, NCH<sub>2</sub>), 27.4 (s, CH<sub>2</sub>), 13.8 (d, J<sub>CP</sub> = 40.2 Hz, PCH); MS (ES<sup>+</sup>): m/z: 567.1 [MH<sup>+</sup>]; HRMS (ES<sup>+</sup>): calcd for C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>OPPd,

567.0829; found, 567.0833. elemental analysis for  $C_{30}H_{25}N_2OPPd \cdot 1.2CH_2Cl_2$ : calcd, C 56.03, H 4.13, N 4.19; found, C 55.55, H 3.94, N 4.77.

### Synthesis of complex [11a](OTf)

TfOH (0.5 M in  $CH_3CN$ , 158  $\mu L$ , 0.079 mmol) was added at  $-40^\circ C$  to a solution of complex **10** (0.045 g, 0.079 mmol) in  $CH_3CN$  (10 mL). The mixture was warmed to room temperature for 2 hours. After filtration over Celite, the solvent was removed under vacuum, and complex [11a](OTf) was obtained as a pale yellow powder (0.056 g, 94%).  $^{31}P\{^1H\}$  NMR (162 MHz,  $CD_3CN$ ,  $25^\circ C$ ):  $\delta = 29.0$  (s);  $^1H$  NMR (400 MHz,  $CD_3CN$ ,  $25^\circ C$ )  $\delta = 7.85$ – $7.80$  (m, 5H,  $H_{Ar}$ ), 7.67–7.63 (m, 3H,  $H_{Ar}$ ), 7.51–7.43 (m, 8H,  $H_{Ar}$ ), 7.33 (d,  $J_{HH} = 8.2$  Hz, 1H,  $H_{Ar}$ ), 7.05 (t,  $J_{HH} = 7.4$  Hz, 1H,  $H_{Ar}$ ), 6.93 (brs, 1H,  $H_{Ar}$ ), 6.76 (d,  $J_{HH} = 8.2$ , Hz, 1H,  $H_{Ar}$ ), 6.62 (t,  $J_{HH} = 7.7$  Hz, 1H,  $H_{Ar}$ ), 4.02–3.95 (m, 1H,  $NCH_2$ ), 3.84–3.78 (m, 1H,  $NCH_2$ ), 3.73–3.68 (m, 1H, PCH), 2.60–2.50 (m, 1H,  $CH_2$ ), 2.15–2.05 (m, 1H,  $CH_2$ );  $^{13}C\{^1H\}$  NMR (101 MHz,  $CD_3CN$ ,  $25^\circ C$ ):  $\delta = 158.8$  (s,  $N_2C$ ), 152.4 (s,  $C_{Ph}$ ), 134.7 (d,  $J_{CP} = 10.6$  Hz,  $CH_{Ph}$ ), 134.5 (d,  $J_{CP} = 3.0$  Hz,  $CH_{Ph}$ ), 130.3 (d,  $J_{CP} = 12.8$  Hz,  $CH_{Ph}$ ), 128.9 (s,  $CH_{Ph}$ ), 127.8 (s,  $C_{Ph}$ ), 123.8 (d,  $J_{CP} = 86.8$  Hz,  $C_{Ph}$ ), 123.3 (s,  $CH_{Ph}$ ), 122.7 (q,  $J_{CF} = 320.9$  Hz,  $CF_3$ ), 121.8 (s,  $CH_{Ph}$ ), 121.0 (s,  $CH_{Ph}$ ), 119.3 (s,  $CH_{Im}$ ), 114.8 (s,  $CH_{Im}$ ), 50.9 (d,  $J_{CP} = 21.1$  Hz,  $NCH_2$ ), 26.7 (s,  $CH_2$ ), 5.7 (d,  $J_{CP} = 32.2$  Hz, PCH); MS ( $ES^+$ ):  $m/z$ : 567.1 [ $M - CH_3CN - CF_3SO_3$ ] $^+$ ; HRMS ( $ES^+$ ): calcd for  $C_{30}H_{26}N_2OPPd$ , 567.0829; found, 567.0859.

### Synthesis of complex [11b](OTf)

*t*-butyl isocyanide (6.87  $\mu L$ , 0.059 mmol) was added at  $-78^\circ C$  to a solution of complex [11a](OTf) (0.03 g, 0.039 mmol) in  $CH_2Cl_2$  (10 mL). The mixture was warmed to room temperature for 2 hours. After filtration over Celite, the solvent was removed under vacuum, and complex [11b](OTf) was obtained as a pale yellow powder (0.03 g, 95 %).  $^{31}P\{^1H\}$  NMR (162 MHz,  $CD_2Cl_2$ ,  $25^\circ C$ ):  $\delta = 31.8$  (s);  $^1H$  NMR (400 MHz,  $CD_2Cl_2$ ,  $25^\circ C$ )  $\delta = 7.89$ – $7.84$  (m, 5H,  $H_{Ar}$ ), 7.72–7.68 (m, 5H,  $H_{Ar}$ ), 7.58–7.54 (m, 5H,  $H_{Ar}$ ), 7.47 (brs, 1H,  $H_{Ar}$ ), 7.28–7.25 (m, 1H,  $H_{Ar}$ ), 7.13–7.09 (m, 1H,  $H_{Ar}$ ), 7.05 (brs, 1H,  $H_{Ar}$ ), 6.90 (d,  $J = 8.2$ , Hz, 1H,  $H_{Ar}$ ), 6.65 (t,  $J_{HH} = 7.7$  Hz, 1H,  $H_{Ar}$ ), 4.09–4.05 (m, 2H,  $NCH_2$ ), 3.36–3.29 (m, 1H, PCH), 2.38–2.30 (m, 1H,  $CH_2$ ), 1.57–1.41 (m, 1H,  $CH_2$ ), 1.18 (s, 9H, *t*Bu);  $^{13}C\{^1H\}$  NMR (101 MHz,  $CD_2Cl_2$ ,  $25^\circ C$ ):  $\delta = 158.2$  (s,  $N_2C$ ), 158.0 (s,  $C_{Ph}$ ), 134.5 (d,  $J_{CP} = 3.0$  Hz,  $CH_{Ph}$ ), 134.3 (d,  $J_{CP} = 10.6$  Hz,  $CH_{Ph}$ ), 130.3 (d,  $J_{CP} = 12.8$  Hz,  $CH_{Ph}$ ), 128.4 (s,  $CH_{Ph}$ ), 125.0 (s,  $C_{Ph}$ ), 123.2 (d,  $J_{CP} = 82.5$  Hz,  $C_{Ph}$ ), 122.7 (s,  $CH_{Ph}$ ), 122.4 (s,  $CH_{Ph}$ ), 121.3 (q,  $J_{CF} = 320.9$  Hz,  $CF_3$ ), 120.2 (s,  $CH_{Ph}$ ), 118.7 (s,  $CH_{Im}$ ), 114.8 (s,  $CH_{Im}$ ), 58.4 (s,  $C(CH_3)_3$ ), 51.0 (d,  $J_{CP} = 21.1$  Hz,  $NCH_2$ ), 30.0 (s,  $CH_3$ ), 27.0 (s,  $CH_2$ ), 3.3 (d,  $J_{CP} = 32.7$  Hz, PCH); MS ( $ES^+$ ):  $m/z$ : 567.1 [ $M - tBuNC$

– CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>; HRMS (ES<sup>+</sup>): calcd for C<sub>30</sub>H<sub>26</sub>N<sub>2</sub>OPPd, 567.0829; found, 567.0842. \* The <sup>13</sup>C NMR resonance of the CN quaternary carbon atom of coordinated *t*-BuNC was not observed.

**Palladium-Catalyzed Allylation of Aldehydes by Pincer Complexes:** Representative procedure for the allylation of benzaldehyde with allyltributyltin in the presence of palladium complex [12a](OTf)<sub>2</sub>.

To a mixture of benzaldehyde (27 mg, 26 μl, 0.25 mmol) and Pd complex [12a](OTf)<sub>2</sub> (14 mg, 0.0127 mmol, 5.0 mol %) in DMF (0.6 mL) was added allyltributyltin (94 μl, 0.30 mmol) under nitrogen. The solution was stirred at 60 °C for 18 hours. The reaction mixture was then quenched with water and the product was extracted with diethyl ether (3 x 5 mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude residue was purified by chromatography on silica gel with pentane/EtOAc (9/1 to 8/2) to afford the homoallylic alcohol as colorless oil (28 mg, 75%). The <sup>1</sup>H and <sup>13</sup>C NMR data obtained are in agreement with the corresponding literature.<sup>37</sup>

### Single-crystal X-ray diffraction analyses

Intensity data of [4](OTf), [7]Br<sub>2</sub>, [8](OTf), [9](OTf)<sub>2</sub>, and **10** were collected at low temperature on an Apex2 Bruker equipped with a 30W air-cooled microfocus Mo source (λ = 0.71073 Å). The structures were solved using SUPERFLIP,<sup>38</sup> and refined by means of least-squares procedures using CRYSTALS.<sup>39</sup> Atomic scattering factors were taken from the international tables for X-ray crystallography. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using a riding model. Absorption corrections were introduced using the program MULTISCAN.<sup>40</sup>

### Electrochemistry data

Voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100 on Pd complexes [4a](OTf), [5a](OTf)<sub>2</sub>, **10**, and [11a](OTf). Experiments were performed at room temperature in an homemade airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of *ca* 1 cm<sup>2</sup> apparent surface. The working electrode was a Pt microdisk (0.5 mm diameter). Voltammograms were recorded in dry CH<sub>3</sub>CN solution (≈ 10<sup>-3</sup> M) in the presence of 0.1 M *n*-tetrabutylammonium triflate as the supporting electrolyte, under nitrogen at 25 °C. In reference 14, the value of +2.00 V given for the oxidation of complex [12a](OTf)<sub>2</sub> corresponds to its second oxidation potential.

## Computational details

Geometries were fully optimized at the PBE-D3/6-31G\*\*/LANL2DZ\* (Pd) level of calculation using Gaussian 09.<sup>41</sup> The star in LANL2DZ\*(Pd) refers to *f*-polarization functions derived by Ehlers *et al.*<sup>42</sup> for Pd, that have been added to the LANL2DZ(Pd) basis set. Vibrational analysis was performed at the same level as the geometry optimization in order to check the obtention of a minimum on the potential energy surface. Gibbs free energies were calculated at 298.15 K. Electron Localization Function (ELF) analysis and Quantum Theory of Atoms in Molecules (QTAIM)<sup>43</sup> topological analyses were performed with the TopMoD package.<sup>44</sup> The topological analysis of the electron density yields a partition of the molecular space into atomic basins. The topological analysis of the ELF gradient field yields a partition of the molecular space into non-overlapping electronic domains, classified into core, valence bonding and nonbonding basins.<sup>45-48</sup> These basins are in one-to-one correspondence to the core, lone or shared pairs of the Lewis model. A core basin contains a nucleus X (except a proton) and is designated as C(X). A valence bonding basin referred to as V(X,Y, ..) lies between two or more core basins. Among chemical reactivity descriptors of the “conceptual DFT”, Fukui functions are suitable for probing soft sites of reactants that are involved in orbital-controlled interactions with electrophiles, nucleophiles or radicals. The Fukui function was introduced by Parr and Yang as the response of the electron density of the molecular system to a change in the global number of electrons.<sup>49</sup> It can be expressed as the derivative of the electron density  $\rho(r)$  with respect to the number of electrons N, calculated at a constant external potential  $v(r)$ .

In this work, frontier molecular orbital (FMO) Fukui functions (in which the electron density is approximated by densities of the FMOs) condensed within QTAIM<sup>50</sup> or ELF<sup>51</sup> topological partitions have been used.  $f_X^\square(r) = \int_X |\square_{KS}^F(r)|^2 dr$  is therefore the contribution of the FMO F ( $\square = -$  : F = HOMO ;  $\square = +$  : F = LUMO) to the atomic QTAIM basin or to the core or valence ELF basin X. These Fukui indices are confined into the 0-1 range and they sum up to one:  $0 \leq f_X^\square \leq 1$  et  $\sum_X f_X^\square = 1$ . The larger the value of the *f* index, the more reactive the corresponding basin X.

## Supporting Information

The supporting Information of this article can be found under <https://...>

- <sup>31</sup>P, <sup>1</sup>H and <sup>13</sup>C NMR spectra for all new compounds,
- Crystallographic table for [4](OTf), [7]Br<sub>2</sub>, [8](OTf), [9](OTf)<sub>2</sub>, and 10,
- Optimized structures of pincer Pd complexes 7<sup>2+</sup>, 11<sup>+</sup>, 12<sup>2+</sup> and 13<sup>+</sup>.

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## Notes

The authors declare no competing financial interests

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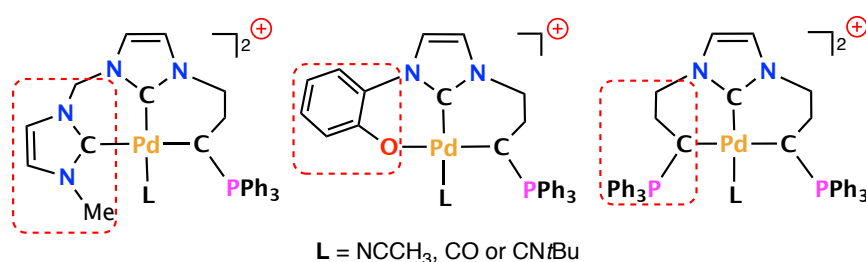
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The coordinating properties and catalytic performances of NHC, phenolate and phosphonium ylide donor moieties are evaluated through the preparation of an isostructural family of NHC core, phosphonium ylide-based palladium(II) pincer complexes.