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# Diverse C-Coordination modes of NHC-Tricyclohexylphosphonium Ylide Ligands in Palladium(II) Complexes

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**ABSTRACT:** Thanks to the  $^+PCy_3$  substituents unlikely to undergo intramolecular C–H activation, a Pd(II) complex  $[(C,C,C)PdCl](OTf)$  exhibiting the neutral  $LX_2$ -type NHC, diphosphonium bis(ylide) pincer ligand was selectively prepared by a double deprotonation of the  $[(NHC)PdCl_2(Py)]$  precursor with *t*BuOK. The influence on the  $^+PCy_3$  substituents on the overall electronic properties of this pincer scaffold was evaluated by IR spectroscopy data of the corresponding Pd–CO adduct revealing its stronger electron-donating character compared to the structurally related NHC core pincer bearing  $^+PPh_3$  extremities. Treatment of the electron-rich pincer complex  $[(C,C,C)PdCl](OTf)$  with AgOTf led to the C,C-chelating NHC-phosphonium ylide Pd(II) complex  $[(C,C)Pd(OTf)Cl](OTf)$  via the oxidatively induced homolytic cleavage of a Pd–ylide bond. In the presence of stronger base (KHMDS or LDA) cyclometalation of a  $^+P-Cy$  substituent was observed affording a constraint Pd(II) complex featuring the unique anionic  $LX_3$ -type C,C,C-C-NHC, diphosphonium tris(ylide) ligand.

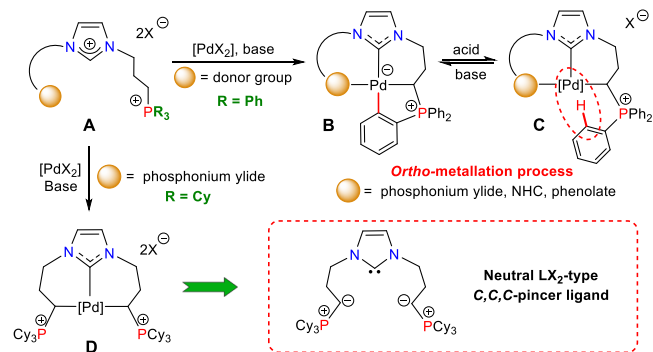
## INTRODUCTION

Beyond its essential role in the field of organic chemistry, carbon is also a major actor in coordination chemistry.<sup>1</sup> Considering carbon as a coordinating element, two distinct cases are to be distinguished depending on whether the C-donor is of anionic or neutral nature with alkyl/aryl groups and carbenes behaving as respective prototypes of these two categories of carbon ligands.<sup>2</sup> In search of phosphine mimics for catalytic purposes, C-centered ligands were more recently considered demonstrating over time their enormous potential in this field, especially since the advent of NHC ligands.<sup>3</sup> Chelating systems exhibiting only carbon extremities of neutral nature remain fairly limited, being mainly constituted of poly-NHC<sup>4</sup> and to a much lesser extend of bis-ylide ligands.<sup>2,5</sup> The association between NHCs and phosphonium ylides, both acting as strongly  $\sigma$ -donating and weakly  $\pi$ -accepting neutral ligands, is an integral part of this area of interest as illustrated by the development over the past two decades of various architectures combining these two carbon fragments,<sup>6</sup> the ylide possibly being a carbene substituent<sup>7</sup> or located in remote position from the carbene to minimize electronic and steric interactions.<sup>8</sup>

In accordance with the second scenario, chelating NHC-triphenylphosphonium ylide ligands featuring an insulating C<sub>3</sub> propyl spacer were recently devised in the bi-,<sup>9</sup> tri-<sup>10</sup> and tetradentate<sup>11</sup> series and coordinated to various Pd(II) centers. In the pincer series, the electron-rich character of the ligand was found to be beneficial for the stabilization of Pd–CO adducts<sup>10a,10d</sup> and the Pd-catalyzed allylation of aldehydes.<sup>10b</sup> While in the synthesis of bi- and tetradentate NHC-ylide derivatives no C–H bond activation process was observed,<sup>9,11</sup> in the pincer series (Scheme 1, *top*) the meridional tridentate coordination mode which leaves an open site was shown to favor via the base assisted  $Csp^2$ -H bond activation of a

$^+P-C_6H_5$  substituent the formation of *ortho*-metalated Pd(II) complexes **B** from *N*-phosphonio-substituted imidazolium salts **A**.<sup>10</sup> To obtain NHC core phosphonium ylide-based pincer Pd(II) complexes of type **C** in a pure form, an additional step was thus required consisting in the acidic cleavage of the C<sub>aryl</sub>-Pd bond of *ortho*-metalated Pd(II) complexes **B**, this process being totally reversible under basic conditions (Scheme 1, *top*).<sup>10</sup> With the aim to overcome this reactivity, we are now considering the introduction of  $^+PCy_3$  extremities which should lead to NHC-phosphonium ylide pincer complexes of type **D** possessing *a priori* increased electron density at the metal center and being more resistant to any C–H activation process (Scheme 1, *bottom*).

**Scheme 1. Known Route to NHC Core, Phosphonium Ylide-Based Pincer Pd(II) Complexes C (R = Ph) via *ortho*-Metalated Species B (R = Ph) and Targeted NHC Core, Diphosphonium Bis(Ylide) Pincer Pd(II) Complexes D (R = Cy).**



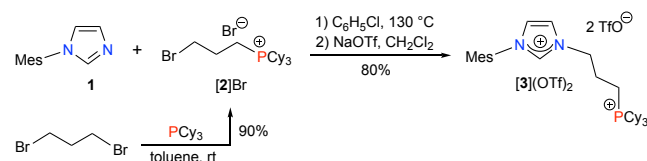
Indeed, cyclohexyl substituents characterizing by a strong inductive effect are expected to decrease the degree of positive charge on phosphorus atom and thus enhance the donor prop-

erties of the *C*-ylidic center. This effect was not well documented in literature certainly due to the lower availability of trialkylphosphines compared to their triarylated analogues, the lack of synthetic methods and the supposed instability of trialkylphosphonium ylide complexes. These limitations resulted in a small number of such metal complexes as illustrated with the few examples of structurally characterized representatives based on trisopropyl-<sup>12</sup> and tricyclohexylphosphonium ylide ligands.<sup>13</sup> It is worth mentioning that there has been recently a growing craze in tricyclohexylphosphonium ylides<sup>14</sup> as strongly donating substituents of phosphine ligands for the development of highly active Pd(II) catalysts.<sup>15</sup> In this general context and considering our persistent interest for the design of new carbon-based ligand platforms, we describe herein the preparation of *C,C,C*-NHC core, diphosphonium bis(ylide) Pd(II) pincer complexes of type **D** from the readily available *N*-tricyclohexylphosphonio-substituted imidazolium salt **A** (Scheme 1).

## RESULTS AND DISCUSSION

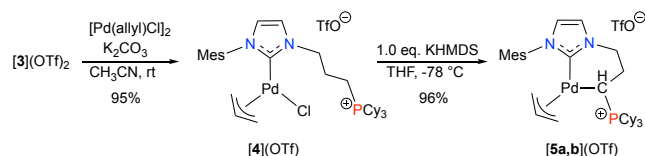
**Synthesis and Spectroscopic Characterization of a *C,C*-NHC, Tricyclohexylphosphonium Ylide Pd(II) Complex [5a,b](OTf).** Before evaluating the influence of the <sup>+</sup>PCy<sub>3</sub> extremities on the stability of phosphonium ylide-based pincer complexes, the role of this cationic fragment was first investigated in the bidentate series. For this purpose, 1-mesitylimidazole **1** was reacted with (3-bromopropyl)tricyclohexylphosphonium bromide [2]Br prepared in 90% yield from 1,3-dibromopropane and PCy<sub>3</sub> (Scheme 2). After heating the reaction at 130 °C in C<sub>6</sub>H<sub>5</sub>Cl followed by an anion metathesis reaction with NaOTf in CH<sub>2</sub>Cl<sub>2</sub>, the *N*-<sup>+</sup>PCy<sub>3</sub>-substituted imidazolium salt [3](OTf)<sub>2</sub> was isolated in 80% overall yield. The structure of [3](OTf)<sub>2</sub> was confirmed by the presence of characteristic single <sup>1</sup>H and <sup>31</sup>P NMR resonances at δ<sub>H</sub> 9.20 ppm and δ<sub>P</sub> 31.8 ppm for the N<sub>2</sub>CH imidazolium and the <sup>+</sup>PCy<sub>3</sub> moiety, respectively.

**Scheme 2. Synthesis of *N*-[(CH<sub>2</sub>)<sub>3</sub>PCy<sub>3</sub>]<sup>+</sup> Substituted Imidazolium Salt [3](OTf)<sub>2</sub> from 1-Mesitylimidazole **1**.**



Expecting a significant difference of *pK*<sub>a</sub> values between the imidazolium and phosphonium moieties, greater than that observed in the related Im(CH<sub>2</sub>)<sub>3</sub><sup>+</sup>PPh<sub>3</sub> series,<sup>9</sup> a sequential strategy to coordinate the two carbon donors was selected. Thus, [3](OTf)<sub>2</sub> was treated with an excess of K<sub>2</sub>CO<sub>3</sub> in the presence of 0.5 equiv. [PdCl(allyl)]<sub>2</sub> in CH<sub>3</sub>CN at room temperature (Scheme 3). Following these conditions, the [(NHC)PdCl(allyl)] complex [4](OTf) featuring a pending <sup>+</sup>PCy<sub>3</sub> chain was isolated in 95% yield. The selective coordination of the carbene center was assessed by <sup>1</sup>H NMR spectroscopy through the disappearance of the N<sub>2</sub>CH imidazolium fragment and the presence of a single phosphonium resonance at δ<sub>P</sub> 32.8 ppm in the <sup>31</sup>P NMR spectrum. The structure of this compound was confirmed by X-ray diffraction (*vide infra*). In order to coordinate the <sup>+</sup>PCy<sub>3</sub> extremity, complex [4](OTf) was then treated with one equiv. of a strong base such as KHMDS in THF. The targeted *C,C*-chelating Pd(II) complex [5a,b](OTf) was thus isolated in 96% yield as a mixture

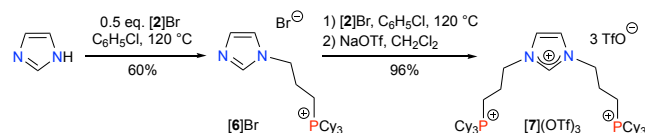
**Scheme 3. Access to Cationic NHC Pd(II) Complexes [4](OTf) and [5a,b](OTf) with Pendant and Coordinated <sup>+</sup>PCy<sub>3</sub> Chain, Respectively.**



(55/45) of two diastereomers originating for the presence of the stereogenic ylidic center and the slow flip of the  $\pi$ -allyl coligand (Scheme 3). Remarkably, complex [5a,b](OTf) was found to be stable for weeks at room temperature in solid state and in solution under a nitrogen atmosphere.<sup>8a,9</sup> It is also likely that the strongly chelating  $\pi$ -allyl ligand prevented any C–H bond activation of a <sup>+</sup>P–Cy substituent during the synthesis of [5a,b](OTf) despite the use of basic conditions. The <sup>31</sup>P NMR spectrum of [5a,b](OTf) displayed characteristic lower field resonances (major: δ<sub>P</sub> 39.2 ppm; minor: δ<sub>P</sub> 40.1 ppm) compared to that of the precursor [4](OTf) (δ<sub>P</sub> 32.8 ppm) in agreement with the formation of a Pd–ylide bond. The CH ylide moiety was also unveiled by <sup>13</sup>C NMR spectroscopy on the basis of the high-field doublets observed at δ<sub>CH</sub> –2.4 ppm (<sup>1</sup>J<sub>CP</sub> = 21.4 Hz) and δ<sub>CH</sub> –3.3 ppm (<sup>1</sup>J<sub>CP</sub> = 21.5 Hz) for the two isomers. The cationic character of [5a,b](OTf) was unambiguously confirmed by ESI mass spectroscopy (*m/z* 653.3 [M – OTf]<sup>+</sup>). To the best of our knowledge, [5a,b](OTf) stands as the first complex of a chelating NHC-phosphonium ylide featuring <sup>+</sup>PCy<sub>3</sub> substituents and as a rare example of a metal complex containing a <sup>+</sup>PCy<sub>3</sub> ylide ligand.<sup>13</sup>

**Synthesis and Spectroscopic Characterization of NHC, Di(tricyclohexylphosphonium) Pd(II) Complexes Exhibiting Mono-, Bis- and Tris(ylide) Extremities.** After the successful preparation of NHC-ylide Pd(II) complex [5a,b](OTf) being stable in the presence of two strong carbon donors, we then focused on the related pincer system. Thanks to the conditions developed in the <sup>+</sup>PPh<sub>3</sub> series,<sup>10a-c</sup> the *N*-tricyclohexylphosphonio-substituted imidazole [6]Br was synthesized in 60% yield by reacting 1*H*-imidazole with 0.5 equiv. of phosphonium salt [2]Br in C<sub>6</sub>H<sub>5</sub>Cl at 120 °C (Scheme 4). From [6]Br, the desired bis(*N*-phosphonio)imidazolium salt [7](OTf)<sub>3</sub> was then isolated in 96% yield after successive reaction with one equiv. of [2]Br in C<sub>6</sub>H<sub>5</sub>Cl at 120 °C and Br/OTf anion exchange in CH<sub>2</sub>Cl<sub>2</sub>. It should be noted that attempts to obtain the imidazolium salt [7](OTf)<sub>3</sub> in a one-pot manner by treating 1*H*-imidazole with an excess of [2]Br in C<sub>6</sub>H<sub>5</sub>Cl at 120 °C in the presence of K<sub>2</sub>CO<sub>3</sub> led to a non-selective reaction thus making the purification of [7](OTf)<sub>3</sub> difficult. In the <sup>31</sup>P NMR spectra, both cationic salts displayed a single signal in the typical range for <sup>+</sup>PCy<sub>3</sub> derivatives ([6]Br: δ<sub>P</sub> 32.0 ppm; [7](OTf)<sub>3</sub>: δ<sub>P</sub> 32.4 ppm). The deshielded <sup>1</sup>H NMR resonance of the N<sub>2</sub>CH signal in [7](OTf)<sub>3</sub> (δ<sub>H</sub> 9.22 ppm) compared to that of [6]Br (δ<sub>H</sub> 7.66 ppm) confirms the *N*-quaternization of the imidazole moiety.

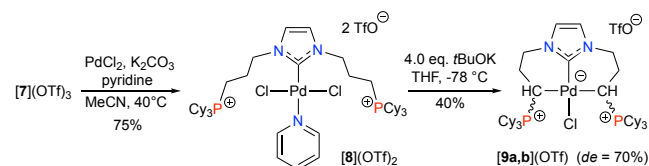
**Scheme 4. Sequential Preparation of *N*-[(CH<sub>2</sub>)<sub>3</sub>PCy<sub>3</sub>]<sup>+</sup> Substituted Imidazolium Salt [7](OTf)<sub>3</sub> from 1*H*-Imidazole.**



Targeting the preparation of a pincer complex from the pre-ligand [7](OTf)<sub>3</sub>, the latter was treated with a stoichiometric amount of PdCl<sub>2</sub> in the presence of the K<sub>2</sub>CO<sub>3</sub>/pyridine system in MeCN at 40 °C.<sup>16</sup> These conditions allowed the formation of the dicationic NHC core PdCl<sub>2</sub>(Py) complex [8](OTf)<sub>2</sub> with two pending <sup>+</sup>PCy<sub>3</sub> chains in 75% yield (Scheme 5). The formation of [8](OTf)<sub>2</sub> was clearly indicated by <sup>1</sup>H NMR spectroscopy with the disappearance of the N<sub>2</sub>CH imidazolium signal and the appearance of three resonances at δ<sub>H</sub> 8.87, 7.94 and 7.49 ppm for the pyridine nucleus. The <sup>31</sup>P NMR singlet observed at δ<sub>P</sub> 32.8 ppm is in favor of a symmetrical molecule with an unchanged environment for the two <sup>+</sup>PCy<sub>3</sub> fragments.

Gratifyingly in the presence of an excess of *t*BuOK, complex [8](OTf)<sub>2</sub> could be converted in a THF solution to the expected pincer complex [9a,b](OTf) by C-coordination of the two lateral <sup>+</sup>PCy<sub>3</sub> chains (Scheme 5). This complex [9a,b](OTf) appeared to be air-stable both in solid state and in solution being isolated after purification by column chromatography on silica gel in 40% yield as a 85/15 mixture of two diastereomers. The major diastereomer [9a](OTf) could be obtained in a pure form after recrystallization in a MeCN/Et<sub>2</sub>O mixture at room temperature. Based on the results of a X-ray diffraction study (*vide infra*) it was attributed to the *trans* isomer (*dl* form) with the two sterically hindered <sup>+</sup>PCy<sub>3</sub> groups on either side of the Pd coordination plane. In the <sup>31</sup>P NMR spectrum, the occurrence of two isomers for [9a,b](OTf) was indicated by two deshielded singlets (major [9a](OTf): δ<sub>P</sub> 40.6 ppm; minor [9b](OTf): δ<sub>P</sub> 40.7 ppm) compared to that of the precursor ([8](OTf)<sub>2</sub>: δ<sub>P</sub> 32.8 (s) ppm). <sup>13</sup>C NMR spectroscopy confirmed the presence of two upfield CH ylidic doublets (major [9a](OTf): δ<sub>C</sub> -0.6 ppm (d, <sup>1</sup>J<sub>CP</sub> = 23.2 Hz); minor

**Scheme 5. Sequential Synthesis of the NHC, Diphosphonium Bis(ylide) Pd(II) Pincer Complex [9a,b](OTf) from Imidazolium Salt [7](OTf)<sub>3</sub>.**



**Table 1. Selected <sup>31</sup>P and <sup>13</sup>C NMR Chemical Shifts (ppm) in CD<sub>3</sub>CN Solution with Signal Multiplicity and J<sub>CP</sub> Coupling Constants (Hz) in Parenthesis for Phosphonium Ylide-Based Pd(II) Complexes [9a](OTf), [10](OTf)<sub>2</sub>, [13](OTf)<sub>2</sub>, and [14](OTf).**

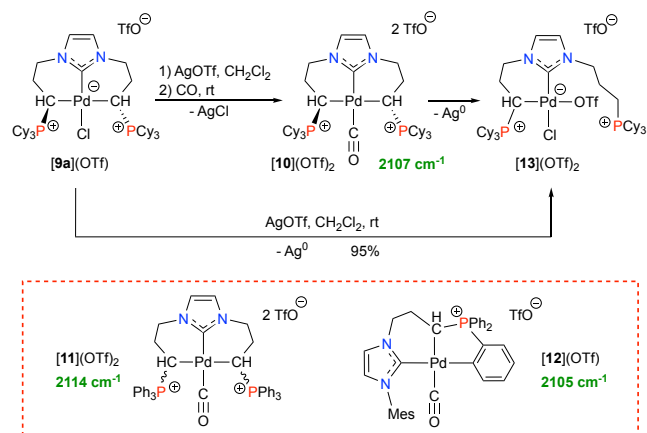
	[9a](OTf)	[10](OTf) <sub>2</sub> <sup>a</sup>	[13](OTf) <sub>2</sub>	[14](OTf)
δ <sub>P</sub>	40.6 (s)	41.7 (s)	41.2 (s); 32.8 (s)	40.9 (s); 28.6 (s)
δ <sub>N<sub>2</sub>C</sub>	167.4 (s)	166.8 (s)	155.7 (s)	171.5 (s)
				-3.4.
δ <sub>PCH</sub>	-0.6 (d, 23.2)	0.6 (d, 25.2)	2.8 (d, 23.0)	(d, 13.1); -8.9 (d, 46.5)
δ <sub>P(cy)</sub>	-	-	-	17.1 (d, 20.2)

<sup>a</sup> NMR data was recorded in CD<sub>2</sub>Cl<sub>2</sub>.

[9b](OTf): δ<sub>C</sub> 2.9 ppm (d, <sup>1</sup>J<sub>CP</sub> = 25.7 Hz)). As already observed in the <sup>+</sup>PPh<sub>3</sub> pincer series,<sup>10a,b</sup> the N<sub>2</sub>C carbon atom exhibited a significant shift upon coordination of the ylide moieties (major [9a](OTf): δ<sub>C</sub> 167.4 ppm; minor [9b](OTf): δ<sub>C</sub> 162.8 ppm; [8](OTf)<sub>2</sub>: δ<sub>C</sub> 150.9 ppm) (Table 1). Such a trend seems to be specific to the pincer case as no downfield shift of the <sup>13</sup>C NMR carbenic resonance was observed in the bidentate series upon conversion of the NHC complex [4](OTf) (δ<sub>C</sub> 178.8 ppm) to NHC-phosphonium ylide complex [5a,b](OTf) (δ<sub>C</sub> 176.1 and 176.4 ppm). ESI mass spectroscopy (9<sup>+</sup>: *m/z* 849.4 [M - OTf]<sup>+</sup>) evidenced the existence of a Pd-Cl bond suggesting thus for pincer complex [9a,b](OTf) a palladate form with a non-coordinating TfO<sup>-</sup> anion to compensate the two <sup>+</sup>PCy<sub>3</sub> moieties. It is worth mentioning that [9a,b](OTf) represents the first Pd(II) pincer complex featuring <sup>+</sup>PCy<sub>3</sub> extremities and comes to complete the restricted family of phosphonium ylide-based pincer-type complexes.<sup>10,17</sup>

To evaluate and compare the donating character of the ligand in [9a,b](OTf) with related phosphonium ylide-based pincer ligands, we then turned to the preparation of a Pd-CO adduct. For this purpose, the cationic pincer [9a](OTf) was first treated with sodium salts such as NaOTf or NaBARF in CH<sub>2</sub>Cl<sub>2</sub> at room temperature followed by CO gas bubbling through the solution for 20 min. No reaction being observed under these conditions, the metal-coordinated chloride in [9a](OTf) was finally abstracted with AgOTf following the same experimental protocol (Scheme 6, *top*). <sup>31</sup>P NMR monitoring indicated 95% conversion with the appearance of a new singlet at δ<sub>P</sub> 41.7 ppm. The formation of Pd-CO pincer [10](OTf)<sub>2</sub> was unambiguously established by <sup>13</sup>C NMR spectroscopy with the presence of a deshielded signal at δ<sub>C</sub> 186.5 ppm for the CO co-ligand. The chemical shifts of carbenic and ylidic carbon atoms appeared to be slightly affected by the nature of the *trans*-coordinated NHC ligand ([10](OTf)<sub>2</sub>: δ<sub>N<sub>2</sub>C</sub> 166.8 ppm (s); δ<sub>PCH</sub> 0.6 ppm (d, <sup>1</sup>J<sub>CP</sub> = 25.2 Hz); [9a](OTf): δ<sub>N<sub>2</sub>C</sub> 167.4 ppm (s); δ<sub>PCH</sub> -0.6 ppm (d, <sup>1</sup>J<sub>CP</sub> = 23.2 Hz) (Table 1). The corresponding IR ν<sub>CO</sub> band was found at 2107 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub> solution. The examination of experimental ν<sub>CO</sub> frequency of related carbonyl Pd(II) pincer complexes exhibiting phosphonium ylide donor extremities (Scheme 6, *bottom*)

**Scheme 6. Substitution of Chloride Ligand at the Pd Center in Complex [9a](OTf) with CO in the Presence of AgOTf and its evolution to the C,C-NHC, phosphonium ylide Pd(II) complex [13](OTf)<sub>2</sub> (top). Known Pd(II)-CO Pincer Complexes Featuring Phosphonium Ylide Extremity with Corresponding ν<sub>CO</sub> Bands Frequencies (bottom).**



revealed that the substitution of  $^+\text{PPh}_3$  groups by  $^+\text{PCy}_3$  ones induces a shift to lower frequency of about  $7\text{ cm}^{-1}$  demonstrating the greater electronic donation of the *C,C,C*-pincer ligand of **[10](OTf)<sub>2</sub>** compared to that of **[11](OTf)<sub>2</sub>** featuring  $^+\text{PPh}_3$  ends.<sup>10a,b</sup> It was also found that the globally neutral *LX*<sub>2</sub>-type ligand of **[10](OTf)<sub>2</sub>** competes well in term of donating properties with the anionic *LX*<sub>2</sub>-type ligand of pincer **[12](OTf)** based on a NHC-ylide-aryl architecture (Scheme 6, *bottom*).<sup>10d</sup>

Noteworthy, the Pd–CO complex **[10](OTf)<sub>2</sub>** was found to be too unstable to be isolated in a pure form being characterized by a  $t_{1/2}$  of about 4 h. Monitoring the reaction by multinuclear NMR experiments in  $\text{CD}_2\text{Cl}_2$  shown the slow formation of a new compound **[13](OTf)<sub>2</sub>** with concomitant precipitation of metallic silver which might be due to the presence of residual AgCl obtained during the initial chloride abstraction step and difficult to remove by filtration to its propensity to form colloidal solutions. The structure of **[13](OTf)<sub>2</sub>** was first assigned on the basis of the  $^{31}\text{P}$  NMR spectrum which exhibited two single resonances in the phosphonium salt ( $\delta_{\text{P}}$  32.8 ppm) and phosphonium ylide regions ( $\delta_{\text{P}}$  41.2 ppm), respectively. The linkage of the CH ylide fragment was confirmed from the upfield shift of the corresponding  $^{13}\text{C}$  NMR resonance ( $\delta_{\text{CH}}$  2.8 ppm (d,  $^1J_{\text{CP}} = 23.0\text{ Hz}$ ) while the pending  $\text{CH}_2^+\text{PCy}_3$  moiety was evidenced by the lower field doublet signal ( $\delta_{\text{CH}_2}$  13.7 ppm (d,  $^1J_{\text{CP}} = 41.4\text{ Hz}$ ). On the other hand, mass spectroscopy (**13**<sup>+</sup>:  $m/z$  425.2 [(M – 2 OTf)/2]<sup>+</sup>) revealed the existence of a Pd–Cl linkage with a dicationic character in favor of the presence of two TfO<sup>–</sup> anions. However, the recording of the  $^{19}\text{F}$  NMR spectrum at 25 °C and at –80 °C despite a broadening of the signal in the latter case did not allow to differentiate between the two TfO<sup>–</sup> anions (Figures S35–36). DOSY NMR experiments were also carried out in solvents of different polarity ( $\text{CD}_2\text{Cl}_2$ ,  $\text{CD}_3\text{CN}$ ) on **[13](OTf)<sub>2</sub>**, phosphonium salts **[2]Br** and **[7](OTf)<sub>3</sub>** exhibiting small and large size respectively, and structurally close Pd(II) complexes **[8](OTf)<sub>2</sub>**, **[9a,b](OTf)** to exclude a dinuclear arrangement based on a Pd<sub>2</sub>(μ-Cl)<sub>2</sub> core.<sup>18</sup> According to all these data, the structure of **[13](OTf)<sub>2</sub>** was attributed to the *C,C*-chelating NHC-phosphonium ylide palladate complex bearing a pending  $^+\text{PCy}_3$  group (Scheme 6, *top*).

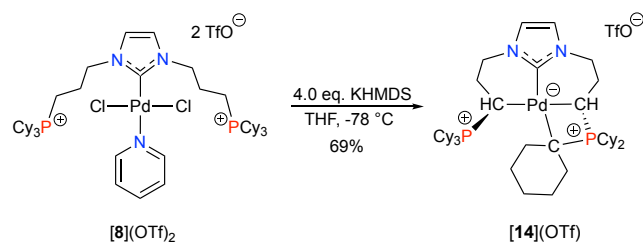
Assuming that the occurrence of a redox process between Pd(II) and Ag(I) type-species may be responsible for the intriguing formation of **[13](OTf)<sub>2</sub>**, electrochemical measurements were performed on the pincer complex **[9a](OTf)**. The latter was found to be irreversibly oxidized in a  $\text{CH}_2\text{Cl}_2$  solution with a  $E_{\text{p}}^{\text{ox}}$  value of +1.05 V/SCE (Pt electrode,  $\text{CH}_2\text{Cl}_2$ ,  $n\text{Bu}_4\text{OTf}$ , 200 mV/s). Examination of the  $E_{\text{p}}^{\text{red}}$  of AgOTf (+0.61 V/SCE) measured in the same experimental conditions indicated that the reaction between **[9a](OTf)** and AgOTf is not thermodynamically favored.<sup>19</sup> However, the reaction of complex **[9a](OTf)** with 2.2 equiv. of AgOTf in  $\text{CH}_2\text{Cl}_2$  at room temperature afforded after 48 h metallic silver and the same complex **[13](OTf)<sub>2</sub>** isolated in 95% yield (Scheme 6, *top*). These results show that despite the endergonic oxidation of **[9a](OTf)<sub>2</sub>** by AgOTf, the overall process became feasible due to the use of an excess of oxidant and the shift of the electron-transfer equilibrium to the products namely the precipitation of Ag(0), this being a typical feature of irreversible oxidants.<sup>20</sup> Noteworthy, the one-electron oxidation of d<sub>8</sub> Pd(II) dialkyl complexes was reported to induce the homolytic cleavage of a Pd–alkyl bond forming an alkyl radical and the corresponding cationic Pd(II) monoalkyl complexes.<sup>21</sup> It is there-

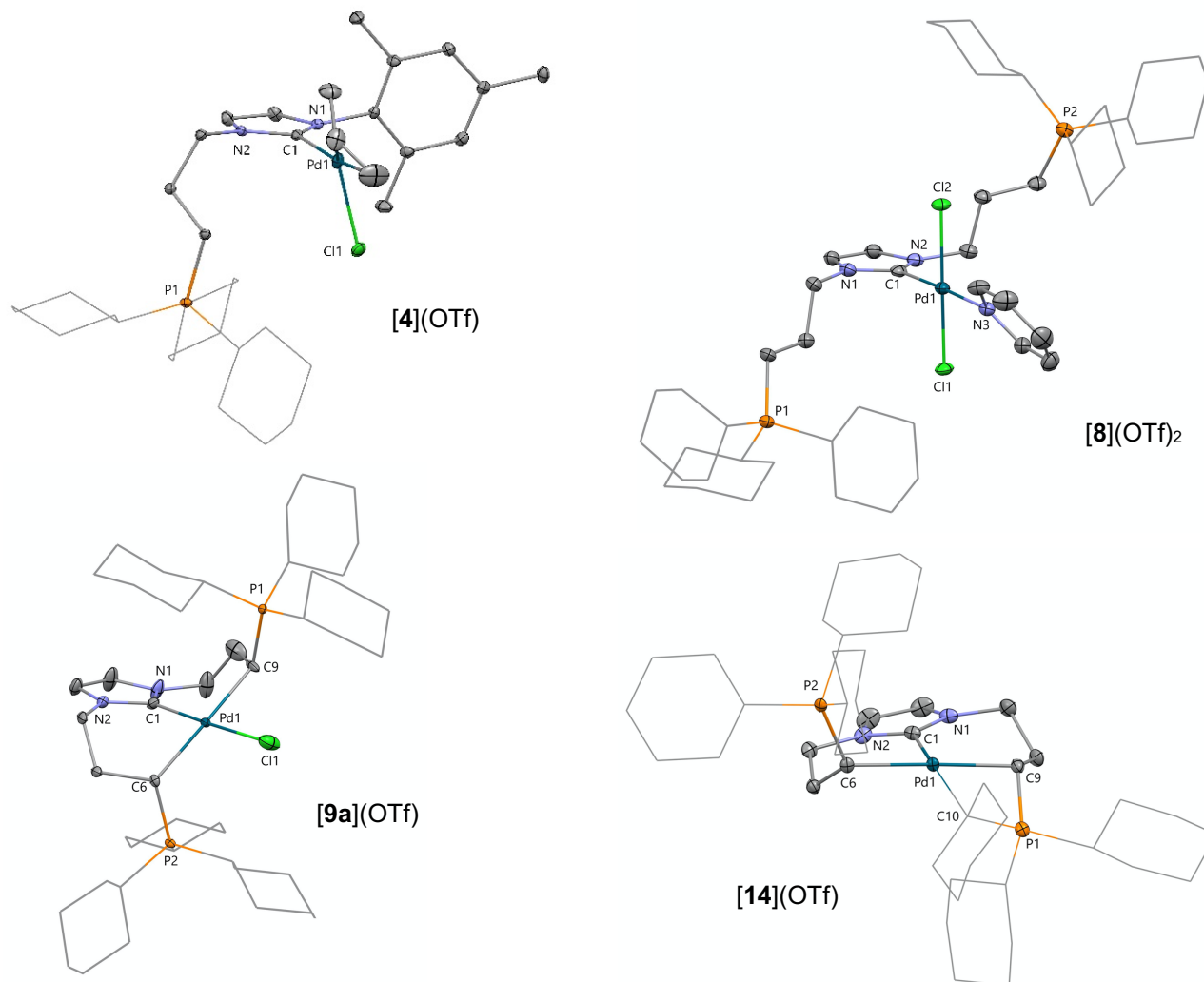
fore reasonable to propose that a similar redox transformation can occur in the case of the electron-rich pincer palladate complex **[9a](OTf)**. The oxidation would induce the homolytic cleavage of one of the two Pd–ylide bonds leading to an intermediate species characterizing by a coordinatively unsaturated 14-electron Pd(II) center and a side cation radical of type  $[-\text{CH}_2\text{CH}_2\text{CH}^+\text{PPh}_3]$ , which would be stabilized by the coordination of a TfO<sup>–</sup> anion and hydrogen atom abstraction from the reaction medium, respectively. We assume here that the hydrogen atom may come from residual solvents ( $\text{Et}_2\text{O}$ , MeCN) present in **[9a](OTf)** since no deuteration of the  $\text{CH}_2^+\text{PCy}_3$  fragment of complex **[13](OTf)<sub>2</sub>** was observed when pincer **[9a](OTf)** was reacted with AgOTf in  $\text{CD}_2\text{Cl}_2$ .<sup>22</sup>

As we have just observed, the introduction of  $^+\text{PCy}_3$  extremities was found to be beneficial for the preparation of the NHC core, diphosphonium bis(ylide) Pd(II) pincer complex **[9a,b](OTf)** since no compound resulting from *Csp*<sup>3</sup>–H activation was evidenced with the selected deprotonation conditions (*t*BuOK in THF).<sup>23</sup> However by reacting the NHC precursor **[8](OTf)<sub>2</sub>** with an excess of a stronger base such as KHMDS or LDA in THF, the formation of the cyclometalated Pd complex **[14](OTf)** was observed, the latter being isolated in 69 % yield after chromatography on silica gel (Scheme 7). The  $^{31}\text{P}$  NMR spectrum of **[14](OTf)** exhibited only two singlets at  $\delta_{\text{P}}$  40.9 and  $\delta_{\text{P}}$  28.6 ppm, thus showing the occurrence of a unique diastereomer attributed to the *trans* isomer with the two cationic moieties on either side of the Pd coordination plane. The linkage of two CH ylide moieties was apparent for the upfield shift of the corresponding  $^{13}\text{C}$  NMR signals with appropriate multiplicity ( $\delta_{\text{CH}}$  –3.4 ppm ( $^1J_{\text{CP}} = 13.1\text{ Hz}$ );  $\delta_{\text{CH}}$  –8.9 ppm ( $^1J_{\text{CP}} = 46.5\text{ Hz}$ ). The  $^{13}\text{C}$  NMR spectrum highlighted also the presence of the shielded doublet of the cyclometalated quaternary carbon atom ( $\delta_{\text{C}}$  17.1 ppm ( $^1J_{\text{CP}} = 20.2\text{ Hz}$ )) (Table 1). The cationic nature of complex **[14](OTf)** was assigned by ESI mass spectroscopy (**14**<sup>+</sup>:  $m/z$  813.5 [M – OTf]<sup>+</sup>). Noteworthy, the formation of this compound can result either from the base-assisted *Csp*<sup>3</sup>–H bond activation at the Pd(II) center or by the generation of the diylide moiety upon deprotonation of the C–H bond of a  $^+\text{P}$ -cyclohexyl group followed by its coordination to the metal, but the available experimental data did not allow to distinguish between these two mechanisms.

The structure of complex **[14](OTf)** is unique in several aspects. The Pd(II) atom is indeed bonded to four carbon atoms of different nature (carbenic (*C-sp*<sup>2</sup>) and phosphonioalkyl (*C-sp*<sup>3</sup>)) being formally coordinated by three strongly donating carbon fragments which behave in an independent manner due to the presence of insulating propyl bridges, namely a NHC, a phosphonium ylide and a phosphonium diylide. More generally, phosphonium diylides have long been known in coordination chemistry as powerful nucleophiles due to their anionic

**Scheme 7. Synthesis of the Cyclometalated Pd(II) Complex [14](OTf) Exhibiting an Anionic C,C,C-Chelating Ligand from [8](OTf)<sub>2</sub>.**





**Figure 1.** Perspective views of the cationic part of NHC Pd(II) complexes [4](OTf), [8](OTf)<sub>2</sub>, [9a](OTf), and [14](OTf) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and triflate anions are omitted for clarity and cyclohexyl rings are shown as wireframe. Selected bond lengths (Å) and bond angles (°) for complexes [4](OTf) and [8](OTf)<sub>2</sub>. [4](OTf) (molecule A) : C1–N1 1.363(4); C1–N2 1.359(4); C1–Pd1 2.041(3); Pd1–Cl1 2.3906(9); N1–C1–N2 104.0(3); N1–C1–Pd1 129.2(2); C1–Pd1–Cl1 95.80(9). [8](OTf)<sub>2</sub>: C1–N1 1.330(7); C1–N2 1.343(7); C1–Pd1 1.961(6); Pd1–Cl1 2.3046(14); Pd1–N3 2.093(5); N1–C1–N2 105.8(5); C1–Pd1–Cl1 86.52(16); C1–Pd1–N3 177.9(2).

character.<sup>24</sup> However, most of them of general formulae [R<sub>2</sub>P(CHR')<sub>2</sub>]<sup>+</sup> are defined by the presence of two identical C-ylidic atoms and only few examples of structurally characterized Pd(II) diylide complexes are known.<sup>25</sup> Complex [14](OTf) stands thus as a unique example of a Pd(II) complex exhibiting an unsymmetrical coordinating diylide unit characterized by X-ray diffraction analysis.<sup>26</sup>

**X-ray Diffraction Studies of NHC Pd(II) Complexes [4](OTf), [8](OTf)<sub>2</sub>, [9a](OTf) and [14](OTf).** Some of the prepared complexes were characterized by X-ray diffraction studies, namely the *N*-[(CH<sub>2</sub>)<sub>3</sub>PCy<sub>3</sub>]<sup>+</sup> substituted monodentate NHC Pd(II) complexes [4](OTf) and [8](OTf)<sub>2</sub>, and the NHC, phosphonium ylide-based Pd(II) complexes [9a](OTf) and [14](OTf) (Figure 1, Table 2).<sup>27</sup> In [4](OTf) and [8](OTf)<sub>2</sub>, the coordinated planes defined by a quasi-square planar environment are not far from being orthogonal to the NHC ring ([4](OTf): dihedral angle N1–C1–Pd1–Cl1 68.78°; [8](OTf)<sub>2</sub>: dihedral angle N1–C1–Pd1–Cl2 88.81°) with chloride and pyridine co-ligands located in respective *cis* (C1–Pd1–Cl1 95.80(9)°) and *trans* (C1–Pd1–N3 177.9(2)°) position to the

**Table 2.** Selected bond lengths (Å) and bond angles (°) for Pd(II) complexes [9a](OTf) and [14](OTf).

Complex	[9a](OTf)	[14](OTf)
C1–Pd1	1.939(5)	2.019(4)
C6–Pd1	2.181(4)	2.143(4)
C9–Pd1	2.161(4)	2.097(4)
X (Cl1 or C10)–Pd1	2.3291(15)	2.161(4)
C9–P1	1.794(5)	1.756(4)
C6–P2	1.792(4)	1.788(4)
C10–P1	–	1.806(4)
C1–Pd1–X (Cl1 or C10)	178.00(14)	162.29(16)
C6–Pd1–C9	174.40(19)	177.21(16)
C1–Pd1–C6	88.28(17)	90.37(16)
C9–Pd1–C10	–	77.01(16)
τ <sub>4</sub>	0.05	0.14

NHC. The N<sub>2</sub>C–Pd bond distances ([**4**](OTf): C1–Pd1 2.041(3) Å; [**8**](OTf)<sub>2</sub>: C1–Pd1 1.961(6) Å) are in good agreement with those already reported in structurally close cationic NHC Pd(II) complexes.<sup>9–11</sup> To compare the geometry of pincer and cyclometalated Pd complexes [**9a**](OTf) and [**14**](OTf), the most pertinent metrical data are collected in Table 2. In both cases, the Pd(II) atom adopts a square planar geometry with a stronger deviation in [**14**](OTf) as indicated by the tau parameter value  $\tau_4$  (0.05 vs. 0.14).<sup>28</sup> While the two P<sup>+</sup>-ylides present a mutual *trans* arrangement ([**9a**](OTf): C6–Pd1–C9 174.40(19)°; [**14**](OTf): 177.21(16)°), the position *trans* relative to the central NHC is respectively occupied by a chloride ([**9a**](OTf): C1–Pd1–Cl1 178.00(14)°) and a quaternary carbon atom ([**14**](OTf): C1–Pd1–C10 162.29(16)°). As common feature, certainly to minimize steric and electrostatic constraints, the two phosphonium moieties are located on either side of the metal coordination plane conferring a *R*<sub>C6</sub>,*R*<sub>C9</sub> (*S*<sub>C6</sub>,*S*<sub>C9</sub>) configuration. The C-coordination of the two ylides results in both complexes in the presence of two strongly distorted fused 6-membered palladacycles as already observed in the related <sup>+</sup>PPh<sub>3</sub> pincer series.<sup>10a,b</sup> In [**14**](OTf), the uncommon cyclometalation of a <sup>+</sup>P–Cy substituent led to the formation of a very tight 4-membered ring fused to the two 6-membered rings, the strained environment being indicated in particular by the C10–Pd1 bond distance (2.161(4) Å) longer than that of the three other C–Pd bond distances (C1–Pd1 2.019(4) Å; C6–Pd1 2.143(4) Å; C9–Pd1 2.097(4) Å). Noteworthy in the same complex [**14**](OTf), the formation of the C10–Pd bond is accompanied with the elongation of the NHC–Pd distance ([**9a**](OTf): C1–Pd1 1.939(5) Å; [**14**](OTf): 2.019(4) Å) and concomitant shortening of the two ylide–Pd distances ([**9a**](OTf): C6–Pd1 2.181(4) Å, C9–Pd1 2.161(4) Å; [**14**](OTf): C6–Pd1 2.143(4) Å, C9–Pd1 2.097(4) Å), a change which might be partly rationalized by the stronger *trans* influence of an alkyl-like carbon atom compared to that of a chloride atom.<sup>29</sup> Concerning the charge distribution, the two phosphonium positive charges are compensated in both complexes by a palladate negative charge and a non-coordinating triflate anion.

## CONCLUSION

The methodology recently developed in the <sup>+</sup>PPh<sub>3</sub> series of chelating NHC-ylide ligands was reported here to be applicable to the <sup>+</sup>PCy<sub>3</sub> case thus providing a practical synthesis of a new family of *N*-substituted <sup>+</sup>PCy<sub>3</sub> imidazolium salts and ensuing monodentate NHC Pd(II) complexes bearing pending <sup>+</sup>PCy<sub>3</sub> groups. By contrast, a significant difference of reactivity was observed in the pincer series, during the coordination of the C-ylidic extremities. Indeed, the <sup>+</sup>PCy<sub>3</sub> substituents more reluctant to C–H bond activation than <sup>+</sup>PPh<sub>3</sub> substituents were demonstrated to be beneficial to the direct preparation of a *C,C,C*-NHC, diphosphonium bis(ylide) palladate pincer complex without first going through an *ortho*-metalated Pd species. The electronic donation of this new pincer platform evaluated on the basis of IR  $\nu_{CO}$  frequency of corresponding Pd–CO adducts was determined to be higher than that of the related pincer ligand exhibiting <sup>+</sup>PPh<sub>3</sub> ends. Selective oxidative cleavage of one Pd–ylide bond in pincer complex upon treatment with AgOTf represents an elegant route to a *C,C*-chelating NHC, phosphonium ylide complex. Finally, it was demonstrated that strong bases could lead to a formal activation of the *Csp*<sup>3</sup>–H bond of a <sup>+</sup>P–Cy substituent to afford an unprecedented cyclometalated palladate complex exhibiting

the anionic *C,C,C,C*-NHC, diphosphonium tris(ylide) ligand. The investigation of the catalytic properties of these carbon-based Pd(II) complexes associating NHC and phosphonium ylide donors will be considered in the near future.

## 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. A liquid nitrogen/ethanol slush bath was used to maintain samples at the desired low temperature. 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 μm).

Solution IR spectra were recorded in 0.1 mm CaF<sub>2</sub> cells using a Perkin Elmer Frontier FT-IR spectrometer and given in cm<sup>-1</sup>. <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C NMR spectra were obtained on Bruker AV400 or NEO600 spectrometers. NMR chemical shifts  $\delta$  are in ppm, with positive values to high frequency referenced against the residual signals of deuterated solvents for <sup>1</sup>H and <sup>13</sup>C and 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” using a Xevo G2 QToF (Waters) spectrometer. 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”.

Voltammetric measurements were carried out with a potentiostat Autolab PGSTAT100 controlled by GPES 4.09 software. Experiments were performed at room temperature in a homemade airtight three-electrode cell consisting of a Pt working electrode (*d* = 0.5 mm), a platinum wire (*S* = 1 cm<sup>2</sup>) as counter electrode, and a saturated calomel electrode (*SCE*) separated from the solution by a bridge compartment as a reference. Before each measurement, the working electrode was cleaned with a polishing machine (Presi P230, P4000). The measurements were carried out in dry CH<sub>2</sub>Cl<sub>2</sub> under argon atmosphere using 0.1 M [*n*Bu<sub>4</sub>N](OTf) (Fluka, 99% puriss electrochemical grade) as supporting electrolyte and typically 10<sup>-3</sup> M sample concentration.

**Synthesis of phosphonium salt [2]Br.** A solution of 1,3-dibromopropane (12.6 g, 62.0 mmol) and PCy<sub>3</sub> (3.5 g, 12.0 mmol) in toluene (70 mL) was stirred at rt for 24 hours. After removal of the solution by decantation, the remaining solid was washed with toluene (3 × 20 mL) to remove the excess of 1,3-dibromopropane and dried under vacuum to afford [2]Br as a white powder (5.2 g, 90%). <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  3.70–3.73 (m, 2H, CH<sub>2</sub>), 2.71–2.79 (m, 2H, CH<sub>2</sub>), 2.50–2.61 (m, 3H, CH<sub>3</sub>), 2.20–2.28 (m, 2H, CH<sub>2</sub>), 1.87–2.02 (m, 12H, CH<sub>2</sub>Cy), 1.74–1.79 (m, 3H, CH<sub>2</sub>Cy), 1.21–1.58 (m, 15H, CH<sub>2</sub>Cy). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  32.0 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  34.2 (d, *J*<sub>CP</sub> = 16.7 Hz, CH<sub>2</sub>), 29.8 (d, *J*<sub>CP</sub> = 40.2 Hz, CH), 26.9 (d, *J*<sub>CP</sub> = 3.9 Hz, CH<sub>2</sub>), 26.2 (d, *J*<sub>CP</sub> = 11.8 Hz, CH<sub>2</sub>), 25.9 (d, *J*<sub>CP</sub> = 3.4 Hz, CH<sub>2</sub>), 25.1 (d, *J*<sub>CP</sub> = 1.6 Hz, CH<sub>2</sub>), 14.5 (d, *J*<sub>CP</sub> = 44.8 Hz, PCH<sub>2</sub>). MS (ES<sup>+</sup>): *m/z*: 401.2 [M – Br]<sup>+</sup>. HRMS (ES<sup>+</sup>): calcd. for C<sub>21</sub>H<sub>39</sub>BrP 401.1973; found 401.1976 ( $\epsilon_r$  = 0.7 ppm). Anal. Found, C 52.30, H 8.55. Calcd. for C<sub>21</sub>H<sub>39</sub>Br<sub>2</sub>P: C, 52.29; H, 8.15.

**Synthesis of pre-ligand [3](OTf)<sub>2</sub>.** 1-Mesitylimidazole **1** (1.0 g, 5.37 mmol) and [2]Br (1.72 g, 3.58 mmol) were heated at 130 °C in C<sub>6</sub>H<sub>5</sub>Cl (30 mL) for 15 hours. After evaporation of the solvent under vacuum, the crude residue and NaOTf (1.23 g, 7.20 mmol) were stirred in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at rt for 4 hours. After filtration over Celite and evaporation of the solvent, [3](OTf)<sub>2</sub> (2.31 g, 80%) was obtained as a white powder. <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  9.20 (s, 1H, N<sub>2</sub>CH), 8.23 (s, 1H, CH<sub>im</sub>), 7.16 (s, 1H, CH<sub>im</sub>), 6.97 (s, 2H, CH<sub>Me</sub>), 4.62–4.66 (m, 2H, NCH<sub>2</sub>), 2.35–2.48 (m, 7H, CH<sub>2</sub> + CH<sub>Cy</sub>),

2.30 (s, 3H,  $CH_{3Mes}$ ), 2.00 (s, 6H,  $CH_{3Mes}$ ), 1.70–1.95 (m, 15H,  $CH_{2Cy}$ ), 1.20–1.60 (m, 15H,  $CH_{2Cy}$ ).  $^{31}P\{^1H\}$  NMR (162 MHz,  $CDCl_3$ , 25 °C):  $\delta$  31.8 (s).  $^{13}C\{^1H\}$  NMR (100.6 MHz,  $CDCl_3$ , 25 °C):  $\delta$  141.4 (s,  $C_{Mes}$ ), 137.1 (s,  $N_2CH$ ), 134.1 (s,  $C_{Mes}$ ), 130.6 (s,  $C_{Mes}$ ), 129.9 (s,  $CH_{Mes}$ ), 124.4 (s,  $CH_{Im}$ ), 123.7 (s,  $CH_{Im}$ ), 120.7 (q,  $J_{CF} = 320.9$  Hz,  $CF_3$ ), 49.7 (d,  $J_{CP} = 19.3$  Hz,  $NCH_2$ ), 30.2 (d,  $J_{CP} = 40.2$  Hz,  $CH_{Cy}$ ), 26.9 (d,  $J_{CP} = 4.2$  Hz,  $CH_2$ ), 26.4 (d,  $J_{CP} = 11.9$  Hz,  $CH_2$ ), 25.3 (s,  $CH_2$ ), 24.0 (d,  $J_{CP} = 3.2$  Hz,  $CH_2$ ), 21.1 (s,  $CH_{3Mes}$ ), 17.3 (s,  $CH_{3Mes}$ ), 12.8 (d,  $J_{CP} = 46.2$  Hz,  $PCH_2$ ). MS ( $ES^+$ ):  $m/z$ : 657.3 [ $M - CF_3SO_3$ ] $^+$ . HRMS ( $ES^+$ ): calcd. for  $C_{34}H_{53}F_3N_2O_3PS$  657.3467; found 657.3477 ( $\epsilon_r = 1.5$  ppm). Anal. Found, C, 52.18; H, 6.93; N, 3.35. Calcd. for  $C_{35}H_{53}F_6N_2O_6PS_2$ : C, 52.10; H, 6.62; N, 3.47.

**Synthesis of complex [4](OTf).** A mixture of  $[Pd(All)Cl_2]$  (0.01 g, 0.031 mmol), pre-ligand [3](OTf) $_2$  (0.05 g, 0.062 mmol) and anhydrous  $K_2CO_3$  (0.03 g, 0.18 mmol) was dissolved in MeCN (20 mL) and stirred at rt for 15 hours. After filtration over Celite and evaporation of the solvent, [4](OTf) was obtained as a white powder (0.049 g, 95%). Recrystallization from MeCN/Et $_2$ O at rt gave pale yellow crystals, some of them being suitable for X-ray diffraction analysis.  $^1H$  NMR (600.1 MHz,  $CD_3CN$ , 75 °C): \* $\delta$  7.50 (brs, 1H,  $CH_{Im}$ ), 7.17 (brs, 1H,  $CH_{Im}$ ), 7.03 (brs, 2H,  $CH_{Mes}$ ), 5.18 (brs, 1H,  $CH_{All}$ ), 4.44 (brs, 2H,  $NCH_2$ ), 4.05 (m, 1H,  $CH_{2All}$ ), 2.97 (m, 1H,  $CH_{2All}$ ), 2.43–2.51 (m, 3H,  $CH_{Cy}$ ), 2.33 (s, 3H,  $CH_{3Mes}$ ), 2.27–2.31 (m, 4H,  $CH_2$ ), 2.07 (brs, 6H,  $CH_{3Mes}$ ), 1.87–1.91 (m, 8H,  $CH_2$ ), 1.76–1.79 (m, 4H,  $CH_2$ ), 1.54–1.61 (m, 8H,  $CH_2$ ), 1.36–1.48 (m, 12H,  $CH_2$ ).  $^{31}P\{^1H\}$  NMR (243 MHz,  $CD_3CN$ , 75 °C):  $\delta$  32.8 (brs). \* $^{13}C\{^1H\}$  NMR (150.9 MHz,  $CD_3CN$ , 75 °C):  $\delta$  178.8 (s,  $N_2C$ ), 140.5 (s,  $C_{Mes}$ ), 137.4 (s,  $C_{Mes}$ ), 136.7 (s,  $C_{Mes}$ ), 130.2 (s,  $CH_{Mes}$ ), 125.3 (s,  $CH_{Im}$ ), 123.2 (s,  $CH_{Im}$ ), 122.6 (q,  $J_{CF} = 321.6$  Hz,  $CF_3$ ), 118.0 (brs,  $CH_{All}$ ), 73.3 (brs,  $CH_{2All}$ ), 52.0 (d,  $J_{CP} = 16.6$  Hz,  $NCH_2$ ), 50.8 (brs,  $CH_{2All}$ ), 31.3 (d,  $J_{CP} = 40.8$  Hz,  $CH_{Cy}$ ), 28.0 (d,  $J_{CP} = 4.5$  Hz,  $CH_2$ ), 27.5 (d,  $J_{CP} = 12.1$  Hz,  $CH_2$ ), 26.4 (s,  $CH_2$ ), 25.0 (s,  $CH_2$ ), 21.3 (s,  $CH_{3Mes}$ ), 18.5 (s,  $CH_{3Mes}$ ), 14.2 (d,  $J_{CP} = 43.8$  Hz,  $PCH_2$ ). MS ( $ES^+$ ):  $m/z$ : 327.2 [ $M - (CF_3SO_3 + Cl)$ ] $^{2+}$ . HRMS ( $ES^+$ ): calcd. for  $C_{36}H_{57}N_2PPd$  327.1654; found 327.1656 ( $\epsilon_r = 0.6$  ppm). The compound [4](OTf) was assessed to be >95% pure by  $^1H$ ,  $^{31}P$  and  $^{13}C$  NMR spectroscopy. \* The rapid flip of the  $\pi$ -allyl co-ligand in solution prevents to assign with exactitude the corresponding  $^1H$  and  $^{13}C$  NMR resonances.

**Synthesis of complex [5a,b](OTf).** A solution of KHMDs (0.5 M in toluene, 95  $\mu$ L, 0.047 mmol) was added at –40 °C to a solution of complex [4](OTf) (0.04 g, 0.047 mmol) in THF (5 mL). The mixture was slowly warmed to rt and stirred for 2 hours. After filtration over Celite, the solvent was removed under vacuum, and complex [5a,b](OTf) (0.036 g, 96%) was obtained as a pale yellow powder as a mixture of two diastereomers (55/45) assigned in NMR spectra as  $^a$ major isomer;  $^b$ minor isomer.  $^1H$  NMR (400 MHz,  $CD_3CN$ , 25 °C):  $\delta$  7.39 $^a$  (brs, 1.2H,  $CH_{Im}$ ), 7.36 $^b$  (brs, 1H,  $CH_{Im}$ ), 7.06–7.09 $^{a,b}$  (m, 6.6H,  $CH_{Mes}$ ,  $CH_{Im}$ ), 4.68–4.84 $^{a,b}$  (m, 2.2H,  $CH_{All}$ ), 4.21–4.31 $^{a,b}$  (m, 2.2H,  $NCH_2$ ), 3.86–3.92 $^a$  (m, 1.2H,  $NCH_2$ ), 3.67–3.73 $^b$  (m, 1H,  $NCH_2$ ), 3.54–3.57 $^a$  (m, 1.2H,  $CH_{2All}$ ), 3.31–3.34 $^b$  (m, 1H,  $CH_{2All}$ ), 2.93–2.99 $^b$  (m, 1H,  $CH_{2All}$ ), 2.53–2.55 $^a$  (m, 1.2H,  $CH_{2All}$ ), 2.29–2.37 $^{a,b}$  (m, 6.6H,  $CH_{Cy}$ ), 2.37 $^a$  (s, 3.6H,  $CH_{3Mes}$ ), 2.36 $^b$  (s, 3H,  $CH_{3Mes}$ ), 2.20–2.30 $^{a,b}$  (m, 2.2H,  $CH_{2All}$ ), 2.16 $^b$  (s, 3H,  $CH_{3Mes}$ ), 2.04 $^a$  (s, 3.6H,  $CH_{3Mes}$ ), 1.80–2.00 $^{a,b}$  (m, 2.2H,  $CH_{2All}$ ), 1.97 $^a$  (s, 3.6H,  $CH_{3Mes}$ ), 1.94 $^b$  (s, 3H,  $CH_{3Mes}$ ), 1.80–2.40 $^{a,b}$  (m, 2.2H,  $PCH$ ), 1.30–2.00 $^{a,b}$  (m, 70.4H,  $CH_2$ ).  $^{31}P\{^1H\}$  NMR (162 MHz,  $CDCl_3$ , 25 °C):  $\delta$  40.1 $^b$  (s), 39.2 $^a$  (s).  $^{13}C\{^1H\}$  NMR (100.6 MHz,  $CD_3CN$ , 25 °C):  $\delta$  176.4 $^b$  (s,  $N_2C$ ), 176.1 $^a$  (s,  $N_2C$ ), 140.1 $^a$  (s,  $C_{Mes}$ ), 138.3 $^b$  (s,  $C_{Mes}$ ), 136.9 $^a$  (s,  $C_{Mes}$ ), 136.4 $^b$  (s,  $C_{Mes}$ ), 136.2 $^b$  (s,  $C_{Mes}$ ), 136.0 $^a$  (s,  $C_{Mes}$ ), 129.8 $^{a,b}$  (s,  $CH_{Mes}$ ), 129.7 $^{a,b}$  (s,  $CH_{Mes}$ ), 129.6 $^{a,b}$  (s,  $CH_{Mes}$ ), 123.5 $^a$  (s,  $CH_{Im}$ ), 123.2 $^a$  (s,  $CH_{Im}$ ), 123.1 $^b$  (s,  $CH_{Im}$ ), 123.0 $^b$  (s,  $CH_{Im}$ ), 121.2 $^{a,b}$  (q,  $J_{CF} = 321.0$  Hz,  $CF_3$ ), 117.1 $^b$  (s,  $CH_{All}$ ), 116.3 $^a$  (s,  $CH_{All}$ ), 59.8 $^b$  (s,  $CH_{2All}$ ), 58.9 $^a$  (s,  $CH_{2All}$ ), 56.8 $^a$  (s,  $CH_{2All}$ ), 55.8 $^b$  (s,  $CH_{2All}$ ), 54.3 $^a$  (d,  $J_{CP} = 19.2$  Hz,  $NCH_2$ ), 54.1 $^b$  (d,  $J_{CP} = 19.7$  Hz,  $NCH_2$ ), 32.7 $^a$  (d,  $J_{CP} = 43.2$  Hz,  $CH$ ), 32.6 $^b$  (d,  $J_{CP} = 43.2$  Hz,  $CH$ ), 29.1 $^a$  (d,  $J_{CP} = 1.9$  Hz,  $CH_2$ ), 29.0 $^b$  (d,  $J_{CP} = 2.0$  Hz,  $CH_2$ ), 28.2 $^{a,b}$  (d,  $J_{CP} = 3.5$  Hz,  $CH_2$ ), 28.1 $^{a,b}$  (d,  $J_{CP} = 3.5$  Hz,  $CH_2$ ), 28.0 $^{a,b}$  (d,  $J_{CP} = 3.9$  Hz,  $CH_2$ ), 27.9 $^{a,b}$  (d,  $J_{CP} = 11.1$  Hz,  $CH_2$ ), 27.8 $^{a,b}$  (s,  $CH_2$ ), 27.7 $^{a,b}$  (d,  $J_{CP} = 8.1$  Hz,  $CH_2$ ), 27.6 $^{a,b}$  (d,  $J_{CP} = 11.1$  Hz,  $CH_2$ ), 27.5 $^{a,b}$  (d,  $J_{CP} = 10.1$  Hz,  $CH_2$ ), 26.4 $^{a,b}$  (brs,  $CH_2$ ), 21.1 $^{a,b}$  (s,  $CH_{3Mes}$ ), 19.2 $^b$  (s,  $CH_{3Mes}$ ), 19.0 $^a$  (s,  $CH_{3Mes}$ ), 17.9 $^b$  (s,  $CH_{3Mes}$ ), 17.8 $^a$  (s,  $CH_{3Mes}$ ), –2.4 $^b$  (d,  $J_{CP} = 21.4$  Hz,  $PCH$ ), –3.3 $^a$  (d,  $J_{CP} = 21.5$  Hz,

$PCH$ ). MS ( $ES^+$ ):  $m/z$ : 653.3 [ $M - CF_3SO_3$ ] $^+$ . HRMS ( $ES^+$ ): calcd. for  $C_{36}H_{56}N_2PPd$  653.3216; found 653.3234 ( $\epsilon_r = 2.7$  ppm). Anal. Found: C, 54.95; H, 7.10; N, 3.91. Calcd. for  $C_{37}H_{56}F_3N_2O_3PPdS$ : C, 55.32; H, 7.03; N, 3.49.

**Synthesis of phosphonium salt [6]Br.** 1*H*-imidazole (0.3 g, 4.37 mmol) and [2]Br (1.0 g, 2.07 mmol) were heated at 120 °C in  $C_6H_5Cl$  (30 mL) for 15 hours. After evaporation of the solvent, the crude residue was washed with a saturated aqueous  $NaHCO_3$  solution (20 mL). The aqueous layer was extracted several times with  $CH_2Cl_2$  (4 $\times$ 80 mL) and the combined organic phase was dried over  $Na_2SO_4$ . After evaporation of the solvent and drying under vacuum [6]Br (0.58 g, 60%) was obtained as a white powder.  $^1H$  NMR (400.1 MHz,  $CDCl_3$ , 25 °C):  $\delta$  7.66 (brs, 1H,  $N_2CH$ ), 7.19 (brs, 1H,  $CH_{Im}$ ), 7.03 (brs, 1H,  $CH_{Im}$ ), 4.40 (t,  $J_{HH} = 7.1$  Hz, 2H,  $NCH_2$ ), 2.56–2.65 (m, 2H,  $CH_2$ ), 2.36–2.49 (m, 3H,  $CH_{Cy}$ ), 2.12–2.20 (m, 2H,  $CH_2$ ), 1.76–1.93 (m, 15H,  $CH_{2Cy}$ ), 1.22–1.52 (m, 15H,  $CH_{2Cy}$ ).  $^{31}P\{^1H\}$  NMR (162 MHz,  $CDCl_3$ , 25 °C):  $\delta$  32.0 (s).  $^{13}C\{^1H\}$  NMR (100.6 MHz,  $CDCl_3$ , 25 °C):  $\delta$  137.7 (s,  $N_2CH$ ), 129.6 (s,  $CH_{Im}$ ), 119.3 (s,  $CH_{Im}$ ), 46.3 (d,  $J_{CP} = 15.6$  Hz,  $NCH_2$ ), 29.8 (d,  $J_{CP} = 40.4$  Hz,  $CH_{Cy}$ ), 26.8 (d,  $J_{CP} = 3.9$  Hz,  $CH_2$ ), 26.3 (d,  $J_{CP} = 12.0$  Hz,  $CH_2$ ), 25.2 (s,  $CH_2$ ), 24.9 (d,  $J_{CP} = 5.0$  Hz,  $CH_2$ ), 12.5 (d,  $J_{CP} = 44.6$  Hz,  $PCH_2$ ). MS ( $ES^+$ ):  $m/z$ : 389.3 [ $M - Br$ ] $^+$ . HRMS ( $ES^+$ ): calcd. for  $C_{24}H_{42}N_2P$  389.3086; found 389.3083 ( $\epsilon_r = 0.8$  ppm). Anal. Found: C, 60.61; H, 8.57; N, 6.12. Calcd. for  $C_{24}H_{42}BrN_2P$ : C 61.40; H, 9.02; N, 5.97.

**Synthesis of pre-ligand [7](OTf) $_3$ .** Compounds [6]Br (0.30 g, 0.64 mmol) and [2]Br (0.33 g, 0.70 mmol) were heated at 120 °C in  $C_6H_5Cl$  (15 mL) for 15 hours. After evaporation of the solvent, the crude residue and  $NaOTf$  (0.38 g, 2.24 mmol) were stirred in  $CH_2Cl_2$  (20 mL) at rt for 4 hours. After filtration over Celite, evaporation of the solvent and drying under vacuum, [7](OTf) $_3$  (0.71 g, 96%) was obtained as a white powder.  $^1H$  NMR (400.1 MHz,  $CDCl_3$ , 25 °C):  $\delta$  9.22 (s, 1H,  $N_2CH$ ), 7.63 (s, 2H,  $CH_{Im}$ ), 4.42–4.48 (m, 4H,  $NCH_2$ ), 2.35–2.48 (m, 14H,  $CH_2 + CH_{Cy}$ ), 1.77–1.97 (m, 30H,  $CH_{2Cy}$ ), 1.29–1.57 (m, 30H,  $CH_{2Cy}$ ).  $^{31}P\{^1H\}$  NMR (162 MHz,  $CDCl_3$ , 25 °C):  $\delta$  32.4 (s).  $^{13}C\{^1H\}$  NMR (100.6 MHz,  $CDCl_3$ , 25 °C):  $\delta$  136.0 (s,  $N_2CH$ ), 122.9 (s,  $CH_{Im}$ ), 120.7 (q,  $J_{CF} = 320.9$  Hz,  $CF_3$ ), 49.5 (d,  $J_{CP} = 18.7$  Hz,  $NCH_2$ ), 29.9 (d,  $J_{CP} = 40.2$  Hz,  $CH_{Cy}$ ), 26.9 (d,  $J_{CP} = 3.9$  Hz,  $CH_2$ ), 26.3 (d,  $J_{CP} = 11.9$  Hz,  $CH_2$ ), 25.3 (s,  $CH_2$ ), 22.9 (d,  $J_{CP} = 3.6$  Hz,  $CH_2$ ), 12.5 (d,  $J_{CP} = 46.4$  Hz,  $PCH_2$ ). MS ( $ES^+$ ):  $m/z$ : 1009.5 [ $M - CF_3SO_3$ ] $^+$ . HRMS ( $ES^+$ ): calcd. for  $C_{47}H_{81}N_2O_6F_6P_2S_2$  1009.4915; found 1009.4915 ( $\epsilon_r = 0.0$  ppm). Anal. Found: C, 49.58; H, 6.14; N, 2.34. Calcd. for  $C_{48}H_{81}F_9N_2O_6P_2S_3$ : C, 49.73; H, 7.04; N, 2.42.

**Synthesis of complex [8](OTf) $_2$ .** A mixture of [7](OTf) $_3$  (0.10 g, 0.08 mmol),  $PdCl_2$  (0.015 g, 0.08 mmol), anhydrous  $K_2CO_3$  (0.12 g, 0.80 mmol) and pyridine (7.6  $\mu$ L, 0.09 mmol) was stirred at 40 °C in MeCN (5 mL) for 48 hours. After filtration over Celite and evaporation of the solvent under vacuum, [8](OTf) $_2$  (0.082 g, 75%) was obtained as a pale yellow powder. Recrystallization from MeCN/Et $_2$ O at –20 °C gave pale yellow crystals, some of them being suitable for X-ray diffraction analysis.  $^1H$  NMR (400.1 MHz,  $CD_3CN$ , 25 °C):  $\delta$  8.87 (d, 2H,  $J_{HH} = 4.0$  Hz,  $CH_{Py}$ ), 7.94 (t, 1H,  $J_{HH} = 4.0$  Hz,  $CH_{Py}$ ), 7.49 (t, 2H,  $J_{HH} = 8.0$  Hz,  $CH_{Py}$ ), 7.34 (s, 2H,  $CH_{Im}$ ), 4.67 (t, 4H,  $J_{HH} = 7.1$  Hz,  $NCH_2$ ), 2.34–2.48 (m, 14H,  $CH_2 + CH_{Cy}$ ), 1.29–1.96 (m, 60H,  $CH_{2Cy}$ ).  $^{31}P\{^1H\}$  NMR (162 MHz,  $CD_3CN$ , 25 °C):  $\delta$  32.8 (s).  $^{13}C\{^1H\}$  NMR (100.6 MHz,  $CD_3CN$ , 25 °C):  $\delta$  152.0 (s,  $CH_{Py}$ ), 150.9 (s,  $N_2C$ ), 140.0 (s,  $CH_{Py}$ ), 125.9 (s,  $CH_{Py}$ ), 124.1 (s,  $CH_{Im}$ ), 121.5 (q,  $J_{CF} = 320.9$  Hz,  $CF_3$ ), 51.4 (d,  $J_{CP} = 17.0$  Hz,  $NCH_2$ ), 30.2 (d,  $J_{CP} = 40.9$  Hz,  $CH_{Cy}$ ), 27.3 (d,  $J_{CP} = 3.8$  Hz,  $CH_2$ ), 27.1 (d,  $J_{CP} = 12.1$  Hz,  $CH_2$ ), 25.9 (s,  $CH_2$ ), 24.6 (d,  $J_{CP} = 4.1$  Hz,  $CH_2$ ), 13.7 (d,  $J_{CP} = 45.3$  Hz,  $PCH_2$ ). MS ( $ES^+$ ):  $m/z$ : 1114.4 [ $M - OTf$ ] $^+$ . HRMS ( $ES^+$ ): calcd. for  $C_{51}H_{85}Cl_2F_6N_3O_6P_2PdS$  1114.4163; found 1114.4165 ( $\epsilon_r = 0.2$  ppm). Anal. Found: C, 48.51; H, 6.76; N, 3.38. Calcd. for  $C_{52}H_{85}Cl_2F_6N_3O_6P_2PdS_2$ : C, 49.35; H, 6.77; N, 3.32.

**Synthesis of complex [9a,b](OTf).** A mixture of solid *t*BuOK (0.036 g, 0.32 mol) and complex [8](OTf) $_2$  (0.10 g, 0.08 mol) was cooled to –78 °C and THF (5 mL) was added. The suspension was slowly warmed to rt and stirred for 16 hours. After evaporation of the solvent, the solid residue was dissolved in  $CH_2Cl_2$  (10 mL) and filtered over Celite. After purification by chromatography on silica gel ( $CH_2Cl_2$ /AcOEt: 9/1), [9a,b](OTf) (0.032 g, 40%) was obtained as a yellow solid and as a mixture of two diastereomers (*trans/cis*: 85/15).



The major isomer [9a](OTf) was isolated in pure form as a white powder after recrystallization from a MeCN/Et<sub>2</sub>O mixture at rt. Single crystals of this isomer suitable for X-ray diffraction analysis were obtained under the same conditions.

*Trans*-isomer [9a](OTf): <sup>1</sup>H NMR (400.1 MHz, CD<sub>3</sub>CN, 25 °C): δ 7.08 (s, 2H, CH<sub>im</sub>), 4.15–4.19 (m, 2H, NCH<sub>2</sub>), 3.72–3.79 (m, 2H, NCH<sub>2</sub>), 2.54–2.63 (m, 6H, CH<sub>Cy</sub>), 2.41–2.49 (m, 2H, PCH), 2.05–2.15 (m, 2H, CH<sub>2</sub>), 1.64–2.00 (m, 32H, CH<sub>2</sub> + CH<sub>2Cy</sub>), 1.24–1.31 (m, 30H, CH<sub>2Cy</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>3</sub>CN, 25 °C): δ 40.6 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CD<sub>3</sub>CN, 25 °C): δ 167.4 (s, N<sub>2</sub>C), 122.2 (q, *J*<sub>CF</sub> = 322.2 Hz, CF<sub>3</sub>), 121.0 (s, CH<sub>im</sub>), 53.2 (d, *J*<sub>CP</sub> = 16.2 Hz, NCH<sub>2</sub>), 32.2 (d, *J*<sub>CP</sub> = 42.4 Hz, CH<sub>Cy</sub>), 28.3 (d, *J*<sub>CP</sub> = 3.0 Hz, CH<sub>2</sub>), 28.0 (d, *J*<sub>CP</sub> = 4.0 Hz, CH<sub>2</sub>), 27.8 (d, *J*<sub>CP</sub> = 11.1 Hz, CH<sub>2</sub>), 27.4 (d, *J*<sub>CP</sub> = 11.1 Hz, CH<sub>2</sub>), 27.0 (s, CH<sub>2</sub>), 26.7 (s, CH<sub>2</sub>), –0.6 (d, *J*<sub>CP</sub> = 23.2 Hz, PCH).

*Cis*-isomer [9b](OTf): <sup>1</sup>H NMR (600.1 MHz, CD<sub>3</sub>CN, 25 °C): δ 7.06 (s, 2H, CH<sub>im</sub>), 4.10–4.15 (m, 2H, NCH<sub>2</sub>), 3.85–3.94 (m, 2H, CH<sub>2</sub>), 2.75–2.85 (m, 6H, CH<sub>Cy</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, CD<sub>3</sub>CN, 25 °C): δ 40.7 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz, CD<sub>3</sub>CN, 25 °C): δ 162.8 (s, N<sub>2</sub>C), 122.2 (q, *J*<sub>CF</sub> = 322.1 Hz, CF<sub>3</sub>), 121.8 (s, CH<sub>im</sub>), 52.0 (brs, NCH<sub>2</sub>), 34.0 (d, *J*<sub>CP</sub> = 33.2 Hz, CH<sub>Cy</sub>), 2.9 (d, *J*<sub>CP</sub> = 25.7 Hz, PCH). All other <sup>1</sup>H and <sup>13</sup>C NMR signals are hidden by the signals of the major isomer. MS (ES<sup>+</sup>): *m/z*: 407.2 [(M – OTf – Cl)<sub>2</sub>]<sup>+</sup>; 849.4 [M – OTf]<sup>+</sup>. HRMS (ES<sup>+</sup>): calcd. for C<sub>45</sub>H<sub>78</sub>N<sub>2</sub>P<sub>2</sub>Pd 407.2346; found 407.2346 (*ε*<sub>r</sub> = 0.0 ppm); calcd. for C<sub>45</sub>H<sub>78</sub>N<sub>2</sub>P<sub>2</sub>PdCl 849.4377; found 849.4350 (*ε*<sub>r</sub> = 3.2 ppm). The compound [9a](OTf) was assessed to be >95% pure by <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR spectroscopy.

**Synthesis of complex [10](OTf)<sub>2</sub>.** A mixture of solid [9a](OTf) (0.015 g, 0.015 mmol) and AgOTf (0.005 g, 0.018 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and stirred for 5 min at rt. Carbon monoxide was then bubbled through the solution for 20 min. at the same temperature. A quasi-full conversion was observed by <sup>31</sup>P NMR spectroscopy of the aliquot. After filtration over Celite, the solvent was removed under vacuum, and [10](OTf)<sub>2</sub> was dissolved in CD<sub>2</sub>Cl<sub>2</sub> and characterized by multi-nuclear NMR and IR spectroscopy. <sup>1</sup>H NMR (400.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ 7.34 (s, 2H, CH<sub>im</sub>), 4.44–4.50 (m, 2H, NCH<sub>2</sub>), 3.83 (t, 2H, *J*<sub>H-H</sub> = 12.0 Hz, NCH<sub>2</sub>), 3.09–3.17 (m, 2H, PCH), 2.38–2.43 (m, 2H, CH<sub>2</sub>), 2.19–2.28 (m, 6H, CH<sub>Cy</sub>), 1.63–1.98 (m, 32H, CH<sub>2</sub> + CH<sub>2Cy</sub>), 1.13–1.40 (m, 30H, CH<sub>2Cy</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ 41.7 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C): δ 186.5 (s, Pd–CO), 166.8 (s, N<sub>2</sub>C), 122.4 (s, CH<sub>im</sub>), 120.9 (q, *J*<sub>CF</sub> = 321.2 Hz, CF<sub>3</sub>), 52.7 (d, *J*<sub>CP</sub> = 14.4 Hz, NCH<sub>2</sub>), 32.2 (d, *J*<sub>CP</sub> = 41.4 Hz, CH<sub>Cy</sub>), 28.0 (d, *J*<sub>CP</sub> = 4.0 Hz, CH<sub>2</sub>), 27.6 (d, *J*<sub>CP</sub> = 4.0 Hz, CH<sub>2</sub>), 27.3 (d, *J*<sub>CP</sub> = 10.1 Hz, CH<sub>2</sub>), 27.2 (d, *J*<sub>CP</sub> = 10.1 Hz, CH<sub>2</sub>), 26.1 (s, CH<sub>2</sub>), 25.8 (s, CH<sub>2</sub>), 0.6 (d, *J*<sub>CP</sub> = 25.2 Hz, PCH). IR (CH<sub>2</sub>Cl<sub>2</sub>): ν<sub>CO</sub> 2107 cm<sup>-1</sup>. Complex [10](OTf)<sub>2</sub> was not isolated because it evolves slowly (t<sub>1/2</sub> ~ 4 h) to complex [13](OTf)<sub>2</sub>.

**Synthesis of complex [13](OTf)<sub>2</sub>.** A mixture of solid [9a](OTf) (0.015 g, 0.015 mmol) and AgOTf (0.009 g, 0.033 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and stirred for 48 hours at rt. After filtration over Celite, the solvent was removed under vacuum, and [13](OTf)<sub>2</sub> (0.016 g, 95%) was obtained as a brown powder. <sup>1</sup>H NMR (400.1 MHz, CD<sub>3</sub>CN, 25 °C): δ 7.37 (s, 1H, CH<sub>im</sub>), 7.35 (s, 1H, CH<sub>im</sub>), 4.16–4.32 (m, 3H, NCH<sub>2</sub>), 4.03–4.09 (m, 1H, NCH<sub>2</sub>), 3.49–3.56 (m, 1H, PCH), 2.46–2.55 (m, 3H, CH<sub>Cy</sub>), 2.35–2.39 (m, 2H, PCH<sub>2</sub>), 2.14–2.24 (m, 7H, CH<sub>2</sub>, CH<sub>Cy</sub>), 1.74–1.98 (m, 15H, CH<sub>2Cy</sub>), 1.52–1.68 (m, 15H, CH<sub>2Cy</sub>), 1.23–1.48 (m, 30H, CH<sub>2Cy</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>3</sub>CN, 25 °C): δ = 41.2 (s), 32.8 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CD<sub>3</sub>CN, 25 °C): δ 155.7 (s, N<sub>2</sub>C), 123.9 (s, CH<sub>im</sub>), 122.6 (s, CH<sub>im</sub>), 122.2 (q, *J*<sub>CF</sub> = 322.2 Hz, CF<sub>3</sub>), 54.0 (d, *J*<sub>CP</sub> = 12.1 Hz, NCH<sub>2</sub>), 51.2 (d, *J*<sub>CP</sub> = 18.2 Hz, NCH<sub>2</sub>), 32.4 (d, *J*<sub>CP</sub> = 41.4 Hz, CH<sub>Cy</sub>), 30.4 (d, *J*<sub>CP</sub> = 41.4 Hz, CH<sub>Cy</sub>), 28.4 (d, *J*<sub>CP</sub> = 3.0 Hz, CH<sub>2</sub>), 27.7 (d, *J*<sub>CP</sub> = 4.0 Hz, CH<sub>2</sub>), 27.6 (d, *J*<sub>CP</sub> = 11.1 Hz, CH<sub>2</sub>), 27.5 (s, CH<sub>2</sub>), 27.4 (s, CH<sub>2</sub>), 27.3 (s, CH<sub>2</sub>), 27.2 (d, *J*<sub>CP</sub> = 12.1 Hz, CH<sub>2</sub>), 27.1 (d, *J*<sub>CP</sub> = 11.1 Hz, CH<sub>2</sub>), 26.7 (s, CH<sub>2</sub>), 26.3 (s, CH<sub>2</sub>), 26.0 (s, CH<sub>2</sub>), 23.4 (d, *J*<sub>CP</sub> = 4.0 Hz, CH<sub>2</sub>), 13.7 (d, *J*<sub>CP</sub> = 41.4 Hz, PCH<sub>2</sub>), 2.8 (d, *J*<sub>CP</sub> = 23.0 Hz, PCH). MS (ES<sup>+</sup>): *m/z*: 425.2 [(M – 2 OTf)<sub>2</sub>]<sup>+</sup>. HRMS (ES<sup>+</sup>): calcd. for C<sub>45</sub>H<sub>79</sub>N<sub>2</sub>P<sub>2</sub>PdCl 425.2227; found 425.2232 (*ε*<sub>r</sub> = 1.2 ppm). The compound [13](OTf)<sub>2</sub> was assessed to be >95% pure by <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR spectroscopy.

**Synthesis of complex [14](OTf).** A solution of KHMDs (0.5 M in toluene, 632 μL, 0.32 mmol) was added at –78 °C to a solution of complex [8](OTf)<sub>2</sub> (0.10 g, 0.08 mmol) in THF (5 mL). The mixture was slowly warmed to rt and stirred for 12 hours. After evaporation of the solvent, the solid residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and filtered over Celite. Purification by chromatography on silica (CH<sub>2</sub>Cl<sub>2</sub>/AcOEt) gave complex [14](OTf) (0.051 g, 69%) as a brown solid. Recrystallization from MeCN/Et<sub>2</sub>O at –20 °C gave pale yellow crystals, some of them being suitable for X-ray diffraction analysis. <sup>1</sup>H NMR (400.1 MHz, CD<sub>3</sub>CN, 25 °C): δ 6.96 (d, 1H, *J*<sub>H-H</sub> = 4.0 Hz, CH<sub>im</sub>), 6.85 (d, 1H, *J*<sub>H-H</sub> = 4.0 Hz, CH<sub>im</sub>), 4.05–4.15 (m, 2H, NCH<sub>2</sub>), 3.87–3.94 (m, 1H, NCH<sub>2</sub>), 3.59–3.66 (m, 1H, NCH<sub>2</sub>), 1.18–2.64 (m, 71H, CH<sub>2</sub> + PCH + CH<sub>Cy</sub> + CH<sub>2Cy</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>3</sub>CN, 25 °C): δ 40.9 (s), 28.6 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CD<sub>3</sub>CN, 25 °C): δ 171.5 (s, N<sub>2</sub>C), 122.8 (s, CH<sub>im</sub>), 120.3 (s, CH<sub>im</sub>), 122.2 (q, *J*<sub>CF</sub> = 322.0 Hz, CF<sub>3</sub>), 54.0 (d, *J*<sub>CP</sub> = 20.2 Hz, NCH<sub>2</sub>), 51.7 (s, NCH<sub>2</sub>), 47.3 (d, *J*<sub>CP</sub> = 10.1 Hz, CH<sub>Cy</sub>), 36.2 (s, CH<sub>2</sub>), 35.4 (s, CH<sub>2</sub>), 33.3 (brd, *J*<sub>CP</sub> = 44.4 Hz, CH<sub>Cy</sub>), 31.3 (d, *J*<sub>CP</sub> = 53.5 Hz, CH<sub>Cy</sub>), 30.2 (d, *J*<sub>CP</sub> = 4.0 Hz, CH<sub>2</sub>), 29.8 (d, *J*<sub>CP</sub> = 4.0 Hz, CH<sub>2</sub>), 29.6 (brs, CH<sub>2</sub>), 28.7 (d, *J*<sub>CP</sub> = 6.1 Hz, CH<sub>2</sub>), 28.7 (s, CH<sub>2</sub>), 28.4 (s, CH<sub>2</sub>), 28.4 (d, *J*<sub>CP</sub> = 11.1 Hz, CH<sub>2</sub>), 28.3 (d, *J*<sub>CP</sub> = 8.1 Hz, CH<sub>2</sub>), 28.2 (d, *J*<sub>CP</sub> = 10.1 Hz, CH<sub>2</sub>), 28.0 (d, *J*<sub>CP</sub> = 7.1 Hz, CH<sub>2</sub>), 27.9 (d, *J*<sub>CP</sub> = 11.1 Hz, CH<sub>2</sub>), 27.8 (s, CH<sub>2</sub>), 27.7 (s, CH<sub>2</sub>), 27.6 (s, CH<sub>2</sub>), 27.5 (d, *J*<sub>CP</sub> = 3.0 Hz, CH<sub>2</sub>), 27.0 (brs, CH<sub>2</sub>), 26.8 (brs, CH<sub>2</sub>), 17.1 (d, *J*<sub>CP</sub> = 20.2 Hz, PC), –3.4 (d, *J*<sub>CP</sub> = 13.1 Hz, PCH), –8.9 (d, *J*<sub>CP</sub> = 46.5 Hz, PCH). MS (ES<sup>+</sup>): *m/z*: 813.5 [M – OTf]<sup>+</sup>. HRMS (ES<sup>+</sup>): calcd. for C<sub>45</sub>H<sub>77</sub>N<sub>2</sub>P<sub>2</sub>Pd 813.4597; found 813.4614 (*ε*<sub>r</sub> = 2.1 ppm). The compound [14](OTf) was assessed to be >95% pure by <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR spectroscopy.

**Single-crystal X-ray diffraction analyses for complexes [4](OTf), [8](OTf)<sub>2</sub>, [9a](OTf), and [14](OTf).** Single crystals suitable for X-ray diffraction were coated with paratone oil and mounted onto the goniometer. The X-ray crystallographic data were obtained at low temperature from a Bruker Apex2 diffractometer (Mo Kα radiation source, λ = 0.71073 Å, graphite monochromator) equipped with an Oxford Cryosystem. The structures have been solved with ShelXS86,<sup>30</sup> Superflip<sup>31</sup> or ShelXT<sup>32</sup> and refined by means of least-squares procedures on F or F<sup>2</sup> using the PC version of the program CRYSTALS.<sup>33</sup> The scattering factors for all the atoms were used as listed in the International Tables for X-ray Crystallography.<sup>34</sup> Absorption correction was performed using a MULTISCAN procedure.<sup>35</sup> All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry and U[iso](H) (in the range 1.2–1.5 times U[eq] of the parent atom), after which the positions were refined with riding constraints. The unit cell of complex [4](OTf) contained two crystallographically independent molecules having close metrical parameters and one of triflate anions was founded to be disordered in 0.8/0.2 occupation ratio. For [8](OTf)<sub>2</sub>, it was not possible to resolve some diffuse electron-density residuals attributed to enclosed solvent molecules and SQUEEZE facility from PLATON was applied to remove their contribution.<sup>36</sup> In the structure of complex [14](OTf) one of Cy substituents belonging to monoyleide moiety presented a statistic disorder with 0.65/0.35 occupation ratio. Detailed crystallographic data and structural refinement parameters are given in Table S1 in the SI.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

<sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR spectra for all new compounds, <sup>19</sup>F NMR spectra for [13](OTf)<sub>2</sub>, IR spectrum for [10](OTf)<sub>2</sub> and additional crystallographic data for complexes [4](OTf), [8](OTf)<sub>2</sub>, [9a](OTf), and [14](OTf) (PDF).

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### Notes

The authors declare no competing financial interest.

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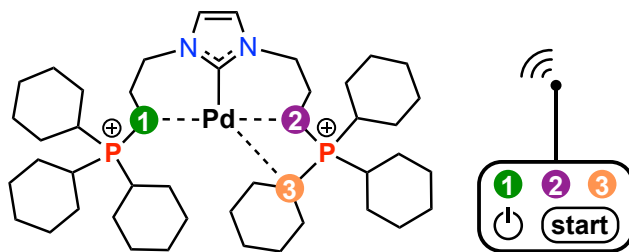
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- (19) The reaction between Pd(CO) complex [10](OTf)<sub>2</sub> and AgOTf was also found to be thermodynamically unfavorable, the E<sub>p</sub><sup>ox</sup> value of [10](OTf)<sub>2</sub> being measured at 1.92V/SCE (Pt electrode, CH<sub>2</sub>Cl<sub>2</sub>, nBu<sub>4</sub>OTf, 200 mV/s).
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