

# Platinum(0)-Catalyzed Intramolecular Addition of a C–H Bond onto the P=C Bond of a Phosphaalkene

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The phosphaalkene *E*-Mes\*P=CHPh (1) reacts with a stoichiometric amount of  $[Ni(COD)_2]$  at room temperature for 15 h in hexanes to afford the 1-P-benzyl-benzophospholane 2, which results from the formal addition of the C-H bond of one *tert*-butyl group onto the P=C double bond. The formulation of benzophospholane 2 was confirmed by an X-ray diffraction study of the corresponding trans  $[Pd(2)Cl_2]$  complex 3a (meso complex). Formation of 2 was also achieved by using a catalytic amount of the [Pt(PCy<sub>3</sub>)<sub>2</sub>] catalyst (20 mol %) in hexanes at 65 °C for 15 h. Extension of this procedure to the bis-phosphaalkene  $[(E)-Mes^*P=CH]_2-(m-C_6H_4)$  (4) afforded the corresponding bisbenzophospholane, which was recovered as a mixture of diastereomers 5a and 5b. On the basis of DFT calculations a complete mechanistic pathway was proposed in the case of nickel. The overall mechanism involves a preliminary complexation of 1 at Ni to afford a 12 VE  $\eta^1$ -complex, which then evolves to yield the 14 VE  $\eta^2$ -species featuring coordination of one C-H of a *tert*-butyl group. Insertion of nickel into this C-H bond followed by the formation of a P-C bond between phosphorus and the methyl group affords a 14-VE hydrido complex featuring a  $\eta^3$ -benzyl ligand. Isomerization of this species through complexation of the phosphorus atom of the benzophospholane unit and decomplexation of the phenyl group affords a 14-VE species, which undergoes a reductive elimination to finally yield the 12-VE Ni complex of 2. A similar mechanism was proposed in the case of platinum considering that the catalytically active species is the 12-VE [Pt(PMe<sub>3</sub>)] complex. In good agreement with NMR data this mechanism involves, as the most stable intermediate, a 16-VE complex featuring the benzophospholane ligand, which is coordinated to the [Pt(H)(PMe<sub>3</sub>)] fragment through the phosphorus atom lone pair and the benzylic carbon atom. NMR data and DFT calculations confirm that, in this intermediate, the hydride is located *trans* to the phosphorus atom of the benzophospholane ligand.

## Introduction

Phosphaalkenes, the phosphorus equivalents of alkenes and imines, constitute a very peculiar class of compounds.<sup>1</sup> Thanks to their electronic properties, which profoundly differ from that of their nitrogen counterparts, they have found numerous applications in coordination chemistry, for example, in the stabilization of very electron rich metal fragments.<sup>2</sup> They also found important applications as ligands in homogeneous catalysis in transformations of important synthetic value.<sup>3</sup> In addition, the presence of both a polarized  $\sigma$ -system and a genuine  $\pi$ -system makes them interesting and versatile precursors of acyclic and cyclic

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# Article

tertiary phosphines through reactions with the P=C double bond (additions of nucleophiles at phosphorus, epoxidation, cycloadditions).<sup>1</sup> More recently, they were also employed as precursors of phosphorus polymeric materials through radical and anionic polymerization and copolymerization processes.<sup>4</sup> An interesting parallel can therefore be drawn between the reactivity of phosphaalkenes and that of alkenes. The challenge consisting in duplicating the chemistry of alkenes to phosphaalkenes still remains of utmost importance. As part of a study on the reactivity of kinetically stabilized phosphaalkenes toward zerovalent group 10 complexes, we recently found that intramolecular addition of a C-H bond onto a P=C double bond could be stoichiometrically and catalytically promoted by Ni(0) and Pt(0) complexes, respectively. Herein we report on these experimental finding as well as on a complete theoretical DFT study that allows us to propose a rational mechanism in both cases.

#### **Results and Discussion**

Unlike what we had initially expected, reacting *E*-Mes\*-P=CHPh (Mes\* = 2,4,6-tri-*tert*-butylphenyl) (1) with [Ni(CO-D)<sub>2</sub>] in a 1 to 1 ratio in hexanes (mixture of isomers) at room temperature did not afford a Ni(0) complex of 1. Indeed, monitoring the reaction by <sup>31</sup>P NMR spectroscopy revealed the formation of a single new phosphorus derivative, 2, which appears as a singlet at much higher field ( $\delta = -7.2$  ppm) than 1 ( $\delta = 259$  ppm). The formation of compound 2 was also accompanied by deposition of metallic nickel (eq 1).



Compound 2, which was found to be oxygen sensitive, was obtained as a pale yellow solid after usual workup with a 60% yield. The formulation of 2, a 1-P-benzyl benzophospholane, was established on the basis on <sup>1</sup>H and <sup>13</sup>C NMR and mass spectrometry, as well as elemental data. In particular, two new signals, each integrating for one hydrogen atom, are observed for the two diastereotopic benzylic hydrogens at 3.00 and 2.61 ppm. They each appear as a doublet of doublets resulting from the coupling with the adjacent P atom  $({}^{2}J_{P-H} = 6.3 \text{ Hz} \text{ and } {}^{2}J_{P-H} = 6.0 \text{ Hz},$  respectively) and with each other  $({}^{2}J_{H-H} = 13.3 \text{ Hz})$ . This was further confirmed by an X-ray crystal structure study of its  $PdCl_2$  complex. Indeed, reaction of 2 with half an equivalent of [Pd(COD)Cl<sub>2</sub>] in toluene at 110 °C overnight cleanly afforded diastereomeric complexes **3a**,**b**, which were formed in a 3 to 2 ratio, respectively, and isolated with a combined 92% yield (eq 2). Unfortunately, 3a and 3b could



Figure 1. Molecular structure of complex 3a with thermal ellipsoids projected at the 50% probability level. The numbering is arbitrary and different from that used in the <sup>13</sup>C NMR spectrum. Selected bond distances (Å) and angles (deg): Pd–P-(1) 2.3345(7), P(1)–C(1) 1.833(2), P(1)–C(8) 1.835(2), Pd–P(1') 2.3345(7), Pd–(Cl1) 2.3109(6), P(1)–Pd–Cl(1) 86.48(2), P-(1)–Pd–P(1') 180.0, Pd–P(1)–C(1) 110.6(1), Pd–P(1)–C(8) 116.8(1), C(1)–P(1)–C(8) 94.2(1).

not be separated during the workup, but single crystals of complex **3a**, which is the *meso*-complex, were obtained by slowly cooling a solution of the mixture of the two complexes in hexanes at -25 °C. According to the <sup>1</sup>H and <sup>13</sup>C NMR data of **3a** and **3b**, which are very similar, we can reasonably assume that complex **3b** also adopts a *trans* geometry.



A view of one molecule of 3a is presented in Figure 1, and the most significant metric parameters are listed in the corresponding legend. Crystal data of complex 3a are reported in Table 1. As can be seen, 1 is a very bulky ligand, which probably does not favor the formation of a *cis*-[PdCl<sub>2</sub>] complex. Apart from this, the structure of 3a does not deserve further comment.

Further experiments were carried out to evidence the formation of intermediates in the formation of **2**, but, whatever the experimental conditions used, the <sup>31</sup>P NMR spectrum of the crude reaction mixture revealed only the presence of compounds **1** and **2**. The use of catalytic conditions  $(20\% \text{ of Ni}(\text{COD})_2)$  did not allow a full conversion to be reached, and the reaction stopped very rapidly, with a concomitant precipitation of metallic Ni. Addition of PCy<sub>3</sub> as a stabilizing ligand of nickel to form a soluble, and hopefully more stable, Ni(0) complex was also attempted  $(5\% \text{ Ni}(\text{COD})_2 \text{ and } 10\% \text{ PCy}_3)$ , but it did not yield further improvement. Finally, the transformation with a stoichiometric amount of Ni nanoparticles stabilized by TOP (tri-*n*-octylphosphine) was also attempted, but no conversion was observed.<sup>5</sup>

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Table 1. Crystallographic Data for Complex 3a

empirical formula	$C_{50}H_{70}Cl_2P_2Pd(CH_2Cl_2)$
mol wt	1080.15
cryst habit	yellow block
cryst size (mm)	$0.24 \times 0.24 \times 0.22$
cryst syst	orthorhombic
space group	Pbca
a (Å)	16.311(1)
b (Å)	17.109(1)
c (Å)	19.404(1)
$V(Å^3)$	5415.0(5)
Z	4
calcd density ( $g \text{ cm}^{-3}$ )	1.325
abs coeff $(cm^{-1})$	0.731
$2\rho_{\rm max}$ (deg)	30.03
F(000)	2256
index ranges	-7 to 22; -23 to 16; -26 to 18
no. of collected/indep reflns	15758/7427
no. of reflns used	3971
R <sub>int</sub>	0.0326
abs corr	multiscan; 0.8441 min, 0.8558 max
no. of params refined	285
no. of reflns/param	13
final $R1^a/wR2^b$ $(I \ge 2\sigma I)$	0.0444/0.1207
goodness of fit on $F^2$	0.918
diff peak/hole (e $Å^{-3}$ )	1.043(0.079)/-0.481(0.079)
${}^{a}\mathbf{R}1 = \sum   F_{0}  -  F_{0}   / \sum  F_{0} , {}^{b}\mathbf{y}$	$wR2 = (\sum w   F_0  -  F_0  ^2 / \sum w  F_0 ^2)^{1/2}.$

With the aim of developing a catalytic version of this rearrangement, further experiments were also conducted with the heavier congeners of the group 10 metals. In first attempts, palladium was tested in the form of the  $[Pd(dba)_2]$  complex. The use of 20 mol % of catalyst at 65 °C for 20 h yielded a conversion of only 5%. The use of PCy<sub>3</sub> as a stabilizing ligand of palladium (1 equiv with regard to the catalyst) yielded the same conversion. Finally, the most satisfying results were obtained by replacing nickel by platinum. Indeed, reaction of 1 with 10 mol % of the 14-VE [Pt(PCy<sub>3</sub>)<sub>2</sub>] complex at 65 °C for 60 h in hexanes cleanly afforded **2** with a 80% yield (eq 3). A similar conversion was obtained with 20 mol % of catalyst after heating at 65 °C for 15 h.

$$1 \xrightarrow{[\text{Pt}(\text{PCy}_3)_2(10 \text{ mol }\%)]{\text{hexanes, 65 °C, 60 h}}} 2$$
(3)

Having found an efficient catalytic formation of benzophospholane **2** from phosphaalkene **1**, we wished to extend this procedure to the formation of the corresponding bisbenzophospholane, a potential precursor of a PCP pincer ligand.<sup>6</sup> Toward this goal, the bis-phosphaalkene **4** was synthesized. Reaction of **4** with 20 mol % of the [Pt-(PCy<sub>3</sub>)<sub>2</sub>] catalyst at 65 °C in hexanes for 15 h cleanly afforded

## Scheme 1. Formation of a Benzophospholane from Mes\*P=CH<sub>2</sub> Catalyzed by AlCl<sub>3</sub>



the bis-benzophospholane **5** as a mixture of diastereomers in a 1:1 ratio with a 82% yield. Compound **5** was recovered as a white oxygen-sensitive solid after usual workup and identified by conventional NMR methods, mass spectrometry, and elemental analysis (eq 4).



Mechanism of the H Migration. The formation of benzophospholane 2 results from the transfer of one hydrogen atom of one *tert*-butyl group to the C-carbon atom of the phosphaalkene. This type of rearrangement is not totally unprecedented since Gates et al. reported on the reactivity of Mes\*P=CH<sub>2</sub> toward MX<sub>3</sub> (M = Al, Ga) in 2002.<sup>7</sup> Interestingly, they showed that, under catalytic conditions, an intramolecular C-H activation took place to afford the corresponding 1-P-methyl benzophospholane. On the basis of isotopic labeling experiments, they proposed a convincing mechanism relying on the transient formation of a phosphenium species that further inserts into the C-H bond of a *tert*butyl group to form a P-H bond, followed by H migration on the neighboring methylene fragment. The mechanism proposed is depicted in Scheme 1.

Formation of **2** cannot be rationalized following a similar pathway since under the conditions used no cationic species are expected to be formed upon reacting  $[Ni(COD)_2]$  or  $[Pt(PCy_3)_2]$  with **1**. In order to shed some light on our transformation, DFT calculations were carried out in the case of both nickel and platinum (see Experimental Section for further details). In this study we did not consider the complete substitution scheme of the Mes\* group. Indeed, as the *para tert*-butyl group is not expected to play a significant role in the transformation, it was replaced by a H atom.

**Mechanism with Ni.** In the case of nickel, examination of the <sup>1</sup>H NMR data of the crude reaction mixture revealed that the COD ligand is released during the process. As mentioned

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Figure 2. Computed energetic pathway for the transformation of 1 into 2 in the case of nickel. Energies are given in kcal/mol.

above, when a ligand  $(PCy_3 \text{ with } Ni(COD)_2 \text{ or } TOP \text{ on } Ni nanoparticles)$  was present, no reaction occurred. Therefore, all our calculations were conducted assuming that no other ligand apart from 1 is linked to nickel during the transformation. The complete computed energetic pathway is presented in Figure 2.

Nickel can bind to ligand 1 either through the lone pair of 1 ( $\eta^1$ -coordination) or through the  $\pi$ -system ( $\eta^2$ -coordination). Calculations revealed that the 12-VE  $\eta^1$ -complex  $I_{Ni}$  is less stable than the 14-VE  $\eta^2$ -species  $II_{Ni}$  by 23.6 kcal/ mol. Interestingly,  $II_{Ni}$  involves the  $\eta^2$ -coordination of a C-H bond (d(Ni-H) = 1.727 Å, d(Ni-C) = 2.155 Å, d(C-C)H) = 1.138 Å) of one methyl group of one the *tert*-butyl groups on the highly unsaturated Ni center. As expected, this complex is the precursor of the Ni(II) hydride species  $III_{Ni}$ , which results from the insertion of nickel into the C-H bond  $(II_{Ni}-TS-III_{Ni})$ . As can be seen, this intramolecular C-H oxidative addition is quite facile, requiring a small activation barrier ( $\Delta E^{\dagger} = +11.1$  kcal/mol). Activation of an aliphatic C-H bond by a late transition metal, especially on the  $\alpha$ position of a P-aryl group such as  $P(o-tol)(R)_2$  or  $P(R)_2$ Mes, to yield the cyclometalated product was already reported,<sup>8</sup> as well as other C-H bond activations on aliphatic phosphine complexes of various transition metals.<sup>9</sup> Complex  $III_{Ni}$  is a 16-VE species in which both the P=C double bond and one C=C bond of the phenyl ring are coordinated to Ni. From this hydride complex, the next step involves the formation of the P–C bond to yield the benzophospholane complex  $IV_{Ni}$ through an exothermic process ( $\Delta E = -8.9$  kcal/mol). Complex  $IV_{Ni}$  is a 14-VE species that features coordination of a  $\eta^3$ -benzyl ligand. A view of the transition state (III<sub>Ni</sub>- $TS-IV_{Ni}$ ) is presented in Figure 3, and the most significant metric parameters are listed in the corresponding legend. We then found that complex  $IV_{Ni}$  can isomerize into the 14-VE species  $V_{Ni}$ , which involves coordination of the phosphorus



Figure 3. View of the theoretical structure of  $III_{Ni}$ -TS-IV<sub>Ni</sub>. Selected bond distances (Å) and angles (deg): P-C(1) 1.786, C(1)-C(2) 1.433, C(2)-C(3) 1.437, C(3)-Ni 2.110, C(2)-Ni 2.103, C(1)-Ni 2.029, P-Ni 2.282, H-Ni 1.502, C(4)-Ni 2.020, C(4)-P 2.389, H-Ni-P 133.218, H-Ni-C(1) 165.872, H-Ni-C(2) 127.200, H-Ni-C(3) 92.252, H-Ni-C(4) 89.883, Ni-C(4)-P 61.676, C(4)-P-Ni 51.170, P-Ni-C(4) 67.154.

atom lone pair of the benzophospholane unit. The two complexes possess very similar energy, and the isomerization involves here again a weak activation barrier of  $\Delta E^{\pm} = +10.3$  kcal/mol.

Finally it appears that the structure of complex  $V_{Ni}$  is well adapted to the final reductive elimination, which affords the 12-VE  $\eta^1$ -complex Ni(0) VI<sub>Ni</sub>. This reductive elimination process is the rate-determining step of the whole process ( $\Delta E^{\ddagger} = +14.3 \text{ kcal/mol}$ ), which is highly exothermic (from I<sub>Ni</sub> to VI<sub>Ni</sub>  $\Delta E = -27.6 \text{ kcal/mol}$ ). Importantly, we note that all the energetic barriers involved in this computed pathway are compatible with the experimental conditions used.

**Mechanism with Pt.** Having proposed a mechanism for the stoichiometric transformation involving nickel, we then turned our attention to the platinum-catalyzed process. In contrast to the reaction promoted by Ni(0) species described above, monitoring the catalytic experiments by <sup>31</sup>P NMR revealed that a few intermediates could be observed in the case of both the mono-phosphaalkene **1** and the bis-phosphaalkene **4**. However, because of the catalytic loadings, these species were observed in minor amounts, which prompted us to carry out stoichiometric reactions in C<sub>6</sub>D<sub>6</sub> to attempt the identification of some intermediates by

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Figure 4. Computed energetic pathway for the transformation of 1 into 2 using [Pt(PMe<sub>3</sub>)] as catalyst. Energies are given in kcal/mol.

 ${}^{31}P{}^{1}H{}$  and  ${}^{1}H{}$  NMR. Essentially the same intermediates were observed in the two cases, showing that the two phosphaalkene moieties in 4 react independently and successively and that the phosphorus atoms are not electronically coupled. The reaction between 1 and  $[Pt(PCy_3)_2]$  was highly informative, even in the early stages. Indeed, within 15 min, the <sup>31</sup>P NMR spectrum showed the presence of the two starting materials ( $\delta = 257$  ppm for 1 and 62 ppm for  $[Pt(PCy_3)_2]$ ), but also the formation of a new complex (roughly the same intensity as 1) and the release of 1 equiv of PCy<sub>3</sub> as well as the final product. This complex is characterized by an AMX spin system pattern with two very different  $J_{Pt-P}$  coupling constants and a relatively small  ${}^{2}J_{P-P}$  coupling constant, attesting to a *cis* location of the two phosphine groups:<sup>10</sup> at  $\delta = -31.0$  ppm ( ${}^{1}J_{Pt-P} = 984$  Hz,  ${}^{2}J_{P-P} = 27.9$  Hz) and  $\delta = +51.7$  ppm ( ${}^{1}J_{Pt-P} = 2952$ Hz,  ${}^{2}J_{P-P} = 27.9$  Hz). Importantly, recording of the corresponding <sup>1</sup>H NMR spectrum indicated that this intermediate is a platinum hydrido complex ( ${}^{1}J_{H-Pt} = 1711$  Hz) and that the hydride ligand is located trans to the upfield shifted phosphorus atom ( ${}^{2}J_{H-P} = 176$  Hz). This was confirmed by the  ${}^{31}$ P spectrum, in which the signal at -31.0 ppm is further split because of the large  ${}^{2}J_{H-P}$  coupling constant of 176 Hz. According to the <sup>31</sup>P NMR spectroscopy, this stoichiometric reaction afforded, after 2 h at room temperature, compound **2** and the catalytic precursor  $[Pt(PCy_3)_2]$ , which has been partly re-formed. Overall, this mechanistic study provided the following key points for the DFT calculations: (a) 1 equiv of  $PCy_3$  is released during the process; (b) a complex featuring two types of phosphines and one hydride ligand is an observable intermediate.

Calculations were thus undertaken and, in order to save computation time, the remaining coordinated  $PCy_3$  was modelized by a PMe<sub>3</sub> group. The overall energetic pathway is presented in Figure 4. From a mechanistic point of view, this energetic pathway is quite similar to that proposed in the case of nickel. The first step of the mechanism involves coordination of the phosphaalkene onto the 12-VE [Pt(PMe<sub>3</sub>)] fragment. Contrary to the analogous nickel species  $II_{Ni}$ , formation of the  $\eta^2$ -complex  $II_{Pt}$  is slightly exothermic.  $II_{Pt}$  is a 14-VE complex that features only a very weak agostic interaction with one hydrogen atom of one tertbutyl group (d(Pt-H) = 2.220 Å, d(C-H) = 1.108 Å vs1.099 Å for the two other C-H bonds of the methyl group). Like in the case of nickel, formation of complex III<sub>Pt</sub>, which results from the insertion of the platinum fragment into the C-H bond, is an exothermic process ( $\Delta E = +6.6 \text{ kcal/mol}$ ) that requires an activation barrier of  $\Delta E^{\pm} = +14.6$  kcal/mol (through II<sub>Pt</sub>-TS-III<sub>Pt</sub>). Complex III<sub>Pt</sub> is a tetracoordinated 16-VE hydrido complex that adopts a distorted square-planar geometry ( $CH_2-Pt-H = 70.7^\circ$ , H-Pt-P $(of PMe_3) = 77.7^\circ$ ). Like in the case of nickel, the following step is the ring closure forming the benzophospholane ring. This step, which also requires a relatively weak activation energy  $(\Delta E^{\dagger} = +11.4 \text{ kcal/mol through } III_{Pt} - TS - IV_{Pt})$ , was found to be much more exothermic ( $\Delta E = -22.6$  kcal/ mol) than in the case of nickel. The new complex formed, IV<sub>Pt</sub>, is a 16-VE hydrido complex that involves the  $\eta^3$ coordination of a benzylic ligand. The second part of the mechanism is also similar to that proposed in the case of nickel apart from the formation of the 16-VE hydrido complex  $VI_{Pt}$ , which could not be rationalized without considering that IVPt first undergoes decomplexation of the arene moiety to afford the 14-VE hydrido complex  $V_{Pt}$ , which adopts T-shaped geometry (no acceptable transition state structure connecting IV<sub>Pt</sub> to VI<sub>Pt</sub> was found). Importantly, we found that VIPt lies at lower energy than the other hydrido intermediates. Therefore one can reasonably assume that this intermediate corresponds to the hydrido complex observed in both the <sup>1</sup>H and <sup>31</sup>P NMR spectra. As expected, the hydride ligand is located *trans* to the benzophospholane ligand (the most upfield shifted phosphorus signal), the two

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Figure 5. View of the theoretical structure of VIPt-TS-VIIPt. Selected bond distances (Å) and angles (deg): P(1)-C 1.910, C-H 1.525, H-Pt 1.640, C-Pt 2.175, P(1)-Pt 2.434, Pt-P(2) 2.233, Pt-P(1)-C 58.630, P(1)-C-H 120.501, P(1)-C-Pt 72.802, C-H-Pt 86.763, P(1)-Pt-H 92.294, P(1)-Pt-P(2) 136.485, H-Pt-P(2) 130.256.

phosphines being fixed in a cis arrangement. Furthermore, another important piece of data is given by the small magnitude of the  ${}^{1}J$  coupling constant (984 Hz) between platinum and the benzophospholane ligand. This phenomenon is not totally unprecedented, and we already noted that  $\eta^2$ -coordination of a  $\lambda^4$ -phosphinine anion to the cationic [Pt(PPh<sub>3</sub>)Cl]<sup>+</sup> fragment resulted in a decrease of the magnitude of this  ${}^{1}J_{Pt-P}$  coupling constant ( ${}^{1}J_{Pt-P} = 2793$  Hz to be compared with  ${}^{1}J_{Pt-P} = 4752$  Hz for the PPh<sub>3</sub> ligand).<sup>11</sup> To some extent, there is an analogy between the two species since complex VIPt can also be regarded as the complexation of a phosphinomethanide ligand  $(R_1R_1P-C(-)R_3R_4)$  to the cationic  $[Pt(H)(PCy_3)]^+$  fragment. Finally, the last step of the transformation is the reductive elimination, which yields the 14-VE Pt(0) complex VII<sub>Pt</sub>, which adopts a linear geometry. The activation barrier needed to promote this transformation (through VIPt-TS-VIIPt) was found to be quite similar to that computed in the case of nickel ( $\Delta E^{\ddagger} = +14.1 \text{ vs } 14.3$ kcal/mol). A view of the computed structure of VIPt-TS-VII<sub>Pt</sub> is presented in Figure 5, and the most relevant metric parameters are listed in the corresponding legend. Finally, our calculations also revealed that complex  $VII_{Pf}$ reacts with released PMe<sub>3</sub> to regenerate the  $[Pt(PMe_3)_2]$ complex (not depicted in the scheme for the sake of clarity), in good agreement with NMR observations made during the stoichiomertic experiment. Indeed, the conversion of VIIPt  $(+ PMe_3)$  into the free benzophospholane and  $[Pt(PMe_3)_2]$ was found to be exothermic ( $\Delta E = -9.9$  kcal/mol).

## Conclusion

In this study, we have evidenced the first example of a metalmediated addition of a C-H bond onto a phosphorus-carbon double bond. Interestingly, this rearrangement was also successfully extended to a bis-phosphaalkene such as 4, thus yielding a new class of pincer ligands featuring benzophospholane as pendant ligands. Although no experiments have been carried out in this direction, one may reasonably expect that this rearrangement could also be extended to functional phospaalkenes featuring other aromatic substituents at the carbon atom. Furthermore, the appreciable kinetic stability of intermediates such as VIPt also offers interesting perspectives because of the presence of a potentially reactive Pt-H bond. All these developments are currently underway in our laboratories and will be reported in due course.

#### **Experimental Section**

Synthesis. All reactions were routinely performed under an inert atmosphere of argon or nitrogen using Schlenk and glovebox techniques and dry deoxygenated solvents. Dry hexanes and tetrahydrofuran were obtained by distillation from Na/benzophenone. Dry dichloromethane was distilled on P2O5 and dry toluene on metallic Na. Nuclear magnetic resonance spectra were recorded on a Bruker AC-300 SY spectrometer operating at 300.0 MHz for <sup>1</sup>H, 75.5 MHz for <sup>13</sup>C, and 121.5 MHz for <sup>31</sup>P. Solvent peaks are used as internal reference relative to Me<sub>4</sub>Si for <sup>1</sup>H and <sup>13</sup>C chemical shifts (ppm); <sup>31</sup>P chemical shifts are relative to an 85% H<sub>3</sub>PO<sub>4</sub> external reference. Coupling constants are given in hertz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; v, virtual; p, pseudo. Compounds 1 and 4 were prepared using the Phospha-Wittig approach, which relies on the reaction of [Mes\*P=PMe<sub>3</sub>] with the corresponding aldehydes.<sup>12</sup> Ni(COD)<sub>2</sub>,<sup>13</sup> [Pd(COD)Cl<sub>2</sub>],<sup>14</sup> [Pd(dba)<sub>2</sub>],<sup>15</sup> and [Pt(PCy<sub>3</sub>)<sub>2</sub>]<sup>16</sup> were prepared according to reported procedures. All other reagents and chemicals were obtained commercially and used as received. Elemental analyses were performed by the "Service d'Analyse du CNRS", at Gif sur Yvette, France.

Synthesis of Compound 2. Phosphaalkene 1 (100 mg, 0.27 mmol) was dissolved in 30 mL of distilled and degassed hexanes in a glovebox. Then, [Pt(PCy<sub>3</sub>)<sub>2</sub>] (41 mg, 0.05 mmol) was added, and the resulting solution was stirred in a oil bath at 65 °C for 15 h. After checking by <sup>31</sup>P NMR for complete disappearance of the starting product, the solvent was removed in vacuo. The solid obtained was then dissolved in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and then filtered over a pad of silica gel under an inert atmosphere in a Schlenk filter and eluted with another 150 mL of dry CH2Cl2. Solvent was then removed in vacuo. Compound 2 was obtained as a white solid; yield 80% (80 mg). HRMS: C<sub>25</sub>H<sub>35</sub>P calcd 366.2476 g·mol<sup>-1</sup>, found 366.2488 g·mol<sup>-1</sup>. Anal. Calcd [C<sub>25</sub>H<sub>35</sub>P] (366.5): C 81.92, H 9.63. Found: C 82.17, H 9.56.



<sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  -7.7 (s); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.28 (dd, 1H, <sup>4</sup>J<sub>P-C</sub> = 4.0 Hz, <sup>4</sup>J<sub>H-H</sub> = 1.7 Hz, *H*C5), 7.00–6.87 (m, 5H, H aromatic), 6.80 (t, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.3 Hz, H<sub>p</sub> of C<sub>6</sub>H<sub>5</sub>), 3.00 (dd,

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1H,  ${}^{2}J_{P-H} = 6.3$  Hz,  ${}^{2}J_{H-H} = 13.3$  Hz, CH<sub>2</sub> benzyl group), 2.61 (dd, 1H,  ${}^{2}J_{P-H} = 6.0$  Hz,  ${}^{2}J_{H-H} = 13.3$  Hz, CH<sub>2</sub> benzyl group), 1.60–1.52 (m, 2H, CH<sub>2</sub> of benzophospholane), 1.40 (s, 9H, t-Bu group grafted on C6), 1.16 (s, 3H, Me of benzophospholane), 1.08 (s, 9H, t-Bu group grafted on C4), 0.90 (s, 3H, Me of benzophospholane);  ${}^{13}C{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  158.9 (s, C2), 152.7 (d,  ${}^{2}J_{P-C} = 13.8$  Hz, C6), 152.4 (s, C4), 139.6 (d,  ${}^{2}J_{P-C} = 8.0$  Hz, C<sub>ipso</sub> of phenyl), 136.2 (d,  ${}^{2}J_{P-C} = 24.1$  Hz, C1) 129.7 (d,  ${}^{3}J_{P-C} = 7.5$  Hz, C<sub>o</sub> of phenyl), 128.7 (s, C<sub>m</sub> of phenyl), 126.0 (d,  ${}^{5}J_{P-C} = 2.3$  Hz, C<sub>p</sub> of phenyl), 122.0 (d,  ${}^{3}J_{P-C} = 4.2$  Hz, C5), 119.0 (s, C3), 46.7 (d,  ${}^{2}J_{P-C} = 6.9$  Hz, C-C2), 38.1 (d,  ${}^{1}J_{P-C} = 24.1$  Hz, CH<sub>2</sub> benzyl group), 37.7 (d,  ${}^{3}J_{P-C} = 1.7$  Hz, C of t-Bu grafted on C4), 34.2 (d,  ${}^{3}J_{P-C} = 4.0$  Hz, Me of benzophospholane), 35.1 (s, C of t-Bu group grafted on C4), 34.2 (d,  ${}^{3}J_{P-C} = 4.0$  Hz, Me of benzophospholane), 33.8 (s, Me of benzophospholane), 32.7 (d,  ${}^{4}J_{P-C} = 8.6$  Hz, Me of t-Bu group grafted on C4).

Synthesis of Complex 3a. Compound 2 (75.5 mg, 0.21 mmol) was dissolved in 50 mL of distilled and degassed toluene in a Schlenk tube. Then, [Pd(COD)Cl<sub>2</sub>] (29.4 mg, 0.10 mmol) was added, and the resulting clear solution was stirred in a oil bath at 110 °C for 15 h. After checking the <sup>31</sup>P NMR for complete disappearance of the starting product, solvent was removed *in vacuo* and the product extracted from the resulting solid using  $2 \times 50$  mL of petroleum ether. The liquid phase was filtered, and the solvent was evaporated. The product is obtained as a bright yellow solid. Yield: 92% (86.3 mg). Anal. Calcd for [C<sub>50</sub>-H<sub>70</sub>Cl<sub>2</sub>P<sub>2</sub>Pd] (910.4): C 65.97, H 7.75. Found: C 65.81, H 7.79.



meso-Diastereomer:  ${}^{31}P{}^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  29.5 (s);  ${}^{1}H$ NMR  $\delta$  7.57 (m, 2H, C5–H), 7.05 (m, 6H, H<sub>o</sub> and H<sub>p</sub> of C<sub>6</sub>H<sub>5</sub>), 6.86 (d,  ${}^{4}J_{P-H} = 1.4$  Hz, 2H, C3-H), 6.66 (s, 4H, H<sub>m</sub> of phenyl), 3.81 (m, 2H, CH<sub>2</sub> benzyl group), 3.30 (dt,  ${}^{2}J_{H-H} = 15.4$  Hz,  ${}^{2}J_{P-H} = 4.7$  Hz, 2H, CH<sub>2</sub> benzyl group), 2.68 (d,  ${}^{2}J_{H-H} = 14.9$ Hz, 2H, CH<sub>2</sub> of benzophospholane), 1.83-1.78 (m, CH<sub>2</sub> of benzophospholane), 1.77 (s, 18H, Me of t-Bu group on C6), 1.28 (s, 18H, Me of t-Bu group on C4), 1.18 (s, 3H, Me of benzophospholane), 0.50 (s, 3H, Me of benzophospholane);  $^{13}C{^{1}H}$  NMR  $\delta$  158.5 (s, C2), 154.0 (s, C4), 151.8 (m, C6), 134.5 (m, C<sub>ipso</sub> of C<sub>6</sub>H<sub>5</sub>), 129.6 (s, C<sub>o</sub> of C<sub>6</sub>H<sub>5</sub>) 127.3 (s, C<sub>m</sub> of C<sub>6</sub>H<sub>5</sub>), 125.7 (s, C<sub>p</sub> of C<sub>6</sub>H<sub>5</sub>), 123.6 (m, C5), 123.4 (m, C1), 118.2  $(d, {}^{3}J_{P-C} = 4.6 \text{ Hz}, \text{C3}), 43.83(\text{s}, \text{C-C2}), 37.0 \text{ (s, C of t-Bu group)}$ grafted on C6), 34.5 (m, CH<sub>2</sub> of benzophospholane) 34.2 (s, C of t-Bu group on C4), 34.1 (m, CH<sub>2</sub> of benzyl group), 33.1 (s, Me of benzophospholane), 32.8 (s, Me of t-Bu group grafted on C6), 32.2 (s, Me of t-Bu group grafted on C4) 30.0 (s, Me of benzophospholane).

*rac*-Diastereoisomer: <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 30.0 (s); <sup>1</sup>H NMR δ 7.57 (m, 2H, C5–H), 7.05 (m, 6H, H<sub>o</sub> and H<sub>p</sub> of C<sub>6</sub>H<sub>5</sub>), 6.83 (d, <sup>4</sup>J<sub>P-H</sub> = 1.4 Hz, 2H, C3–H), 6.64 (s, 4H, H<sub>m</sub> of phenyl) 3.86 (m, 2H, CH<sub>2</sub> benzyl group), 3.40 (dt, <sup>2</sup>J<sub>H-H</sub> = 15.4 Hz, <sup>2</sup>J<sub>P-H</sub> = 4.7 Hz, 2H, CH<sub>2</sub> benzyl group), 2.56 (d, <sup>2</sup>J<sub>H-H</sub> = 14.9 Hz, 2H, CH<sub>2</sub> of benzophospholane), 1.83–1.78 (m, CH<sub>2</sub> of benzophospholane), 1.83–1.78 (m, CH<sub>2</sub> of benzophospholane), 1.79 (s, 18H, Me of t-Bu group on C6), 1.25 (s, 18H, Me of t-Bu group on C4), 1.14 (s, 3H, Me of benzophospholane), 0.42 (s, 3H, Me of benzophospholane); <sup>13</sup>C{<sup>1</sup>H} NMR δ 158.7 (s, C2), 154.0 (s, C4), 151.8 (m, C6), 134.5 (m, C<sub>ipso</sub> of C<sub>6</sub>H<sub>5</sub>), 123.6 (m, C5), 123.4 (m, C1), 118.2 (d, <sup>3</sup>J<sub>P-C</sub> = 4.6 Hz, C3), 43.78 (s, <u>C</u>-C2), 37.1 (s, C of t-Bu group

grafted on C6), 34.6 (m, CH<sub>2</sub> of benzophospholane), 34.2 (s, C of t-Bu group on C4), 33.9 (m, CH<sub>2</sub> benzyl group), 33.0 (s, Me of benzophospholane), 32.7 (s, Me of t-Bu group grafted on C6), 32.2 (s, Me of t-Bu group grafted on C4) 29.7 (s, Me of benzophospholane).

**Synthesis of Compound 5.** Bis-phosphaalkene **4** (100 mg, 0.15 mmol) was dissolved in 30 mL of distillated and degassed hexanes in a glovebox. Then,  $[Pt(PCy_3)_2]$  (23 mg, 0.03 mmol) was added, and the resulting solution was stirred in a oil bath at 65 °C for 15 h. After checking by <sup>31</sup>P NMR for complete disappearance of the starting product, the solvent was removed *in vacuo*. The solid obtained was dissolved in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and then filtered over a pad of silica gel under an inert atmosphere in a Schlenk filter and eluted with another 150 mL of dry CH<sub>2</sub>Cl<sub>2</sub>. Solvent was removed *in vacuo*. Compound **5** (a mixture of **5a** and **5b**) was obtained as a white solid; yield 82% (82 mg): HRMS C<sub>44</sub>H<sub>64</sub>P<sub>2</sub> calcd 654.4483 g·mol<sup>-1</sup>, found 654.4480 g·mol<sup>-1</sup>. Anal. Calcd [C<sub>44</sub>H<sub>64</sub>P<sub>2</sub>] (654.9): C 80.69, H 9.85. Found: C 80.88, H 9.79.



Diastereomer **5a**: <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  –7.5 (s); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.54 (m, 2H, C5-H), 7.26 (s, 1H, C7-H), 7.20 (s, 2H, C3-H), 7.15 (s, 2H, C9-H), 7.12 (s, 1H, C10-H), 3.28 (dd, 2H, <sup>2</sup>J<sub>H-H</sub> = 13.3 Hz, <sup>2</sup>J<sub>P-H</sub> = 7.1 Hz, CH<sub>2</sub> of benzyl group), 2.90 (dd, 2H, <sup>2</sup>J<sub>H-H</sub> = 13.3 Hz, <sup>2</sup>J<sub>P-H</sub> = 5.7 Hz, CH<sub>2</sub> of benzyl group), 2.2–1.8 (m, 4H, CH<sub>2</sub> of benzophospholane) 1.67 (s, 18H, Me of t-Bu group grafted on C6), 1.48 (s, 6H, Me of benzophospholane), 1.34 (s, 18H, Me of t-Bu group grafted on C4), 1.20 (s, 6H, Me of benzophospholane); <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$  157,6 (d, <sup>2</sup>J<sub>P-C</sub> = 1.1 Hz, C2), 151.3 (d, <sup>2</sup>J<sub>P-C</sub> = 14.4 Hz, C6), 151.0 (s, C4), 138.4 (d, <sup>2</sup>J<sub>P-C</sub> = 8 Hz, C8), 134.9 (d, <sup>1</sup>J<sub>P-C</sub> = 23 Hz, C1), 129.6 (m, C7), 127.5 (s, C10), 125.8 (d, <sup>3</sup>J<sub>P-C</sub> = 6.3 Hz, C9), 120.6 (d, <sup>3</sup>J<sub>P-C</sub> = 4.0 Hz, C5), 117.6 (s, C3), 45.3 (d, <sup>2</sup>J<sub>P-C</sub> = 6.9 Hz, C-C2), 36.6 (d, <sup>1</sup>J<sub>P-C</sub> = 1.7 Hz, C of t-Bu group grafted on C6), 35.0 (d, <sup>1</sup>J<sub>P-C</sub> = 10.3 Hz, CH<sub>2</sub> of benzophospholane), 32.4 (s, Me of benzophospholane), 30.3 (s, Me of t-Bu group grafted C4).

(s, Me of t-Bu group grafted C4). Diastereomer **5b**:  ${}^{31}P{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  -7.6 (s);  ${}^{1}H$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.54 (dd, 2H,  ${}^{4}J_{P-H} = 1.9$  Hz,  ${}^{4}J_{H-H} = 1.4$  Hz, C5-H), 7.26 (s, 1H, C7-H), 7.20 (s, 2H, C3-H), 7.15 (s, 2H, C9-H), 7.12 (s, 1H, C10-H), 3.29 (dd, 2H,  ${}^{2}J_{H-H} = 13.3$  Hz,  ${}^{2}J_{P-H} = 7.1$  Hz, CH<sub>2</sub> benzyl), 2.90 (dd, 2H,  ${}^{2}J_{H-H} = 13.3$  Hz,  ${}^{2}J_{P-H} = 5.7$  Hz, CH<sub>2</sub> benzyl), 2.2–1.8 (m, 4H, CH<sub>2</sub> of benzophospholane), 1.67 (s, 18H, Me of t-Bu group grafted on C6), 1.50 (s, 6H, Me of benzophospholane), 1.33 (s, 18H, Me of t-Bu group grafted on C4), 1.21 (s, 6H, Me of benzophospholane);  ${}^{13}C{}^{1}H{}$  NMR  $\delta$ 157,5 (d,  ${}^{2}J_{P-C} = 1.1$  Hz, C2), 151.3 (d,  ${}^{2}J_{P-C} = 14.4$  Hz, C6), 151.0 (s, C4), 138.4 (d,  ${}^{2}J_{P-C} = 8$  Hz, C8), 135.0 (d,  ${}^{1}J_{P-C} = 23$  Hz, C1), 129.6 (m, C7), 127.5 (s, C10), 125.8 (d,  ${}^{3}J_{P-C} = 6.3$ Hz, C9), 120.7 (d,  ${}^{3}J_{P-C} = 4.0$  Hz, C5), 117.7 (s, C3), 45.3 (d,  ${}^{2}J_{P-C} = 6.9$  Hz, C-C2), 36.9 (d,  ${}^{1}J_{P-C} = 12.1$  Hz, CH<sub>2</sub> of benzophospholane), 36.3, (d,  ${}^{3}J_{P-C} = 1.7$  Hz, C of t-Bu group grafted on C6), 35.5 (d,  ${}^{3}J_{P-C} = 10.3$  Hz, CH<sub>2</sub> benzyl), 33.7 (s, C of t-Bu group grafted on C4), 32.9 (vt,  ${}^{3}J_{P-C} = 9.8$  Hz, Me of t-Bu group grafted on C6), 30.3 (s, Me of t-Bu group grafted on C4). **Computational Details.** All calculations were performed with the Gaussian 03W set of programs<sup>17</sup> using the B3PW91 functional.<sup>18</sup> The 6-31G\* basis set was used for all H, C, and P atoms, and the LANL2TZ(f) basis set<sup>19</sup> was used to describe the nickel and the platinum atoms. For each computed structure the minimum energy was characterized by vibration frequencies calculations. Transition structures were localized using the synchronous transit-guided quasi-Newton (STQN) method.<sup>20</sup>

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**X-ray Crystallography.** Data were collected at 150.0(1) K on a Nonius Kappa CCD diffractometer using a Mo K $\alpha$  ( $\lambda$ , 0.71070 Å) X-ray source and a graphite monochromator. All data were measured using phi and omega scans. Experimental details are described in Table 1. The crystal structures were solved using SIR 97<sup>21</sup> and Shelx1-97.<sup>22</sup> ORTEP drawings were made using ORTEP III for Windows.<sup>23</sup>

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**Supporting Information Available:** Crystal data and structure refinement details, atomic coordinates and equivalent isotropic displacement parameters, a complete list of bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates, and equivalent isotropic displacement parameters for complex **3a**. Computed Cartesian coordinates, the three lower frequencies, and energies of all theoretical structures. This material is available free of charge via the Internet at http:// pubs.acs.org.

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