

## Transient Palladadiphosphanlycarbenes: Singlet Carbenes with an “Inverse” Electronic Configuration ( $p_{\pi}^2$ instead of $\sigma^2$ ) and Unusual Transannular Metal–Carbene Interactions ( $\pi_{C\rightarrow Pd}$ Donation and $\sigma_{Pd\leftarrow C}$ Back-donation)

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**Abstract:** Upon treatment with  $[PdCl(allyl)]_2$ , asymmetrically substituted  $\alpha,\alpha'$ -diphosphanly diazo compounds eliminate dinitrogen to afford C-chlorodiphosphanlymethanide complexes in high yields. In the presence of a chloride-abstracting agent, such as sodium tetraphenylborate, the C-chlorodiphosphanlymethanide complexes react with pyridine and trimethylphosphine, readily affording the corresponding nitrogen and phosphorus ylides. The postulated intermediate in this process, namely palladadiphosphanlycarbenes, could not be spectroscopically characterized, but their transient formation was chemically supported further by a Lewis base exchange reaction between pyridine and 4-dimethylaminopyridine. This hypothesis has also been substantiated by computing the corresponding dissociation energy using two model systems featuring methyl groups at the phosphorus. Of particular interest, density functional theory calculations reveal that these palladadiphosphanlycarbenes have a singlet ground state with an “inverse”  $p_{\pi}^2$  electronic configuration and a distorted geometry associated with unusual transannular metal–carbene interactions ( $\pi_{C\rightarrow Pd}$  donation and  $\sigma_{Pd\leftarrow C}$  back-donation).

Over the past two decades, transition metal complexes featuring stable aminocarbenes,<sup>1</sup> especially *N*-heterocyclic carbenes (NHCs),<sup>2</sup> as ligands have attracted considerable interest and found numerous synthetic applications.<sup>3</sup> Comparatively, the coordination chemistry of the other well-known family of stable

carbenes,<sup>4</sup> namely phosphinocarbenes (PCs), is much less developed, and only a few PC complexes are known.<sup>5</sup> Indeed, despite the preceding discovery of stable PCs,<sup>6</sup> it was not until 2002 that direct complexation of a stable PC was reported with the isolation and structural characterization of complex **A**<sup>7</sup> (Figure 1). In addition, the scope of stable PCs has been recently extended to *P*-heterocyclic carbenes (PHCs), and the ensuing complexes **B** have been described.<sup>8</sup> Apart from direct complexation of stable species, a few alternative routes give access to

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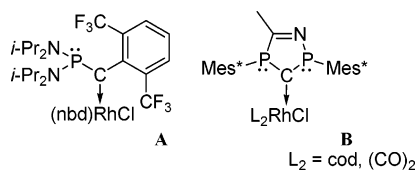
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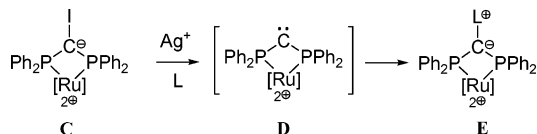
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**Figure 1.** Structure of (di)phosphino carbene complexes **A** and **B** (nbd = 2,5-norbornadiene, cod = 1,4-cyclooctadiene).

#### Scheme 1<sup>a</sup>



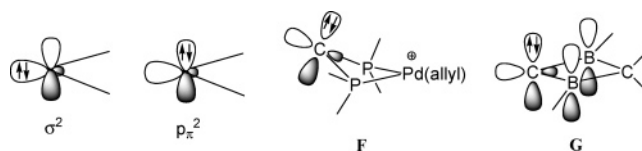
<sup>a</sup> [Ru] = Ru(*t*-BuNC)<sub>4</sub>; L = Py, THT (tetrahydrothiophene).

PC complexes, such as the heterofunctionalization of carbyne complexes<sup>9</sup> and the C–H activation of ligated PMe<sub>3</sub>.<sup>10</sup> More recently, Le Floch et al. took advantage of the propensity of dithioacetals for desulfurization to prepare PHC zirconocene complexes.<sup>11</sup>

Another significant breakthrough in this area has been reported by Ruiz et al., with the generation of the transient metalladiphosphanylcarbene **D** by iodide abstraction from **C** and its *in situ* trapping with Lewis bases, leading to the corresponding adducts **E** (Scheme 1).<sup>12,13</sup>

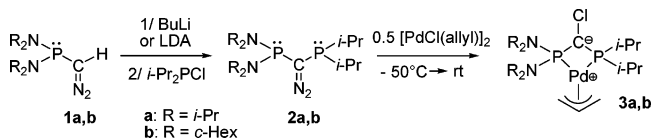
Taking into account the extreme moisture sensitivity of free PCs, we became interested in using their considerably more robust diazo precursors and have reported the coordination of an  $\alpha$ -diazo phosphine to Rh(I) fragments with retention of the diazo moiety.<sup>14</sup> These results prompted us to investigate the coordination properties of related diphosphanyl diazo compounds, and we describe here (i) the unexpected preparation of diphosphanylmethanide complexes related to **C**, (ii) a Lewis base exchange reaction that supports the hypothesis of the transient formation of palladadiphosphanylcarbenes **F** (Figure 2), and (iii) the very unusual  $p_{\pi}^2$  electronic configuration of singlet carbenes **F** predicted by density functional theory (DFT) calculations.

The  $p_{\pi}^2$  configuration is usually found among the excited states of singlet carbenes, whose ground state adopts the  $\sigma^2$



**Figure 2.**  $\sigma^2$  and  $p_{\pi}^2$  electronic configurations of singlet carbenes and structure of palladadiphosphanylcarbenes **F** and cyclic diborylcarbenes **G**.

#### Scheme 2



configuration (Figure 2).<sup>15</sup> Accordingly, “inverse” singlet carbenes featuring a  $p_{\pi}^2$  ground state have neither been isolated nor characterized, and only the putative cyclic diborylcarbenes **G** have been predicted to adopt such an unusual configuration.<sup>16</sup> This peculiar situation has been attributed to strong  $\pi$ -interactions between the doubly occupied  $p_{\pi}$  orbital at carbon and the vacant 2p orbitals at boron. Similarly, for palladadiphosphanylcarbenes **F**, DFT calculations reveal significant interactions between the carbene lone pair and vacant orbitals at phosphorus, but also unusual transannular PdC interactions, the nature of which ( $\pi_{C-Pd}$  donation/ $\sigma_{Pd-C}$  back-donation) is opposite to that usually encountered in Fischer-type carbene complexes ( $\sigma_{C-M}$  donation/ $\pi_{M-C}$  back-donation).

## Results and Discussion

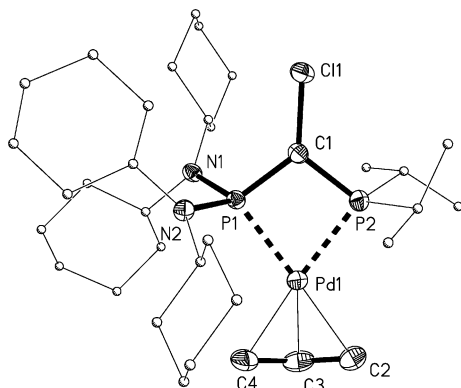
### Synthesis and Characterization of Palladium Complexes

**3.** The introduction of bulky amino groups at phosphorus is known to efficiently stabilize  $\alpha$ -phosphino diazo compounds,<sup>17</sup> but also to make the complexation of the phosphine to a metal center rather difficult. With a view to studying the coordination behavior of diphosphanyl diazo compounds, the unsymmetrically substituted derivatives **2** were thus considered as promising candidates due the combination of a bis(diisopropylamino)- (**2a**) or bis(dicyclohexylamino)phosphino group (**2b**) with a less sterically demanding and electronically active diisopropylphosphino group (Scheme 2). As detailed below, no significant difference was found between the properties of **2a** and **2b**, but the diisopropylamino- and dicyclohexylamino-substituted variations were developed in parallel for convenient NMR characterization and X-ray diffraction analysis.

Hetero-functionalization of diazo compounds is most commonly achieved by reacting metalated diazo precursors with electrophiles. Although this strategy may be limited, in some instances, by concurrent formation of nitrile–imines resulting from the reaction at the terminal nitrogen rather than at carbon,<sup>18</sup> it proved efficient for the preparation of the desired diphosphino diazo compounds. Treatment of the known precursors **1**<sup>17a</sup> with *n*-BuLi or lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at  $-78$  °C, followed by addition of chlorodiisopropy-

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**Figure 3.** Thermal ellipsoid diagram (50% probability) of **3b**. For clarity, the cyclohexyl and isopropyl groups are simplified and only one position of the disordered meso carbon atoms of the allyl group is shown. Selected bond lengths (Å) and angles (°): P1–C1 1.727(3), P2–C1 1.733(3), C1–Cl1 1.778(3), P1–Pd1 2.3160(7), P2–Pd1 2.2886(7), Pd1–C2 2.216(3), Pd1–C3 2.164(4), Pd1–C4 2.218(3), C2–C3 1.366(5), C3–C4 1.384(5), P1–C1–P2 103.80(14), P1–C1–Cl1 130.18(16), P2–C1–Cl1 125.91(15), P1–Pd1–P2 72.49(2).

lphosphine, afforded **2a** (viscous red oil, 84% yield) and **2b** (orange powder, 83% yield).

Derivatives **2** readily and cleanly reacted with  $[\text{Pd}(\mu\text{-Cl})(\text{allyl})_2]$  in dichloromethane (DCM) at room temperature. The decomposition of the diazo moiety was apparent from the visible evolution of  $\text{N}_2$ , while the high solubility in pentane of the resulting complexes **3** suggested a neutral structure. The coordination of the  $\text{P}(i\text{-Pr})_2$  group to palladium was indicated by the deshielding of the corresponding  $^{31}\text{P}$  NMR signal (from  $\delta = -2.5$  to  $+40$  ppm for **3a**). Although the signal of the  $\text{P}(\text{NR}_2)_2$  group was only slightly shielded (**2a**,  $+66$  ppm; **3a**,  $+61$  ppm), the presence of doublets of doublets for the three allylic carbon atoms suggested that both phosphorus centers were coordinated to the palladium. The  $\eta^3$  coordination of the allyl fragment was retained, as deduced from the  $^{13}\text{C}$  chemical shifts of the  $\text{CH}_2$  (63 and 54 ppm) and  $\text{CH}$  moieties (116 ppm). Despite the elimination of  $\text{N}_2$ , the signal for the central carbon atom was only marginally affected by coordination (**2a**, 33 ppm,  $J_{\text{PC}} = 71$  and 36 Hz; **3a**, 39 ppm,  $J_{\text{PC}} = 47$  and 39 Hz). In order to unambiguously establish the structure of complexes **3**, single crystals of **3b** were grown from a saturated pentane solution at  $-30$  °C, and an X-ray diffraction study was performed (Figure 3, Tables 1 and 2). Both phosphorus atoms are indeed coordinated to the palladium center, and the chlorine atom was found to have migrated from the palladium to the central carbon. Overall, complexes **3** adopt a zwitterionic four-membered metallacyclic structure, with formal negative and positive charges located on carbon and palladium, respectively. This situation is reminiscent of that observed in diphosphanylmethanide complexes  $(\text{R}_2\text{PCR}'\text{PR}_2)\text{ML}_n$  that are generally prepared by deprotonation of ligated methylenediphosphines.<sup>19</sup> The PIC1P2Pd four-membered ring of **3b** is perfectly planar, with a very acute P1PdP2 angle ( $72.5^\circ$ ) and a rather wide PIC1P2 angle ( $103.8^\circ$ ). The central carbon atom is in a planar environment (sum of bond angles =  $360^\circ$ ) and symmetrically

bonded to the two phosphorus atoms. The CP bond distances (1.73 Å) are rather short and in the range typical of those observed in phosphorus ylides, indicating noticeable interaction between the negative carbon atom and the  $\sigma^4$  phosphorus centers (negative hyperconjugation). Finally, the  $\eta^3$ -allyl moiety is symmetrically coordinated to the palladium (Pd–C4 and Pd–C2 bond lengths of 2.22 Å/C2–C3 and C3–C4 bond lengths of 1.38 Å), despite the electronic and steric dissymmetry of the PCP ligand.

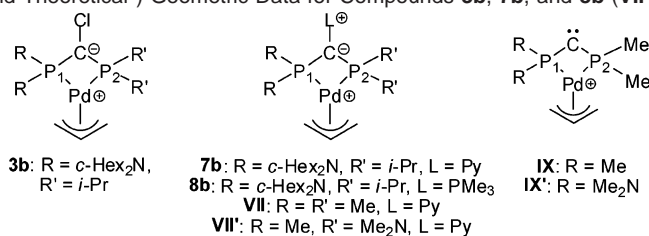
From a mechanistic viewpoint, the formation of complexes **3** most probably results from the initial cleavage of the chloride bridges of  $[\text{Pd}(\mu\text{-Cl})(\text{allyl})_2]$  induced by the diisopropyl phosphino group of **2**, leading to complexes **4** (Scheme 3). A possible route to **3** would then involve nitrogen elimination to give the phosphinocarbenes **5a,b**,<sup>20</sup> followed by ring closure and chlorine migration. Alternatively, the proximity of the second phosphino group to the metal center in **4** may favor the formation of the cyclic ion pair complexes **6**, and then after elimination of  $\text{N}_2$ , the chloride counteranion could add to the carbene center. Aiming at discriminating experimentally between these two pathways, the reaction between **2** and  $[\text{Pd}(\mu\text{-Cl})(\text{allyl})_2]$  was monitored by  $^{31}\text{P}$  NMR. Unfortunately, no intermediate could be detected even at low temperature ( $-80$  °C), suggesting that the first step is rate determining. However, when the reaction was performed in THF instead of DCM, and in the presence of sodium tetraphenylborate, we were pleased to detect by  $^{31}\text{P}$  NMR a new compound, which was rapidly converted into the final complex **3**. The  $^{31}\text{P}$  NMR data for this intermediate (Table 3) are very comparable to those of **3**, suggesting a similar four-membered metallacyclic structure. In addition, a strong infrared absorption for a CNN vibration was observed at  $2048\text{ cm}^{-1}$ , indicating the presence of the diazo moiety. All these data are consistent with the second pathway involving intermediates **6**.

#### Nucleophilic Displacement from the Palladium Complexes

**3**. Ruiz et al. have demonstrated that *C*-halogeno diphosphanylmethanide complexes react with Lewis bases such as pyridine and tetrahydrothiophene in the presence of silver salts to give the corresponding substitution products.<sup>12</sup> Complexes **3** were also found to react cleanly with pyridine in the presence of silver trifluoromethanesulfonate or sodium tetraphenylborate, quantitatively affording the corresponding ion pair complexes **7a,b** (Scheme 4). Complex **7b** was subjected to a single-crystal X-ray diffraction analysis (Figure 4, Tables 1 and 2). Accordingly, it was found that replacement of the chlorine atom for a pyridine moiety at carbon has only a limited geometric impact. In particular, the PIC1P2 angle decreases by less than  $2^\circ$  (from  $103.8^\circ$  to  $102.0^\circ$ ) and the P1PdP2 angle increases only slightly (from  $72.5^\circ$  to  $73.9^\circ$ ). The fairly small twist of the pyridine ring relative to the PdPCP plane ( $32^\circ$ ) and the rather short C1N3 bond length (1.42 Å) indicate noticeable CN double bond character. A more sterically hindered Lewis base such as trimethylphosphine also reacts with complexes **3** in the presence of sodium tetraphenylborate, affording complex **8b**, which has been fully characterized, including an X-ray analysis. The bond lengths and angles measured for **8b** are very similar to those of **3b** and **7b**, but the four-membered PIC1P2Pd ring slightly deviates from planarity (angle between the PPdP and PCP

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**Table 1.** Selected Experimental (and Theoretical<sup>a</sup>) Geometric Data for Compounds **3b**, **7b**, and **8b** (**VII'** and **IX'**)

compound	R/R'	L	P <sub>1</sub> C	P <sub>2</sub> C	P <sub>1</sub> Pd	P <sub>2</sub> Pd	CPd	P <sub>1</sub> CP <sub>2</sub>	P <sub>1</sub> PdP <sub>2</sub>	ΣCα
<b>3b</b>	<i>c</i> -Hex <sub>2</sub> N/ <i>i</i> -Pr		1.727	1.733	2.316	2.289	2.86	103.80	72.49	359.9
<b>7b</b>	<i>c</i> -Hex <sub>2</sub> N/ <i>i</i> -Pr	Py	1.769	1.776	2.297	2.286		102.0	73.89	360.0
<b>VII</b>	Me/Me	Py	1.80	1.80	2.34	2.34	3.00	102.1	73.7	360.0
<b>VII'</b>	Me <sub>2</sub> N/Me	Py	1.79	1.80	2.33	2.34	3.01	101.1	72.8	360.0
<b>8b</b>	<i>c</i> -Hex <sub>2</sub> N/ <i>i</i> -Pr	PMe <sub>3</sub>	1.764	1.771	2.314	2.285		99.01	71.55	360.0
<b><sup>1</sup>IX</b>	Me/Me		1.71	1.71	2.38	2.38	2.25	129.7	80.8	
<b><sup>3</sup>IX</b>	Me/Me		1.82	1.82	2.37	2.37	2.88	110.1	77.8	
<b><sup>1</sup>IX'</b>	Me <sub>2</sub> N/Me		1.69	1.71	2.37	2.35	2.27	135.1	83.2	
<b><sup>3</sup>IX'</b>	Me <sub>2</sub> N/Me		1.82	1.81	2.36	2.36	2.89	108.3	77.2	

<sup>a</sup> At the B3PW91 level.**Table 2.** Crystallographic Data for Complexes **3b**, **7b**, and **8b**

	<b>3b</b>	<b>7b</b>	<b>8b</b>
formula	C <sub>34</sub> H <sub>63</sub> ClN <sub>2</sub> P <sub>2</sub> Pd	C <sub>65</sub> H <sub>92</sub> BCl <sub>4</sub> N <sub>3</sub> P <sub>2</sub> Pd	C <sub>61</sub> H <sub>92</sub> BN <sub>2</sub> P <sub>3</sub> Pd
formula weight	703.65	1236.37	1063.49
cryst system, space group	triclinic, <i>P</i> $\bar{1}$	orthorhombic, <i>Pna</i> 2 <sub>1</sub>	monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , Å	10.364(1)	36.164(4)	17.119(4)
<i>b</i> , Å	12.560(2)	12.575(1)	16.313(4)
<i>c</i> , Å	14.176(2)	13.970(2)	21.541(5)
α, deg	91.410(2)		
β, deg	99.142(2)		110.272(4)
γ, deg	101.852(2)		
<i>V</i> , Å <sup>3</sup>	1779.9(4)	6352.6(12)	5643(2)
<i>Z</i>	2	4	4
<i>d</i> <sub>calcd</sub> , Mg/m <sup>3</sup>	1.313	1.293	1.252
absorp coeff, mm <sup>-1</sup>	0.711	0.552	0.453
no. total reflections	15032	28987	32210
no. unique reflections	7235	8692	11621
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0333	0.0516	0.0427
w <i>R</i> 2 (all data)	0.0891	0.1062	0.1075
(Δ/ <i>r</i> ) <sub>max</sub> (e Å <sup>-3</sup> )	0.898 and -0.418	0.631 and -0.713	0.655 and -0.679

**Table 3.** Selected <sup>31</sup>P NMR and IR Data for Compounds **2a**, **3a**, and **6a**

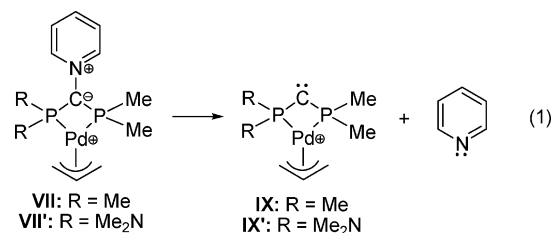
	δ (ppm)			ν <sub>CN2</sub> (cm <sup>-1</sup> )
	( <i>i</i> -Pr) <sub>2</sub> N <sub>2</sub> P	P( <i>i</i> -Pr) <sub>2</sub>	<i>J</i> <sub>PP</sub> (Hz)	
<b>2a</b>	66.4	-2.5	128	2012
<b>3a</b>	61.2	40.1	22	
<b>6a</b>	50	36	13	2048

planes, 170.9°). This distortion most probably results from steric crowding between the PMe<sub>3</sub> group and the neighboring sterically demanding *i*-Pr and *c*-Hex substituents. Finally, noticeable negative hyperconjugation between the central carbon atom and the three phosphorus centers is suggested by the shortness of the associated CP bonds (1.74–1.77 Å).

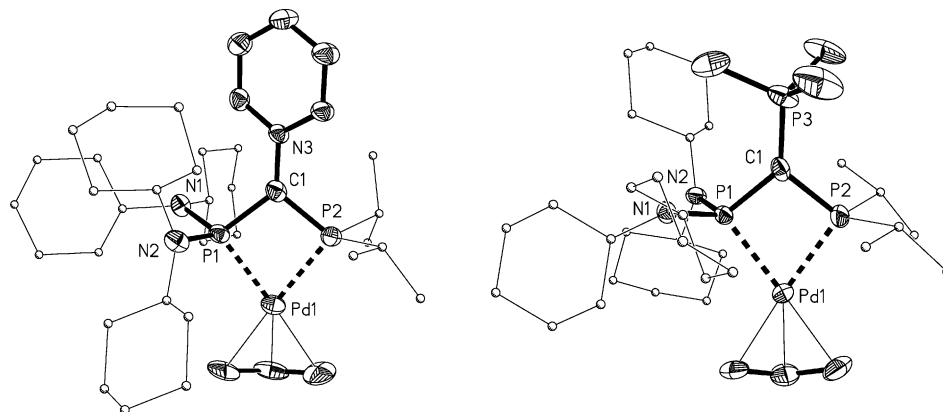
As pointed out by Ruiz et al.,<sup>12</sup> complexes such as **7** and **8** might be envisaged as Lewis base adducts of the corresponding metalladiphosphanylcarbenes **9**. All our efforts to spectroscopically characterize these carbenes upon chloride abstraction failed. Aiming at demonstrating their possible formation by dissociation of adducts **7** and **8**, we turned our attention to Lewis base exchange reactions. Indeed, the pyridine adduct **7b** was found to react spontaneously and cleanly with dimethylaminopyridine (1 equiv) in DCM at room temperature (Scheme 5).

The structure of the resulting exchange adduct **10b** was unambiguously deduced by the similarity of its spectroscopic data with those of **7b**. This reaction is most likely driven by the enhanced donating properties of 4-dimethylaminopyridine (DMAP), resulting in a stronger CN bond. From a mechanistic viewpoint, nucleophilic attack of DMAP at the carbon atom of **7b** seems rather unlikely, and the reaction most probably proceeds via a dissociative pathway involving carbene **9b**.

In order to further support the transient formation of metalladiphosphanylcarbenes **9** in this exchange reaction, the dissociation of the pyridine adducts was investigated computationally (eq 1). Pyridine and the model compounds **VII** and

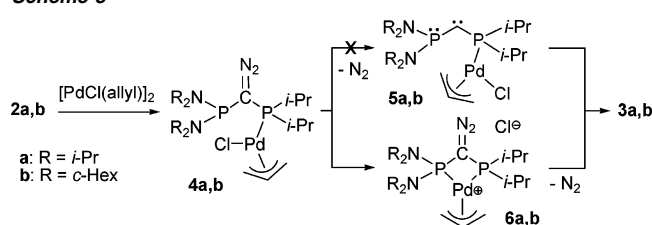


**IX**, featuring methyl groups at phosphorus, were optimized (Table 1). The dissociation energy for the Lewis base adduct

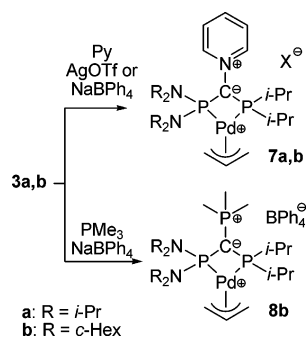


**Figure 4.** Thermal ellipsoid diagrams (50% probability) of **7b** (left) and **8b** (right). For clarity, the cyclohexyl and isopropyl groups are simplified. Only one position is shown for the disordered isopropyl groups at phosphorus and meso carbon atoms of the allyl group. The tetraphenylborate anion has been omitted. Selected bond lengths (Å) and angles (°): **7b**, P1–C1 1.769(5), P2–C1 1.776(6), C1–N3 1.424(7), P1–Pd1 2.2969(15), P2–Pd1 2.2862(15), P1–C1–P2 102.0(3), P1–C1–N3 129.8(4), P2–C1–N3 128.2(4), P1–Pd1–P2 73.89(5); **8b**, P1–C1 1.764(3), P2–C1 1.771(3), C1–P3 1.741(3), P1–Pd1 2.3142(9), P2–Pd1 2.2845(10), P1–C1–P2 99.01(16), P1–C1–P3 133.41(18), P2–C1–P3 127.58(18), P1–Pd1–P2 71.55(3).

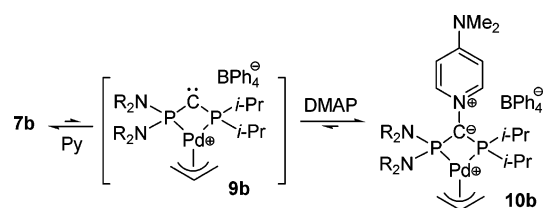
### Scheme 3



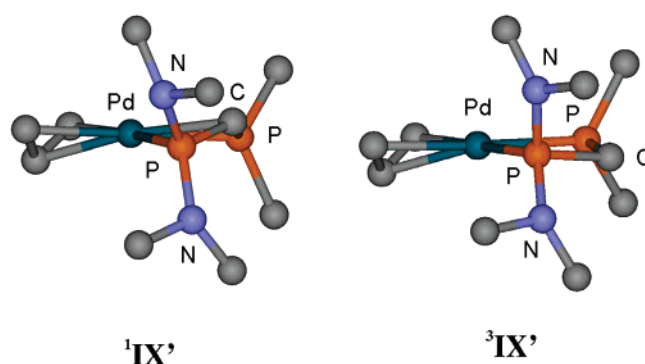
### Scheme 4



### Scheme 5



was thereby estimated to be  $\Delta G = 29.7 \text{ kcal}\cdot\text{mol}^{-1}$ . A slightly smaller dissociation energy ( $28.6 \text{ kcal}\cdot\text{mol}^{-1}$ ) was found when amino groups were introduced at one of the phosphorus centers (model compounds **VII'** and **IX'**). These values are suggestive of spontaneous exchange reactions at room temperature. For comparison, a dissociation energy of  $63.3 \text{ kcal}\cdot\text{mol}^{-1}$  was predicted for the extrusion of the parent singlet carbene  $\text{CH}_2$  from the corresponding pyridinium ylide.<sup>21</sup> This suggests that metalladiphosphanycarbenes **9** should benefit from some



**Figure 5.** Optimized structures for singlet and triplet metalladiphosphanycarbenes **IX'** (hydrogen atoms have been omitted for clarity).

significant electronic stabilization, the precise nature of which is not obvious, since both phosphorus lone pairs are engaged in the coordination of the metal and are therefore not prone to interact with the carbene center.

**Metalladiphosphanycarbenes 9 (IX).** Careful attention was paid to the electronic structure of the model metalladiphosphanycarbene **IX'** (Figure 5), and an unprecedented stabilization mode was thereby evidenced for the singlet state. The corresponding triplet state was also optimized as a reference structure, only weak interaction between the carbene center and its surroundings being anticipated in this case. The first unexpected geometric feature of singlet carbene **1IX'** is the noticeable deviation from planarity of the four-membered PCPPd ring (angles of  $154.5^\circ$  between the PPdP and PCP planes). This situation is in marked contrast with the perfectly planar conformations found for the corresponding triplet state **3IX'** as well as the pyridine adduct **VII'**. Moreover, the PCP angle of metalladiphosphanycarbenes is noticeably wider in the singlet state ( $135.1^\circ$ ) than in the triplet state ( $108.3^\circ$ ), in contrast to the situation found for most carbenes.<sup>22</sup> Importantly, a considerable shortening of the PdC distance on going from **3IX'** (2.89 Å) to **1IX'** (2.27 Å) is observed. This observation raises the question of the possible involvement of a transannular interaction between the carbene center and the metal (sum of van der Waals radii, 3.33 Å). This question also arises from the rather large

(21) Combined with laser flash photolysis techniques, the formation of pyridinium ylides has proven to be a powerful tool to study transient carbenes: Jackson, J. E.; Platz, M. In *Advances in Carbene Chemistry*; Brinker, U. H. Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, p 89.

(22) (a) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485. (b) Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* **1978**, *100*, 1333.

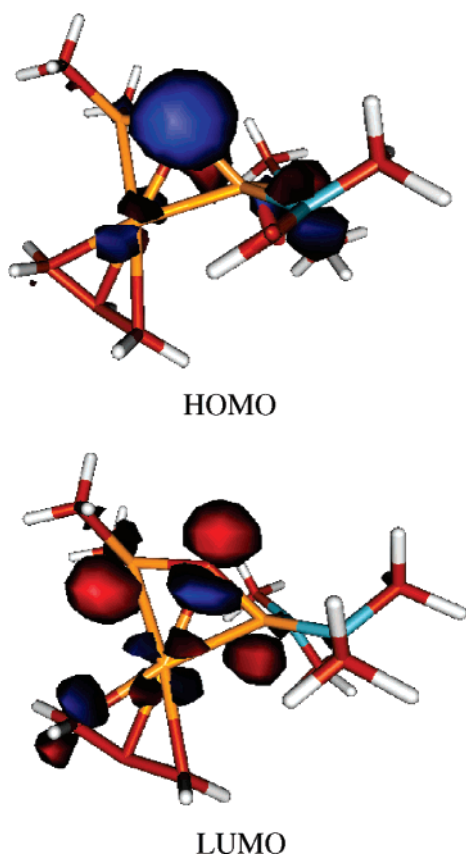


Figure 6. Plots of the frontier orbitals for  $^1\text{IX}'$ .

singlet/triplet gap predicted for metalladiphosphanylcarbenes,  $^1\text{IX}'$  being about  $14.5 \text{ kcal}\cdot\text{mol}^{-1}$  more stable than  $^3\text{IX}'$ . Indeed, this value is comparable in magnitude to that predicted for diphosphinocarbenes,<sup>23</sup> although both phosphorus lone pairs in  $\text{IX}'$  are engaged in coordination and therefore cannot efficiently stabilize the singlet state.

More insight into the electronic structure of singlet metalladiphosphanylcarbene  $^1\text{IX}'$  was gained from its frontier orbitals. Indeed, the carbene lone pair (HOMO) was found to be of p symmetry with an almost perpendicular orientation relative to the carbene coordination plane, while the carbene vacant orbital (LUMO) is located approximately along the CPd axis (Figure 6). This  $p_{\pi}^2$  electronic configuration is in marked contrast with the  $\sigma^2$  electronic configuration normally observed for singlet carbenes (Figure 2). As mentioned in the introduction, only the putative cyclic diborylcarbenes **G** have been predicted to adopt such a  $p_{\pi}^2$  configuration due to strong  $\pi$ -interaction between the doubly occupied  $p_{\pi}$  orbital at carbon and the vacant  $2p$  orbitals at boron.<sup>16</sup> At first glance, a comparable situation may be found in  $^1\text{IX}'$ . Indeed, it is clearly apparent from the short CP bond lengths ( $1.69$ – $1.71 \text{ \AA}$ ) that the doubly occupied  $p_{\pi}$  orbital at carbon interacts with the  $\sigma^4$  phosphorus centers (negative hyperconjugation). Although these interactions probably play an important role in the “inverse” electronic configuration of metalladiphosphanylcarbenes, they cannot explain the geometric distortion predicted for  $^1\text{IX}'$ . At this stage, the

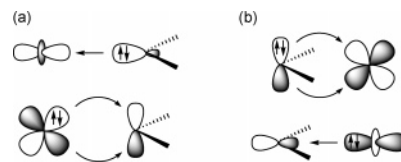


Figure 7. Schematic representations of the MC interactions involved in Fischer-type carbene complexes (a) and in metalladiphosphinocarbenes (b).

noticeable contribution of Pd-centered d-orbitals in the HOMO and LUMO of  $^1\text{IX}'$  strongly suggested the presence of transannular interactions between the carbene and the metal. This situation was confirmed by Natural Bonding Analysis (NBO).<sup>24</sup> At the second-order donor–acceptor interaction level, the carbene lone pair was indeed predicted to be delocalized over empty orbitals centered at both phosphorus ( $40 \text{ kcal}\cdot\text{mol}^{-1}$ ) and palladium ( $20 \text{ kcal}\cdot\text{mol}^{-1}$ ). In addition to this  $\pi$  donation from the carbene to the palladium center, some  $\sigma$  back-donation from the metal to the carbene was also apparent ( $7 \text{ kcal}\cdot\text{mol}^{-1}$ ). This bonding situation is completely opposite to that normally encountered in Fischer-type carbene complexes<sup>25</sup> ( $\sigma_{\text{C}\rightarrow\text{M}}$  donation/ $\pi_{\text{M}\rightarrow\text{C}}$  back-donation) (Figure 7). Although the  $\pi_{\text{C}\rightarrow\text{M}}/\sigma_{\text{M}\rightarrow\text{C}}$  interactions involved in metalladiphosphanylcarbenes are not comparable in strength to those present in normal Fischer-type carbene complexes, they are apparently strong enough to enforce the butterfly geometry and to favor to some extent the  $p_{\pi}^2$  configuration. The resulting stabilization of such carbenes should also be related to the relative propensity of the corresponding pyridine adducts for dissociation.

## Conclusion

A new route to C-chlorodiphosphanylmethanide complexes has been evidenced by reacting the diphosphino diazo compounds **2** with  $[\text{Pd}(\mu\text{-Cl})(\text{allyl})]_2$ . The resulting complexes **3** were found to react readily with pyridine and trimethylphosphine in the presence of a chloride-abstracting agent to give the corresponding adducts **7** and **8**. The spontaneous Lewis base exchange reaction observed between pyridine and DMAP substantiates the possible dissociation of such adducts and therefore the transient formation of the corresponding metalladiphosphanylcarbenes **9**. Although these carbenes could not be spectroscopically characterized, DFT calculations supported their possible formation, since relatively low dissociation energies are predicted for model systems. According to DFT calculations and NBO analyses, singlet metalladiphosphanylcarbenes adopt a distorted geometry associated with an “inverse”  $p_{\pi}^2$  electronic configuration. This peculiar situation has been attributed to stabilizing interactions between the carbene lone pair and vacant orbitals at phosphorus and to transannular PdC interactions, the nature of which ( $\pi_{\text{C}\rightarrow\text{Pd}}$  donation and  $\sigma_{\text{Pd}\rightarrow\text{C}}$  back-donation) is opposite to that usually encountered in Fischer-type carbene complexes.

From these results, the characterization of singlet carbenes adopting a  $p_{\pi}^2$  electronic configuration appears to be a realistic goal. In this regard, metalladiphosphanylcarbenes should be considered as promising candidates, since variation of the metal fragment and phosphorus substituents may allow further stabilization of such species.

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(24) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(25) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons: New York, 1994. (b) Vyboishchikov, S. F.; Frenking, G. *Chem. Eur. J.* **1998**, *4*, 1428.

## Experimental Section

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra were recorded on Bruker AC200, WM250, AMX400, and AMX500 spectrometers.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported in ppm relative to  $\text{Me}_4\text{Si}$  as external standard.  $^{31}\text{P}$  NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85%  $\text{H}_3\text{PO}_4$ . Infrared spectra were recorded on a Perkin-Elmer 1725X FT-IR spectrometer. Mass spectra were obtained on a Ribermag R10 10E instrument. The bis-(diisopropylamino)- and bis(dicyclohexylamino)phosphinodiazomethanes **1a,b** were prepared according to the literature procedure.<sup>17a</sup>

**Synthesis of Diazo Compound 2a.** *n*-BuLi (8.3 mmol) was added at  $-80^\circ\text{C}$  to a THF solution (20 mL) of bis(diisopropylamino)phosphinodiazomethane (8.3 mmol, 2.26 g). After 30 min, chlorodiisopropylphosphine (8.3 mmol, 1.32 mL) was added at  $-80^\circ\text{C}$ , and the solution was stirred for 15 min. After the solution warmed to room temperature, the solvent was removed under vacuum. The crude residue was extracted with pentane (20 mL) and quickly filtered through neutral activated alumina. After evaporation of the solvent, **2a** was obtained as a red oil (2.7 g, 84%).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  66.4 (d,  $^2J_{\text{PP}} = 128$  Hz,  $\text{PNi-Pr}_2$ ),  $-2.5$  (d,  $^2J_{\text{PP}} = 128$  Hz,  $\text{Pi-Pr}_2$ ).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.27 (ddd, 6 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $^3J_{\text{HP}_2} = 16.4$  Hz,  $^5J_{\text{HP}_1} = 1.1$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 1.28 (ddd, 6 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $^3J_{\text{HP}_2} = 16.4$  Hz,  $^5J_{\text{HP}_1} = 1.3$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 1.31 (d, 12 H,  $^3J_{\text{HH}} = 6.4$  Hz,  $\text{CH}_3\text{Ni-Pr}$ ), 1.43 (d, 12 H,  $^3J_{\text{HH}} = 6.4$  Hz,  $\text{CH}_3\text{Ni-Pr}$ ), 1.90 (sept, 2 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $\text{CHi-Pr}$ ), 3.49 (sept d, 4 H,  $^3J_{\text{HH}} = 6.4$  Hz,  $^3J_{\text{HP}_1} = 1.6$  Hz, CHN).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  19.5 (d,  $^2J_{\text{CP}_2} = 8$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 20.4 (dd,  $^2J_{\text{CP}_2} = 20$  Hz,  $^4J_{\text{CP}_1} = 3$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 24.7 (d,  $^3J_{\text{CP}_1} = 7$  Hz,  $\text{CH}_3\text{Ni-Pr}$ ), 25.3 (dd,  $^1J_{\text{CP}_2} = 3$  Hz,  $^3J_{\text{CP}_1} = 8$  Hz,  $\text{CHi-Pr}$ ), 25.6 (dd,  $^1J_{\text{CP}_2} = 18$  Hz,  $^3J_{\text{CP}_1} = 2$  Hz,  $\text{CHi-Pr}$ ), 33.0 (dd,  $^1J_{\text{CP}_1} = 36$  Hz,  $^1J_{\text{CP}_2} = 71$  Hz,  $\text{CN}_2$ ), 48.0 (d,  $^2J_{\text{CP}_1} = 13$  Hz,  $\text{CHNi-Pr}$ ). IR (diethyl ether):  $\nu_{\text{CN}_2}$  2012  $\text{cm}^{-1}$ .

**Synthesis of Diazo Compound 2b.** A freshly prepared LDA solution from diisopropylamine (1.71 mmol, 0.240 mL) and BuLi (1.71 mmol, 1.12 mL) in THF (5 mL) was added at  $-80^\circ\text{C}$  to a solution of bis-(dicyclohexylamino)phosphino diazomethane (1.71 mmol, 738 mg) in THF (10 mL). After 30 min, chlorodiisopropylphosphine (1.71 mmol, 0.272 mL) was added at  $-80^\circ\text{C}$  and stirred for a further 15 min. The solution was warmed to rt and the volatiles were removed under vacuum. The crude residue was extracted with pentane and quickly filtered through celite and neutral activated alumina. After evaporation of the solvent, compound **2b** was obtained as an orange powder. Recrystallisation from  $\text{Et}_2\text{O}$  at  $-30^\circ\text{C}$  led to compound **2b** as orange crystals (778 mg, 83%): mp  $54^\circ\text{C}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  67.6 (d,  $^2J_{\text{PP}} = 132$  Hz,  $\text{PNC-Hex}_2$ ),  $-3.8$  (d,  $^2J_{\text{PP}} = 132$  Hz,  $\text{Pi-Pr}_2$ ); IR (THF)  $\nu_{\text{CN}_2}$  2015  $\text{cm}^{-1}$ .

**Synthesis of Palladium Complexes 3a,b.** A  $\text{CH}_2\text{Cl}_2$  solution (4 mL) of  $[\text{PdCl}(\text{allyl})]_2$  dimer (0.3 mmol, 110 mg) was added at  $-80^\circ\text{C}$  to a solution of diazo derivative **2a** (0.7 mmol) or **2b** (0.7 mmol) in 4 mL of  $\text{CH}_2\text{Cl}_2$ . The solution was warmed to room temperature and stirred for 1 h. After evaporation of the solvent, the crude residue was extracted with  $4 \times 10$  mL of pentane, yielding **3a** as a yellow oily residue (277 mg, 85%).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  61.2 (d,  $^2J_{\text{PP}} = 22$  Hz,  $\text{PNi-Pr}_2$ ), 40.1 (d,  $^2J_{\text{PP}} = 22$  Hz,  $\text{Pi-Pr}_2$ ).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.10 (dd, 3 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $^3J_{\text{HP}_2} = 18.0$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 1.16 (dd, 3 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $^3J_{\text{HP}_2} = 18.0$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 1.18 (dd, 3 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $^3J_{\text{HP}_2} = 15.2$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 1.27 (d, 6 H,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CH}_3\text{Ni-Pr}$ ), 1.28 (d, 6 H,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CH}_3\text{Ni-Pr}$ ), 1.31 (d, 6 H,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CH}_3\text{Ni-Pr}$ ), 1.34 (d, 6 H,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CH}_3\text{Ni-Pr}$ ), 2.18 (sept d, 1 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $^4J_{\text{HP}_1} = 1.2$  Hz,  $\text{CHi-Pr}$ ), 2.24 (sept d, 1 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $^4J_{\text{HP}_1} = 1.2$  Hz,  $\text{CHi-Pr}$ ), 2.42 (ddd, 1 H,  $^3J_{\text{HH}} = 13.2$  Hz,  $^5J_{\text{HP}_1} = 12.4$  Hz,  $^5J_{\text{HP}_2} = 1.2$  Hz,  $\text{CH}_2(\text{allyl})$ ), 2.60 (ddd, 1 H,  $^3J_{\text{HH}} = 13.2$  Hz,  $^5J_{\text{HP}_1} = 5.2$  Hz,  $^5J_{\text{HP}_2} = 8.0$  Hz,  $\text{CH}_2(\text{allyl})$ ), 3.82 (d, 2 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $\text{CH}_2(\text{allyl})$ ), 4.11 (sept d, 2 H,  $^3J_{\text{HH}} = 6.8$  Hz,  $^3J_{\text{HP}_1} = 18.4$  Hz, CHN), 4.15 (sept d, 2 H,  $^3J_{\text{HH}} = 6.8$  Hz,  $^3J_{\text{HP}_1} = 18.8$  Hz, CHN), 4.91 (m, 1 H,  $\text{CH}(\text{allyl})$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  19.9 (s,  $\text{CH}_3i\text{-Pr}$ ), 20.0 (s,  $\text{CH}_3i\text{-Pr}$ ), 20.7

(d,  $^2J_{\text{CP}_2} = 6$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 20.8 (d,  $^2J_{\text{CP}_2} = 6$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 24.5 (d,  $^3J_{\text{CP}_1} = 3$  Hz,  $\text{CH}_3\text{Ni-Pr}$ ), 24.6 (d,  $^3J_{\text{CP}_1} = 2$  Hz,  $\text{CH}_3\text{Ni-Pr}$ ), 24.9 (d,  $^3J_{\text{CP}_1} = 3$  Hz,  $\text{CH}_3\text{Ni-Pr}$ ), 25.3 (d,  $^3J_{\text{CP}_1} = 3$  Hz,  $\text{CH}_3\text{Ni-Pr}$ ), 27.6 (dd,  $^1J_{\text{CP}_2} = 18$  Hz,  $^3J_{\text{CP}_1} = 5$  Hz,  $\text{CHi-Pr}$ ), 27.8 (dd,  $^1J_{\text{CP}_2} = 18$  Hz,  $^3J_{\text{CP}_1} = 4$  Hz,  $\text{CHi-Pr}$ ), 39.2 (dd,  $J_{\text{CP}_1} = 39$  Hz,  $J_{\text{CP}_2} = 47$  Hz,  $\text{CCl}_1$ ), 47.4 (d,  $^2J_{\text{CP}_1} = 10$  Hz, CHN), 47.7 (d,  $^2J_{\text{CP}_1} = 11$  Hz, CHN), 53.8 (dd,  $J_{\text{CP}_1} = 42$  Hz,  $J_{\text{CP}_2} = 5$  Hz,  $\text{CH}_2(\text{allyl})$ ), 63.2 (dd,  $J_{\text{CP}_1} = 12$  Hz,  $J_{\text{CP}_2} = 30$  Hz,  $\text{CH}_2(\text{allyl})$ ), 116.4 (dd,  $J_{\text{CP}_1} = 9$  Hz,  $J_{\text{CP}_2} = 5$  Hz,  $\text{CH}(\text{allyl})$ ). **3b** was obtained as yellow crystals by recrystallization from toluene at  $-30^\circ\text{C}$  (367 mg, 87%), mp  $148^\circ\text{C}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  62.2 (d,  $^2J_{\text{PP}} = 17$  Hz,  $\text{PNC-Hex}_2$ ), 36.5 (d,  $^2J_{\text{PP}} = 17$  Hz,  $\text{Pi-Pr}_2$ ). MS (FAB): 705  $[\text{M} + \text{H}]^+$ .

**Synthesis of Palladium Complexes 7a,b.** At  $-80^\circ\text{C}$ , pyridine (0.52 mmol, 0.042 mL) was added to a DCM solution (3 mL) of **3a** (0.52 mmol, 283 mg) or **3b** (0.52 mmol, 364 mg). The solution was warmed to  $-30^\circ\text{C}$  and transferred by canula to a suspension of  $\text{NaBPh}_4$  (0.57 mmol, 195 mg) in DCM (5 mL). The resulting suspension was warmed to room temperature and stirred for 30 min.  $\text{NaCl}$  was filtered off, and the solvent was evaporated. Recrystallization from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  afforded **7b** as yellow crystals (482 mg, 87%), mp  $167\text{--}169^\circ\text{C}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CH}_2\text{Cl}_2$ ):  $\delta$  30.9 (d,  $J_{\text{PP}} = 4.4$  Hz,  $\text{Pi-Pr}_2$ ), 66.0 (br,  $\text{PNC-Hex}_2$ ). **7a** was also isolated and characterized (400 mg, 85%).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  34.1 (d,  $J_{\text{PP}} = 4.9$  Hz,  $\text{Pi-Pr}_2$ ), 68.7 (d,  $J_{\text{PP}} = 4.9$  Hz,  $\text{PNi-Pr}_2$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.00 (br, 3 H,  $\text{CH}_3i\text{-Pr}$ ), 1.14 (br, 3 H,  $\text{CH}_3i\text{-Pr}$ ), 1.21 (br, 3 H,  $\text{CH}_3i\text{-Pr}$ ), 1.24 (br, 3 H,  $\text{CH}_3i\text{-Pr}$ ), 1.24–1.32 (br, 12 H,  $\text{CH}_3\text{N}$ ), 1.42 (br, 12 H,  $\text{CH}_3\text{N}$ ), 2.41 (br, 1 H,  $\text{CHi-Pr}$ ), 2.50 (br, 1 H,  $\text{CHi-Pr}$ ), 2.76 (br, 2 H,  $\text{CH}_2(\text{allyl})$ ), 3.86 (br, 2 H, CHN), 3.95 (br, 2 H, CHN), 4.23 (br, 1 H,  $\text{CH}_2(\text{allyl})$ ), 4.32 (br, 1 H,  $\text{CH}_2(\text{allyl})$ ), 5.16 (m, 1 H,  $\text{CH}(\text{allyl})$ ), 6.85 (br, 3 H,  $\text{CHPy}$ ), 6.95 (br, 4 H,  $\text{CHBPh}$ ), 7.10 (br, 8 H,  $\text{CHBPh}$ ), 7.52 (br, 8 H,  $\text{CHBPh}$ ), 7.82 (br, 2 H,  $\text{CHPy}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  20.8 (s,  $\text{CH}_3i\text{-Pr}$ ), 21.0 (s,  $\text{CH}_3i\text{-Pr}$ ), 22.5 (d,  $J_{\text{CP}_2} = 8.7$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 22.9 (d,  $J_{\text{CP}_2} = 8.1$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 24.3 (d,  $J_{\text{CP}_1} = 4.7$  Hz,  $\text{CH}_3\text{Ni-Pr}$ ), 24.4 (d,  $J_{\text{CP}_1} = 4.0$  Hz,  $\text{CH}_3\text{Ni-Pr}$ ), 26.0 (s,  $\text{CH}_3\text{Ni-Pr}$ ), 26.2 (s,  $\text{CH}_3\text{Ni-Pr}$ ), 28.9 (dd,  $J_{\text{CP}_1} = 5.7$  Hz,  $J_{\text{CP}_2} = 30.4$  Hz,  $\text{CHi-Pr}$ ), 29.2 (dd,  $J_{\text{CP}_1} = 3.9$  Hz,  $J_{\text{CP}_2} = 30.5$  Hz,  $\text{CHi-Pr}$ ), 49.6 (d,  $J_{\text{CP}_1} = 11.0$  Hz,  $\text{CHNi-Pr}$ ), 50.6 (d,  $J_{\text{CP}_1} = 11.5$  Hz,  $\text{CHNi-Pr}$ ), 60.3 (dd,  $J_{\text{CP}_1} = 42.0$  Hz,  $J_{\text{CP}_2} = 5.3$  Hz,  $\text{CH}_2(\text{allyl})$ ), 65.5 (dd,  $J_{\text{CP}_1} = 13.1$  Hz,  $J_{\text{CP}_2} = 30.7$  Hz,  $\text{CH}_2(\text{allyl})$ ), 119.2 (dd,  $J_{\text{CP}_1} = 10.1$  Hz,  $J_{\text{CP}_2} = 6.2$  Hz,  $\text{CH}(\text{allyl})$ ), 122.1 (s,  $\text{CHBPh}$ ), 126.0 (q,  $J_{\text{CB}} = 2.7$  Hz,  $\text{CHBPh}$ ), 127.8 (s,  $\text{CHPy}$ ), 131.7 (s,  $\text{CHPy}$ ), 133.3 (s,  $\text{CHPy}$ ), 136.8 (s,  $\text{CHBPh}$ ), 164.6 (q,  $J_{\text{CB}} = 49.3$  Hz,  $\text{CBPh}$ );  $\text{C}_{\text{ylide}}$  was not observed.

**Synthesis of Palladium Complex 8b.** To a THF solution (5 mL) of **3b** (0.37 mmol, 258 mg) was added trimethylphosphine (0.37 mmol, 0.370 mL) at room temperature. This solution was transferred by canula to a suspension of  $\text{NaBPh}_4$  (0.40 mmol, 137 mg) in 1.5 mL of THF previously cooled to  $-80^\circ\text{C}$ . The suspension was warmed to room temperature and stirred for 1 h. The solvent was evaporated, and the solid was washed with  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL) and extracted with DCM (5 mL). Crystallization from a THF solution and slow diffusion of  $\text{Et}_2\text{O}$  at room temperature afforded **8b** as pale yellow crystals (322 mg, 82%), mp  $214\text{--}216^\circ\text{C}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.5 (dd,  $J_{\text{P}_3\text{P}_1} = 16$  Hz,  $J_{\text{P}_3\text{P}_2} = 7$  Hz,  $\text{PMe}_3$ ), 26.9 (dd,  $J_{\text{P}_2\text{P}_1} = 82$  Hz,  $J_{\text{P}_2\text{P}_3} = 7$  Hz,  $\text{Pi-Pr}_2$ ), 63.8 (dd,  $J_{\text{P}_1\text{P}_2} = 82$  Hz,  $J_{\text{P}_1\text{P}_3} = 16$  Hz,  $\text{PNC-Hex}_2$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.17 (dd, 3 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $^5J_{\text{HP}_2} = 19.2$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 1.22 (m, 12 H,  $\text{CH}_3\text{-Hex}$ ), 1.28 (dd, 3 H,  $^3J_{\text{HH}} = 6.8$  Hz,  $^5J_{\text{HP}_2} = 18.8$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 1.29 (dd, 3 H,  $^3J_{\text{HH}} = 7.4$  Hz,  $^5J_{\text{HP}_2} = 17.6$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 1.31 (dd, 3 H,  $^3J_{\text{HH}} = 7.8$  Hz,  $^5J_{\text{HP}_2} = 16.9$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 1.63 (d, 9 H,  $^2J_{\text{HP}_3} = 12.4$  Hz,  $\text{PMe}_3$ ), 1.68–2.04 (m, 28 H,  $\text{CH}_2\text{-Hex}$ ), 2.15 (sept d, 1 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $^5J_{\text{HP}_1} = 3.2$  Hz,  $^5J_{\text{HP}_2} = 10.4$  Hz,  $\text{CHi-Pr}$ ), 2.28 (sept d, 1 H,  $^3J_{\text{HH}} = 7.2$  Hz,  $^5J_{\text{HP}_1} = 3.2$  Hz,  $^5J_{\text{HP}_2} = 10.4$  Hz,  $\text{CHi-Pr}$ ), 2.70 (m, 2H,  $\text{CH}_2(\text{allyl})$ ), 3.51 (m, 4 H,  $\text{CHNc-Hex}$ ), 4.04 (m, 1 H,  $\text{CH}_2(\text{allyl})$ ), 4.14 (t,  $J_{\text{HH}} = 8.4$  Hz,  $^5J_{\text{HP}_1} = 8.4$  Hz,  $\text{CH}_2(\text{allyl})$ ), 5.12 (m, 1 H,  $\text{CH}(\text{allyl})$ ), 6.95 (t, 4 H,  $J_{\text{HH}} = 7.2$  Hz,  $\text{CHBPh}$ ), 7.10 (t,  $J_{\text{HH}} = 7.2$  Hz,  $\text{CHBPh}$ ), 7.38 (br, 8 H,  $\text{CHBPh}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  16.9 (d,  $J_{\text{CP}} = 57.3$  Hz,  $\text{PMe}_3$ ), 20.0 (d,  $J_{\text{CP}_2} = 2.6$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 20.1 (d,  $J_{\text{CP}_2} = 2.7$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 22.6 (d,  $J_{\text{CP}_2} = 6.0$  Hz,  $\text{CH}_3i\text{-Pr}$ ), 22.7 (d,  $J_{\text{CP}_2} = 6.1$

Hz, CH<sub>3</sub>*i*-Pr), 26.1 (s, CH<sub>2</sub>*c*-Hex), 26.2 (s, CH<sub>2</sub>*c*-Hex), 27.9 (s, CH<sub>2</sub>*c*-Hex), 28.0 (br, CH<sub>2</sub>*c*-Hex), 29.0 (dd,  $J_{CP1} = 5.0$  Hz,  $J_{CP2} = 18.6$ , CH*i*-Pr), 29.1 (dd,  $J_{CP1} = 5.0$  Hz,  $J_{CP2} = 18.6$ , CH*i*-Pr), 33.7 (ddd,  $J_{CP1} = 33.2$  Hz,  $J_{CP2} = 23.4$  Hz,  $J_{CP3} = 58.3$ , C<sub>ylide</sub>), 35.5 (d,  $J_{CP1} = 3.3$  Hz, CH<sub>2</sub>*c*-Hex), 35.6 (d,  $J_{CP1} = 3.5$  Hz, CH<sub>2</sub>*c*-Hex), 35.8 (d,  $J_{CP1} = 2.7$  Hz, CH<sub>2</sub>*c*-Hex), 36.0 (d,  $J_{CP1} = 2.3$  Hz, CH<sub>2</sub>*c*-Hex), 57.8 (dd,  $J_{CP1} = 45.6$  Hz,  $J_{CP2} = 7.0$  Hz, CH<sub>2</sub>(allyl)), 59.1 (d,  $J_{CP1} = 10.2$  Hz, CHN*c*-Hex), 59.4 (d,  $J_{CP1} = 10.8$  Hz, CHN*c*-Hex), 65.8 (dd,  $J_{CP1} = 15.5$  Hz,  $J_{CP2} = 33.0$  Hz, CH<sub>2</sub>(allyl)), 119.2 (dd,  $J_{CP1} = 11.6$  Hz,  $J_{CP2} = 6.7$  Hz, CH(allyl)), 122.2 (s, CH<sub>BPh</sub>), 126.1 (q,  $J_{CB} = 2.7$  Hz, CH<sub>BPh</sub>), 136.3 (s, CH<sub>BPh</sub>), 164.4 (q,  $J_{CB} = 49.3$  Hz, C<sub>BPh</sub>). MS (FAB): 743 [M]<sup>+</sup>.

**Synthesis of Palladium Complex 10b.** To a DCM solution (1 mL) of **7b** (0.085 mmol, 60 mg) was added DMAP (0.085 mmol, 11 mg) in DCM (1 mL) at -80 °C. The solution was warmed to room temperature and stirred for 1 h. After evaporation of the solvent, the solid was washed with Et<sub>2</sub>O, affording **10b** as a yellow powder (89 mg, 94%), mp 188–190 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 31.4 (d,  $J_{PP} = 8$  Hz, P*i*-Pr<sub>2</sub>), 60.6 (br, P*Nc*-Hex<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.01 (dd, 3 H,  $^3J_{HH} = 7.2$  Hz,  $J_{HP2} = 16.2$  Hz, CH<sub>3</sub>*i*-Pr), 1.14 (dd, 6 H,  $^3J_{HH} = 7.1$  Hz,  $J_{HP2} = 17.4$  Hz, CH<sub>3</sub>*i*-Pr), 1.18 (dd, 3 H,  $^3J_{HH} = 6.9$  Hz,  $J_{HP2} = 18.0$  Hz, CH<sub>3</sub>*i*-Pr), 2.19 (sept d, 1 H,  $^3J_{HH} = 7.0$  Hz,  $J_{HP2} = 7.1$  Hz, CH*i*-Pr), 2.29 (sept d, 1 H,  $^3J_{HH} = 7.1$  Hz,  $J_{HP2} = 7.1$  Hz, CH*i*-Pr), 2.55 (s, 6 H, NMe<sub>2</sub>), 2.62 (m, 2 H, CH<sub>2</sub>(allyl)), 3.46 (m, 4 H, CHN*c*-Hex), 4.08 (m, 2 H, CH<sub>2</sub>(allyl)), 5.05 (m, 1H, CH(allyl)), 6.02 (d, 2 H,  $J_{HH} = 7.8$  Hz, CH<sub>DMAP</sub>), 6.90 (t, 4 H,  $J_{HH} = 7.2$  Hz, CH<sub>BPh</sub>), 7.05 (t<sub>like</sub>, 8 H,  $J_{HH} = 7.5$  Hz, CH<sub>BPh</sub>), 7.46 (br, 8 H, CH<sub>BPh</sub>), 7.69 (d, 2 H,  $J_{HH} = 7.8$  Hz, CH<sub>DMAP</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>): δ 20.2 (s, CH<sub>3</sub>*i*-Pr), 20.3 (s, CH<sub>3</sub>*i*-Pr), 20.8 (d,  $J_{CP2} = 5.7$  Hz, CH<sub>3</sub>*i*-Pr), 21.2 (d,  $J_{CP2} = 5.5$  Hz, CH<sub>3</sub>*i*-Pr), 25.8 (s, CH<sub>2</sub>*Nc*-Hex), 25.9 (s, CH<sub>2</sub>*Nc*-Hex), 27.4 (s, CH<sub>2</sub>*Nc*-Hex), 27.5 (s, CH<sub>2</sub>*Nc*-Hex), 27.6 (s, CH<sub>2</sub>*Nc*-Hex), 27.7 (s, CH<sub>2</sub>*Nc*-Hex), 28.3 (dd,  $J_{CP1} = 5.3$  Hz,  $J_{CP2} = 17.9$  Hz, CH*i*-Pr), 28.4 (dd,  $J_{CP1} = 6.2$  Hz,  $J_{CP2} = 17.9$  Hz, CH*i*-Pr), 35.6 (d,  $J_{CP1} = 2.9$  Hz, CH<sub>2</sub>*c*-Hex), 35.7 (d,  $J_{CP1} = 2.9$  Hz, CH<sub>2</sub>*c*-Hex), 35.9 (s, CH<sub>2</sub>*c*-Hex), 36.0 (s, CH<sub>2</sub>*c*-Hex), 39.7 (s, NMe<sub>2</sub>), 56.3 (dd,  $J_{CP1} = 43.9$  Hz,  $J_{CP2} = 5.1$  Hz, CH<sub>2</sub>(allyl)), 58.0 (d,  $J_{CP1} = 9.8$  Hz, CHN*c*-Hex), 58.5 (d,  $J_{CP1} = 9.8$  Hz, CHN*c*-Hex), 64.3 (dd,  $J_{CP1} = 13.7$  Hz,  $J_{CP2} = 31.1$  Hz, CH<sub>2</sub>(allyl)), 65.3 (dd,  $J_{CP1} = 36.2$  Hz,  $J_{CP2} = 42.3$  Hz, C<sub>ylide</sub>), 107.4 (s, CH<sub>DMAP</sub>), 117.6 (dd,  $J_{CP1} = 10.2$  Hz,  $J_{CP2} = 5.9$  Hz, CH(allyl)), 121.6 (s, CH<sub>BPh</sub>), 125.5 (s, CH<sub>BPh</sub>), 136.3 (s, CH<sub>BPh</sub>), 141.5 (s, CH<sub>DMAP</sub>), 164.2 (q,  $J_{CB} = 49.3$  Hz, C<sub>BPh</sub>).

**X-ray Crystallographic Studies of Complexes 3b, 7b, and 8b.** Crystal data for all structures are presented in Table 2. Data for all structures were collected at 193(2) K using an oil-coated shock-cooled

crystal on a Bruker-AXS CCD 1000 diffractometer ( $\lambda = 0.71073$  Å). Semiempirical absorption corrections were employed.<sup>26</sup> The structures were solved by direct methods (SHELXS-97)<sup>27</sup> and refined using the least-squares method on  $F^2$ .<sup>28</sup>

**Computational Details.** Palladium and phosphorus were treated with a Stuttgart–Dresden pseudopotential in combination with their adapted basis set.<sup>29</sup> In all cases, the basis set has been augmented by a set of polarization function (f for Pd and d for P).<sup>30</sup> Carbon, nitrogen, and hydrogen atoms have been described with a 6-31G(d,p) double- $\zeta$  basis set.<sup>31</sup> Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91.<sup>32</sup> Geometry optimizations were carried out without any symmetry restrictions; the nature of the *extrema* (*minimum*) was verified with analytical frequency calculations. All computations described herein were performed with the Gaussian 98<sup>33</sup> suite of programs. The electronic density was analyzed using the Natural Bonding Analysis (NBO) technique.<sup>24</sup>

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**Supporting Information Available:** Computational details (Z-matrices) and complete ref 33 (PDF); X-ray crystallographic data for complexes **3b**, **7b**, and **8b** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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