# Study of Insertion of Olefins and/or Carbon Monoxide into Phosphine-Imine Palladium Methyl Complexes

K. Rajender Reddy, K. Surekha, Gene-Hsiang Lee, Shie-Ming Peng, Jwu-Ting Chen, and Shiuh-Tzung Liu\*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

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Palladium methyl complexes with a phosphine-imine ( $\mathbf{P} \sim \mathbf{N}$ ) bidentate ligand, [Pd( $\mathbf{P} \sim \mathbf{N}$ )-MeCl] (1),  $[Pd(\mathbf{P} \sim \mathbf{N})Me(\mathbf{C}H_3CN)](BF_4)$  (2), and  $[Pd(\mathbf{P} \sim \mathbf{N})Me(PPh_3)](BF_4)$  (3), are treated with CO to result in the corresponding Pd-acyl complexes **4**-**6**. NMR studies indicate the formation of a sole isomer with the acyl group cis to the phosphine donor. The neutral complex 4 and the triphenylphosphine-substituted complex 6 cannot serve for the insertion of ethylene. However, the acetonitrile complex 5 appears to be active in the insertion reaction with various alkenes as well as ethylene/CO (E-CO) co-oligomerization, resulting in the products 7-14and 16, which have been isolated and characterized by spectroscopic methods. X-ray structures of 1, 2, 3, 4, 7, 10, 11, and 13 are revealed.

## Introduction

Insertion of small unsaturated molecules into the metal-carbon bond is an important step for the metalcatalyzed reactions of C-C bond formation.<sup>1</sup> Among them, the alternating insertion of carbon monoxide and olefins into metal-carbon bonds leading to the formation of polyketones by various palladium complexes has received considerable interest.<sup>2</sup> It is known that the coordinating ability of the ligand and its steric environments generally control the efficiency of the catalyst. In this regard, palladium-based catalysts with symmetrical bidentate phosphorus [P-P]<sup>3</sup> or nitrogen [N-N]<sup>4</sup> donor atoms are found to be very effective. A number of stoichiometric and theoretical studies have provided valuable information on mechanistic aspects of migratory insertion of CO and olefins into Pd-alkyl and Pdacyl bonds, respectively.<sup>5-7</sup>

Recently, interest in searching for new catalysts with unsymmetrical bidentate ligands has been increasing,8-11 particularly with P-N ligands.<sup>12,13</sup> Although the palladium complexes with phosphino-oxazolines ligands in

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### Study of Insertion of Olefins

asymmetric catalysis have been reported,<sup>14</sup> ligands with phosphorus and  $\pi$ -accepting imine nitrogen donors in palladium-catalyzed reactions show very promising activity for homo- and copolymerization.<sup>13</sup> Unlike the symmetrical counterparts, the soft and hard nature of phosphorus and nitrogen, combined with their trans effecting nature, are expected to influence the binding properties of the substrates as well as migratory insertion with keen discerning ability. Isolation and characterization of the insertion intermediates with P-N ligands can contribute valuable information on the reactivity of these catalysts.<sup>13</sup> Some preliminary results concerning the insertions of CO with various functionalized alkenes and alkynes in cationic palladium complexes  $[Pd(\mathbf{P} \sim \mathbf{N})(Me)L]^+$  from our laboratory were reported recently.<sup>15</sup> Continuing this trend, we report the synthesis and detailed structural characterization of both neutral and cationic palladium complexes and their reactivity toward CO and various olefins.

### Results

**Preparation of Ligand and the [Pd(P~N)MeCl]] Complex.** The phosphine–imine ligand was prepared by simple condensation of 2-(diphenylphosphino)aniline<sup>16</sup> with excess benzaldehyde and characterized by spectroscopic methods. Substitution reaction of Pd-(COD)MeCl<sup>17</sup> with the **P**~**N** ligand in a THF solution provided the neutral methyl palladium complex [Pd-(**P**~**N**)MeCl] (1) in excellent yield. Recrystallization

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 Table 1. Selected IR and NMR Data of Free

 Ligand and Its Palladium Complexes<sup>a,b</sup>

	${\scriptstyle {{\cal V}_{C=N},}\atop{cm^{-1}}}$	$\mathcal{V}_{(N=CMe)},$ cm <sup>-1</sup>	<sup>I</sup> H NMR Pd–C <i>H</i> <sub>3</sub>	-HC=N	<sup>31</sup> P NMR
<b>P</b> ∼N	1625			8.12	-14.5
1	1611		0.88 (d,	8.62	35.4
2	1609	2322, 2289	${}^{3}J_{\rm PH} = 2.9)$ 0.58 (d, ${}^{3}J_{\rm PH} = 1.6)$	9.26	38.6
3	1610		$0.77 \text{ (dd,} ^{3}J_{\rm PH} = 6.1)$	8.61	30.8 and 27.5 ( $^2J_{\rm PP} = 381$ Hz)

<sup>a</sup> In KBr. <sup>b</sup>In CDCl<sub>3</sub>, ppm, J in Hz.



Figure 1. ORTEP plot of complex 1.

from dichloromethane and hexane gave the analytically pure product. Spectroscopic analysis confirms the structure of the complex (Table 1). A downfield shift of ca. 50 ppm with respect to the free ligand reflects the coordination of the phosphine to the palladium metal.<sup>18,19</sup> Appearance of a single peak in the <sup>31</sup>P NMR for the complex suggests the formation of a single isomer. The stereochemistry of the methyl group cis to the phosphorus was established from its <sup>1</sup>H NMR spectra, where the methyl group bound to the palladium appears as a doublet with a coupling constant  $J_{\rm P-H} \approx 3.0$  Hz, which is in the typical range for the *cis*-[PdMeCl(P–N)] complexes.<sup>12a,20</sup>

Further confirmation of cis-geometry for **1** is obtained from the X-ray structural analysis. The ORTEP diagram for **1**, as shown in the Figure 1, indicates the square planar geometry around the palladium metal center with the phosphine and methyl groups being cis to each other. Selected bond lengths and angles are listed in the Table 2, which are in agreement with the reported [Pd(P-N)RX] complexes.<sup>12b,20</sup>

**Preparation of the Cationic**  $[Pd(P \sim N)Me(L)]^+ \{L = CH_3CN \text{ or } PPh_3\}$  **Complexes**. The cationic complex **2** is prepared by the treatment of **1** with AgBF<sub>4</sub> in a mixture of dichloromethane and acetonitrile solution (Scheme 1). After the removal of AgCl by filtration, the solution was evaporated to a small volume and the desired complex was precipitated upon the addition of

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Table 2. Selected Bond Distances (Å) and Angles (deg) of Palladium Complexes

					•	•		-	
	1	2	3	4	7	9	10	11	13
Pd-C1 Pd-Cl1	2.029(6) 2.375(2)	2.045(4)	2.075(7)	1.983(3) 2.3777(7)	2.022(5)	2.003(9)	2.026(4)	2.059(3)	2.034(5)
Pd-N1 Pd-N2	2.224(4)	2.198(3) 2.112(3)	2.183(5)	2.284(2)	2.208(3)	2.182(7)	2.191(3)	2.148(3)	2.175(4)
Pd-P1 Pd-P2	2.196(2)	2.2075(9)	2.312(2) 2.333(2)	2.2495(7)	2.180(1)	2.186(2)	2.186(9)	2.212(1)	2.189(1)
$\begin{array}{c} Pd{-}O1 \\ C1{-}Pd{-}P1 \\ P1{-}Pd{-}N1 \\ C1{-}Pd{-}N1 \\ N1{-}Pd{-}C11 \\ C1{-}Pd{-}C11 \\ C11{-}Pd{-}P1 \\ N1{-}Pd{-}N2 \\ C1{-}Pd{-}N2 \\ N2{-}Pd{-}P1 \\ N1{-}Pd{-}P2 \end{array}$	91.6(2) 81.37(11) 172.7(2) 98.56(11) 88.1(2) 170.96(7)	90.38(13) 83.28(7) 173.61(14) 99.05(11) 87.3(2) 173.61(9)	92.2(2) 79.49(14) 170.9(2) 101.29(13)	97.48(9) 78.90(6) 176.18(11) 97.85(6) 85.92(9) 169.78(3)	2.143(3) 92.7(2) 82.98(9) 175.2(2)	2.127(4) 95.4(3) 81.6(2) 175.4(4)	2.148(3) 93.05(13) 83.36(8) 176.03(14)	2.161(2) 95.89(12) 82.76(7) 177.72(14)	2.112(3) 94.8 (2) 82.37(10) 175.6(2)
C1-Pd-P2 P2-Pd-P1 N1-Pd-O1 C1-Pd-O1 O1-Pd-P1			87.7(2) 163.97(7)		103.53(12) 80.9(2) 172.79(9)	101.8(3) 81.3(4) 176.5(3)	103.39(11) 80.0(2) 171.31(8)	99.27(10) 81.68(13) 168.34(8)	99.03(13) 83.5(2) 173.44(9)
	_			Schem	e 1				
	(	P Pd N	le AgBF <sub>4</sub>	$\binom{P}{N} \stackrel{+}{Pd}$	Me PPh	$\frac{3}{N}$	Pd Pd BF <sub>4</sub> -PPh <sub>3</sub>		
		1		:	2		3		
				PPh N-P	$p^2 \equiv \mathbf{P} \sim \mathbf{N}$				

ether. Selected IR and NMR data of the complexes are also shown in Table 1.

The presence of two low-intensity bands at 2322 and 2289 cm<sup>-1</sup> in the IR spectrum, which are assigned to the coordinated acetonitrile, is comparable to the reported palladium complexes.<sup>13a</sup> Phosphorus-31 NMR again shows only one signal corresponding to the formation of a single isomer. The peaks are slightly downfield shifted (1-2 ppm) compared to the less electrophilic neutral analogues. A slightly smaller hydrogen-phosphorus coupling ( $J_{P-H} \approx 1.6$  Hz) for the methyl hydrogen atoms is observed.<sup>13a</sup> X-ray structural analysis of **2** (Figure 2) also confirms the cis-arrangement of phosphine and methyl group and the coordination of acetonitrile to palladium as well. Selected bond lengths and angles are given in Table 2. The triphenylphosphinesubstituted complex 3 was prepared by substitution reaction of  $\mathbf{2}$  with PPh<sub>3</sub> in dichloromethane solution, and its characterization was performed by both <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy (Table 1).<sup>21</sup> In addition, the X-ray structure of 3 (Figure 3) was obtained.

**CO and Ethylene Insertions into Neutral and Cationic Palladium Complexes.** Insertion reactions of CO into the Pd–C bond for complexes **1–3** were monitored by <sup>31</sup>P NMR. In a typical experiment, a CDCl<sub>3</sub> solution of the respective complex (10–15 mg) was bubbled with CO for 30 min, and the <sup>31</sup>P NMR and <sup>1</sup>H



**Figure 2.** Molecular diagram of the cation  $[(\mathbf{P} \sim \mathbf{N})Pd(Me)-(NCCH_3)]^+$ .

NMR indicated the formation of the acyl product. The resulting acyl complexes 4-6 were isolated in stable solid form as described in Experimental Section. Selected spectroscopic data for the acyl derivatives are shown in Table 3.

Infrared absorption for the C=O stretching band appears in the range  $1688-1705 \text{ cm}^{-1}$ , which is typical for the acyl complexes.<sup>13a</sup> <sup>31</sup>P NMR signals for **4**-**6** suggest the formation of one inserted product in each case. It is noticed that complex **5** exhibits relatively

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Figure 3. Structure of complex 3.

Table 3. Selected IR and NMR Data of the<br/>Inserted Products<sup>a,b</sup>

	$C=O^{c}$			
	$\nu$ (cm <sup>-1</sup> )	<sup>1</sup> H NMR Pd $-R$	-HC=N	<sup>31</sup> P NMR
4	1688	2.23 (s, -COCH <sub>3</sub> )	8.55 (m)	14.8
5	1705	1.76 (s, -COCH <sub>3</sub> )	9.11 (s)	18.4
6	1694	1.79 (s)	8.62 (s)	16.5 and 12.5
				$(^{2}J_{\rm PP}=250)$
7	1636	1.86 (t, $J = 7.0$ , Pd-CH <sub>2</sub> )	9.15 (s)	36.7
8		2.72 (s, -COCH <sub>2</sub> )	9.07 (s)	19.9
9	1712 (f)	1.89 (m, 5H,	9.20 (s)	36.8
	1629 (c)	CH <sub>2</sub> , CH <sub>3</sub> )		
10	1630	0.93 (t, 3H) (10a)	9.14	36.3
		1.33 (d, 3H) ( <b>10b</b> )	9.18	39.5
11	1708,	2.51 (s, Pd-CH)	9.29 (s)	37.3
	1686 (f)			
	1630 (c)			
12	1610 (c)	3.46 (m, Pd-CH)	9.11 (s)	31.2
13	1626 (c)	1.32 (d, Pd-CH)	9.19 (s)	35.3
14	1713 (f)	5.15 (s, Pd-CH)	9.15 (s)	35.7
	1610 (c)			
15	1620 (c)	5.27 (s, Pd-CH)	9.30 (s)	34.7
16		1.83 (t, Pd-CH <sub>2</sub> )	9.26 (s)	37.7

 $^a$  In KBr.  $^b$ In CDCl3, in ppm, J in Hz.  $^c({\rm f})$  free carbonyl, (c) coordinated carbonyl.

better stability and can be isolated at room temperature and kept at 0  $^\circ C$  for several days.

Insertion of ethylene into the palladium-acyl bond was achieved by bubbling ethylene through a solution of dichloromethane containing the complex 5. The NMR spectrum of the resulting reaction mixture was taken immediately. Complete conversion of 5 into 7 was done within 1 h. The <sup>31</sup>P NMR spectrum shows a downfield shift representing the palladium-alkyl bond formation. Appearance of one <sup>31</sup>P signal indicates the formation of only one isomer. The IR spectrum shows a C=O stretching band at 1636 cm<sup>-1</sup>, which is shifted about 70  $cm^{-1}$  to lower wavenumber with respect to that of 5,<sup>5i,6e</sup> indicating the coordination of the acyl-oxygen to the palladium center. Both <sup>1</sup>H and <sup>13</sup>C NMR support the formation of the insertion products (Table 3). It is noticed that the compound 7 is much more stable than the acyl complex 5 presumably due to the chelation effect. The detailed structure of 7 is confirmed by its X-ray single-crystal structural analysis (Figure 4). No insertion of the ethylene molecule into the Pd-acyl bond of 4 and 6 was observed. Bubbling for a longer period  $(\sim 24 \text{ h})$  resulted in the precipitation of palladium black.



Figure 4. ORTEP plot of complex 7.

Further CO insertion into 7 in dichloromethane was not successful, but could be done in acetonitrile or a mixture of acetonitrile and dichloromethane. Apparently, the coordinating solvent is necessary to stabilize the resulting acyl product, as observed in prior cases.<sup>13d</sup> The crystal structures of complex 8 and the subsequent ethylene-inserted one 9 have been reported in our preliminary communication, Scheme 2.15 The Pd-C1 bond distances in 7 [2.022(5) Å] and 9 [2.003(9) Å] are comparable with those in the diimine analogues, and the Pd-O1 bond distances in 7 [2.143(3) Å] and 9 [2.127-(4) Å] are in agreement with those in the diphosphine complexes.<sup>6e,22</sup> The formation of a five-membered (C,O) chelation product via olefin insertions into the Pd-acyl bond is known.<sup>2c</sup> Nevertheless further insertion by CO and the fact that it serves as a catalyst for CO/ethylene copolymerization in complex 9 indicate that the phosphine-imine system may be promising for the use of insertion processes.<sup>15</sup>

Insertion of Functionalized Olefins into 5. Insertion of propene with 5 leads to the formation of two mixed species (10a and 10b) in 1:1 ratio according to the <sup>1</sup>H and <sup>31</sup>P NMR spectroscopic data. On the other hand, complex 5 undergoes regiospecific insertions (2,1insertion) with methyl acrylate or styrene to provide 11 and 12, respectively, as shown in Scheme 3. The insertion of norbornene into 5 proceeds exclusively from the exo-face to give the product 13. Such face-selective insertion of norbornene into the Pd-acyl bond was also observed with bidentate nitrogen and bis(phosphine) complexes earlier.<sup>6e,22</sup> The complexes **10–13** are isolated in solid form and characterized by spectroscopic methods (Table 3) and by X-ray structural analysis. The molecular structure of 13 is illustrated in Figure 5, and selected bond distances and angles are summarized in Table 2.

It is generally known that olefin insertion into a Pd– acyl bond is faster than into the Pd–alkyl bond. Experimental evidence also suggests that the formation of the five-membered (C,O) chelation product provides the extra stability to avoid competing  $\beta$ -hydride elimination. In all instances investigated in this work, consecutive insertion of alkene molecules is not feasible, i.e., no insertion of alkene into Pd–C<sub>(alkyl)</sub>, except that

<sup>(22)</sup> Brumbaugh, J. S.; Whittle, R. R.; Parvez, M.; Sen, A. Organometallics **1990**, *98*, 1735.







Figure 5. Structure of complex 13.

vinyl acetate can insert into **5** and **2** to yield **14** and **15**, respectively.<sup>15</sup>



**Copolymerization.** Taking advantage of the feasibility of the stepwise insertion of CO/ethylene (E-CO) in **2**, the use of **2** as the catalyst for copolymerization is

investigated. In an autoclave was placed the 27 mg of catalyst in dichloromethane (70 mL), and 40 psi each of CO and ethylene was stirred at room temperature for 48 h. The resulting white solid was filtered and washed with 5 N HCl, followed by water and acetone, respectively. A small amount of polymer product (440 mg) was formed. It appears that complex **2** is not a very efficient catalyst for E-CO copolymerization. However, such reaction allows us to isolate the rare species of a metal-capped E-CO copolymer. The reaction proceeds at room temperature for 4 h, and an E-CO oligomeric palladium complex 16 was acquired. It was characterized by spectroscopic methods. <sup>1</sup>H NMR and mass spectra are shown in Figures 6 and 7, which clearly evidence the attached ethylene/CO oligomeric units to palladium metal. By NMR integration, the average repeating units of each chain have been estimated to be 14.



## Discussion

In this work, we demonstrate that the unsymmetric  $\mathbf{P}{\sim}\mathbf{N}$  bidentate tends to allow single regioisomers in each insertion process. Since the migratory insertion could change the coordination site for the carbon-bound ligand, one might expect to see the kinetic products with the carbon ligand being trans or cis to phosphine.



Figure 6. (a) <sup>1</sup>H NMR spectrum of complex 2. (b) <sup>1</sup>H NMR spectrum of complex 7. (c) <sup>1</sup>H NMR spectrum of complex **16**, the metal-capped oligomer.



Figure 7. (a) FAB mass spectrum of complex 16 in the range m/z 900–1300. (b) Expansion of m/z at 1102, which is consistent with formula of  $[(\mathbf{P} \sim \mathbf{N}) Pd(CH_2CH_2CO)_{11}CH_3]^+$ . (c) Simulated pattern of the formula of  $[(\mathbf{P} \sim \mathbf{N})Pd(CH_2CH_2 - \mathbf{N})Pd(CH_2CH_2 -$  $CO)_{11}CH_3]^+$ .

However, only one of that kind of intermediate with a carbon ligand cis to phosphine is observed in our studies. This is similar to the carbonylation of other known P-N palladium complexes<sup>13a,d</sup> and suggests that a rapid isomerization process must occur during the insertion steps. This outcome is consistent with Pearson's antisymbiotic effect.<sup>23</sup>

The Pd-acyl complexes with weak coordinating ligands such as acetonitrile can be subjected to decarbonylation, which accounts for the unstable nature of some Pdacyl complexes.<sup>5d,6e,g,10a</sup> The deinsertion process can be hindered by strongly coordinating or inert ligands such as chloride or phosphines. Indeed, acyl complexes 4 and 6 are found to be stable at 25 °C. Curiously, the cationic palladium acyl complex 5 with a weak coordinating acetonitrile is stable and allows us to utilize it for further studies of alkene and alkyne insertions.<sup>15</sup> Luinstra and co-workers also demonstrated the isolation of CO-inserted products with mixed bidentate P-N ligands.<sup>13a</sup> Like compound 5, the stable Pd-acyl complex 17 with an unsymmetric P–O ligand was reported by Braunstein and co-workers recently.<sup>11a</sup> In fact, we demonstrated that the metal-capped polymeric species **16** can be isolated under copolymerization conditions, indicating that the  $P \sim N$  bidentate plays a role in stabilization of the palladium-attached carbon ligand, which also explains the lower catalytic activity in copoylermization; that is, every metal center can carry only one polymer chain.



Complex 5 shows reactivity toward insertion with various alkenes.  $\alpha$ -Olefins such as styrene, methyl acrylate, or vinyl acetate undergo a regioselective insertion (2,1-insertion). Norbornylene undergoes insertion selectively at the exo-face. Only propene gives a mixture of 1,2- and 2,1-inserted products. This selectivity is consistent with most of the other insertion instances, in which the coordinating orientation of the olefin would determine the regio- or stereoproperties of the products.

Unlike the diimine-palladium complexes, neither 2 nor **5** can serve as a polymerization catalyst for olefins, even for ethylene. Our previous study indicates that complex 2 mediates the dimerization and trimerization of ethylene,<sup>24</sup> but shows no reactivity toward propene or styrene. On the other hand, alternating insertion of CO and olefins in **2** or **5** is facile, indicating the greater activation barrier for olefin insertion than that of COinsertion reactions.<sup>5a,6d</sup>

The crystallographic results in this work confirm that the ligands of the P,N chelates always have the carbon ligand seated trans to the imine donors. The configurations of the coordinating atoms in complexes are in typical square planar geometry, as expected. The bond distances and bond angles are in the normal range, except the angles of N-Pd-P (Tables 2) are smaller, due to o-phenylene linkage. Whether the angle of N-Pd-P is related to the activity of insertion is currently under investigation.

#### Conclusion

The designed P~N ligand in this work allows the formation of a stable five-membered chelation product

 <sup>(23)</sup> Pearson, R. G. *Inorg. Chem.* 1973, *12*, 712.
 (24) Chen, J.-T.; Liu, S.-T.; Zhao, K.-Q. *J. Chin. Chem. Soc.* 2000, 47, 279.

with palladium complexes. The mixed soft and hard donors of phosphorus and nitrogen in the palladium complexes influence the binding stability of the substrates and ligand migration and results in the isolation of various new inserted intermediates, including a rare palladium-capped oligomer. This result allows the opportunity to build block polymerizations.

### **Experimental Section**

**General Information.** All reactions, manipulations, and purifications steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried with CaH<sub>2</sub> and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used as received unless otherwise stated. 2-(Diphenylphosphino)aniline and Pd(COD)MeCl were prepared according to literature procedures.<sup>16,17</sup>

Nuclear magnetic resonance spectra were recorded in CDCl<sub>3</sub> on either a Bruker AC-E 200 or AM-300 spectrometer. Chemical shifts are given in parts per million relative to Me<sub>4</sub>S for <sup>1</sup>H and relative to 85%  $H_3PO_4$  for <sup>31</sup>P NMR. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series II) as KBr pallets, unless otherwise noted.

**Synthesis of P**~**N Ligand.** To freshly distilled benzaldehyde (16 mL, 0.15 mol) was added 2-(diphenylphosphino)aniline (6.0 g, 0.02 mol) under nitrogen, and the mixture was stirred at room temperature under vacuum. Completion of the reaction was monitored by <sup>31</sup>P NMR, which took 6–7 h. The reaction mixture was poured into cold methanol and kept at low temperature overnight. The desired ligand P~N was crystallized as a white solid (5.2 g, 65%). IR (KBr): 1625 cm <sup>-1</sup>(C=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.84–7.31 (m, 17 H), 7.63 (m, 2 H), 8.12 (s, 1 H). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  –14.5. Anal. Calcd for C<sub>25</sub>H<sub>20</sub>NP: C 82.17; H, 5.52; N, 3.83. Found: C, 81.84; H, 5.79; N, 3.67. FABMS: 366 (M<sup>+</sup>).

**Complex 1.** To a colorless solution of Pd(COD)MeCl (265 mg, 1 mmol) in THF (5 mL) was added an equal molar amount of the ligand in a THF solution (5 mL). The mixture was stirred under N<sub>2</sub> at room temperature. After 15 min a white solid began to precipitate, and the solution was stirred for another 30 min. The resulting mixture was cooled, and the white solid was filtered and washed with ether and dried under vacuum (470 mg, 90%). IR (KBr): 1611 (C=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.88 (d, 3 H, J = 2.9 Hz), 7.13–7.60 (m, 17 H), 8.53 (m, 2 H), 8.62 (s, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  0.87 (Pd–Me), 168.9 (C=N). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  35.4. Anal. Calcd for C<sub>26</sub>H<sub>23</sub>NPClPd: C, 59.8, H, 4.43, N, 2.68. Found: C, 59.9; H, 4.78; N, 2.28.

**Complex 2.** To a solution of the neutral complexes **1** (0.5 mmol) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> was added a stoichiometric amount of AgBF<sub>4</sub> in 5 mL of CH<sub>3</sub>CN under nitrogen, and the reaction mixture was stirred at room temperature for 1 h. The resulting white AgCl precipitate was filtered through silica gel, and the solvent was evaporated to a small amount. Upon addition to Et<sub>2</sub>O, a precipitate was deposited, which was filtered and dried under vacuum, resulting in 262 mg (85%) of pure product. IR (KBr): 1609 (C=N), 2322 and 2289 (C=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.58 (d, 3 H, J = 1.60 Hz), 1.80 (s, 3 H), 7.09–8.04 (m, 17 H), 8.23 (d, 2 H, J = 7.0 Hz), 9.26 (s, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  -2.09 (Pd–Me), 1.81 (Pd–NCMe), 169.6 (C=N). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  38.6. Anal. Calcd for C<sub>28</sub>H<sub>26</sub>N<sub>2</sub>PBF<sub>4</sub>Pd: C, 54.70; H, 4.26; N, 4.55. Found: C, 54.66; H, 4.17; N, 4.36. FABMS: 486.1 (M<sup>+</sup> – CH<sub>3</sub>CN).

**Complex 3.** To a solution of the cationic complexes **2** (0.5 mmol) in 20 mL of THF was added a stoichiometric amount of PPh<sub>3</sub> under nitrogen, and the reaction mixture was stirred for 1 h. The solvent was removed under vacuum, and the residue was washed with  $Et_2O$  and dried under vacuum, resulting in 355 mg (85%) of pure product. IR (KBr): 1610

(C=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.77 (t, 3 H, J = 6.1 Hz), 7.0– 7.82 (m, 32 H), 8.05 (d, 2 H, J = 6.8 Hz), 8.61 (s, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  –0.16 (Pd–Me), 172.1 (C=N). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  30.8 and 27.5 (d, <sup>2</sup> $J_{PP} = 381$  Hz). Anal. Calcd for C<sub>44</sub>H<sub>38</sub>NP<sub>2</sub>BF<sub>4</sub>Pd: C, 63.20; H, 4.58; N, 1.67. Found: C, 62.98; H, 4.70; N, 1.60. FABMS: 749.1 (M<sup>+</sup>).

**General Procedure for Preparation of Complexes 4–6.** To a solution of 1-3 (0.25 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, continuous bubbling of carbon monoxide for 2-4 h resulted in the formation of the corresponding CO-inserted product. The resulting solution was cooled and filtered through silica gel (small amount of Pd black formation was observed in all these reactions), and the filtrate was evaporated to a small volume. The desired complex was precipitated by addition of diethyl ether.

**Complex 4.** (80%) IR (KBr): 1688 (C=O), 1610 s (C=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.23 (s, 3 H), 7.23–7.64 (m, 17 H), 8.44 (m, 1 H), 8.55 (m, 1 H). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  14.8. Anal. Calcd for C<sub>27</sub>H<sub>23</sub>NOPClPd: C, 58.9; H, 4.21; 2.54. Found: C, 58.35; H, 4.41; N, 2.34.

**Complex 5.** (75%) IR (KBr): 1705 (C=O), 1610 (C=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.76 (s, 3 H), 1.99 (s, 3 H), 7.18–7.70 (m, 16 H), 8.28 (s, 1 H), 8.46 (s, 2 H), 9.11 (s, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  2.0 (Pd–NC*C*H<sub>3</sub>), 37.3 (CO*C*H<sub>3</sub>), 169.4 (*C*=N), 226.8 (Pd-*C*OMe). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  18.4. FABMS: 514 (M<sup>+</sup> – CH<sub>3</sub>CN).

**Complex 6.** (80%) IR (KBr): 1694 (C=O), 1608 (C=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.79 (s, 3 H), 7.14–7.83 (m, 32 H), 8.18 (d, 2 H, J = 6.7 Hz), 8.62 (s, 1 H). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  16.5 and 12.5 (d, trans, <sup>2</sup>*J*<sub>PP</sub> = 250 Hz). Anal. Calcd for C<sub>45</sub>H<sub>38</sub>NOP<sub>2</sub>-BF<sub>4</sub>Pd: C, 62.5; H, 4.43; N, 1.62. Found: C, 61.6; H, 4.47; N, 1.57. FABMS: 777.1(M<sup>+</sup>).

**Complex 7.** To a solution of **5** (100 mg) in 5 mL of  $CH_2Cl_2$  was bubbled ethylene for 1 h. The resulting solution was filtered through silica gel and evaporated to a small volume. The desired product was precipitated by addition of  $Et_2O$  (74 mg, 72%). IR (KBr): 1636 (C=O), 1609 (C=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.86 (t, 2 H, J = 7.0 Hz, Pd– $CH_2$ ), 2.18 (s, 3 H, COCH<sub>3</sub>), 3.10 (t, 2 H, J = 7.0,  $-CH_2CO$ ), 7.23–7.69 (m, 17 H), 8.29 (m, 2 H), 9.15 (s, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  21.6 (Pd– $CH_2$ ), 27.5 (CO $CH_3$ ), 50.4 ( $CH_2$ –CO), 232.9 (CH<sub>3</sub> $COCH_2$ ). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  36.7. Anal. Calcd for C<sub>30</sub>H<sub>29</sub>NOPBF<sub>4</sub>Pd: C, 56.49; H, 4.58; N, 2.19. Found: C, 55.54; H, 4.37; N, 2.21. FABMS: 550.9 (M<sup>+</sup>).

**Complex 8.** To a solution of **7** (50 mg) in 2 mL of CH<sub>3</sub>CN was bubbled carbon monoxide for 1 h, and the resulting solution was filtered through silica gel and evaporated to a small amount at low temperature and precipitated by adding to an Et<sub>2</sub>O solution. The resulting pale yellow solid was filtered and dried under vacuum. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.77 (s, 3 H, Pd–NCC*H*<sub>3</sub>), 1.94 (s, 3 H, COC*H*<sub>3</sub>), 2.26 (br, 2 H, PdCOC*H*<sub>2</sub>), 2.72 (br, 2 H, COCH<sub>2</sub>C*H*<sub>2</sub>), 7.19–7.69 (m, 16 H), 7.89 (s, 1 H), 8.26 (s, 2 H), 9.07 (s, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  29.3 (CO*C*H<sub>3</sub>), 37.4 (*C*H<sub>2</sub>CO), 44.5 (PdCO*C*H<sub>2</sub>), 206.6 (*C*OCH<sub>3</sub>), 223.1 (Pd*C*O). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  19.9.

**Complex 9.** To a CH<sub>2</sub>Cl<sub>2</sub> solution of the above complex **8** was bubbled ethylene gas for 2 h. The solution was filtered through silica gel, concentrated to a small amount, and precipitated by adding to an Et<sub>2</sub>O solution. The solid was filtered and dried under vacuum. IR (KBr): 1712 (C=O, free), 1629 (C=O, coordinated), 1609 (C=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.89 (m, 5 H, COC*H*<sub>3</sub> + PdCOC*H*<sub>2</sub>), 2.32 (t, 2 H, *J* = 7 Hz), 2.77 (t, 2 H, *J* = 7 Hz), 3.03 (t, 2 H, *J* = 7.0 Hz), 7.18–7.95 (m, 17 H), 8.30 (m, 2 H), 9.20 (s, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  20.7, 29.1, 33.7, 36.7, 48.9, 206.3, 231.3. <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  36.8.

**General Procedure for Preparation of 10–14.** To a solution of **5** (100 mg, 0.15 mmol) in 5 mL of  $CH_2Cl_2$  was added the corresponding olefin in excess (5–10 mmol), and the reaction mixture was stirred for 1–3 h. The resulting solution was filtered through silica gel and evaporated to a small volume. The desired complex was precipitated by addition of ether.

**Complex 10.** (80%) IR (KBr): 1630 (C=O, coordinated). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.93 (t, 3 H, 50%, 7.6 Hz), 1.33 (d, 3 H, 50%, 7.3 Hz), 1.66 (m, 1 H, 50%), 2.03 (m, 1 H, 50%), 2.15 (s, 3 H, 50%), 2.21 (s, 3 H, 50%), 2.33 (m, 1 H, 50%), 2.69 (m, 1 H, 50%), 2.97 (m, 1 H, 50%), 3.17 (m, 1 H, 50%), 7.29–8.38 (m, 19 H), 9.16 (s, 1 H, 50%), 9.21 (s, 1 H, 50%). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  36.3, 39.5. Anal. Calcd for C<sub>30</sub>H<sub>29</sub>NOPBF<sub>4</sub>Pd: C, 55.9; H, 4.54; N, 2.17. Found: C, 56.34; H, 4.53; N, 2.13. FABMS: 556.2 (M<sup>+</sup>).

**Complex 11.** (78%) IR (KBr): 1708, 1686 (C=O, free), 1630 (C=O, coordinated). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.20 (s, 3 H), 2.51 (s, 1 H), 2.93 (m, 2 H), 3.50 (s, 3 H), 7.21–7.67 (m, 16 H), 8.04 (m, 1 H), 8.44 (d, 2 H, J = 7.5 Hz), 9.29 (s 1 H). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  37.3. Anal. Calcd for C<sub>31</sub>H<sub>29</sub>NO<sub>3</sub>PBF<sub>4</sub>Pd: C, 54.13; H, 4.25; N, 2.03. Found: C, 53.49; H, 4.32; N, 1.89. FABMS: 600.2 (M<sup>+</sup>).

**Complex 12.** (75%) IR (KBr): 1610 (C=O, coordinated). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.28 (s, 3 H), 2.95 (d, 1 H, J = 2.0 Hz), 3.17 (s, 2 H), 3.46 (m, 1 H), 6.69–7.58 (m, 21 H), 7.86 (s, 1 H), 8.40 (s, 2 H), 9.11 (s, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  27.7 (CO*C*H<sub>3</sub>), 44.8 (CH*C*H<sub>2</sub>), 55.8 (*C*HCH<sub>2</sub>), 168.5 (*C*=N), 232.5 (*C*OCH<sub>3</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  31.2. Anal. Calcd for C<sub>35</sub>H<sub>31</sub>NOPBF<sub>4</sub>Pd: C, 59.56; H, 4.43; N, 1.98. Found: C, 58.96; H, 4.63; N, 1.79. FABMS: 618.2 (M<sup>+</sup>).

**Complex 13.** (78%) IR (KBr): 1626 (C=O, coordinated). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.49 (s, 1 H), 1.15 (m, 2 H), 1.32 (d, 1 H, J= 9.7 Hz), 1.49 (m, 1 H), 1.81 (d, 1 H, J= 9.9 Hz), 1.91 (m, 1 H), 2.04 (s, 1 H), 2.10 (s, 3 H), 2.48 (s, 1 H), 2.77 (d, 1 H, J= 6.5 Hz), 7.40–7.93 (m, 17 H), 8.40 (m, 2 H), 9.19 (s, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  27.0 (CO*C*H<sub>3</sub>), 29.3, 30.2, 36.8, 43.1, 53.5, 71.2, 169.1 (*C*=N), 234.7 (COCH<sub>3</sub>). <sup>31</sup>P NMR (CDCl<sub>3</sub>): 35.3. Anal. Calcd for C<sub>34</sub>H<sub>33</sub>NOPBF<sub>4</sub>Pd: C, 58.69; H, 4.78; N, 2.01. Found: C, 57.58; H, 4.83; N, 1.89. FABMS: 608.2 (M<sup>+</sup>).

**Complex 14.** (75%) IR (KBr): 1713 (C=O, free), 1610 (C=O, coordinated). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.92 (s, 3 H), 2.12 (s, 3 H), 2.78 (s, 2 H), 5.12 (s, 1 H), 7.19–7.93 (m, 17 H), 8.60 (s, 2 H), 9.15 (s, 1 H). <sup>31</sup>P NMR (CDCl<sub>3</sub>): 35.7. Anal. Calcd for C<sub>31</sub>H<sub>29</sub>NO<sub>3</sub>PBF<sub>4</sub>Pd: C, 54.13; H, 4.25; N, 2.03. Found: C, 53.68; H, 4.41; N, 1.78. FABMS: 600.2 (M<sup>+</sup>).

**Complex 15.** To a solution of **2** (100 mg, 0.16 mmol) in  $CH_2Cl_2$  was added excess vinyl acetate, and the reaction mixture was refluxed at 80 °C for about 24 h. The resulting solution was filtered through silica gel, evaporated to a small amount, and precipitated into ether. The pale white solid was filtered and dried under vacuum (75 mg, 70%). IR (KBr): 1620 (C=O, coordinated). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.04 (t, 3 H, *J* = 7.1 Hz), 1.59 (m, 2 H), 2.0 (s, 3 H), 5.27 (m, 1 H), 7.24–8.10 (m, 17 H), 8.41 (d, 2 H, *J* = 7.5 Hz), 9.3 (s, 1 H). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  34.7. Anal. Calcd for C<sub>30</sub>H<sub>29</sub>NO<sub>2</sub>PBF<sub>4</sub>Pd: C, 54.61; H, 4.43; N, 2.12. Found: C, 54.12; H, 4.49; N, 1.91.

**Complex 16.** To an autoclave (100 mL) were loaded the palladium complex **2** (60 mg) in CH<sub>2</sub>Cl<sub>2</sub>(10 mL), CO (50 psi), and ethylene (50 psi), and the mixture was stirred at room temperature. Reaction stopped after 4 h, and the resulting clear solution was filtered through silica gel and evaporated, which provided a transparent polymeric material (120 mg). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.83 (t, 2 H), 2.13 (s, 4 H), 2.28 (m, 6 H), 2.66 (br, ~48 H), 3.0 (t, 2 H), 7.24–8.10 (m, 17 H), 8.28 (d, 2 H, J = 6.3 Hz), 9.26 (s, 1 H). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  37.7.

**Crystallography.** Crystals suitable for X-ray determination were obtained for **1**, **2**, **3**, **4**, **7**, **10**, **11**, and **13** by slow diffusion of hexane into a dichloromethane solution at room temperature. Cell parameters were determined by a Siemens SMART CCD or a CAD-4 diffractometer. Selected bond distances and bond angles are collected in Table 2. Other crystallographic data are deposited as Supporting Information.

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**Supporting Information Available:** Complete description of the X-ray crystallographic structure determination of **1**, **2**, **3**, **4**, **7**, **10**, **11**, and **13** including figures of ORTEP plots and tables of crystal data, atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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