Single and Multiple Insertion of Alkynes into Pd−Acyl and Pd−Aryl Bonds in Cationic Palladium Complexes with Phosphine−Imine (P∼N) Ligands

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Neutral and cationic Pd(II)−alkyl and Pd(II)−aryl complexes with phosphine−imine (P∼N) ligands show unusual reactivity toward alkynes. No insertion of alkyne has been observed into the neutral palladium complexes or the cationic Pd−alkyl complex. On the other hand, smooth insertion of alkynes into the cationic complexes $[(P\sim N)Pd(COMe)(MeCN)]^+$ (**4**) and $[(P\sim N)Pd(Ph)(MeCN)]^+$ (**5**) was observed, resulting in the formation of single- and double-insertion products, respectively. All the inserted products were isolated and characterized by spectroscopic methods. Single-crystal X-ray analyses for some alkyne insertion complexes indicate that the products are stabilized by intramolecular coordination via either a carbonyl oxygen or a π-phenyl coordination with η^2 mode. Higher order insertions of ethyl propiolate in the complexes $[(P\sim N)Pd(Ph)(MeCN)]^+$ (**5**) and $[(P\sim N)Pd(C(Ph)=C(Ph)C(Ph)=CPh_2)(MeCN)]^+$ (**13**) leading to the oligomeric species are found to proceed smoothly, but disubstituted alkynes such as diphenylacetylene do not undergo such insertion.

Introduction

In recent years, late transition metal complex catalyzed polymerization and copolymerization reactions via insertion/coordination mechanisms have drawn much interest.[1,2] Studies of stoichiometric insertion in transition-metal complexes with various supporting ligands have provided valuable information on the mechanistic aspects of such reactions. The majority of these works deal with olefins and/or carbon monoxide.[3−8] Although there have been many reports in the literature about the polymerization of alkynes using transition-metal catalysts, mechanistic details are still rare and unclear.[9] Recently, Nayori has demonstrated that rhodium(I) complexes react via 2,1-insertion to afford stereoregular poly(phenylacetylene)s with cis-transoidal structures.[10]

Investigation into the stepwise insertion of alkynes into Pd−carbon bonds has shown that a number of organo-palladium complexes are able to allow the tri-

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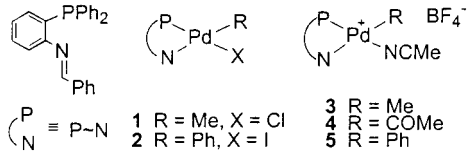
Chart 1. P∼N Ligand and Complexes 1−5



merization of alkyne molecules. However, the accompanying cyclization process leading to the stable carbocyclic moiety stops further insertion.[11−15] Such a process of cyclization was observed by Brookhart[16] and Osakada[17] with use of electrophilic palladium−diimine complexes, which are known to be good catalysts for olefin polymerization.

There has been much research interest in palladium catalysts with the ligands of mixed nitrogen and phosphorus donors[18] because of the different nature of P and N donor atoms.[19] Indeed, we have shown that various insertion intermediates of alkene and alkyne can be isolated with the use of cationic methyl palladium phosphorus−imine $[MePd(P\sim N)]^+$ complexes.[20,21] In continuation of this work, we describe the insertion of alkynes into palladium−acyl and palladium−aryl bonds of cationic palladium complexes with phosphorus−imine (P∼N) ligands. The resulting species with inserted alkynes might serve as intermediates leading to the oligo(alkyne).

Results

Synthesis and Characterization of Palladium Complexes. Ligand and metal complexes used for the present studies are shown in Chart 1. Complexes **1**−**4** were synthesized according to the previously reported procedures.[20,21] Complex **5** was prepared by the reaction of **2** with $AgBF_4$ in a mixed solution of dichloromethane and acetonitrile. Analytically pure product **5**, which was characterized by spectroscopic methods, was obtained in good yield (Table 1). The coordination of acetonitrile in **5** was confirmed by an IR spectrum in which the stretching bands appear at 2320 and 2292 cm^{-1} and was consistent with the earlier reported complexes.[20b] Both ^1H and ^{31}P NMR spectral data reveal the formation of only one isomeric product in which the aryl group is disposed cis to the phosphine. Both ^1H and ^{31}P NMR signals for complex **5** also show that the imine proton and phosphorus signals are shifted downfield compared to those for its neutral analogue **2**. Such a NMR discrepancy between cationic and neutral complexes was in accordance with our prior observation of phosphine−imine palladium complexes.[20b]

Table 1. Selected Spectral Data of Palladium Complexes

complex	$\nu_{C=N}$[a]	^1H NMR[b] −*HC*=N	^{31}P NMR[b]
1	1611	8.62 (s)	35.4
2	1611	8.64 (s)	22.8
3	1609	9.26 (s)	38.6
4	1610	9.11 (s)	18.4
5	1617	9.37 (s)	32.1

[a] In KBr, in cm^{-1}. [b] In $CDCl_3$, in ppm.

Reactivity of Palladium Complexes toward Alkynes by NMR Studies. Complexes **1**−**5** were subjected to NMR studies in chloroform-*d* or acetone-d_6 to probe the reactivity toward various alkynes. In a typical experiment 5−10 mg of the complex and 1−3 equiv of alkynes were dissolved in the deuterated solvent. The mixture was then monitored by both ^1H and ^{31}P NMR spectroscopy at certain time intervals. No significant spectral change was observed for several hours for the neutral palladium complexes **1** and **2** with phenylacetylene or diphenylacetylene in acetone-d_6. Slow decomposition of the complex resulted after longer times. Similarly, phenylacetylene does not undergo insertion in $[Pd(P\sim N)Me(NCMe)]^+$ in acetone-d_6.

However, it was indeed found that the insertion of phenylacetylene and diphenylacetylene into Pd−C took place smoothly in complexes **4** and **5**. Upon the treatment of phenylacetylene with **4** in acetone-d_6, the ^{31}P resonance at δ 18.4 for **4** disappeared within 1 h, accompanied by the appearance of a new signal at δ 38.8 ppm, which was later identified as the insertion product **8**. Insertion of diphenylacetylene into complex **5** was also observed overnight. A broad intense ^{31}P signal gradually grew in at 20.2 ppm. The product was later identified as a species with double alkyne insertion, **13** (see below). It is evident that the reactivity of palladium complexes toward alkynes is quite dependent on the ancillary ligand around the metal center, which affects the metal−carbon bond.

Insertion of Alkynes into Pd−C_{acyl} Bonds. The results from insertion of various alkynes into the Pd−C_{acyl} bonds of **4** are summarized in Scheme 1. Complexes **6**−**10** (except **8**) were isolated in good yields by treating the complex **4** with the respective alkynes (ca. 3 equiv) in dichloromethane solution at room temperature. Complex **8** could be isolated in moderate yield from a stoichiometric amount of the complex **4** and phenylacetylene in acetone. All of the resulting products (**6**−**10**) were characterized by spectroscopic methods. Complexes **6**, **7**, and **10** were further characterized by single-

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Scheme 1. Insertion of Various Alkynes into Pd−C_{acyl}

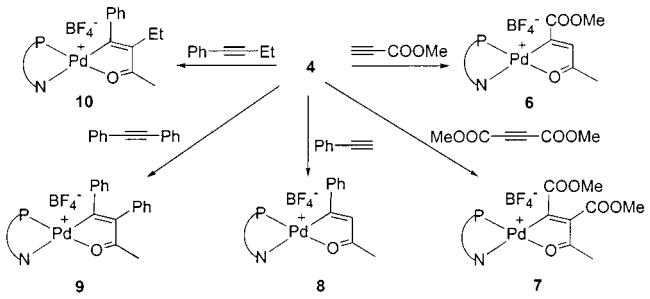

Table 2. Selected Spectral Data of the Inserted Products

complex	$\nu_{C=O}$[a]	^{1}H NMR[b] HC=N	^{31}P NMR[b]
6	1607,[c] 1708[d]	9.49 (s)	43.0
7	1602,[c] 1721[d]	9.59 (s)	42.9
8	1610[c]	9.60 (s)[e]	38.8[e]
9	1606	9.39 (s)	39.8
10	1607	9.35 (s)	38.9
11	1626,[c] 1684[d]	9.52 (s)[e]	39.0[e]
12	1644,[c] 1714,[d] 1731[d]	9.56 (s)	41.3
13		8.63 (d)	21.6

[a] In KBr, in cm^{-1}. [b] In $CDCl_3$ (unless otherwise noted), in ppm. [c] Free carbonyl. [d] Coordinated carbonyl. [e] In acetone-d_6.

crystal structural analysis. Selected spectroscopic data are shown in Table 2. The IR spectra of the products show C=O stretching bands around 1602−1608 cm^{-1}. A large shift from the position of the free carbonyl group was generally observed for the coordination of the C=O group to the palladium(II) metal ion.[22,23] As expected, these values were lower in wavenumber by ∼20 cm^{-1} as compared to those of the alkene insertion analogues,[20b] due to the conjugated carbonyl system of the alkyne-inserted products. As for the free carbonyl groups in **6** and **7**, bands of $\nu_{C=O}$ appeared at 1708 and 1721 cm^{-1}, respectively. In all instances, ^{31}P NMR showed a single peak, indicating the formation of only one isomer. We also observed a regioselective 2,1-insertion with unsymmetrical alkynes leading to the formation of the products **6**, **8**, and **10**, where the vinyl carbon with a bulky group is attached to the metal center. Such selectivity was also found in the insertion of alkyne with palladacycles reported earlier.[13b] All the insertion products are fairly stable in the solid state as well as in solution.

ORTEP diagrams for **6**, **7**, and **10** are shown in Figures 1−3, respectively. Selected bond lengths and bond angles are listed in Table 3. The molecular geometry around the metal ion in all these three complexes was a square-planar arrangement, with two coordination sites occupied by phosphorus and nitrogen donor atoms and the other two by carbonyl oxygen and vinyl carbon atoms. The cis arrangement of the vinylic carbon and phosphine is consistent with the spectroscopic data. The formation of five-membered chelates via the vinyl carbon and carbonyl oxygen could be one of the factors that stabilize the resulting products. Such an arrangement was also observed in products of olefin insertion into Pd−acyl complexes with the P∼N ligands.[24,25] No major deviations were observed in bond lengths. The

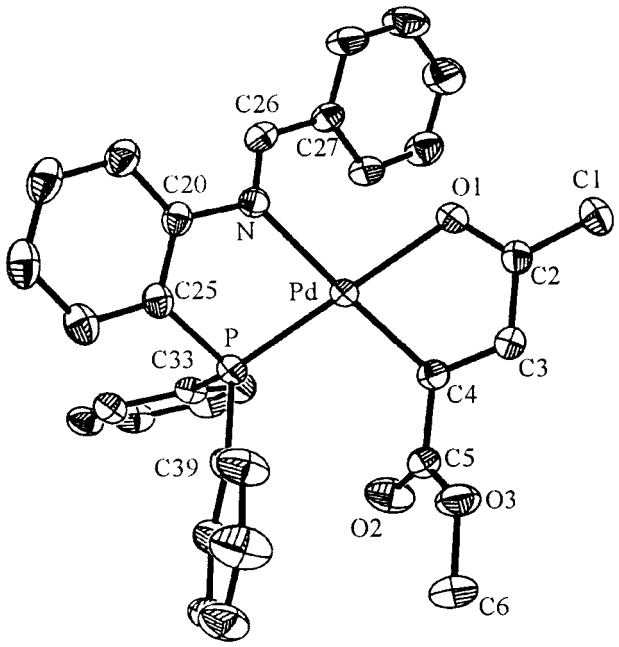

Figure 1. ORTEP plot of the cationic part of complex **6**.

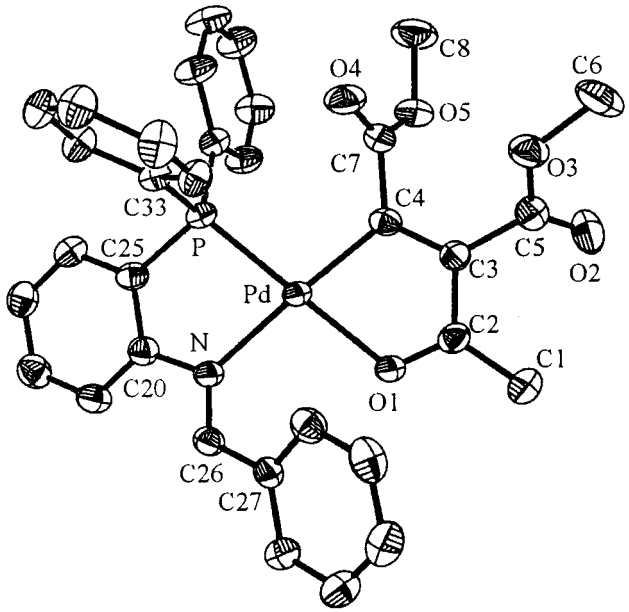

Figure 2. Molecular structure of the cationic part of complex **7**.

average metal−ligand distances are comparable to those of earlier reported systems where the vinyl carbon is trans to the imine and the carbonyl oxygen is trans to the phosphine.[26] Least-squares planes calculated for the metal and coordinated atoms also show a perfect square-planar geometry.

Insertion of Alkynes into Pd−C_{aryl} Bonds. In contrast to complex **4**, which undergoes single alkyne insertion, complex **5** allows double insertion of various alkynes, except phenylacetylene, into the Pd−C_{aryl} bond

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Table 3. Selected Bond Distances (Å) and Angles (deg) of Palladium Complexes

	6	7	10		12	13
Pd−C4	1.988(3)	2.000(4)	2.005(8)	Pd−C5	1.986(2)	2.010(3)
Pd−N	2.121(3)	2.106(3)	2.130(7)	Pd−N	2.111(2)	2.164(2)
Pd−P	2.2145(8)	2.2146(11)	2.221(2)	Pd−P	2.2106(7)	2.2357(7)
Pd−O1	2.140(2)	2.116(3)	2.100(6)	Pd−O1	2.139(2)	
				Pd−C56		2.418(3)
				Pd−C57		2.461(3)
C4−Pd−P	100.28(10)	100.19(11)	102.9(3)	C5−Pd−P	97.41(7)	93.60(7)
P−Pd−N	82.30(8)	82.95(8)	82.7(2)	P−Pd−N	83.79(6)	81.84(6)
C4−Pd−N	177.33(12)	175.50(13)	173.5(3)	C5−Pd−N	177.87(9)	172.42(9)
N−Pd−O1	97.38(10)	97.42(10)	94.4(2)	N−Pd−O1	94.04(7)	
C4−Pd−O1	79.99(12)	79.80(13)	80.6(3)	C5−Pd−O1	85.41(9)	
O1−Pd−P	174.76(7)	174.04(8)	170.5(2)	O1−Pd−P	160.61(5)	
				C5−Pd−C56		78.67(10)
				N−Pd−C56		108.91(8)
				P−Pd−C56		125.87(7)
				C5−Pd−C57		84.45(10)
				N−Pd−C57		101.93(8)
				P−Pd−C57		159.57(7)

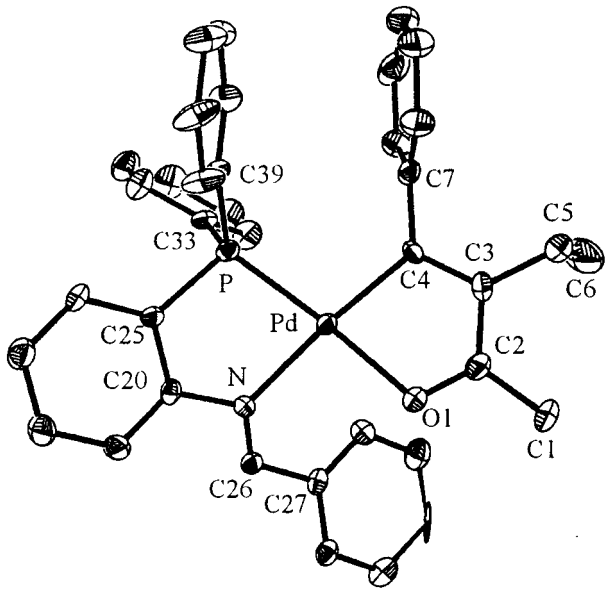


Figure 3. ORTEP drawing of $[(P{\sim}N)Pd\{(Ph)C{=}C(Et)\text{-}COCH_3\}]^+$.

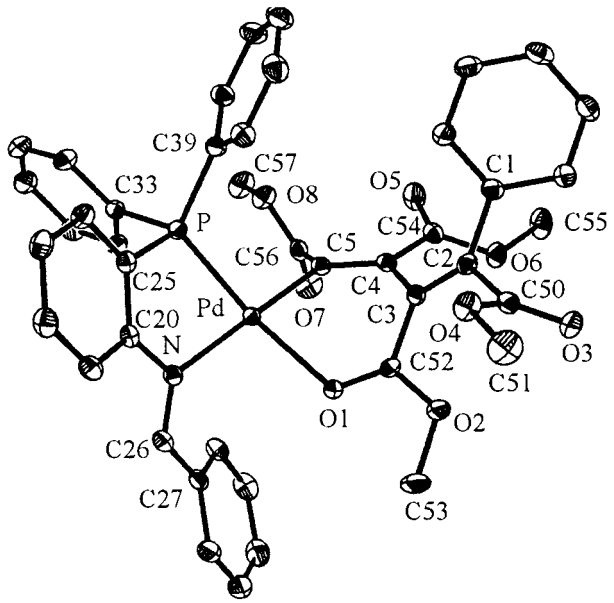
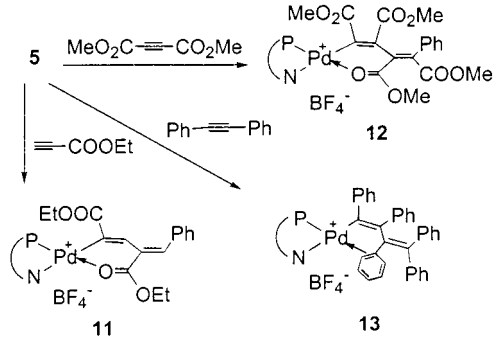


Figure 4. Molecular structure of the cationic part of complex **12**.

Scheme 2. Insertion of Alkynes into Pd−C_{aryl}



to yield compounds **11**−**13** (Scheme 2). Spectroscopic analysis established the structures of complexes **11**−**13** (Table 2). IR spectra for the compounds **11** and **12** evidence two sets of carbonyl stretching frequencies (1626 and 1684 cm^{-1} for **11**; 1644, 1714, and 1741 cm^{-1} for **12**), corresponding to coordinated and free carbonyl groups, respectively. The ^1H and ^{13}C NMR spectral data also support the formation of double-insertion products for **11** and **12**. The ^1H NMR spectrum for **11** shows two sets of signals corresponding to $-CH_3$ (at 0.86 and 1.05 ppm) and $-OCH_2$ (at 3.53 and 3.77 ppm) groups. Similarly, the spectrum for **12** shows four different signals for −OMe groups, indicating that it contains two inserted alkyne units. For the compound **13**, infrared and ^1H and ^{13}C NMR spectral data were not sufficiently informative because only aromatic groups exist in the complex. However, FAB mass spectral data provided the evidence for double insertions in all these instances. In the cases of the complexes **12** and **13**, the X-ray structural analyses confirm our identification of the coordination mode of the doubly inserted alkynes.

The ORTEP plots for **12** and **13** are shown in Figures 4 and 5. Selected bond lengths and angles are shown in Table 3. A distorted-square-planar arrangement around the palladium metal ion was observed in **12** and **13**, with the donors being phosphorus (P1), imino nitrogen (N1) and vinyl carbon (C1). The fourth site in **12** was occupied by the carbonyl oxygen (O1), whereas in **13** it was occupied by a π-phenyl group with η^2 mode. Such intramolecular coordination modes via oxygen or π-bond-

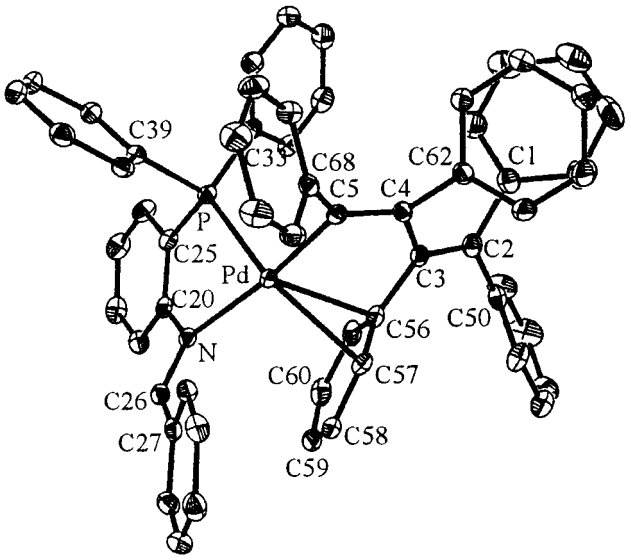


Figure 5. ORTEP plot of [(P∼N)Pd{(Ph)C═C(Ph)C(Ph)═C(Ph)$_2$}]$^+$.

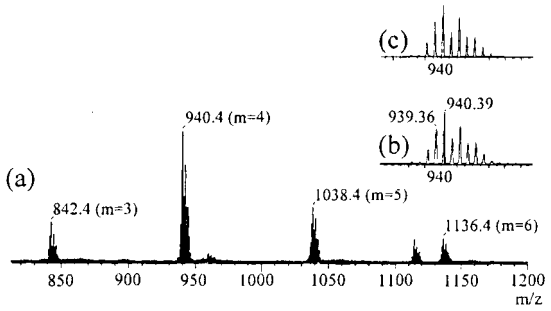


Figure 6. FAB mass spectra of **5**, showing (a) multiple insertion of EP into **5**, (b) expansion at *m*/*z* 940, and (c) calculated mass pattern at *m*/*z* 940 for $C_{51}H_{49}NO_8PPd$.

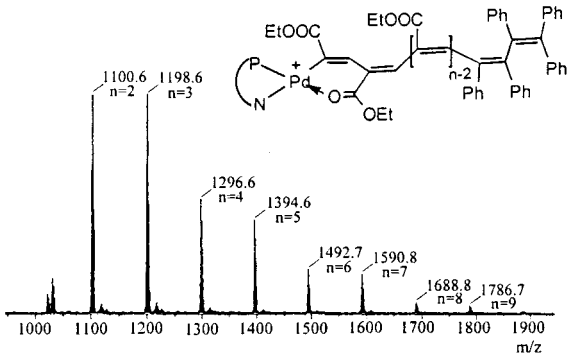


Figure 7. FAB mass spectrum of poly(alkyne).

ing have been observed in previous reactions involving alkyne insertion into Pd−C bonds.[13a,14,27] The bond lengths between the Pd and P, N, and carbon donor atoms for **12** and **13** are within the ranges of and comparable to those of compounds **6**, **7**, and **10** (see Table 3). A large deviation was found in the bond angle of P−Pd−O1 (160.61(5)°) in **12**. The bond distances between the metal and π-bond in **13** are longer than those reported in π-olefin palladium complexes. This is explained by the larger trans influence of the phosphine situated trans to the π-bond in **13**.[13a,27]

Stepwise Insertion Studies. In the above sections, we have shown that regioselective insertion products have been isolated and characterized. To examine the possibility of controlled insertions with alkyne and CO or alkynes, several experiments have been carried out. Attempts to carry out the second insertion of CO into **6**−**10** have not been successful. Either atmospheric or higher pressures of carbon monoxide in various solvents generally led to the decomposition of the complexes with the formation of palladium black.

However, stepwise insertion of alkynes to form oligomeric species with the cationic aryl complex **5** was observed. The reaction of **5** with ethyl propiolate in an equal molar ratio after 2 h forms a mixture of the double-insertion product **11** and unreacted starting material **5** in a 1:1 ratio, which was confirmed by ^{1}H and ^{31}P NMR. Such results suggest that the double insertions are more preferable than single insertion. Interestingly, the FAB mass spectrum (Figure 6) for the reaction of **5** and excess ethyl propiolate shows formation of the higher insertion units (n = 3−6). Furthermore, complex **13** underwent further insertion with excess ethyl propiolate. The FAB mass spectrum (Figure 7) of the reaction mixture clearly shows the multiple insertion of ethyl propiolate. As shown in Figure 7, the values *m*/*z* 1100.6, 1198.6, and 1296.6 correspond to the alkyne-inserted products with n = 2−4, even up to n = 9 (*m*/*z* 1786.7). However, such higher order insertions were not observed in the reactions using DMAD and DPA to react with **13**, presumably due to the steric hindrance of the disubstituted alkynes.

Discussion

This study proves neutral and cationic palladium complexes with phosphine−imine (P∼N) ligands showing unusual reactivity toward alkynes. The ligand confers both electronic and steric influence on the metal center and plays a key role in stabilizing the alkyne-inserted intermediates. As for **1** and **2**, chloride and iodide could prevent the coordination of alkyne to the metal center, which is essential to the migratory insertion pathway.

One possible reason for the different reactivities among the complexes **3**−**5** toward alkynes may be due to the electrophilicity at the metal centers imparted by the ancillary ligands. The metal centers for **4** and **5** appear to be more electrophilic than that of **3**, on the basis of the π-bonding tendencies of acyl and aryl ligands, resepectively. The ^{31}P chemical shifts for these complexes, which are in the order **4** < **5** < **3** (respective to 85% H_3PO_4, Table 1), also qualitatively support that the complex **4** with an acyl group is the most electrophilic in nature. Indeed, complex **4** shows the best reactivity among others in such alkyne insertions. Such a reactivity difference is similar to that observed in the insertion of olefin into Pd−acyl vs Pd−alkyl bonds.[2c] Of course, the formation of the stable five-membered chelate in the inserted product is also the driving force for the acceleration of the insertion process.

The reaction of **4** with various alkynes led to the formation of the stable single-inserted products **6**−**10**. Unlike the stepwise insertions with ethylene and CO, as observed in cationic palladium complexes with diphosphine[2c] as well as phosphine−imine ligands,[20a,b]

(27) Zhao, G.; Wang, Q.-G.; Mak, T. C. W. *J. Organomet. Chem.* **1999**, *574*, 311.

further insertions of CO/alkyne into **6**−**10** were not successful. This is presumably due to the stronger oxygen coordination through the five-membered chelate. As shown in the crystallographic data, these five-membered chelating rings adopt to the perfectly planar geometry. The higher stability of the chelating ring might stop the further insertion of alkyne with **6**−**10**. Unlike the cationic palladium complexes with symmetrical diimine ligands, which were very active toward functional groups attached to the growing oligomer, we observed a stepwise insertion without formation of any cyclization product.[16−23]

FAB mass analysis as well as the characterization of insertion intermediates clearly indicate the stepwise insertion of alkynes into the cationic Pd−aryl complex **5**. Double insertions were found as the major products, which were stabilized by intramolecular coordination through donor atoms, such as carbonyl oxygen in **11** and **12** or a π-coordination from the aryl group in **13**. Similar to compound **12**, a palladium complex with the 2,2′-bipyridine ligand prepared by Osakada and co-workers did not show such a coordination mode.[17b]

Insertion of higher units of EP and DMAD with **5** and **13**, respectively, clearly illustrates that metal-capped oligomeric species which were stabilized by intramolecular coordination of π-donor can readily open up a coordination site for the incoming alkyne (i.e., bonding through the phenyl ring from the growing chain does occur readily for the incoming alkyne molecule to allow further chain growth). However, the metal centers in complexes **6**−**10**, which grow into the stable five-membered chelating ring, are coordination-saturated; thus, the polymerization process is disfavored. Clearly, the design of catalysts for the polymerization of alkynes needs a fine-tuning of the metal system in which migratory insertion of alkynes is facile.

It was reported by Brookhart and co-workers that the cationic diimine−palladium complexes mediate the trimerization of alkynes, leading to the formation of alkylidene−cyclopentenyl palladium complexes,[16] which are inactive toward further insertion of alkynes for polymerization. However, this kind of cyclized product was not observed in our studies with the phosphine−imine ligand system. This indicates that the P∼N ligand combination might differentiate the coodination site and the trans effect as well. In addition, a weaker chelating ring effect (six-membered) in complex **13** might also assist in opening the coordination site for the incoming alkyne. Stability induced by intramolecular coordination through functional groups as well as the pre- or post-insertion isomerization observed with unsymmetrical ligands may also be the reason for the lower activity of these complexes.[28]

In this study, we have demonstrated novel alkyne insertion reactions with the cationic phosphine−imine palladium complexes. It is clear that the mixed-donor ligand as well as the reacting substrates affect the migratory insertion path of alkynes. The complexes with unsymmetrical ligands, which can differentiate between the migratory insertion of alkynes over the intramolecular cyclization, may be promising candidates for polymerization of alkynes. Steric influences of the P∼N ligands as well as reactions with other unsymmetrical ligands are presently under investigation.

(28) Dekker, G. P. C. M.; Buijs, A.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Smeets, W. J. J.; Spek, A. L.; Wang, Y. F.; Stam, C. H. *Organometallics* **1992**, *11*, 1937.

Experimental Section

General Information. All reactions, manipulations, and purification steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried over CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used as received unless otherwise stated. Complexes **1**−**4** were prepared by our earlier reported procedures.[20,21]

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ or acetone-d_6 on either a Bruker AC-E 200 or AM-300 spectrometer. Chemical shifts are given in parts per million relative to Me_4S for ^1H and ^{13}C NMR and relative to 85% H_3PO_4 for ^{31}P NMR. Due to the complexity of the aromatic region, chemical shifts of nonaromatic carbons were reported. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II) as KBr pellets, unless otherwise noted.

Complex 5. To a solution of the neutral complex **2** (0.5 mmol) in 20 mL of CH_2Cl_2 was added a stoichiometric amount of $AgBF_4$ in 5 mL of CH_3CN under nitrogen, and the mixture was stirred at room temperature for 1 h. The resulting white AgCl precipitate was filtered through silica gel, and the solution was evaporated to a small volume. Upon addition to Et_2O, a precipitate was deposited, which was filtered and dried under vacuum, resulting in 262 mg (85%) of pure product. IR (KBr): 2320, 2292 cm^{-1} (C≡N), 1617 (C═N, coordinated). ^1H NMR ($CDCl_3$): δ 1.79 (s, 3 H, −*Me*), 6.78−7.77 (m, 21 H, Ar *H*), 8.24 (m, 1 H, Ar *H*), 8.48 (s, 1 H, Ar *H*), 9.37 (s, 1 H, −HC═N). ^{31}P NMR ($CDCl_3$): δ 32.1. Anal. Calcd for $C_{33}H_{28}N_2PBF_4Pd$: C, 58.56; H, 4.17; N, 4.14. Found: C, 57.89; H, 4.09; N, 3.98. FABMS: 548.1 ($M^+ - CH_3CN$).

General Procedure for the Preparation of 6−10. To a solution of **4** (100 mg, 0.15 mmol) in CH_2Cl_2(5 mL) was added the corresponding alkyne (nearly 3 equiv), and the mixture was stirred for 1−3 h. The resulting solution was filtered through Celite and evaporated to a small volume. The desired complexes **6**, **7**, **9**, and **10** were precipitated by addition of ether, filtered, and dried under vacuum. On the other hand the complex **8** was prepared by reacting the complex **4** (0.17 mmol) with 1 equiv of phenylacetylene in acetone (2 mL). The white solid precipitated by stirring the reaction mixture at room temperature for 2 h and was filtered, washed with a small amount of acetone/ether, and dried under vacuum.

Complex 6. Yield: 80%. IR (KBr): 1708, 1607 cm^{-1} (C═O, coordinated). ^1H NMR ($CDCl_3$): δ 2.15 (s, 3 H, −CO*Me*), 2.94 (s, 3 H, −O*Me*), 6.62 (s, 1 H, −C*H*═), 6.93−7.77 (m, 16 H, Ar *H*), 8.23−8.37 (m, 3 H, Ar *H*), 9.49 (s, 1 H, −*H*C═N). ^{13}C NMR ($CDCl_3$): δ 27.1, 50.1, 172.1, 184.4, 218.7. ^{31}P NMR ($CDCl_3$): δ 43.0. Anal. Calcd for $C_{31}H_{27}NO_3PBF_4Pd$: C, 54.30; H, 3.96; N, 2.04. Found: C, 53.95; H, 4.21; N, 1.87.

Complex 7. Yield: 80%. IR (KBr): 1721, 1602 cm^{-1} (C═O, coordinated). ^1H NMR ($CDCl_3$): δ 2.22 (s, 3 H, −CO*Me*), 2.81 (s, 3 H, −O*Me*), 3.67 (s, 3 H, −O*Me*), 6.88−7.78 (m, 16 H, Ar *H*), 8.24−8.38 (m, 3 H, Ar *H*), 9.59 (s, 1 H, −*H*C═N). ^{13}C NMR ($CDCl_3$): δ 28.8, 51.6, 52.7, 170.6, 173.4, 192.5, 217.3. ^{31}P NMR ($CDCl_3$): δ 42.9. Anal. Calcd for $C_{33}H_{29}NO_5PBF_4Pd$: C, 53.20; H, 3.93; N, 1.88. Found: C, 52.94; H, 4.09; N, 1.89. FABMS: 656.0 (M^+).

Complex 8. Yield: 57%. IR (KBr): 1610 cm^{-1} (C═O, coordinated). ^1H NMR (acetone-d_6): δ 2.25 (s, 3 H, −CO*Me*), 6.23 (s, 1 H, −C*H*═), 6.84−8.15 (m, 22 H, Ar *H*), 8.80 (d, 2 H, J = 3.5 Hz, Ar *H*), 9.12 (s, 1 H, −*H*C═N). ^{31}P NMR ($CDCl_3$): δ 38.8. Anal. Calcd for $C_{35}H_{29}NOPBF_4Pd$: C, 59.73; H, 4.15; 1.99. Found: C, 59.44; H, 3.99; N, 1.67. FABMS: 616.1 (M^+).

Complex 9. Yield: 80%. IR (KBr): 1606 cm^{-1} (C═O, coordinated). ^1H NMR ($CDCl_3$): δ 1.85 (s, 3 H, −CO*Me*), 6.37−

Table 4. Selected Crystallographic Data of Complexes 6, 7, 10, 12, and 13

	6	7	10	12	13
formula	$C_{31.5}H_{28}BClF_4NO_3PPd$	$C_{33}H_{29}BF_4NO_5PPd$	$C_{37}H_{33}BF_4NOPPd$	$C_{49}H_{53}BF_4NO_{12}PPd$	$C_{59}H_{45}BF_4NPPd$
fw	728.18	743.75	731.82	1072.10	992.14
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a, Å	12.5765(1)	18.242(4)	12.3198(1)	16.9538(5)	10.2153(3)
b, Å	12.7653(2)	10.257(2)	13.8352(2)	17.2030(5)	13.2332(4)
c, Å	12.7816(1)	19.028(4)	20.1515(4)	17.0361(5)	17.7982(6)
α, deg	114.151(1)	90	90	90	100.863(1)
β, deg	116.522(1)	112.65(3)	94.233(1)	99.977(1)	100.379(1)
γ, deg	94.510(1)	90	90	90	90.292(1)
V, Å^3	1587.20(3)	3286(1)	3425.39(9)	4893.5(2)	2322.3(1)
Z	2	4	4	4	2
D_{calcd}, Mg/m^3	1.524	1.504	1.419	1.455	1.419
F(000)	734	1504	1488	2208	1016
cryst size, mm	0.40 × 0.35 × 0.15	0.35 × 0.25 × 0.20	0.20 × 0.20 × 0.40	0.30 × 0.25 X 0.20	0.40 × 0.25 × 0.20
θ range, deg	1.85−26.37	1.31−25.00	1.79−25.00	1.56−27.50	1.19−25.00
no. of rflns collected	19 497	18 632	19 655	50 290	26 317
no. of indep rflns (R_{int})	6486 (0.027)	5792 (0.0437)	6032 (0.0759)	11 232 (0.0356)	8172 (0.0203)
refinement method	full-matrix least squares on F^2				
R1 ($I > 2\sigma(I)$)	0.0389	0.0372	0.1166	0.0368	0.0318
wR2 ($I > 2\sigma(I)$)	0.1081	0.1106	0.2472	0.0981	0.0792
goodness of fit on F^2	1.025	0.892	1.612	1.060	1.064

7.69 (m, 26 H, Ar *H*), 8.14 (s, 1 H, Ar *H*), 8.58 (s, 1 H, Ar *H*), 9.39 (s, 1 H, −*H*C═N). ^{13}C NMR ($CDCl_3$): *δ* 27.6 (d, J_{P-C} = 1.92 Hz), 171.4, 190.2, 217.5. ^{31}P NMR ($CDCl_3$): *δ* 39.8. Anal. Calcd for $C_{41}H_{33}NOPBF_4Pd$: C, 63.1; H, 4.26; N, 1.79. Found: C, 62.85; H, 4.53; N, 1.65. FABMS: 644.2 (M^+).

Complex 10. Yield: 80%. IR (KBr): 1607 (C═O, coordinated). ^{1}H NMR ($CDCl_3$): *δ* 0.76 (t, 3 H, *J* = 7.4 Hz, −CH_2*Me*), 1.79 (m, 2 H, −C*H*$_2$Me), 2.08 (s, 3 H, −CO*Me*), 6.46−8.11 (m, 22 H, Ar *H*), 8.49 (d, 2 H, *J* = 6.6 Hz, Ar *H*), 9.35 (s, 1 H, −*H*C═N). ^{13}C NMR ($CDCl_3$): *δ* 14.7, 23.0, 26.2, 171.3, 195.0, 218.3. ^{31}P NMR ($CDCl_3$): *δ* 38.9. Anal. Calcd for $C_{37}H_{33}NOPBF_4Pd$: C, 60.72; H, 4.54; N, 1.91. Found: C, 60.47; H, 4.60; N, 1.66. FABMS: 644.2 (M^+).

General Procedure for the Preparation of 11−13. To a solution of **5** (100 mg, 0.15 mmol) in 2 mL of acetone was added the corresponding alkyne (2.5 equiv). The resulting mixture was stirred at room temperature overnight. The reaction mixture was filtered through Celite and evaporated to a small volume. The desired complex was precipitated by addition of ether; the solids were filtered and dried under vacuum.

Complex 11. Yield: 71%. IR (KBr): 1684 cm^{-1} (C═O, free), 1626 (C═O, coordinated). ^{1}H NMR (acetone-d_6): *δ* 0.86 (t, 3 H, *J* = 7.12 Hz, −CH_2*Me*), 1.05 (t, 3 H, *J* = 7.12 Hz, −OCH_2*Me*), 3.53 (m, 2 H, −C*H*$_2$Me), 3.77 (m, 2 H, −OC*H*$_2$−), 7.25−8.12 (m, 24 H, Ar *H* and −C*H*═), 8.77 (d, 2 H, *J* = 6.7 Hz, Ar *H*), 9.52 (s, 1 H, −*H*C═N). ^{13}C NMR ($CDCl_3$): *δ* 13.58, 13.62, 60.8, 65.5, 170.0, 171.0. ^{31}P NMR ($CDCl_3$): *δ* 41.2. FABMS: 744.2 (M^+).

Complex 12. Yield: 74%. IR (KBr): 1731, 1714 cm^{-1} (C═O, free), 1644 (C═O, coordinated). ^{1}H NMR (acetone-d_6): *δ* 3.03 (s, 3 H, −O*Me*), 3.37 (s, 3 H, −O*Me*), 3.38 (s, 3 H, −O*Me*), 3.79 (s, 3 H, −O*Me*), 7.09−7.83 (m, 21 H, Ar *H*), 8.38 (m, 1 H, Ar *H*), 8.63 (d, 2 H, *J* = 7 Hz, Ar *H*), 9.56 (s, 1 H, −*H*C═N). ^{13}C NMR ($CDCl_3$): *δ* 51.43, 51.63, 53.18, 56.03, 160.72, 166.52, 172.0, 174.5. ^{31}P NMR ($CDCl_3$): *δ* 41.5. Anal. Calcd for $C_{43}H_{37}NO_8PBF_4Pd$: C, 56.15; H, 4.05; N, 1.52. Found: C, 56.03; H, 3.98; N, 1.49. FABMS: 832.0 (M^+).

Complex 13. Yield: 72%. IR (KBr): 1614 cm^{-1} (C═N, coordinated). ^{1}H NMR ($CDCl_3$): *δ* 6.48−7.81 (m, 42 H, Ar *H*), 8.33 (d, 2 H, *J* = 7.2 Hz, Ar *H*), 8.63 (d, 1 H, *J* = 2.8 Hz, −*H*C═N). ^{13}C NMR ($CDCl_3$): *δ* 142.3, 143.39, 144.9, 146.9, 153.8, 154.0, 169.5. ^{31}P NMR ($CDCl_3$): *δ* 21.6. Anal. Calcd for $C_{59}H_{45}NPBF_4Pd$: C, 71.42; H, 2.05; N, 1.41. Found: C, 71.28; H, 1.98; N, 1.39. FABMS: 904.4 (M^+).

Crystallography. Crystals suitable for X-ray determination were obtained for **6**, **7**, **10**, **12**, and **13** by slow diffusion of hexane into a dichloromethane solution at room temperature. Cell parameters were determined by either a Siemens SMART CCD or a CAD-4 diffractometer. Crystal data for complexes **6, 7**, **10**, **12**, and **13** are listed in Table 4, and their ORTEP plots are shown in Figures 1−5, respectively (labels of phenyl groups are omitted for clarity). Other crystallographic data are deposited as Supporting Information.

Acknowledgment. We thank the National Science Council for financial support (Grant No. NSC89-2113-M-002-070).

Supporting Information Available: Complete descriptions of the X-ray crystallographic structure determination of **6**, **7**, **10**, **12**, and **13**, including tables of crystal data, atomic coordinates, isotropic and anisotropic thermal parameters, and bond distances and angles; crystallographic data in CIF format are also given. This material is available free of charge via the Internet at http://pubs.acs.org.

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