Reactions of Cationic Palladium(II) Methyl and Vinyl Complexes with Alkynes

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$[(phen)Pd(CH_3)(OEt_2)]^+[BAr'_4]^-$ (phen = 1,10 phenanthroline, Ar′ = 3,5-$(CF_3)_2C_6H_3$) reacts with RC≡CR′ to form the η^2-alkyne complexes $[(phen)Pd(CH_3)(\eta^2\text{-}RC{\equiv}CR']^+[BAr'_4]^-$ (**5a**, R = R′ = $SiMe_3$; **5b**, R=C_6H_5, R′ = H). In contrast, the reaction of the diimine complexes $[(ArN{=}C(R)C(R){=}NAr)Pd(CH_3)(NCCH_3)]^+[BAr'_4]^-$ (**1**−**3**) (Ar = 2,6-$(CH_3)_2C_6H_3$, 2,6-(*i*-Pr)$_2C_6H_3$; R = H, CH_3, $^1/_2$BIAN) with HC≡CR′ (R′ = H, *t*-Bu) yielded the alkyne insertion products $[(ArN{=}C(R)C(R){=}NAr)Pd(CH{=}C(R)CH_3)(NCCH_3)]^+[BAr'_4]^-$ (**3**) while the reaction of 1-hexyne with **1a** yielded a mixture of the 2,1- and 1,2-insertion products $[(N{-}N)Pd(C(C_4H_9){=}CHCH_3)(NCCH_3)]^+[BAr'_4]^-$ and $[(N{-}N)Pd(CH{=}C(C_4H_9)(CH_3)(NCCH_3)]^+[BAr'_4]^-$, respectively. The vinyl complexes $[(N{-}N)Pd(CH{=}CRCH_3)(NCCH_3)]^+[BAr'_4]^-$ react with acetylene to form the η^1-dienyl complexes $[(N{-}N)Pd(CH{=}CHCH{=}CRCH_3)(NCCH_3)]^+[BAr'_4]^-$, which then react with acetylene and rearrange to form the novel 5-ethylidene-2-cyclopenten-1-yl complexes $[(N{-}N)Pd(\eta^3\text{-}C(CH_3)(R)C_5H_5)]^+[X]^-$. (R = H, *t*-Bu; X = BAr'_4, O_3SCF_3) (**8**).

Introduction

The reactions of alkynes with late transition metal hydrido, alkyl, and aryl complexes have been the subject of much research.[1] In many cases, alkyne insertion into the metal−hydrogen or metal−carbon σ-bond occurs, yielding a vinyl complex. Although such a reaction represents the first step in the polymerization of alkynes via a coordination/insertion pathway,[2] there is little mechanistic information concerning the details of such processes for late transition metal systems.[3−5] Several rhodium- and platinum-based catalysts for the polymerization of alkynes have been reported,[6] but the nature of the catalyst resting state and the specific details of the chain growth for these systems have not been investigated. Noyori[7] has reported that the well-characterized σ-acetylide complex, Rh(C≡C−Ph)(norbornadiene)$(PPh_3)_2$, initiates a living polymerization of phenylacetylene, which supports the operation of a coordination/insertion mechanism for this family of catalysts.

Recent studies in these and other laboratories have focused on the use of cationic Pd(II) methyl complexes as precatalysts for olefin dimerization,[8] oligomerization, and polymerization,[9,10] olefin hydrosilation and dehydrogenative silation,[11] and ethylene/CO copolymerization.[12−15] In particular, the square-planar Pd(II) diimine complexes (**1**−**3**) are versatile precatalysts for the homo- and copolymerization of α-olefins.[9,10]

The goal of this work was to examine the reactivity of the cationic methyl complexes **1**−**4** with alkynes in

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(2) In some cases, it has been shown that vinyl complexes are inert toward further insertion of alkynes, see: (a) Etienne, M.; Mathieu, R.; Donnadieu, B. *J. Am. Chem. Soc.* **1997**, *119*, 3218. (b) Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5505.

(3) For examples of alkyne dimerization catalysts, see refs 3a−d. Mechanistic studies suggest that carbon−carbon bond formation occurs via acetylide migration to a vinyl ligand. (a) Rappert, T.; Yamamoto, A. *Organometallics* **1994**, *13*, 4984. (b) Jun, C.-H.; Lu, Z.; Crabtree, R. H. *Tetrahedron Lett.* **1992**, *47*, 7119 (c) Bianchini, C.; Frediani, P.; Masi, D.; Peruzini, M.; Zanobini, F. *Organometallics* **1994**, *13*, 4616. (d) Barbaro, P.; Bianchini, C.; Peruzini, M.; Polo, A.; Zanobini, F. *Inorg. Chim. Acta* **1994**, *220*, 5. (e) Slugovc, C.; Merciter, K.; Zobertz, E.; Schmid, R.; Kirchner, K *Organometallics* **1996**, *15*, 3998.

(4) For references to numerous examples of alkyne polymerization by d^0 early transition metal catalysts, see: (a) Gibson, H. W.; Porchan, J. M. In *Encyclopedia of Polymer Science and Engineering* 2nd ed.; Kvoschwitz, J. I., Ed.; Wiley and Sons: New York, 1984; Vol. 1, p 87. (b) Simionescu, C. I.; Percec, V. *Prog. Polym. Sci.* **1982**, *8*, 133. (c) Shirakawa, H.; Masuda, T.; Takeda, K. In *The Chemistry of Triple-Bonded Functional Groups*; Patai, S., Ed.; Wiley: Chichester, 1994; Suppl. C2, Chapter 17.

(5) For examples of niobium, tantalum, molybdenum, and tungsten alkyne polymerization catalysts which operate via metal alkylidene intermediates, see: (a) Schrock, R. R.; Luo, S.; Lee, J. C., Jr.; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3883. (b) Schlund, R.; Schrock, R. R.; Crowe, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8004. (c) Katz, T. J.; Ho, T.-H.; Shih, N.-Y.; Ying, Y.-C., Stuart, V. I. W. *J. Am. Chem. Soc.* **1984**, *106*, 2658. (d) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1987**, *81*, 121.

(6) (a) Furlani, A.; Napoletano, C.; Russo, M. V. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 75. (b) Furlani, A.; Licoccia, S.; Russo, M. V. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 991. (c) Goldberg, Y.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1994**, 1209. (d) Tabata, M.; Wang, Y.; Yokota, K *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 1113.

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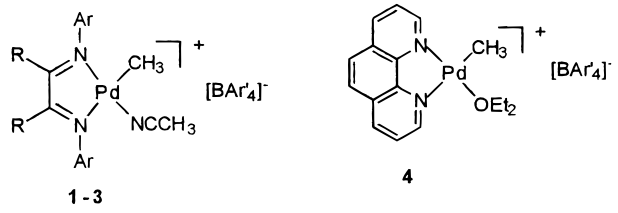
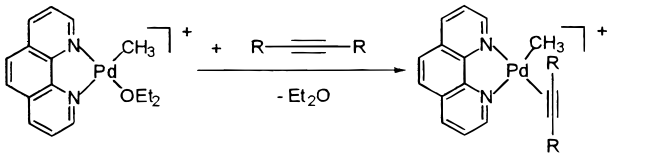


an effort to generate Pd(II) methyl alkyne adducts and study their migratory insertion reactions, as well as to determine whether such complexes could function as effective alkyne oligomerization or polymerization catalysts. We report here the results of these studies.

Results and Discussion

1. Formation of Alkyne Adducts. [(phen)Pd(CH$_3$)(OEt$_2$)]$^+$[BAr′$_4$]$^-$ (**4**) reacts with bis(trimethylsilyl)-acetylene to form the η^2-alkyne adduct [(phen)-Pd(CH$_3$)(η^2−Me$_3$SiC≡CSiMe$_3$)]$^+$[BAr′$_4$]$^-$ (**5a**) (eq 1). **5a**



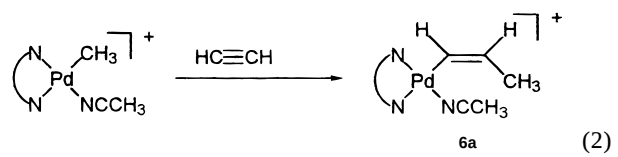
(1)

is a thermally stable, colorless crystalline solid and is moderately air- and water-stable. No evidence for migratory insertion of alkyne into the palladium−methyl bond was observed.

The reaction of [(phen)Pd(CH$_3$)(OEt$_2$)]$^+$[BAr′$_4$]$^-$ with phenylacetylene at −78 °C in CD_2Cl_2 yielded a complex whose ^{1}H NMR spectrum was consistent with the formulation [(phen)Pd(CH$_3$)(η^2−C$_6$H$_5$C≡CH)]$^+$[BAr′$_4$]$^-$ (**5b**). In the presence of excess phenylacetylene, exchange between free and coordinated phenylacetylene was observed at −60 °C, as evidenced by a broadening of the coordinated PhC≡C*H* peak (5.05 ppm). CD_2Cl_2 solutions of **5b** were unstable above −40 °C, transforming into an unidentifiable mixture of products.

The diimine complexes, [(N−N)Pd(CH$_3$)(NCCH$_3$)]$^+$-[BAr′$_4$]$^-$ (**1**−**3**), did not react with bis(trimethylsilyl)-acetylene or diphenylacetylene, perhaps for steric reasons. Less hindered alkynes reacted rapidly with **1**−**3** to insert into the Pd−CH$_3$ bond. This will be discussed in the next section.

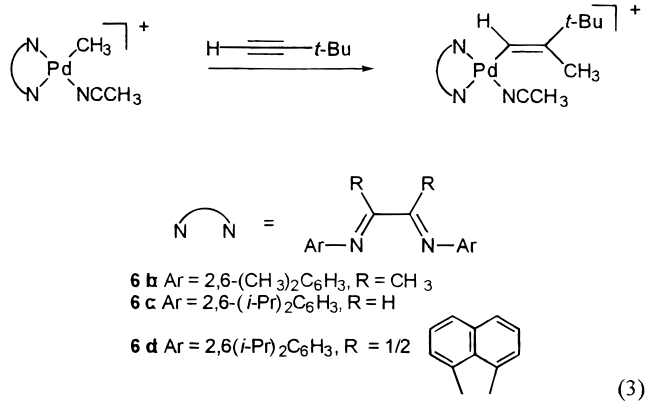
2. Migratory Insertion of Alkynes. A. Acetylene. The reaction of **3a** with acetylene in CD_2Cl_2 at −60 °C yields the η^1−vinyl complex [(Ar$_2$BIAN)Pd-(CH=CHCH$_3$)(NCCH$_3$)]$^+$ (**6a**), eq 2. The vincinal coupling constant between the vinylic protons (J_{HH} = 6 Hz) suggests that the insertion occurs with cis geometry.[16] No intermediate species were observed by ^{1}H NMR spectroscopy. Qualitatively, the insertion of acetylene occurs faster than the analogous insertion reaction of ethylene.



(2)

6a can be isolated as a thermally stable orange solid if excess acetylene is removed from the reaction mixture prior to warming. **6a** shows no evidence of isomerizing into an η^3-allyl complex or an η^2-vinyl complex. When complexes containing less bulky supporting ligands (**1b**,**c**, **2**, **4**) are reacted with acetylene in CD_2Cl_2 at −60 °C, vinyl complexes analogous to **6a** are observed by ^{1}H NMR spectroscopy, but these complexes are difficult to isolate in pure form due to their rapid reaction with a second equivalent of acetylene (see below).

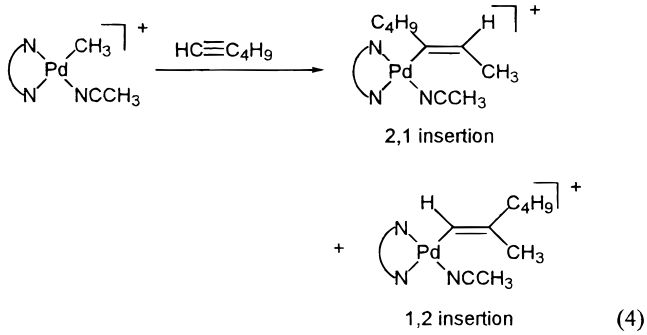
B. *tert*-Butylacetylene. Complexes **1b**, **2**, and **3** react with *tert*-butylacetylene in dichloromethane at 25 °C to form the η^1-vinyl complexes [(N−N)PdCH=C(*t*-Bu)(CH$_3$)(NCCH$_3$)]$^+$[BAr′$_4$]$^-$ (**6b**−**d**). From the NMR data, it cannot be determined whether alkyne insertion has occurred in a cis or trans fashion; however, steric arguments, and the observed preference for cis insertion of acetylene suggest that cis addition is likely (eq 3).



(3)

Complexes **6b**−**d** are thermally stable solids and show no evidence of converting into η^3-allyl or η^2-vinyl complexes.

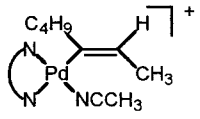
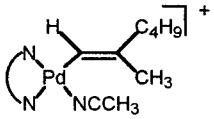
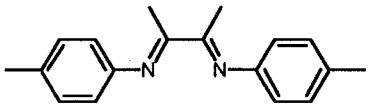
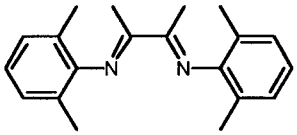
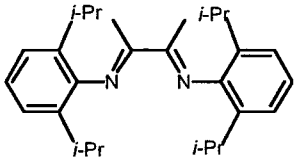
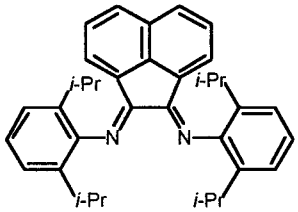
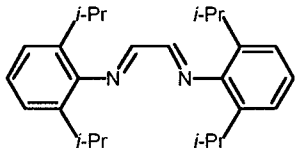
C. 1-Hexyne. Complexes **1a**−**c**, **2**, and **3** were allowed to react with 1-hexyne (0.8 equiv) in $CDCl_3$ at 25 °C, eq 4. A mixture of the 1,2-insertion product [(N−N)Pd(CH=C(C$_4$H$_9$) (CH$_3$))(NCCH$_3$)]$^+$ and the 2,1-insertion product [(N−N)Pd(C(C$_4$H$_9$)=CHCH$_3$)(NCCH$_3$)]$^+$ was



(4)

(16) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*, 2nd ed.; VCH: New York, 1993.

Table 1. Ligand Influence on the Regiochemistry of the Reaction of 1-Hexyne with $[(N\text{-}N)Pd(CH_3)(NCCH_3)]^+[BAr'_4]^-$ ($CDCl_3$, 25 °C)

entry number		 2,1 insertion	 1,2 insertion
1.		71%	29%
2.		51%	49%
3.		30%	70%
4.		35%	65%
5.		56%	44%

formed.[17] The relative amounts of the two insertion products are shown in Table 1.

For a given ligand backbone (complexes **1a**−**c**), the percentage of 1,2-insertion increases as the steric demands of the ligand aryl substituents increase (2,6-(i-Pr)$_2$C$_6$H$_3$ > 2,6-(CH$_3$)$_2$C$_6$H$_3$ > 4-CH$_3$C$_6$H$_4$). Likewise, for a given aryl substituent (2,6-(i-Pr)$_2$C$_6$H$_3$), the percentage of 1,2-insertion increases as the steric demand of the ligand backbone increases (**1** > **3** ≫ **2**).

The results with 1-hexyne and *tert*-butylacetylene suggest that the regiochemistry of alkyne insertion is governed by the steric demands of both the metal center and the alkyne. 2,1-Insertion is favored when there is little steric hindrance (entries 1 and 2), but when there is substantial steric congestion at the metal center (entries 3−5) or there is a bulky substituent on the alkyne (eq 3), 1,2-insertion is favored. If the alkyne must lie approximately in the square plane formed by the metal and the diimine ligand for migratory insertion to occur (eq 5), then the observed preference for 1,2-insertion when the alkyne substituents and/or the diimine are bulky can be explained by steric repulsion between the alkyne substituent R and the aryl substituents of the diimine disfavoring the 2,1-insertion.

There have been several studies on the insertion of alkynes into cyclometalated Ni(II) and Pd(II) complexes.[18−23] For these neutral complexes, alkyne insertion occurs only at 10 °C. The alkyne insertion

(17) In the presence of excess 1-hexyne, the vinyl complexes react to form the second insertion products as a mixture of regioisomers. Qualitatively, the 1,2-insertion products reacted more rapidly than the 2,1-insertion products; the second insertion reactions were significantly slower than the first insertion reactions. For this reason, a slight deficit (0.8 equiv) of 1-hexyne was used.

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(19) Ryabov, A. D.; van Eldik, R.; Le Borgne, G.; Pfeffer, M. *Organometallics* **1993**, *12*, 1386.
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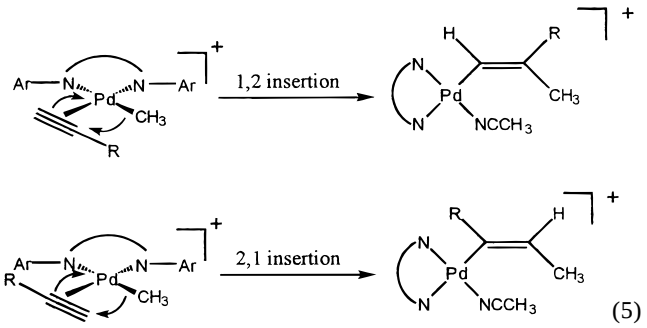
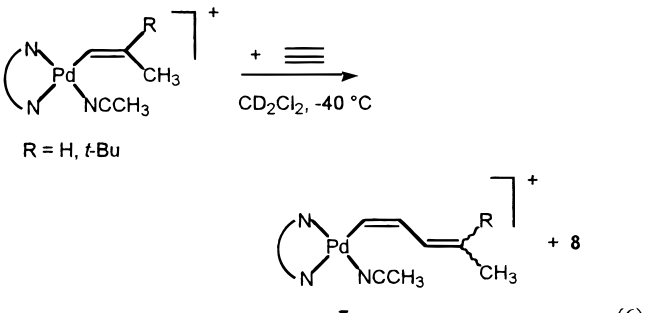
(21) Dupont, J.; Pfeffer, M.; Daran, J.-C.; Gouteron, J. *J. Chem. Soc., Dalton Trans.* **1988**, 2421.



(5)

reactions reported here occur at significantly lower temperatures (−60 °C); this enhanced reactivity is attributed to the higher electrophilicity of the cationic Pd(II) complexes.

3. Reactions of $[(N-N)Pd(CH=CHR)(NCCH_3)]^+[BAr'_4]^-$ (R = H, *t*-Bu) with Alkynes. The reactions of the η^1-vinyl complexes with acetylene were investigated by low-temperature ^1H NMR spectroscopy. At −20 °C, **6b** reacts with acetylene to form a new product whose ^1H NMR spectrum is consistent with the formulation $[(N-N)Pd(CH=CHCH=CH(t\text{-}Bu)(NCCH_3)]^+[BAr'_4]^-$ (**7**). Qualitatively, the insertion of acetylene into the Pd−vinyl bond is slower than the insertion of acetylene into the Pd−methyl bond. However, quantitative measurements were not possible since the formation of **7** is competitive with the formation of another product, **8** (eq 6).



7 (6)

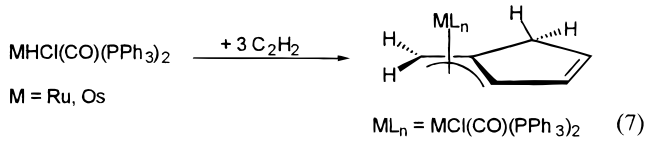
In the presence of excess acetylene at −40 °C, **7** is eventually converted into **8a**. A variety of complexes with the same connectivity as **8a** can be more conveniently prepared by purging CH_2Cl_2, Et_2O, or CH_3CN solutions of **1a**−**c**, **2**−**4** , or **6a**−**d** with acetylene at 25 °C. **8a**−**d** are isolated as highly crystalline, air- and water-stable solids whose colors range from deep green to deep purple and red. ^1H and ^{13}C NMR spectroscopy and elemental analyses revealed that CH_3CN was not present in **8a**−**d** and that a total of 3 equiv of alkyne was incorporated. Furthermore, the connectivity of the coupled alkyne fragment was similar in all of the complexes. In particular, one unusual feature was noted in the ^1H and ^{13}C NMR spectra. Two signals (1H each) were observed between 2.8 and 3.0 ppm, which were coupled to each other with an extremely high geminal coupling constant (J_{HH} = 24 Hz). ^1H and COSY spectra revealed that these protons exhibit a very weak coupling with one vinylic proton. ^{13}C NMR spectroscopy revealed that a CH_2 group was present in the fragment resulting from the coupled alkyne, suggesting that isomerization had occurred. However, the connectivity of the incorporated alkynes was not readily determined from the spectral data alone.

The connectivity of the coupled alkyne fragment in **8d** was determined by X-ray crystallography; however, the structure was disordered and accurate bond distances could not be determined. As shown in Scheme 1, the three alkyne fragments have coupled to form a 5-ethylidene-2-cyclopenten-1-yl fragment, which coordinates to the metal in an allylic fashion. The exact position of the double bond could not be determined from the X-ray data.

The structural information provides an explanation for the unusual features observed in the ^1H NMR spectra. The two signals coupled to each other with J_{HH} = 24 Hz are the methylenic protons of the cyclopentadienyl ring; high $^2J_{HH}$ values have been observed for hydrogens of an sp^3-hybridized carbon adjacent to a vinylic center.[16] The ^1H and COSY NMR spectra of **8a** reveal that the methylenic protons exhibit weak coupling to only one proton on the noncoordinated double bond. No coupling of the methylenic protons to the allylic proton was observed, suggesting that the connectivity is best represented by **8** rather than **8′**.

One possible mechanism for the formation of **8** is shown in Scheme 2. The first and second insertion of acetylene have been directly observed. Following the insertion of the third equivalent of acetylene, the next step is intramolecular cyclization resulting from migratory insertion of the pendant double bond into the Pd−C bond. β-Hydride elimination would yield a fulvene complex, which undergoes rapid rearrangement to form **8** (Scheme 2). The fact that the third insertion product cannot be observed suggests that the intramolecular cyclization and rearrangement are rapid relative to the alkyne insertion reactions.

A similar transformation has recently been reported by Roper and co-workers.[24] The hydride complexes $MHCl(CO)(PPh_3)_2$ (M = Ru, Os) react with 3 equiv of acetylene to form the 5-methylene-2-cyclopenten-1-yl complexes (eq 7). The connectivity of the coupled alkyne



(7)

fragment in the Ru and Os systems is similar to that proposed for **8**.

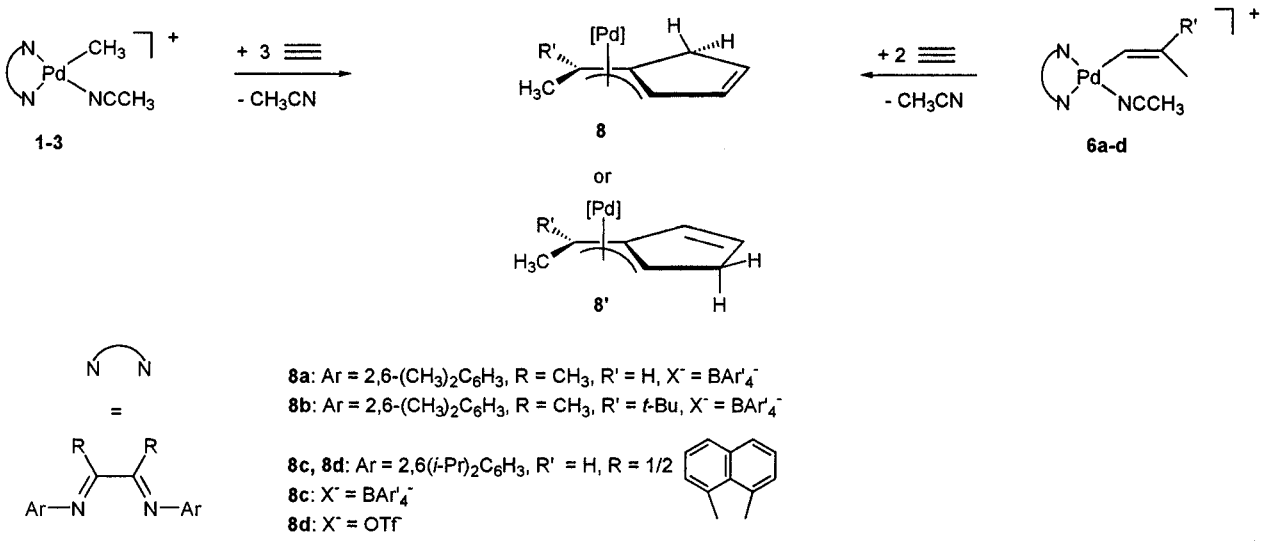
On the basis of the proposed mechanism for formation of **8**, we investigated whether the intramolecular cyclization was disfavored in the presence of more strongly coordinating neutral ligands or counterions; such ligands might bind strongly enough to the metal to inhibit formation of the chelate or allyl complexes. All attempts to prevent formation of **8** by changing to a coordinating solvent (CH_3CN, THF) or switching to a more coordinating counterion (triflate) were unsuccessful. Likewise, lowering the reaction temperature (to increase the

(22) Albert, J.; Granell, J.; Sales, J.; Solans, X. *J. Organomet. Chem.* **1989**, *379*, 177.

(23) . Tao, W.; Silverberg, L. J.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1989**, *8*, 2550.

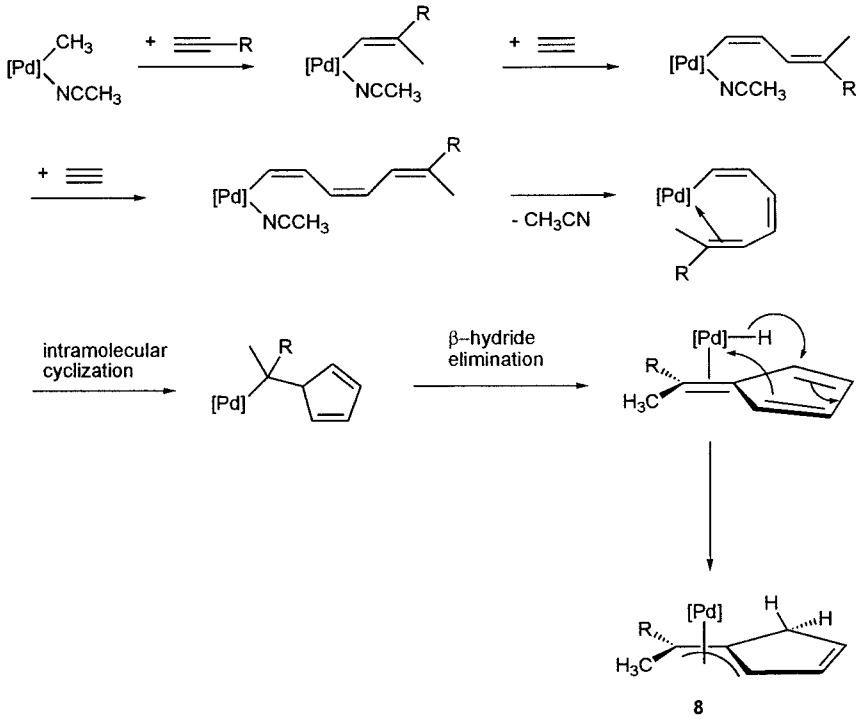
(24) Irvine, G. J.; Roper, W. R.; Wright, L. J. 213th National Meeting of the American Chemical Society, San Franscisco, CA, April 1997.

Scheme 1. Reaction of 1−3 or 6a−d with Excess Acetylene[a]



[a] [Pd] = (N-N)Pd$^+$.

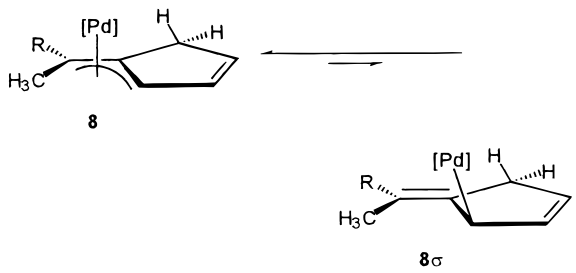
Scheme 2. Proposed Mechanism for the Formation of 8[a]



[a] [Pd] = (N-N)Pd$^+$; R = H, *t*-Bu.

amount of acetylene in solution), changing the substituents on the diimine ligand, or switching to the phenanthroline complexes (**4**) resulted in the formation of complexes analogous to **8a**−**d**.

At 25 °C in CH_2Cl_2, the cyclic compounds **8a**−**d** did not react with excess acetylene, ethylene, H_2, or CO. Likewise, no reaction was observed between **8a**−**d** and HCl, pyridine, or $HSiEt_3$. Since such substrates are normally quite reactive toward cationic Pd(II) alkyl complexes such as **1**−**4** or vinyl complexes such as **6a**−**d**, these results suggest that the equibrium between the π-allyl structure **8** and a σ-alkyl structure **8**σ lies strongly in favor of the π-allyl, perhaps for steric reasons (eq 8).



(8)

The results reported here illustrate one problem associated with the design of cationic, highly electrophilic complexes for use as polymerization catalysts, namely, that even if migratory insertion reactions with unsaturated substrates occur readily, reactive functionalities attached to the growing oligomer chain can

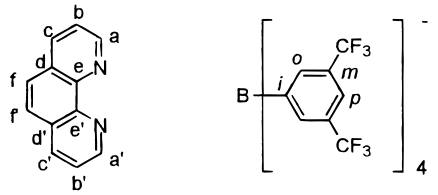
compete with external substrate for the vacant coordination site at the metal. If there is an equilibrium between chelation and coordination of monomer, then polymerizations are still possible; this is the case in the alternating copolymerization of C_2H_4/CO by **4**[12] or the copolymerization of methylacrylate and ethylene by **1**−**3**.[10] However, if the chelate does not open readily or if an intramolecular reaction occurs between the metal center and a site of unsaturation on the chelate, then polymerization reactions are strongly disfavored. This is the case in the formation of **8a**−**d**, when cyclization and rearrangement to an allylic structure result in complexes that are inert toward further insertion reactions with alkynes, alkenes, or carbon monoxide. Thus, the rational design of late transition metal catalysts for the polymerization of alkynes will require a precise tuning of the steric and electronic factors to develop systems in which migratory insertion reactions of alkynes are facile but in which intramolecular cyclization is disfavored.

Experimental Section

General. Unless otherwise noted, all reactions were conducted under an atmosphere of dry, deoxygenated argon using standard Schlenk techniques or in a Vacuum Atmospheres glovebox. Pentane, hexane, ether, toluene, and tetrahydrofuran were distilled from sodium benzophenone ketyl under a nitrogen atmosphere prior to use. Dichloromethane was distilled from P_4O_{10} under a nitrogen atmosphere. CD_2Cl_2 (CIL) was dried over CaH_2 under argon and was degassed and vacuum transferred. $CDCl_3$ was used as received. (phen)PdMe$_2$,[12] H(OEt$_2$)$_2$BAr′$_4$,[25] and complexes **1a**−**c**, **2**−**4**[8,9] were prepared according to reported procedures. Acetylene was purchased from Matheson and used without further purification. Alkynes were purchased from Aldrich and used without further purification.

Routine NMR spectra were recorded on a Varian XL-400, Varian Gemini 300 MHz, or Bruker AC-200 NMR spectrometer. Low-temperature NMR spectra were recorded on a Varian XL-400 spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to residual protio solvent peaks and solvent ^{13}C peaks, respectively. Elemental analyses were performed by Oneida Laboratories.

The atom-labeling schemes for the phenanthroline and ((CF$_3$)$_2$C$_6$H$_3$)$_4$B$^-$ counterion resonances are as follows:



The ^{1}H NMR resonances were assigned into groups of a, b, c, f or a, a′, b, b′, c′ or according to their characteristic coupling patterns. The ^{13}C NMR resonances were assigned in pairs such as C$_a$ or C$_{a'}$ and C$_{a'}$ or C$_a$ based on their chemical shifts and $^1J_{CH}$.

The ^{1}H and ^{13}C NMR data attributed to the counterion BAr′$_4^-$ (Ar′ = 3,5(CF$_3$)$_2$C$_6$H$_3$) follow. These are consistent for all cationic complexes examined and are not included in each compound characterized below. ^{1}H NMR (CD_2Cl_2): δ 7.72 (8, H$_o$), 7.56 (4, H$_p$). ^{1}H chemical shifts are accurate to within ±0.02 ppm. ^{13}C NMR (CD_2Cl_2): δ 162.1 (q, J_{C-B} = 50 Hz, C$_i$), 135.2 (C$_o$), 129.3 (q, $^2J_{C-F}$ = 31 Hz, C$_m$), 125.0 (q, J_{C-F} = 272 Hz, *C*F$_3$), 117.8 (C$_p$). ^{13}C NMR chemical shifts and coupling constants are consistent to within ±1 ppm and ±2 Hz, respectively. Note: because of the large number of aromatic peaks (100−160 ppm) from complexes containing the acenaphthene backbone, the ^{13}C spectra for these complexes were difficult to assign and full spectral data are usually not included here.

[(phen)Pd(CH$_3$)(Me$_3$SiC≡CSiMe$_3$)]$^+$[BAr′$_4$]$^-$ (5a). Solid (phen)Pd(CH$_3$)$_2$ (116 mg, 0.37 mmol) and [H(OEt$_2$)$_2$][BAr′$_4$] (365 mg, 0.37 mmol) were combined. The reaction flask was cooled to −30 °C, and Et$_2$O (10 mL) and CH_2Cl_2 (5 mL) were added. The resulting slurry was allowed to warm to 25 °C to dissolve solid (phen)Pd(CH$_3$)$_2$, and then the solution was cooled to −30 °C. Bis(trimethylsilyl)acetylene was added, and colorless microcrystals formed. The mixture was allowed to warm to room temperature, and the solid dissolved. The mixture was stirred for 1 h, and then the volume was reduced to 5 mL in vacuo and cooled slowly to −78 °C. Colorless needles formed and were washed with 10 mL of cold Et$_2$O, collected, and dried (yield = 285 mg; 59%). ^{1}H NMR (CD_2Cl_2, 20 °C): δ 8.95 (δ, 1, phen H$_a$), 8.71 (d, 1, phen H$_{a'}$), 8.59 (dd, 1, phen H$_c$), 8.54 (dd, 1, phen H$_{c'}$), 8.05 (s, 2, phen H$_d$), 8.00 (dd, 1, phen H$_b$), 7.92 (dd, 1, phen H$_{b'}$), 1.06 (s, 3, PdC*H*$_3$), 0.32 (s, 18, Si(C*H*$_3$)$_3$). ^{13}C NMR (CD_2Cl_2): δ 147.2, 145.2 (C$_a$, C$_{a'}$), 146.2, 143.2 (C$_e$, C$_{e'}$), 139.7, 138.4 (C$_c$, C$_{c'}$), 129.9, 129.3 (C$_f$, C$_{f'}$), 126.8, 126.5 (C$_d$, C$_{d'}$), 124.6, 124.4 (C$_b$, C$_{b'}$), 103.6 (Me$_3$Si*C*≡*C*SiMe$_3$), 7.9 (Pd*C*H$_3$), −1.7 (Si*Me*$_3$). Anal. Calcd for $C_{53}H_{41}N_2BF_{24}PdSi_2$: C, 47.67; H, 3.09; N, 2.10. Found: C, 47.83; H, 3.04; N, 1.94.

[(phen)Pd(CH$_3$)(C$_6$H$_5$≡CH)]$^+$[BAr′$_4$]$^-$ (5b). In a drybox, solid **4** (45 mg, 0.036 mmol) was loaded into a 5-mm NMR tube. CD_2Cl_2 (700 μL) was added at −78 °C, and the tube was shaken briefly to dissolve the solid. Phenylacetylene (5 μL, 0.045 mmol) was added via syringe, and the sample was inserted into a precooled (−78 °C) NMR probe. ^{1}H NMR (CD_2Cl_2, −78 °C): δ 8.92 (d, 1, phen H$_a$), 8.68 (d, 1, phen H$_{a'}$), 8.58 (d, 1, phen H$_b$), 8.50 (d, 1, phen H$_{b'}$), 7.99 (s, 2, phen H$_{d,\ -d'}$), 7.84 (m, 2, phen H$_{b,\ -b'}$), 5.05 (s, 1, PhC≡C*H*), 1.18 (s, 3, Pd−C*H*$_3$).

[BIAN(Ar)$_2$Pd(CH=CHMe)(NCCH$_3$)]$^+$[BAr′$_4$]$^-$ (Ar = 2,6-C$_6$H$_3$(*i*-Pr)$_2$) (6a). Solid **3** (270 mg, 0.18 mmol) was dissolved in 15 mL of dichloromethane. The solution was cooled to −70 °C, and acetylene gas was bubbled through the solution for 5 min. The mixture was allowed to stir at −70 °C for 30 min and then was placed under an active vacuum. After 5 min, the cooling bath was removed and the mixture was allowed to warm as dichloromethane was removed in vacuo. An orange-brown solid was isolated and recrystallized from a mixture of dichloromethane and pentane at 25 °C. Orange-brown crystals were collected and dried (yield = 159 mg, 58%). ^{1}H NMR (CD_2Cl_2): δ 6.42−8.12 (m, 12 total, BIAN + Ar), 4.80 (m, 1, PdCH=C*H*CH$_3$), 4.61 (d, 1, J_{HH} = 6 Hz, PdC*H*=CHCH$_3$), 3.22, 3.15 (sept, 2 each, C*H*Me$_2$), 1.88 (C*H*$_3$CN), 1.78 (d, 3, PdCH-CHC*H*$_3$), 1.40, 1.30, 1.02, 0.87 (d, 6 each, CH*Me*$_2$). Anal. Calcd for $C_{73}H_{60}N_3BF_{24}Pd$: C, 56.48; H, 3.89; N, 2.71. Found: C, 56.24; H, 3.92; N, 2.34.

[(ArN=C(Me)−C(Me)=NAr)Pd(CH=CMe(*t*-Bu))(NCCH$_3$)]$^+$[BAr′$_4$]$^-$ (Ar = 2,6-C$_6$H$_3$(Me)$_2$) (6b). [(ArN=C(Me)−C(Me)=NAr)Pd(CH$_3$)(NCCH$_3$)]$^+$[BAr′$_4$]$^-$ (282 mg, 0.21 mmol) was dissolved in 10 mL of dichloromethane, and *tert*-butylacetylene (30μ L, 0.26 mmol) was added. The mixture became orange and was allowed to stir for 30 min. Dichloromethane was removed in vacuo, and the resulting yellow glassy solid was washed with hexane and dried (yield = 192 mg, 64%). ^{1}H NMR (CD_2Cl_2): δ 7.21, 7.16 (m, 6 total, Ar), 4.27 (s, 1, PdC*H*), 2.25, 2.17, 2.15, 2.14 (s, 18 total, N=C(C*H*$_3$) + ArC*H*$_3$), 1.85, 1.75 (s, 3 each, C*H*$_3$CN + PdCH=C(*t*-Bu)-(C*H*$_3$)), 0.61 (s, 9, *t*-Bu). ^{13}C NMR ($CDCl_3$): δ 146.4 (C$_{iso}$, note: the two C$_{ipso}$ peaks are apparently coincident), 142.6, 142.3 (Ar C$_{para}$), 129.0, 128.8 (Ar C$_{meta}$), 122.6, 122.2 (Ar C$_{ortho}$), 120.8 (CH$_3$*C*N), 37.3 (=C(*C*H$_3$)), 28.8 (C*Me*$_3$), 28.7 (*C*Me$_3$), 19.7,

(25) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

19.5, 18.7, 17.6, 17.5 (N=C*CH*$_3$ and Ar*CH*$_3$), 1.7 (*CH*$_3$CN). Anal. Calcd for $C_{61}H_{52}N_3BF_{24}Pd$: C, 52.33; H, 3.74; N, 3.00. Found: C, 52.41; H, 3.82; N, 2.19.

[(ArN=C(H)−C(H)=NAr)Pd(CH=CMe(*t*-Bu))(NCCH$_3$)]$^+$-[BAr′$_4$]$^-$ (Ar = 2,6-C$_6$H$_3$(*i*-Pr)$_2$) (6c). Following the above procedure, an orange powder was isolated in 79% yield. ^{1}H NMR (CD_2Cl_2): δ 8.26 (d, 2, Ar), 7.27−7.37 (m, 4, Ar), 4.48 (s, 1, PdC*H*), 3.16, 3.06 (sept, 2 each, C*H*Me$_2$), 1.88, 1.80 (s, 3 each, C*H*$_3$CN + PdCH=C(*t*-Bu)(C*H*$_3$)), 1.39, 1.37, 1.25, 1.17 (d, 6 each, CH*Me*$_2$), 0.63 (*t*-Bu). ^{13}C NMR (CD_2Cl_2): δ 167.5, 161.6 (*C*=N), 147.4, 142.8 (Ar C$_{ipso}$), 139.4, 138.5 (Ar C$_{para}$), 129.6, 129.4 (Ar C$_{meta}$), 124.4, 124.3 (Ar C$_{ortho}$), 123.4 (*CH*$_3$CN), 37.6 (*C*Me$_3$), 29.4 (C*Me*$_3$), 29.5, 29.3 (CH*Me*$_2$), 25.1, 23.9, 22.3, 19.7 (CH*Me*$_2$), 2.6 (*CH*$_3$CN). Anal. Calcd for $C_{67}H_{64}N_3BF_{24}Pd$: C, 54.21; H, 4.34; N, 2.83. Found: C, 53.87; H, 4.13; N, 2.42.

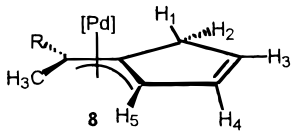
[(BIAN)(Ar)$_2$Pd(CH=CMe(*t*-Bu))(NCCH$_3$)]$^+$[BAr′$_4$]$^-$ (Ar = 2,6-C$_6$H$_3$(*i*-Pr)$_2$) (6d). [(BIAN)(Ar)$_2$Pd(CH$_3$)(NCCH$_3$)]$^+$-[BAr′$_4$]$^-$ (525 mg, 0.34 mmol) was dissolved in 20 mL of dichloromethane, and *tert*-butylacetylene (45 μL, 0.40 mmol) was added via syringe. The resulting orange solution was allowed to stir for 30 min. Dichloromethane was removed in vacuo, leaving an orange microcrystalline solid which was recrystallized from a CH_2Cl_2/hexane mixture at −30 °C. Orange cubes were collected and dried (370 mg, 68%). ^{1}H NMR (CD_2Cl_2): δ 6.5−8 (m, 12, BIAN + Ar), 4.47 (s, 1, PdC*H*), 3.40, 3.35 (sept, 2 each, C*H*Me$_2$), 1.87, 1.86 (s, 3 each, PdCH=C(*t*-Bu)(C*H*$_3$) + C*H*$_3$), 1.46, 1.38, 1.08, 0.93 (d, 6 each, CH*Me*$_2$), 0.68 (s, 9, *t*-Bu). Anal. Calcd for $C_{77}H_{68}N_3BF_{24}Pd$: C, 57.50; H, 4.26; N, 2.61. Found: C, 57.59; H, 4.04; N, 2.30.

Reactions of [(ArN=C(R)−C(R)=NAr)Pd(CH$_3$)(NCCH$_3$)]-$^+$[BAr′$_4$]$^-$ with 1-Hexyne: Regiochemistry of Insertion. Solid **1**−**3** (0.03 mmol) was loaded into a 5-mm NMR tube and dissolved in $CDCl_3$ (0.7 mL). 1-Hexyne (2.5 μL, 0.022 mmol) was then added via syringe; the sample was shaken 3 times and inserted into a NMR probe. The relative amounts of 1,2-insertion and 2,1-insertion were analyzed by the relative integrals of the peaks attributed to PdC*H*=C(CH$_3$)(C$_4$H$_9$) and PdC(C$_4$H$_9$)=C*H*(CH$_3$), respectively (Table 1). Note: a deficit (0.7 equiv) of 1-hexyne was used in order to prevent the vinyl complexes that are formed from reacting with excess alkyne.[17] ^{1}H NMR data for the vinylic protons is given below. Due to the large number of overlapping ligand peaks in the aromatic and aliphatic regions, the remainder of the peaks are difficult to assign and are not listed below.

^{1}H NMR ($CDCl_3$, 25 °C). **1a** + 1-hexyne: δ 3.58 (s, PdC*H*=C(CH$_3$)(C$_4$H$_9$)), 3.96 (q, J_{HH} = 7 Hz, PdC(C$_4$H$_9$)=C*H*(CH$_3$)). **1b** + 1-hexyne: δ 4.08 (s, PdC*H*=C(CH$_3$)(C$_4$H$_9$)), 4.39 (q, J_{HH} = 7 Hz, PdC(C$_4$H$_9$)=C*H*(CH$_3$)). **1c** + 1-hexyne: δ 4.53 (s, PdC*H*=C(CH$_3$)(C$_4$H$_9$)), 4.27 (q, J_{HH} = 8 Hz, PdC(C$_4$H$_9$)=C*H*(CH$_3$)). **2** + 1-hexyne: δ 4.26 (s, PdC*H*=C(CH$_3$)(C$_4$H$_9$)), 4.44 (q, J_{HH} = 7 Hz, PdC(C$_4$H$_9$)=C*H*(CH$_3$)). **3** + 1-hexyne: δ 4.28 (s, PdC*H*=C(CH$_3$)(C$_4$H$_9$)), 4.48 (q, J_{HH} = 7 Hz, PdC(C$_4$H$_9$)=C*H*(CH$_3$)).

Observation of [(ArN=C(CH$_3$)C(CH$_3$)NAr)PdCH=CHCH=CHC(*t*-Bu)(CH$_3$)]$^+$ (Ar = 2,6-(CH$_3$)$_2$C$_6$H$_3$) (7). Solid **6b** (25 mg, 0.018 mmol) was loaded into a 5-mm NMR tube and dissolved in 0.7 mL of CD_2Cl_2. The solution was cooled to −78 °C, and acetylene (1 mL, 0.044 mmol) was added via gastight syringe. The sample was then inserted into a precooled (−78 °C) NMR probe. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 6.37 (d, 1, J_{HH} = 11 Hz, PdC*H*=CH), 5.50 (dd, 1, J_{HH} = 11, 6 Hz, PdCH=C*H*CH), 4.75 (dd, 1, J_{HH} = 6 Hz, PdCH=CHC*H*). The terminal CH$_3$ and *t*-Bu peaks could not be unambiguously assigned due to the presence of substantial amounts of **6b** and **8b**.

Formation of 8a−d. In a typical procedure, solid [(ArN=C(R)−C(R)=NAr)Pd(CH$_3$)(NCCH$_3$)]$^+$[BAr′$_4$]$^-$ or [(ArN=C(R)-C(R)=NAr)Pd(CH=C(*t*-Bu)(CH$_3$)(NCCH$_3$)]$^+$[BAr′$_4$]$^-$ was loaded into a Schlenk flask. The solid was dissolved in CH_2Cl_2, and acetylene was bubbled through the solution for 5 min at 25 °C. CH_2Cl_2 and CH_3CN were then removed in vacuo, yielding a microcrystalline powder which was then recrystallized from CH_2Cl_2/pentane. Triflate complexes were prepared in a similar manner. The peaks associated with the coupled tris(alkyne) fragment are labeled according to the following assignments.



[(ArN=C(CH$_3$)C(CH$_3$)=NAr)Pd(η^3-CH(CH$_3$)C$_5$H$_5$)]$^+$-[BAr′$_4$]$^-$ (Ar = 2,6-(CH$_3$)$_2$C$_6$H$_3$) (8a). Purple crystals were prepared in the manner described above from **1b** (103 mg, 0.078 mmol) and acetylene (yield = 78 mg, 68%) ^{1}H NMR (CD_2Cl_2, 25 °C): δ 7.2−7.4 (m, 6 total, Ar), 6.44 (br d, 1, J_{HH} = 6 Hz, H$_4$), 4.92 (d, 1, J_{HH} = 6 Hz, H$_3$), 4.64 (br s, 1, H$_5$), 3.88 (q, 1, J_{HH} = 6 Hz, C*H*CH$_3$), 2.93, 2.78 (d, 1 each, J_{HH} = 24 Hz, H$_1$ and H$_2$), 2.31, 2.27, 2.17, 2.14, 1.95, 1.77 (s, 3 each, diimine C*H*$_3$), 0.39 (d, 3, J_{HH} = 6 Hz, CHC*H*$_3$). ^{13}C NMR (coupled alkyne fragment only) (CD_2Cl_2, 25 °C): δ 101.1 (d, J_{CH} = 179 Hz, cyclopentadienyl), 97.8 1 (d, J_{CH} = 178 Hz, cyclopentadienyl), 83.4 1 (d, J_{CH} = 166 Hz, cyclopentadienyl), 70.1 (d, J_{CH} = 154 Hz, cyclopentadienyl), 40.2 (t, J_{CH} = 132 Hz, *C*H$_3$H$_4$). Note: the peak corresponding to the internal allylic carbon could not be located and may be hidden under diimine or BAr′$_4$ peaks. Anal. Calcd for $C_{59}H_{45}N_2BF_{24}Pd$: C, 52.29; H, 3.34; N, 2.07. Found: C, 52.28; H, 3.19; N, 1.96.

[(ArN=C(CH$_3$)C(CH$_3$)=NAr)Pd(η^3-C(*t*-Bu)(CH$_3$)C$_5$H$_5$)]$^+$-[BAr′$_4$]$^-$ (Ar = 2,6-(CH$_3$)$_2$C$_6$H$_3$) (8b). Orange-brown crystals were prepared from **6b** (250 mg, 0.19 mmol) and acetylene in the manner described above (yield = 215 mg, 80%). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 7.2−7.4 (m, 6 total, Ar), 6.43 (d, 1, J_{HH} = 6 Hz, H$_3$), 4.76 (dd, 1, J_{HH} =2 Hz, 6 Hz, H$_4$), 4.10 (d, 1, J_{HH} = 2 Hz, H$_5$), 3.04, 2.75 (d, 1 each, J_{HH} = 24 Hz, H$_1$ and H$_2$), 2.33, 2.20, 2.13, 2.12, 1.98, 1.73 (s, 3 each, Ar−C*H*$_3$, N=CC*H*$_3$), 0.87 (s, 9, *t*-Bu), 0.80 (s, 3, C(*t*-Bu)(C*H*$_3$)). ^{13}C NMR (coupled alkyne fragment only) (CD_2Cl_2, 25 °C): δ 97.4, 85.5, 44.4, 41.1 (cyclopentadienyl). Note: the peaks corresponding to the internal and quaternary terminal allylic carbons could not be located. Anal. Calcd for $C_{63}H_{53}N_2BF_{24}Pd$: C, 53.62; H, 3.78; N, 1.99. Found: C, 53.72; H, 3.61; N, 1.87.

[(BIAN)(NAr)$_2$)Pd(η^3-CH(CH$_3$)C$_5$H$_5$)]$^+$[BAr′$_4$]$^-$ (Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$) (8c). In a modification of the above procedure, acetylene was bubbled through a CH_3CN solution of [(BIAN)(NAr)$_2$Pd(CH$_3$)(NCCH$_3$)]$^+$[BAr′$_4$]$^-$ (370 mg, 0.24 mmol). After acetylene addition had ceased, green crytals formed on the sides of the flask and were collected, washed with CH_3CN, and dried (yield = 276 mg, 74%). ^{1}H NMR (coupled alkyne fragment only) (CD_2Cl_2, 25 °C): 6.55 (d, 1, J_{HH} = 6 Hz, H$_4$), 5.34 (d, 1, J_{HH} = 6 Hz, H$_3$), 4.96 (s, 1, H$_5$), 4.15 (q, 1, J_{HH} = 6 Hz, C*H*CH$_3$), 2.93, 2.80 (d, 1 each, J_{HH} = 24 Hz, H$_1$ and H$_2$), 0.61 (d, 3, J_{HH} = 6 Hz, CHC*H*$_3$). ^{13}C NMR (coupled alkyne fragment only) (CD_2Cl_2, 25 °C): δ 104.6, 98.4, 83.9, 70.3 (cyclopentadienyl vinylic *C*), 40.0 (cyclopentadienyl *C*H$_2$), 14.2 (CH*C*H$_3$). Note: the peak corresponding to the internal allylic carbon could not be located and may be hidden under diimine or BAr′$_4$ peaks. Anal. Calcd for $C_{75}H_{61}N_2BF_{24}Pd$: C, 57.62; H, 3.90; N, 1.79. Found: C, 57.49; H, 3.85; N, 1.78.

[(BIAN)(NAr)$_2$)Pd(η^3-CH(CH$_3$)C$_5$H$_5$)]$^+$[O$_3$SCF$_3$]$^-$ (Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$) (8d). Green crystals were formed from **3b** (282 mg, 0.35 mmol) and acetylene according to the above procedure (yield = 225 mg, 76%). NMR data for the cationic portion of the molecule matched that of **8c**. Anal. Calcd for $C_{44}H_{49}N_2F_3O_3PdS$: C, 62.22; H, 5.81; N, 3.30. Found: C, 62.43; H, 5.71; N, 3.02.

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