Acrylonitrile Insertion Reactions of Palladium Alkyl Complexes that Contain Neutral or Anionic Bidentate Phosphine Ligands

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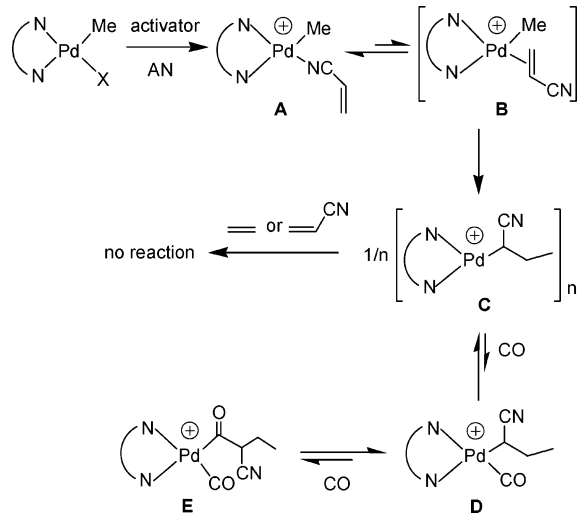
The reactions of acrylonitrile (AN) with palladium alkyl complexes that contain bisphosphine ligands, P∧P = $Ph_2P(CH_2)_3PPh_2$ (**a**, dppp), $Me_2P(CH_2)_2PMe_2$ (**b**, dmpe), $[Ph_2B(CH_2PPh_2)_2]^-$ (**c**, Ph_2BP_2), were studied. (P∧P)PdMeCl (**1a**,**b**) reacts with $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ and AN to form N-bound AN adducts $(P∧P)PdMe(NCCH{=}CH_2)^+$ (**3a**,**b**). **3b** inserts AN to form $[(dmpe)Pd(CHEtCN)]_n^{n+}$ (**4b**). Sequential reaction of [ASN][$(Ph_2BP_2)PdMe_2$] (**1c**, ASN = 5-azoniaspiro[4.4]nonane) with $[HNMe_2Ph][B(C_6F_5)_4]$ and AN affords the N-bound adduct $(Ph_2BP_2)PdMe(NCCH{=}CH_2)$ (**3c**), which reacts to form $[(Ph_2BP_2)$-Pd(CHEtCN)$]_n$ (**4c**). IR data suggest that the Pd units of **4b**,**c** are aggregated by PdCHEtCN- - -Pd bridges. **4b** reacts with PPh_3 to form $(dmpe)Pd(CHEtCN)(PPh_3)^+$ (**5b**). **4c** reacts with PMe_3 and with pyridine (py) to form $(Ph_2BP_2)Pd(CHEtCN)(L)$ (L = PMe_3 (**6c**), py (**7c**)). The characterization of **5b**, **6c**, and **7c** confirms the 2,1 AN insertion of **3b**,**c**. The rate constants for AN insertion ($k_{obs,AN}$, 23 °C) vary in the order **3c** ($1.12(3) \times 10^{-3}$ s^{-1}) > **3b** ($3.33(5) \times 10^{-5}$ s^{-1}) > **3a** (no reaction). Electron-rich metal centers and incorporation of an anionic charge in the P∧P ligand promote insertion, probably by favoring formation of a reactive π-bound AN complex.

Introduction

The development of metal-catalyzed insertion polymerization reactions of acrylonitrile (AN) is an attractive goal. Polyacrylonitrile (PAN) and AN copolymers are important materials with diverse applications and are currently prepared by anionic or radical polymerization.[1] Hydrogenated nitrile butadiene rubbers (HNBRs), which are in effect linear copolymers of ethylene and AN, are prepared by radical copolymerization of butadiene and AN followed by hydrogenation. Synthesis of these materials by metal-catalyzed insertion polymerization/copolymerization may provide improved control over polymer composition, structure, and properties through tuning of the catalyst structure.[2]

Previously we investigated the reactions of AN with Pd ethylene dimerization/polymerization catalysts that contain bidentate N-donor ligands (N∧N).[3] As shown in Scheme 1, $(N∧N)PdMe^+$ species that contain bis-imidazole, bis-pyridine, or diimine ligands (N∧N) form N-bound $(N∧N)PdMe(NCCH{=}CH_2)^+$ adducts (**A**). The bis-imidazole and bis-pyridine complexes undergo 2,1 AN insertion to yield $(N∧N)Pd(CHEtCN)^+$ products (**C**), which aggregate by PdCHEtCN- - -Pd bridging. The diimine complex [{(2,6-^{i}Pr_2-C_6H_3)N=CMeCMe=N(2,6-^{i}Pr_2-C_6H_3)}PdMe$(NCCH{=}CH_2)$][$B(C_6F_5)_4$] does not insert AN at 23 °C; however, Baird reported that the analogous B{3,5-$(CF_3)_2$-C_6H_3}$_4^-$ salt does undergo insertion to yield $(N∧N)Pd(CHEtCN)(NCCH{=}CH_2)^+$, which was characterized by ESI-MS and partial NMR data.[4] These insertions are presumed to proceed via intermediate C=C π-bound AN adducts (**B**), which were not observed. The overall insertion rates for $(N∧N)PdMe(NCCH{=}CH_2)^+$ species vary in the order N∧N = bis-imidazole > bis-pyridine > diimine, which parallels the order of electron-richness at the Pd center based on ν_{CO} data for the corresponding $(N∧N)Pd\{C(=O)Me\}(CO)^+$ species. Isomerization of the N-bound adducts **A** to the C=C π-bound adducts **B** is critical for insertion, and highly electron-deficient $(N∧N)PdMe(NCCH{=}CH_2)^+$ species for which the N-bound adduct is strongly favored are poor candidates for insertion. In parallel work, Weiss, Piers, and co-workers showed that $(L∧L)PdMe(NCCH_3)$ complexes containing ancillary bidentate phenoxydiazene or phenoxyaldi-

Scheme 1



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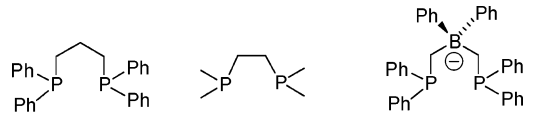
mine ligands (L∧L) also form N-bound AN adducts, which undergo 2,1 AN insertion to form (L∧L)Pd(CHEtCN) species that dimerize and trimerize by PdCHEtCN---Pd bridging.[5] Incorporation of an anionic $-BF_3$ group on the ancillary L∧L ligand increased the AN insertion rate, and both neutral and anionic (L∧L)PdMe(NCCH═CH_2) species insert faster than (N∧N)PdMe(NCCH═CH_2)$^+$ species, again indicating that increasing the negative charge at the metal center enhances the overall AN insertion rate.

The [(N∧N)Pd(CHEtCN)]$_n^{n+}$ species **C** formed in Scheme 1 do not react with ethylene or AN. However, [(N∧N)Pd(CHEtCN)]$_n^{n+}$ species that contain bis-imidazole ligands, which are the strongest donors among the N∧N ligands studied, do react with CO to form (N∧N)Pd(CHEtCN)(CO)$^+$ complexes (**D**). More interestingly, (bim)Pd(CHEtCN)(CO)$^+$ (bim = CH_2-(*N*-Me-imidazol-2-yl)$_2$) undergoes slow, reversible CO insertion to form (bim)Pd{C(═O)CHEtCN}(CO)$^+$ (**E**), which demonstrates that insertions into Pd−CHRCN bonds are possible. However, this process is much slower than CO insertion of (bim)PdMe(CO)$^+$ species, which is normally very fast. This difference in reactivity results from the electron-withdrawing effect of the α-CN substituent in **D**.

These initial studies suggest that the key obstacles to incorporation of AN in insertion polymerization/copolymerization reactions are: (a) slow overall AN insertion rates for highly electrophilic catalysts due to the preference for N-coordination over C═C π-coordination of AN; (b) the tendency of $L_nM\{CH(CN)CH_2R\}$ species to aggregate by $MCH(CH_2R)$-CN---M bridging, due to the high Lewis basicity of the α-CN group; and (c) the low insertion reactivity of $L_nM\{CH(CN)$-$CH_2R\}$(substrate)$^+$ species due to the deactivating effect of the α-CN group. Additionally, metal catalysts may initiate anionic or radical AN polymerization.[6,7]

To begin to address these issues, we have investigated the reactivity of palladium methyl complexes that contain bidentate phosphine ligands (P∧P). The softer character of phosphorus donors compared to nitrogen donors[8,9] may enhance C═C π-complexation of AN and, therefore, increase the overall AN insertion rate. Additionally, the stronger trans influence of phosphorus donors versus nitrogen donors[8a,b] may labilize the PdCHEtCN---Pd interactions in the insertion product aggregates and promote insertions into Pd−CHEtCN bonds.



a, dppp **b**, dmpe **c**, Ph_2BP_2

2130 ca. 2121 2108

Figure 1. Ancillary ligands (P∧P) used in this work and ν_{CO} values (in cm^{-1}) for the terminal CO ligands in the corresponding [(P∧P)-Pd{C(═O)Me}(CO)]$^{n+}$ complexes (n = 1 for **a**,**b** and 0 for **c**). The ν_{CO} value for **b** is estimated from that for the corresponding dippp complex.[11]

Results

Probe Complexes. "(P∧P)PdMe^{n+}" species (n = 0 or 1) containing the bidentate phosphine ligands $Ph_2P(CH_2)_3PPh_2$ (**a**, dppp), $Me_2P(CH_2)_2PMe_2$ (**b**, dmpe), or $[Ph_2B(CH_2PPh_2)_2]^-$ (**c**, Ph_2BP_2), which are shown in Figure 1, were studied in this work. The electrophilic character of [(P∧P)PdMe]$^{n+}$ (n = 1 for **a**, **b**; 0 for **c**) species can be assessed by the ν_{CO} values for the terminal CO ligands in the corresponding [(P∧P)Pd{C(═O)-Me}(CO)]$^{n+}$ complexes, which are listed in Figure 1.[10a,11] On the basis of these values, the electrophilic character of [(P∧P)-PdMe]$^{n+}$ is expected to vary in the order **a** > **b** > **c**. Ligands **a** and **c** are more sterically demanding than **b**. Cationic/zwitterionic [(P∧P)PdMe]$^{n+}$ species based on **a**−**c** catalyze the copolymerization of ethylene and CO, and (P∧P)PdMe-(ethylene)$^+$ complexes containing ligands **a** or **b** catalytically dimerize ethylene.[11a,12]

Generation of [(P∧P)PdMe(NCCH═CH_2)]$^{n+}$ Complexes (3a−c). The reaction of (P∧P)PdMeCl (**1a**,**b**) with 0.5 equiv of $[Li(Et_2O)_{2.8}][B(C_6F_5)_4]$ yields dinuclear [{(P∧P)PdMe}$_2$(μ-Cl)]$^+$ complexes (**2a**,**b**) quantitatively (eq 1).[13] Addition of excess AN to **2a**,**b** in the presence of 0.5 equiv of $[Li(Et_2O)_{2.8}]$-$[B(C_6F_5)_4]$ results in quantitative formation of (P∧P)PdMe-(NCCH═CH_2)$^+$ complexes (**3a**,**b**, eq 1).

The reaction of (dmpe)$PdMe_2$ with $[HNMe_2Ph][B(C_6F_5)_4]$ quantitatively generates (dmpe)PdMe(NMe_2Ph)$^+$ and methane within 10 min at −78 °C. Addition of AN results in quantitative formation of **3b** (eq 2).

The reaction of [ASN][(Ph_2BP_2)$PdMe_2$] (**1c**, ASN = 5-azonia-spiro[4.4]nonane)[10] with $[HNMe_2Ph][B(C_6F_5)_4]$ at −78 °C, followed by addition of excess AN and warming to −60 °C, yields (Ph_2BP_2)PdMe(NCCH═CH_2) (**3c**) cleanly (eq 3).

The ^{1}H and ^{13}C NMR AN resonances of **3a**−**c** are only slightly shifted from the free AN positions. For example, the ^{1}H NMR AN resonances for **3c** (−60 °C, CD_2Cl_2) appear at δ 6.06 (d, J = 12, 1H, H_{cis}), 5.78 (d, J = 18, 1H, H_{trans}), and 5.39 (dd, J = 18, 12; 1H, H_{int}), shifted upfield by <0.5 ppm from

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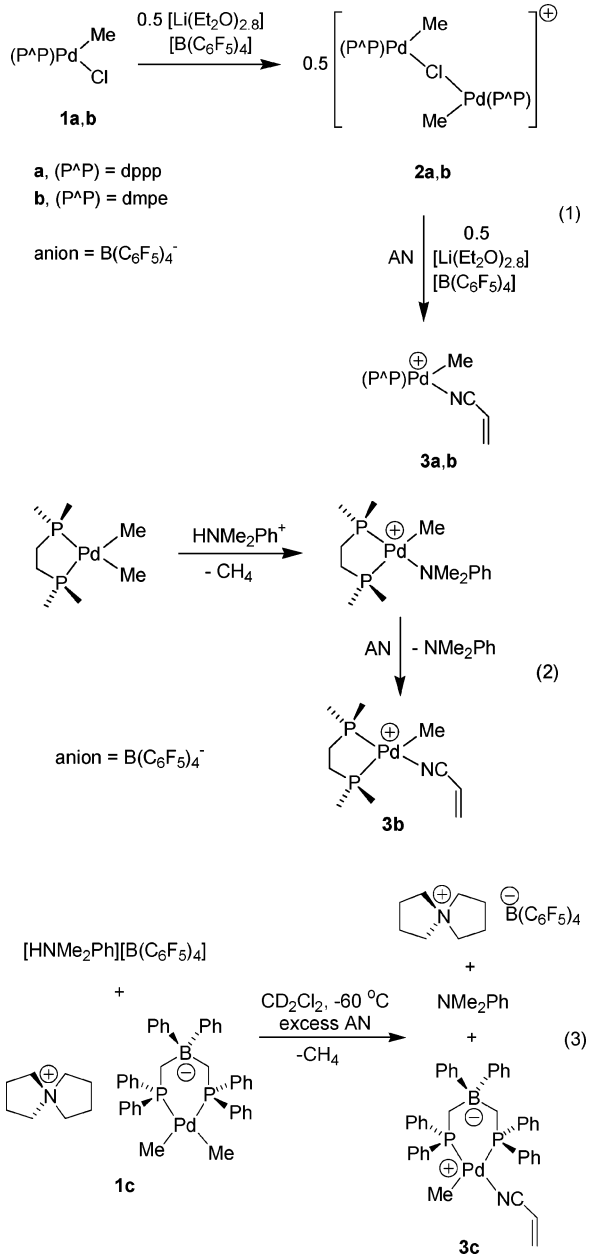
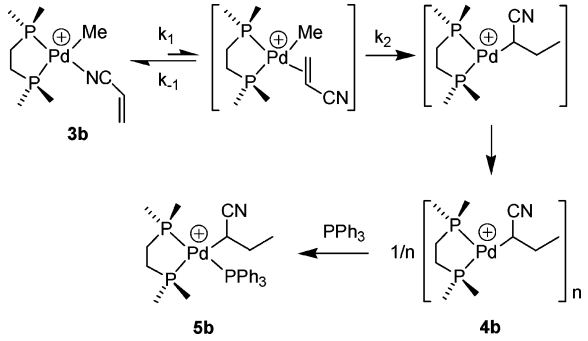


the corresponding free AN resonances. The ^{13}C NMR AN resonances of **3c** appear at δ 141.8 (C_{ter}), 120.3 (CN), and 105.2 (C_{int}), within 5 ppm of the corresponding free AN positions. These data are consistent with N-coordination of the AN ligand.[3,14] In contrast, for C═C π-bound AN complexes, the ^1H and ^{13}C NMR AN resonances are normally shifted far upfield from the free AN positions.[15,16] The IR ν_{CN} values for **3a** (2227 cm^{-1}) and **3b** (2220 cm^{-1}) are slightly lower than that for free AN (2230 cm^{-1}).[17] The presence of AN was confirmed by the ESI mass spectra of **3a**,**b**, in which the (P∧P)PdMe(NCCH═CH$_2$)$^+$ ions are the major cations observed.

Scheme 2



Acrylonitrile Insertion of 3b. Complex **3a** is stable at 23 °C for several days. No evidence for AN insertion of **3a** was observed up to 60 °C, at which temperature significant decomposition occurred. In contrast, **3b** undergoes 2,1 insertion at 23 °C to afford (dmpe)Pd(CHEtCN)$^+$, which is believed to form as a mixture of [(dmpe)Pd(CHEtCN)]$_n^{n+}$ aggregate species (**4b**, Scheme 2). ^1H NMR monitoring experiments show that **3b** is completely consumed within 2 days, but no free AN is consumed in this reaction. No intermediates in the conversion of **3b** to **4b** were observed by NMR. The observed first-order rate constant for conversion of **3b** to **4b** determined by NMR monitoring of the disappearance of the Pd-Me resonance of **3b** is $k_{obs,AN} = 3.33(5) \times 10^{-5}$ s^{-1} at 23 °C. This rate constant can be expressed as $k_{obs,AN} = k_1k_2/(k_{-1} + k_2)$, making the steady-state assumption for the unobserved π-complex intermediate (Scheme 2). Compound **4b** is stable in CD_2Cl_2 solution at 23 °C for at least 10 days.

The NMR spectra of **4b** are complex. For example, the ^{31}P NMR spectrum of **4b** contains five sets of resonances, indicating the presence of five chemically inequivalent, unsymmetrical dmpe environments. The ESI mass spectrum of **4b** contains a prominent signal for the (dmpe)Pd(CHEtCN)$^+$ cation, but does not contain signals for aggregated species. The IR ν_{CN} band for **4b** appears at 2218 cm^{-1}. These results do not provide definitive evidence for the structure of **4b**. It is likely that **4b** is aggregated by PdCHEtCN---Pd bridges, as observed previously for the (N∧N)Pd(CHEtCN)$^+$ analogues and the structurally characterized complex [(N∧O)Pd(CHEtCN)]$_3$ (N∧O = bulky phenoxydiazene),[3,5,18] but the aggregates dissociate under ESI-MS conditions.

Although attempts to isolate **4b** using $B(C_6F_5)_4^-$ as the counterion were unsuccessful, the corresponding $B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4^-$ salt was isolated. The reaction of **1b** with 1 equiv of Na[$B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4$] and 10 equiv of AN in CH_2Cl_2 affords

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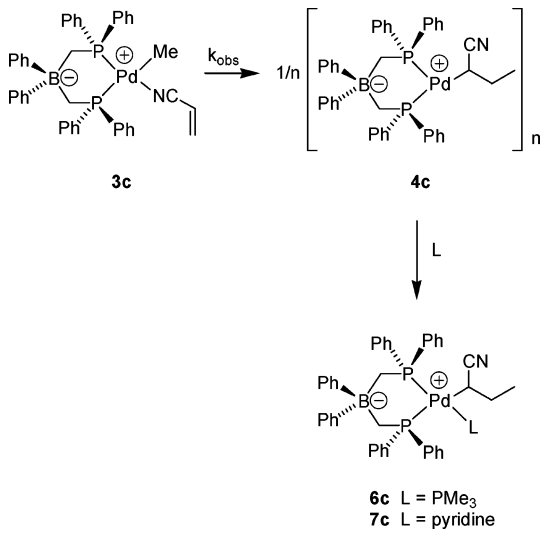
Scheme 3



analytically pure [(dmpe)Pd(CHEtCN)][B{3,5-$(CF_3)_2$-C_6H_3}$_4$] (**4b′**) as a pale yellow solid in 63% yield.

To confirm the presence of a PdCHEtCN unit in **4b** and hence that 2,1 AN insertion occurs as proposed in Scheme 2, the derivatization of **4b** by Lewis base complexation was explored. Complex **4b** does not react with excess CH_3CN or THF at 23 °C in CD_2Cl_2 solution. However, as shown in Scheme 2, **4b** reacts quantitatively with 1 equiv of PPh_3 to yield (dmpe)Pd(CHEtCN)$(PPh_3)^+$ (**5b**, $B(C_6F_5)_4^-$ salt). The ^{1}H NMR spectrum of **5b** contains a multiplet at δ 1.81 for the PdC*H*(CN)CH_2CH_3 methine hydrogen, multiplets at δ 1.47 and 1.10 for the diastereotopic PdCH(CN)C*H*$_2$CH$_3$ methylene hydrogens, and a triplet at δ 0.89 for the PdCH(CN)CH_2C*H*$_3$ methyl group. The COSY spectrum shows correlations between these resonances that are consistent with the PdCH(CN)CH_2CH_3 structure. The ^{13}C{^{1}H} NMR spectrum of **5b** contains a doublet (J_{CP} = 86 Hz) at δ 15.1 for the Pd*C*HEtCN methine carbon. The ^{31}P NMR spectrum of **5b** contains a PPh_3 resonance with the expected ^{31}P coupling at δ 28.1 (dd, J = 367, 37), which is shifted downfield from the free PPh_3 position (δ −5.0). The ESI mass spectrum of **5b** contains a prominent signal for the cation of **5b**. The IR spectrum of **5b** contains a ν_{CN} band at 2188 cm^{-1}, similar to the ν_{CN} value observed for (bim)Pd(CHEtCN)$(PPh_3)^+$ (2192 cm^{-1}).[3] The reduction in ν_{CN} on going from **4b** (2218 cm^{-1}) to **5b** (2188 cm^{-1}) is consistent with the change from the postulated bridging coordination of the Pd(CHEtCN) unit in **4b** to terminal coordination in **5b**.

Attempts to isolate **5b** using $B(C_6F_5)_4^-$ as the counterion were unsuccessful, but the corresponding B{3,5-$(CF_3)_2$-C_6H_3}$_4^-$ salt was isolated. The reaction of **4b′** with 1 equiv of PPh_3 yields [(dmpe)Pd(CHEtCN)(PPh_3)][B{3,5-$(CF_3)_2$-C_6H_3}$_4$] (**5b′**) as an analytically pure, pale yellow solid.[19]

Acrylonitrile Insertion of 3c. Complex **3c** also inserts AN to yield [(Ph_2BP_2)Pd(CHEtCN)]$_n$ (**4c**, Scheme 3). The observed first-order rate constant for AN insertion of **3c**, $k_{obs,AN}$ = 1.12(3) × 10^{-3} s^{-1} at 23 °C, is ca. 33 times greater than that for **3b**. The ^{31}P and ^{11}B NMR spectra of **4c** contain three major sets of Ph_2BP_2 ligand resonances, implying the presence of three inequivalent unsymmetrical (Ph_2BP_2)Pd environments. The ^{1}H NMR spectrum of **4c** contains three triplets at δ 0.89, 0.34, and −0.20 ppm, which is consistent with the presence of three inequivalent −CH(CN)CH_2C*H*$_3$ units. The major anion observed in the ESI mass spectrum of **4c** taken in the presence of [Bu_3(CH_2Ph)N]Cl is [(Ph_2BP_2)Pd(CHEtCN)Cl]$^-$. The IR spectrum of **4c** contains a ν_{CN} band at 2215 cm^{-1}, similar to the value for **4b**. These results suggest that **4c** has an aggregated structure but, as for **4b**, do not provide convincing evidence regarding this issue. Complex **4c** is stable in CD_2Cl_2 solution at 23 °C for at least 10 days.

Complex **4c** does not react with PPh_3, but does react with PMe_3 to form (Ph_2BP_2)Pd(CHEtCN)(PMe_3) (**6c**, Scheme 3). The 1D and 2D NMR spectra of **6c** confirm the presence of a Pd(CHEtCN) group. The IR ν_{CN} band for **6c** appears at 2179 cm^{-1}, ca. 36 cm^{-1} below the value for **4c**. The reduction of ν_{CN} on going from **4c** to **6c** is consistent with the aggregation of **4c** by PdCHEtCN---Pd bridging. The analogous pyridine adduct (Ph_2BP_2)Pd(CHEtCN)(py) (**7c**) is formed in a similar manner (Scheme 3) and displays similar spectroscopic properties. These results confirm the characterization of **4c** as a 2,1 AN insertion product.

Reactivity of 4b,c. Neither **4b** nor **4c**, nor their derivatives **5b**, **6c**, or **7c**, react with excess AN at 23 °C in CD_2Cl_2 solution. Also, **4b**,**c** do not react with ethylene or CO (20 atm, 23 °C).

Conclusion

(P∧P)PdMe$^+$ complexes **2a**,**b** and the zwitterionic species (Ph_2BP_2)Pd(Me) (**2c**) form N-bound AN adducts **3a**−**c**. The C=C π-bound isomers were not detected. The preference for N-coordination over π-coordination of AN is consistent with the poor back-bonding ability of these square-planar d^8 Pd(II) systems. (dmpe)PdMe(NCCH=CH_2)$^+$ (**3b**) and **3c** undergo 2,1 insertion of AN. The observed first-order rate constants for AN insertion vary in the order **3c** > **3b** > **3a** (no reaction), which parallels the order of the electron-richness of the Pd center, as assessed by the ν_{CO} values in the corresponding [(P∧P)Pd{C(=O)Me}(*CO*)]$^{n+}$ species. In particular, the introduction of an anionic charge in the backbone of the dppp ligand of **3a** to give **3c** dramatically increases the AN insertion rate. The increased negative charge at Pd probably destabilizes the N-bound adduct and favors isomerization to the reactive π-complex and, therefore, promotes AN insertion. These results are consistent with earlier studies of (N∧N)PdMe(NCCH=CH_2)$^+$ and (L∧L)PdMe(NCCH=CH_2) species (L∧L = bulky phenoxydiazene or phenoxyaldimine ligand).[3,5] Complexes **4b**,**c** do not react with AN, ethylene, or CO, which precludes AN polymerization or copolymerization by these systems.

Experimental Section

General Procedures. All manipulations were performed under purified nitrogen or vacuum using standard Schlenk or high-vacuum techniques or in a nitrogen-filled drybox unless otherwise noted. Nitrogen was purified by passage through columns of activated molecular sieves and Q-5 oxygen scavenger. Chlorinated solvents and acrylonitrile (AN) were distilled from CaH_2 and stored under vacuum prior to use. PMe_3 and pyridine were purchased from Aldrich and dried over 4 Å molecular sieves. PPh_3, CO, [Bu_3(CH_2Ph)N]Cl, and ethylene were purchased from Aldrich and used as received. [$HNMe_2Ph$][$B(C_6F_5)_4$], [$Li(Et_2O)_{2.8}$][$B(C_6F_5)_4$], and Na[B{3,5-$(CF_3)_2$-C_6H_3}$_4$] were obtained from Boulder Scientific and used as received. Compounds **1c**,[10a] **1a**,**b**, **2a**,**b**,[13] and (dmpe)$PdMe_2$[20] were prepared by literature procedures.

NMR spectra were recorded in sealed tubes on a Bruker AMX-500 spectrometer at ambient temperature unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported versus Me_4Si and were

(19) The molecular structure of **5b′** was confirmed by X-ray crystallography. However, a detailed discussion of this structure is not warranted due to disorder in the PCH_2CH_2P and CHEtCN units of the cation and the CF_3 units of the anion.

determined by reference to the residual solvent peaks. ^{11}B, ^{19}F, and ^{31}P chemical shifts were referenced to external neat $BF_3{\cdot}Et_2O$, $CFCl_3$, and H_3PO_4 respectively. Coupling constants are reported in Hz. In the NMR assignments for AN, H_{cis} and H_{trans} refer to the hydrogens that are cis and trans to H_{int}, respectively. NMR spectra of $B(C_6F_5)_4^-$ and $B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4^-$ salts contain anion resonances at the free anion positions.[21,22] Samples of CD_2Cl_2 solutions of **2a**,**b** and species generated in situ from **2a**,**b** contain LiCl. NMR spectra of species derived from [(dmpe)PdMe(NMe_2Ph)][$B(C_6F_5)_4$] contain resonances for free NMe_2Ph.[23] NMR spectra of **3c** and species derived from this species contain resonances for free NMe_2-Ph and free $[ASN]^+$ (ASN = 5-azoniaspiro[4.4]nonane).[24] NMR spectra for species generated in the presence of excess AN contain resonances for free AN.[25]

ESI-MS experiments were performed with a HP Series 1100 MSD instrument using direct injection via syringe pump (ca. 10^{-6} M solutions). For **4c**, **6c**, and **7c**, $[Bu_3(CH_2Ph)N]Cl$ (ca. 1.0 wt %) was added to CH_2Cl_2 solutions of the samples to generate anionic chloride complexes. Good agreement between observed and calculated isotope patterns was observed in all cases. In each case, the listed *m*/*z* value corresponds to the most intense peak in the isotope pattern. IR spectra were recorded on a Nicolet NEXUS 470 FT-IR spectrometer. Unless otherwise noted, IR spectra were recorded for neat samples using the Nicolet Smart Miracle ATR accessory after the evaporation of the solvent.

[(dmpe)PdMe(NMe_2Ph)][$B(C_6F_5)_4$]. An NMR tube was charged with (dmpe)$PdMe_2$ (7.8 mg, 0.027 mmol) and [$HNMe_2Ph$]-[$B(C_6F_5)_4$] (21.8 mg, 0.027 mmol), and CD_2Cl_2 (0.6 mL) was added by vacuum transfer at −78 °C. The tube was vigorously agitated, resulting in a pale yellow solution. The tube was maintained at −78 °C for 10 min and then transferred to the NMR probe at −60 °C. NMR spectra showed that (dmpe)PdMe(NMe_2Ph)$^+$ had formed quantitatively. ^1H NMR (CD_2Cl_2, −60 °C): δ 7.39 (t, J = 8, 2H, *m*-Ph), 7.31 (d, J = 8, 2H, *o*-Ph), 7.19 (t, J = 8, 1H, *p*-Ph), 2.91 (s, 6H, N*Me*$_2$Ph), 1.78 (m, 2H, PCH_2), 1.54 (d, J = 11, 6H, PMe), 1.46 (m, 2H, PCH_2), 0.68 (d, J = 8, 6H, PMe), 0.36 (d, J = 7, 3H, PdMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 154.1 (Ph C1), 129.8 (Ph C2), 126.0 (Ph C4), 119.2 (Ph C3), 50.2 (N*Me*$_2$Ph), 28.0 (dd, J = 30, 25; PCH_2), 25.5 (dd, J = 30, 9; PCH_2), 13.2 (d, J = 37, PMe), 10.7 (d, J = 17, PMe), 8.2 (dd, J = 91, 7; PdMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 37.5 (d, J = 19), 15.4 (d, J = 19).

[(dppp)PdMe(NCCH═CH_2)][$B(C_6F_5)_4$] (3a). A solution of [{(dppp)PdMe}$_2$(μ-Cl)][$B(C_6F_5)_4$] (**2a**, 0.0088 mmol) and [Li-$(Et_2O)_{2.8}$][$B(C_6F_5)_4$] (0.0088 mmol) in CD_2Cl_2 (0.6 mL) was generated in an NMR tube, and AN (0.13 mmol) was added by vacuum transfer at −196 °C. The tube was warmed to −78 °C, resulting in immediate formation of a slurry of a white solid in a pale yellow supernatant. ^1H NMR spectra showed that **3a** had formed quantitatively. Exchange of free and coordinated AN is fast on the NMR chemical shift time scale at −60 °C. ^1H NMR (CD_2Cl_2, −60 °C, in the presence of 0.19 M free AN): δ 7.52−7.33 (m, 20H, Ph), 6.25 (br d, J = 17, H_{trans} of free and coordinated AN), 6.11 (d, J = 12, H_{cis} of free and coordinated AN), 5.67 (br, H_{int} of free and coordinated AN), 2.57 (m, 2H, PCH_2), 2.51 (m, 2H, PCH_2), 1.82 (m, 2H, CH_2), 0.35 (dd, J = 7, 3; 3H, PdMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C, in the presence of 0.19 M free AN): δ 138.4 (br, C_{ter} of free and coordinated AN), 132.8 (d, J = 11), 132.6 (d, J = 11), 131.5, 130.9, 129.5 (d, J = 38), 128.9 (d, J = 11), 128.7 (d, J = 11), 127.5 (d, J = 57), 117.4 (br, *C*N of free and coordinated AN), 107.0 (br, C_{int} of free and coordinated AN), 26.8 (dd, J = 34, 9; PCH_2), 25.2 (d, J = 22, PCH_2), 17.9 (CH_2), 10.5 (d, J = 85, PdMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 28.2 (d, J = 54), −2.9 (d, J = 54). The ^{13}C NMR assignments for AN were confirmed by a DEPT-135 experiment. The chemical shifts for the coordinated AN at −60 °C in CD_2Cl_2 (δ_{coord}) are related to the observed weighted averages of the chemical shifts ($\delta_{average}$) for free (δ_{free}) and coordinated (δ_{coord}) AN and the mole fractions of free (χ_{free}) and coordinated (χ_{coord}) AN by eq 4:

$$\delta_{average} = \delta_{free}\chi_{free} + \delta_{coord}\chi_{coord} \quad (4)$$

and are as follows: ^1H NMR δ 6.31 (H_{trans}), 6.24 (H_{cis}), 5.54 (H_{int}); ^{13}C NMR δ 140.3 (C_{ter}), 118.0 (CN), 105.7 (C_{int}). ESI-MS: Major cations observed [(dppp)PdMe(NCCH═CH_2)]$^+$ calcd *m*/*z* 586.1, found 586.0; [(dppp)Pd(Me)]$^+$ calcd *m*/*z* 533.1, found 532.9. IR (neat): ν_{CN} = 2227 cm^{-1}.

[(dmpe)PdMe(NCCH═CH_2)][$B(C_6F_5)_4$] (3b) from 2b. This complex was generated in CD_2Cl_2 (0.6 mL) from [{(dmpe)PdMe}$_2$-(μ-Cl)][$B(C_6F_5)_4$] (**2b**, 0.020 mmol), [Li($Et_2O)_{2.8}$][$B(C_6F_5)_4$] (0.020 mmol), and AN (0.20 mmol) using the procedure for **3a**. ^1H NMR spectra showed that **3b** had formed quantitatively. Exchange of free and coordinated AN is fast on the NMR chemical shift time scale at −60 °C. ^1H NMR (CD_2Cl_2, −60 °C, in the presence of 0.27 M free AN): δ 6.29 (br, H_{trans} of free and coordinated AN), 6.15 (br, H_{cis} of free and coordinated AN), 5.73 (br, H_{int} of free and coordinated AN), 1.95 (m, 2H, PCH_2), 1.69 (m, 2H, PCH_2), 1.51 (d, J = 11, 6H, PMe), 1.40 (d, J = 9, 6H, PMe), 0.25 (dd, J = 7, 3; 3H, PdMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C, in the presence of 0.27 M free AN): δ 138.9 (br, C_{ter} of free and coordinated AN), 117.7 (br, *C*N of free and coordinated AN), 107.0 (br, C_{int} of free and coordinated AN), 29.6 (dd, J = 36, 22; PCH_2), 24.4 (dd, J = 30, 8; PCH_2), 12.6 (d, J = 36, PMe), 11.9 (d, J = 18, PMe), 1.9 (d, J = 94, PdMe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 42.5 (d, J = 24), 26.4 (d, J = 24). The chemical shifts for the coordinated AN at −60 °C in CD_2Cl_2 determined from the observed weighted average chemical shifts for free and coordinated AN and the mole fractions of free and coordinated AN as shown in eq 4 are as follows: ^1H NMR δ 6.49 (H_{trans}), 6.39 (H_{cis}), 5.89 (H_{int}); ^{13}C NMR δ 142.1 (C_{ter}), 119.3 (CN), 106.2 (C_{int}). ESI-MS: Major cations observed [(dmpe)PdMe(NCCH═CH_2)]$^+$ calcd *m*/*z* 324.0, found 324.0; [(dmpe)Pd(Me)]$^+$ calcd *m*/*z* 271.0, found 271.0. IR (neat): ν_{CN} = 2220 cm^{-1}.

[(dmpe)PdMe(NCCH═CH_2)][$B(C_6F_5)_4$] (3b) from [(dmpe)-PdMe(NMe_2Ph)][$B(C_6F_5)_4$]. An NMR tube containing a solution of [(dmpe)PdMe(NMe_2Ph)][$B(C_6F_5)_4$] (0.027 mmol) in CD_2Cl_2 (0.6

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(21) NMR data for free $B(C_6F_5)_4^-$: $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 148.5 (dm, J = 234, C2), 138.6 (dm, J = 246, C4), 136.6 (dm, J = 243, C3), 123.6 (br, C1). ^{19}F NMR (CD_2Cl_2): δ −133.2 (br s, 2F, *o*-F), −163.7 (t, J = 23, 1F, *p*-F), −167.6 (t, J = 19, 2F, *m*-F). ^{11}B NMR (CD_2Cl_2): δ −16.6 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 147.5 (dm, J = 241, C2), 137.8 (dm, J = 238, C4), 135.8 (dm, J = 249, C3), 123.6 (br, C1). ^{19}F NMR (CD_2Cl_2, −60 °C): δ −133.7 (br s, 2F, *o*-F), −163.0 (t, J = 23, 1F, *p*-F), −167.0 (t, J = 19, 2F, *m*-F). ^{11}B NMR (CD_2Cl_2, −60 °C): δ −16.5 (s).

(22) NMR data for $B\{3,5\text{-}(CF_3)_2\text{-}C_6H_3\}_4^-$: ^1H NMR (CD_2Cl_2): δ 7.72 (s, 8H, H2), 7.55 (s, 4H, H4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 162.1 (q, J_{CB} = 234, C1), 135.1 (C2), 129.2 (q, J_{CF} = 32, C3), 125.0 (q, J_{CF} = 273, CF_3), 117.8 (m, C4). ^{19}F NMR (CD_2Cl_2): δ −62.8 (s). ^{11}B NMR (CD_2Cl_2): δ −6.7 (s).

(23) (a) NMR data for free NMe_2Ph: ^1H NMR (CD_2Cl_2): δ 7.20 (m, 2H, *o*-Ph), 6.72 (m, 2H, *m*-Ph), 6.67 (t, J = 7, 1H, *p*-Ph), 3.03 (s, 6H, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 151.1 (C1), 129.3 (C2), 116.6 (C4), 112.8 (C3), 40.7 (Me). ^1H NMR (CD_2Cl_2, −60 °C): δ 7.18 (m, 2H, *o*-Ph), 6.67 (m, 2H, *m*-Ph), 6.63 (t, J = 7, 1H, *p*-Ph), 2.88 (s, 6H, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 150.2 (C1), 128.7 (C2), 115.8 (C4), 111.9 (C3), 40.3 (Me). (b) If excess [$HNMe_2Ph$][$B(C_6F_5)_4$] is used in the generation of **3c**, the excess $HNMe_2Ph^+$ undergoes fast H^+ exchange with NMe_2Ph and a single set of $NMe_2Ph/HNMe_2Ph^+$ resonances at the weighted average of the chemical shifts of these species is observed.

(24) NMR data for free $[ASN]^+$: ^1H NMR (CD_2Cl_2): δ 3.19 (m, 8H, N($CH_2CH_2)_2$), 2.11 (m, 8H, N($CH_2CH_2)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 63.8 (N($CH_2CH_2)_2$), 22.3 (N($CH_2CH_2)_2$). ^1H NMR (CD_2Cl_2, −60 °C): δ 3.06 (m, 8H, N($CH_2CH_2)_2$), 2.03 (m, 8H, N($CH_2CH_2)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 62.2 (N($CH_2CH_2)_2$), 21.3 (N($CH_2CH_2)_2$).

(25) NMR data for free AN: ^1H NMR (CD_2Cl_2, 23 °C): δ 6.21 (d, J = 18, 1H, H_{trans}), 6.07 (d, J = 12, 1H, H_{cis}), 5.67 (dd, J = 18, 12.0, 1H, H_{int}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 138.0 (C_{ter}), 117.3 (*C*N), 108.2 (C_{int}). ^1H NMR (CD_2Cl_2, −60 °C): δ 6.24 (d, J = 18, 1H, H_{trans}), 6.09 (d, J = 12, 1H, H_{cis}), 5.69 (dd, J = 18, 12.0, 1H, H_{int}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 138.1 (C_{ter}), 117.3 (*C*N), 107.2 (C_{int}).

mL) was cooled to −196 °C, and AN (0.023 mmol, ca. 0.85 equiv) was added by vacuum transfer. The tube was warmed to −78 °C and vigorously agitated, resulting in a pale yellow solution. The tube was maintained at −78 °C for 10 min and then transferred to the NMR probe at −60 °C. A ^{1}H NMR spectrum showed that [(dmpe)PdMe(NCCH═CH_2)][B(C_6F_5)$_4$] (**3b**) had formed quantitatively based on AN, i.e., 85% yield based on Pd. The NMR and IR data for **3b** generated by this method are nearly identical to those for **3b** generated from **2b**. NMR data for coordinated AN: ^{1}H NMR (CD_2Cl_2, −60 °C) δ 6.52 (d, J = 18, 1H, H_{trans} of coordinated AN), 6.41 (d, J = 11, 1H, H_{cis} of coordinated AN), 5.91 (dd, J = 18,11; 1H, H_{int} of coordinated AN); ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C) δ 143.0 (C_{ter} of coordinated AN), 119.2 (*C*N of coordinated AN), 105.4 (C_{int} of coordinated AN). The ^{13}C NMR assignments were confirmed by a DEPT-135 experiment. IR (neat): ν_{CN} = 2219 cm^{-1}.

(Ph$_2$BP$_2$)PdMe(NCCH═CH$_2$) (3c). A solution of [ASN][(Ph$_2$BP$_2$)PdMe$_2$] (**1c**, 11.8 mg, 0.0140 mmol) and [HNMe$_2$Ph][B(C_6F_5)$_4$] (11.4 mg, 0.0140 mmol) in CD_2Cl_2 (0.6 mL) was generated in an NMR tube at −78 °C and cooled to −196 °C, and AN (0.017 mmol, 1.2 equiv) was added by vacuum transfer. The tube was warmed to −78 °C, resulting in the immediate formation of a clear, colorless solution. The tube was transferred to an NMR probe at −60 °C. ^{1}H NMR spectra showed that **3c** had formed quantitatively. Separate sharp ^{1}H NMR resonances for free and coordinated AN were observed at −60 °C. ^{1}H NMR (CD_2Cl_2, −60 °C): δ 7.36−7.05 (m, 20H, Ph), 6.82−6.60 (m, 10H, Ph), 6.06 (d, J = 12, H_{cis} of coordinated AN), 5.78 (d, J = 18, H_{trans} of coordinated AN), 5.39 (dd, J = 18, 12; H_{int} of coordinated AN), 1.91 (dd, J = 15, 3; 2H, PCH_2), 1.76 (d, J = 13, 2H, PCH_2), −0.11 (d, J = 7, 3H, PdMe). ^{13}C{^{1}H} NMR (CD_2Cl_2, −60 °C): δ 141.8 (C_{ter} of coordinated AN), 135.7 (d, J = 33), 133.0 (d, J = 52), 132.8 (d, J = 11), 132.5 (d, J = 11), 131.3, 130.9, 128.7, 128.6 (d, J = 6), 127.5 (d, J = 11), 127.2 (d, J = 11), 125.8, 121.7, 120.3 (d, J = 13, *C*N of coordinated AN), 105.2 (C_{int} of coordinated AN), 20.8 (br, P*C*H$_2$B), 17.9 (CH_2), 15.5 (br, P*C*H$_2$B), 7.4 (d, J = 87, PdMe). ^{31}P{^{1}H} NMR (CD_2Cl_2, −60 °C): δ 38.9 (d, J = 48), 14.1 (d, J = 48). ^{11}B NMR (CD_2Cl_2, −60 °C): δ −14.3.

[(dmpe)Pd(CHEtCN)]$_n^{n+}$ (4b, B(C$_6$F$_5$)$_4^-$ salt). An NMR tube containing a solution of [(dmpe)PdMe(NCCH═CH_2)][B(C_6F_5)$_4$] (**3b**, 0.039 mmol) and AN (0.16 mmol) in CD_2Cl_2 (0.6 mL) was maintained at 23 °C and monitored periodically by NMR. The NMR signals associated with **3b** disappeared after 2 days. The volatiles were removed under vacuum to yield a pale yellow solid. The solid was redissolved in CD_2Cl_2 (0.6 mL). NMR and ESI-MS analyses showed that [(dmpe)Pd(CHEtCN)]$_n^{n+}$ species (**4b**) were present. The NMR yield for **4b** was 90%. In a similar experiment with more frequent ^{1}H NMR monitoring, the first-order rate constant for conversion of **3b** to **4b** was determined from the disappearance of the PdMe ^{1}H NMR resonance to be k_{obs}(23 °C) = 3.33(5) × 10^{-5} s^{-1} at 23 °C ([AN] = 0.028 M, 1.2 equiv vs **3b**). ^{1}H NMR (CD_2Cl_2) for **4b**: Major resonances δ 2.26−2.03 (m, 3H, PC*H*$_2$ and PdC*H*(CN)), 2.03−1.72 (m, 4H, PC*H*$_2$ and PdCH(CN)C*H*$_2$), 1.72−1.64 (m, 6H, PMe), 1.64−1.46 (m, 6H, PMe), 1.15−1.00 (m, 3H, PdCH(CN)CH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 49.1 (d, J = 18, 1P), 48.8 (d, J = 18, 1P), 48.7 (d, J = 18, 1P), 47.3 (d, J = 18, 5P), 47.0 (d, J = 18, 1P), 46.8 (d, J = 18, 5P), 46.4 (d, J = 18, 1P), 45.4 (d, J = 18, 1P), 44.3 (d, J = 18, 1P), 43.7 (d, J = 18, 1P). ESI-MS: Major cation observed (dmpe)Pd(CHEtCN)$^+$ calcd *m*/*z* 324.0, found 323.8. IR (neat): ν_{CN} = 2218 cm^{-1}.

Alternatively, **3b** was generated by the reaction of [(dmpe)PdMe(NMe$_2$Ph)][B(C_6F_5)$_4$] (0.022 mmol) with AN (0.13 mmol) in CD_2Cl_2 (0.6 mL). The conversion from **3b** to **4b** was monitored periodically by NMR. The first-order rate constant for conversion of **3b** to **4b**, measured from the disappearance of the PdMe ^{1}H NMR resonance, was k_{obs}(23 °C) = 3.5(1) × 10^{-5} s^{-1} at 23 °C ([AN] = 0.18 M, 5 equiv vs **3b**). The NMR, ESI-MS, and IR data for **4b** generated by this method are very similar to the data for **4b** generated from **2b**.

[(dmpe)Pd(CHEtCN)]$_n^{n+}$ (4b′, B{3,5-(CF$_3$)$_2$-C$_6$H$_3$}$_4^-$ salt). A flask was charged with (dmpe)PdMeCl (**1b**, 0.11 g, 0.35 mmol) and Na[B{3,5-(CF$_3$)$_2$-C$_6$H$_3$}$_4$] (0.28 g, 0.32 mmol), and CH_2Cl_2 (40 mL) was added at −78 °C by vacuum transfer. The pale yellow slurry was vigorously stirred for 5 min at 23 °C. The flask was cooled to −196 °C, and AN (0.20 mL, 3.0 mmol) was added by vacuum transfer. The flask was warmed to 23 °C, and the mixture was stirred for 2 days to yield a slurry of a white solid in a yellow supernatant. The mixture was filtered through Celite, and the filtrate was dried under vacuum to afford a pale yellow solid (0.24 g, 63%). Anal. Calcd for $C_{42}H_{34}BF_{24}NP_2Pd$: C, 42.47; H, 2.89; N, 1.16. Found: C, 42.18; H, 3.05; N, 1.16. The NMR data for **4b′** are very similar to the data for **4b**, except for the anion resonances.

[(Ph$_2$BP$_2$)Pd(CHEtCN)]$_n$ (4c). An NMR tube containing a solution of (Ph$_2$BP$_2$)PdMe(NCCH═CH_2) (**3c**, 0.015 mmol) and AN (0.66 mmol) in CD_2Cl_2 (0.6 mL) was maintained at 23 °C and monitored periodically by NMR. The NMR signals associated with **3c** disappeared after 2 h. The volatiles were removed under vacuum to yield an off-white solid. The solid was redissolved in CD_2Cl_2 (0.6 mL). NMR and ESI-MS analyses showed that [(Ph$_2$BP$_2$)Pd(CHEtCN)]$_n$ (**4c**) was present. The NMR yield for **4c** was 95%. In a similar experiment with more frequent ^{1}H NMR monitoring, the first-order rate constant for conversion of **3c** to **4c** was determined from the disappearance of the PdMe ^{1}H NMR resonance to be k_{obs}(23 °C) = 1.12(3) × 10^{-3} s^{-1} at 23 °C ([AN] = 0.028 M, 1.2 equiv vs **3c**). ^{1}H NMR (CD_2Cl_2) of **4c**: Major resonances δ 7.63−6.30 (m, 90H, Ph), 2.04−1.07 (m, 19H, PC*H*$_2$ and PdC*H*(CN)C*H*$_2$), 0.89 (t, J = 7, 3H, PdCH(CN)CH$_2$C*H*$_3$), 0.69 (m, 2H, PdCH(CN)C*H*$_2$), 0.34 (t, J = 7, 3H, PdCH(CN)CH$_2$C*H*$_3$), −0.20 (t, J = 7, 3H, PdCH(CN)CH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): Major resonances δ 38.7 (d, J = 45, 1P), 38.1 (d, J = 45, 1P), 37.9 (d, J = 45, 1P), 18.6 (d, J = 45, 1P), 15.5 (d, J = 45, 1P), 15.3 (d, J = 45, 1P). ^{11}B NMR (CD_2Cl_2): Major resonances δ −13.8 (br), −14.3 (br), −15.2 (br). ESI-MS in CH_2Cl_2/[Bu$_3$(CH$_2$Ph)N]Cl, major anion observed: [(Ph$_2$BP$_2$)Pd(CHEtCN) + Cl$^-$] calcd *m*/*z* 772.2, found 772.2. IR (neat): ν_{CN} = 2215 cm^{-1}.

[(dmpe)Pd(CHEtCN)(PPh$_3$)][B(C$_6$F$_5$)$_4$] (5b). Solid PPh_3 (10.3 mg, 0.0390 mmol) was added to an NMR tube containing solid [(dmpe)Pd(CHEtCN)]$_n^{n+}$ (**4b**, B(C_6F_5)$_4^-$ salt, 0.0390 mmol). The tube was evacuated, and CD_2Cl_2 (0.6 mL) was added by vacuum transfer at −78 °C. The tube was vigorously agitated to yield an off-white solution and was then warmed to 23 °C. After 5 min, NMR spectra showed that (dmpe)Pd(CHEtCN)(PPh$_3$)$^+$ (**5b**) had formed quantitatively. ^{1}H NMR (CD_2Cl_2): δ 7.66−7.50 (m, 15H, PPh_3), 2.08 (m, 2H, PCH_2), 1.92 (m, 2H, PCH_2), 1.85 (dd, J = 11, 3; 3H, PMe), 1.81 (m, 1H, PdC*H*(CN)), 1.75 (dd, J = 11, 3; 3H, PMe), 1.47 (m, 1H, PdCH(CN)C*H*$_2$), 1.10 (m, 1H, PdCH(CN)C*H*$_2$), 0.90 (d, J = 11, 3H, PMe), 0.77 (d, J = 11, 3H, PMe), 0.50 (t, J = 7, 3H, PdCH(CN)CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 134.4 (d, J = 12, *o*-PPh_3), 132.6 (d, J = 3, *p*-PPh_3), 129.9 (d, J = 10, *m*-PPh_3), 128.4 (d, J = 44, PPh_3 C_{ipso}), 128.1 (*C*N), 28.2−27.5 (m, P*C*H$_2$*C*H$_2$P), 25.3 (m, PdCH(CN)*C*H$_2$), 15.8 (d, J = 8, PdCH(CN)CH$_2$*C*H$_3$), 15.1 (d, J = 86, Pd*C*H(CN)CH$_2$), 12.6 (d, J = 23, PMe), 12.0 (d, J = 23, PMe), 11.7 (dd, J = 26, 3; PMe), 10.7 (dd, J = 26, 3; PMe). The assignments of the PPh_3 resonances are based on the size of J_{P-C} and are consistent with the trend observed in free PPh_3.[26] ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 36.4 (dd, J = 367, 32; *P*CH$_2$), 28.3 (dd, J = 37, 32; *P*CH$_2$), 28.1 (dd, J = 367, 37; *P*Ph$_3$). Key ^{1}H−^{1}H COSY correlations δ/δ: 1.81 (PdC*H*(CN))/1.47 (PdCH(CN)C*H*$_2$); 1.81 (PdC*H*(CN))/1.10 (PdCH(CN)C*H*$_2$); 1.47 (PdCH(CN)C*H*$_2$)/1.10 (PdCH(CN)C*H*$_2$); 1.47 (PdCH(CN)C*H*$_2$)/0.50 (PdCH(CN)CH$_2$C*H*$_3$); 1.10 (PdCH(CN)C*H*$_2$)/0.50 (PdCH(CN)-

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CH_2CH_3). Key $^1H-^{13}C$ HMQC correlations δ $^1H/\delta$ ^{13}C: 1.81 (PdC*H*(CN))/15.1 (Pd*C*H(CN)); 1.47 (PdCH(CN)CH_2)/25.3 (PdCH(CN)*C*H_2); 1.10 (PdCH(CN)CH_2)/25.3 (PdCH(CN)*C*H_2); 0.50 (PdCH(CN)CH_2CH_3)/15.8 (PdCH(CN)CH_2*C*H_3). ESI-MS: Major cations observed (dmpe)Pd(CHEtCN)$(PPh_3)^+$ calcd *m*/*z* 586.1, found 586.0. IR (neat): $\nu_{CN} = 2188$ cm^{-1}.

[(dmpe)Pd(CHEtCN)(PPh_3)][B{3,5-(CF_3)$_2$-C_6H_3}$_4$] (5b′). A flask was charged with (dmpe)PdMeCl (**1b**, 0.11 g, 0.34 mmol) and Na[B{3,5-(CF_3)$_2$-C_6H_3}$_4$] (0.29 g, 0.32 mmol), and CH_2Cl_2 (40 mL) was added at −78 °C by vacuum transfer. The pale yellow slurry was warmed to 23 °C and vigorously stirred for 5 min. The flask was cooled to −196 °C, and AN (0.20 mL, 3.0 mmol) was added by vacuum transfer. The flask was warmed to 23 °C, and the mixture was stirred for 2 days to yield a slurry of a white solid in a pale yellow supernatant. A solution of PPh_3 (85 mg, 0.32 mmol) in CH_2Cl_2 (5.0 mL) was added by syringe. The mixture was stirred for 10 h at 23 °C to afford a white slurry in a yellow supernatant. The mixture was filtered through Celite, and the filtrate was dried under vacuum to afford a pale yellow solid (0.30 g, 65%). Anal. Calcd for $C_{66}H_{45}BF_{24}N_3PPd$: C, 49.69; H, 3.41; N, 0.97. Found: C, 49.58; H, 3.60; N, 0.71. The NMR data for **5b′** are identical with the data for **5b** except for the anion resonances.

(Ph_2BP_2)Pd(CHEtCN)(PMe_3) (6c). An NMR tube containing a solution of [(Ph_2BP_2)Pd(CHEtCN)]$_n$ (**4c**, 0.015 mmol) in CD_2Cl_2 (0.6 mL) was cooled to −196 °C, and PMe_3 (0.015 mmol) was added by vacuum transfer. The tube was warmed to 23 °C and vigorously agitated, resulting in an off-white solution. After 5 min at 23 °C, NMR spectra showed that (Ph_2BP_2)Pd(CHEtCN)(PMe_3) (**6c**) had formed in 90% yield. ^1H NMR (CD_2Cl_2): δ 7.58−7.10 (m, 20H, Ph), 6.67 (m, 10H, Ph), 1.97 (m, 4H, PCH_2B), 1.79 (m, 1H, PdC*H*(CN)), 1.38 (m, 1H, PdCH(CN)CH_2), 0.98 (dd, $J = 9$, 2; 9H, PMe_3), 0.54 (t, $J = 7$, 3H, PdCH(CN)CH_2CH_3), 0.43 (m, 1H, PdCH(CN)CH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 136.6 (d, $J =$ 34), 134.8 (d, $J = 11$), 132.9 (d, $J = 10$), 132.7 (d, $J = 10$), 131.6 (d, $J = 4$), 130.8 (d, $J = 2$), 130.7 (d, $J = 2$), 130.2 (s), 130.0 (d, $J = 2$), 128.8 (d, $J = 8$), 128.4 (d, $J = 11$), 128.3 (d, $J = 5$), 128.2 (d, $J = 4$), 126.5 (s), 122.2 (d, $J = 2$), 25.2 (br, P*C*H_2B), 23.9 (br m, PdCH(CN)*C*H_2), 20.6 (br, P*C*H_2B), 16.0 (d, $J = 8$, PdCH(CN)CH_2*C*H_3), 15.5 (d, $J = 25$, PMe_3), 14.1 (dd, $J = 87$, 5; Pd*C*H(CN)). Assuming free rotation of the phenyl groups, there should be a total of 24 phenyl carbon signals. However, only 15 phenyl carbon signals were observed, most likely because some are coincident due to the distance of the phenyl group from the stereogenic center. The *C*N resonance was not observed. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.5 (dd, $J = 370$, 53; *P*CH_2), 19.0 (dd, $J =$ 53, 33; *P*CH_2), −21.0 (dd, $J = 370$, 33; *P*Me_3). ^{11}B NMR (CD_2Cl_2): δ −15.0. Key $^1H-^1H$ COSY correlations δ/δ: 1.79 (PdC*H*(CN))/1.38 (PdCH(CN)CH_2); 1.38 (PdCH(CN)CH_2)/0.54 (PdCH(CN)CH_2CH_3); 1.38 (PdCH(CN)CH_2)/0.43 (PdCH(CN)CH_2); 0.54 (PdCH(CN)CH_2CH_3)/0.43 (PdCH(CN)CH_2). Key $^1H-^{13}C$ HMQC correlations δ $^1H/\delta$ ^{13}C: 1.97 (PCH_2B)/25.2 (P*C*H_2B); 1.97 (PCH_2B)/20.6 (P*C*H_2B); 1.79 (PdC*H*(CN))/14.1 (Pd*C*H(CN)); 1.38 (PdCH(CN)CH_2)/23.9 (PdCH(CN)*C*H_2); 0.54 (PdCH(CN)CH_2CH_3)/16.0 (PdCH(CN)CH_2*C*H_3); 0.43 (PdCH(CN)CH_2)/23.9 (PdCH(CN)*C*H_2). ESI-MS in CH_2Cl_2/[Bu_3(CH_2Ph)N]Cl, major anion observed: [(Ph_2BP_2)Pd(CHEtCN) + Cl^-] calcd *m*/*z* 772.2, found 772.1. IR (neat): $\nu_{CN} = 2179$ cm^{-1}.

(Ph_2BP_2)Pd(CHEtCN)(C_5H_5N) (7c). Pyridine (0.14 mmol) was added by vacuum transfer to an NMR tube containing [(Ph_2BP_2)Pd(CHEtCN)]$_n$ (**4c**, 0.014 mmol) in CD_2Cl_2 (0.6 mL) at −196 °C. The tube was warmed to 23 °C and vigorously agitated, resulting in a clear, colorless solution. After 30 min, the volatiles were removed under vacuum, and the remaining off-white solid was redissolved in CD_2Cl_2 (0.6 mL) to yield a colorless solution. NMR spectra showed that (Ph_2BP_2)Pd(CHEtCN)(C_5H_5N) (**7c**) had formed in 87% yield. ^1H NMR (CD_2Cl_2): δ 8.21 (dd, $J = 5$, 2; 2H, *o*-py), 7.60−6.94 (m, 24H, Ph and py), 6.87−6.61 (m, 10H, Ph), 1.99 (m, 4H, PCH_2B), 1.25 (m, 1H, PdC*H*(CN)), 0.77 (m, 2H, PdCH(CN)CH_2), 0.35 (t, $J = 7$, 3H, PdCH(CN)CH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 151.2 (br, *o*-py), 137.8 (s, *p*-py), 136.0 (d, $J =$ 37), 135.1 (d, $J = 48$), 134.6 (d, $J = 11$), 134.0 (d, $J = 11$), 132.4 (d, $J = 9$), 131.9 (d, $J = 9$), 131.6 (d, $J = 10$), 130.9 (s), 130.2 (d, $J =$ 16), 128.5 (d, $J = 5$), 128.4 (d, $J = 6$), 128.3 (d, $J = 11$), 127.6 (d, $J = 8$, *C*N), 126.5 (s), 125.3 (br, *m*-py), 122.4 (s), 24.1 (d, $J =$ 4, PdCH(CN)*C*H_2), 21.8 (br, P*C*H_2B), 19.5 (d, $J = 90$, Pd*C*H(CN)), 17.4 (br, P*C*H_2B), 15.9 (d, $J = 9$, PdCH(CN)CH_2*C*H_3). Assuming free rotation of the phenyl groups, there should be a total of 24 phenyl carbon signals. However, only 15 phenyl carbon signals were observed, most likely because some are coincident due to the distance of the phenyl group from the stereogenic center. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 34.9 (d, $J = 48$), 21.6 (d, $J = 48$). Key $^1H-^{13}C$ HMQC correlations δ $^1H/\delta$ ^{13}C: 1.25 (PdC*H*(CN))/19.5 (Pd*C*H(CN)); 0.77 (PdCH(CN)CH_2)/24.1 (PdCH(CN)*C*H_2); 0.35 (PdCH(CN)CH_2CH_3)/15.9 (PdCH(CN)CH_2*C*H_3). ^{11}B NMR (CD_2Cl_2): δ −14.7. ESI-MS in CH_2Cl_2/[Bu_3(CH_2Ph)N]Cl, major anion observed: [(Ph_2BP_2)Pd(CHCNEt) + Cl^-] calcd *m*/*z* 772.2, found 772.1. IR (neat): $\nu_{CN} = 2175$ cm^{-1}.

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