N−C Cleavage in Pincer PNP Complexes of Palladium

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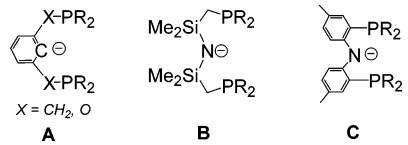
Several new N-methylated diarylamine-based PNP pincer ligands have been prepared. The synthesis of these ligands is modular and allows incorporation of a variety of substituents that change the solubility and the stereoelectronic properties of the ligand as well as allow for the introduction of a sensitive ^{19}F NMR spectroscopic probe. The reactions of PN(Me)P ligands with PdX_2 (X = Cl, OAc) initially proceed with formation of an adduct, (PN(Me)P)-PdX_2, that may exist in either the neutral or the ionic forms. These adducts are unreactive in the case of PPh_2-bearing ligands, but with the more donating PPr^i_2-bearing ligands, the adduct evolves into square planar (PNP)PdX with irreversible loss of MeX. Thus, the feasibility of cleavage of an unstrained N−C bond by Pd^{II} is demonstrated. The N−C cleavage is accelerated by decreasing the solvent polarity. The mechanism may involve either N−C oxidative addition or a nucleophilic attack (external or internal) of X^- on the Me group of the N-bound PN(Me)P ligand.

Formation and cleavage of carbon−nitrogen bonds at transition metal centers is crucial to our understanding of the catalytic processes involving these transformations. Reductive elimination of aromatic amines is the key C−N bond-forming step in the Pd- and Ni-catalyzed aromatic amination.[1] Studies of well-defined examples of C−N bond formation have yielded valuable mechanistic insight into this process.[2] On the other hand, cleavage of C−N bonds must be involved in the metal-catalyzed hydrodenitrogenation of petroleum.[3] Studies of well-defined examples of C−N cleavage on transition metal centers are very few and include a recent example from our group.[4,5a] In the spirit of the principle of microscopic reversibility the information obtained in studies of C−N bond forming reactions is complementary to that obtained from C−N bond cleavage studies.



We have recently developed a new type of PNP pincer ligand based on the bis(*ortho*-phosphinoaryl)amine motif (**C**).[5] Two other groups reported similar ligands, varying by the substitution pattern on P and on the aromatic rings.[6,7] Our interest in the pincer PNP framework is partly based on the extraordinary chemistry that the PCP family of ligands (**A**) gave rise to.[8] The salient property of the PCP complexes is their robustness and well-defined geometry. The anionic PNP ligands may be expected to benefit from the same in terms of robustness but give rise to different reactivity where the difference between the N- and C-donor sites is emphasized. The anionic PNP ligand that has been explored most thoroughly in organometallic chemistry so far is the disilylamido PNP ligand (**B**) of Fryzuk et al.[9,10] The advantages of **C** over **B** are that it offers increased rigidity and is devoid of β-hydrogens and moisture-sensitive functionalities such as N−Si bonds.[10d]

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We have reported certain aspects of the chemistry of Pd, Rh, and Ir with ligand **C**. Upon entry into the Pd chemistry we discovered the facile N−H cleavage by Pd^{II}.[5a] A later report showed that both N−H and N−C oxidative addition took place in the Rh^{I} and Ir^{I} complexes.[5b] These reactions are partly driven by the strong preference of the pincer ligand to bind to the transition metal as a meridional, anionic PNP. We were then intrigued by the possibility of the similarly induced N−C cleavage chemistry in the case of Pd^{II} analogues. In the present report we describe the facile cleavage of unstrained N−C bonds by Pd^{II} centers in a pincer ligand environment. That N−C bonds are *cleaved* by Pd^{II} is particularly striking considering the widespread use of Pd-based catalysts in aromatic and allylic aminations, i.e., C−N bond *forming* reactions.[1,11]

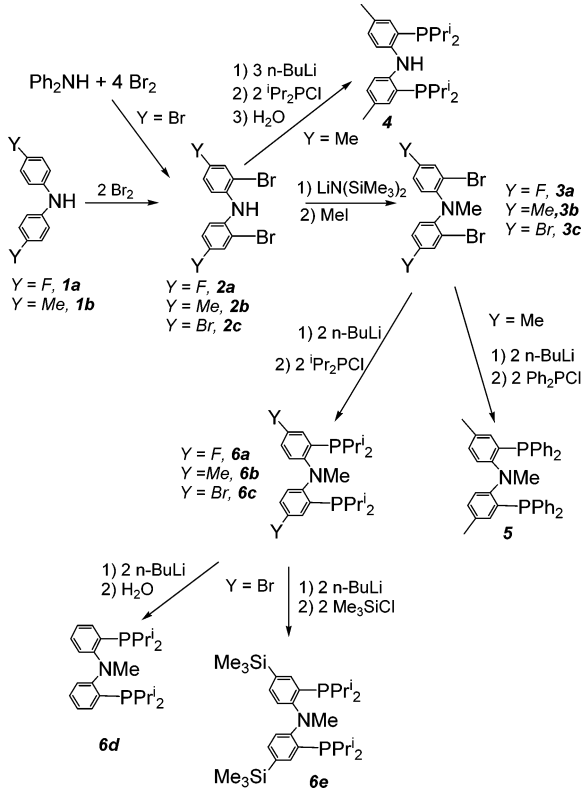
Our investigations should be taken in the proper context of other examples of the C−X (X = H, C, O, N) bond cleavage reactions in the topologically similar PCP and PCN pincer systems.[8,12,13] The chief difference in our case is that X (here, N) and not C is the central donor site of our pincer framework. Milstein et al. have described catalytic hydrogenative cleavage of C−N bonds in a (PCN)Rh system at 180 °C.[8,13] In contrast, in the present report we observe room-temperature cleavage that is effected by a less basic metal (Pd^{II} vs Rh^{I}) and without the need for H_2. Chaudhury et al. reported a C−N cleavage reaction involving Pd; however, in that case it was a Pd^{II}-assisted alcoholysis of an aminal, a cleavage of a rather labile C−N bond.[14]

In addition to the N−C cleavage chemistry, we also present the versatility of our synthetic approach to the PNP pincer ligands that allows synthesis of ligands with different stereo and electronic properties, solubility, and convenient built-in spectroscopic probes.

Results

Preparation of Ligands. We have previously reported the preparation of ligands **4** and **6b**.[5] The methodology used in the synthesis of **6b** is easily adaptable to preparation of a series of ligands where the substituents *para* to the amine functionality can be varied (ligands **6a**−**e**) as well as the substituents on the phosphorus atom (ligand **5**) (Scheme 1). The diarylamines **1a**,**b** were prepared by the Buchwald−Hartwig protocol from the corresponding aniline and bromoarene.[1] We found that the combination of DPPF/Pd-

Scheme 1



$(OAc)_2$ was superior as a catalyst to catalysts derived from BINAP, PCy_3, biphenyl-PBu^t_2, and either $Pd(OAc)_2$ or $Pd_2(dba)_3$. We also found that sodium *tert*-pentoxide was a more convenient base than $NaOBu^t$ for the amination because of the higher solubility of $NaOCMe_2$-Et. This allowed us to use substantially smaller amounts of solvent for the amination reactions. Bromination of **1a**,**b** was optimized to give high isolated yields of **2a**,**b**.[15] Compound **2c** was obtained in high yield by tetrabromination of the commercially available diphenylamine. Compounds **3a**−**c** were obtained by methylation of the Li salt of **2a**−**c** with MeI in THF. This reaction is essentially quantitative if a small excess of $LiN(SiMe_3)_2$ is used as the base. $LiN(SiMe_3)_2$ is superior to *n*-BuLi for generation of the Li salt of **2a**−**c** because *n*-BuLi also undergoes Li/Br exchange. Lithium−bromine exchange with *n*-BuLi in ether was used to generate in situ the dilithio derivatives of **3a**−**c**, which were subsequently allowed to react with either Ph_2PCl (to give **5**) or $^iPr_2$-PCl (to give **6a**−**c**). The lithiation and phosphination proceed nearly quantitatively in all cases. The preferential Li/Br exchange with *ortho*-bromines in **3c** has been used by others.[16] Using Li/Br exchange again, **6c** can be further functionalized by lithiation and subsequent hydrolysis (to give **6d**) or silylation (to give **6e**).

Compounds **5**, **6b**, and **6c** can be easily isolated as colorless or off-white solids. Compounds **6a**, **6d**, and **6e** are extremely lipophilic and do not crystallize from pentane or hexamethyldisiloxane. Moderate *isolated* yields of solid **6a** were obtained by trituration of a concentrated pentane solution of **6a** with MeOH. When using freshly purchased *n*-BuLi (Acros) and distilled

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$^{i}Pr_2PCl$ (Aldrich), crude **6a**−**c** (and thence **6d**,**e**) are obtained >98% pure by NMR. Therefore, crude **6a**, **6d**, and **6e** can be used in solution. We tested **6e** for its sensitivity to air. A solution of **6e** in acetone was left to evaporate in the air, and after 24 h the remaining oil was dissolved in C_6D_6. ^{31}P NMR analysis revealed that only ca. 10% decomposition to unidentified products occurred. Presumably, **6a**−**d** are also insignificantly air-sensitive. It has been our experience that they can be handled in the air briefly without detectable decomposition.

All of the ligands **5** and **6** were characterized by solution multinuclear NMR techniques. All of these ligands display C_{2v} symmetry in solution. The ^{31}P chemical shifts for **6a**−**e** are similar (δ ca. -6 ± 1 ppm), but distinguishable from each other. The diastereotopicity of the two methyl groups within each ^{i}Pr group is evident from the ^{13}C and ^{1}H NMR spectra. The ligand **6a** is additionally characterized by its ^{19}F NMR resonance (δ −123.2 ppm). The protons of the N−CH_3 group in **5** and **6a**−**e** resonate at ca. +3.0−3.6 ppm.

Reactions of ^{Y}PN(Me)P^{R} (6) with Pd(COD)Cl$_2$. Stirring **6** and $Pd(COD)Cl_2$ in C_6D_6 or toluene initially led to the formation of a suspension of a yellow solid in a reddish solution. Continued stirring at ambient temperature overnight or at 100 °C for 1 h resulted in a homogeneous red solution. The ^{31}P NMR and ^{1}H NMR analysis demonstrated the near quantitative formation of **9** with concomitant release of chloromethane and free 1,5-COD. Complexes **9a**−**e** displayed C_{2v} symmetry in solution on the NMR time scale at 22 °C: one singlet resonance (δ ca. $+49 \pm 1$ ppm) in the $^{31}P\{^{1}H\}$ NMR spectrum, one methine resonance and two methyl resonances arising from the isopropyl groups in the ^{1}H NMR spectrum. The solid-state structure of (^{Me}PNP^{iPr})-PdCl (**9b**) was reported previously.[5b]

Upon mixing **6c** with $Pd(COD)Cl_2$ in CD_2Cl_2 at ambient temperature, a homogeneous yellow solution was produced. After 10 min, a relatively broad resonance of **7c** (δ +44.2 ppm, $\Delta\nu_{1/2} = 154$ Hz) was observed by the ^{31}P NMR spectroscopy alongside traces of **9c**. After 20 h at ambient temperature, the ^{31}P NMR indicated >98% conversion to **9c**.

We isolated the yellow solid initially produced upon mixing **6c** with $Pd(COD)Cl_2$ in C_6D_6. This solid was insoluble in toluene or C_6D_6, but it dissolved well in $CDCl_3$ or CD_2Cl_2. The NMR data and the solubility are consistent with the assignment of this material as **7c.** **7c** displays four different methyl and two methine resonances of the i-Pr groups in its ^{1}H NMR spectrum. Compound **7a** was isolated analogously. The solubility of **7a** and **7c** was consistent with the ionic formulation; however the equilibrium between **7** and **7*** can be easily envisioned in solution.

We chose to probe the identity of **7a** by synthesizing **10a**, which differs from **7a** only by the anion. We used Me_3SiOTf to exchange the chloride counterion for triflate in **7a** prepared in situ. The yellow **10a** was isolated as a microcrystalline solid that was essentially insoluble in hydrocarbons but dissolved well in more polar solvents. The triflate anion is much more weakly coordinating than chloride, and we expected **10a** to exist as a distinctly ionic species. In addition to the appropriate solubility observations, this was confirmed by the X-ray diffraction study in the solid state (vide infra) and by observation of the characteristic ^{19}F NMR resonance of an anionic triflate in solution. We surmised that if **7a** is indeed ionic, it should give rise to an ^{1}H NMR spectrum identical to that of **10a**. We found that the ^{1}H NMR spectrum of **7a** becomes increasingly similar to that of **10a** with increasing polarity of the solvent. In DMSO, the two ^{1}H NMR spectra are essentially identical. These observations are consistent with a solvent-dependent equilibrium between **7a** and **7a*** with the more polar solvents favoring the ionic isomer **7a**. Alternatively, tight ion pairing in **7a** in solvents of lesser polarity may be responsible for the difference in the ^{1}H NMR spectra of **7a** and **10a**. In contrast to **7a**, **10a** is thermally stable. Thermolysis of **10a** in CD_2Cl_2 (50 °C, 72 h) or in fluorobenzene (100 °C, 96 h) did not result in any NMR-observable change.

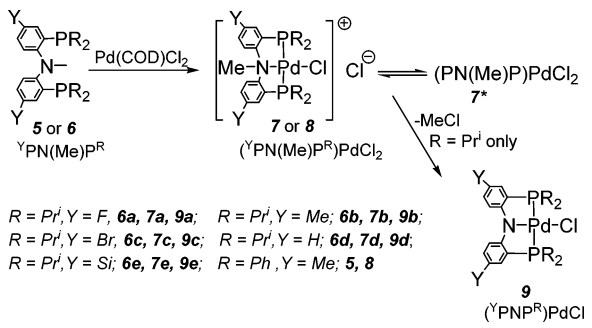
Prompted by the difference in the reactivity of **7** and **10**, we investigated the influence of the solvent polarity on the rate of conversion of **7a** to **9a** in different solvents in the presence and in the absence of added $[Bu_4N]Cl$. The reaction rate order in different solvents was found to be THF > $CDCl_3 \approx CD_2Cl_2$ > acetone ≫ CH_3NO_2 > DMSO, i.e., decreasing with the increasing solvent polarity. In DMSO, even after 2 days at ambient temperature, only a trace of **9a** could be observed. Thermolysis at 100 °C for 6 h was sufficient to effect quantitative (^{19}F NMR evidence) conversion to **9a** in all solvents. Addition of $[Bu_4N]Cl$ was found to accelerate the reaction in all solvents.

Reaction of ^{Me}PN(Me)P^{Ph} (5) with Pd(COD)Cl$_2$. Vigorous stirring of **5** with $Pd(COD)Cl_2$ in toluene resulted in the formation of a copious amount of a yellow solid. This solid was insoluble in hydrocarbons but dissolved well in acetonitrile, $CDCl_3$, and CD_2Cl_2. The NMR data and the solubility are consistent with this material being **8**. In contrast to the behavior of **7**, thermolysis of this compound in toluene, fluorobenzene, or acetonitrile at 100 °C for 18 h did not result in any observable change.

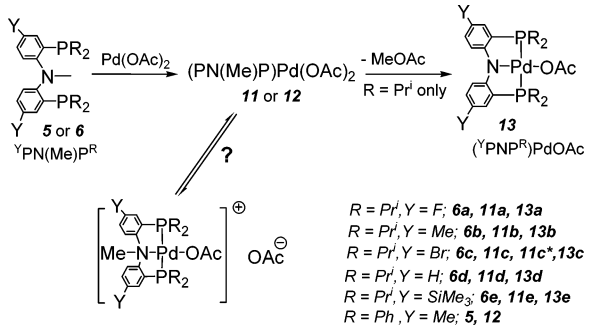
Reaction of ^{Y}PN(Me)P^{R} (6) with Pd(OAc)$_2$. Mixing **6b**−**e** and $Pd(OAc)_2$ in C_6D_6 or toluene resulted in the formation of a homogeneous reddish solution. The ^{31}P NMR analysis 10 min after mixing revealed the formation of **11** alongside a small amount of **13**. Monitoring the resulting solution by NMR showed gradual conversion of **11** to **13** with the concomitant production of MeOAc. In all cases, 24 h at 22 °C or 2 h at 80 °C was sufficient to achieve >95% conversion to **13**. Alternative synthesis of **13b** has been reported previously.[5b] The reaction of **6a** with $Pd(OAc)_2$ in C_6D_6 produced a copious amount of precipitate, but after 48 h at 22 °C, full conversion to **13a** was achieved. It is possible that the equilibrium between the neutral and ionic forms of **11** exists (Scheme 3), similarly to the case of **7**. Interestingly, in the more polar solvent CH_2Cl_2 the conversion of **11** to **13** was much less clean, resulting in a significant amount of P-containing side products in addition to **13**. Complexes **13** displayed C_{2v} symmetry on the NMR time scale. The identity of (^{F}PNP^{iPr})PdOAc (**13a**) in the solid state was confirmed by an X-ray diffraction study (vide infra).

The synthesis of **14c** was accomplished by abstracting acetate from **11c** with 1 equiv of Me_3SiOTf. Unlike **10**,

Scheme 2



Scheme 3



14c reacts further with excess Me_3SiOTf to give **15c**. **15c** gave rise to two different ^{19}F NMR resonances, consistent with the proposed formulation. Apparently, the high oxophilicity of Si allows abstraction of both acetate groups from **11** but only of one chloride from **7**. Thermolysis of **14c** in fluorobenzene or dioxane at 100 °C for 8 h led to the formation of a complex mixture of unidentified products and Pd black.

Reaction of ^{Me}PN(Me)P^{Ph} (5) with Pd(OAc)$_2$. Mixing **5** with $Pd(OAc)_2$ in C_6D_6 resulted in the formation of a homogeneous solution of **12**. **12** displayed broad resonances in the ^1H NMR and the ^{31}P NMR (δ 23.0, $\Delta\nu_{1/2}$ = 28 Hz) spectra. Thermolysis of **12** in C_6D_6 at 100 °C for 5 h lead to the formation of a complex mixture of unidentified products.

Solid-State Structures of 10c (Figure 1) and 13a (Figure 2). The X-ray diffraction study revealed an approximately square planar environment about Pd in **13a**. The P−Pd−P angle in **13a** is 168.16(6)°, which is slightly larger than that for **9b**.[5a] The Pd−N distances in **13a** and **9b** differ by less than 0.01 Å, reflecting the similar trans-influence of Cl and OAc. On the other hand, the Pd−O distance in **13a** is ca. 0.13 Å shorter than in Milstein's (PCP)Pd(O_2CCF_3).[12h] The difference can be only partly attributed to the lesser donicity of trifluoroacetate versus acetate and is probably primarily due to the higher trans-influence of C in PCP versus N in PNP.

The environment about the Pd center was also found to be approximately square planar in the cation of **10c**. The conformation of the aromatic rings in **10c** is different from that in **13a**, consistent with the need to accommodate a tetrahedral N in **10c**. The Pd−N distance in **10c** (amine donor) is somewhat longer than in **13a** (amide donor), but surprisingly only by 0.034(9) Å. The cation of **10c** is isoelectronic with the previously reported (^{Me}PN(Me)P^{iPr})RhCl (**17**).[5b] While qualitatively the structures of **10c** and **17** are similar, the environment about Pd in **10c** is closer to the idealized square planar geometry and the bonds to the ligands are shorter by a larger margin (cf. Pd−N, 2.049(8) Å, P−Pd−P, 164.42(10)°, in **10c**; Rh−N, 2.160(15) Å, P−Rh−P, 155.3(2)°, in **17**) than can be attributed to the inherent difference in the sizes of Pd and Rh. The greater Lewis acidity of the *cationic* Pd center in **10c** is probably responsible for the shorter bonds. That leads to the Pd being held tighter "inside" the pincer ligand, deviating less from the ideally preferred square planar geometry.

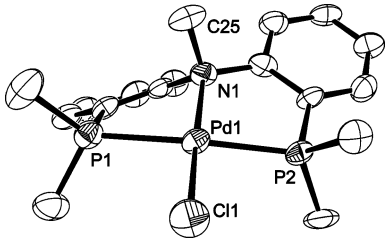


Figure 1. ORTEP drawing (50% probability ellipsoids) of the cation of [(PN(Me)P)PdCl][OTf] (**10c**). Omitted for clarity: the triflate anion, all H atoms, the Me groups of the ^{i}Pr, Br atoms *para* to N. Selected bond distances (Å) and angles (deg): Pd−Cl1, 2.214(3); Pd−C25, 2.750(3); Pd−P1, 2.338(3); Pd−P2, 2.274(3); N1−Pd−Cl1, 175.0(3); N1−Pd−P1, 87.2(3); N1−Pd−P2, 84.8(3); P1−Pd−Cl1, 94.67(11); P2−Pd−Cl1, 94.35(12).

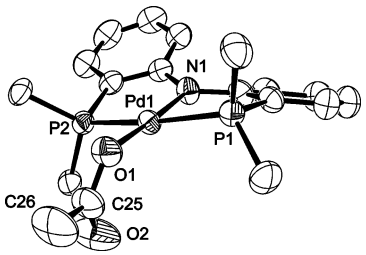


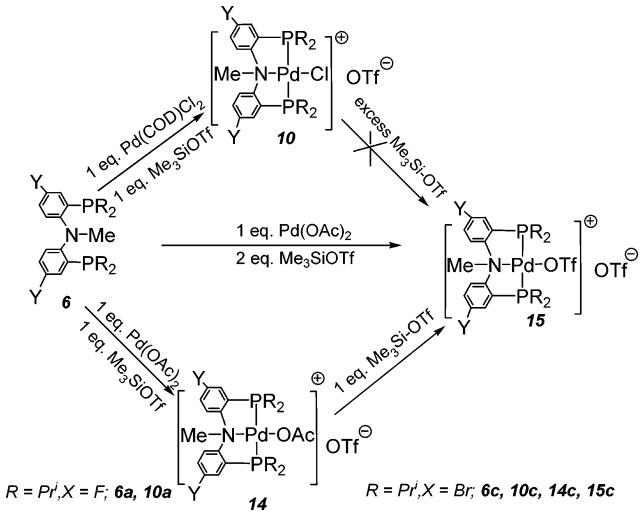
Figure 2. ORTEP drawing (50% probability ellipsoids) of (^{F}PNP^{iPr})PdOAc (**13a**). Omitted for clarity: all H atoms, the Me groups of the ^{i}Pr, F atoms *para* to N. Selected bond distances (Å) and angles (deg): Pd1−N1, 2.015(5); Pd1−P1, 2.2739(17); Pd1−P2, 2.2852(17); Pd1−O1, 2.028(4); P2−Pd1−N1, 84.12(16); N1−Pd1−P1, 84.05(16); P2−Pd1−O1, 98.77(16); N1−Pd1−O1, 174.6(2); P1−Pd1−O1, 92.99(16).

Kinetic Study of the Reaction of 6c with Pd(OAc)$_2$. We undertook a variable-temperature NMR study of the reaction of **6c** with $Pd(OAc)_2$ in C_6D_6 in the 9−41 °C range. It was found at all temperatures that the transformation of the initially formed adduct **11c** follows a first-order rate law. The activation parameters were determined: $\Delta H^{\ddagger}$ = 23.5(15) kcal/mol, $\Delta S^{\ddagger}$ = 3(5) eu, $\Delta G^{\ddagger}_{298}$ = 22.5(30) kcal/mol. We also investigated the kinetics of the reactions of other ligands **6** with $Pd(OAc)_2$ at ca. 25 °C. For all ligands, a first-order rate law was followed. **11b** reacted (to give **12b**) the fastest, and **11a**, the slowest. In addition, NMR analysis indicated that evolution of **11a** gave rise to a significant (ca. 30%) amount of products (unidentified at this point) other than **12b**.

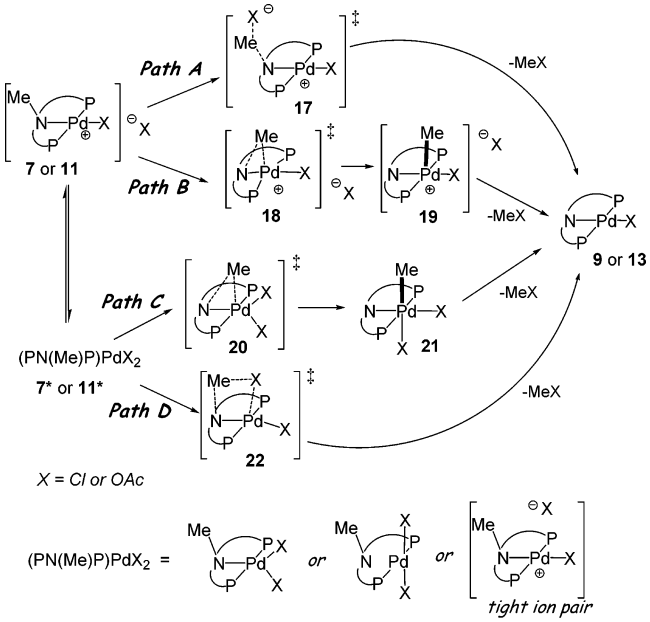
Discussion

Ligand Versatility. We have demonstrated that our synthetic approach to the PNP pincer ligand framework allows us to easily modify the substituents on P and

Scheme 4



Scheme 5



trans to N on the aromatic ring. The variation of the substituents on P affects the overall electronic and steric properties of the PNP ligand to a much greater degree than the variation of the aromatic ring substituents. However, only a few of the required R_2PCl starting materials are available commercially, and most are quite expensive. Our ability to introduce different substituents in the *para*-position of the diarylamine framework (economically!) is much greater. While this changes the steric properties negligibly and the electronic properties only moderately, such substitution can be used to dramatically change the solubility of the ligand. While we have not pursued this here, it is easy to envision introduction of highly lipo-, hydro-, or fluorophilic groups to increase solubility of PNP complexes respectively in hydrocarbons, water, or fluorous phase,[17] or linkers for immobilizing the PNP ligand on solid supports. The other purpose of the *para*-substitution is to introduce a spectroscopic probe. This is realized in (although not limited to) ligand **6a**, which displays a convenient ^{19}F NMR "spectroscopic handle". Because of its higher sensitivity, ^{19}F NMR is far superior to ^{31}P NMR for detecting low concentrations of PNP-containing species.

The exploration of the N−Me cleavage is partly of interest as a way of attaching an *anionic* PNP ligand to transition metal centers. The lithiation/phosphination in the *ortho*-brominated diarylamines proceeds more cleanly with an N−Me central moiety instead of an N−H, and so a greater variety of PNP ligands are accessible in the N-methylated form.

Mechanistic Considerations. Several mechanisms for the cleavage of an N−Me bond in **7** or **11** can be envisaged (Scheme 5). Compound **7** can exist in either the ionic or neutral form. The exact identity of the neutral form **7*** is unclear. It could have either a five-coordinate Pd center or a four-coordinate one (if N is not bound to Pd). On the other hand, the "neutral form" may simply be a contact ion pair that is formed in solvents of lesser polarity. For other various neutral PNP ligands, the ionic forms [(PNP)PdCl]Cl have been reported, but C−N cleavage was not observed.[18] While five-coordinate Pd^{II} compounds are rare, they are not unknown, particularly with chelating ligands.[19] On the basis of the high hydrocarbon solubility (not observed for **11a**, however), compounds **11b**−**e** do not dissociate acetate ion readily and can be considered to exist exclusively in the neutral form **11*** under the conditions of the observed N−C cleavage in C_6D_6. Thus paths A and B are less likely for the N−C cleavage in **11**. The relation between the solvent polarity and the rate of N−Me cleavage in **7** is reminiscent of the same relationship for S_N2 decomposition of tetraalkylammonium halides. Increasing solvent polarity decreases the rate of these reactions, classed as type III (cationic electrophile + anionic nucleophile) by Ingold.[20] However, this similarity alone is not sufficient to confirm path A as the operating mechanism. The path A mechanism fails to explain why N−C cleavage proceeds in **7** and **11** but not **8** or **12**. On the contrary, changing from the more electron-donating PPr^i_2 to PPh_2 should accelerate the reaction according to path A, if any impact is to be registered at all. The exact effects of the various substituents *para* to N are difficult to quantify because their effect will be transmitted differently to the metal via P (*meta*-effect) and N (*para*-effect).[21] However, the relative rates of the N−C cleavage in **11a**−**e** generally indicate that the most basic ligand (**6b**) gives the fastest reaction, while the presumably least basic ligand (**6a**) gives the slowest reaction. The dependence of the rate on the basicity of the PNP ligand is much easier to reconcile with a mechanism that involves oxidative

(17) Gladysz, J. A.; Curran, D. P. *Tetrahedron* **2002**, *58*, 3823.

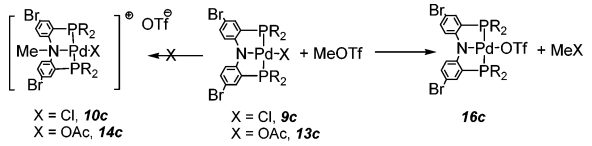
(18) (a) Hii, K. K.; Thornton-Pett, M.; Jutand, A.; Tooze, R. P. *Organometallics* **1999**, *18*, 1887. (b) Reddy, V. V. S. *J. Mol. Catal.* **1988**, *45*, 73. (c) Taqui Khan, M. M.; Taqui Khan, B.; Begum, S. *J. Mol. Catal.* **1988**, *45*, 305. (d) Hillebrand, S.; Bartkowska, B.; Bruckmann, J.; Kruger, C.; Haenel, M. W. *Tetrahedron Lett.* **1998**, *39*, 813. (e) Vasapollo, G.; Nobile, C. F.; Sacco, A. *J. Organomet. Chem.* **1985**, *296*, 435.

(19) (a) Fernandez, D.; Garcia-Seijo, M. I.; Kegl, T.; Petocz, G.; Kollar, L.; Garcia-Fernandez, M. E. *Inorg. Chem.* **2002**, *41*, 4435. (b) Albano, V. G.; Castellari, C.; Cucciolito, M. E.; Panunzi, A.; Vitagliano, A. *Organometallics* **1990**, *9*, 1269. (c) Sakai, T.; Taira, Z.; Yamazaki, S.; Ama, T. *Polyhedron* **1989**, *8*, 1989.

(20) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell Uniiversity Press: Ithaca and London, 1969; pp 457−463.

(21) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

Scheme 6

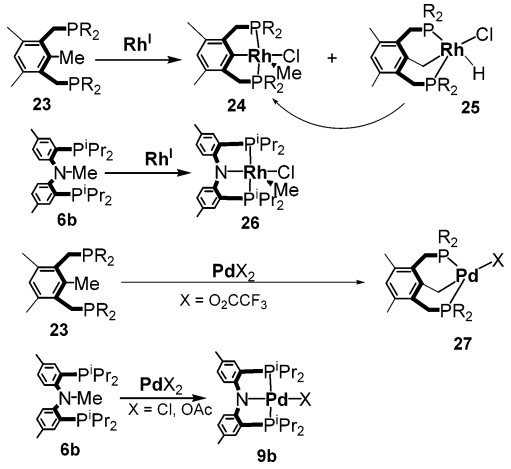


addition of N−Me to the Pd center to give **19** or **21** (path B or C). The high thermal stability of **10** shows that N−Me oxidative addition in the cation of **7** is *thermodynamically unfavorable* but does not exclude it as a *kinetically accessible* step. However, if path B was operative, with the rate-limiting N−Me oxidative addition (via TS **18** to give **19**) in the cationic species (of **7** or of **11**) preceded by the dissociative preequilibrium, then acceleration, rather than retardation, of the reaction by the polar solvents should be expected.

Paths C and D are generally in agreement with experimental observations. Solvents of lesser polarity (and/or addition of Cl^-) will shift the equilibrium farther toward the neutral form **7*** and thus accelerate the overall reaction. The more basic ligand will make the Pd center more electron-rich (and thus more capable of oxidatively adding N−Me to give **21**) but also will make the Cl ligand on Pd somewhat more nucleophilic (lowering the energy of **22**). The results of the kinetic investigations of the N−C cleavage in **11** are also in agreement with a "nonionic" mechanism. The first-order rate law and the small value of $\Delta S^{\ddagger}$ are consistent with an intramolecular process. The intramolecular N−C oxidative addition to Rh^I in (^{Me}PN(Me)P^{iPr})RhCl was also found to have a near-zero $\Delta S^{\ddagger}$.[5b] The cation of **10**, the Pd isoelectronic analogue of (^{Me}PN(Me)P^{iPr})RhCl, does not undergo N−C oxidative addition even under much harsher conditions probably because cationic Pd^{II} is more electron-poor than neutral Rh^I. However, addition of Cl^- to the cation of **10** (to give **7***) would make the Pd center more electron-rich, and path C cannot be ruled out based on the thermal stability of **10**. While +4 is a relatively high oxidation state for Pd, Pd^{IV} intermediates are often invoked, and there are a number of examples of well-characterized organopalladium(IV) compounds.[22] The absence of N−C cleavage reactivity for **10** and **14** (e.g., with loss of MeOTf, MeCl, or MeOAc) is apparently not of thermodynamic origin. If this were true, one might expect N-methylation to occur upon reaction of either **9** or **13** with MeOTf. Instead, we observed exchange of X (X = Cl, OAc) and OTf groups at 22 °C in C_6D_6 (Scheme 6). This is related to the halide exchange we previously reported in the reaction of **9b** with MeI. While these observations do not rule out the thermodynamic unfavorability of the loss of MeX from **10** or **14**, they do indicate that these processes are (also) kinetically inaccessible.

In summary, perhaps only path B can be ruled out based on the available experimental evidence. Further studies involving various N−R cleavages (R ≠ Me) and other metals of group 10 may assist in the elucidation of the mechanism. For instance, if R possesses β-hydrogens, an oxidative addition pathway may give rise to an olefin byproduct via β-hydrogen elimination from the Pd^{IV}−R intermediate.

Scheme 7



Milstein et al. suggested mechanistic possibilities similar to our path A or D for the O−Me cleavage by Pd^{II} in a pincer ligand environment.[12g] In that case too, the mechanistic uncertainty remained. In a related earlier example by Shaw et al., O−Me cleavage by Pt^{II} proceeded more readily in *o*-diphenylphosphinoanisole compared with *o*-dialkylphosphinoanisoles.[23] This is in contrast to our observations presently reported in regard to the inactivity of **8** and **12** but not **7** and **11**. Thus it remains unclear whether O−Me and N−Me cleavage may proceed by the same mechanism.

Decomposition of Acetate-Containing Compounds. The thermolysis of **12** in benzene or toluene (but not of **8**) produced a mixture of unidentified products (including Pd metal) with no evidence for N−C cleavage. The reduction of $Pd(OAc)_2$ by phosphines to Pd(0) is well documented.[24] This is a competitive pathway that is preferred to N−C cleavage for the less basic ligand **5**. The unselective decomposition of **14** (not observed for **10**) and the side-products observed upon evolution of **11** in polar solvents presumably is related to the acetate-assisted reduction to Pd(0) as well. This reaction is particularly fast for bidentate phosphines, such as dppp,[24a] to which a neutral ligand **6** can be likened. It is necessary to emphasize that the *amido*/acetate complexes **13** are thermally stable and can be heated at 100 °C without apparent decomposition.

Comparison with PCP Systems. The reactivity of N-methylated PNP ligands with late transition metals differs from the reactivity of the topologically similar C-methylated PCP ligands of Milstein et al. (Scheme 7). In reactions with Rh^I, both the C−CH_3 (**24**, thermodynamically preferred) and the CCH_2−H oxidative addition products (**25**) were observed with the PCP ligand,[12b] while only the N−CH_3 oxidative addition product (**26**) was observed with the PNP ligand.[5a] With

(22) For selected examples of organopalladium(IV) compounds see: (a) Canty, A. J.; Denney, M. C.; Skelton, B. W.; White, Allan H. *Organometallics* **2004**, *23*, 1122. (b) Sobanov, A. A.; Vedernikov, A. N.; Dyker, G.; Solomonov, B. N. *Mendeleev Commun.* **2002**, 14. (c) Canty, A. J.; Hoare, J. L.; Patel, J.; Pfeffer, M.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 2660. (d) Kruis, D.; Markies, B. A.; Canty, A. J.; Boersma, J.; van Koten, G. *J. Organomet. Chem.* **1997**, *532*, 235. (e) Duecker-Benfer, C.; van Eldik, R.; Canty, A. J. *Organometallics* **1994**, *13*, 2412.

(23) Jones, C. E.; Shaw, B. L.; Turtle, B. L. *J. Chem. Soc., Dalton Trans.* **1974**, 992.

(24) (a) Amatore, C.; Jutand, A.; Thuilliez, A. *Organometallics* **2001**, *20*, 3241. (b) Csakai, Z.; Skoda-Foldes, R.; Kollar, L. *Inorg. Chim. Acta* **1999**, *286*, 93. (c) Amatore, C.; Blart, E.; Genet, J. P.; Jutand, A.; Lemaire-Audoire, S.; Savignac, M. *J. Org. Chem.* **1995**, *60*, 6829.

Pd^{II}, only the CCH_2-H cleavage product (**27**)[12h] was observed with PCP, while the exclusive $N-CH_3$ cleavage is reported here with PNP. Activation of α-C−H bonds in amines has been reported with Ir and Ru.[25] The higher preference for the N−C cleavage versus the putative NCH_2-H cleavage may be attributed to the kinetic mobility of the methyl group on N (more electrophilic Me). In addition, oxidative addition of the diarylamine N−Me bond may be thermodynamically more favorable than that of an aryl C−Me bond relative to C−H oxidative addition.

Conclusion

In summary, we have demonstrated the facile, room-temperature cleavage of nitrogen−carbon bonds in the $(^{Y}PN(Me)P^{R})PdX_2$ complexes (X = Cl, OAc). The reaction proceeds faster for the more donating PNP ligands and is accelerated by the decreasing solvent polarity. $(^{Y}PN(Me)P^{R})PdCl_2$ easily dissociates into $[(^{Y}PN(Me)P^{R})PdX]^+$ and Cl^- in polar solvents. Replacement of one or both chlorides by a weakly coordinating triflate stops the N−Me cleavage. The mechanistic investigations rule out the oxidative addition in $[(^{Y}PN(Me)P^{R})PdX]^+$ and indicate that association of $[(^{Y}PN(Me)P^{R})PdX]^+$ and X^- is involved in the cleavage of the N−Me bond. The results are consistent with either an N−Me oxidative addition $(^{Y}PN(Me)P^{R})PdX_2$ or a nucleophilic attack of X on the Me group. The overall ease of the N−Me cleavage can be partly ascribed to the rigidity of the pincer backbone favoring a meridionally bound anionic PNP ligand.

Experimental Section

General Considerations. Unless specified otherwise, all manipulations were performed under an argon atmosphere using standard Schlenk line or glovebox techniques. Toluene, ethyl ether, C_6D_6, THF, and isooctane were dried over NaK/Ph_2CO/18-crown-6, distilled or vacuum transferred, and stored over molecular sieves in an Ar-filled glovebox. $CDCl_3$ and CH_2Cl_2 were dried with and then distilled or vacuum transferred from CaH_2. Diisopropylchlorophosphine (Aldrich) was vacuum transferred, leaving a small amount of yellow oil behind. Bis(4-methylphenyl)amine (**1b**),[5b] 2,2′-dibromo-4,4′-dimethyldiphenylamine (**2b**),[5b] 2,2′,4,4′-tetrabromodiphenylamine (**2c**),[15] *N*-methyl-2,2′-dibromo-4,4′-dimethyldiphenylamine (**3b**),[5a] *N*-methyl-2,2′,4,4′-tetrabromodiphenylamine (**3c**),[15] **6b**,[5b] and $[(COD)PdCl_2]$[26] were prepared according to published procedures. All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 400 (^{1}H NMR, 399.755 MHz; ^{13}C NMR, 100.518 MHz; ^{31}P NMR, 161.822 MHz) spectrometer. Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR spectra, the residual solvent peak was used as an internal reference. ^{31}P NMR spectra were referenced externally using 85% H_3PO_4 at δ 0 ppm. ^{19}F NMR spectra were referenced externally to 1.0 M CF_3CO_2H in $CDCl_3$ at δ −78.5 ppm.

(^{Me}PN(Me)P^{Ph}) (5). Under Ar, *n*-BuLi (0.8 mL of a 2.5 M solution in hexanes, 2.0 mmol) was slowly added to a solution of *N*-methyl-2,2′-dibromo-4,4′-dimethyldiphenylamine (369 mg, 1.0 mmol) in 50 mL of Et_2O at −35 °C. The mixture was allowed to warm to ambient temperature and stirred for 3 h, and then it was cooled to −35 °C. Diphenylchlorophosphine (359 μL, 2.0 mmol) was added to the mixture, and it was allowed to warm to ambient temperature while stirring. After 2 h, the volatiles were removed in vacuo, the residue was dissolved in 20 mL of toluene, and the precipitate was filtered off. The filtrate was collected, and the volatiles were removed in vacuo. The resulting solid was washed with 2 × 5 mL of isooctane and then dried in vacuo. A yellow solid was obtained (290 mg, 50% yield). ^{1}H NMR (C_6D_6): δ 7.48 (m, 8H, Ar-*H*), 7.12 (m, 2H, Ar-*H*), 6.98−7.02 (m, 12H, Ar-*H*), 6.82 (m, 2H, Ar-*H*), 6.72 (m, 2H, Ar-H), 3.06 (s, 3H, NMe), 1.88 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 154.1 (t), 138.6 (t), 137.3, 133.7 (t), 132.3, 131.5 (t), 130.3, 128.0, 127.8, 123.2, 45.4, 20.7. ^{31}P NMR (C_6D_6): δ −18.3.

(^{F}PN(Me)P^{iPr}) (6a) and (^{F}PNP^{iPr})Pd(OAc) (13a). 3a (4.00 g, 10.6 mmol) was dissolved in 30 mL of ether, and n-BuLi (9.50 mL of a 2.5 M solution in hexanes, 21.2 mmol) was added to it via syringe. The resulting yellow-orange solution was stirred for 3 min, and then chlorodiisopropylphosphine (3.37 mL, 21.2 mmol) was added. The solution became nearly colorless, and a copious amount of white precipitate separated. The mixture was stirred for 2 h, and then the volatiles were removed in vacuo. The residue was triturated with isooctane, extracted with pentane, and filtered. The filtrate was treated with silica gel and filtered through a layer of silica gel on a glass frit. The resulting solution contained >90% pure **6a**. We were unable to induce **6a** to crystallize at −35 °C out of solutions in pentane, *n*-hexane, or hexamethyldisiloxane. An oily mass was formed upon removal of volatiles. Treatment of this oil with methanol caused formation of a white amorphous solid. It was filtered off and washed with methanol to give, after drying in vacuo, 1.74 g (36%) of >99% pure **6a**. The combined filtrates contained ca. 90% pure **6a**, but we were unable to isolate more of it in a solid form. All the volatiles were removed from this solution, the residue was dissolved in toluene, and 1.23 g (5.5 mmol) of palladium acetate was added to it. The mixture was heated at 110 °C for 1 h, during which time it turned deep red. The volatiles were removed, and the residue was dissolved in ether and passed through a layer of silica gel. Removal of the volatiles and washing of the resulting red solid with pentane gave 1.37 g of (^{F}PNP^{iPr})Pd(OAc) (**13a**) that contained ca. 1 equiv of AcOH. Drying in vacuo at 100 °C overnight, followed by recrystallization, gave 1.28 g (13%) of **13a**. Data for **6a**: ^{1}H NMR (C_6D_6): δ 7.16 (dd, J_{HH} = 3 Hz, J_{HF} = 8 Hz, 2H, Ar-*H*), 6.75 (ddd, J_{HH} = 3 Hz, J_{HH} = 9 Hz, J_{HF} = 8 Hz, 2H, Ar-*H*), 6.61 (m, 2H, Ar-*H*), 3.27 (s, 3H, N-CH_3), 1.83 (m, 4H, C*H*Me$_2$), 1.06 (dd, 13 Hz, 7 Hz, 12H, CH*Me*$_2$), 0.85 (dd, 13 Hz, 7 Hz, 12H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 159.2 (d, 243 Hz, C-F), 154.6 (m, C-N), 135.7 (m), 125.1 (m), 120.2 (d, 20 Hz), 116.0 (d, 22 Hz), 46.3 (t, 9 Hz), 24.7 (m, CH), 20.7 (m, CH_3), 20.2 (m, CH_3). ^{31}P NMR (C_6D_6): δ −6.3. ^{19}F NMR (C_6D_6): δ −123.2 (br s). Data for **13a**: ^{1}H NMR (C_6D_6): δ 7.25 (m, 2H, Ar-*H*), 6.66 (m, 2H, Ar-*H*), 6.60 (m, 2H, Ar-*H*), 2.17 (s, 3H, O_2C-CH_3), 2.08 (m, 4H, C*H*Me$_2$), 1.25 (app. quartet (dvt), 8 Hz, 12H, CH*Me*$_2$), 0.94 (app. q (dvt), 8 Hz, 12H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 175.8 (O_2C-CH$_3$), 160.4 (t, J_{CP} = 10 Hz, *C*-N), 154.6 (dvt, J_{CF} = 241 Hz, J_{CP} = 4 Hz, C-F), 120.4 (vtd, J_{CP} = 18 Hz, J_{CF} = 5 Hz), 118.5 (d, J_{CF} = 22 Hz), 118.1 (d, J_{CF} = 21 Hz), 116.2 (app. q, 7 Hz), 24.5 (t, J_{CP} = 12 Hz, *C*HMe$_2$), 23.0 (s, O_2C-*C*H$_3$), 18.1 (t, J_{CP} = 2 Hz, CH*Me*$_2$), 17.4 (s, CH*Me*$_2$). ^{31}P NMR (C_6D_6): δ 48.0. ^{19}F NMR (C_6D_6): δ −130.4 (m).

(^{Br}PN(Me)P^{iPr}) (6c). *n*-BuLi (8.0 mL of a 2.5 M solution in hexanes, 20.0 mmol) was slowly added to a solution of **3c** (4.99 g, 10.0 mmol) in 100 mL of Et_2O at −35 °C. The mixture was allowed to warm to ambient temperature and stirred for 3 h, and then it was cooled to −35 °C. Diisopropylchlorophosphine (3.21 mL, 20.0 mmol) was added to the mixture, and it was allowed to warm to ambient temperature while stirring. After 24 h, the volatiles were removed in vacuo, the residue was dissolved in 50 mL of toluene, and the precipitate was filtered off. The filtrate was collected, and the volatiles were removed in vacuo. The resulting solid was washed with 2 × 20 mL of

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isooctane and then dried in vacuo. A light yellow solid was obtained (3.32 g, 60% yield). ^{1}H NMR (C_6D_6): δ 7.59 (s, 2H, Ar-*H*), 7.18 (dd, 2H, J = 9 Hz, J = 4 Hz, Ar-*H*), 6.46 (dd, 2H, J = 9 Hz, J = 4 Hz, Ar-*H*), 3.23 (s, 3H, NCH_3), 1.80 (m, 4H, C*H*Me$_2$), 1.01 (dd, 12H, CH*Me*$_2$,), 0.83 (dd, 12H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 157.2, 136.9, 136.1, 132.7, 126.0, 116.9, 46.1, 24.9, 20.9, 20.2. ^{31}P NMR (C_6D_6): δ −5.2.

(^{H}PN(Me)P^{iPr})Me (6d). *n*-BuLi (0.8 mL of a 2.5 M solution in hexanes, 2.0 mmol) was slowly added to a solution of **6c** (573 mg, 1.0 mmol) in 40 mL of Et$_2$O at −35 °C. The mixture was allowed to warm to ambient temperature and stirred for 3 h, and then degassed distilled water (36 μL, 2.0 mmol) was added to the mixture. After 30 min, the volatiles were removed in vacuo, and the residue was dissolved in 50 mL of toluene and then was passed through silica gel. The filtrate was collected, and the volatiles were removed in vacuo. A light yellow oil was obtained (332 mg, 80% yield). ^{1}H NMR (C_6D_6): δ 7.34 (d, 2H, J = 8 Hz, Ar-*H*), 7.05 (dvt, 2H, Ar-*H*), 6.90 (m, 4H, Ar-*H*), 3.48 (s, 3H, NCH_3), 2.01 (m, 4H, C*H*Me$_2$), 1.16 (dd, 12H, CH*Me*$_2$,), 0.95 (dd, 12H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 158.9, 134.5, 132.5, 129.9, 124.4, 123.1, 46.4, 25.4, 21.1, 20.5. ^{31}P NMR (C_6D_6): δ −6.4

(^{Si}PN(Me)P^{iPr})Me (6e). *n*-BuLi (0.8 mL of a 2.5 M solution in hexanes, 2.0 mmol) was slowly added to a solution of **6c** (573 mg, 1.0 mmol) in 40 mL of Et$_2$O at −35 °C. The mixture was allowed to warm to ambient temperature and stirred for 3 h, and then it was cooled to −35 °C. Trimethylsilyl chloride (254 μL, 2.0 mmol) was added to the mixture, and it was allowed to warm to ambient temperature while stirring. After 24 h, the volatiles were removed in vacuo, and the residue was dissolved in 30 mL of toluene and then was passed through silica gel. The filtrate was collected, and the volatiles were removed in vacuo. A light yellow oil was obtained (466 mg, 88% yield). ^{1}H NMR (C_6D_6): δ 7.77 (s, 2H, Ar-*H*), 7.30 (d, 2H, J = 8 Hz, Ar-*H*), 6.93 (d, 2H, J = 9 Hz, J = 4 Hz, Ar-*H*), 3.55 (s, 3H, NCH_3), 2.15 (m, 4H, C*H*Me$_2$), 1.20 (dd, 12H, CH*Me*$_2$,), 1.03 (dd, 12H, CH*Me*$_2$), 0.26 (s, 12H, Si*Me3*). ^{13}C NMR (C_6D_6): δ 159.6, 139.8, 134.9, 133.3, 131.4, 123.8, 46.2, 24.8, 21.2, 20.5, −0.6. ^{31}P NMR (C_6D_6): δ −6.1.

[(^{F}PN(Me)P^{iPr})PdCl]Cl (7a). (COD)PdCl$_2$ (14 mg, 0.050 mmol) was added to the solution of **6a** (23 mg, 0.05 mmol) in C_6D_6 in a J-Young tube, and immediately some yellow solid precipitated. The solution was decanted, and the resulting solid was washed with pentane and dried in vacuo. This solid consisted of **7a** and unreacted (COD)PdCl$_2$. Data for **7a** follow. ^{1}H NMR (CD_2Cl_2): δ 8.46 (m, 2H, Ar-*H*), 7.77 (m, 2H, Ar-*H*), 7.32 (m, 2H, Ar-*H*), 6.24 (s, (COD)PdCl$_2$), 4.07 (s, N-CH_3), 2.82 (m, 4H, C*H*Me$_2$), 2.34(s, (COD)PdCl$_2$), 1.13−1.55 (m, 24H, CH*Me*$_2$,). ^{31}P NMR (C_6D_6): δ 43.6. ^{19}F NMR (CD_2Cl_2): δ −113.1 (m).

7b and **7c** were isolated analogously. Data for **7b** follow. ^{1}H NMR (CD_2Cl_2): δ 7.82 (d, 2H, Ar-*H*), 7.71 (d, 2H, Ar-*H*), 7.46 (s, 2H, Ar-*H*), 6.24 (s, (COD)PdCl$_2$), 3.92 (s, N-CH_3), 2.33−2.89 (m, C*H*Me$_2$, Ar-C*H*3, (COD)PdCl$_2$), 1.18−1.55 (m, 24H, CH*Me*$_2$). ^{31}P NMR (C_6D_6): δ 43.9. Data for **7c** follow. ^{1}H NMR ($CDCl_3$): δ 8.40 (d, 2H, Ar-*H*), 8.11 (d, 2H, Ar-*H*), 7.65 (s, 2H, Ar-*H*), 6.30 (s, (COD)PdCl$_2$), 4.23 (s, 3H, N-CH_3), 2.82 (m, C*H*Me$_2$), 2.56 (m, C*H*Me$_2$ (COD)PdCl$_2$), 1.18−1.53 (m, 24H, CH*Me*$_2$,). ^{31}P NMR (C_6D_6): δ 44.0.

Observation of 7a in Different Deuterated Solvents. (COD)PdCl$_2$ (14 mg, 0.050 mmol) was added to the solution of **6a** (23 mg, 0.05 mmol) in various deuterated solvents, and homogeneous yellow solutions were produced (**7a** + COD). ^{1}H NMR ($CDCl_3$): δ 8.48 (m, 2H, Ar-*H*), 7.55 (m, 2H, Ar-*H*), 7.25 (m, 2H, Ar-*H*), 5.54 (COD), 4.12 (s, N-CH_3), 2.78 (m, 4H, C*H*Me$_2$), 2.32 (COD), 1.18−1.51 (m, 24H, CH*Me*$_2$). ^{1}H NMR (CD_3COCD_3): δ 8.10 (m, 2H, Ar-*H*), 7.87 (m, 2H, Ar-*H*), 7.63 (m, 2H, Ar-*H*), 5.48 (COD), 4.08 (s, N-CH_3), 3.08 (m, 4H, C*H*Me$_2$), 2.30(COD), 1.22−1.53 (m, 24H, CH*Me*$_2$). ^{1}H NMR (DMSO-d_6): δ 7.98 (m, 2H, Ar-*H*), 7.84 (m, 2H, Ar-*H*), 7.66 (m, 2H, Ar-*H*), 5.49 (COD), 3.84 (s, N-CH_3), 3.04 (m, 2H, C*H*Me$_2$), 2.95 (m, 2H, C*H*Me$_2$), 2.28(COD), 1.03−1.47 (m, 24H, CH*Me*$_2$).

(^{F}PNP^{iPr})PdCl (9a). (^{F}PNP^{iPr})Pd(OAc) (**13a**) (1.25 g, 2.08 mmol) was dissolved in 10 mL of fluorobenzene and was treated with ca. 2 mL of Me$_3$SiCl. The mixture was stirred for 5 h, and then it was filtered through a layer of silica gel. The volatiles were removed from the filtrate in vacuo, and the red solid residue was washed with pentane and dried in vacuo. Yield: 1.00 g (83%). ^{1}H NMR (C_6D_6): δ 7.25 (m, 2H, Ar-*H*), 6.67 (m, 2H, Ar-*H*), 6.60 (m, 2H, Ar-*H*), 2.09 (m, 4H, C*H*Me$_2$), 1.29 (app. quartet (dvt), 8 Hz, 12H, CH*Me*$_2$), 0.97 (app. q (dvt), 8 Hz, 12H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 160.4 (t, J_{CP} = 10 Hz, *C*-N), 154.6 (dvt, J_{CF} = 237 Hz, J_{CP} = 5 Hz, C-F), 120.6 (vtd, J_{CP} = 18 Hz, J_{CF} = 5 Hz), 118.5 (d, J_{CF} = 23 Hz), 118.1 (d, J_{CF} = 21 Hz), 116.0 (app. q, 7 Hz), 24.9 (t, J_{CP} = 11 Hz, *C*HMe$_2$), 18.4 (br s, CH*Me*$_2$), 17.7 (s, CH*Me*$_2$). ^{31}P NMR (C_6D_6): δ 47.4. ^{19}F NMR (C_6D_6): δ −130.3 (m).

Preparation of (^{Me}PNP^{iPr})PdCl (9b). (COD)PdCl$_2$ (428 mg, 1.50 mmol) was added to **6b** (665 mg, 1.5 mmol) in 20 mL of toluene with stirring, and the color of the solution rapidly changed to dark red. The mixture was heated at 100 °C for 1 h while being stirred, and then the resulting mixture was passed through Celite. The volatiles were removed from the filtrate in vacuo to produce 0.504 g (88% yield) of a purple solid product that was >99% pure as judged by NMR. The NMR data matched that reported previously.[5b]

Compounds 9c−e were prepared from (COD)PdCl$_2$ (428 mg, 1.5 mmol) and **6c−e** (1.51 mmol), respectively, in a manner analogous to **9b**. Yields and NMR data are given below.

(^{Br}PNP^{iPr})PdCl (9c) (85%). ^{1}H NMR (C_6D_6): δ 7.18 (m, 4H, Ar-*H*), 6.95 (d, 2H, J = 6 Hz, Ar-*H*), 2.01 (m, 4H, C*H*Me$_2$), 1.25 (app. q, dvt, 12H, CH*Me*$_2$), 0.93 (app. q, dvt, 12H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 162.3 (t), 134.9, 134.3, 123.1 (t), 117.6, 108.3 (t), 24.9 (t, J_{C-P} = 12 Hz, *C*HMe$_2$), 18.3 (CH*Me*$_2$), 17.6 (CH*Me*$_2$). ^{31}P NMR (C_6D_6): δ 48.7.

(^{H}PNP^{iPr})PdCl (9d) (80%). ^{1}H NMR (C_6D_6): δ 7.71 (d, 2H, J = 8 Hz, Ar-*H*), 6.90 (m, 4H, Ar-*H*), 6.46 (m, 2H, Ar-H), 2.24 (m, 4H, C*H*Me$_2$), 1.39 (app. q, dvt, 12H, CH*Me*$_2$), 1.07 (app. q, dvt, 12H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 164.1 (t, J_{C-P} = 11 Hz), 133.3, 131.8, 120.1 (t, J_{C-P} = 8 Hz), 117.6, 116.8, 25.1 (t, J_{C-P} = 12 Hz, *C*HMe$_2$), 18.8 (CH*Me*$_2$), 18.1 (CH*Me*$_2$). ^{31}P NMR (C_6D_6): δ 48.5.

(^{Si}PNP^{iPr})PdCl (9e) (89%). ^{1}H NMR (C_6D_6): δ 7.80 (d, 2H, J = 8 Hz, Ar-*H*), 7.38 (s, 2H, Ar-H), 7.21 (d, 2H, J = 8 Hz, Ar-*H*), 2.38 (m, 4H, C*H*Me$_2$), 1.40 (app. q, dvt, 12H, CH*Me*$_2$), 1.12 (app. q, dvt, 12H, CH*Me*$_2$), 0.25 (s, 18H, SiMe$_3$). ^{13}C NMR (C_6D_6): δ 164.3 (t, J = 11 Hz), 138.3, 136.9, 120.0 (t, J = 8 Hz), 116.8, 24.9 (t, J_{C-P} = 12 Hz, *C*HMe$_2$), 18.6 (CH*Me*$_2$), 17.8 (CH*Me*$_2$), −0.7 (SiCH$_3$). ^{31}P NMR (C_6D_6): δ 49.3.

Preparation of [(^{F}PN(Me)P^{iPr}))PdCl]$^+$OTf $^-$ (10a). A mixture of (COD)PdCl$_2$ (43 mg, 0.15 mmol) and Me$_3$SiOTf (28 μL, 0.15 mmol) in CH_2Cl_2 was stirred for 30 min followed by the addition **6a** (69 mg, 0.15 mmol) at ambient temperature. The volatiles were removed in vacuo, and yellow solid was obtained. Recrystallization from fluorobenzene gave a light yellow crystalline solid. Yield: 91 mg (71%). ^{1}H NMR ($CDCl_3$): δ 8.02 (m, 2H, Ar-H), 7.52 (m, 2H, Ar-*H*), 7.29 (m, 2H, Ar-*H*), 3.92 (s, 3H), 2.82 (m, 4H), 1.52 (app. q, dvt, 6H, CH*Me*$_2$), 1.43 (m, 12H, CH*Me*$_2$), 1.25 (app. q, dvt, 6H). ^{13}C NMR ($CDCl_3$): δ 163.2 (m), 160.7 (m), 152.8 (m), 129.4 (m), 127.0 (m), 120.9 (d, J = 23 Hz), 119.7 (d, J = 23 Hz), 65.3, 27.1 (t, *C*HMe$_2$), 26.8 (t), 19.1, 18.5, 18.4, 18.1 (CH*Me*$_2$). ^{31}P NMR ($CDCl_3$): δ 43.5. ^{19}F NMR ($CDCl_3$): δ −80.8 (O_3SCF_3), −111.5 (Ar-*F*). ^{1}H NMR (CD_3COCD_3): δ 8.02 (m, 2H, Ar-*H*), 7.86 (m, 2H, Ar-*H*), 7.60 (m, 2H, Ar-*H*), 4.08 (s, N-CH_3), 3.08 (m, 4H, C*H*Me$_2$), 1.26−1.59 (m, 24H, CH*Me*$_2$). ^{31}P NMR (CD_3COCD_3): δ 46.1. ^{19}F NMR (CD_3COCD_3): δ −80.4, −113.7. ^{1}H NMR (DMSO): δ 7.96 (m, 2H, Ar-*H*), 7.83 (m, 2H, Ar-*H*), 7.65 (m, 2H, Ar-*H*), 3.84 (s, N-CH_3), 3.03 (m, 2H, C*H*Me$_2$), 2.94 (m, 2H,

C*H*Me$_2$), 1.03−1.47 (m, 24H, CH*Me$_2$*). ^{31}P NMR (DMSO): δ 46.7. ^{19}F NMR (DMSO): δ −79.9, −113.3.

Preparation of [(^{Br}PN(Me)P^{iPr})PdCl]$^+$OTf$^-$ (10c). (COD)PdCl$_2$ (57 mg, 0.20 mmol) was added to the solution of **6c** (115 mg, 0.20 mmol) in 5 mL of toluene at ambient temperature, followed by the addition of Me$_3$SiOTf (49 μL, 0.30 mmol). The reaction mixture stood for 5 days at ambient temperature, and a copious amount of yellow crystalline precipitate formed. The precipitate was separated by decantation, dissolved in fluorobenzene, and passed through Celite. The volatiles were removed from the resulting filtrate, and a yellow solid was obtained (94 mg, 75%). ^{1}H NMR (CDCl$_3$): δ 7.89 (d, 2H, J = 8 Hz, Ar-H), 7.83 (d, 2H, J = 8 Hz, Ar-*H*), 7.70 (s, 2H, Ar-*H*), 3.91 (s, 3H), 2.82 (m, 4H), 1.52 (app. q, m, 6H, CH*Me$_2$*), 1.43 (m, 12H, CH*Me$_2$*), 1.19 (app. q, dvt, 6H). ^{13}C NMR (CDCl$_3$): δ 155.9 (t, J = 7 Hz), 136.9, 136.0, 130.3 (t, J = 13 Hz), 126.4 (t), 124.5, 64.8, 27.0 (t, *C*HMe$_2$), 26.8 (t), 19.3, 18.7, 18.5, 18.2 (CH*Me$_2$*). ^{31}P NMR (CDCl$_3$): δ 44.5. ^{19}F NMR (CDCl$_3$): δ −80.8. Anal. Calcd (Found) for $C_{26}H_{37}NBr_2F_3SO_3ClP_2Pd$: C, 36.24 (36.32); H, 4.30 (4.28).

(^{Me}PN(Me)P^{Ph})Pd(OAc)$_2$ (12). Pd(OAc)$_2$ (22.4 mg, 0.100 mmol) was added into the solution of **5** (57.9 mg, 0.1 mmol) in 1 mL of C$_6$D$_6$, and the solution changed to red quickly. Let it stand for 2 h at ambient temperature. All of the volatiles were removed in vacuo, and a red solid was obtained. ^{1}H NMR (C$_6$D$_6$): δ 8.07 (m, 8H, Ar-H), 6.49−7.05 (m, 18H, Ar-*H*), 1.92 (s, 3H, N-Me), 1.82 (s, 6H, Ar-Me), 1.63 (s, 6H, OAc). ^{31}P NMR (C$_6$D$_6$): δ 20.1.

Preparation of (^{Me}PNP^{iPr})PdOAc (13b). Pd(OAc)$_2$ (336 mg, 1.50 mmol) was added to **6b** (665 mg, 1.5 mmol) in 20 mL of toluene with stirring, and the color of the solution rapidly changed to red. The mixture was stirred at ambient temperature overnight, and then the resulting mixture was passed through Celite. The volatiles were removed from the filtrate in vacuo, and the resulting red solid product was washed with pentane and dried in vacuo. Yield: 800 mg (90%). The NMR data matched that reported previously.[5b] Anal. Calcd (Found) for $C_{28}H_{43}NO_2P_2Pd$: C, 56.66 (56.34); H, 7.25 (7.04).

Compounds 13c−e were prepared from Pd(OAc)$_2$ (336 mg, 1.50 mmol) and **6c−e** (1.51 mmol), respectively, in a manner analogous to **13b**. Yields and NMR data are given below.

(^{Br}PNP^{iPr})PdOAc (13c) (83%). ^{1}H NMR (C$_6$D$_6$): δ 7.10 (m, 4H, Ar-*H*), 6.93 (d, 2H, J = 8 Hz, Ar-*H*), 2.12 (s, 3H, COCH$_3$), 2.01 (m, 4H, C*H*Me$_2$), 1.20 (app. q, dvt, 12H, CH*Me$_2$*), 0.93 (app. q, dvt, 12H, CH*Me$_2$*). ^{13}C NMR (C$_6$D$_6$): δ 175.5, 162.3 (t), 134.7, 134.2, 122.8 (t), 117.8, 108.3 (t), 24.9 (t, J_{C-P} = 12 Hz, *C*HMe$_2$), 22.9 (s, O2C-*C*H$_3$), 18.1 (CH*Me$_2$*), 17.3 (CH*Me$_2$*). ^{31}P NMR (C$_6$D$_6$): δ 48.5.

(^{H}PNP^{iPr})PdOAc (13d) (86%). ^{1}H NMR (C$_6$D$_6$): δ 7.64 (d, 2H, J = 8 Hz, Ar-H), 6.87 (m, 4H, Ar-*H*), 6.45 (d, 2H, J = 8 Hz, Ar-*H*), 2.25 (m, 4H, C*H*Me$_2$), 2.21 (s, 3H, COCH$_3$), 1.35 (app. q, dvt, 12H, CH*Me$_2$*), 1.03 (app. q, dvt, 12H, CH*Me$_2$*). ^{13}C NMR (C$_6$D$_6$): δ 176.0, 164.3 (t), 133.2, 131.7, 119.7 (t), 117.4, 116.9 (t), 24.67 (t, J_{C-P} = 12 Hz, *C*HMe$_2$), 23.0, 18.5 (CH*Me$_2$*), 17.7 (CH*Me$_2$*). ^{31}P NMR (C$_6$D$_6$): δ 48.2.

(^{Si}PNP^{iPr})PdOAc (13e) (85%). ^{1}H NMR (C$_6$D$_6$): δ 7.72 (d, 2H, J = 8 Hz, Ar-H), 7.32 (s, 2H, Ar-*H*), 7.18 (d, 2H, J = 8 Hz, Ar-*H*), 2.37 (m, 4H, C*H*Me$_2$), 2.18 (s, 3H, COCH$_3$), 1.33 (app. q, dvt, 12H, CH*Me$_2$*), 1.10 (app. q, dvt, 12H, CH*Me$_2$*), 0.25 (s, 18H, SiMe$_3$). ^{13}C NMR (C$_6$D$_6$): δ 175.3, 164.5 (t), 138.3, 136.8, 127.3 (t), 119.6, 116.9 (t), 24.6 (t, J_{C-P} = 12 Hz, *C*HMe$_2$), 23.1, 20.1 (CH*Me$_2$*), 18.4 (CH*Me$_2$*), −0.7 (SiMe$_3$). ^{31}P NMR (C$_6$D$_6$): δ 48.7.

Preparation of [(^{Me}PN(Me)P^{iPr})PdOAc]$^+$OTf$^-$ (14b). Pd(OAc)$_2$ (45 mg, 0.20 mmol) was added to the solution of **6b** (89 mg, 0.20 mmol) in 5 mL of toluene at ambient temperature, followed by the addition of Me$_3$SiOTf (33 μL, 0.20 mmol). The reaction mixture stood for 5 days at ambient temperature, and a brown oil separated. The oil was separated by decantation, washed with toluene, dissolved in fluorobenzene, and passed through Celite. The volatiles were removed from the resulting filtrate, and a brown oil was obtained (106 mg, 70%). ^{1}H NMR (CDCl$_3$): δ 7.66 (d, 2H, J = 8 Hz, Ar-H), 7.54 (d, 2H, J = 8 Hz, Ar-*H*), 7.40 (s, 2H, Ar-*H*), 3.83 (s, 3H), 2.71 (m, 4H), 2.45 (s, 6H), 1.97 (s, 3H), 1.14−1.47 (m, 24H, CH*Me$_2$*). ^{13}C NMR (CDCl$_3$): δ 176.7, 154.9 (t, J = 8 Hz), 140.8, 134.1, 133.9, 126.1 (t, J = 13 Hz), 123.8, 64.0, 26.8 (t, *C*HMe$_2$), 25.6 (t), 21.7, 20.6, 18.8, 18.4, 18.3, 17.4 (CH*Me$_2$*). ^{31}P NMR (CDCl$_3$): δ 41.9. ^{19}F NMR (CDCl$_3$): δ −80.7.

[(^{Br}PN(Me)P^{iPr})PdOAc]$^+$OTf$^-$ (14c) was prepared analogously to 14b (yield: 78%). ^{1}H NMR (CDCl$_3$): δ 7.87 (d, 2H, J = 8 Hz, Ar-H), 7.82 (d, 2H, J = 8 Hz, Ar-*H*), 7.66 (s, 2H, Ar-*H*), 3.88 (s, 3H), 2.71 (m, 4H), 1.96 (s, 3H), 1.18−1.51 (m, 24H, CH*Me$_2$*). ^{13}C NMR (CDCl$_3$): δ 175.7, 155.6 (t), 136.5, 135.6, 129.6, 126.2 (t), 123.8, 62.5, 26.8 (m, *C*HMe$_2$), 25.5, 21.5, 18.5, 18.2, 18.0, 17.1 (CH*Me$_2$*). ^{31}P NMR (CDCl$_3$): δ 42.5. ^{19}F NMR (CDCl$_3$): δ −80.7.

Preparation of [(^{Br}PN(Me)P^{iPr})PdOTf]$^+$OTf$^-$ (15c). Pd(OAc)$_2$ (45 mg, 0.20 mmol) was added to a solution of **6c** (115 mg, 0.20 mmol) in 5 mL of toluene at ambient temperature, followed by the addition of Me$_3$SiOTf (66 μL, 0.40 mmol). The reaction mixture stood for 5 days at ambient temperature, and a brown oil formed. The oil was separated by decantation, washed with toluene, dissolved in fluorobenzene, and passed through Celite. The volatiles were removed from the resulting filtrate, and a brown oil was obtained (148 mg, 76%). ^{1}H NMR (CDCl$_3$): δ 7.94 (d, 2H, J = 8 Hz, Ar-H), 7.84 (d, 2H, J = 8 Hz, Ar-*H*), 7.76 (s, 2H, Ar-*H*), 4.05 (s, 3H), 3.03 (m, 2H, C*H*Me$_2$), 2.73 (m, 2H, C*H*Me$_2$), 1.48 (m, 12H), 1.35 (dvt, 6H), 1.21 (dvt, 6H, CH*Me$_2$*). ^{13}C NMR (CDCl$_3$): δ 156.1 (t, J = 8 Hz), 137.6, 136.3, 129.9, 126.4, 125.0, 66.4, 26.8 (m, *C*HMe$_2$), 19.4, 18.8, 18.0, 17.4 (CH*Me$_2$*). ^{31}P NMR (CDCl$_3$): δ 50.9. ^{19}F NMR (CDCl$_3$): δ −80.7 (free OTf$^-$), −78.2 (Pd-OTf).

Preparation of (^{Br}PNP^{iPr})PdOTf (16c). MeOTf (1.5 uL, 0.010 mmol) was added to **13c** (7.5 mg, 0.010 mmol) in 0.5 mL of C$_6$D$_6$ at ambient temperature. This was allowed to stand for 6 h, and the NMR analysis showed that all of **13c** was converted to a new complex and MeOAc. The resulting purple solution was passed through Celite. The volatiles were removed from the filtrate in vacuo, and the resulting purple solid product was washed with pentane, dried in vacuo, and redissolved in C$_6$D$_6$ for NMR characterization. ^{1}H NMR (C$_6$D$_6$): δ 7.11 (s, 2H, Ar-*H*), 7.00 (d, 2H, J = 8 Hz, Ar-H), 6.86 (d, 2H, J = 8 Hz, Ar-*H*), 2.14 (m, 4H, C*H*Me$_2$), 1.21 (dvt, 12H, CH*Me$_2$*), 0.85 (dvt, 12H, CH*Me$_2$*). ^{13}C NMR (C$_6$D$_6$): δ 162.6 (t), 134.8, 134.5, 120.9, 118.5, 109.5 (t), 24.9, 18.2 (CH*Me$_2$*), 17.6 (CH*Me$_2$*). ^{31}P NMR (C$_6$D$_6$): δ 54.4. ^{19}F NMR (C$_6$D$_6$): δ −79.2.

X-ray Structure Determination. Single crystals of **10c** and **13a** suitable for X-ray diffraction measurements were obtained by recrystallization from fluorobenzene and ether, respectively. Crystals were mounted in glass capillaries. Data collection was carried out at room temperature (low-temperature apparatus was not available) on a CAD-4 Turbo diffractometer equipped with Mo Kα radiation.[27] For **10c** and **13a**, data were collected to $2\theta_{max}$ = 25.0° and 30.4°, respectively, the lower 2θ value corresponding to poorer crystal quality for **10c**. For **13c**, which crystallized in space group $P2_12_12_1$, the absolute configuration of the crystal was established by a Flack parameter refinement.

The structures were solved by direct methods (SIR92).[28] Full-matrix least squares refinement was carried out using the Oxford University Crystals for Windows system.[29] All ordered non-hydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were fixed at

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calculated geometric positions and updated after each least-squares cycle. The occupancies of the O and F atoms of the triflate anion were refined as two rotameric sets. The occupancies were constrained to sum to 1.0; the occupancy of the major component was 0.662(12). A PLATON analysis of void volume for compound **10c** revealed a void volume of 64 Å^3 per asymmetric unit. Missing solvent could not be located on electron density difference maps, nor could the voids be successfully modeled using the PLATON SQUEEZE[30,31] technique. A full report on the structures is available as CIF files for **10c** and **13a**.

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Supporting Information Available: Experimental details and characterization data for **1a**, **2a**, and **3a**; experimental details of the kinetic studies; graphic NMR spectra for **6a**−**e**, **7a**, **9a**−**e**, **10a**, **12**, **14b**,**c**, **15c**, and **16c**; and crystallographic information for **10c** and **13a** in the form of CIF files. This material is available via the Internet free of charge at http://pubs.acs.org.

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