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Published on Web 01/25/2005

Insertion of Acrylonitrile into Palladium Methyl Bonds in Neutral and Anionic Pd(II) Complexes

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Abstract: The reactions of a series of Pd(II) methyl compounds of general formula $LPd(NCCH_3)CH_3$, where L is a bulky phenoxydiazene or phenoxyaldimine ligand with the polar olefin acrylonitrile (AN), are reported. The compounds react with an excess of AN to give the products of 2,1 insertion into the Pd−Me bond, yielding dimers and/or trimers which feature bridging α-cyano groups. The reactions were studied by low temperature ^{1}H NMR spectroscopy, revealing an initial formation of compounds featuring N-bound AN, which isomerized to an (unobserved) π-bound species that rapidly underwent 2,1 insertion into the Pd−Me bond. Intermediate oligomeric complexes retaining a Pd−Me function were observed at low [AN] in these reactions. Under pseudo first-order conditions, k_{obs} values of 8.5×10^{-5} to 2.68×10^{-3} M^{-1} (−22 °C to 10 °C, 100 equiv of AN) and activation parameters of $\Delta H^{\ddagger} = 14.4(5)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -19(5)$ eu were obtained in one case. Comparison of the overall rates of insertion between two $LPd(NCCH_3)CH_3$, differing in the overall charge on the supporting ligand L, showed that the complex bearing a negatively charged ligand reacts with AN twice as fast as one with no anionic charge. The rates of insertion in both of these complexes are significantly faster than reported rates for analogous reactions in cationic Pd(II) derivatives, indicating that increasing the negative charge on the complex enhances the rate of AN insertion. These results provide fundamental mechanistic insights into a crucial reaction for incorporation of polar comonomers into alpha olefins via a coordination polymerization mechanism.

Introduction

While tremendous success in the controlled polymerization of aliphatic olefins by homogeneous, single-site catalysts has been attained in the past 15 years,[1] the development of organotransition metal compounds capable of incorporating comonomers with polar functions remains a significant challenge in polymerization catalysis.[2] Currently, polymers or copolymers integrating polar monomers are prepared via relatively uncontrollable radical or anionic initiation polymerization processes.[3] While polymers that incorporate polar groups have useful properties, it is likely that even more functional materials could be discovered if the stereo and regiocontrol bestowed by single site catalysts could be deployed in an effective coordination polymerization process for these monomers.

While there have been some late metal based catalysts that are reportedly able to incorporate polar monomers via an insertion mechanism,[4] direct evidence for this is rare and some of these examples[5] involve monomers in which the polar function is relatively far-removed from the olefinic locus of insertion. Polar monomers such as acrylates or vinyl halides, in which the polar group is directly bonded to the olefinic moiety to be inserted, are the most desirable polar monomers but provide several challenges to be overcome if a coordination insertion process is to be viable (Scheme 1). The first obstacle involves the preference of binding for the substrate; for olefin insertion to take place, it is clear that the olefinic moiety must bind at some point to the metal center. Since the catalysts for olefin polymerization are generally electrophilic in nature, there is a tendency for polar monomers to preferentially bind the metal through the polar function in a σ bonding mode. Thus, there must at least be an equilibration to the π bound form involving the olefin function, if not a clear preference for π bonding, in order for insertion to take place at appropriate rates. Assuming a π bound complex from which insertion can take place is

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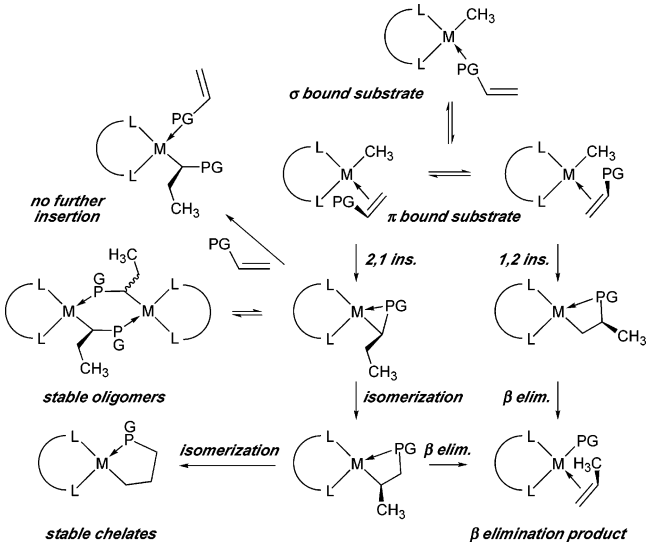
10.1021/ja044119+ CCC: $30.25

Scheme 1



accessible, the next challenge involves control of the regiochemistry of insertion. Vinyl monomers with polar groups generally exhibit a tendency to undergo kinetic 2,1 insertion, since the polarity of the 4-centered transition state disfavors electron withdrawing groups in the β position.[6] These 2,1 products, however, may undergo isomerization to the 1,2 isomer with the polar group now on the β carbon and facile β-PG elimination processes often ensue,[7,8] poisoning the catalyst toward further reactivity.[9] In other instances, the polar group simply forms a stable chelate to the metal from the β position, blocking the vacant coordination site necessary to take up further equivalents of monomer. In yet another scenario, the polar group can facilitate oligomerization of catalyst sites by binding to the vacant site of a separate catalyst molecule. All of these proclivities have a tendency to preclude further steps in a polymerization reaction. Finally, even if one can design a catalyst that effectively binds the polar monomer through the olefin and regioselectively inserts the monomer to an alkyl with an a polar group that is relatively stable toward isomerization or oligomerization processes, a final challenge is likely to be encountered. The electron withdrawing nature of the polar group tends to raise the barrier toward its migration to a coordinated olefin since it is significantly less nucleophilic than an unfunctionalized alkyl ligand. Thus, while it may be possible to exert some control on the insertion of the polar comonomer into M−C bonds, subsequent insertions of aliphatic olefins or polar comonomers may be prohibited by the presence of the polar substituents, even if it is nonchelating.

Acrylonitrile (AN) is a particularly challenging polar comonomer given its high tendency to polymerize via radical[10] or anionic[11] processes. Indeed, there are several transition metal complexes that have been reported to be active for the polymerization of AN,[12] but in only a handful of cases has the mode of polymerization been elucidated. In these cases, anionic[13] or radical[14] mechanisms have been shown to be operative, while some reports invoke enchainment via a group transfer mechanism.[15] Furthermore, the nitrile function is a relatively good donor and though complexes of AN exhibiting bonding via the olefinic π electrons are known,[16] N-bound isomers are energetically competitive, particularly for hard metals. Little is known regarding the barrier to isomerization between N-bound and π-bound[17] AN isomers,[18] and when N-bound complexes dominate, insertion is precluded.[19] When π bonding is accessible, kinetically or thermodynamically, products consistent with 2,1 AN insertion into M−P[20] or M−C[21] bonds have led authors to invoke this as a mechanistic possibility but direct observation of these reactions has not, to our knowledge, been reported.

While suitable catalysts for AN enchainment via a coordinative mechanism are currently not known, computational investigations[22] point to certain key characteristics one might expect in a candidate catalyst. To encourage a π bonding mode involving the olefinic function of the monomer, softer late transition metal-based catalysts would be more effective than

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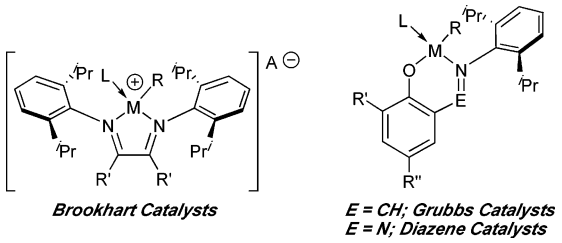
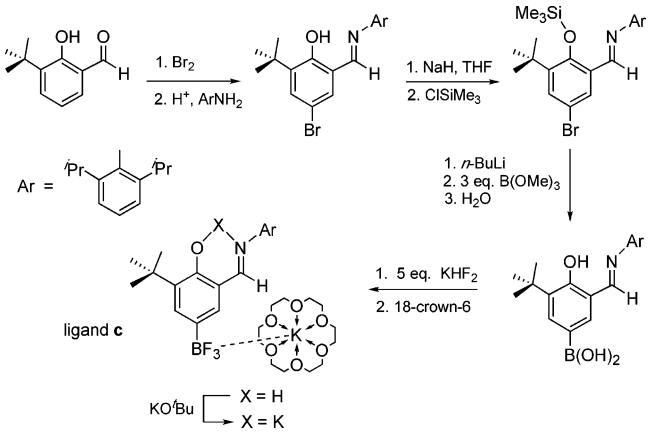
Chart 1



the harder early metal systems known to polymerize olefins. Indeed, it is well-recognized that late metal catalysts, such as Brookhart's cationic diimine nickel and palladium catalysts,[4] or Grubbs' neutral salicylaldiminato nickel catalysts[5,23] (Chart 1), offer significantly greater "functional group tolerance" than do, for example, the cationic group 4 metallocenium family of catalysts. In comparing the Brookhart and Grubbs classes of catalysts, Deubel and Ziegler have shown that the catalysts incorporating the second row metal palladium actually favor π bonding over σ bonding for AN since the greater separation in the *n*s/*n*p and *n*d levels ($n = 4,5$) allows for more effective back-bonding to the AN than in the nickel compounds where $n = 3$.[22c] Furthermore, since the N-bound σ binding mode has a strong electrostatic component, the cationic Brookhart catalysts more strongly favor this detrimental bonding mode than the neutral Grubbs systems.[22c] In fact, it was shown that for the Pd salicylaldiminato catalysts, π bonding is expected to be the favored mode of bonding for AN. The calculations also show that, for the π bound isomer of the AN complex, the barrier to insertion into an M−C bond is comparable to that found for ethylene, suggesting that the insertion of AN might be experimentally observable in such systems.[24]

Given the above discussion, we have targeted neutral palladium complexes incorporating bulky salicylaldiminato donors and closely related ligands incorporating a diazene function (Chart 1) as good candidates for studying AN insertion into metal alkyl bonds. Furthermore, extending the idea that neutral catalysts are more likely to engage in π bonding than cationic derivatives, we have developed a negatively charged[25] version of the Grubbs salicylaldiminato ligand framework to compare with the neutral versions. These ligands use established motifs for engendering polymerization activity, such as the 2,6-diisopropyl aryl substituent on the imine nitrogen, and a *tert*-butyl group *ortho* to the phenoxy donor, to provide a polymerization-relevant environment for this model study. We find that 2,1 insertion of AN in these complexes is facile and present results that corroborate some of the predictions of theory, but at the same time underscore that some of the problems presented in Scheme 1 are significant. The computational results mentioned above notwithstanding, Jordan and co-workers have found that several cationic Pd methyl complexes also undergo these reactions, indicating that π-bound AN complexes are also accessible in these systems, although the N-bound isomers dominate as determined by spectroscopic methods. Their results are described in a companion paper[26] and comparisons are made when appropriate.

Scheme 2



Results and Discussion

Ligand and Palladium Complex Syntheses. The bulky diazene[27] (**a** series) and salicylaldiminato[5,23,28] (**b** series) ligands were prepared according to literature procedures using the appropriate amine/aldehyde or phenol/diazonium salt precursors and converted to their alkali metal salts using standard reagents and procedures. The synthesis of the salicylaldiminato ligand **c**, bearing an anionic group, is outlined in Scheme 2. Bromination of 3-*tert*-butyl-2-hydroxy-benzaldehyde[29] in the *para* position was accomplished using Br_2[30] and the crude solid was reacted with 2,6-diisopropylaniline in methanol to prepare the brominated salicylaldimine in 54% yield. Protection of the phenolic group with a trimethylsilyl group via deprotonation with NaH and quenching with $ClSiMe_3$ gave the silyl ether as a yellow solid in quantitative yield after evaporation of all the volatiles. The anionic BF_3 group was installed using a procedure recently reported by Fröhn,[31] involving lithium−halogen exchange by reaction with one equivalent of *n*-BuLi in cold THF (−78 °C, yellow solution) followed by quenching with an excess of $B(OMe)_3$ and letting the mixture warm to room temperature

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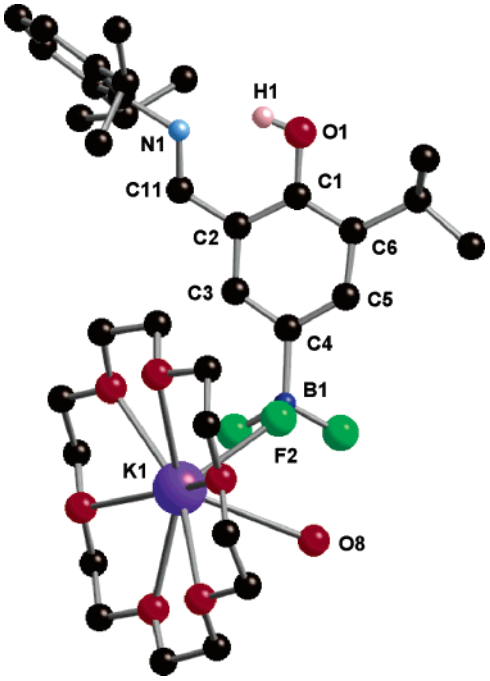


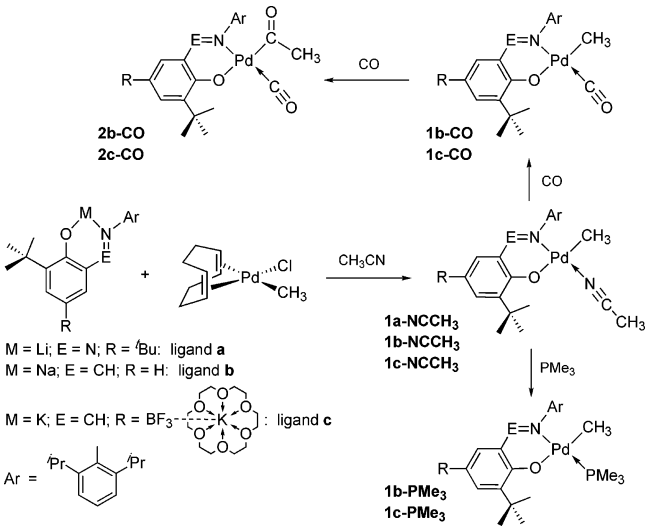
Figure 1. Crystalmaker diagram of the structure of the phenolic form of borate functionalized ligand **c**. Selected bond distances (Å): C(1)−O(1), 1.360(2); C(11)−N(1), 1.280(2); C(4)−B(1), 1.601(3); B(1)−F(1), 1.402(2); B(1)−F(2), 1.426(3); B(1)−F(3), 1.403(2); F(1)−K(1), 3.1533(15); F(2)−K(1), 2.6570(13); F(3)−K(1), 4.376. Selected bond angles (deg): O(1)−C(1)−C(2), 119.84(14); C(1)−C(2)−C(11), 121.16(16); C(2)−C(11)−N(1), 122.67(15); C(11)−N(1)−C(12), 122.08(14). Selected torsion angles (deg): O(1)−C(1)−C(2)−C(11), 0.2(2); C(1)−C(2)−C(11)−N(1), −3.4(3); C(11)−N(1)−C(12)−C(13), −79.2(2); C(11)−N(1)−C(12)−C(17), −106.59(19).

(almost colorless). Addition of water immediately formed the boronic acid and hydrolyzed the O−Si bond. The crude product was dissolved in methanol whereupon treatment with an aqueous solution of KHF_2 converted the boronic acid to the potassium trifluoroborate salt, which was recrystallized from an acetone/pentane solution and isolated in 56% yield. Stirring equimolar mixtures of the ligand and 18-crown-6 in toluene for 24 h followed by removal of the volatiles yielded pure [K-18-Crown-6][4-BF_3-*t*-BuG(OH)] as a beige solid. It was then deprotonated with 1.2 equivalent of KO*t*Bu in a CH_3CN solution at room temperature. The ligand and all the intermediates were completely characterized by NMR spectroscopy, elemental analysis and in the case of the proteo ligand **c** (X = H, Scheme 2) by X-ray diffraction studies.

The molecular structure of the proteo ligand **c** is shown in Figure 1; benzene molecules (1.5) and water cocrystallized with in the centro-symmetric P-1 space group. The structure shows that the potassium cation is strongly bonded by the six oxygens of the crown ether (average K−O distance: 2.87(7) Å) and a water molecule). A fluorine atom (F2) also comes to close contact with the potassium (K1−F2 distance: 2.6570(13) Å) while the two other fluorine atoms are much further away (more than 3.15 Å). As a result, boron−fluorine distances are not equivalent, B1−F2 distance being elongated (B1−F2: 1.426 Å > B1−F1 ≈ B1−F3: 1.402 Å). Metrical parameters in the rest of the structure are normal. The diisopropylphenyl group is roughly perpendicular to the phenolic group and the acidic proton of the phenol function is oriented toward the nitrogen of the imine.

Palladium methyl complexes incorporating these ligands and stabilized by coordinated acetonitrile can be prepared via

Scheme 3



reaction of alkali metal salts of the ligands and (COD)Pd(Cl)-Me[32] as shown in Scheme 3. Acetonitrile was condensed (−78 °C) onto a mixture of the deprotonated ligand and one equivalent of (COD)Pd(Cl)Me. After the solution was warmed to room temperature and stirred for a few hours, filtration gave a clear, bright yellow solution from which pure compounds **1-NCCH$_3$** were isolated as light yellow solids after removal of the solvent in vacuo. The main difference between the neutral complexes **1a,b-NCCH$_3$** and the anionic **1c-NCCH$_3$** is their solubility properties, **1a,b-NCCH$_3$** being completely soluble in hexanes, while **1c-NCCH$_3$** needing more polar solvents to dissolve. Compounds **1-NCCH$_3$** are stable as solids when stored under inert atmosphere and low temperature, but exhibit a tendency to decompose at room temperature in solvents other than acetonitrile, depositing Pd(0). Typically, solutions of compounds **1-NCCH$_3$** were kept at −78 °C and NMR spectra measured at −20 °C to prevent decomposition. The ^{1}H NMR signals for the isopropyl group, as well as the Pd−Me moiety provide good spectroscopic handles to confirm the preparation of the complexes. When the ligands are not coordinated to the metal center, only one doublet is observed for the CH(CH_3)$_2$; upon coordination to the Pd, the rotation of the aryl group is hindered and two separate doublets are observed. The signals for the Pd−CH_3 group are found characteristically at higher field at 0.0 and −0.1 ppm for **1a,b-NCCH$_3$**, respectively and slightly further upfield at −0.22 ppm for anionic **1c-NCCH$_3$**. In nOe experiments, enhancement in the aryl isopropyl methines was observed upon irradiation of the palladium methyl group, while no enhancement in the *tert*-butyl group was seen. This indicates that in these compounds the Pd-methyl occupies the site trans to the phenoxide oxygen. Assignment of this structure is consistent with the results of Ziegler and co-workers, who have shown computationally that the isomer with Me trans to the phenoxide is the most stable isomer.

Crystallographic analysis of the structures of **1a-NCCH$_3$** and **1b-NCCH$_3$** confirm that the methyl groups occupy the position trans to the phenoxy donor in these compounds. Both **1a-NCCH$_3$** and **1b-NCCH$_3$** crystallize with two independent

(32) Preparation of (COD)Pd(Me)Cl: Rülke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier: C. J.; van Leeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769.

Table 1. Selected Bond Distances (Å) and Angles (deg) of **1a-NCCH$_3$** and **1b-NCCH$_3$**

parameter	**1a-NCCH$_3$**	parameter	**1b-NCCH$_3$**
Pd(1)−C(27)	2.021(4)	Pd(1)−C(1)	2.004(5)
Pd(1)−N(1)	1.978(3)	Pd(1)−N(1)	2.013(3)
Pd(1)−O(1)	2.050(3)	Pd(1)−O(1)	2.062(3)
Pd(1)−N(3)	2.018(4)	Pd(1)−N(2)	2.001(4)
N(2)−N(1)	1.285(4)	C(8)−N(1)	1.292(6)
N(3)−C(28)	1.136(5)	N(2)−C(25)	1.132(6)
O(1)−Pd(1)−N(1)	90.36(12)	O(1)−Pd(1)−N(1)	91.66(13)
N(1)−Pd(1)−C(27)	95.47(17)	N(1)−Pd(1)−C(1)	93.40(18)
C(27)−Pd(1)−N(3)	88.88(17)	C(1)−Pd(1)−N(2)	87.92(19)
N(3)−Pd(1)−O(1)	85.60(13)	N(2)−Pd(1)−O(1)	87.19(14)
O(1)−Pd(1)−C(27)	173.03(17)	O(1)−Pd(1)−C(1)	173.98(18)
N(1)−Pd(1)−N(3)	173.92(14)	N(1)−Pd(1)−N(2)	176.92(15)
Pd(1)−O(1)−C(1)	125.9(2)	Pd(1)−O(1)−C(2)	127.7(3)
O(1)−C(1)−C(2)	123.4(3)	O(1)−C(2)−C(7)	122.4(4)
C(1)−C(2)−N(2)	127.1(4)	C(2)−C(7)−C(8)	124.3(4)
C(2)−N(2)−N(1)	124.6(3)	C(7)−C(8)−N(1)	130.5(4)
N(2)−N(1)−Pd(1)	127.2(3)	C(8)−N(1)−Pd(1)	122.6(3)
Pd(1)−N(1)−C(15)−C(16)	−82.9(4)	Pd(1)−N(1)−C(13)−C(14)	78.6(4)
Pd(1)−N(1)−C(15)−C(20)	96.0(4)	Pd(1)−N(1)−C(13)−C(18)	−99.2(4)
N(2)−N(1)−C(15)−C(16)	92.6(4)	C(8)−N(1)−C(13)−C(14)	−98.4(5)
N(2)−N(1)−C(15)−C(20)	−88.5(5)	C(8)−N(1)−C(13)−C(18)	83.7(5)

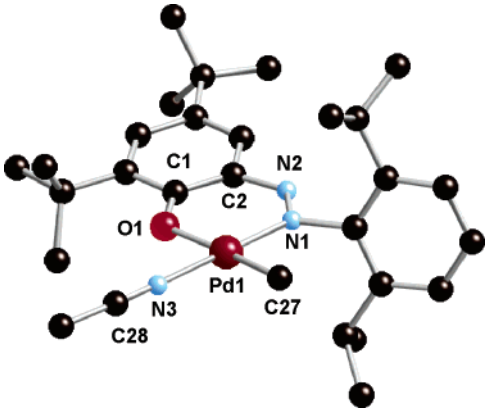


Figure 2. Crystalmaker diagram of the structure of **1a-NCCH$_3$**. See Table 1 for selected metrical data.

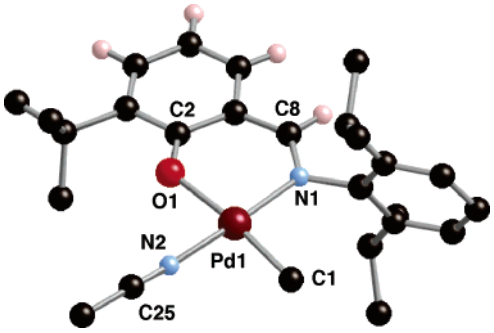


Figure 3. Crystalmaker diagram of the structure of **1b-NCCH$_3$**. See Table 1 for selected metrical data.

molecules in the unit cell, along with solvents of crystallization, but the metrical parameters within the two molecules do not differ significantly. Figure 2 shows the structure of **1a-NCCH$_3$**, while Figure 3 shows that of **1b-NCCH$_3$**; Table 1 gives a comparison of selected metrical parameters for the two related compounds. For both, the coordination environment around the Pd center is square planar with minimal distortion, the largest angle being the N(1)−Pd−CH$_3$ angle due to the sterically bulky *N*-aryl group. The Pd−O and Pd−N bonds are slightly shorter in the diazene complex **1a-NCCH$_3$**, indicating this ligand is a

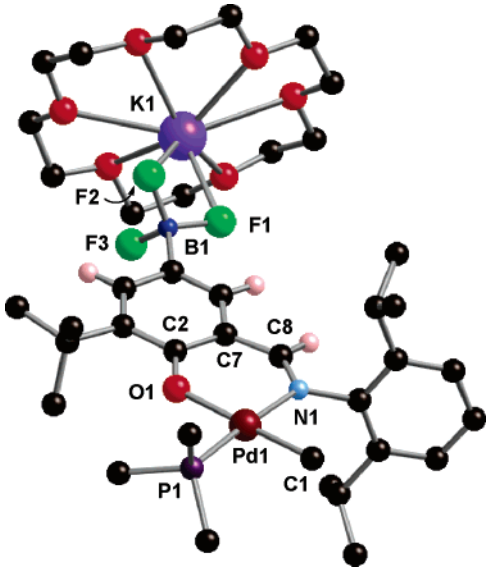


Figure 4. Crystalmaker diagram of the structure of **1c-PMe$_3$**. See Table 2 for selected metrical data.

marginally better donor; corresponding increases in the Pd−CH$_3$ and Pd−NCCH$_3$ distances are observed.

Ligand substitution reactions using PMe$_3$ or CO occur rapidly to produce the complexes **1-L**; in the case of CO, insertion to form the acyl complexes **2-CO** is facile. The phosphine complexes were fully characterized for identification purposes in experiments described below and are generally much more stable than the acetonitrile adducts toward deposition of Pd(0) in solution. In addition to characteristic resonances in the ^{1}H NMR spectra, they exhibit peaks in the ^{31}P NMR spectra in the regions around −3 ppm for L = PMe$_3$. The X-ray structure of complex **1c-PMe$_3$** was obtained and demonstrates that the ligand bearing the anionic borate center coordinates the Pd similarly to the parent ligand; the molecular structure is shown in Figure 4, while pertinent metrical data are given in Table 2. Aside from the presence of the −BF$_3$K(18-crown-6) moiety and the substitution of CH$_3$CN for PMe$_3$, the structure is geometrically identical and metrically quite similar to that observed for **1b-**

Table 2. Selected Bond Distances (Å) and Angles (deg) of **1c-PMe$_3$**

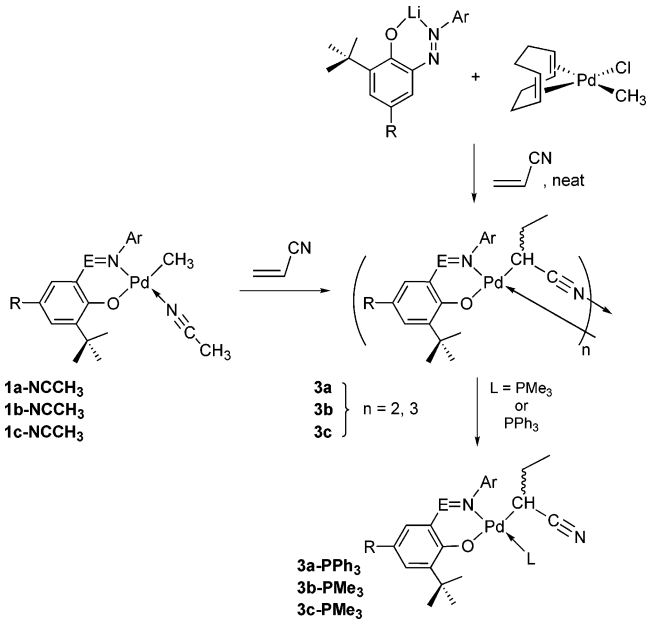
parameter	**1c-PMe$_3$**
Pd(1)−C(1)	2.041(5)
Pd(1)−N(1)	2.093(3)
Pd(1)−O(1)	2.097(3)
Pd(1)−P(1)	2.2273(13)
C(8)−N(1)	1.296(5)
C(5)−B(1)	1.602(7)
B(1)−F(1)	1.412(7)
B(1)−F(2)	1.386(8)
B(1)−F(3)	1.387(7)
K(1)−F(1)	2.716(3)
K(1)−F(2)	2.905(4)
K(1)−F(3)	3.125(4)
O(1)−Pd(1)−N(1)	89.27(13)
N(1)−Pd(1)−C(1)	92.36(17)
C(1)−Pd(1)−P(1)	85.41(15)
P(1)−Pd(1)−O(1)	93.07(9)
O(1)−Pd(1)−C(1)	177.08(19)
N(1)−Pd(1)−P(1)	176.50(11)
Pd(1)−O(1)−C(2)	129.0(3)
O(1)−C(2)−C(7)	122.5(4)
C(2)−C(7)−C(8)	125.0(4)
C(7)−C(8)−N(1)	130.4(4)
C(8)−N(1)−Pd(1)	122.9(3)
Pd(1)−N(1)−C(13)−C(14)	−99.7(4)
Pd(1)−N(1)−C(13)−C(18)	79.9(5)
C(8)−N(1)−C(13)−C(14)	79.5(5)
C(8)−N(1)−C(13)−C(18)	−100.9(5)

NCCH$_3$ (Figure 3). Slight elongation of the Pd−C, N and O bonds is observed in **1c-PMe$_3$**, but this may be due to the greater steric presence of the PMe$_3$ ligand in comparison to the more rodlike acetonitrile donor rather than any electronic perturbation caused by the anionic substituent.

The carbonyl derivatives were prepared to acquire a quantitative measure of the effect of the ligand on the π back-donating capacity of the palladium center. The reactions were monitored by ^{1}H NMR spectroscopy, which showed that compounds **1b,c-CO** rapidly formed at low temperature and then more slowly converted to the acyl carbonyl compound **2** over the course of a few hours. Carbonyl stretching frequencies for the coordinated CO ligand in compounds **2-CO** were 2088 cm^{-1} for **2b-CO** and 2085 cm^{-1} for anionic compound **2c-CO**. A comparison between the latter two indicates that the effect of the anionic BF$_3$ group on the electron density at Pd is not profound, but measurable. In comparison to cationic Pd complexes incorporating a hard NN donor set, these compounds are considerably more electron rich, since ν_{CO} values of ∼2120−2130 cm^{-1} are observed in the cationic systems.[26,33]

Insertion of Acrylonitrile Into Pd−Me Bonds. The acetonitrile adducts of compounds **1** all react with an excess of pure, dry AN to afford products that were determined to be oligomers of the product of 2,1 insertion in which the α-cyano alkyl group coordinates to the Pd center of another molecule (Scheme 4). In NMR tube reactions, free acetonitrile was apparent in the medium. Reactions were carried out in THF at room temperature and the products were isolated via evaporation of the volatiles and washed before analysis by NMR spectroscopy and mass spectrometry. Alternatively, the oligomeric product mixture containing the diazene ligand **a** could be generated directly from

Scheme 4



the lithium salt of the ligand and (COD)Pd(Cl)Me using AN as the solvent (Scheme 4). These observations all suggest that the α-cyano group is a stronger Lewis base than the free nitrile groups present, enthalpically favoring oligomerization.

While sparingly soluble in aromatic solvents, the products of these reactions were soluble in chlorinated solvents such as methylene chloride. The ^{1}H NMR spectra, however, were exceedingly complex due to the presence of both dimers and trimers (and possibly higher oligomers), each with the potential to consist of a mixture of diastereomers given that the α cyano carbon is chiral. Similar diastereomeric mixtures for dimers of chiral α-cyano Pd alkyls have been observed previously.[34]

The features of the spectra for the neutral compounds **3a** and **3b** were quite similar, particularly in the region associated with the isopropyl methine resonances, suggesting a similar constitution for these mixtures. In the ^{1}H NMR spectrum of salicylaldiminato derivative **3b**, the region associated with the aldimine proton (∼7.5 ppm) is quite informative. Five singlets are evident, a 1:1:1 group of three and another 1:1 group of two at approximately half the intensity of the first group. We tentatively assign the less intense pair to a 1:1 mixture of syn and anti dimers. In the case of a trimeric structure, because of the identical constitution of the three chiral centers, there are only two diastereomeric pairs of enantiomers possible, one in which the relative stereochemistry for each center is the same, and one in which two are the same and one is opposing. In the former (RRR/SSS), a C_3 axis exchanges the homotopic ligand environments and one singlet for the aldimine proton would be expected in the ^{1}H NMR spectrum. In the RRS/SSR pair,[35] however, the Pd centers cannot be exchanged by any symmetry operation and so three aldimine resonances in a 1:1:1 ratio is expected. Since this is what is observed, it appears that trimer formation in these systems is diastereoselective for this pair of enantiomers. Interestingly, the ^{1}H NMR spectrum for the anionic compound **3c** was somewhat simplified, and only two prominent

(33) Carfagna, C.; Gatti, G.; Martini, D.; Pettinari, C. *Organometallics* **2001**, *20*, 2175. (b) Carfagna, C.; Formica, M.; Gatti, G.; Musco, A.; Pierleoni, A. *Chem. Commun.* **1998**, 1113. (c) Binotti, B.; Carfagna, C.; Gatti, G.; Martini, D.; Mosca, L.; Pettinari, C. *Organometallics* **2003**, *22*, 1115.

(34) Ruiz, J.; Rodriguez, V.; Lopez, G.; Casabo, J.; Molins, E.; Miravitlles, C. *Organometallics* **1999**, *18*, 1177.

(35) This diastereomer is identical to the RSR/SRS and SSR/RSS pairs.

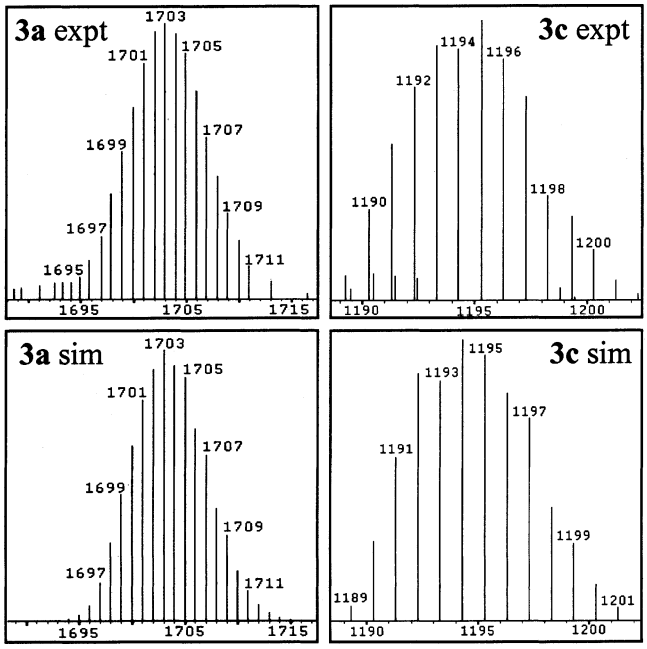


Figure 5. Left: experimental and simulated FD mass spectrum of **3a** ($Pd_3C_{90}H_{129}N_9O_3$) Right: experimental and simulated ESI mass spectrum of dimeric **3c** ($Pd_2C_{54}H_{70}N_4O_2B_2F_6K$).

aldimine peaks in an approximately 1:1 ratio were observed, suggesting that two diastereomeric dimers dominate the solution chemistry of this species.

The NMR spectroscopic evidence for the assignment of mainly dimers and trimers for compounds **3** was augmented by mass spectrometry data, which showed strong parent peaks corresponding to the trimer for **3a** ($M^+ = 1703$, FD MS) and dimer for the anionic complex **3c** ($M^- = 1195$, ESI MS).[36] Figure 5 shows the parent peaks for these two compounds along with the simulated spectra based on the expected isotopic distribution, showing excellent agreement in both cases. In the spectrum for **3a**, peaks at M = 1137 and 567 indicate the presence of the dimer and monomer, respectively; likely the monomer arises from fragmentation. The spectrum for the anionic complex **3c** contains no evidence for trimeric species but a peak at $M^+ = 508$ is indicative of a monomer fragment. The lack of evidence for the trimer is consistent with the solution NMR data which indicate that in **3c** the dimeric diasteromers dominate.

X-ray quality crystals were obtained from solutions of the diazene complex **3a** and analysis provided further confirmation of the assignments made on the basis of the NMR and MS data described above. The structure is shown in Figure 6 and selected metrical data is given in Table 3. The structure shows that insertion of AN has occurred with 2,1 regiochemistry, producing α-cyano propyl ligands that occupy the position trans to the phenoxy donor at each Pd center. Trimerization occurs through the lone pair of the α-cyano group. As suggested by the NMR spectroscopy for **3b**, the diastereomer observed for **3a** in the solid state is the RRS/SSR pair, rendering the Pd centers heterotopic. Despite their chemical inequivalence, the metrical parameters associated with each center are quite similar, and in addition are comparable to those found for **1a-NCCH$_3$** (Table 1). The Pd−C bonds are slightly longer than that observed in **1a-NCCH$_3$**, likely a reflection of the greater steric bulk of the α-cyano alkyl group vs methyl.

Treatment of mixtures **3** with one equivalent of PMe_3 or PPh_3 based on Pd resulted in breaking of the dimers and trimers into

(36) The parent peak for **3c** indicates loss of two 18-crown-6 molecules and one potassium ion is facile. Attempts to obtain ESI data for the neutral **3b** mixture were unsuccessful, but we assume on the basis of the similarity in the NMR data that the conclusions regarding the composition of oligomers **3a** can be extended to the salicylaldimine compounds **3b**.

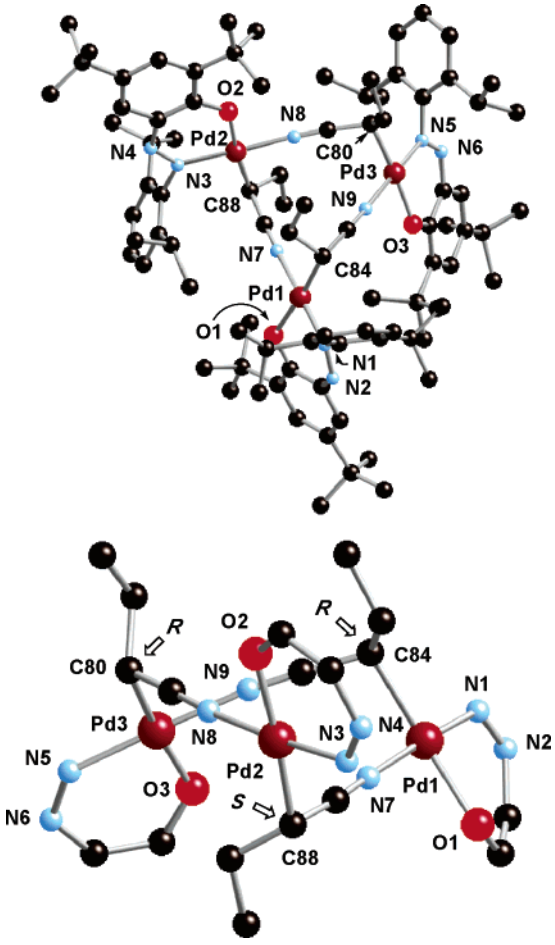


Figure 6. Crystalmaker diagram of the structure of the trimer of **3a**. Top, the full molecule; bottom, the Pd_3 core of the molecule. See Table 3 for selected metrical data.

Table 3. Selected Bond Distances (Å) and Angles (deg) of **3a**

parameter	3a	3a	3a
	Pd(1)	Pd(2)	Pd(3)
Pd−C	2.058(6)	2.073(7)	2.069(6)
Pd−N_{ligand}	1.979(5)	1.998(6)	1.960(6)
Pd−O(1)	2.012(4)	2.022(5)	2.030(4)
Pd−$N_{cyanoalkyl}$	2.005(6)	2.000(6)	2.008(6)
N−N_{ligand}	1.279(7)	1.285(8)	1.278(8)
O−Pd−N_{ligand}	88.33(19)	90.7(2)	90.1(2)
N_{ligand}−Pd−C	95.3(2)	95.0(3)	94.2(2)
C−Pd−$N_{cyanoalkyl}$	88.0(2)	88.6(2)	87.9(2)
$N_{cyanoalkyl}$−Pd−O	88.6(2)	85.8(2)	87.76(19)
O−Pd−C	174.5(2)	174.4(2)	175.0(2)
N_{ligand}−Pd−$N_{cyanoalkyl}$	175.3(2)	176.3(2)	177.9(2)
Pd−O−$C_{ipso(O)}$	122.4(3)	126.1(4)	125.4(3)
O−$C_{ipso(O)}$−$C_{ipso(N)}$	121.7(3)	122.2(4)	121.6(4)
$C_{ipso(O)}$−$C_{ipso(N)}$−N	126.9(3)	129.0(4)	129.5(4)
$C_{ipso(N)}$−N−N_{ligand}	122.1(5)	125.6(6)	123.1(5)
N−N_{ligand}−Pd	126.2(4)	126.3(5)	129.0(4)
Pd−$N_{cyanoalkyl}$−C	177.6(6)	174.8(6)	174.5(5)
$N_{cyanoalkyl}$−C−C_{Pd}	176.3(7)	176.0(7)	176.6(7)
Pd−C−CN	104.6(4)	101.6(4)	103.2(4)

phosphine stabilized monomers **3-PR$_3$** as shown in Scheme 4, significantly simplifying the NMR spectra since now a single species dominates in solution. In the case of PMe_3, addition of more than one equivalent of phosphine resulted in formation of Pd(0) species, so careful control of the phosphine stoichiometry is necessary in these reactions. Diagnostic patterns for the α-cyanopropyl group were found in the signal for the α-CH(CN) moiety, which coupled to the two diastereotopic methylene protons as well as the phosphine phosphorus atom, and the signal for the methyl group which exhibited coupling only to the methylene protons, appearing as a pseudo triplet. ^{31}P NMR chemical shifts were in the range expected for PMe_3 or PPh_3 complexes of a Pd alkyl complex with these ligands, suggesting that the alkyl group maintains its position trans to the phenoxy donor.

NMR Investigations of the Reactions of 1-NCCH$_3$ with AN. The complexities of AN insertion reactions are summarized in Scheme 1; the reaction is further complicated in the case of compounds **1-NCCH$_3$** due to the dissymmetry of the ligand donor, which creates the possibility of geometric isomers. However, in the presence of excess donor, interconversion of these isomers should be rapid[37] and in the discussion below, we assume that this is the case, given that for the most part a large excess of AN is employed. Thus, although insertion of AN into the Pd−Me bonds of compounds **1-NCCH$_3$** presumably leads to products with the α-cyanoalkyl group trans to the imine function of the ligand, these are not observed and isomerize rapidly to the more thermodynamically stable isomer with the alkyl trans to the phenoxy donor.

To gain further insight into the details concerning the reaction of AN with compounds **1-NCCH$_3$**, the reaction of **1b-NCCH$_3$** was examined by variable temperature ^{1}H NMR spectroscopy. Similar experiments with the diazene complex **1a-NCCH$_3$** and the anionic **1c-NCCH$_3$** indicated a qualitatively identical reaction course; for practical reasons (solubility issues, more spectroscopic information) we focus on the experiments utilizing **1b-NCCH$_3$** in the following discussion.

When **1b-NCCH$_3$** is reacted with 1.0 equiv of AN at −80 °C in CD_2Cl_2, signals for both free and bound $NCCH_3$ are observed, and two resonances at −0.26 and −0.30 ppm indicate the presence of two Pd−Me containing species in solution. The region for the AN vinyl protons shows two sets of resonances, one for free AN and one due to N-bound AN, shifted only by ∼0.2 ppm upfield of the resonances for free AN. Typically, π-bound AN exhibits more severely shifted resonances for these protons,[16,38] and no signals for π-bound AN are observed in any of these experiments. The relative intensities of the Pd−Me signals indicate that the ratio of **1b-NCCH$_3$** to **1b-*n*-AN** is about 1:1 at −80 °C. When the sample is warmed to −30 °C, the ratio of **1b-NCCH$_3$** to **1b-*n*-AN** changes slightly and a third Pd−Me species appears (∼10% total); since it is in this temperature regime and above that insertion of AN ensues, we assign this peak, which intensifies as the equivalency of AN used decreases to 0.5, to the Pd−Me containing dimers **4b−L** shown in Scheme 5. Although free AN and acetonitrile are present, this dimer forms because the α cyano group is the most basic nitrile group in the system. Further warming results in consumption of all the AN in the system and formation of dimers and trimers **3a**. When only 0.5 equiv of AN are used, **4b-*n*-NCCH$_3$** can also be identified among the final products.

When **1b-NCCH$_3$** is reacted with a 10−190-fold excess of AN at −78 °C, the equilibrium at the top of Scheme 5 shifts completely to **1b-*n*-AN**; all of the acetonitrile present is free by ^{1}H NMR spectroscopy. As these samples are warmed to temperatures where product formation is observed, the Pd-Me

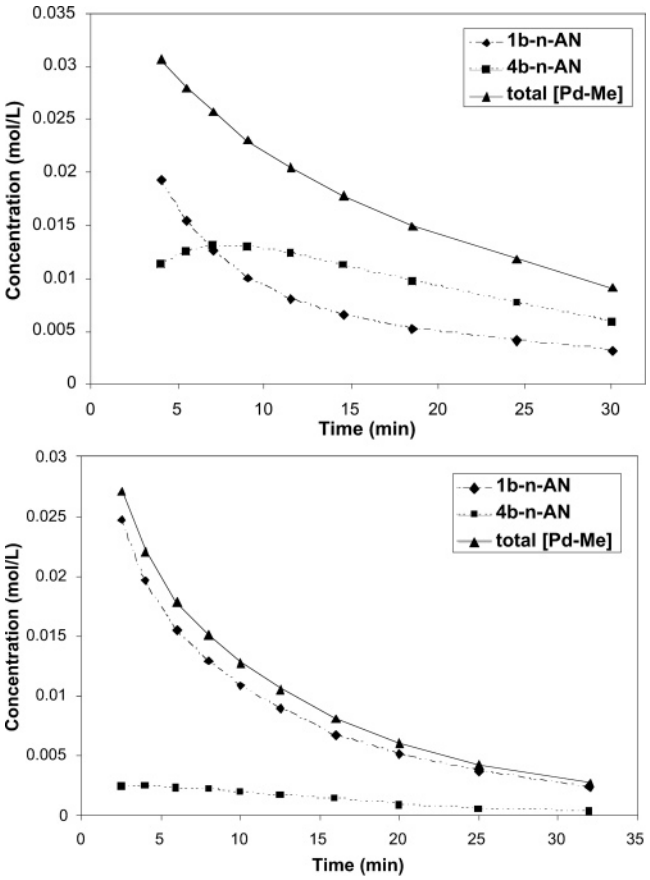
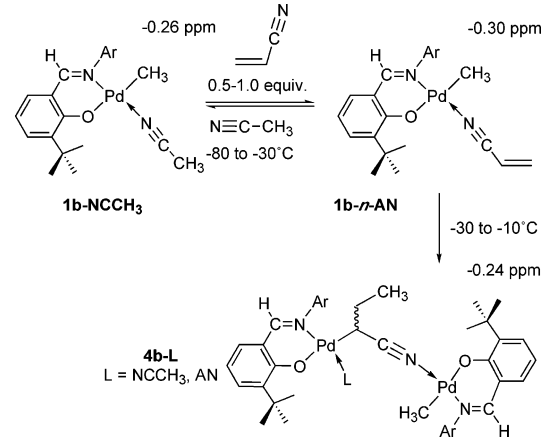


Figure 7. (a) Concentration vs Time plot for **1b-*n*-AN** and **4b-*n*-AN** (10 equiv of AN, 3.1 °C). (b) Concentration vs Time plot for **1b-*n*-AN** and **4b-*n*-AN** (190 equiv of AN, 3.1 °C).

Scheme 5



(37) While four coordinate complexes of Ni(II) are subject to rapid isomerization via tetrahedral intermediates, analogous Pd(II) compounds are generally more resistant to isomerization in the absence of excess donor ligand; however, interchange of these isomers by an associative mechanism is facile when such donor is present. (b) Jun, H.; Young Jr., V. G.; Angelici, R. J. *Organometallics* **1994**, *13*, 2444. (c) Wakatsuki, Y.; Yamazaki, H.; Grutsch, P. A.; Santhanam, M.; Kutal, C. *J. Am. Chem. Soc.* **1985**, *107*, 8153.

(38) See for example: Albano, V. G.; Castellari, C.; Cucciolito, M. E.; Panunzi, A.; Vitagliano, A. *Organometallics* **1990**, *9*, 1269.

Table 4. Observed Rate Constants for the Reactions of Compounds **1** with AN

complex	AN (equiv)	T (°C)	k_{obs} ($\times 10^{-5}$) (M^{-1})
1b-NCCH$_3$	20	−22.8	4.83
1b-NCCH$_3$	20	−15.0	13.0
1b-NCCH$_3$	20	−5.0	39.3
1b-NCCH$_3$	20	3.1	95.8
1b-NCCH$_3$	20	9.8	193
1b-NCCH$_3$	100	−22.8	8.5
1b-NCCH$_3$	100	−15.0	18.2
1b-NCCH$_3$	100	−5.0	65.8
1b-NCCH$_3$	100	3.1	123.0
1b-NCCH$_3$	100	9.8	267.5
1b-NCCH$_3$	10	3.1	75.5
1b-NCCH$_3$	40	3.1	108.3
1b-NCCH$_3$	60	3.1	117
1b-NCCH$_3$	80	3.1	120.8
1b-NCCH$_3$	190	3.1	127.2
1c-NCCH$_3$	20	3.1	215
1c-NCCH$_3$	100	3.1	316.8

signal for **1b-*n*-AN** begins to diminish, while that for the dimer **4b-*n*-AN** increases to a maximum and then disappears as the reaction approaches completion. At low concentrations of AN, the waxing and waning of **4b-*n*-AN** is more prominent; a typical concentration vs time plot for the Pd−Me containing species is shown in Figure 7a. However, at high loadings of AN, **4b** never comprises more than 5% of the total concentration of Pd−Me present (Figure 7b).

Observed rate constants for the disappearance of Pd-Me can be evaluated by integration of the signals for both **1b-*n*-AN** and **4b-*n*-AN** and constructing pseudo first-order plots on the basis of the disappearance of total [Pd-Me].[39] These plots are linear over the course of the reaction, and k_{obs} may be evaluated as a function of [AN]; values for k_{obs} in all of these experiments are collected in Table 4. A plot of k_{obs} vs [AN] (Figure 8a) shows saturation behavior, with saturation being reached at about 100 equiv of AN at 3.1 °C. These results may be interpreted on the basis of the mechanism depicted in Scheme 6. In the presence of an excess of AN, formation of **1b-*n*-AN** is essentially quantitative and upon warming to the temperature regime where product formation ensues, **1b-*n*-AN** is in equilibrium with the (unobserved) π bound isomer **1b-*p*-AN** with an equilibrium constant K_{eq}. This species undergoes rapid insertion to give the transiently stable insertion product, which rapidly coordinates AN and in the process isomerizes to **3b-*n*-AN**. This species can undergo oligomerization to dimers and trimer **3b**, or react with **1b-*n*-AN** to give the dimeric intermediate Pd−Me complex **4b-*n*-AN**, which we observe spectroscopically. As the concentration of this species builds up, it can react with free AN to generate one equivalent of **3b-*n*-AN**, which forms product, and one equivalent of **1b-*n*-AN** and re-enters the reaction scheme. As the concentration of AN increases, then, the persistence of **4b-*n*-AN** diminishes.

Although an inverse plot of $1/k_{obs}$ vs 1/[AN] (Figure 8b) is linear, the complicated nature of the reaction scheme presented in Scheme 6 (in particular the effect of **4b-*n*-AN** on the equilibrium K_{eq}) muddies the interpretation of this plot and does not necessarily allow for straightforward evaluation of K_{eq} and k_{ins}.[40] Clearly, however, at high [AN], where the concentration build-up of **4b-*n*-AN** is negligible over the course of the reaction, and the equilibrium between **1b-*n*-AN** and **1b-*p*-AN** is saturated, k_{obs} approaches k_{ins}. By evaluation of k_{obs} at various temperatures under near saturation conditions (100 equivalents of AN), an Eyring plot (Figure 9) can be constructed and the activation parameters of $\Delta H^{\ddagger} = 14.4(5)$ kcal mol^{-1} and $\Delta S^{\ddagger} = -19(5)$ eu for k_{ins} extracted. This corresponds to a $\Delta G^{\ddagger}$ of ∼20.2

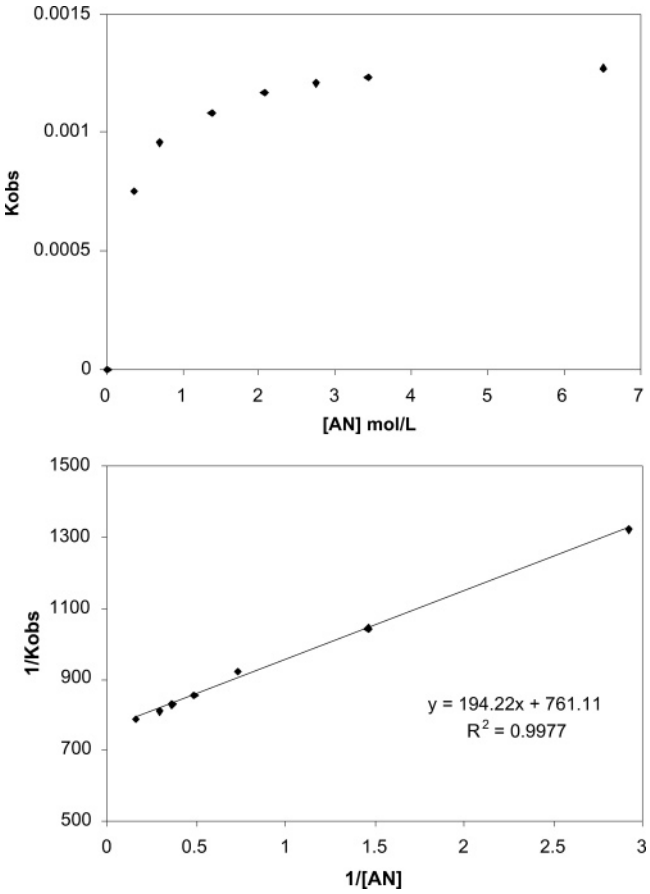
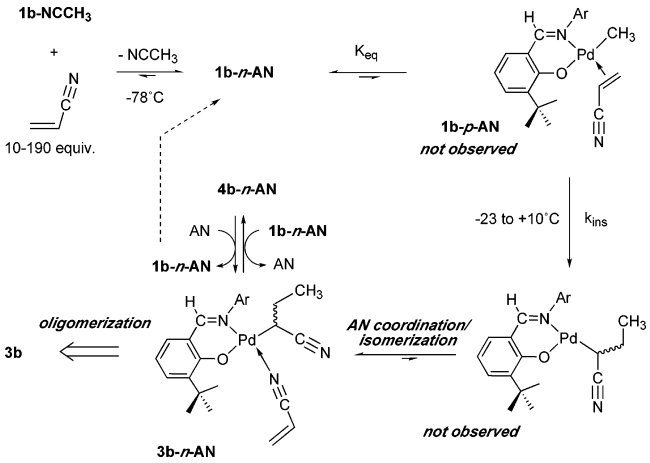


Figure 8. (a) Plot of k_{obs} vs [AN] in the reaction of **1b-*n*-AN** with AN. (b) Plot of $1/k_{obs}$ vs 1/[AN] in the reaction of **1b-*n*-AN** with AN.

Scheme 6



(39) Treatment of the data in this way is a simplification given that formation and involvement of the dimer **4b-*n*-AN** modifies the order in [Pd−Me] somewhat. However, pseudo first order plots constructed by monitoring the disappearance of only **1b-*n*-AN** exhibit curvature, while inclusion of the Pd-Me signal for **4b-*n*-AN** leads to linear plots.

(40) Wilkins, R. G. *The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes;* Alyn and Bacon, Inc., Boston, 1974; pp 26−31.

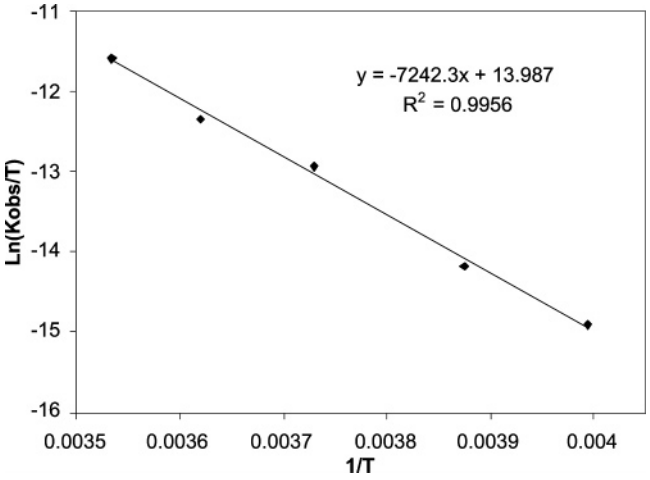


Figure 9. Eyring plot for the disappearance of **1b-*n*-AN** under saturation conditions at various temperatures.

kcal mol^{-1} at 25 °C. Although the $\Delta S^{\ddagger}$ value is subject to considerable experimental uncertainty, given the narrow temperature range we were able to access, it is comparable to that reported by Brookhart et al. (−14(7) eu) for the insertion of π bound methyl acrylate into the Pd−Me bond of a cationic diimine complex akin to that shown in Chart 1.[4b] The overall barrier is slightly higher than that calculated (17.6 kcal mol^{-1}) by Ziegler et al.[22d] and that found by Brookhart et al. for the insertion of methyl acrylate (17.4 kcal mol^{-1}) in the cationic compounds.[4b] Interestingly, in some of Brookhart's systems, O-bound methyl acrylate was observed at low temperatures, but for this carbonyl containing monomer, the isomerization to the π-bound species necessary for insertion has a comparable or slightly lower barrier than that for insertion. In the AN system, it appears that isomerization of **1b-*n*-AN** to **1b-*p*-AN** is rate limiting.[41] Given the differences in coordination geometry for these two polar monomers (i.e., bent for the O-bound methyl acrylate vs linear for the N-bound AN) this is not too surprising.

Relative Rates of Insertion in Neutral vs. Anionic Complexes. The effect of charge on the overall rate of insertion is of interest in designing compounds that exhibit facile insertion rates. For example, while the character of the reactions of cationic Pd-Me complexes, where N-bound AN is even more thermodynamically favored, appears to be similar to these reactions, overall insertion rates are somewhat slower.[26] Given this trend, complexes bearing an anionic charge should encourage π-bonding (i.e., increase K_{eq}) and increase the overall rate of insertion.

The ionic nature of compound **1c-NCCH$_3$** made monitoring the reaction with AN somewhat more technically challenging than for the neutral **1b-NCCH$_3$** as described above, but we were able to obtain values for k_{obs} under nonsaturation (20 equivalents of AN) and near-saturation (100 equiv) conditions. In both cases, the observed rate constants were nearly twice as large as those observed for the neutral complex under identical conditions (Table 4), showing that the ligand bearing the anionic group imparts a positive influence on the kinetics of AN insertion into the Pd−Me bond. These observations were corroborated by the experiment outlined in Scheme 7, a competition experiment designed to give a direct comparison of the relative rates of insertion of AN into the Pd-Me bonds of **1b-NCCH$_3$** and **1c-NCCH$_3$** by setting up a competition for 1 equiv of AN and the two complexes. To distinguish between the two, complex **1b-NCCH$_3$** was selectively deuterium labeled in the Pd−Me position, yielding ***d$_3$*-1b-NCCH$_3$**. A 1:1 mixture of this species and **1c-NCCH$_3$** was treated with one equivalent of AN (0.5 equiv based on total Pd) and allowed to form a complex mixture of unreacted compounds **1**, product oligomers ***d$_3$*-3** and mixed dimers **4**. These mixtures were then treated with 2 equiv of PMe_3 to yield the more simple mixture shown to the right of Scheme 7. As shown in Figure 10, the ratio of ***d$_3$*-3b-PMe$_3$** to ***d$_3$*-1b-PMe$_3$** was determined by ^{2}H NMR spectroscopy to be 0.39:0.61, while the ratios of ***d$_3$*-1b-PMe$_3$** to **1c-PMe$_3$** and ***d$_3$*-3b-PMe$_3$** to **3c-PMe$_3$** were found to be 0.67:0.33 and 0.42:0.58 by ^{31}P NMR spectroscopy. These assignments were possible since each of these compounds were made and identified separately as described above in Schemes 3 and 4.

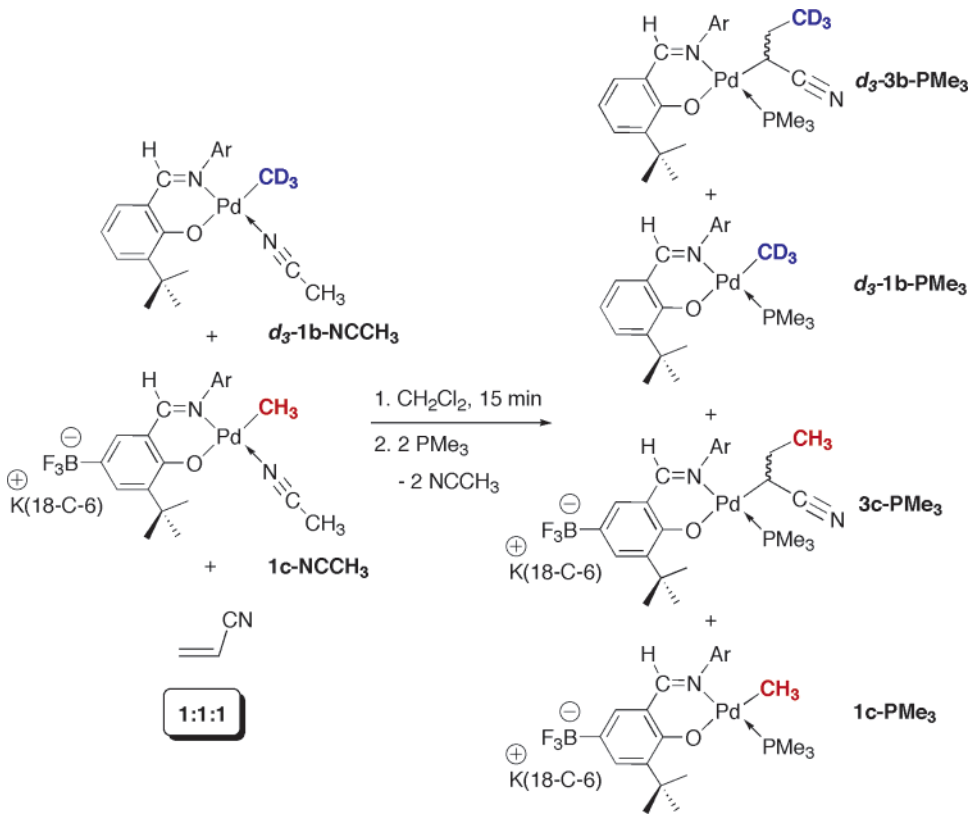
Taking the average of the ratios obtained shows that the insertion of AN into the Pd−Me bond of the complex containing the borate functionalized ligand occurs with an overall rate roughly 1.6× as fast as the insertion into the Pd−Me bond of the conventional neutral catalyst. This is consistent with the ratio of k_{obs} obtained by direct monitoring of the two reactions as described above.

These experiments do not identify the reason for the increased macroscopic rate of insertion vis-à-vis improved access to the π-bound isomer of the AN complex (K_{eq}), or an enhanced migratory insertion rate (k_{ins}), but do illustrate that the concept of using anionically charged catalysts to improve reactivity toward polar comonomers is moderately successful. Computational results suggest that the largest effect of increasing the negative charge on the complex should have a positive effect on K_{eq}, but increase the barrier to insertion.[22e] Since we are unable to reliably deconvolute these two parameters from the data at hand, we cannot comment on the most likely origin of the higher rates observed for the anionic compound **1c-NCCH$_3$**. However, we note that based on the n_{CO} stretches in compounds **2b,c-CO**, the change in electron density at the metal center is slight upon introduction of the BF_3K(18-crown-6) group and thus perhaps the effect on K_{eq} would be expected to be minimal. The observation of larger rates for k_{obs} under near saturation conditions (AN = 100 equiv) suggests that the insertion rate may be inherently larger for the complex supported by borate bearing ligand **c** in comparison to its noncharged analogue. In any case, the result is encouraging in light of the apparently modest effect on the electron density at the metal that the positioning and nature of the anionic group (BF_3) has in this case. Situating the anionic group in a position closer to the metal center may lead to enhanced effects in this regard.

Conclusions. The development of catalysts capable of incorporating polar comonomers, and particularly acrylate derivatives, requires a detailed understanding of the factors that favor π-coordination of these monomers and insertion via a conventional four centered coordination mechanism. It appears based on this and other studies[22,26] that the barriers to insertion for such monomers are not the crux of the problem, but that

(41) Little is known about the mechanism of this isomerization, but it appears to be influenced by the presence of free [AN], suggesting it is associative in character. A pathway involving bimolecular species with bridging AN ligands is conceivable, since complexes with such bridging AN ligands are known.[41b,c] Further studies on the nature of this isomerization process are underway. (b) Johmann, F.; tom Dieck, H.; Kruger, C.; Tsay, Y. H. *J. Organomet. Chem.* **1979**, *171*, 353. (c) Massaux, M.; le Bihan, M.-T.; Chevalier, R. *Acta Cryst. Sect. B* **1977**, *33*, 2084.

Scheme 7



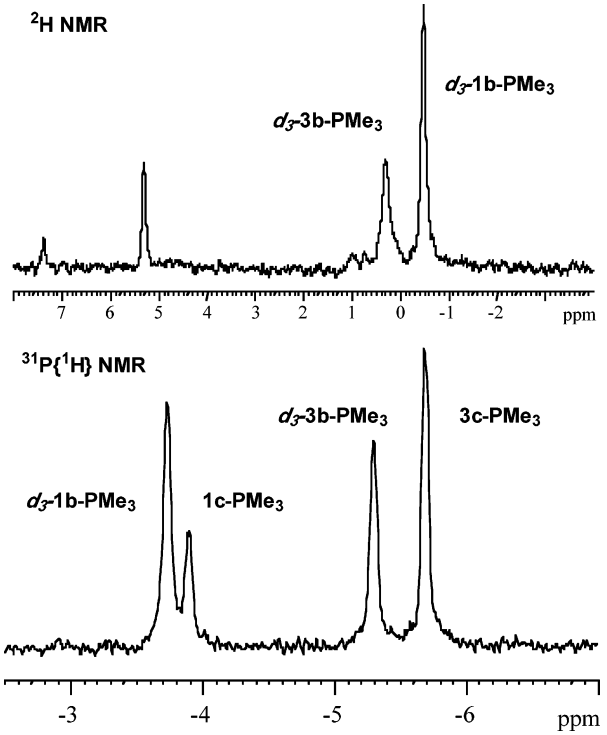


Figure 10. ^{2}H (top) and $^{31}P\{^{1}H\}$ (bottom) NMR spectra for the competition experiment depicted in Scheme 7.

the dominance of coordination of polar functions (both in the monomer and in the products of insertion) must be overcome to give insertion a chance to occur with any degree of efficiency. To this end, we have shown that neutral Pd(II) methyl compounds, while favoring N-bound acrylonitrile, undergo isomerization to the π-bound isomer[22] which undergoes rapid 2,1 insertion to give α-cyanopropyl derivatives that readily associate to give dimers and trimers via the α-cyano groups. Furthermore, we have shown that incorporation of an anionically charged group into the salicylaldiminato ligand framework can enhance the overall insertion rate for AN, although the effect is modest in the system studied. New generation negatively charged ligands are being explored in an attempt to increase this rate enhancement further.

While we have demonstrated that it is possible to observe 2,1 insertion of AN into Pd−carbon bonds, this is just the first challenge in developing a transition metal catalyst capable of copolymerizing AN and related monomers with, for example, ethylene. The dimers and trimers formed after insertion are quite robust and although they can be ruptured with strong donors such as PMe_3, they do not react with ethylene or carbon monoxide under conditions where they do not decompose first. Furthermore, preliminary experiments utilizing compounds **3a,b-PR$_3$** indicate that these species are also unreactive toward small molecules that might be expected to undergo insertion into the Pd-α-cyanopropyl bond. Thus, while a first insertion of AN can be observed and enhanced by going from cationic to neutral to anionic complexes, subsequent chain growth reactions appear to become more energetic challenging as the charge on the metal increases. Interestingly, Jordan and co-workers have observed insertion of CO into an α-cyanoalkyl derived from AN insertion into the Pd−Me bond of a cationic complex with a strongly electron donating N_2 ligand set,[26] suggesting that a subtle balance of charge, or an ability to modulate the charge at the metal may prove a useful strategy for further catalyst design modification.

Experimental Section

General Procedures. All operations were performed under a purified argon atmosphere using glovebox or vacuum line techniques. Toluene,

Table 5. Crystal Data, Data Collection and Structure Refinement Parameters

	anionic l	**1a-NCCH$_3$**	**1b-NCCH$_3$**	**1c-PMe$_3$**	**3a**
formula	$C_{35}H_{54}BF_3KNO_7$. 1.5 C_6D_6 · 0.5 H_2O	$C_{29}H_{43}N_3OPd$. 0.5 *n*-hexane	$C_{26}H_{36}N_2OPd$. 0.22 CH_2Cl_2	$C_{39}H_{65}BF_3KNO_7P$ Pd. 1.5 CH_3CN	$C_{90}H_{128}N_9O_3Pd_3$ x CH_2Cl_2
cryst color/habit	beige block	yellow needle	yellow needle	yellow block	yellow block
dimensions, mm	0.20 × 0.15 × 0.09	0.40 × 0.03 × 0.01	0.20 × 0.06 × 0.04	0.14 × 0.11 × 0.10	0.10 × 0.10 × 0.02
symmetry	triclinic	triclinic	orthorombic	triclinic	monoclinic
space group	P −1	P −1	Pbcn	P −1	P 2_1/c
a, Å	8.5510(10)	13.9617(12)	23.574(2)	14.004(4)	23.5116(12)
b, Å	10.112(2)	14.0737(11)	14.380(3)	16.841(5)	17.1359(8)
c, Å	26.361(5)	17.2592(14)	31.490(4)	21.172(6)	27.4042(14)
α, deg	91.776(5)	93.220(4)		85.573(17)	
β, deg	98.641(5)	110.871(3)		80.042(16)	113.717(2)
γ, deg	99.773(10)	98.433(3)		88.58(2)	
volume, Å^3	2217.1(7)	3112.9(4)	10675(3)	4903(2)	10108.5(9)
Z	2	4	16	4	4
D(calcd) (g cm^{-1})	1.249	1.230	1.288	1.308	1.119
diffractometer	Nonius KappaCCD	Siemens P4	Nonius KappaCCD	Nonius KappaCCD	Siemens P4
T (K)	173(2)	153(2)	173(2)	173(2)	153(2)
λ, Å (Mo Kα)	0.71073	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	0.18	0.621	0.757	0.553	0.573
scan type	*ω* scan	*ω* scan	*ω* scan	*ω* scan	*ω* scan
θ_{max}, °	27.5	31.53	25.0	27.5	28.00
h,*k*,*l* range	$-11 \le h \le 11$	$-20 \le h \le 20$	$-28 \le h \le 27$	$-18 \le h \le 18$	$-31 \le h \le 31$
	$-13 \le k \le 13$	$-20 \le k \le 20$	$-17 \le k \le 17$	$-21 \le k \le 21$	$-22 \le k \le 22$
	$-34 \le l \le 34$	$-24 \le l \le 24$	$-37 \le l \le 37$	$-27 \le l \le 27$	$-36 \le l \le 36$
refl collected/ind.	18589/10103	47987/19140	17626/9370	40813/21810	115473/24308
absorption correction	multiscan method	SADABS	multiscan method	multiscan method	SADABS
T (min, max)	0.964, 0.984	0.670673, 1.00000	0.863, 0.970	0.927, 0.947	0.548361, 1.00000
R, w*R*2	0.048, 0.104	0.0496, 0.0898	0.045, 0.109	0.063, 0.125	0.0816, 0.1919
GOF	1.00	0.765	1.06	1.09	0.939

Hexane, and THF were dried and purified by passing through activated alumina and Q5 columns[42] or have been purchased dry form Aldrich. Dichloromethane and acetonitrile were dried over CaH_2 and distilled under reduced pressure. Deuterated NMR solvents: d_2-dichloromethane (CD_2Cl_2), d_3-acetonitrile (CD_3CN), and *d*-chloroform ($CDCl_3$) were dried and distilled over CaH_2. ^{1}H, ^{2}H, ^{13}C, and ^{31}P NMR 1D and 2D-experiments were performed on Bruker AC-200, AMX-300, DRV-400, DPX400, and DRX700 spectrometers. Data are given in ppm using the residual solvent signals or internal TMS for calibration of the ^{1}H, ^{2}H, and ^{13}C spectra. ^{31}P spectra were referenced to external H_3PO_4. Elemental analyses were performed in the microanalytical laboratory of the Department of Chemistry (University of Calgary) or at the Bayer Industry Sevices laboratory for element- and water analysis (Bayer AG, Leverkusen). IR spectra were recorded on a Nicolet NEXUS 470 FT-IR spectrometer using KBr plates and given in reciprocal centimeters (cm^{-1}). UV−Vis-Spectra were recorded on a Varian Cary 4 spectrometer at 25 °C. X-ray crystallography was performed on suitable crystals coated in paratone or perfluoropolyether oil and mounted on a Nonius KappaCCD diffractometer (University of Calgary) or a Siemens P4 diffractometer equipped with a SMART-CCD-1000 area detector, a MACScience Co. rotating anode, and a Siemens LT2 low-temperature device (Bayer AG). Crystal data and refinement details are given in Table 5. Field desorption mass spectrometry (FD−MS) analyses were carried out with a MAT 900 double focusing magnetic sector instrument (ThermoFinnigan Inc., San Jose, CA, USA/ThermoFinnigan MAT GmbH, Bremen, Germany) equipped with PATRIC-detector, while Electron spray ionization mass spectrometry (ESI−MS) analyzes were carried out on a Bruker Esquire 3000 instrument equipped with an Agilent *model 1100* LC source. (COD)Pd(Me)Cl[32] was prepared by literature procedures.

Synthesis of 2,4-Di*tert*-butyl-6-[2,6-diisopropyl-phenylazo)phenol [N$_2$,OH]. 2,6-diisopropylaniline (20 mmol), isoamylnitrite (2.9 g, 3.4 mL, 25 mmol) and BF_3·OEt_2 (3.1 g, 2.8 mL, 22 mmol) were mixed in CH_2Cl_2 (200 mL) at −10 °C. Within 1 h, the diazonium salt precipitated and was isolated by filtration at −10 °C. The diazonium salt was then suspended in THF (50 mL) at −20 °C and transferred onto a basic solution of sodium phenolate in ethanol/water prepared by dissolving the phenol (20 mmol) in a minimum amount of ethanol and adding NaOH (10 g, 250 mmol) dissolved in 100 mL water. The reaction mixture was warmed to 25 °C and stirred for 15 h obtaining a system with two phases. Hexane (50 mL) was added. The organic layer was separated washed first with 3 M HCl and then successive portions of water until neutralized. The organic phase was dried with Na_2SO_4 and all volatiles removed under high vacuum. The dye was isolated by flash chromatography (silica gel, hexane/CH_2Cl_2 3/1). A pure compound was obtained by crystallization from methanol at −20 °C which was dried in high vacuum over P_2O_5. Yield: 70%. Mp.: 82 °C. ^{1}H NMR ($CDCl_3$): *δ* (ppm) 13.2 (1H, O*H*), 7.80 (s, 1H, Ar*H*), 7.50 (s, 1H, Ar*H*), 7.25−7.32 (m, 3H, Ar*H*), 3.05 (septet, 2H, $^3J_{H-H}$ = 7.8 Hz, *i*-Pr C*H*), 1.49 (s, 9H, *t*-Bu*H*), 1.37 (s, 9H, *t*-Bu*H*), 1.20 (d, 12H, $^3J_{H-H}$ = 7.8 Hz, *i*-Pr C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): *δ* (ppm) 149.8 (Ar), 148.5 (Ar), 141.3 (Ar), 140.2 (Ar), 137.9 (Ar), 136.9 (Ar), 128.6 (Ar *C*H), 128.2 (Ar *C*H), 127.7 (Ar *C*H), 123.7 (Ar *C*H), 35.4 (*t*-Bu *C*), 34.3 (*t*-Bu *C*), 31.4 (*t*-Bu *C*H$_3$), 29.5 (*t*-Bu *C*H$_3$), 27.9 (*i*-Pr *C*H), 23.7 (*i*-Pr *C*H$_3$,). Anal. for $C_{26}H_{38}N_2O$: C, 79.0; H, 10.4; N, 6.9; Calcd: C, 79.14; H, 9.71; N, 7.10.

Synthesis of Lithio-2,4-Di-*tert*-butyl-6-[2,6-diisopropyl-phenylazo)phenolate [N$_2$,O]Li. The azo dye, [N$_2$,OH], (14.2 mmol) was dissolved in 150 mL THF and cooled to −78 °C. *n*-BuLi (2.7 M solution in heptane, 5.8 mL, 15.6 mmol) was added and the reaction mixture was stirred for 1 h at −78 °C. After being warmed to 25 °C, all of the volatiles were removed under high vacuum, and the residue was dissolved in 60 mL *n*-hexane. The pure compound was obtained by crystallization at −20 °C. After isolation and drying under high vacuum, it could be used without any further purification. Yield: quantitative.

Synthesis of 5-Bromo-3-*tert*-butyl-2-hydroxy-benzaldehyde). Bromine (8.025 g, 50.2 mmol) in 15 mL of 1,2-dichloroethane was added over 2 h to a stirred solution of 3-*tert*-butyl-2-hydroxy-benzaldehyde (9.0 g, 50.2 mmol) in 25 mL of 1,2-dichloroethane at 0 °C. Further stirring (1 h) and removal of the volatiles yielded crude 5-bromo-3-

(42) Otwinowski, Z.; Minor, W. *Methods Enzymol*. **1997**, *276*, 307.

tert-butyl-2-hydroxy-benzaldehyde (12.65 g, 98% yield) as a beige solid. Purification can be achieved by chromatography (silica gel, hex/ethyl acetate). ^{1}H NMR ($CDCl_3$): δ (ppm) 11.74 (s, 1H, O*H*), 9.82 (s, 1H, imine *H*), 7.59 (d, 1H, $^4J_{H-H}$ = 2.44 Hz, Ar*H*), 7.52 (d, 1H, $^4J_{H-H}$ = 2.40 Hz, Ar*H*), 1.41 (s, 9H, *t*-Bu*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 196.94 (*C*═O), 160.17 (*C*−OH), 141.10 (*C*−*t*Bu), 136.95, 133.58, 121.65 (*C*−CHO), 111.11 (*C*−Br), 34.90 (*t*-Bu *C*), 28.98 (*t*-Bu *C*H_3). Anal. for $C_{11}H_{13}BrO_2$: C, 51.59; H, 5.11. Calcd: C, 51.38; H, 5.10.

Synthesis of 4-Bromo-2-*tert*-butyl-6-[(2,6-diisopropyl-phenylimino)-methyl]-phenol. 5-Bromo-3-*tert*-butyl-2-hydroxy-benzaldehyde (3.0 g, 11.7 mmol) and 2,6-diisopropylaniline (2.76 g, 15.5 mmol) were stirred in 20 mL of methanol for 24 h at room temperature. Removal of all the volatiles and purification by column (silica gel, hexanes) yielded pure 4-Bromo-2-*tert*-butyl-6-[(2,6-diisopropyl-phenylimino)-methyl]-phenol as a bright yellow solid (2.70 g, 56% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 13.70 (s, 1H, O*H*), 8.25 (s, 1H, imine *H*), 7.51 (d, 1H, $^4J_{H-H}$ = 2.44 Hz, Ar*H*), 7.33 (d, 1H, $^4J_{H-H}$ = 2.48 Hz, Ar*H*), 7.21 (s, 3H, ArH), 3.00 (septet, 2H, $^3J_{H-H}$ = 6.88 Hz, *i*-Pr C*H*), 1.50 (s, 9H, *t*-Bu*H*), 1.21 (d, 12H, $^3J_{H-H}$ = 6.88 Hz, *i*-Pr CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 166.06 (*C*═N), 159.75 (*C*−OH), 145.79 (*C*−N), 140.53 (*C*-*t*Bu), 138.75 (*C*−*i*Pr), 133.24, 132.29, 125.65, 123.35, 119.78 (*C*−C═N), 110.14 (*C*-Br), 35.23 (*t*-Bu *C*), 29.20 (*t*-Bu *C*H_3), 28.15 (*i*-Pr *C*H), 23.62 (*i*-Pr *C*H_3). Anal. for $C_{23}H_{30}BrNO$: C, 66.17; H, 7.42; N, 3.22. Calcd: C, 66.34; H, 7.26; N, 3.36.

Synthesis of (5-Bromo-3-*tert*-butyl-2-trimethylsilanyloxy-benzylidene)−(2,6-diisopropyl-phenyl)-amine. THF (120 mL) was condensed onto a mixture of 4-bromo-2-*tert*-butyl-6-[(2,6-diisopropyl-phenylimino)-methyl]-phenol (3.4 g, 8.17 mmol) and KH (0.5 g, 12.5 mmol) and stirred for 1 h at room temperature. The mixture was then cooled to 0 °C. $SiMe_3Cl$ (2 mL, 15.7 mmol) was added; the resultant mixture was stirred for another hr at room temperature and filtered. All of the volatiles were removed under high vacuum to obtain the desired product as a pale yellow solid in quantitative yield. ^{1}H NMR ($CDCl_3$): δ (ppm) 8.42 (s, 1H, imine *H*), 8.21 (d, 1H, $^4J_{H-H}$ = 2.88 Hz, Ar*H*), 7.55 (d, 1H, $^4J_{H-H}$ = 2.88 Hz, Ar*H*), 7.13 (m, 3H, ArH), 2.95 (septet, 2H, $^3J_{H-H}$ = 6.81 Hz, *i*-Pr C*H*), 1.42 (s, 9H, *t*-Bu*H*), 1.17 (d, 12H, $^3J_{H-H}$ = 6.81 Hz, *i*-Pr CH_3), 0.24 (s, 9H, Si(CH_3)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 157.99 (*C*═N), 154.47 (*C*−O), 148.87 (*C*−N), 143.87 (*C*−*t*Bu), 137.45 (*C*−*i*Pr), 133.40, 129.56 (*C*−C═N), 128.27, 124.16, 122.92, 114.91 (*C*−Br), 35.07 (*t*-Bu *C*), 30.21 (*t*-Bu *C*H_3), 27.80 (*i*-Pr *C*H), 23.58 (*i*-Pr *C*H_3), 1.74 (Si(*C*H_3)$_3$). Anal. for $C_{26}H_{38}BrNOSi$: C, 64.17; H, 8.02; N, 2.73. Calcd: C, 63.92; H, 7.84; N, 2.87.

Synthesis of (5-trifluoroborate-3-*tert*-butyl-2-trimethylsilanyloxy-benzylidene)−(2,6-diisopropyl-phenyl)-amine [4-KBF$_3$-*t*-BuG(OH)]. To a solution of (5-bromo-3-*tert*-butyl-2-trimethylsilanyloxy-benzylidene)−(2,6-diisopropyl-phenyl)-amine (0.5 g, 1.02 mmol) in THF (50 mL) at −78 °C, was added *n*-BuLi (0.7 mL of a 1.6 M solution in hexanes, 1.13 mmol). After the mixture was stirred at the same temperature for 2 h, $B(OMe)_3$ (2 mL, 17.8 mmol) was added dropwise and the mixture was allowed to warm to room temperature over a 30 min period. Water (10 mL) was then added and the solution stirred for another 30 min. The mixture was extracted with Et_2O and the volatiles of the organic part were removed under vacuum. The residue was dissolved in methanol (30 mL) and an aqueous solution of KHF_2 (1 mL, 0.39 g/mL) was added. After the mixture was stirred for 1 h, all of the volatiles were removed. The product was extracted with acetone and dried under high vacuum overnight, washed with pentane, and dried. Pure product (450 mg, 54% yield) was obtained after recrystallization from an acetone/pentane solution. ^{1}H NMR (CD_3CN): δ (ppm) 13.24 (s, 1H, O*H*), 8.33 (s, 1H, imine *H*), 7.60 (s, 1H, Ar*H*), 7.39 (s, 1H, Ar*H*), 7.17 (m, 3H, ArH), 3.00 (septet, 2H, $^3J_{H-H}$ = 6.88 Hz, *i*-Pr C*H*), 1.46 (s, 9H, *t*-Bu*H*), 1.15 (d, 12H, $^3J_{H-H}$ = 6.88 Hz, *i*-Pr CH_3). ^{13}C-{^{1}H} NMR (CD_3CN): δ (ppm) 169.74 (*C*═N), 159.65 (*C*-OH), 147.50 (*C*−N), 139.63 (*C*−^{i}Pr), 135.57, 135.08, 134.90, 125.92, 123.97, 118.50, 35.27 (*t*-Bu *C*), 30.04 (*t*-Bu *C*H_3), 28.76 (*i*-Pr *C*H), 23.62 (*i*-Pr *C*H_3). Anal. for $C_{23}H_{30}BF_3KNO$: C, 63.79; H, 7.09; N, 2.75. Calcd: C, 62.30; H, 6.82; N, 3.16.

Synthesis of [K-18-Crown-6][4-BF$_3$-*t*-BuG(OH)]. [4-KBF$_3$-*t*-BuG-(OH)] (252 mg, 0.568 mmol) and 18-Crown-6 (150 mg, 0.568 mmol) were stirred in toluene (15 mL) for 24 h. Removal of the solvent gave pure [K-18-crown-6][4-BF$_3$-*t*-BuG(OH)] in quantitative yield. ^{1}H NMR (CD_3CN): δ (ppm) 13.22 (s, 1H, O*H*), 8.35 (s, 1H, imine *H*), 7.62 (s, 1H, Ar*H*), 7.39 (s, 1H, Ar*H*), 7.22 (m, 3H, ArH), 3.55 (s, crown ether), 3.05 (septet, 2H, $^3J_{H-H}$ = 6.88 Hz, *i*-Pr C*H*), 1.46 (s, 9H, *t*-Bu*H*), 1.16 (d, 12H, $^3J_{H-H}$ = 6.88 Hz, *i*-Pr CH_3). ^{13}C{^{1}H} NMR (CD_3CN): δ (ppm) 170.49 (*C*═N), 159.35 (*C*−OH), 147.95 (*C*-N), 140.08 (*C*−^{i}Pr), 135.39, 126.19, 124.29, 70.99 (crown ether), 35.43 (*t*-Bu *C*), 30.15 (*t*-Bu *C*H_3), 29.05 (*i*-Pr *C*H), 23.84 (*i*-Pr *C*H_3). Anal. for $C_{35}H_{54}BF_3KNO_7$: C, 59.08; H, 7.52; N, 1.75. Calcd: C, 59.40; H, 7.69; N, 1.98.

Synthesis of [K-18-Crown-6][4-BF$_3$-*t*-BuG(OK)]. [[K-18-Crown-6][4-BF$_3$-*t*-BuG(OH)] (601 mg, 0.849 mmol) and KO*t*Bu (125 mg, 1.02 mmol) were stirred in acetonitrile (30 mL) for 1.5 h. Crude product, obtained by removal of the solvent, was dissolved in 2 mL THF, then, ca. 20 mL of Et_2O was added to precipitate the deprotonated ligand. Filtration and washing with 2 portions of Et_2O (30 mL) gave pure [K-18-crown-6][4-BF$_3$-*t*-BuG(OK)].

Synthesis of 1a-NCCH$_3$. The lithium salt [N_2,O]Li (1.75 g, 4.38 mmol) was dissolved in acetonitrile (20 mL) at 0 °C and transferred to (COD)Pd(Me)Cl (1.16 g, 4.38 mmol) dissolved in acetonitrile (20 mL) at 0 °C. The mixture was stirred for 15 min at 0 °C and for another 3 h at 25 °C. All volatiles were then removed under high vacuum and the residue was extracted with *n*-hexane. The solution was concentrated and the compound crystallized within 2 days at −20 °C. Yield: 1.76 g, 72%. Dp: 120−123 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.49 (d, $^4J_{H-H}$ = 2.6 Hz, 1H, Ar*H*), 7.38 (d, $^4J_{H-H}$ = 2.6 Hz, 1H, Ar*H*), 7.38 (d, $^4J_{H-H}$ = 2.6 Hz, 1H, Ar*H*), 7.2 (m, 3H, Ar*H*), 2.32 (s, 3H, CH_3CN), 1.48 (s, 9H, *t*-Bu*H*), 1.32 (d, $^3J_{H-H}$ = 7.0 Hz, 6H, *i*-Pr CH_3), 1.25 (s, 9H, *t*-Bu*H*), 1.09 (d, $^3J_{H-H}$ = 7.0 Hz, 6H, *i*-Pr CH_3), 0.00 (s, 3H, Pd-Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 155.7, 140.6 (Ar *C*H), 130.7 (Ar *C*H), 129.1 (Ar *C*H), 127.0 (Ar *C*H), 123.1 (Ar *C*H), 119.0 (*C*H_3*C*N), 35.8 (*t*-Bu *C*), 33.9 (*t*-Bu *C*), 31.1 (*t*-Bu *C*H_3), 29.6 (*t*-Bu *C*H_3), 27.6 (*i*-Pr *C*H), 24.5 (*i*-Pr *C*H_3), 22.6 (*i*-Pr *C*H_3), 4.5 (*C*H_3CN), −5.7 (Pd-*C*H_3). IR: 3069 (w), 2959 (s), 2906 (m), 2886 (m), 1616, 1482, 1456, 1391, 1360, 1323, 1271, 1253, 1227, 1145. MS (FD)[%] (toluene): 555 [100, M^+]. Anal. for $C_{29}H_{43}N_3OPd$: C, 62.6; H, 7.7; N, 6.9; calcd. C, 62.64; H, 7.79; N, 7.56.

Synthesis of 1b-NCCH$_3$. The sodium salt of the bulky salicylaldiminato ligand (0.236 g, 0.55 mmol) and (COD)Pd(Me)Cl (0.145 g, 0.55 mmol) were weighed into a round-bottom flask in a glovebox, placed on a frit assembly and transferred to the vacuum line. Acetonitrile (10 mL) was condensed onto the solids at −78 °C and the reaction was warmed to room temperature. Upon warming, the yellow solution became turbid and was allowed to stir for an additional 3 h. The reaction was filtered, and the solids washed until the filtrate was colorless. The solvent was then removed in vacuo and the sample was isolated as a light yellow solid, which was pure by NMR spectroscopy. (0.250 g, 91% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.67 (s, 1H, imine *H*), 7.35 (d, 1H, $^3J_{H-H}$ = 7.11 Hz, Ar*H*), 7.20 (m, 3H, Ar*H*), 6.97 (d, 1H, $^3J_{H-H}$ = 7.95 Hz, Ar*H*), 6.39 (t, 1H, $^3J_{H-H}$ = 7.46 Hz, Ar*H*), 3.47 (septet, 2H, $^3J_{H-H}$ = 6.81 Hz, *i*-Pr C*H*), 2.29 (s, 3H, NCCH_3), 1.49 (s, 9H, *t*-Bu*H*), 1.30 (d, 6H, $^3J_{H-H}$ = 6.81 Hz, *i*-Pr CH_3), 1.10 (d, 6H, $^3J_{H-H}$ = 6.81 Hz, *i*-Pr CH_3), −0.10 (s, 3H, Pd−CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 168.31 (*C*−O), 166.10 (*C*═N), 147.91 (N−*C*), 141.30 (*C*−*i*Pr), 134.35, 131.17, 126.30, 123.20, 122.99 (*C*−*t*Bu), 119.27 (*C*−C═N), 117.91 (*C*≡N), 111.80 (Ar *C*H), 35.22 (*t*-Bu *C*), 29.52 (*t*-Bu *C*H_3), 27.68 (*i*-Pr *C*H), 24.84 (*i*-Pr *C*H_3), 22.73 (*i*-Pr *C*H_3), 2.88 (*C*H_3-CN), −5.15 (Pd-*C*H_3). Anal. for $C_{26}H_{36}N_2OPd$: C, 62.34; H, 7.21; N, 5.88. Calcd: C, 62.58; H, 7.27; N, 5.61.

Synthesis of 1b-PMe$_3$. PMe_3 (0.102 mmol) was condensed onto a frozen THF solution (25 mL) of **1b-NCCH$_3$** (51 mg, 0.102 mmol). The mixture was warmed to room temperature and stirred for 2 h.

Filtration and evaporation of all the volatiles gave pure **1b-PMe$_3$** as a yellow solid (38 mg, 70% yield). ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.91 (d, $^3J_{H-P}$ = 11.98 Hz, 1H, imine *H*), 7.28 (dd, $^3J_{H-H}$ = 7.18 Hz, $^4J_{H-H}$ = 1.80 Hz, 1H, Ar*H*), 7.18 (m, 3H, Ar*H*), 6.95 (dd, $^3J_{H-H}$ = 7.78 Hz, $^4J_{H-H}$ = 1.62 Hz, 1H, Ar*H*), 6.39 (t, $^3J_{H-H}$ = 7.51 Hz, 1H, Ar*H*), 3.27 (septet, 2H, $^3J_{H-H}$ = 6.83 Hz, *i*-Pr C*H*), 1.44 (d, $^2J_{H-P}$ = 10.24 Hz, 9H, PCH_3), 1.42 (s, 9H, *t*-Bu*H*), 1.20 (d, 6H, $^3J_{H-H}$ = 6.88 Hz, *i*-Pr CH_3), 1.05 (d, 6H, $^3J_{H-H}$ = 6.88 Hz, *i*-Pr CH_3), −0.42 (d, $^3J_{H-P}$ = 3.88 Hz, 3H, Pd−CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 168.05 (*C*-O), 166.73 (*C*═N), 147.82 (N−*C*), 141.16 (*C*-*i*Pr), 140.61 (*C*−*t*Bu), 135.54, 131.36, 125.89, 123.18, 119.39 (*C*−C═N), 111.82, 35.24 (*t*-Bu *C*), 29.09 (*t*-Bu *C*H_3), 27.75 (*i*-Pr *C*H), 24.78 (*i*-Pr *C*H_3), 22.45 (*i*-Pr *C*H_3), 15.1 (d, $^1J_{C-P}$ = 31.7 Hz, P*C*H_3), −4.28 (d, $^2J_{C-P}$ = 13.7 Hz, Pd-*C*H_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ (ppm) −3.73. Anal. for ($C_{27}H_{42}$NOPPd): C, 60.17; H, 7.97; N, 2.52. Calcd: C, 60.73; H, 7.93; N, 2.62.

Synthesis of 1b-CO. 1b-NCCH$_3$ (25 mg, 0.051 mmol) in CD_2Cl_2 was frozen, evacuated and exposed to an atmosphere of CO. The mixture was kept at −78 °C and ^{1}H NMR spectrum taken at −60 °C. ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.90 (s, 1H, imine *H*), 7.33 (d, $^3J_{H-H}$ = 7.24 Hz, 1H, Ar*H*), 7.21 (m, 3H, Ar*H*), 7.00 (d, $^3J_{H-H}$ = 7.99 Hz, 1H, Ar*H*), 6.43 (t, $^3J_{H-H}$ = 7.56 Hz 1H, Ar*H*), 3.01 (septet, 2H, $^3J_{H-H}$ = 6.64 Hz, *i*-Pr C*H*), 1.99 (free CH_3CN) 1.36 (s, 9H, *t*-Bu*H*), 1.16 (d, 6H, $^3J_{H-H}$ = 6.75 Hz, *i*-Pr CH_3), 0.97 (d, 6H, $^3J_{H-H}$ = 6.69 Hz, *i*-Pr CH_3), 0.06 (s, 3H, Pd−CH_3). Traces of **2b-CO** are also found in this spectrum.

Synthesis of 1c-NCCH$_3$. The dipotassium salt of ligand **c** (312 mg, 0.42 mmol) and (COD)Pd(Me)Cl (111 mg, 0.42 mmol) were weighed into a round-bottom flask in the glovebox, placed on a frit assembly, and transferred to the vacuum line. Acetonitrile (25 mL) was condensed onto the solids at −78 °C and the reaction was warmed to room temperature. Upon warming, the yellow solution became turbid and was allowed to stir for an additional 2 h. The reaction was filtered, and the solvent was removed in vacuo. The product was isolated as a light yellow solid, which was pure by NMR spectroscopy (320 mg, 88% yield). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.68 (s, 1H, imine *H*), 7.62 (s, 1H, Ar*H*), 7.23 (s, 1H, Ar*H*), 7.16 (m, 3H, Ar*H*), 3.57 (1, 24H, crown ether), 3.50 (septet, 2H, $^3J_{H-H}$ = 6.81 Hz, *i*-Pr C*H*), 2.26 (s, 3H, NCCH_3), 1.49 (s, 9H, *t*-Bu*H*), 1.25 (d, 6H, $^3J_{H-H}$ = 6.33 Hz, *i*-Pr CH_3), 1.05 (d, 6H, $^3J_{H-H}$ = 6.99 Hz, *i*-Pr CH_3), −0.22 (s, 3H, Pd−CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ (ppm) 167.86 (*C*−O), 166.60 (*C*═N), 148.44 (N−*C*), 141.61 (*C*−^{i}Pr), 138.05, 136.48 (*C*−BF_3), 125.80, 122.94, 118.77 (*C*−C═N), 117.68 (*C*≡N), 69.94 (crown ether), 35.05 (*t*-Bu *C*), 29.86 (*t*-Bu *C*H_3), 27.49 (*i*-Pr *C*H), 24.89 (*i*-Pr *C*H_3), 22.70 (*i*-Pr *C*H_3), 2.86 (*C*H_3CN), −5.89 (Pd-*C*H_3). Anal. for $C_{38}H_{59}BF_3KN_2O_7$-Pd: C, 52.89; H, 6.76; N, 3.09. Calcd: C, 52.52; H, 6.84; N, 3.22.

Synthesis of 1c-PMe$_3$. PMe_3 (0.078 mmol) was condensed on a frozen THF solution (25 mL) of **1c-NCCH$_3$** (68 mg, 0.078 mmol). The mixture was warmed to room temperature and stirred for 2 h. Filtration and evaporation of all the volatiles led to the isolation of crude **1c-PMe$_3$** as a yellow solid (48 mg, 68% yield). ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.89 (d, $^3J_{H-P}$ = 12.33 Hz, 1H, imine *H*), 7.46 (s, 1H, Ar*H*), 7.18 (m, 3H, Ar*H*), 7.06 (s, 1H, Ar*H*), 3.55 (s, crown ether), 3.30 (m, 2H, *i*-Pr C*H*), 1.44 (d, $^2J_{H-P}$ = 10.24 Hz, 9H, PCH_3), 1.42 (s, 9H, *t*-Bu*H*), 1.19 (d, 6H, $^3J_{H-H}$ = 6.52 Hz, *i*-Pr CH_3), 1.04 (d, 6H, $^3J_{H-H}$ = 6.42 Hz, *i*-Pr CH_3), −0.48 (d, $^3J_{H-P}$ = 2.91 Hz, 3H, Pd−CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 167.34 (*C*═N), 167.28 (*C*−O), 148.27 (N−*C*), 141.40 (*C*-^{i}Pr), 138.75, 137.91, 135.99, 125.51, 122.99, 118.61 (*C*−C═N), 70.05 (crown ether), 35.12 (*t*-Bu *C*), 29.46 (*t*-Bu *C*H_3), 27.65 (*i*-Pr *C*H), 24.83 (*i*-Pr *C*H_3), 22.46 (*i*-Pr *C*H_3), 15.15 (d, $^1J_{C-P}$ = 31.46 Hz, P*C*H_3), −4.59 (d, $^2J_{C-P}$ = 14.2 Hz, Pd-*C*H_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ (ppm) −3.85. Anal. for ($C_{39}H_{65}NO_7PBF_3$-KPd): C, 50.84; H, 6.98; N,1.51. Calcd: C, 51.80; H, 7.25; N, 1.55.

Synthesis of 1c-CO. 1c-NCCH$_3$ (22 mg, 0.025 mmol) in CD_2Cl_2 was frozen, evacuated and exposed to an atmosphere of CO. The mixture was kept at −78 °C and ^{1}H NMR spectrum taken at −70 °C. ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.87 (s, 1H, imine *H*), 7.45 (s, 1H, Ar*H*), 7.18 (m, 3H, Ar*H*), 7.01 (s, 1H, Ar*H*), 3.52 (crown ether), 3.03 (septet, 2H, $^3J_{H-H}$ = 6.53 Hz, *i*-Pr C*H*), 1.99 (free CH_3CN) 1.41 (s, 9H, *t*-Bu*H*), 1.18 (d, 6H, $^3J_{H-H}$ = 6.68 Hz, *i*-Pr CH_3), 0.99 (d, 6H, $^3J_{H-H}$ = 6.69 Hz, *i*-Pr CH_3), 0.05 (s, 3H, Pd−CH_3). Traces of **2c-CO** are also found in this spectrum.

Synthesis of 2b-CO. 1b-NCCH$_3$ (25 mg, 0.051 mmol) in CD_2Cl_2 was frozen, evacuated and exposed to an atmosphere of CO. The mixture was kept at −78 °C and ^{1}H NMR spectrum taken at 0 °C after 2 h. ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.96 (s, 1H, imine *H*), 7.40 (dd, $^3J_{H-H}$ = 7.42 Hz, $^4J_{H-H}$ = 1.84 Hz, 1H, Ar*H*), 7.21 (m, 3H, Ar*H*), 7.05 (dd, $^3J_{H-H}$ = 7.85 Hz, $^4J_{H-H}$ = 1.83 Hz, 1H, Ar*H*), 6.43 (t, $^3J_{H-H}$ = 7.60 Hz 1H, Ar*H*), 3.28 (septet, 2H, $^3J_{H-H}$ = 6.85 Hz, *i*-Pr C*H*), 2.68 (s, 3H, O═CCH_3), 1.99 (free CH_3CN), 1.33 (s, 9H, *t*-Bu*H*), 1.33 (d, 6H, *i*-Pr CH_3), 1.11 (d, 6H, $^3J_{H-H}$ = 6.83 Hz, *i*-Pr CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 218.74 (Pd−*C*O), 184.44 (free *C*O), 174.22 (Pd−*C*OCH_3), 167.11 (*C*═N), 165.10 (*C*−O), 150.80 (N−*C*), 140.90 (*C*−*t*Bu), 139.66 (*C*−*i*Pr), 134.91, 132.37, 126.72, 123.74, 119.50 (free CH_3*C*N), 114.72 (*C*−C═N), 39.18 (Pd−CO*C*H_3), 35.14 (*t*-Bu *C*), 29.13 (*t*-Bu *C*H_3), 28.12 (*i*-Pr *C*H), 24.84 (*i*-Pr *C*H_3), 22.92 (*i*-Pr *C*H_3), 2.14 (free *C*H_3CN). IR (KBr pellets; cm^{-1}): 2088 (ν_{CO}, coord C≡O), 1733 (ν_{CO}, acyl-C═O), 1610 (ν_{CN}, C═N).

Synthesis of 2c-CO. 1c-NCCH$_3$ (22 mg, 0.025 mmol) in CD_2Cl_2 was frozen, evacuated and exposed to an atmosphere of CO. The mixture was kept at −78 °C and ^{1}H NMR spectrum taken at 0 °C after 2 h. ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.95 (s, 1H, imine *H*), 7.60 (s, 1H, Ar*H*), 7.19 (m, 4H, Ar*H*), 3.56 (crown ether), 3.31 (septet, 2H, $^3J_{H-H}$ = 6.78 Hz, *i*-Pr C*H*), 2.67 (s, 3H, O═CCH_3), 1.98 (free CH_3CN), 1.36 (s, 9H, *t*-Bu*H*), 1.33 (d, 6H, $^3J_{H-H}$ = 6.80 Hz, *i*-Pr CH_3), 1.10 (d, 6H, $^3J_{H-H}$ = 6.83 Hz, *i*-Pr CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 220.63 (Pd−*C*O), 174.61 (Pd−*C*OCH_3), 167.69 (*C*═N), 163.96 (*C*-O), 151.36 (N−*C*), 139.92 (*C*−*i*Pr), 138.22, 137.02, 126.39, 123.60, 123.20, 118.72, 70.19 (crown ether), 39.41 (Pd−CO*C*H_3), 34.98 (*t*-Bu *C*), 29.51 (*t*-Bu *C*H_3), 28.08 (*i*-Pr *C*H), 24.90 (*i*-Pr *C*H_3), 22.96 (*i*-Pr *C*H_3), 2.15 (free *C*H_3CN). IR (KBr pellets; cm^{-1}): 2085 (ν_{CO}, coord C≡O), 1724 (ν_{CO}, acyl-C═O), 1603 (ν_{CN}, C═N).

Synthesis of 3a. [N_2,O]Li (1.5 mmol) was dissolved in acrylonitrile (10 mL) and transferred to a solution of (COD)Pd(Me)Cl (1.5 mmol) in acrylonitrile (5 mL) at 0 °C. The resulting suspension was stirred for 15 h at 25 °C. After removal of all volatiles the residue was extracted with toluene and filtered; the toluene was removed and replaced by *n*-hexane. A pure reddish-purple compound was obtained by crystallization at −20 and −78 °C. Yield: 74%. Mixture of diastereomers: ^{1}H NMR ($CDCl_3$): δ (ppm) 7.1−7.4 (Ar*H*) 3.60 (septet, $^3J_{H-H}$ = 6.7 Hz, *i*-Pr C*H*), 3.46 (septet, $^3J_{H-H}$ = 6.7 Hz, *i*-Pr C*H*), 3.33 (septet, $^3J_{H-H}$ = 6.7 Hz, *i*-Pr C*H*), 3.15 (septet, $^3J_{H-H}$ = 6.7 Hz, *i*-Pr C*H*), 3.06 (septet, $^3J_{H-H}$ = 6.7 Hz, *i*-Pr C*H*), 2.87 (septet, $^3J_{H-H}$ = 6.7 Hz, *i*-Pr C*H*), 2.14 (m, CH_3CH_2), 1.95 (m, CH_3CH_2), 1.59 (d, $^3J_{H-H}$ = 6.7 Hz, *i*-Pr CH_3), 1.47 (d, $^3J_{H-H}$ = 6.7 Hz, *i*-Pr CH_3), 1.38 (m, CH_3CH_2), 1.32 (d, $^3J_{H-H}$ = 6.7 Hz, *i*-Pr CH_3), 1.28 (d, $^3J_{H-H}$ = 6.7 Hz, *i*-Pr CH_3), 1.25 (s, *t*-Bu*H*), 1.24 (s, *t*-Bu*H*), 1.23 (s, *t*-Bu*H*), 1.22 (s, *t*-Bu*H*), 1.19 (s, *t*-Bu*H*), 1.14 (s, *t*-Bu*H*), 1.11 (d, $^3J_{H-H}$ = 6.7 Hz, *i*-Pr CH_3), 1.00 (t, $^3J_{H-H}$ = 5.4 Hz, CH_3), 0.91 (dd, C*H*CN), 0.88 (dd, C*H*CN), 0.61 (dd, C*H*CN), 0.42 (t, $^3J_{H-H}$ = 5.4 Hz, CH_3). MS (FD)[%] (toluene): 1703 [100, M^+, trimer], 1137 [20, dimer], 567[20, monomer]. IR: 2235 (s, ν_{CN}). UV−vis [toluene]: λ_{max}: 501 nm; ϵ: 56135. Anal. for ($C_{30}H_{43}N_3OPd)_n$: C, 63.5; H, 7.8; N, 7.2; Calcd. C, 63.43; H, 7.63; N, 7.40.

Synthesis of 3a-PPh$_3$. The oligomer Pd complex **3a** (0.82 g, 0.48 mmol) was dissolved in 10 mL *n*-hexane at 25 °C. Triphenylphosphine (excess) in 20 mL *n*-hexane was added and after 15 min a precipitate was observed. The mixture was stirred for 15 h and the reddish-brown precipitate was isolated by filtration and was dried in high vacuum. Yield: 1.2 g, 86%. ^{1}H−^{1}H−COSY (C_6D_6): δ (ppm) 8.1−8.2 (m, Ar*H*), 7.92 (s, Ar*H*), 7.71 (s, Ar*H*), 7.1−7.3 (m, Ar*H*), 4.24 (septet, 1H, $^3J_{H-H}$ = 6.8 Hz, *i*-Pr C*H*), 3.74 (septet, 1H, $^3J_{H-H}$ = 6.8 Hz, *i*-Pr C*H*), 2.58

(dd, 1H, $^3J_{H-H}$ = 12.0, $^3J_{H-P}$ = 5.0 Hz, CH_2-CHCN), 1.61 (d, 6H, $^3J_{H-H}$ = 6.8 Hz, *i*-Pr CH_3), 1.42 (s, 9H, *t*-Bu*H*), 1.31 (d, 3H, $^3J_{H-H}$ = 6.8 Hz, *i*-Pr CH_3), 1.18 (d, 3H, $^3J_{H-H}$ = 6.8 Hz, *i*-Pr CH_3), 1.01 (m, 1H, CH_3CH_2), 0.94 (s, 9H, *t*-Bu*H*), 0.65 (m, 1H, CH_3CH_2), 0.53 (t, 3H, $^3J_{H-H}$ = 6.4 Hz, CH_3CH_2). ^{1}H-^{13}C−HSQC ($CDCl_3$): δ (ppm) 154.0 (*C*-O), 149.5 (*C*-N), 142.9 (*C*-*t*-Bu), 142.5 (*C*-*i*-Pr), 141.3 (*C*-*i*-Pr), 140.7 (*C*-*i*-Pr), 136.8 (*C*-*t*-Bu), 136.2 (Ar *C*H$_.$, PPh_3), 136.0 (Ar *C*H$_.$, PPh_3), 135.8, 131.9, 131.0 (Ar *C*H$_.$, PPh_3), 130.6, 123.9, 123.6, 35.3 (*t*-Bu *C*), 33.9 (*t*-Bu *C*), 31.2 (*t*-Bu CH_3), 29.7 (*t*-Bu CH_3), 29.0 (*i*-Pr *C*H), 25.2 (*i*-Pr CH_3), 24.9 (*i*-Pr CH_3), 24.0 (*C*H−CN), 22.9 (*i*-Pr CH_3), 22.7 (*i*-Pr CH_3), 14.4 (CH_2CHCN), 0.77 (CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ (ppm) 30.4 ppm. IR: 2192 cm^{-1} (ν_{CN}). MS(FD) (toluene): M^+(829, correct isotope pattern).

Synthesis of 3b. Dry acrylonitrile (136 mg, 2.56 mmol) was added to a stirred solution of **1b-NCCH$_3$** (319 mg, 0.64 mmol) in THF (25 mL) at −78 °C. The solution was stirred for 2 h while warming to room temperature. The volatiles were removed in vacuo and the sample was isolated as an orange solid (305 mg, 93% yield). ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.59, 7.54, 7.53, 7.52, and 7.50 (5 s, imine *H*), 7.32−7.15 (m, Ar*H*), 7.00−6.89 (m, Ar*H*), 6.45−6.30 (m, Ar*H*), 3.73, 3.58, 3.53, 3.36, 3.36, 3.11, 3.02 (m, $^3J_{H-H}$ = 6.5−6.9 Hz, *i*-Pr C*H*), 1.37 (s, *t*-Bu*H*), 1.30−0.90 (m, *i*-Pr CH_3 and Pd−C*H*(CN)CH_2), 0.65 (m, CH-(CN)CH_2CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 166.61, 165.94, 165.85, 165.66 and 165.17 (*C*═N and *C*−O), 147.27, 147.23, 146.98 (N−*C*), 141.53−140.90 (*C*-*i*-Pr), 133.51−123.15 (Ar *C*H and *C*N), 119.07, 118.78, and 118.52 (*C*−*t*Bu and *C*−C═N), 113.01, 112.93, and 112.60 (Ar *C*H), 35.22 and, 35.13 (*t*-Bu *C*), 29.46−28.75 (*t*-Bu CH_3), 27.78−27.58 (*i*-Pr *C*H), 26.01−24.79 (*i*-Pr CH_3), 23.43−22.13 (*i*-Pr CH_3), 14.90−14.10 ($CH_3CH_2CH(CN)$), 10.32−8.43 (CH_3CH_2CH-(CN)). Anal. for $(C_{27}H_{36}N_2OPd)_n$: C, 63.43; H, 7.18; N, 5.59. Calcd: C, 63.46; H, 7.10; N, 5.48.

Synthesis of 3b-PMe$_3$. PMe_3 (0.045 mmol, 1 eq) was added to a frozen CD_2Cl_2 solution of neutral oligomer mixture (23 mg, 0.045 mmol). The mixture was warmed to room temperature and the NMR tube was shaken for 5 min. ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.91 (d, 1H, $^3J_{H-P}$ = 12.3 Hz, imine *H*), 7.33 (d, 1H, $^3J_{H-H}$ = 7.35 Hz, Ar*H*), 7.22 (m, 3H, Ar*H*), 6.97 (dd, 1H, $^3J_{H-H}$ = 7.88 Hz, $^4J_{H-H}$ = 1.74 Hz, Ar*H*), 6.44 (t, 1H, $^3J_{H-H}$ = 7.51 Hz, Ar*H*), 3.23 (septet, 2H, $^3J_{H-H}$ = 6.84 Hz, *i*-Pr C*H*), 1.63 (d, 9H, $^2J_{H-P}$ = 10.73 Hz, PCH_3), 1.41 (s, 9H, *t*-Bu*H*), 1.30, 1.26, 1.08 and 0.99 (4d, 12H, $^3J_{H-H}$ = 6.88 Hz, *i*-Pr CH_3), 1.45 (m, 1H, (C*H*(CN)CH_2CH_3), 1.22 and 1.05 (m, 2H, (CH(CN)CH_2-CH_3), 0.35 (t, 3H, $^3J_{H-H}$ = 7.10 Hz, (CH(CN)CH_2CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 167.51 (*C*═N), 167.05 (*C*−O), 146.70 (N−*C*), 142.03 and 141.28 (*C*−*i*-Pr), 140.53 (Ar *C*−*t*Bu), 135.54 (Ar *C*−H), 132.24 (Ar *C*−H), 128.91 (d, $^3J_{C-P}$ = 6.23 Hz, *C*≡N), 126.97 (Ar *C*−H), 123.65 (Ar *C*−H), 119.46 (*C*−C═N), 112.97 (Ar *C*−H), 35.19 (*t*-Bu *C*), 29.29 (*t*-Bu CH_3), 28.14 and 27.99 (*i*-Pr *C*H), 25.53 and 25.09 (*i*-Pr CH_3), 24.55 (d, $^3J_{C-P}$ = 2.90 Hz, CH(CN)CH_2), 22.42 and 22.08 (*i*-Pr CH_3), 14.26 (CH(CN)CH_2CH_3), 14.17 (d, $^1J_{C-P}$ = 30.76 Hz, PCH_3), 6.05 (d, $^2J_{C-P}$ = 8.92 Hz, Pd-*C*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ (ppm) −5.29.

Synthesis of 3c. Dry acrylonitrile (38.3 g, 0.72 mmol) was added to a stirred solution of **1c-NCCH$_3$** (157 mg, 0.18 mmol) in THF (25 mL) at −78 °C. The solution was stirred for 2 h during which room temperature was reached. All the volatiles were then removed *in vacuo* and the sample was isolated as an orange solid (122 mg, 77% yield). ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.49 and 7.47 (s, imine *H*), 7.42 − 7.12 (m, Ar*H*), 7.07 (s, Ar*H*), 3.52 (s, crown ether), 3.26 (t, $^3J_{H-H}$ = 6.65 Hz, *i*-Pr C*H*), 3.20−2.80 (m, *i*-Pr C*H*), 1.33 (s, *t*-Bu*H*), 1.26, 1.22, 1.04 and 0.95 (m, *i*-Pr CH_3), 1.30 and 1.18 (m, CH(CN)CH_2CH_3), 0.97 and 0.84 (t, $^3J_{H-H}$ = 6.80 Hz, C*H*(CN)CH_2CH_3), 0.53 (t, $^3J_{H-H}$ = 7.08 Hz, CH(CN)CH_2CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 165.69 (*C*═N), 164.92 (*C*−O), 147.03 (N−*C*), 141.85 and 141.60 (*C*−^{i}Pr), 138.05 (Ar *C*−*t*Bu), 137.09 (Ar *C*−H), 136.93 (Ar *C*−H), 133.84 (*C*−BF_3), 129.01 and 128.38 (*C*≡N), 127.06 (Ar *C*−H), 123.69 (Ar *C*−H), 123.48 (Ar *C*−H), 117.88 (*C*−C═N), 70.02 (crown ether), 34.94 (*t*-Bu *C*), 29.46 (*t*-Bu CH_3), 28.02 and 27.76 (*i*-Pr *C*H), 25.86, 24.93, 22.60 and 22.10 (*i*-Pr CH_3), 24.93 (CH(CN)CH_2), 14.59 (CH(CN)CH_2CH_3), 10.27 (d, $^2J_{C-P}$ = 9.46 Hz, Pd-*C*). Anal. for $(C_{39}H_{59}N_2O_7BF_3KPd)_n$: C, 52.71; H, 6.60; N, 3.40. Calcd: C, 53.16; H, 6.75; N, 3.18.

Synthesis of 3c-PMe$_3$. PMe_3 (0.026 mmol, 1 eq) was added to a frozen CD_2Cl_2 solution of anionic oligomer mixture **3c** (23 mg, 0.026 mmol). The mixture was warmed to room temperature and the NMR tube shaken for 5 min. ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.89 (d, $^3J_{H-P}$ = 12.85 Hz, 1H, imine *H*), 7.51 (s, 1H, Ar*H*), 7.20 (m, 3H, Ar*H*), 7.09 (s, 1H, Ar*H*), 3.54 (s, crown ether), 3.27 (septet, $^3J_{H-H}$ = 6.58 Hz 2H, *i*-Pr C*H*), 1.62 (d, $^2J_{H-P}$ = 10.64 Hz, 9H, PCH_3), 1.43 (s, 9H, *t*-Bu*H*), 1.38 (m, 1H, (C*H*(CN)CH_2CH_3), 1.29, 1.25, 1.07 and 0.98 (d, 12H, $^3J_{H-H}$ = 6.72 Hz, *i*-Pr CH_3), 1.22 and 1.03 (m, 2H, (CH(CN)CH_2CH_3), 0.34 (t, $^3J_{H-H}$ = 7.04 Hz, 3H, (CH(CN)CH_2CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 168.09 (*C*═N), 166.13 (*C*−O), 147.17 (N−*C*), 142.27 and 141.50 (*C*−^{i}Pr), 138.67 (Ar *C*−H), 137.81 (Ar *C*−*t*Bu), 136.91 (Ar *C*−H), 129.32 (d, $^3J_{C-P}$ = 6.03 Hz, *C*≡N), 128.35 (*C*−BF_3), 126.58 (Ar *C*−H), 123.44 (Ar *C*−H), 118.70 (*C*−C═N), 70.03 (crown ether), 35.04 (*t*-Bu *C*), 29.63 (*t*-Bu CH_3), 28.08 and 27.87 (*i*-Pr *C*H), 25.63 and 25.16 (*i*-Pr CH_3), 24.54 (CH(CN)CH_2), 22.42 and 22.05 (*i*-Pr CH_3), 14.30 (CH(CN)CH_2CH_3), 14.21 (d, $^1J_{C-P}$ = 30.11 Hz, PCH_3), 5.82 (d, $^2J_{C-P}$ = 9.46 Hz, Pd-*C*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ (ppm) −5.68.

Competition Experiment (Scheme 7). ***d*$_3$-1b-NCCH$_3$** (11 mg, 0.0219 mmol, 1 eq) and **1c-NCCH$_3$** (19 mg, 0.0219 mmol, 1 eq) were dissolved in CH_2Cl_2 (0.7 mL). Acrylonitrile (116 mg of a 1% w/w CH_2Cl_2 solution, 0.0219 mmol, 1 eq) was then added and the NMR tube was shaken and allowed to stand for 20 min. at room temperature. The solution was frozen in liquid nitrogen, the tube evacuated and PMe_3 was added via gas transfer (19.1 mL at 42.4 mmHg and 23 °C, 0.438 mmol, 2 eq). The mixture was warmed to room temperature and shaken for 1−2 min. ^{2}H and ^{31}P NMR specta were recorded unlocked at −20 °C and referenced using naturally abundant deuterated solvent (^{2}H) or external H_3PO_4 in CD_2Cl_2 (^{31}P). The experiment was repeated to confirm the reproducibility of the results. ^{2}H NMR (CH_2Cl_2): δ (ppm) (integration first experiment, integration second experiment, assignment) 0.30 (1.00, 1.00, ***d*$_3$-3b-PMe$_3$**), −0.47 (1.56, 1.55, ***d*$_3$-1b-PMe$_3$**). ^{31}P NMR (CH_2Cl_2): δ (ppm) (integration first experiment, integration second experiment, assignment) −3.73 (0.68, 0.85, ***d*$_3$-1b-PMe$_3$**), −3.89 (0.36, 0.38, **1c-PMe$_3$**), −5.29 (0.73, 0.74, ***d*$_3$-3b-PMe$_3$**), −5.68 (1.00, 1.00, **3c-PMe$_3$**).

NMR Tube Reactions of 1-NCCH$_3$ with Acrylonitrile. 1a-NCCH$_3$ (20 mg) was dissolved at −78 °C in CD_2Cl_2 (650 μL). Acrylonitrile was then transferred to the NMR tube (1−20 eq) and the tube transferred to a pre-cooled NMR probe. Several ^{1}H NMR-experiments have been carried out for complex **1a-NCCH$_3$** at different temperatures in CD_2Cl_2 to examine the exchange of acetonitrile by acrylonitrile and insertion of acrylonitrile into Pd-Me. The exchange of acetonitrile by acrylonitrile (AN) was monitored by observing the signals of coordinated AN and free AN.[43] *Free AN at −30 °C:* ^{1}H NMR (CD_2Cl_2): δ (ppm) 6.33 (d, $^3J_{HH}$ = 17.9 Hz, 1 H, CH_2), 6.18 (d, $^3J_{HH}$ = 11.9 Hz, 1 H, CH_2), 5.77 (dd, $^3J_{H-H}$ = 17.9, 11.9 Hz, 1 H, C*H*CN). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 130.1 (*C*H_2), 117.1 (CH*C*N), 107.3 (*C*HCN). *N−Coordinated AN at −30 °C:* ^{1}H NMR (CD_2Cl_2): δ (ppm) 6.58 (d, $^3J_{H-H}$ = 17.9 Hz, 1H, CH_2), 6.45 (d, $^3J_{H-H}$ = 12.1 Hz, 1H, CH_2), 5.97 (dd, $^3J_{H-H}$ = 17.9, 12.1 Hz, 1H, C*H*CN). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 142.2 (*C*H_2), 106.0 (*C*HCN), 119.1 (CH*C*N). During the exchange proton signals of free acetonitrile at 2.0 ppm have been observed. For comparison in **1a-NCCH$_3$** at −30 C: ^{1}H NMR (CD_2Cl_2): δ (ppm) 2.35 (CH_3CN). No insertion reaction was observed in CD_2Cl_2 at −30 °C when a ratio of AN: **1a-NCCH$_3$** = 20 was used. Upon warming to higher temperatures, the disappearance of **1a-*n*-AN** was monitored over time by observing the decrease of the Pd-Me signal intensity at 0.0 ppm. Similar reactions were studied with **1b-NCCH$_3$**

(43) Rosenblum, M.; Turnbull, M. M., Begum, M. K. *J. Organomet. Chem.* **1987**, *321*, 67.

(12 mg, 1−190 eq AN, total volume: 700 μL) and with **1c-NCCH$_3$** (21 mg, 1−100 eq AN, total volume: 700 μL). Below −30 °C, the acetonitrile ligand is completely replaced by N-bound AN when more 20 eq of AN, or more, are present in solution to form **1b-*n*-AN** and **1c-*n*-AN**, respectively, whereas insertion into the Pd-Me bound is observed above −30 °C.

1b-*n*-AN at −60°C ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.66 (s, 1H, imine *H*), 7.23 (d, $^3J_{H-H}$ = 7.0 Hz, 1H, Ar*H*), 7.14 (m, 3H, Ar*H*), 6.92 (d, $^3J_{H-H}$ = 7.0 Hz, 1H, Ar*H*), 6.47 (d, $^3J_{H-H}$ = 17.8 Hz, 1H, *n*-bound AN), 6.29 (d, $^3J_{H-H}$ = 12.6 Hz, 1H, *n*-bound AN), 6.23 (d, $^3J_{H-H}$ = 18.5 Hz, *free* AN), 6.09 (d, $^3J_{H-H}$ = 13.0 Hz, *free* AN), 5.97 (dd, $^3J_{H-H}$ = 17.8, 12.6 Hz, 1H, *n*-bound AN), 5.77 (dd, $^3J_{H-H}$ = 17.9, 11.9 Hz, *free* AN), 3.23 (septet, $^3J_{H-H}$ = 6.58 Hz, 2H, *i*-Pr C*H*), 1.99 (s, 3H, *free* CH_3CN), 1.36 (s, 9H, *t*-Bu*H*), 1.19 and 0.97 (d, $^3J_{H-H}$ = 6.52 Hz, 6H, *i*-Pr CH_3), −0.25 (s, 3H, Pd−Me). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 167.17 (*C*═N), 165.53 (*C*−O), 146.85 (N−*C*), 142.02 (*n*-bound AN), 140.60 (*C*−^{i}Pr), 140.15 (Ar *C*−H), 138.26 (*free* AN), 137.81 (Ar *C*−*t*Bu), 136.86 (Ar *C*−H), 134.48 (Ar *C*−H), 126.27 (Ar *C*−H), 123.10 (Ar *C*−H), 118.66 (Pd−N*C*), 117.94 (*free* CH_3CN), 117.46 (*free* AN), 111.91 (*C*−C═N), 107.27 (*free* AN), 106.21 (Pd−NC*C*), 35.01 (*t*-Bu *C*), 28.66 (*t*-Bu CH_3), 27.38 (*i*-Pr *C*H), 24.62 and 22.15 (*i*-Pr CH_3), 2.28 (free CH_3CN), −4.87 (Pd-*C*).

1c-*n*-AN at −60°C ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.62 (s, 1H, imine *H*), 7.42 (s, 1H, Ar*H*), 7.14 (m, 4H, Ar*H*), 7.05 (s, 1H, Ar*H*), 6.47 (d, $^3J_{H-H}$ = 17.4 Hz, 1H, *n*-bound AN), 6.34 (d, $^3J_{H-H}$ = 12.6 Hz, 1H, *n*-bound AN), 6.23 (d, $^3J_{H-H}$ = 18.3 Hz, *free* AN), 6.09 (d, $^3J_{H-H}$ = 13.0 Hz, *free* AN), 5.97 (dd, $^3J_{H-H}$ = 17.4, 12.6 Hz, 1H, *n*-bound AN), 5.77 (dd, $^3J_{H-H}$ = 18.3, 11.9 Hz, *free* AN), 3.52 (crownether), 3.29 (septet, $^3J_{H-H}$ = 6.68 Hz, 2H, *i*-Pr C*H*), 1.99 (s, 3H, *free* CH_3CN), 1.39 (s, 9H, *t*-Bu*H*), 1.20 and 1.04 (d, $^3J_{H-H}$ = 6.62 Hz, 6H, *i*-Pr CH_3), −0.30 (s, 3H, Pd−Me). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (ppm) 166.80 (*C*═N), 166.16 (*C*−O), 147.52 (N−*C*), 141.72 (*n*-bound AN), 141.18 (*C*−^{i}Pr), 138.19 (*free* AN), 137.44 (Ar *C*−*t*Bu), 136.10 (Ar *C*−H), 128.50 (Ar *C*−H), 123.02 (Ar *C*−H), 118.10 (Pd−N*C*), 117.75 (*free* CH_3CN), 117.42 (*free* AN), 108.20 (*C*−C═N), 107.36 (*free* AN), 106.66 (Pd−NC*C*), 69.95 (crownether), 34.98 (*t*-Bu *C*), 29.24 (*t*-Bu CH_3), 27.78 (*i*-Pr *C*H), 24.76 and 22.30 (*i*-Pr CH_3), 2.29 (free CH_3CN), −5.34 (Pd-*C*).

Kinetic Studies of AN Insertion in the Pd−Me Bond: Complex **1b-NCCH$_3$** or **1c-NCCH$_3$** (0.024 mmol. 12 and 21 mg respectively) was dissolved in CD_2Cl_2 at −78 °C. A CD_2Cl_2 solution of acrylonitrile (1 to 190 eq) was then syringed to the NMR tube (total volume: 700 μL) and the tube transferred to a NMR probe set at different temperature from −22.8 to +9.8 °C. The temperature in the probe was measured accurately using a thermocouple device. Disappearance of the total [Pd-Me], which include **1-*n*-AN** as well as a new species identified as **4-*n*-AN**, was used to monitor the reaction at set temperatures and amounts of AN. The obtained k_{obs} are listed in Table 4.

Acknowledgment. This paper is dedicated to Professor John E. Bercaw on the occasion of his 60th birthday. Funding for this work was provided by Bayer Polymers (Leverkusen). The authors thank Prof. Richard Jordan (Chicago) for stimulating discussions and for sharing unpublished work prior to publication; we also thank Dr. Miklos Szabo (University of Calgary) for his insights. T. W. would like to thank Dr. Matthias Jank and Dr. Joachim Wesener for technical support and helpful discussions concerning NMR and MS measurements. L.F.G. would like to thank the Natural Science and Engineering Research Council of Canada and the Alberta Ingenuity Fund for postdoctoral fellowships and Prof. Hans Vogel and Dr. Dean McIntyre (Biological Sciences, University of Calgary) for the use of their 400 MHz NMR spectrometer and technical assistance with the kinetic experiments.

Supporting Information Available: ORTEP diagrams for the structurally characterized compounds (borate bearing ligand, **1a-NCCH$_3$**, **1b-NCCH$_3$**, **1c-PMe$_3$**, and **3a**, 5 pages, print/PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA044119+