Protonolysis Approach to the Catalytic Amination of Olefins with Bis(phosphine)palladium(II) Dialkyls

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Several compounds of the general type $PdR_2(PR_3)_2$, where R = alkyl and $(PR_3)_2$ = monodentate or chelating alkyl- or arylphosphines, catalyze the addition of aniline to acrylonitrile. Acrolein, methyl acrylate, and crotonitrile also act as substrates for aniline addition with $Pd(CH_3)_2$(dmpe) catalyst, where dmpe = 1,2-bis(dimethylphosphino)ethane. All the catalysts require 1 equiv of H^+ cocatalyst, provided as NH_3Ph^+. The mechanism proposed for catalysis involves protonolysis of a Pd–R bond to form $PdR(PR_3)_2^+$. This species can bind acrylonitrile and add NH_2R to form $PdRR'(PR_3)_2$, with $R' = -C(CN)HCH_2(NH_2R)^+$, which can be detected in solution by NMR spectroscopy. The net effect is the regeneration of a new palladium dialkyl complex and an H^+ source to continue the catalytic cycle. Catalyst stabilities vary in the order **7**, $Pd(CH_3)_2(PMe_3)_2$ < **1**, $Pd(CH_3)_2$(dmpe) ≈ **2**, $Pd(CH_3)_2$(dppe) < **3**, $Pd[CH_2Si(CH_3)_3]_2$(dmpe) ≈ **4**, $Pd[CH_2Si(CH_3)_3]_2$(dppe) < **5**, $PdMe[(t\text{-}Bu_2)P(CH_2)_2CH(CH_2)_2P(t\text{-}Bu)_2]$. Complex **5** forms a catalyst active for hundreds of turnovers with no loss of activity. Catalytic turnover rates at 30 °C increase in the order **3** ≈ **2** < **1** < **7** < **5**. The unexpected high activity of the sterically hindered catalyst **5** is partly attributed to its crowded binding site. NMR studies show it favors coordination of acrylonitrile over aniline, in contrast to **1**.

Introduction

Alkylamines find use in the production of surfactants, polyamide fibers, and fertilizers and as specialty chemicals, such as solvents. The amine functionality also occurs in many natural products and medicinal chemicals. Currently most alkylamines are synthesized by the reaction between ammonia and an alcohol in the presence of hydrogen over acidic metal-supported oxide catalysts.[1] Since most alcohols are synthesized from simple olefins,[2] direct amination of an olefin would be economically advantageous. Besides its industrial importance, this reaction would have many applications in organic synthesis. The syntheses of alkyl-substituted amines by the addition of amines to olefins are mostly favorable thermodynamic processes.[3] Some of these reactions are exothermic but have equilibrium constants near unity. When reaction temperatures increase, they become less favorable. Therefore, it is desirable to catalyze the addition of amines to olefins under mild reaction conditions.

Attempts at catalytically adding NH_3 to ethylene over heterogeneous catalysts date back to 1954. Howk et al. reported 0.7% conversion to alkylated amine, at temperatures of 199–250 °C and pressures of ethylene between 380 and 1000 atm, with metallic sodium.[4] Other catalysts include MoO_3 on alumina at 175–300 °C,[5] palladium on alumina at 120 °C,[6] and zeolite acid catalysis at 400 °C.[7] Most of these studies do not report yields or catalyst efficiencies.

Homogeneous catalysts for the amination of olefins have also been explored. Solutions of $RhCl_3$ or $RuCl_3 \cdot xH_2O$,[8] in addition to Zr, Nb, Ta[9] and alkali-metal amides,[10] have all proved effective for the amination of ethylene by dialkylamines at reasonably low temperatures (<150 °C) and pressures. Alkali-metal amides have also shown activity toward catalyzing the addition of ammonia to ethylene and propylene, but conversions were drastically reduced.[10] Several of these relatively simple catalysts exhibit extreme air and moisture sensitivity. A comprehensive review has appeared recently.[11]

Advances in the chemistry of late-metal nitrogen compounds[12] has led to the investigation of possible homogeneous organometallic mediated catalytic pathways for the amination of olefins. One viable mechanism that has received attention[13,14] is shown in Scheme I. This involves oxidative addition of the N–H bond of an amine to a coordinatively unsaturated metal center to produce a hydrido amido complex. Insertion of an olefin into the metal–nitrogen bond generates a hydrido alkyl complex. Reductive elimination of the hydrido alkylamine product regenerates the coordinatively unsaturated ML_n species. Each step in this proposed catalytic cycle has been observed

(1) Schweizer, A. E.; Fowlkes, R. L.; McMakin, J. H.; Whyte, T. E., Jr. In *Encyclopedia of Chemistry and Technology*; Othmer, K., Ed.; John Wiley and Sons: 3rd Ed.; Vol. 2, 1978, p 272–283.
(2) Sherman, P. D., Jr.; Kavasmaneck, P. R. In *Encyclopedia of Chemistry and Technology*; Othmer, K., Ed.; John Wiley and Sons: 3rd ed.; Vol. 9, 1980, p 344–350.
(3) Benson, S. W. *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2nd ed.; John Wiley and Sons: New York, NY, 1976.
(4) Howk, B. W.; Little, E. L.; Scott, S. L.; Whitman, G. M. *J. Am. Chem. Soc.* **1954**, *76*, 1899.
(5) Uhlmann, L. *Wissenschaftliche Zeitschrift der Technischen Hochschule fur Chemie Leuna-Merseburg*; **1963**, *5*, 263.
(6) McClain, D. M. *U.S. Patent* **1968**, 3,412,158.
(7) (a) Peterson, J. O. H.; Fales, H. S. *U.S. Patent* **1981**, 4,307,250. (b) Peterson, J. O. H.; Fales, H. S. *U.S. Patent* **1983**, 4,375,002A. (c) Deeba, M.; Ambs, W. J. *Eur. Pat. Appl.* **1983**, EP 77016. (d) Deeba, M.; Ford, M. E. *Zeolites* **1990**, *10*, 794.
(8) Coulson, D. R. *Tetrahedron Lett.* **1971**, 429; Gardner, D. M.; Clark, R. T. *Eur. Pat. Appl.* **1981**, EP 39061 Al.
(9) Clerici, M. G.; Maspero, F. *Synthesis* **1980**, *4*, 305.
(10) Pez, G. P.; Galle, J. E. *Pure Appl. Chem.* **1985**, *57*, 1917.
(11) Roundhill, D. M. *Chem. Rev.* **1992**, *92*, 1.
(12) (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163 and references therein. (b) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1 and references therein.
(13) Casalnuvo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738.
(14) (a) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750. (b) Cowan, R. L.; Trogler, W. C. *Organometallics* **1987**, *6*, 2451.

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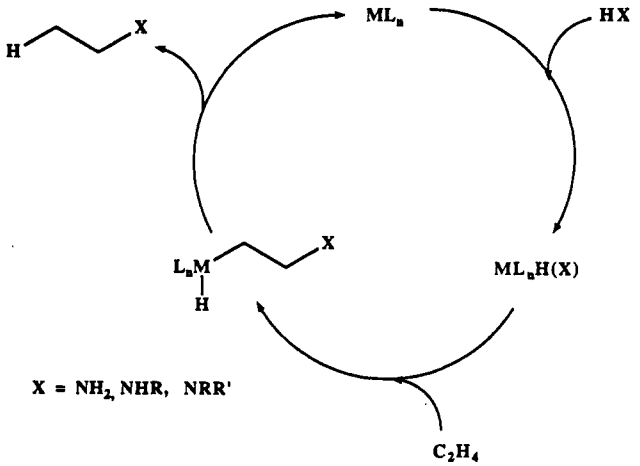
Scheme I. Idealized Cycle for Catalytic Addition of Amines to Ethylene via the N–H Oxidative Addition Pathway



independently. One reaction that appears to proceed by this mechanism has been reported by Casalnuvo, Calabrese, and Milstein.[13] Aniline adds to norbornene in the presence of $IrCl(PEt_3)_2(C_2H_4)_2$ and $ZnCl_2$ in refluxing THF for 3 days. This reaction produces a maximum of six turnovers of product before loss of catalytic activity.

Previously we showed that the reaction between *trans*-$Pt(H)(NO_3)(PEt_3)_2$ and sodium anilide yields *trans*-$PtH[N(H)Ph](PEt_3)_2$.[14] Olefin insertion into the platinum–nitrogen bond produces the corresponding platinum hydrido alkyl, which reductively eliminates alkyl-substituted amine on heating. The resulting "$Pt(PEt_3)_2$" metal species is trapped by excess olefin as a platinum(0) olefin complex and does not oxidatively add the N–H bond of excess aniline. Attempts to increase the reactivity by use of the chelating dmpe ($Me_2PCH_2CH_2PMe_2$) ligand were unsuccessful.[15]

For late transition metals, reports of the oxidative addition of N–H bonds to a single coordinatively unsaturated metal center are rare.[13,16] with the exception of activated or chelated N–H bonds.[17] Reactivity studies suggest that N–H reductive elimination dominates the chemistry of the platinum-group hydrido amido complexes.[14,15,18] The weaker bond strength of the M–N bond in comparison to M–O and M–C[19] bonds, together with the bond strength order N–H > O–H > C–H, suggests that the amination of olefins with a platinum group metal bis(phosphine) complex catalyst will be difficult to achieve by the mechanism shown in Scheme I.[15]

These considerations led us to explore alternative pathways for olefin amination. The addition of amines to coordinated olefins occurs with several late-transition-metal systems.[20] Binding of alkene to the metal center sufficiently activates the olefin for nucleophilic attack.[21] This was first reported for platinum by Panunzi et al.,[22] who described the addition of amines to *cis*-$PtCl_2$(olefin)-(PR_3) complexes to produce new platinum alkyls. Addition of amines to solutions containing bis(benzonitrile)palladium(II) chloride and olefin in THF at low temperature results in the formation of new palladium–alkyl bonds.[23] In both cases, the metal alkyls derive from nucleophilic attack of amine on coordinated olefin. The inherent stability of the platinum- and palladium–alkyl bonds formed impedes their cleavage. Platinum–alkyl bonds in the former system were cleaved by addition of HCl or $NaBH_4$. These reactions produce an N-alkylated amine and a catalytically inactive platinum(trialkylphosphine) chloro-bridged dimer. Alkylamine product along with palladium hydrides and palladium metal were recovered on hydrogenation of the palladium–alkyl systems. The one report of catalytic amination of olefins by palladium involves the cyclization of tethered aminoolefins,[24] with benzoquinone as a sacrificial oxidant. Lanthanide-metal complexes exhibit similar cyclization catalysis,[25] with the advantage that a sacrificial reagent is not required.

Protonolysis of the metal–alkyl bond with an ammonium salt acid provides a potential way to make these reactions catalytic. This approach requires a more electron-rich metal center. The reaction between $PdMe_2$(dmpe) and [NHRR'R''][X] (eq 1) provides an example of such reactivity.[26] When X is a noncoordinating anion, such as $[BPh_4]^-$, cleavage of the palladium–carbon bond extrudes methane and yields cationic palladium amine complexes of the general formula [PdMe(dmpe)(NRR'R'')][X]. This pathway is shown in Scheme II. Protonolysis of a palladium–alkyl bond by 1 equiv of ammonium salt produces complex A in step 1. All the steps involved in the catalytic cycle shown in Scheme II have good precedent in the literature,[23,24,26] and this paper explores that catalytic approach. A similar mechanism has been proposed[27] to explain the cyclization of aminoolefins catalyzed by $PtCl_4^{2-}$ in acidic solution. This particular catalyst suffered from

(15) Seligson, A. L.; Cowan, R. L.; Trogler, W. C. *Inorg. Chem.* **1991**, *30*, 3371.

(16) (a) Koelliker, R.; Milstein, D. *Agnew. Chem., Int. Ed. Engl.* **1991**, *30*, 1707. (b) Casalnuvo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 971. (c) Armor, J. N. *Inorg. Chem.* **1978**, *17*, 203. (d) Armor, J. N. *Inorg. Chem.* **1978**, *17*, 213. (e) Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem.* **1984**, *106*, 5472. (f) Suss-Fink, G. *Z. Naturforsch., B; Anorg. Chem., Org. Chem.* **1980**, *35B*, 454. (g) Sappa, E.; Milone, L. *J. Organomet. Chem.* **1973**, *61*, 383. (h) Lin, Y.; Mayr, A.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* **1984**, *272*, 207. (i) Johnson, B. F. G.; Lewis, J.; Odiaka, T.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *216*, C56. (j) Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1977**, 1328.

(17) (a) Fornies, J.; Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1006. (b) Schaad, D. R.; Landis, C. R. *J. Am. Chem. Soc.* **1990**, *112*, 1628. (c) Park, S.; Johnson, M. P.; Roundhill, D. M. *Organometallics* **1989**, *8*, 1700. (d) Hedden, D.; Roundhill, D. M. *Inorg. Chem.* **1986**, *25*, 9. (e) Park, S.; Hedden, D.; Roundhill, D. M. *Organometallics* **1986**, *5*, 2151. (f) Hedden, D.; Roundhill, D. M.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 5014. (g) Hedden, D.; Roundhill, D. M. *Inorg. Chem.* **1970**, *9*, 254. (i) Yamamoto, T.; Sano, K.; Yamamoto, A. *Chem. Lett.* **1982**, 907. (j) Nelson, J. H.; Schmidt, D. L.; Henry, R. A.; Moore, D. W.; Jonassen, H. B. *Inorg. Chem.* **1970**, *9*, 2678. (k) Ladipo, F. T.; Merola, J. S. *Inorg. Chem.* **1990**, *29*, 4172. (l) Schadd, D. R.; Landis, C. R. *Organometallics* **1992**, *11*, 2024.

(18) (a) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875.

(19) (a) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444. (b) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.

(20) Gasc, M. B.; Lattes, A.; Perie, J. J. *Tetrahedron* **1983**, *39*, 703.

(21) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308.

(22) Panunzi, A.; DeRenzi, A.; Palumbo, R.; Paiaro, G. *J. Am. Chem. Soc.* **1969**, *91*, 3879.

(23) Akermark, B.; Bäckvall, J. E.; Hegedus, L. S.; Siirala-Hansén, K.; Sjöberg, K. *J. Organomet. Chem.* **1974**, *72*, 127.

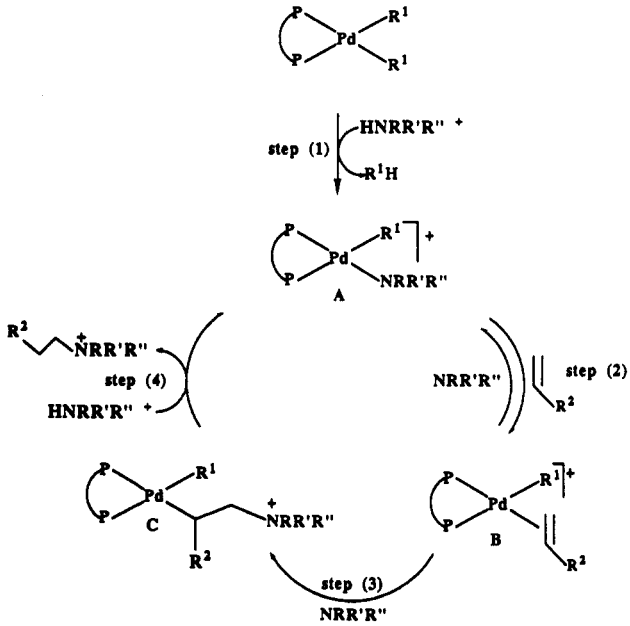
(24) Hegedus, L. S.; Allen, G. F.; Bozell, J. J.; Waterman, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 5800.

(25) (a) Gagné, M. R.; Nolan, S. P.; Marks, T. J. *Organometallics* **1990**, *9*, 1716. (b) Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108. (c) Gagné, M. R.; Brard, L.; Conticello, V. P.; Giardello, M. A.; Stern, C. L.; Marks, T. J. *Organometallics* **1992**, *11*, 2003. (d) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275.

(26) Seligson, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 2520.

(27) Ambüehl, J.; Pregosin, P. S.; Venanzi, L. M.; Consiglio, G.; Bachechi, F.; Zambonelli, L. *J. Organomet. Chem.* **1979**, *181*, 255. Ambüehl, J.; Pregosin, P. S.; Venanzi, L. M.; Ughetto, G.; Zambonelli, L. *J. Organomet. Chem.* **1978**, *160*, 329.

Scheme II. Proposed Catalytic Cycle for Nucleophilic Attack of Amine on Coordinated Olefin Using a Palladium–Alkyl Catalyst



sluggish kinetics (1–67 days at 60 °C) and low catalytic turnovers (3 maximum).

Experimental Section

All reactions were performed under a nitrogen atmosphere by using modified Schlenk and glovebox techniques. Liquids were transferred by syringe (or cannula). Materials obtained from commercial sources were used without further purification, except where noted. Under a nitrogen atmosphere, Et_2O, THF, and C_6D_6 were dried over Na- or K-benzophenone ketyl. Methylene chloride was distilled over CaH_2. Ammonium salts of the type [HNRR′R″][X], where [X] is BPh_4, were prepared by the reaction of $NaBPh_4$ with the corresponding hydrido chloride salt of the amine in H_2O. The BF_4^- salts were synthesized by reacting an amine with $HBF_4{\cdot}Et_2O$ in Et_2O. A sample of $HNPh(CH_2CH_2CN)$ was purchased from Pfaltz and Bauer. $[H_2NPh(CH_2CH_2CN][Cl]$ was synthesized by reacting $HNPh(CH_2CH_2CN)$ with HCl. Acrylonitrile was purified by passing it through a column of activated alumina, followed by vacuum distillation. $PdMe_2(dmpe)$[28] (1), $PdMe_2(dppe)$[29] (2), $Pd(CH_2SiMe_3)_2(dmpe)$[28] (3), $[PdMe(dmpe)(NHEt_2)][BF_4]$,[26] [1,5-bis(di-*tert*-butylphosphino)pentan-3-yl-*C,P,P′*]methylpalladium(II)[29] (5), [1,5-bis(di-*tert*-butylphosphino)pentan-3-yl-*C,P,P′*]palladium(II) tetrafluoroborate[29] (6), and *cis*-$PdMe_2(PMe_3)_2$[28] (7) were prepared according to known procedures.

All NMR spectra were recorded on a GE QE-300 MHz spectrometer equipped with a 5-mm broad-band probe. Proton chemical shifts were referenced to the residual solvent peak in the observed spectra. The $^{31}P\{^1H\}$ NMR spectra were referenced to the deuterated lock solvent, which had been previously referenced to 85% H_3PO_4. All $^{31}P\{^1H\}$ chemical shifts were recorded relative to H_3PO_4, with downfield shifts being positive. Gel permeation chromatography used THF solvent and a Waters Associates chromatograph equipped with a refractive index detector and 500 Å, 10^3 Å, 10^4 Å, and 10^6 Å Ultrastyragel columns. Both distilled and crude acrylonitrile starting material exhibited peaks from oligomers with a molecular weight of approximately 240.

Reaction of 1 with Acrylonitrile and $[NH_3Ph][BPh_4]$ in CD_2Cl_2. Complex 1 (10 mg, 0.03 mmol) and $[NH_3Ph][BPh_4]$ (0.072 g, 0.15 mmol) were loaded in an NMR tube along with acrylonitrile (0.1 mL, 1.5 mmol) and CD_2Cl_2 (0.4 mL). The solution was heated at 35 °C for 2 h and then cooled to room temperature, and ^1H and $^{31}P\{^1H\}$ NMR spectra were taken. Besides excess acrylonitrile and a complex alkyl region (from palladium phosphine complexes in solution), two new resonances were observed in the ^1H NMR spectrum. These were identified by comparison of the spectrum of $[H_2NPh(CH_2CH_2CN)][BPh_4]$, which was synthesized independently. ^1H NMR (CD_2Cl_2): δ 2.62 (t, $^3J_{HH}$ = 7 Hz, 2 H, CH_2CN)1, 2.94 (t, $^3J_{HH}$ = 7 Hz, 2H, H_2PhNCH_2). Complex 2 can also be used as a catalyst under the same conditions.

Reactivity of Other Activated Olefins with 1 and $[NH_3Ph][BPh_4]$. A general procedure for these reactions involves loading 1 (10 mg) and $[NH_3Ph][BPh_4]$ (5 equiv) into an NMR tube with olefin (50 equiv) and CD_2Cl_2. The solutions were heated in a constant-temperature bath at 35 °C for 2 h, and cooled, and ^1H NMR spectra were taken. Table I shows that products formed by the addition of aniline to methyl acrylate, acrolein, and crotonitrile. Detectable amounts of these products did not form in the control reactions without palladium catalyst.

***cis*-Bis((trimethylsilyl)methyl)(bis(diphenylphosphino)ethane)palladium(II), *cis*-$Pd(CH_2SiMe_3)_2(dppe)$ (4).** To a suspension of $PdCl_2(dppe)$ (0.259 g, 0.45 mmol) in Et_2O (20 mL) was added Me_3SiCH_2MgCl (2.70 mL, 1.0 M in Et_2O), and the reaction was stirred for 6 h. The solution was cooled to 0 °C, and the excess Grignard reagent was hydrolyzed by the dropwise addition of H_2O (5 mL). The organic layer was removed and the aqueous layer washed with Et_2O (3 × 5 mL). The combined organic extracts were dried over $MgSO_4$ and filtered through activated charcoal. The solution was reduced to 2 mL, pentane (1 mL) added, and the solution cooled in the freezer to yield colorless crystals of 4: 0.283 g (92%); mp 155–165 °C dec; ^1H NMR (C_6D_6) δ 0.30 (s, 18 H, CH_3), 1.25 (dd, 4 H, $PdCH_2$), 1.88 (d, 4 H, PCH_2), 7.18 and 7.61 (m, 20 H, PC_6H_5); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 38.58 (s). Anal. Calcd for $C_{34}H_{46}Si_2P_2Pd$: C, 60.12; H, 6.83. Found C, 60.06; H, 6.82.

Reaction of 1–5 and 7 with Acrylonitrile, NH_2Ph, and $[NH_3Ph][BPh_4]$ in C_6D_6. Six NMR tubes were loaded with the palladium complexes 1–5 and 7 (0.014 M), $[NH_3Ph][BPh_4]$ (0.014 M), acrylonitrile (2.80 M), NH_2Ph (2.80 M), and $(CH_3)_3SiOSi(CH_3)_3$ (0.014 M) in C_6D_6. The appearance of the product 3-anilinopropionitrile was monitored by ^1H NMR spectroscopy for 6 h at 30 °C, by integration of product versus the $(CH_3)_3SiOSi(CH_3)_3$ internal standard. Turnover data for these reactions are plotted in Figure 1 (except for complex 4, which was too slow to observe under these conditions). The identity of the product was confirmed by comparison to an authentic sample of 3-anilinopropionitrile. ^1H NMR (C_6D_6): δ 2.24 (t, J = 6 Hz, 2 H, CH_2CN), 2.94 (q, J = 6 Hz, 2 H, $HPhNCH_2$), 4.2 (s, (br), 1 H, N*H*). (Note: these resonances shift depending on the acidity of the specific solution.)

Reaction of 1 with $[NH_3Ph][BPh_4]$ and 20 Equiv of Acrylonitrile in CD_2Cl_2. Complex 1 (0.012 g, 0.04 mmol) and $[NH_3Ph][BPh_4]$ (0.017 g, 0.04 mmol) were loaded into an NMR tube and cooled to −78 °C. Acrylonitrile (0.05 mL, 20 equiv) and CD_2Cl_2 (0.40 mL) were added. The NMR tube was placed in the probe at −70 °C and warmed up in 10 °C intervals while observing the ^1H and $^{31}P\{^1H\}$ NMR spectra. At 10 °C new resonances were observed, which could possibly be an intermediate. ^1H NMR (CD_2Cl_2, $[PdMe(dmpe)(NH_2Ph)][BPh_4]$): δ 0.30 (dd, 3 H, $PdCH_3$), 0.93 (d(br), 6 H, PCH_3), 1.48 (d, 6 H, PCH_3), 1.77 (m, 4 H, PCH_2), 6.6–7.6 (m, NC_6H_5 and BC_6H_5). ^1H NMR (CD_2Cl_2, new resonances): δ 2.59 (td, J = 6.5 Hz, J = 3.6 Hz), 3.44 (d, J = 3.6 Hz), 3.57 (d, J = 3.6 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 39.1 (d), 21.06 (d), weak new resonances at 32.43 (d), 23.08 (d). On warming the solution to 25 °C, the ^1H NMR spectrum of the new resonances broadened and became more intense, and the weak $^{31}P\{^1H\}$ NMR resonances at 32.43 and 23.08 gained intensity. Product $[H_2NPh(CH_2CH_2CN)][BPh_4]$ appeared in the ^1H NMR spectra after ~0.5 h at this temperature.

(28) Tooze, R.; Chiu, K. W.; Wilkinson, G. *Polyhedron* **1984**, *3*, 1025.
(29) Seligson, A. L.; Trogler, W. C. *Organometallics*, preceding paper in this issue.

Generation of [Pd(CH$_2$SiMe$_3$)(dmpe)(CH$_2$CHCN)][BPh$_4$]. Complex **3** (0.052 g, 0.12 mmol) and AgBPh$_4$ (0.051 g, 0.12 mmol) were placed into a Schlenk flask and kept in the dark. To this was added acrylonitrile (3 mL), and the solution was stirred for 0.5 h. Activated charcoal was added and the solution stirred for 5 min and then filtered to yield a pale yellow solution. Aliquots of this solution were drawn for NMR analysis. ^{1}H and ^{31}P{^{1}H} NMR resonances obtained for this solution were complex and will be discussed further in the text.

Generation of [Pd(CH$_2$SiMe$_3$)(dmpe)(NH$_2$Ph)][BPh$_4$]. Complex **3** (0.010 g, 0.02 mmol) and [Cp$_2$Fe][PF$_6$] (0.007 g, 0.02 mmol) were loaded in an NMR tube, and to this was added NH$_2$Ph (0.27 mL, 3.0 mmol, 150 equiv) and C$_6$D$_6$ (0.3 mL). ^{1}H NMR (C$_6$D$_6$): δ 0.0 (s, 12 H, Si(C*H*$_3$)$_4$), 0.12 (s, 9 H, SiC*H*$_3$), 0.2 (dd(br)), 2 H, PdC*H*$_2$), 0.37 (d, 6 H, PC*H*$_2$), 0.88 (d, 6 H, PC*H*$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 22.21 (d, $^2J_{PP}$ = 22 Hz), 37.67 (d, $^2J_{PP}$ = 22 Hz).

Kinetics and Turnover Data for the Production of 3-Anilinopropionitrile by the Reaction between 5, [NH$_3$Ph][BPh$_4$], Acrylonitrile, and NH$_2$Ph in C$_6$D$_6$. A typical run was done as follows: A solution of **5** (0.24 mL, 2.1 × 10^{-3} M) in C$_6$D$_6$ (also containing a predetermined amount of hexamethyldisiloxane as an integration standard) was added to an NMR tube containing NH$_2$Ph (0.023 mL), acrylonitrile (0.016 mL), [NH$_3$Ph][BPh]$_4$ (0.10 mL, 5.1 × 10^{-3} M in C$_6$D$_6$), and C$_6$D$_6$ (0.12 mL). The solution was warmed in the probe to 25 °C, and ^{1}H NMR spectra were taken at set time intervals. Concentrations were calculated by integration of product versus the hexamethyldisiloxane internal standard.

Reaction of 5 with [NH$_3$Ph][BPh$_4$] and 20 Equiv of Acrylonitrile in C$_6$D$_6$. Complex **5** (0.003 g, 0.006 mmol) and [NH$_3$Ph][BPh$_4$] (0.003 g, 0.006 mmol) were loaded into an NMR tube. Addition of acrylonitrile (0.005 mL, 12.5 equiv) and C$_6$D$_6$ (0.45 mL) yielded a colorless solution. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 98.4 (s), 91.9 (s), 91.7 (s).

Reaction of 5 with [NH$_3$Ph][BPh$_4$] and 200 Equiv of Aniline in C$_6$D$_6$. Complex **5** (0.003 g, 0.006 mmol) and [NH$_3$Ph][BPh$_4$] (0.003 g, 0.006 mmol) were loaded into an NMR tube. Addition of aniline (0.11 mL, 200 equiv) and C$_6$D$_6$ (0.35 mL) produced a pale yellow solution. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 82.5 (s br).

Reaction of 5 with [NH$_3$Ph][BPh$_4$] in CD$_3$CN. Complex **5** (0.003 g, 0.006 mmol) and [NH$_3$Ph][BPh$_4$] (0.003 g, 0.006 mmol) were loaded into an NMR tube. Addition of CD$_3$CN (0.45 mL) produced a colorless solution. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 92.7 (s).

Reaction of 6 with Acrylonitrile in CD$_2$Cl$_2$. Complex **6** (0.015 g, 0.03 mmol) was loaded into an NMR tube, dissolved in CD$_2$Cl$_2$ (0.45 mL), and cooled to −70 °C in the NMR probe. After addition of acrylonitrile (1.5 μL, 0.03 mmol), ^{1}H and ^{31}P{^{1}H} NMR spectra were taken. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.29 (m br, 36 H, CC*H*$_3$), 1.62 (m, br), 2.97 (m br, 1 H, PdC*H*), 3.15 (m br), 3.64 (m br), 5.91 (dd, C*H*), 6.41 (dd, C*H*$_2$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 90.95 (s), 95.42 (s).

Results

Catalytic Amination of Activated Olefins by 1, 2, 3, 4, and 7. Activated olefins should exhibit enhanced binding to electron-rich metal centers. They also show a greater tendency toward nucleophilic attack. Acrylonitrile and aniline were chosen to test whether catalysis by Scheme II is possible, because the weak aniline ligand might allow the olefin to compete for binding at the metal center. There is no detectable reaction between acrylonitrile and aniline in the absence of catalyst, under the identical conditions of the palladium catalyzed reactions studied here.

The reaction between [NH$_3$Ph][BPh$_4$] and acrylonitrile in CH$_2$Cl$_2$ at 35 °C, in the presence of catalytic quantities of **1**, yields 3-anilinopropionitrile in its protonated form. Identification of the product was confirmed by comparing

Chart I. Catalyst Precursors Studied

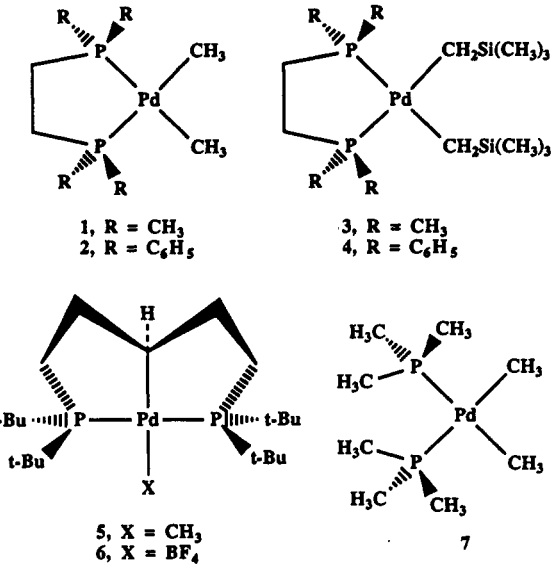


Table I. Results of the Addition of Aniline to Activated Olefins with Catalyst 1

olefin	[addition product][BPh$_4$]	^{1}H NMR resonances (CD$_2$Cl$_2$), ppm
methyl acrylate	H$_2$PhN(CH$_3$)$_2$C(O)OCH$_3$	2.63 (t, ^3J = 7 Hz, 2H), 2.95 (t, ^3J = 7 Hz, 2H)
acrolein	H$_2$PhNCH$_2$CH$_2$C(O)H	2.77 (t, ^3J = 7 Hz, 2H), 2.97 (t, ^3J = 7 Hz, 2H)
crotonitrile	H$_2$PhNCH(CH$_3$)CH$_2$CN	1.45 (d, ^3J = 9 Hz, 3H), 2.62 (dd, ^3J = 9 Hz, 2H), 3.18 (q, ^3J = 9 Hz, 1H)

the ^{1}H NMR spectrum of the reaction solution with an authentic sample. This reaction gave about 10 turnovers of product per mole of catalyst within a 4.5-h period. Decomposition of the catalyst was evident at that time by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy, and no further reactivity was observed. Several other activated olefins were used as substrates. Methyl acrylate, acrolein, and crotonitrile all showed evidence of catalytic behavior (Table I) in the ^{1}H NMR spectrum, while 2-cyclohexen-1-one exhibited none. Complex **2** was also an active catalyst precursor for these reactions. The inherent insolubility of the [NH$_3$Ph][BPh$_4$] and the rapid decomposition of catalyst under these conditions limited further mechanistic studies. With the nonchelating phosphine catalyst in Pd(CH$_3$)$_2$[P(CH$_3$)$_3$]$_2$, **7**, catalytic activity decreased after only 3 turnovers (Figure 1, Table II). The solubility problem with [NH$_3$Ph][BPh$_4$] was eliminated by using free aniline. Aniline, a weak base, has been shown to be a poor ligand in these palladium systems.[26] [PdMe(dmpe)(NH$_2$Ph)]$^+$ is unstable unless excess free aniline is present in solution. At least 1 equiv of NH$_3$Ph$^+$ must be added with the aniline substrate, since a proton source is a requisite cocatalyst.

Two other palladium–alkyl catalyst precursors, Pd(CH$_2$SiMe$_3$)$_2$(dmpe) (**3**) and Pd(CH$_2$SiMe$_3$)$_2$(dppe) (**4**), made it easier to monitor the catalysis reactions spectroscopically. Protonolysis of the palladium–alkyl bond in these compounds yields TMS. This is a convenient internal integration standard for the ^{1}H NMR spectrum. The presence of the bulkier (trimethylsilyl)methyl ligand cis to the active coordination site in **3** and **4** appears to prolong the active life of the catalyst, as compared to **1** and **2**. When the solution of **3** is catalytically active, the Pd–CH$_2$SiMe$_3$ resonance and the free TMS signal are present in comparable amounts. This suggests Pd(CH$_2$SiMe)-

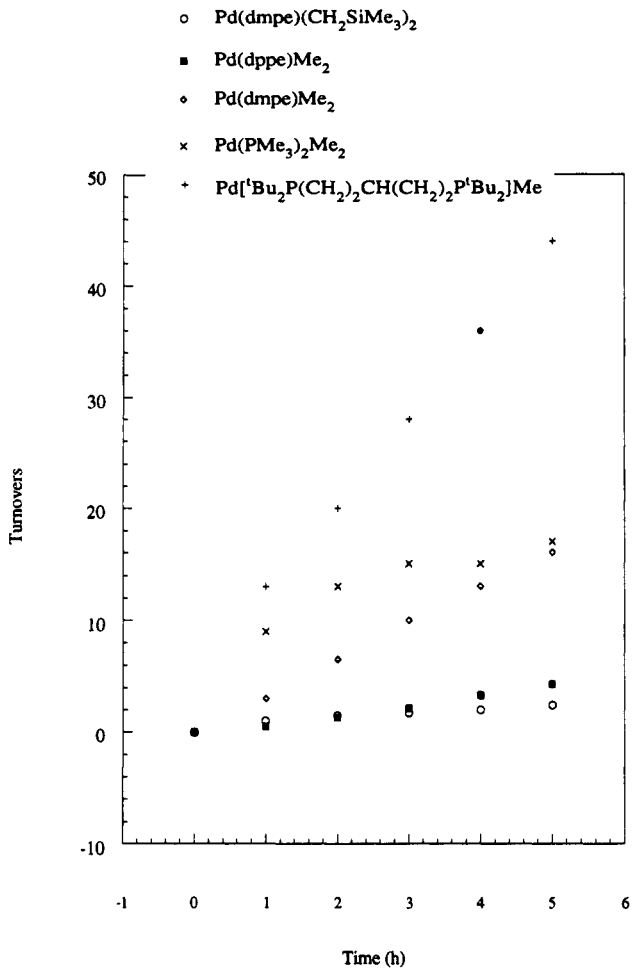


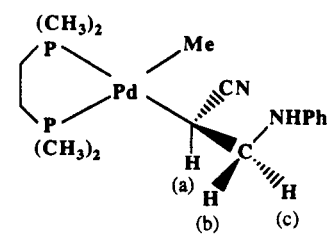
Figure 1. Comparison of the number of turnovers of 3-anilinopropionitrile produced per mole of catalyst for complexes 1, 2, 3, 5, and 7 (0.5%) for the reaction of acrylonitrile with NH_2Ph at 30 °C. Complex 4 showed no appreciable reactivity on this time scale.

$(dmpe)(NH_2Ph)^+$ acts as the catalyst or as a direct precursor to it.

The one-electron oxidative cleavage of palladium–carbon bonds[30] facilitates mechanistic studies of this system. The reaction between 3 and 1 equiv of $AgBPh_4$ in CD_2Cl_2 generates $[Pd(CH_2SiMe_3)(dmpe)][BPh_4]$, which is trapped in the presence of acrylonitrile. The ^1H and $^{31}P\{^1H\}$ NMR spectra are complex and broadened. In the $^{31}P\{^1H\}$ NMR spectra two major species form in solution, although several additional broad resonances appear between δ 30 and 40. Each of the major species exhibits two distinct ^{31}P resonances as expected for a $[Pd(CH_2SiMe_3)(dmpe)L]^+$ complex. Each resonance shows doublet splitting from coupling to a cis phosphorus atom. One species is assigned to $[Pd(CH_2SiMe_3)(dmpe)(NCHC{=}CH_2)][BPh_4]$, where acrylonitrile binds to palladium through the nitrile group [δ 41.7 (J = 19 Hz) and 28.1 (J = 19 Hz)]. The two $^{31}P\{^1H\}$ resonances for this species closely resemble those of $[Pd(CH_2SiMe_3)(dmpe)(NCCH_3)][BPh_4]$.[30] Addition of CH_3CN to the reaction solution generates the acetonitrile complex, completely displacing the original ^{31}P NMR resonances. Acetonitrile is therefore a much better ligand than acrylonitrile. Up to 200 equiv of acrylonitrile can be added to a solution of $[Pd(CH_2SiMe_3)(dmpe)(CH_3CN)]^+$, and none of the resonances for the acrylonitrile complex are observed. The complexity in the NMR spectral data for the acrylonitrile complex appears to be the result of coordination isomerization. Several NMR resonances suggest the olefin-coordinated isomer of $[Pd(CH_2SiMe_3)(dmpe)(CH_2{=}CHCN)][BPh_4]$ is the other major isomer present in solution [^{31}P (CD_2Cl_2): δ 36.3 (J = 22 Hz) and 26.0 (J = 22 Hz)]. Broad multiplets in the ^1H NMR spectrum also appear between 2.5 and 3.2 ppm and are attributed to the olefinic protons of π-bound acrylonitrile. Known cationic olefin complexes of platinum display similar resonances in this spectral region.[31]

The addition of small amounts of aniline to a solution of the acrylonitrile complexes at −40 °C causes several new resonances to appear in the $^{31}P\{^1H\}$ spectrum. Small quantities of $[Pd(CH_2SiMe_3)(dmpe)(NH_2Ph)]^+$ could be identified in the $^{31}P\{^1H\}$ NMR spectrum [δ 37.9 (J = 22 Hz) and 22.2 (J = 22 Hz)]. The authentic aniline complex could be generated by adding $AgBPh_4$ to $Pd(CH_2SiMe_3)_2(dmpe)$ in CD_2Cl_2 with added aniline. On warming the −40 °C solution to 0 °C, several new resonances appear. One possible species present would be a palladium–dialkyl complex, such as $Pd(CH_2SiMe_3)[CH(CN)CH_2NHPh](dmpe)$. This could be observed more clearly in the ^1H NMR spectrum. The formation of 3-anilinopropionitrile was observed simultaneously in the ^1H NMR spectrum to establish that the solution is catalytically active. The monoalkyl cation catalyst can be generated by addition of 1 equiv of $[FeCp_2][PF_6]$ to 3 in the presence of excess aniline. This cleanly produces $[Pd(CH_2SiMe_3)(dmpe)(NH_2Ph)][PF_6]$. When several equivalents of acrylonitrile are added to this solution, 3-anilinopropionitrile is immediately observed to form.

The reaction between 1 and $[NH_3Ph][BPh_4]$ with 20 equiv of acrylonitrile at low (−70 °C) temperature and with warming to 10 °C affords several new resonances in the ^1H NMR spectra. One minor group of proton resonances (Figure 2) can be attributed to the $PdCH(CN)CH_2NHPh$ moiety of the aniline addition product prior to its protolytic cleavage. The diastereotopic protons b and c appear as two doublets at 3.57 and 3.44 ppm in the ^1H NMR spectrum. A single resonance for proton a should appear as a complicated multiplet from coupling to protons b and c and the inequivalent cis and trans phosphines. A triplet of doublets is observed at 2.59 ppm, which is assigned to the proton resonance of a. We emphasize that these were minor components in the reaction mixture; however, species I is expected to be a



I

short-lived intermediate in the proposed catalytic cycle. The ^1H NMR spectrum of the platinum complex $PtH(CH(CN)CH_2NHPh)(PEt_3)_2$[14] displays the diastereotopic protons as doublets at 3.97 and 3.46 ppm and also exhibits a multiplet at 2.46 ppm. These closely resemble the

(30) Seligson, A. L.; Trogler, W. C. *J. Am. Chem. Soc* **1992**, *114*, 7085.

(31) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1973**, 1848.

Table II. Total Amount of Product vs Time for the Addition of Aniline (2.8 M) to Acrylonitrile (2.8 M) with Various Soluble (0.014 M) Palladium Catalysts at 30 °C in C_6D_6 Solvent

	turnovers of product/mol of catalyst				
time (h)	$Pd(CH_2SiMe_3)_2$(dmpe)	$PdMe_2$(dppe)	$PdMe_2$(dmpe)	$PdMe_2(PMe_3)_2$	PdMe[PC_5P]
1.00	1.0	0.5	3.0	9	13
2.00	1.5	1.3	6.5	13	20
3.00	1.7	2.1	10.0	15	28
4.00	2.0	3.3	13.0	15	36
5.00	2.4	4.3	16.0	17	44

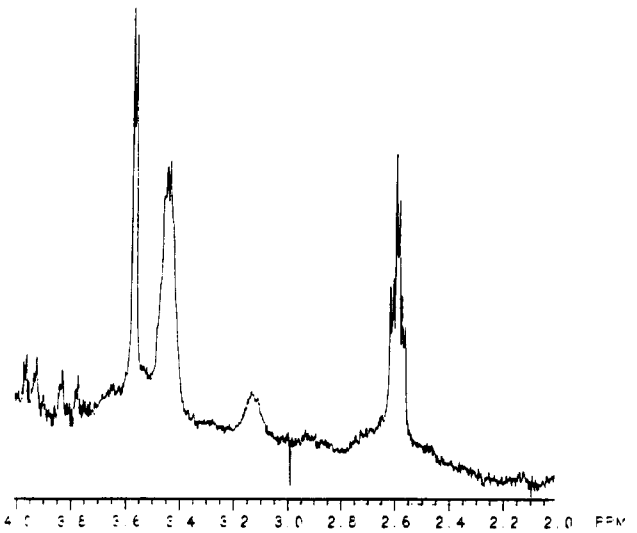


Figure 2. ^{1}H NMR spectrum of resonances attributed to the Pd–CH(CN)CH_2(NHPh) moiety obtained from the reaction between $Pd(CH_3)$(dmpe)$(CH_2{=}CHCN)^+$ and aniline.

resonances discussed above for complex I. The structure of PtH(CH(CN)CH_2NHPh)$(PEt_3)_2$ was established crystallographically. The acidic conditions should cleave the new palladium–carbon bond, which accounts for the instability of I in solution.

Catalytic Reactions Using 5 as a Precursor. The decomposition of the palladium dialkyl catalysts at high turnovers poses a problem for their practical use. The PdR_2L_2-based catalysts, where L_2 is the chelating phosphine dmpe or dppe and R_2 is CH_3 or CH_2SiMe_3, are rendered completely inactive over time, and decomposition products, such as palladium metal, are visually evident. The qualitative NMR studies suggested the essential feature for the catalysts was a stable bis(phosphine) monoalkyl palladium cation. Building a catalyst with a very stable $\widehat{PCP}$ backbone of donor ligands, and sterically protecting the active site from undesired reactivity, might accomplish this goal. One system that fills the requirements is {1,5-bis(di-*tert*-butylphosphino)pentan-3-yl-*C,P,P'*}methylpalladium(II) (**5**).

Catalytic amounts of **5** and $[NH_3Ph][BPh_4]$, combined with aniline and acrylonitrile at room temperature, are almost completely converted to 3-anilinopropionitrile. When additional substrate is added to the reaction solution, more product forms. The active catalyst obtained from **5** is apparently very stable and therefore active for much longer times than 1–4. By NMR spectroscopy the reaction appears to be considerably cleaner.

To better understand why complex **5** generates an improved homogeneous catalyst, identification of intermediate species involved in this process were again pursued by NMR spectroscopy. The reaction between 1 equiv of $[NH_3Ph][BPh_4]$ and **5**, in the presence of excess acrylonitrile, displayed three new resonances in the $^{31}P\{^1H\}$ NMR spectra. These are identical to those observed in the spectrum of an active catalysis solution. To determine whether one of these resonances corresponds to the aniline complex, **5** was combined with 1 equiv of $[NH_3Ph][BPh_4]$ in the presence of a 200-fold excess of aniline. This solution displayed only a weak and broadened resonance at 82.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum, which does not match any of the resonances in the spectrum of the catalysis solution. Therefore, if the aniline complex is present during catalysis, it is present in a very low concentration. Complex **5** was reacted with 1 equiv of $[Cp_2Fe][PF_6]$ in CD_3CN, and a singlet was observed at 94.2 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Similarly, **5** was reacted with 1 equiv of $[NH_3Ph][BPh_4]$ in CD_3CN, which shows a singlet at 92.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum. We assign these shifts to the acetonitrile complex of the {1,5-bis(di-*tert*-butylphosphino)pentan-3-yl-*C,P,P'*}palladium(II) cation. Small chemical shift differences in the $^{31}P\{^1H\}$ NMR spectrum have been observed previously when changing counterions.[26] These resonances are of similar chemical shift to one of the peaks observed in the catalysis solution. Therefore, it is probable that the nitrile-coordinated acrylonitrile complex exists as one of the major species in the catalysis solution.

The addition of 1 equiv of acrylonitrile to **6** in CD_2Cl_2 at −70 °C results in complete conversion of this complex into two new species, as observed by $^{31}P\{^1H\}$ NMR spectroscopy. The chemical shift of the more intense resonance at 90.95 ppm is similar to the nitrile-bound isomer, as discussed above. The second resonance is further downfield at 95.42 and about one-fourth the intensity of the former. In the ^{1}H NMR spectrum of this reaction solution the major resonance for the vinyl acrylonitrile protons shifts downfield 0.2 ppm from its normal chemical shift. This apparently results from nitrile coordination to palladium, as the major species present. Two new weak resonances also appear at 3.15 and 3.64 ppm as a complex triplet and doublet, respectively. The complicated weak coupling could not be resolved due to the poor signal to noise ratio, because of solubility limitations at low temperature. Raising the temperature resulted in broadening of the signals, which would be expected for a fluxional complex. The chemical shifts of these resonances are similar to those for other reported olefin complexes.[31] Therefore, we propose this is the η^2-olefin-coordinated acrylonitrile complex (acrylonitrile)-{1,5-bis(di-*tert*-butylphosphino)pentan-3-yl-*C,P,P'*}-palladium(II) tetrafluoroborate. The coupling of the vinyl protons to the equivalent phosphorus would explain the additional coupling that was poorly resolved. These resonances would correspond to the less intense resonance observed in the $^{31}P\{^1H\}$ NMR spectrum. For **5**, the major species evident in the NMR spectra during catalysis are therefore assigned to the nitrile-bound and π-olefin-bound acrylonitrile complexes.

These results differ significantly from the other Pd(II) catalysts in one respect. The bulky coordination environment in **5** selectively blocks binding of aniline, so the isomeric acrylonitrile complexes form exclusively. Recall that for $Pd(CH_2SiMe_3)(dmpe)^+$ the aniline complex is stable and cannot be displaced by acrylonitrile to a detectable degree. The blocking of NH_2Ph coordination in the **5**-derived catalyst probably results because conelike amines do not fit in the binding site as well as the linear nitrile group or π-bound terminal olefin. The tendency of ligands to bind so that they minimize in-plane steric effects with the *t*-Bu groups on the phosphine ligands is evident in the preceding structural paper. This bias in favor of acrylonitrile binding over aniline may explain the unexpected rapid kinetics for the catalytic activity of **5**. Usually reaction rates for bulky phosphine complexes are sluggish, unless phosphine dissociation occurs in the mechanism. Phosphine dissociation is unlikely for the tridentate chelating ligand in **5**. The high reactivity of **5** can be attributed to a major shift in the position of the equilibrium of step 2 in Scheme II toward the olefin complex.

Reactivity of 1 and 2 with Unactivated Olefins and [NHRR′R″][X]. The reaction between $Pd(dmpe)Me_2$ (**1**), 5 equiv of [HNRR′R″][X] {NRR′R″ = NH_3, NH_2Ph, $NHEt_2$, NH^iPr_2, NMe_3, NEt_3 and X = BF_4}, and 40 equiv of 1-hexene in methylene chloride or THF under reflux conditions yields palladium–amine complex, decomposition products, free amine, ammonium salt, and unreacted 1-hexene. Similar results were observed with ethylene and styrene substrates. Attempts to generate cationic olefin complexes $PdMe(dmpe)(C_2H_4)^+$ or $\overline{Pd[(t\text{-}Bu_2)P(CH_2)_2CH(CH_2)_2P(t\text{-}Bu)_2]}(C_2H_4)^+$ by oxidative cleavage of the Pd–CH_3 bond in noncoordinating solvents failed. Decomposition occurs, as was also observed in the absence of a trapping ligand. Similar exploratory experiments with **5** failed to yield an olefin complex or catalytic activity. The intrinsic instability of the cationic olefin complexes with unactivated olefins appears to be the root of the problem.

Discussion

The reaction between acrylonitrile and $[NH_3Ph][BPh_4]$ with catalytic amounts of cis palladium dialkyls produces the protonated form of 3-anilinopropionitrile. In the absence of catalyst, acrylonitrile reacts with aniline by a Michael addition process only under strongly basic conditions (e.g., refluxing with NaOH). In contrast, the catalysis described here occurs under nearly neutral conditions at 30 °C. The activated olefin substrate apparently facilitates the coordination of the double bond to the active site of the metal complex. Substituting aniline for some of the $[NH_3Ph][BPh_4]$ results in longer activity of the catalyst, shown by the increased number of turnovers of product. One equivalent of $[NH_3Ph][BPh_4]$ per mole of palladium dialkyl is still necessary to initiate catalytic activity, since the catalytic cycle of Scheme II requires 1 equiv of a proton source. The extended activity observed with added aniline probably results from the lower acidity of the solutions. We have observed that the second methyl group of $Pd(CH_3)_2(dmpe)$ can be cleaved with increased ammonium ion concentrations and reaction times. The resulting products of this reaction are inactive toward further catalysis. This may also be a pathway for deactivation of the catalysts, since the reduction of acidity by adding excess aniline prolongs the catalyst life. When **5** is the catalyst precursor, only protonolysis of the single CH_3 group can occur under the same conditions and this catalyst appears to persist indefinitely at 30 °C.

Two effects need to be considered in assessing the effectiveness of the homogeneous catalysts studied: stability and rate. Qualitatively the stabilities parallel the ease with which the second alkyl group is lost from the catalyst by protonolysis. Thus, the highly basic metal center in **7**, which contains sterically accessible alkyl groups, produces a highly active but short-lived catalyst. Complexes **1** and **2** form catalysts of intermediate stability. Complexes **3** and **4** contain bulky alkyl groups that protonate slowly and yield longer lived catalysts. In complex **5**, where the chelating alkyl resists protonation, the catalyst can convert substrate to product without loss of activity. We speculate that at least one alkyl group must remain in the complex throughout the cycle, so an electron-rich dialkyl can be a reactant in the protonolysis step 4 of Scheme II.

The relative activities of the catalysts explored in this study can be compared from plots of their initial rates for the addition of aniline to acrylonitrile shown in Figure 1. The extreme instability of catalyst **7** is evident from the rapid decrease in activity shown in this plot. While Figure 1 provides a useful qualitative comparison, it proved extremely difficult to perform accurate kinetics studies. Although the linearity of individual turnover vs time plots was excellent for most catalysts, the reproducibility was poor (±80%). This does not appear to result from sample decomposition but from oligomers present in acrylonitrile. Gel permeation chromatography of both crude and distilled acrylonitrile show variable amounts of oligomers centered around molecular weight 240. As discussed previously, the key acrylonitrile–palladium complex formed in Scheme II could be detected by NMR spectroscopy; however, acrylonitrile is a very weak ligand. We observed that acetonitrile, an alkyl nitrile, displaces acrylonitrile completely from the metal center. This suggests that the nitrile groups in the acrylonitrile oligomer, which contain alkyl nitrile groups instead of the less basic vinyl nitrile, compete with acrylonitrile for the metal binding site and inhibit catalysis. This would be expected to hinder attempts at rigorous kinetics studies. Nonetheless, the relative rates of the catalysts under identical conditions parallel those shown in Figure 1.

The activities of the catalysts follow the order **5** > **7** > **1** > **2** ≈ **3** > **4**. This can also be rationalized in the context of Scheme II. For complexes **3** and **4** the bulky (trimethylsilyl)methyl groups show slow protonolysis, which appears to be a steric effect. The slowness of the protonation step 1 was evident in the NMR spectral changes that occurred during the reaction. Complex **2** shows a similar retardation of the protonolysis step, which may be attributed to both a steric effect of the phenyl substituents and the reduced electron density at the metal because dppe is a poorer donor ligand than dmpe. For similar reasons **4** is less reactive than **3**. Although the slow protonation could only be observed directly for step 1 of Scheme II, it is reasonable to expect retarded protonation in step 4 as well. The enhanced reactivity of **1** and **7** makes sense because of the low steric hindrance and good electron donor properties of the dmpe and PMe_3 ligands.

The unexpected result in this study was the exceptional activity of **5**, which contains the bulky tridentate P–C–P

donor ligand. Two factors may contribute to the enhanced rate. First, the trans geometry places a strong trans-directing alkyl group from the chelate opposite to the coordination position where catalysis occurs. This should speed up rates of substitution and protonation in the catalytic cycle. Furthermore, the bulky chelate perturbs the equilibrium of step 2 so that species B in the cycle predominates over A. For all the other catalysts examined, the reverse situation holds. We believe this steric effect on the equilibrium provides a significant clue for the development of improved catalysts. It shows that the binding selectivity can be altered to favor olefin complexation in the presence of amines. For unactivated olefin substrates, a change in electron donor properties of the ligand must occur to permit substrate binding. This offers a guide for future efforts.

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