Inorg. Chem. **2009**, *48*, 3699−3709

Palladium N(CH$_2$CH$_2$P^{i}Pr$_2$)$_2$-Dialkylamides: Synthesis, Structural Characterization, and Reactivity

Alexander N. Marziale, Eberhardt Herdtweck, Jörg Eppinger, and Sven Schneider*

Technische Universität München, Department Chemie, Lichtenbergstrasse 4, D-85747 Garching b München, Germany

Received December 2, 2008

Palladium(II) aminodiphosphine PNP pincer complexes [PdR(PNP^H)]PF$_6$ (**1^R**; R = Cl Me, Ph; PNP^H = HN(CH$_2$CH$_2$P^{i}Pr$_2$)$_2$) were prepared. Deprotonation with KO^{t}Bu affords dialkylamides [PdR(PNP)] (**2^R**; R = Cl Me, Ph; PNP = (NCH$_2$CH$_2$P^{i}Pr$_2$)$_2$) in high yield which are stable toward β-H elimination. While AgPF$_6$ oxidizes the amides, cationic amido complexes [PdL(PNP)]PF$_6$ (**3^L**; L = CN^{t}Bu, PMe$_3$) were obtained upon chloride abstraction from **1^{Cl}** with TlPF$_6$. The reaction of amide **2^{Cl}** with MeOTf results in *N*-methylation yielding [PdCl(PNP^{Me})]OTf (**5**) quantitatively. N−H acidities of the amino complexes **1^{Me}** (pK_a = 24.2(1)) and **1^{Ph}** (pK_a = 23.2(1)) were determined in dmso. Complexes **1^{Cl}**, **1^{Me}**, **2^{Cl}** **2^{Me}**, **3^{CNtBu}**, and **5** were structurally characterized by single crystal X-ray diffraction. The amido complexes feature pyramidal nitrogen atoms in the solid state. The molecular structures, high *N*-basicity, and reactivity of the amido complexes can be explained with Pd−N^{amido} bonding that is characterized by strong N→Pd σ-donation and repulsive d_π-p_π π-interactions. This interpretation was confirmed by density functional theory (DFT) calculations of **2^{Cl}**.

Introduction

Palladium catalysis has considerably contributed to the remarkable progress in C−N coupling reactions, as in Hartwig−Buchwald cross-coupling, hydroamination, or oxidative amination of olefins.[1−3] Hartwig−Buchwald type reactions have been studied experimentally and with quantum-chemical calculations.[4,5] In the generally accepted mechanism, arylamine reductive elimination from a three- or four-coordinate palladium(II) amido species has been identified as the crucial step determining the product selectivity.[6] Hartwig and co-workers found that the rate of amine reductive elimination from [(dppf)Pd(Ar)(NMeAr′)] (dppf = [(η^5-C$_5$H$_4$PPh$_2$)$_2$Fe]) correlates qualitatively with the pK_a of the corresponding free amine.[7] Recently, Buchwald and co-workers have examined competetive C−N coupling of aryl- and alkylamine substrates with PhCl catalyzed by [(SPhos)PdCl]$_2$ (SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxy-1,1′-biphenyl) in the presence of NaOCMe$_2$Et as base, resulting in high chemoselectivity toward aryl-ary-

* To whom correspondence should be addressed. E-mail: sven.schneider@ch.tum.de.

(1) (a) Kosugi, M.; Kameyama, M.; Toshihiko, M. *Chem. Lett.* **1983**, 927–928. (b) Paul, F.; Patt, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 5969–5970. (c) Guram, A.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem.* **1995**, *107*, 1456–1459. *Angew. Chem., Int. Ed.* **1995**, *34*, 1348−1350. (d) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609–3612. (e) Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215–7216. (f) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217–7218. (g) Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 13109–13110. (h) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852–860. (i) Hartwig, J. F. *Synlett* **2006**, 1283–1294. (j) Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651–2710.

(2) (a) Johns, A. M.; Utsunomiya, M.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 1828–1839. (b) Sakai, N.; Ridder, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 8134–8135. (c) Johns, A. M.; Sakai, N.; Ridder, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 9306–9307. (d) Cochran, B. M.; Michael, F. E. *J. Am. Chem. Soc.* **2008**, *130*, 2786–2792.

(3) Kotov, V.; Scarborough, C. C.; Stahl, S. S. *Inorg. Chem.* **2007**, *46*, 1910–1923.

(4) (a) Amatore, C.; Broeker, G.; Jutand, A.; Khalil, F. *J. Am. Chem. Soc.* **1997**, *119*, 5176–5185. (b) Amatore, C.; Jutand, A. *Coord. Chem. Rev.* **1998**, *178−180*, 511–528. (c) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 1232–1233. (d) Jordan, R. B. *Organometallics* **2007**, *26*, 4763–4770. (e) Quilong, S.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 7734–7735. (f) Quilong, S.; Ogata, T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 6586–6596.

(5) (a) Kozuch, S.; Amatore, C.; Jutand, A.; Shaik, S. *Organometallics* **2005**, *24*, 2319–2330. (b) Cundari, T. R.; Deng, J. *J. Phys. Org. Chem.* **2005**, *18*, 417–425. (c) Barder, T. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 12003–12010.

(6) (a) Ahekhar, S.; Rydberg, P.; Hartwig, J. F.; Mathew, J. S.; Blackmond, D. G.; Strieter, E. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2006**, *128*, 3584–3591. (b) Hartwig, J. F. *Inorg. Chem.* **2007**, *46*, 1936–1947.

(7) (a) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 4708. (b) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232. (c) Yamashita, M.; Cuevas Vicario, J. V.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 16347.

10.1021/ic802286u CCC: $40.75
Published on Web 03/12/2009

lamine coupling. However, if lithium amides were used as nitrogen source, the chemoselectivity was reversed toward aryl-alkylamine coupling.[8] These results were rationalized with the higher pK_a values of alkyl- versus arylamines.

However, despite the importance of palladium amido complexes in catalysis, structural and thermodynamic data about this class of compounds, for example, pK_a values of amines coordinated to Pd^{II}, remains scarce.[9] Since the pioneering work by Fryzuk et al. on disilylamido complexes,[10] studies about palladium amides have mostly focused on arylamides.[11−13] The reactivity of electron rich complexes bearing covalently bound π-donating ligands, such as amides, is generally attributed to the high ligand nucleophilicity.[14] Both repulsive filled-filled p_π-d_π interactions and high M−N σ-bond polarity have been stressed as an explanation.[15,16] While the π-acceptor ability of silyl and aryl substituents stabilizes the high electron density on the nitrogen by delocalization of the lone pair, terminal alkylamido derivatives bearing β-hydrogens typically suffer from decomposition to metal hydrides.[14,17] Hence, isolable alkylamides of palladium are particularly rare.[11b,18]

In our efforts to study the chemistry of electron-rich alkylamido complexes we have recently reported the isolation of iridium(I) amino and amido complexes with the pincer ligands $HN(CH_2CH_2P^iPr_2)_2$ (PNP^H) and $N(CH_2CH_2P^iPr_2)_2$ (PNP).[19] In contrast to the stable iridum(I) dialkylamides, for Ru^{II}PNP-complexes reversible β-H elimination processes were observed.[20] In this context, we were interested in palladium PNP dialkylamido complexes to obtain thermodynamic and structural information that can be correlated with reactivity patterns which are important to understand catalytic reaction mechanisms. In this manuscript we describe the synthesis and structural characterization of palladium(II) PNP dialkylamido complexes which are stable toward β-H elimination. The reactivity toward electrophiles and oxidizing agents will be reported.

Experimental Section

Materials and Methods. All experiments were carried out under an atmosphere of argon using Schlenk and glovebox techniques. Benzene and tetrahydrofuran (THF) were dried over Na/benzophenone, distilled under argon and deoxygenated prior to use. Diethylether and pentane were dried and deoxygenized by passing through columns packed with activated alumina and Q5, respectively. Deuterated solvents were dried by distillation from Na/K alloy (C_6D_6 and d^8-THF) or stirring over 4 Å molecular sieves and distillation from B_2O_3 (d^6-acetone), respectively, and deoxygenated by three *freeze−pump−thaw* cycles. KO^{t}Bu was purchased from VWR and sublimed prior to use. Palladiumdichloride (ABCR), $AgPF_6$ (ABCR), $TlPF_6$ (ABCR), MeOTf (Aldrich), PMe_3 (Aldrich), CN^{t}Bu (Fluka) were used as purchased. Pyrrol and 2-pyrrolidinone (ACROS) were dried over CaH_2 and distilled prior to use. $HN(CH_2CH_2P^iPr_2)_2$, $[PdCl_2(CH_3CN)_2]$, and [Pd(I)Ph(tmeda)] were prepared as reported in the literature.[21−23]

Analytical Methods. Elemental analyses were obtained from the Microanalytical Laboratory of Technische Universität München. The IR spectra were recorded on a Jasco FT/IR-460 PLUS spectrometer as nujol mulls between KBr plates. NMR spectra were recorded on Jeol Lambda 400 and Bruker DPX 400 spectrometers at room temperature and were calibrated to the residual proton resonance and the natural abundance ^{13}C resonance of the solvent (C_6D_6, $\delta_H = 7.16$ and $\delta_C = 128.06$ ppm; d^6-acetone, $\delta_H = 2.05$ and $\delta_C = 29.84 + 206.26$ ppm). ^{31}P NMR chemical shifts are reported relative to external phosphoric acid (δ 0.0 ppm). Signal multiplicities are abbreviated as: s (singlet), d (doublet), t (triplet), vt (virtual triplet), sp (septet), m (multiplet), br (broad).

Syntheses. $[PdCl(PNP^H)][PF_6]$ (1^{Cl}). $HN(CH_2CH_2P^iPr_2)_2$ (0.100 g; 0.327 mmol) is added to a solution of $PdCl_2(NCMe)_2$ (0.085 g; 0.327 mmol) in THF (5 mL) and stirred for 30 min. $AgPF_6$ (0.081 g; 0.327 mmol) is added to the solution, and the reaction is stirred at room temperature overnight. After filtration the product is precipitated with diethylether and pentanes, washed twice with pentanes, and dried in vacuo to give a yellowish solid. Yield: 0.189 g (0.319 mmol; 99%). Anal. Calcd for $C_{16}H_{37}ClF_6NP_3Pd$ (592.26): C, 32.50; H, 6.14; N, 2.37. Found: C, 32.18; H, 6.43; N, 2.40. IR (cm^{-1}) $\nu = 3239$ (N−H). NMR (d_6-acetone, r.t., [ppm]) ^1H NMR (399.8 MHz): δ 1.34 (dvt, 6H, $^3J_{HH} = 7.0$ Hz, $J_{PH} = 8.7$ Hz, CH_3), 1.39−1.49 (m, 18H, CH_3), 2.20−2.33 (m, 2H, NCH_2CH_2), 2.38−2.49 (m, 4H, $CH(CH_3)_2$+ NCH_2CH_2), 2.58 (m, 2H, $CH(CH_3)_2$), 3.09 (m, 2H, NCH_2), 3.43 (m, 2H, NCH_2), 6.77 (br, 1H, NH). ^{13}C {^1H} NMR (100.6 MHz): δ 17.0 (s, CH_3), 17.4 (s, CH_3), 18.0 (s, CH_3), 18.2 (s, CH_3), 22.9 (vt, $J_{CP} = 9.9$ Hz, PCH_2), 23.6 (vt, $J_{CP} = 12.6$ Hz, $CH(CH_3)_2$), 25.0 (vt, $J_{CP} = 10.7$ Hz, $CH(CH_3)_2$), 56.3 (d, $^2J_{CP} = 9.2$ Hz, NCH_2). ^{31}P {^1H} NMR (161.8 MHz): δ 64.6 (s, P^iPr_2), −143.6 (sp, $^1J_{PF} = 709$ Hz, PF_6). Assignments were confirmed by $^1H-^1H$ COSY and $^1H-^{13}C$ HETCOR spectra.

$[PdMe(PNP^H)][PF_6]$ (1^{Me}). To a solution of 1^{Cl} (0.030 g, 0.051 mmol) in THF (5 mL) is added a solution of MeMgBr in THF (0.170 mL, 0.3M) dropwise, and the solution is stirred at room

(8) Biscoe, M. R.; Barder, T. E.; Buchwald, S. L. *Angew. Chem.* **2007**, *119*, 7370–7373; *Angew. Chem. Int. Ed.* **2007**, *46*, 7232−7235.
(9) Driver, M. S.; Hartwig, J. F. *Organometallics* **1997**, *16*, 5706–5715.
(10) (a) Fryzuk, M. D.; MacNeil, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 3592–3593. (b) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J.; Secco, A. S.; Trotter, J. *Organometallics* **1982**, *1*, 918–930.
(11) (a) Villanueva, L. A.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1992**, *11*, 2963–2965. (b) Villanueva, L. A.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1994**, *13*, 3921–3931.
(12) Yamashita, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 5344–5345.
(13) (a) Fan, L.; Foxman Ozerov, O. V. *Organometallics* **2004**, *23*, 326–328. (b) Fan, L.; Yang, L.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4778–4787. (c) Ozerov, O. V.; Guo, C.; Fan, L.; Foxman, B. M. *Organometallics* **2004**, *23*, 5573–5580. (d) Fafard, C. M.; Chen, C.-H.; Foxman, B. M.; Ozerov, O. V. *Chem. Commun.* **2007**, 4465–4467. (e) Fafard, C. M.; Adhikari, D.; Foxman, B. M.; Mindiola, D. J.; Ozerov, O. V. *J. Am. Chem. Soc.* **2007**, *129*, 10318–10319.
(14) (a) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163–1188. (b) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1–40. (c) Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44–56. (d) Gunnoe, T. B. *Eur. J. Inorg. Chem.* **2007**, *118*, 5–1203.
(15) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25–41.
(16) Holland, P. L.; Andersen, R. A.; Bergman, R. G. *Comments Inorg. Chem.* **1999**, *21*, 115–129.
(17) (a) Diamond, S. E.; Mares, F. *J. Organomet. Chem.* **1977**, *142*, C55–C57. (b) Ryu, S. Y.; Kim, H.; Kim, H. S.; Park, S. *J. Organomet. Chem.* **1999**, *592*, 194–197.
(18) Douthwaite, R. E.; Houghton, J.; Kariuki, B. M. *Chem. Commun.* **2004**, 698–699.
(19) Friedrich, A.; Ghosh, R.; Kolb, R.; Herdtweck, E.; Schneider, S. *Organometallics* **2009**, *28*, 708–718.
(20) Käβ, M.; Friedrich, A.; Drees, M.; Schneider, S. *Angew. Chem.* **2009**, *121*, 922–924; *Angew. Chem. Int. Ed.* **2009**, *48*, 905−907.
(21) Danopoulos, A. A.; Wills, A. R.; Edwards, P. G. *Polyhedron* **1990**, *9*, 2413–2418.
(22) Hartley, F. R.; Murray, S. G.; McAuliffe, C. A. *Inorg. Chem.* **1979**, *18*, 1394–1397.
(23) Alster, P. L.; Boersma, J.; van Koten, G. *Organometallics* **1993**, *12*, 1629–1638.

temperature overnight. Two milliliters of Dioxane are added to the solution, and the reaction is stirred until a white precipitate forms. The reaction is filtered, and the solvent is evaporated in vacuo. The residue is extracted with dichloromethane, and another 2 mL of dioxane are added. The solution is filtered again and evaporated in vacuo. The residue is extracted with THF, and the product is precipitated with diethylether and pentanes. The precipitate is washed twice with pentanes and dried in vacuo to give a yellowish solid. Yield: 0.029 g (0.048 mmol; 95%). Anal. Calcd for $C_{17}H_{40}F_6NP_3Pd$ (571.84): C, 35.70; H, 7.05; N, 2.45. Found: C, 35.49; H, 6.91; N, 2.49. IR (cm^{-1}) ν = 3271 (N−H). NMR (d_6-acetone, r.t., [ppm]) ^{1}H NMR (399.8 MHz): δ 0.44 (t, $^3J_{PH}$ = 5.6 Hz, 3H, PdCH_3), 1.21−1.37 (m, 24H, CH_3), 2.13−2.23 (m, 2H, NCH_2CH_2), 2.33−2.51 (m, 6H, CH(CH_3)$_2$+ NCH_2CH_2), 2.66−2.78 (m, 2H, NCH_2), 3.34−3.49 (m, 2H, NCH_2), 4.93 (br, 1H, NH). ^{13}C {^{1}H} NMR (100.6 MHz): δ −19.5 (t, $^2J_{CP}$ = 5.4 Hz, PdCH_3), 16.9 (s, CH_3), 17.5 (s, CH_3), 18.4 (s, CH_3), 18.5 (s, CH_3), 22.8 (vt, J_{CP} = 12.7 Hz, PCH_2), 24.7 (vt, J_{CP} = 10.0 Hz, CH(CH_3)$_2$), 24.9 (vt, J_{CP} = 11.1 Hz, CH(CH_3)$_2$), 51.7 (s, NCH_2). ^{31}P {^{1}H} NMR (161.8 MHz): δ 52.0 (s, P^iPr_2), −143.6 (sp, $^1J_{PF}$ = 709 Hz, PF_6).

[PdPh(PNP^H)][PF_6] (1^{Ph}). To a solution of Pd(I)Ph(tmeda) (0.670 g, 1.684 mmol) in THF (20 mL) is added a solution of $(PNP)^H$ (0.514 g, 1.684 mmol) in THF (2 mL) dropwise and stirred at room temperature for 30 min. A yellow solid is formed and filtered off. The precipitate is washed with three times diethylether and dried in vacuo. The yellow solid is dissolved in dichloromethane (15 mL), and a solution of $AgPF_6$ (0.185 g, 0.731 mmol) in dichloromethane (5 mL) is added dropwise. The solution is stirred for 15 min until a yellowish-white solid is formed. The precipitate is filtered off and washed twice with diethylether. The product is precipitated from the filtrates with diethylether and pentanes, washed twice with diethylether, and dried in vacuo to give a yellowish solid. Yield: 0.412 g (0.651 mmol; 39%). Anal. Calcd for $C_{22}H_{42}F_6NP_3Pd$ (633.15): C, 41.70; H, 6.68; N, 2.21. Found: C, 42.37; H, 6.26; N, 2.11. IR (cm^{-1}) ν = 3277 (N−H). NMR (d_6-acetone, r.t., [ppm]) ^{1}H NMR (399.8 MHz): δ 1.02−1.11 (m, 12H, CH_3), 1.24 (dvt, 6H, $^3J_{HH}$ = 7.0 Hz, J_{PH} = 8.3 Hz, CH_3), 1.31 (dvt, 6H, $^3J_{HH}$ = 7.0 Hz, J_{PH} = 7.9 Hz, CH_3), 2.19 (m, 4H, NCH_2CH_2), 2.36 (m, 2H, CH(CH_3)$_2$), 2.48 (m, 2H, CH(CH_3)$_2$), 2.79−2.88 (m, 2H, NCH_2), 3.40−3.54 (m, 2H, NCH_2), 5.08 (br, 1H, NH), 6.86 (t, 1H, $^3J_{HH}$ = 7.4 Hz, *para*-C_6H_5), 7.02 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *meta*-C_6H_5), 7.33 (d, 2H, $^3J_{HH}$ = 7.1 Hz, *ortho*-C_6H_5). NMR (d_3-acetonitrile, r.t., [ppm]) ^{13}C {^{1}H} NMR (100.6 MHz): δ 16.9 (s, CH_3), 17.1 (s, CH_3), 17.8 (s, CH_3), 18.1 (s, CH_3), 22.7 (vt, J_{CP} = 9.2 Hz, PCH_2), 23.8 (vt, J_{CP} = 11.5 Hz, CH(CH_3)$_2$), 25.1 (vt, J_{CP} = 10.9 Hz, CH(CH_3)$_2$), 56.3 (d, $^2J_{CP}$ = 10.0 Hz, NCH_2), 123.0 (s, *para*-C_6H_5), 127.7 (s, *meta*-C_6H_5), 136.9 (s, *ortho*-C_6H_5), 143.2 (t, $^2J_{CP}$ = 6.9 Hz, *ipso*-C_6H_5). ^{31}P {^{1}H} NMR (161.8 MHz): δ 49.6 (s, P^iPr_2), −144.4 (sp, $^1J_{PF}$ = 709 Hz, PF_6).

[PdCl(PNP)] (2^{Cl}). $HN(CH_2CH_2P^iPr_2)_2$ (0.105 g; 0.340 mmol) is added to a solution of $PdCl_2(NCMe)_2$ (0.089 g; 0.340 mmol) in THF (5 mL) and stirred for 30 min. KO^{t}Bu (0.038 g; 0.340 mmol) is added to the solution, and the reaction is stirred at room temperature for 2 h. After filtration the solution is evaporated in vacuo to give an orange solid. The solid is dissolved in pentanes and KCl is filtered off. The filtrate is evaporated and dried in vacuo to give an orange solid. Yield: 0.148 g (0.33 mmol; 98%). Anal. Calcd for $C_{16}H_{36}ClNP_2Pd$ (446.28): C, 43.06; H, 8.13; N, 3.14. Found: C, 43.84; H, 7.71; N, 2.73. NMR (C_6D_6, r.t., [ppm]) ^{1}H NMR (399.8 MHz): δ 1.03 (dvt, 12H, $^3J_{HH}$ = 7.0 Hz, J_{PH} = 7.3 Hz, CH_3), 1.38 (dvt, 12H, $^3J_{HH}$ = 7.4 Hz, J_{PH} = 8.4 Hz, CH_3), 1.55 (m, 2H, NCH_2CH_2), 2.03 (m, 4H, CH(CH_3)$_2$), 2.83 (m, 4H, NCH_2CH_2). ^{13}C {^{1}H} NMR (100.6 MHz): δ 17.6 (s, CH_3), 18.8 (s, CH_3), 23.7 (vt, J_{CP} = 9.6 Hz, PCH_2), 24.1 (vt, J_{CP} = 10.7 Hz, CH(CH_3)$_2$), 62.6 (s, NCH_2). ^{31}P {^{1}H} NMR (161.8 MHz): δ 70.1 (s, P^iPr_2). Assignments were confirmed by a ^{1}H−^{13}C HSQC spectrum.

[PdMe(PNP)] (2^{Me}). KO^{t}Bu (0.014 g, 0.115 mmol) is added to a solution of $\mathbf{1^{Me}}$ (0.066 g, 0.115 mmol) in THF (10 mL) at room temperature. The reaction is stirred at room temperature for 30 min. until a white precipitate is formed. After filtration the solution is evaporated in vacuo to give a yellow solid. The solid is dissolved in pentanes and stored at −18 °C for 24 h. A white precipitate is formed. After filtration the solution is evaporated and dried in vacuo to give a yellow solid. Yield: 0.034 g (0.071 mmol; 62%). Anal. Calcd for $C_{17}H_{39}NP_2Pd$ (425.87): C, 47.95; H, 9.23; N, 3.30. Found: C, 46.81; H, 8.88; N, 3.00. NMR (C_6D_6, r.t., [ppm]) ^{1}H NMR (399.8 MHz): δ 0.28 (t, $^3J_{PH}$ = 5.6 Hz, 3H, PdCH_3), 1.02 (dvt, 12H, $^3J_{HH}$ = 6.6 Hz, J_{PH} = 6.8 Hz, CH_3), 1.16 (dvt, 12H, $^3J_{HH}$ = 7.4 Hz, J_{PH} = 7.6 Hz, CH_3), 1.89 (br, 8H, NCH_2CH_2 + CH(CH_3)$_2$), 3.37 (m, 4H, NCH_2CH_2). ^{13}C {^{1}H} NMR (100.6 MHz): δ −23.0 (t, $^2J_{CP}$ = 9.7 Hz, PdCH_3), 17.7 (s, CH_3), 19.0 (s, CH_3), 24.0 (vt, J_{CP} = 10.4 Hz, PCH_2), 24.7 (vt, J_{CP} = 10.7 Hz, CH(CH_3)$_2$), 59.5 (s, NCH_2). ^{31}P {^{1}H} NMR (161.8 MHz): δ 65.2 (s, P^iPr_2).

[PdPh(PNP)] (2^{Ph}). A solution of KO^{t}Bu (0.026 g, 0.229 mmol) in THF (5 mL) is added to a solution of $\mathbf{1^{Ph}}$ (0.145 g, 0.229 mmol) in THF (10 mL) at − 80 °C. The reaction is stirred at −80 °C for 15 min. The solvent is removed in vacuo to give a yellow solid. The solid is dissolved in pentanes, and the solution is filtered. The filtrate is evaporated in vacuo to give a yellow solid. Yield: 0.083 g (0.169 mmol; 74%). Anal. Calcd for $C_{17}H_{39}NP_2Pd$ (487.94): C, 54.15; H, 8.47; N, 2.87. Found: C, 53.46; H, 8.52; N, 2.83. NMR (C_6D_6, r.t., [ppm]) ^{1}H NMR (399.8 MHz): δ 0.95 (m, 24H, CH_3), 1.80 (br, 4H, NCH_2CH_2), 1.89 (m, 4H, CH(CH_3)$_2$), 3.33 (m, 4H, NCH_2CH_2), 7.03 (t, 1H, $^3J_{HH}$ = 7.1 Hz, *para*-C_6H_5), 7.22 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *meta*-C_6H_5), 7.70 (d, 2H, $^3J_{HH}$ = 6.6 Hz, *ortho*-C_6H_5). ^{13}C {^{1}H} NMR (100.6 MHz): δ 16.9 (s, CH_3), 17.9 (s, CH_3), 23.5 (vt, J_{CP} = 10.8 Hz, PCH_2), 24.7 (vt, J_{CP} = 9.2 Hz, CH(CH_3)$_2$), 62.5 (s, NCH_2), 120.7 (s, *para*-C_6H_5), 125.9 (s, *meta*-C_6H_5), 139.5 (s, *ortho*-C_6H_5), 138.6 (t, $^2J_{CP}$ = 5.8 Hz, *ipso*-C_6H_5). ^{31}P {^{1}H} NMR (161.8 MHz): δ 62.7 (s, P^iPr_2).

[Pd(CN^{t}Bu)(PNP)][PF_6] (3^{CNtBu}). A solution of $TlPF_6$ (0.035 g; 0.10 mmol) in THF (10 mL) and CN^{t}Bu (0.0084 g; 0.011 mL; 0.10 mmol) are added to a solution of $\mathbf{2^{Cl}}$ (0.045 g; 0.10 mmol) in THF (10 mL) at −78 °C. The solution is stirred at −78 °C for 1 h and warmed to room temperature. After evaporation of the solvent in vacuo the orange-grayish solid is extracted with benzene and filtered. The product is precipitated upon addition of diethylether and pentanes, washed twice with pentanes, and dried in vacuo to give a yellow solid. Yield: 0.057 g (0.09 mmol; 90%). Anal. Calcd for $C_{21}H_{45}F_6N_2P_3Pd$ (638.93): C, 39.48; H, 7.09; N, 4.38. Found: C, 40.41; H, 7.15; N, 4.32. IR (cm^{-1}) ν = 2186 (C≡N^{t}Bu). NMR (d_6-acetone, r.t., [ppm]) ^{1}H NMR (399.8 MHz): δ 1.26−1.35 (m, 24H, CH_3), 1.60 (s, 9H, CH_3), 2.24 (m, 2H, NCH_2CH_2), 2.53 (m, 4H, CH(CH_3)$_2$), 3.22 (m, 4H, NCH_2CH_2). ^{13}C {^{1}H} NMR (100.6 MHz): δ 17.5 (s, CH_3), 18.9 (s, CH_3), 24.2 (vt, J_{CP} = 11.5 Hz, PCH_2), 25.0 (vt, J_{CP} = 12.3 Hz, CH(CH_3)$_2$), 29.1 (s, C(CH_3)$_3$), 59.6 (s, C(CH_3)$_3$), 61.4 (s, NCH_2), 209.1 (s, CN^{t}Bu). ^{31}P {^{1}H} NMR (161.8 MHz): δ 89.9 (s, P^iPr_2), −143.6 (sp, $^1J_{PF}$ = 710 Hz, PF_6). ^{19}F NMR (376.2 MHz): δ −72.5 (d, $^1J_{PF}$ = 712 Hz, PF_6).

[Pd(PMe_3)(PNP)][PF_6] (3^{PMe3}). A solution of $TlPF_6$ (0.040 g; 0.114 mmol) in THF (5 mL) is added to a solution of $\mathbf{2^{Cl}}$ (0.050 g; 0.112 mmol) in THF (5 mL) at room temperature and stirred for 5 min. A 1 M solution of PMe_3 in THF (0.200 mL; 0.20 mmol) is added dropwise to the reaction, which is stirred at room temperature for 3 h. The solution is filtered, and the filtrate is evaporated in

vacuo to give an orange-grayish solid. The solid is dissolved in benzene, and the solution is filtered again. After removing the solvent the orange solid is dissolved in THF, and the product is precipitated with diethylether and pentanes, washed twice with pentanes, and dried in vacuo to give a yellow-orange solid. The solid is dissolved in benzene and the product is precipitated with diethylehter and pentanes, washed twice with diethylehter and dried in vacuo to give an orange solid. Yield: 0.024 g (0.039 mmol; 35%). Anal. Calcd for $C_{19}H_{45}F_6NP_4Pd$ (631.87): C, 36.11; H, 7.17; N, 2.22. Found: C, 35.86; H, 7.04; N, 2.39. NMR (d_6-benzene/CD_2Cl_2, r.t., [ppm]) ^{1}H NMR (399.8 MHz): δ 0.84−0.95 (m, 24H, CH_3), 1.28 (d, $^2J_{PH}$ = 9.2 Hz, 9H, P(CH_3)$_3$), 1.63 (m, 4H, NCH$_2$CH_2), 1.87 (m, 4H, CH(CH$_3$)$_2$), 2.80 (m, 4H, NCH_2CH$_2$). ^{13}C {^{1}H} NMR (100.6 MHz): δ 17.8 (s, *C*H$_3$), 18.7 (d, $^1J_{CP}$ = 28.3 Hz, P(*C*H$_3$)$_3$), 20.2 (s, *C*H$_3$), 23.0 (vt, J_{CP} = 12.2 Hz, P*C*H$_2$), 26.2 (vt, J_{CP} = 11.9 Hz, *C*H(CH$_3$)$_2$), 60.6 (s, N*C*H$_2$). ^{31}P {^{1}H} NMR (161.8 MHz): δ 81.3 (d, $^2J_{PP}$ = 48.5 Hz, *P*^{i}Pr$_2$), −22.2 (t, $^2J_{PP}$ = 50.5 Hz, *P*(CH$_3$)$_3$), −143.1 (sp, $^1J_{PF}$ = 710.9 Hz, *P*F$_6$).

Reaction of 2^{Ph} with $AgPF_6$. 2^{Ph} (8.8 mg; 18 μmol) is dissolved in THF (0.5 mL) in a J-Young NMR tube, and $AgPF_6$ (4.6 mg; 18 μmol) added at room temperature. A black precipitate immediately forms, and the yellow solution turns colorless. After 5 min the starting material is quantitatively converted to a mixture of $\mathbf{1^{Ph}}$ ($\sim$ 80%) and [PdPh{N(CHCH$_2$P^{i}Pr$_2$)(CH$_2$CH$_2$P^{i}Pr$_2$)}]PF$_6$ (**4**; $\sim$ 20%) by NMR. Selected NMR data of **4** (d_6-acetone, r.t., [ppm]): ^{1}H NMR (399.8 MHz): δ 3.89 (m, 2H, *N* = CHC*H*$_2$), 8.48 (d, $^3J_{HP}$ = 25.3 Hz 1H, *N* = C*H*CH$_2$). ^{31}P {^{1}H} NMR (161.8 MHz): δ 54.3 (d, $^2J_{PP}$ = 351 Hz, *P*^{i}Pr$_2$), 50.1 (d, $^2J_{PP}$ = 351 Hz, *P*^{i}Pr$_2$), −143.6 (sp, $^1J_{PF}$ = 707.4 Hz, *P*F$_6$).

[PdCl(PNP^{Me})][OTf] (5). MeOTf (0.018 g; 0.012 mL; 0.110 mmol) is added to a solution of $\mathbf{2^{Cl}}$ (0.049 g; 0.110 mmol) in toluene (5 mL) and stirred for 10 min until a yellow solid is formed. The solid is filtered off, washed three times with diethylether, and dried in vacuo to give microcrystalline, yellow **5**. Yield: 0.066 g (0.109 mmol; 99%). Anal. Calcd for $C_{18}H_{39}ClF_3NO_3P_2PdS$ (610.39): C, 35.42; H, 6.44; N, 2.29. Found: C, 35.49; H, 6.47; N, 2.32. NMR (d_6-acetone, r.t., [ppm]) ^{1}H NMR (399.8 MHz): δ 1.32−1.52 (m, 24H, CH_3), 2.51 (m, 4H, NCH$_2$CH_2), 2.59−2.79 (m, 4H, CH(CH$_3$)$_2$), 2.99 (s, 3H, NCH_3), 3.16−3.28 (m, 2H, NCH_2), 3.46 (m, 2H, NCH_2). ^{13}C {^{1}H} NMR (100.6 MHz): δ 16.9 (s, *C*H$_3$), 17.5 (s, *C*H$_3$), 18.1 (s, *C*H$_3$), 18.2 (s, *C*H$_3$), 21.9 (vt, J_{CP} = 8.8 Hz, P*C*H$_2$), 23.9 (vt, J_{CP} = 12.3 Hz, *C*H(CH$_3$)$_2$), 25.6 (vt, J_{CP} = 11.9 Hz, *C*H(CH$_3$)$_2$), 46.5 (s, N*C*H$_3$), 66.4 (s, N*C*H$_2$). ^{31}P {^{1}H} NMR (161.8 MHz): δ 60.3 (s, *P*^{i}Pr$_2$). ^{19}F NMR (376.2 MHz): δ −78.7 (s, SO_3CF_3).

pK_a Determinations. The palladium amido compound $\mathbf{2^R}$ (R = CH_3, Ph) and an equimolar amount of the corresponding acid ($\mathbf{2^{Me}}$: 2-pyrrolidinone; $\mathbf{2^{Ph}}$: pyrrole) were dissolved in 0.6 mL of d_6-dmso. Because of fast proton exchange on the NMR time scale one peak resulted in the ^{31}P NMR with a chemical shift δ_{meas} that was located between those of pure $\mathbf{1^R}$ (δ_{1R}) and $\mathbf{2^R}$ (δ_{2R}) in d_6-dmso. The equilibrium molar fractions of $\mathbf{2^R}$ (x_{2R}) and the corresponding $\mathbf{1^R}$ (x_{1R}) conjugate acid cation were derived using

$$\delta_{meas} = x_{1R}\delta_{1R} + x_{2R}\delta_{2R} \quad (1)$$

$$x_{1R} + x_{2R} = 1 \quad (2)$$

pK_a values were calculated from the equilibrium constant (K_{eq}) using the following equations (pK_a(2-pyrrolidinone) = 24.2; pK_a(pyrrole) = 23.0):[24]

$$K_{eq} = x_{2R}^2/x_{1R}^2 \quad (3)$$

$$pK_a(\mathbf{1^R}) = pK_a(\text{ref}) - \log(K_{eq}) \quad (4)$$

X-ray Crystal Structure Determinations. General Procedures. Crystal data and details of the structure determination are presented in Table 1. Suitable single-crystals for the X-ray diffraction studies were grown by diffusion of pentane into THF solutions ($\mathbf{1^{Cl}}$, $\mathbf{1^{Me}}$, $\mathbf{3^{CNtBu}}$, **5**) or slow cooling of saturated pentane solutions to −30 °C ($\mathbf{2^{Cl}}$, $\mathbf{2^{Me}}$). Crystals were stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examinations and data collection were carried out with area detecting systems and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The unit cell parameters were obtained by full-matrix least-squares refinements during the scaling procedures. Data collection was performed at low temperatures (OXFORD CRYOSYSTEMS), each crystal was measured with a couple of data sets in rotation scan modus with either $\Delta\varphi/\Delta\omega$ = 0.5° or 1.0°. Intensities were integrated, and the raw data were corrected for Lorentz, polarization, and arising from the scaling procedure for latent decay. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the Shelxl-97 weighting scheme and stopped at shift/err <0.001. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography. All calculations were performed on an Intel Pentium 4 PC, with the WinGX system, including the programs PLATON, SIR92, SIR97, and SHELXL-97.[25]

Specific Details. $\mathbf{1^{Cl}}$: Data collection was performed with an Oxford Diffraction device (Xcalibur, κ-CCD; sealed tube, Enhance X-ray Source, Spellman, DF3) at T = 153 K. Intensities were corrected for absorption effects during the scaling procedure (T_{max} = 0.8600, T_{min} = 0.5695). Methyl hydrogen atoms were calculated as a part of rigid rotating groups, with d_{C-H} = 0.98 Å and $U_{iso(H)}$ = 1.5$U_{eq(C)}$. All other hydrogen atoms were placed in ideal positions and refined using a riding model, with methylene and methyne d_{C-H} distances of (0.99 and 1.00 Å) and $U_{iso(H)}$ = 1.2$U_{eq(C)}$. In contrast the amine hydrogen atom could be located in the final difference Fourier map and was allowed to refine freely. $\mathbf{1^{Me}}$: Data collection

(24) (a) Bordwell, F. G.; Drucker, G. E.; Fried, H. E. *J. Org. Chem.* **1981**, *46*, 632–635. (b) Bordwell, F. G.; Fried, H. E. *J. Org. Chem.* **1991**, *56*, 4218–4223.

(25) (a) *APEX suite of crystallographic software. APEX 2*, Version 2008.4.; Bruker AXS Inc.: Madison, WI, 2008. (aa) *SAINT, Version 7.56a and SADABS Version 2008/1.*; Bruker AXS Inc.: Madison, WI, 2008. (b) *Data Collection Software and Data Processing Software for Stoe IPDS 2T diffractometer, X-ARERA*, Version 1.26; Stoe & Cie: Darmstadt, Germany, 2004. (c) *Data Processing Software for Stoe IPDS 2T diffractometer, XRED, XSHAPE*, Version 1.26; Stoe & Cie: Darmstadt, Germany, 2004. (d) *CrysAlis Data Collection Software and Data Processing Software for Oxford Xcalibur diffractometer*, Version 1.171; Oxford Diffraction Ltd.: Oxfordshire, U.K., 2005. (e) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838; WinGX Version 1.70.01, January 2005. (f) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *SIR92, J. Appl. Crystallogr.* **1994**, *27*, 435–436. (g) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi Moliterni, A. G. G. A.; Burla, M. C.; Polidori, G.; Camalli, M.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119; SIR97, A New Tool for Crystal Structure Determination and Refinement. (h) *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2. (i) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001. (j) Sheldrick, G. M. *SHELXL-97*, Universität Göttingen: Göttingen, Germany, 1998.

Table 1. Crystallographic Data for $\mathbf{1^{Cl}}$, $\mathbf{1^{Me}}$, $\mathbf{2^{Cl}}$, $\mathbf{2^{Me}}$, $\mathbf{3^{CNtBu}}$, and **5**

	$\mathbf{1^{Cl}}$	$\mathbf{1^{Me}}$	$\mathbf{2^{Cl}}$	$\mathbf{2^{Me}}$	$\mathbf{3^{CNtBu}}$	**5**
formula	$C_{16}H_{37}ClF_6NP_3Pd$	$C_{17}H_{40}F_6NP_3Pd$	$C_{16}H_{36}ClNP_2Pd$	$C_{17}H_{39}NP_2Pd$	$C_{21}H_{45}F_6N_2P_3Pd$	$C_{18}H_{39}ClF_3NO_3P_2PdS$
fw	592.25	571.83	446.27	425.85	638.88	610.38
color/habit	yellowish/fragment	yellowish/fragment	orange/fragment	yellow/fragment	yellow/plate	yellow/fragment
cryst dimensions (mm^3)	0.14 × 0.34 × 0.56	0.20 × 0.30 × 0.30	0.18 × 0.18 × 0.51	0.08 × 0.20 × 0.56	0.25 × 0.53 × 0.63	0.25 × 0.25 × 0.31
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	*Pbcm* (No. 57)	$P2_1/c$ (No. 14)
a, Å	8.6831(1)	8.6804(3)	8.5012(4)	7.6469(6)	9.5853(1)	8.4064(2)
b, Å	15.4168(2)	15.6177(5)	11.6523(7)	8.5660(6)	15.7998(2)	25.1998(4)
c, Å	18.4350(2)	18.5296(8)	21.1295(10)	17.8499(14)	19.5797(2)	13.0821(2)
α, deg	90	90	90	76.172(6)	90	90
β, deg	95.210(1)	94.552(3)	90.537(4)	83.808(6)	90	98.8013(8)
γ, deg	90	90	90	69.326(6)	90	90
V, $Å^3$	2457.62(5)	2504.10(16)	2092.97(19)	1061.88(15)	2965.26(6)	2738.68(9)
Z	4	4	4	2	4	4
T, K	153	173	173	173	153	293
D_{calcd}, g cm^{-3}	1.601	1.517	1.416	1.332	1.431	1.480
μ, mm^{-1}	1.107	0.981	1.163	1.021	0.837	1.007
F(000)	1208	1176	928	448	1320	1256
θ range, deg	2.84−25.38	4.57−26.83	3.99−25.30	4.71−25.30	2.78−25.61	2.89−25.34
index ranges (*h*, *k*, *l*)	±10, ± 18, ± 22	±11, ± 19, ± 23	±10, ± 14, ± 25	±9, ± 10, ± 21	±11, ± 19, ± 23	±9, ± 30, ± 15
no. of rflns collected	45861	33072	15075	11610	52425	34614
no. of indep rflns/R_{int}	4500/0.029	5282/0.039	3695/0.068	3471/0.044	2881/0.025	4615/0.031
no. of obsd rflns ($I > 2\sigma(I)$)	4049	4895	3207	3016	2551	4317
no. of data/ restraints/params	4500/0/265	5282/0/266	3695/0/198	3471/0/199	2881/0/219	4615/0/280
R1/wR2 ($I > 2\sigma(I)$)[a]	0.0276/0.0623	0.0312/0.0769	0.0241/0.0655	0.0215/0.0477	0.0353/0.0782	0.0272/0.0661
R1/w*R*2 (all data)[a]	0.0327/0.0669	0.0347/0.0785	0.0293/0.0664	0.0281/0.0489	0.0419/0.0828	0.0298/0.0687
GOF (on F^2)[a]	1.153	1.080	1.011	0.948	1.158	1.080
largest diff peak and hole (e $Å^{-3}$)	+0.59/−0.60	+0.87/−0.64	+0.49/−0.66	+0.37/−0.34	+1.28/−0.69	+0.44/−0.32

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$; $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

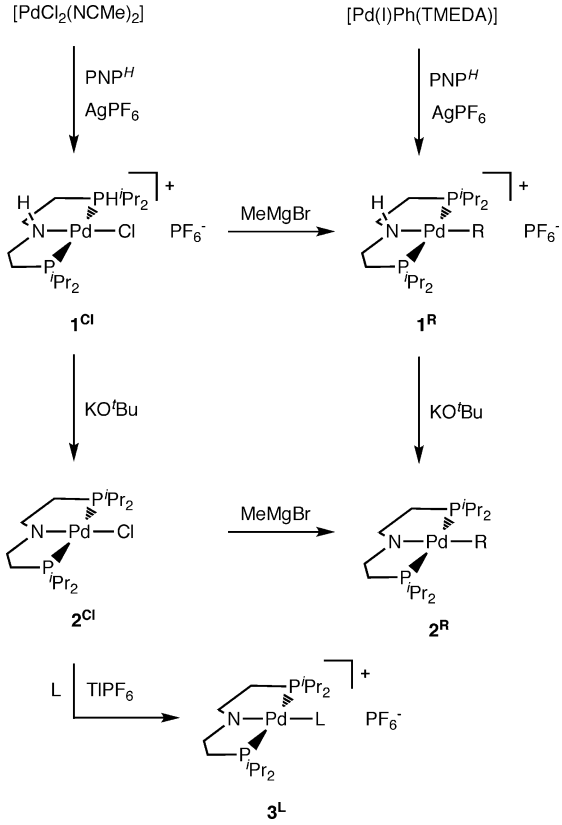
was perfomed with a Stoe device (IPDS 2T, rotating anode, Nonius FR591) at $T = 173$ K. Intensities were corrected for absorption using the DELABS procedure ($T_{max} = 0.819$, $T_{min} = 0.422$). Methyl hydrogen atoms were calculated as a part of rigid rotating groups, with $d_{C-H} = 0.98$ Å and $U_{iso(H)} = 1.5U_{eq(C)}$. All other hydrogen atoms were placed in ideal positions and refined using a riding model, with methylene and methyne d_{C-H} distances of (0.99 and 1.00 Å) and $U_{iso(H)} = 1.2U_{eq(C)}$. In contrast the amine hydrogen atom could be located in the final difference Fourier map and was allowed to refine freely. The compounds $\mathbf{1^{Cl}}$ and $\mathbf{1^{Me}}$ appear to be isostructural. $\mathbf{2^{Cl}}$: Data collection was perfomed with a Stoe device (IPDS 2T, rotating anode, Nonius FR591) at $T = 173$ K. Intensities were corrected for absorption (numerical after crystal shape optimization, $T_{max} = 0.9149$, $T_{min} = 0.7087$). Methyl hydrogen atoms were calculated as a part of rigid rotating groups, with $d_{C-H} = 0.98$ Å and $U_{iso(H)} = 1.5U_{eq(C)}$. All other hydrogen atoms were placed in ideal positions and refined using a riding model, with methylene and methyne d_{C-H} distances of (0.99 and 1.00 Å) and $U_{iso(H)} = 1.2U_{eq(C)}$. $\mathbf{2^{Me}}$: Data collection was perfomed with a Stoe device (IPDS 2T, rotating anode, Nonius FR591) at $T = 173$ K. Intensities were corrected for absorption (numerical after crystal shape optimization, $T_{max} = 0.9215$, $T_{min} = 0.7806$). Methyl hydrogen atoms were calculated as a part of rigid rotating groups, with $d_{C-H} = 0.98$ Å and $U_{iso(H)} = 1.5U_{eq(C)}$. All other hydrogen atoms were placed in ideal positions and refined using a riding model, with methylene and methyne d_{C-H} distances of (0.99 and 1.00 Å) and $U_{iso(H)} = 1.2U_{eq(C)}$. $\mathbf{3^{CNtBu}}$: Data collection was performed with an Oxford Diffraction device (Xcalibur, *κ*-CCD; sealed tube, Enhance X-ray Source, Spellman, DF3) at $T = 153$ K. Intensities were corrected for absorption effects during the scaling procedure ($T_{max} = 0.8100$, $T_{min} = 0.5537$). Methyl hydrogen atoms were calculated as a part of rigid rotating groups, with $d_{C-H} = 0.98$ Å and $U_{iso(H)} = 1.5U_{eq(C)}$. All other hydrogen atoms were placed in ideal positions and refined using a riding model, with methylene and methyne d_{C-H} distances of (0.99 and 1.00 Å) and $U_{iso(H)} = 1.2U_{eq(C)}$. A disorder of the PF_6-anion could be resolved clearly. $\mathbf{3^{CNtBu}}$ is sited on a crystallographic mirror plane passing N1, Pd1, N2, C18, and C20 with a symmetry code for equivalent atoms of *x*, *y*, 1/2 − *z*. **5**: Data collection was perfomed with a Bruker Axs device (APEX II, rotating anode, Bruker Axs FR591) at $T = 293$ K. Intensities were corrected for absorption effects during the scaling procedure ($T_{max} = 0.7750$, $T_{min} = 0.7312$). Methyl hydrogen atoms were calculated as a part of rigid rotating groups, with $d_{C-H} = 0.96$ Å and $U_{iso(H)} = 1.5U_{eq(C)}$. All other hydrogen atoms were placed in ideal positions and refined using a riding model, with methylene and methyne d_{C-H} distances of (0.97 and 0.98 Å) and $U_{iso(H)} = 1.2U_{eq(C)}$.

Density Functional Theory (DFT) Calculations. DFT calculations were performed with GAUSSIAN 03 using the PBE functional.[26,27] Geometry optimizations were run without symmetry or internal coordinate constraints using the Stuttgart-RSC-ECP and corresponding valence basis set for palladium and all-electron split valence double-ζ basis set 6-31+G** for all other elements.[28,29] The optimized structures were verified as being true minima by the absence of negative eigenvalues in the vibrational frequency analysis. Hirshfeld charges were obtained by single-point calculations on the geometry optimized minimum structures using the all-electron DGDZVP basis-set for palladium.[30,31] Orbital expressions were visualized with GaussView via cube files generated from formatted checkpoint files.[32] The orbital energies were obtained from the Mulliken population analysis.

Results and Discussion

Syntheses. Reaction of $HN(CH_2CH_2P^iPr_2)_2$ (PNP^H) with $[PdCl_2(NCMe)_2]$ and subsequent chloride abstraction with $AgPF_6$ gives palladium(II) amino complex $[PdCl(PNP^H)]PF_6$ ($\mathbf{1^{Cl}}$) in quantitative yield (Scheme 1). Methyl complex

Scheme 1. Syntheses of Palladium(II) PNP Amino and Amido Complexes **1**−**3** (PNP^H = $HN(CH_2CH_2P^iPr_2)_2$; R = Me, Ph; L = CN^tBu, PMe_3)



$[PdMe(PNP^H)]PF_6$ ($\mathbf{1^{Me}}$) is easily prepared from $\mathbf{1^{Cl}}$ by salt metathesis with MeMgBr, while reaction with LiMe yields intractable mixtures of several products. Likewise, the reaction of $\mathbf{1^{Cl}}$ with phenyl Grignard-solution suffers from low selectivity. However, phenyl complex $[PdPh(PNP^H)]PF_6$ ($\mathbf{1^{Ph}}$) was isolated in modest yields starting from [Pd(I)Ph(TMEDA)] (TMEDA = $Me_2NCH_2CH_2NMe_2$).

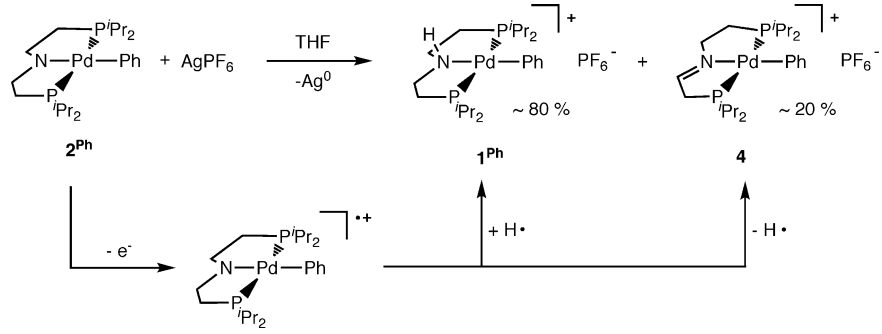
Facile deprotonation of the amino complexes with KO^tBu gives the corresponding neutral palladium(II) amides [PdR(PNP)] ($\mathbf{2^R}$; R = Cl, Me, Ph), which are well soluble in nonpolar solvents such as pentane. Alternatively, $\mathbf{2^{Me}}$ can be prepared from $\mathbf{2^{Cl}}$ with MeMgBr in THF, albeit in lower yield. Owing to the chelating pincer ligand, the highly air sensitive amido complexes are stable in the solid state and in solution toward β-hydride elimination.

Clean chloride abstraction from amide $\mathbf{2^{Cl}}$ was accomplished with $TlPF_6$. In the presence of CN^tBu or PMe_3 the cationic amido complexes $[PdL(PNP)]PF_6$ ($\mathbf{3^L}$; L = CN^tBu, PMe_3) are obtained in moderate ($\mathbf{3^{PMe3}}$) to good yields ($\mathbf{3^{CNtBu}}$), while the corresponding carbonyl complex could not be isolated under CO atmosphere (1 bar). However, the synthesis of cationic Pd^{II} carbonyl complexes typically requires the use of highly non-nucleophilic anions and handling at low temperatures because of labile binding of CO to electrophilic palladium centers.[33]

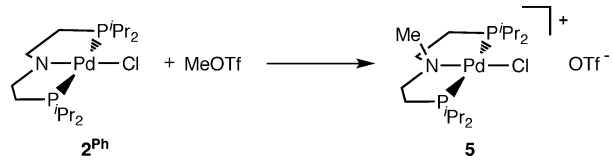
In contrast to the halide abstraction with $TlPF_6$, the addition of silver salts to amido complexes $\mathbf{2^R}$ at room temperature results in immediate precipitation of silver metal. While the reaction of $\mathbf{2^{Cl}}$ with $AgPF_6$ gives several products by ^{31}P NMR, including amino complex $\mathbf{1^{Cl}}$, oxidation of the organic derivatives $\mathbf{2^R}$ (R = Me, Ph) proceeds much more selective. $\mathbf{2^{Ph}}$ reacts with $AgPF_6$ in THF to give around 80% of the amino complex $\mathbf{1^{Ph}}$ and one other product (**4**) accounting for the remaining yield (Scheme 2). While **4** could not be obtained analytically pure, the NMR spectra are in agreement with imino complex $[PdPh\{N(CHCH_2P^iPr_2)(CH_2CH_2P^iPr_2)\}]PF_6$, resulting from dehydrogenation of the PNP pincer in α-position to the nitrogen donor.[34] The presence of the two products suggests that the radical cation $[PdR(PNP)]^{+\bullet}$ is formed as the initial oxidation product. Decomposition pathways via hydrogen atom addition and hydrogen abstraction (Scheme 2) could then account for the formation of $\mathbf{1^{Ph}}$ and **4**, respectively. When the reaction is carried out in d^8-THF, the product distribution of $\mathbf{1^{Ph}}$/**4** is retained (1:0.25 by ^{31}P NMR). However, the signal for the $\mathbf{1^{Ph}}$ N−H proton (4.55 ppm) is strongly diminished, now integrating over 0.2 protons, and deuteration of the amino function was confirmed by ^2H NMR spectroscopy (δ N-D = 4.20 ppm).[35] These results are in agreement with the formation of $[PdPh(PNP^D)]^+$ (∼60%) by deuterium atom transfer from the solvent, and recombination of two [PdR(P-

(26) Frisch, M. J. Trucks, G. W. Schlegel, H. B. Scuseria, G. E. Robb, M. A. Cheeseman, J. R. J. Montgomery, J. A. Vreven, T. Kudin, K. N. Burant, J. C. Millam, J. M. Iyengar, S. S. Tomasi, J. Barone, V. Mennucci, B. Cossi, M. Scalmani, G. Rega, N. Petersson, G. A. Nakatsuji, H. Hada, M. Ehara, M. Toyota, K. Fukuda, R. Hasegawa, J. Ishida, M. Nakajima, T. Honda, Y. Kitao, O. Nakai, H. Klene, M. Li, X. Knox, J. E. Hratchian, H. P. Cross, J. B. Bakken, V. Adamo, C. Jaramillo, J. Gomperts, R. Stratmann, R. E. Yazyev, O. Austin, A. J. Cammi, R. Pomelli, C. Ochterski, J. W. Ayala, P. Y. Morokuma, K. Voth, G. A. Salvador, P. Dannenberg, J. J. Zakrzewski, V. G. Dapprich, S. Daniels, A. D. Strain, M. C. Farkas, O. Malick, D. K. Rabuck, A. D. Raghavachari, K. Foresman, J. B. Ortiz, J. V. Cui, Q. Baboul, A. G. Clifford, S. Cioslowski, J. Stefanov, B. B. Liu, G. Liashenko, A. Piskorz, P. Komaromi, I. Martin, R. L. Fox, D. J. Keith, T. Al-Laham, M. A. Peng, C. Y. Nanayakkara, A. Challacombe, M. Gill, P. M. W. Johnson, B. Chen, W. Wong, M. W. Gonzalez, C. Pople, J. A. *Gaussian03*, Rev. C.02; Gaussian Inc.: Wallingford, CT, 2004.
(27) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
(28) (a) Andrae, D.; Häuβermann, U.; Dolg, M.; Stoll, H.; Preuβ, H. *Theor. Chim. Acta* **1990**, *77*, 123–141. (b) Martin, J. M. L.; Sundermann, A. *J. Chem. Phys.* **2001**, *114*, 3408–3420.
(29) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; DeFrees, D. J.; Pople, J. A.; Gordon, M. S. *J. Chem. Phys.* **1982**, *77*, 3654–3665. (c) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294–301.
(30) Hirshfeld, F. L. *Theoret. Chim. Acta* **1977**, *44*, 129–138.
(31) (a) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560–571. (b) Sosa, C.; Andzelm, J.; Elkin, B. C.; Wimmer, E.; Dobbs, K. D.; Dixon, D. A. *J. Phys. Chem.* **1992**, *96*, 6630–6636.
(32) Dennington, R., II.; Keith, T.; Millam, J. *GaussView V4.1*; Semichem Inc.: Shawnee Mission, KS, 2007.
(33) (a) Hwang, G.; Wang, C.; Aubke, F.; Willner, H.; Bodenbinder, M. *Can. J. Chem.* **1993**, *71*, 1532–1536. (b) Weber, L. *Angew. Chem.* **1994**, *106*, 1131–1133; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1077−1078. (c) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746–4764. (d) Ara, I.; Forniés, J.; Navarro, R.; Sicilia, V.; Urriolabeitia, E. P. *Polyhedron* **1997**, *16*, 1963–1970. (e) Popeney, C.; Guan, Z. *Organometallics* **2005**, *24*, 1145–1155. (f) Burns, C. T.; Jordan, R. F. *Organometallics* **2007**, *26*, 6737–6749.
(34) Coleman, K. S.; Green, M. L. H.; Pascu, S. I.; Rees, N. H.; Cowley, A. R.; Rees, L. H. *J. Chem. Soc., Dalton Trans.* **2001**, 3384–3395.
(35) Some deuteration was also obtained for the *iso*-propyl methyne protons of the pincer ligand by ^2H NMR. We tentatively attribute this observation to H-/D-exchange with THF radicals.

Scheme 2. Oxidation of $\mathbf{2^{Ph}}$ with $AgPF_6$ in THF and Proposed Pathway of Product Formation via a Radical Cation Intermediate



Scheme 3. Reaction of $\mathbf{2^{Cl}}$ with MeOTf



NP)]$^{+\bullet}$ radicals accounting for an equimolar amount of **4** (~20%) and [PdPh(PNP^H)]$^+$ (~20%). Nitrogen centered aminyl radicals are typically transient species, representing pivotal intermediates in radical based C−N coupling reactions,[36] and only few persistent late metal complexes that were described as metal stabilized aminyl radicals have been reported.[37] However, proton coupled electron transfer (PCET) reactions of metal complexes have attracted considerable interest, owing to their importance in various chemical and biological processes,[38] and the oxidative dehydrogenation of amines coordinated to transition metals has been studied extensively.[39]

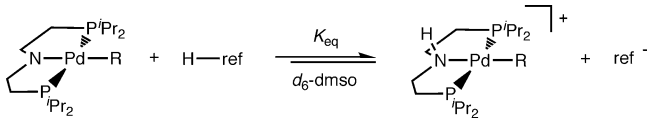
The reactivity of $\mathbf{2^{Cl}}$ toward electrophiles was probed by the reaction with methyl triflate. Quantitative conversion to *N*-methyl amino complex [PdCl(PNP^{Me})]OTf (**5**; PNP^{Me} = $MeN(CH_2CH_2P^iPr_2)_2$) is observed (Scheme 3), as can be expected for a highly nucleophilic amido ligand.[40]

Spectroscopic Characterization. Palladium(II) amino complexes $\mathbf{1^R}$ (R = Cl, Me, Ph) exhibit N−H stretching vibrations between 3239−3277 cm^{-1} in the IR spectra, very close to the free ligand (3285 cm^{-1}), suggesting the absence of N−H hydrogen bonding. The IR stretching vibrations of strong π-acceptor ligands, such as CO or isocyanides, can serve as a probe for the electron density at the metal center. For example, iridium(I) amido complex [Ir(CO)(PNP)] features a carbonyl stretching frequency at particularly low wavenumbers (1908 cm^{-1}) which can be explained by strong Ir→CO back bonding reinforced by a p_N-d_{Ir}-π^*_{CO} push−pull π-interaction.[15,19] As the palladium analogue [Pd(CO)(PNP)]$^+$ could not be prepared, $\mathbf{3^{CNtBu}}$ was synthesized. C≡N stretching vibrations of palladium(II) tert-butylisocyanide complexes are typically found at about 50 to 100 cm^{-1} higher wavenumbers with respect to the free ligand (2136 cm^{-1}), and cationic complexes are located at the upper end of that range.[41,42] Therefore, the frequency of the IR band of $\mathbf{3^{CNtBu}}$ assignable to the C≡N stretch (2186 cm^{-1}) suggests strong electron donation by the dialkylamido ligand, for example, as compared with *trans*-[Pd(C_6F_5)(CN^tBu)(PEt_3)$_2$]ClO_4 (2230 cm^{-1}). However, the molecular structure of $\mathbf{3^{CNtBu}}$ in the solid state, which features a pyramidal amido nitrogen atom (see below), is indicative of predominant N→Pd σ-donation. Note that dialkylamines (pK_a^{dmso} ~ 44) and C_6F_5H (pK_a^{dmso} = 29.0) exhibit a large difference in proton acidity as well.[43,44]

Solution NMR spectra of amino complexes $\mathbf{1^R}$ (R = Cl, Me, Ph) and **5**, featuring one ^{31}P NMR signal and two sets of chemically inequivalent iso-propyl substituents with diastereotopic methyl groups (^{1}H and ^{13}C NMR), are in agreement with a square planar coordination geometry around the Pd center and a pyramidal nitrogen atom. The ^{31}P, ^{1}H, and ^{13}C NMR spectra of amido complexes $\mathbf{2^R}$ (R = Cl, Me, Ph) and $\mathbf{3^L}$ (L = PMe_3, CN^tBu) indicate C_{2v} symmetry on the NMR time scale with a mirror plane defined by the coordination plane of palladium, as was found for isoelec-

(36) (a) Bowman, W. R.; Bridge, C. F.; Brookes, P. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1–14. (b) Bowman, W. R.; Cloonan, M. O.; Krintel, S. L. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2885–2902.
(37) (a) Penkert, F. N.; Weyhermüller, T.; Bill, E.; Hildebrandt, P.; Lecomte, S.; Wieghardt, K. *J. Am. Chem. Soc.* **2000**, *122*, 9663–9673. (b) Büttner, T.; Geier, J.; Frison, G.; Harmer, J.; Calle, C.; Schweiger, A.; Schönberg, H.; Grützmacher, H. *Science* **2005**, *307*, 235–238. (c) Adhikari, D.; Mossin, S.; Basuli, F.; Huffmann, J. C.; Szilagyi, R. K.; Meyer, K.; Mindiola, D. J. *J. Am. Chem. Soc.* **2008**, *130*, 3676–3682. (d) Tejel, C.; Ciriano, M. A.; Pilar del Rio, M.; Hetterscheid, D. G. H.; Tsichlis i Spithas, N.; Smits, J. M. M.; de Bruin, B. *Chem.—Eur. J.* **2008**, *14*, 10932–10936.
(38) (a) Cukier, R. I.; Nocera, D. G. *Annu. Rev. Phys. Chem.* **1998**, *49*, 337–369. (b) Hammes-Schiffer, S. *Acc. Chem. Rev.* **2001**, *34*, 273–281. (c) Meyer, J. M. *Annu. Rev. Phys. Chem.* **2004**, *55*, 363–390. (d) Huynh, M. H. V.; Meyer, T. J. *Chem. Rev.* **2007**, *107*, 5004–5064.
(39) (a) Keene, F. R. *Coord. Chem. Rev.* **1999**, *187*, 121–149. (b) Thiel, W. *Coord. Chem. Rev.* **2003**, *245*, 95–106.
(40) Park, S.; Rheingold, A. L.; Roundhill, D. M. *Organometallics* **1991**, *10*, 615–623.
(41) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21–86.
(42) (a) Otsuka, S.; Nakamura, A.; Yoshida, T. *J. Am. Chem. Soc.* **1969**, *91*, 7196–7198. (b) Otsuka, S.; Tatsuno, K.; Ataka, K. *J. Am. Chem. Soc.* **1971**, *93*, 6705–6706. (c) Empsall, H. D.; Green, M.; Shakshooki, S. K.; Stone, F. G. A. *J. Chem. Soc. (A)* **1971**, 3472–3476. (d) Uson, R.; Fornies, J.; Espinet, P.; Lalinde, E. *J. Organomet. Chem.* **1981**, *220*, 393–399. (e) Uson, R.; Fornies, J.; Espinet, P.; Garcia, A.; Sanau, A. *Transition Met. Chem.* **1983**, *8*, 11–13. (f) Langrick, C. R.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 1233–1238. (g) De Munno, G.; Bruno, G.; Arena, C. G.; Drommi, D.; Faraone, F. *J. Organomet. Chem.* **1993**, *450*, 263–267. (h) Ruiz, J.; Martinez, M. T.; Vincente, C.; Garcia, G.; Lopez, G.; Chaloner, P. A.; Hitchcock, P. B. *Organometallics* **1993**, *12*, 4321–4325. (i) Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1994**, *13*, 441–450. (j) Samar, D.; Fortin, J.-F.; Fortin, D.; Decken, A.; Harvey, P. D. *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 411–429. (k) Cadierno, V.; Diez, J.; Garcia-Alvarez, J.; Gimeno, J.; Nebra, N.; Rubio-Garcia, J. *Dalton Trans.* **2006**, 5593–5604.
(43) pK_a values of dialkylamines in dmso are typically beyond that of dmso (35.1) and were extrapolated: ref 24a.
(44) Predicted from quantum chemical calculations, Shen, K.; Fu, Y.; Li, J.-N.; Liu, L.; Guo, Q.-X *Tetrahedron* **2007**, *63*, 1568–1576.

Scheme 4. Acid-Base Equilibrium Utilized for the Determination of the $\mathbf{1^R}$ (R = Me, Ph) pK_a Values



tronic iridium compounds [Ir(L)(PNP)] (L = CO, C_2H_4, PMe_3).[19,45] While the iridium amides feature almost perfectly planarized nitrogen atoms in the solid state, the molecular structures of palladium complexes $\mathbf{2^R}$ show strong pyramidalization of the N-donor (see below). However, cooling a sample of $\mathbf{2^{Cl}}$ in d^8-toluene did not result in peak broadening in the ^{1}H NMR spectrum down to −40 °C, suggesting low barriers for nitrogen inversion, as typically found for organic amines with electropositive substituents and metal dialkylamides.[46,47]

pK_a Measurements. pK_a values of the amino complexes were determined in d_6-dmso to ensure efficient ion separation.[48] The equilibrium constants from the reaction of $\mathbf{2^R}$ (R = Me, Ph) with a suitable acid (Scheme 4, Href) were derived by NMR and pK_a values calculated by referencing to the pK_a of Href. The right reference was found by screening a range of acids with known pK_a's in dmso.[49] For example, $\mathbf{2^{Me}}$ showed no reaction (^{31}P and ^{1}H NMR) with equimolar amounts of *p*-toluidine (pK_a > 30) or 2-aminopyridine (pK_a = 27.7), minor protonation with diphenylamine (pK_a = 25.0), almost complete conversion to $\mathbf{1^{Me}}$ with pyrrole (pK_a = 23.0), and complete protonation with indene (pK_a = 20.1). Quantitative derivations of the pK_a's were carried out with 2-pyrrolidinone ($\mathbf{2^{Me}}$; pK_a = 24.2) and pyrrole ($\mathbf{2^{Ph}}$), respectively. The pK_a of $\mathbf{1^{Cl}}$ could not be obtained in this way as $\mathbf{2^{Cl}}$ is not stable in dmso, presumably because of halide versus solvent exchange. For the alkyl and aryl complexes pK_a values of 24.2(1) ($\mathbf{1^{Me}}$) and 23.2(1) ($\mathbf{1^{Ph}}$) were derived indicating only a minor influence of the ligands in *trans*-position, that is, the purely σ-donating methyl or the potentially π-accepting phenyl ligands.

The structural analysis of the amino and amido complexes suggests, that the flexible PNP^H and PNP ligands are relatively unstrained (see below). Therefore, we believe that these values can serve as a good general estimate for the acidity of dialkylamines coordinated to palladium(II). To the best of our knowledge this is the first time that pK_a values of palladium alkylamino complexes were measured.

It is well established that metal coordination acidifies amine protons.[40,50] Accordingly, the pK_a values of $\mathbf{1^R}$ (R = Me, Ph) range between those of free dialkylamines (∼44) and dialkylammonium cations (∼10).[51] Low proton acidity (pK_a 31.5 in THF) was reported by Bergman and co-workers for octahedral ruthenium(II) ammonia complex [RuH(NH_3)-(dmpe)$_2$]$^+$ (dmpe = $Me_2PCH_2CH_2PMe_2$).[52] Grützmacher's group has developed a family of dialkylamino and diamino ligands with benzanellated biscycloheptatrienyl substituents, which form stable group 9 amido complexes. Despite the lower metal oxidation state, four-coordinate [Rh(trop$_2$dach)]-OTf (pK_a = 15.7) and five-coordinate [Rh(HNtrop$_2$)(H_2Ntrop)]-OTf (pK_a = 20.6) and [Rh(HNtrop$_2$)(bipy)]OTf (pK_a = 18.7) are considerably more acidic than $\mathbf{1^R}$ in dmso (HNtrop$_2$ = Bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)amine, H_2Ntrop = 5-amino-5*H*-dibenzo[*a*,*d*]cycloheptene, trop$_2$dach = *N*,*N*′-bis(5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)-1,2-diaminocyclohexane, bipy = 2,2′-bipyridine).[53−55] Likewise, iridium(I) complexes [Ir(L)(PNP^H)]PF_6 (L = CO: 14.8; cyclooctene: 16.0) exhibit much lower pK_a values as compared with $\mathbf{1^R}$.[45] While the small amount of pK_a data in non-protic solvents prevents a systematic analysis, regarding the influence of oxidation state, coordination number, and auxiliary ligands, it is noteworthy that the palladium(II) complexes $\mathbf{2^R}$ are the most basic as compared with a series of isoelectronic group 9 dialkylamido complexes.

X-ray Structure Determinations. The molecular structures of $\mathbf{1^{Cl}}$, $\mathbf{1^{Me}}$, $\mathbf{2^{Cl}}$, $\mathbf{2^{Me}}$, $\mathbf{3^{CNtBu}}$, and **5** in the crystal were derived by X-ray crystallography (Figures 1 and 2, Table 2). $\mathbf{2^{Cl}}$, $\mathbf{2^{Me}}$, and $\mathbf{3^{CNtBu}}$ are the first structurally characterized palladium dialkylamido complexes. All structures feature the palladium centers in a distorted square-planar coordination geometry with pincer bite angles in the range of 165.8°−170.2°. P−Ir−P angles found for [Ir(L)(PNP^H)]PF_6 and [Ir(L)(PNP)] (L = CO, C_2H_4, PMe_3) were in the same range.[19,45] The structural parameters of the Pd(PNP^H) fragments in $\mathbf{1^{Cl}}$ and $\mathbf{1^{Me}}$ are almost identical except for the significantly longer Pd−N1 distance of $\mathbf{1^{Me}}$ (ΔD = 0.08 Å) reflecting the stronger methyl *trans*-influence. This observation confirms the structural flexibility of the (PNP)^H pincer which can easily adjust to accommodate different bonding situations around the metal center, particularly in comparison with more rigid PNP pincers, such as Ozerov's phenylene bridged chelate ligands.[13] Therefore, the chelating nature of the (PNP)^H ligand should have a minor effect on chemical properties of the amino moiety, such as pK_a values, and $\mathbf{1^R}$ represent reasonable general models for dialkylamines coordinated to palladium(II). Furthermore, the *N*-methylated amino complex **5** exhibits only minor structural differences as compared to N−H analogue $\mathbf{1^{Cl}}$.

(45) Friedrich, A.; Buchner, M. R.; Herdtweck, E.; Schneider, S., manuscript in preparation.
(46) Stevenson, P. E.; Burkey, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 3061–3064.
(47) Dewey, M. A.; Bakke, J. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1349–1351.
(48) (a) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463. (b) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155–9171.
(49) For an extensive compilation of acidities in dmso, cf. http://www.chem.wisc.edu/areas/reich/pkatable/ (accessed Nov 25, 2008).
(50) (a) Park, S.; Roundhill, D. M.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3972–3974. (b) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781–2794.
(51) Liu, W.-Z.; Bordwell, F. G. *J. Org. Chem.* **1996**, *61*, 4778–4783.
(52) The pK_a value was not corrected for ion pairing effects, Fulton, J. R.; Bouwkamp, M. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 8799–8800.
(53) Maire, P.; Breher, F.; Schönberg, H.; Grützmacher, H. *Organometallics* **2005**, *24*, 3207–3218.
(54) Büttner, T.; Breher, F.; Grützmacher, H. *Chem. Commun.* **2004**, 2820–2821.
(55) Königsmann, M.; Donati, N.; Stein, D.; Schönberg, H.; Harmer, J.; Sreekanth, A.; Grützmacher, H. *Angew. Chem.* **2007**, *119*, 3637–3640. *Angew. Chem. Int. Ed.* **2007**, *46*, 3567−3570.

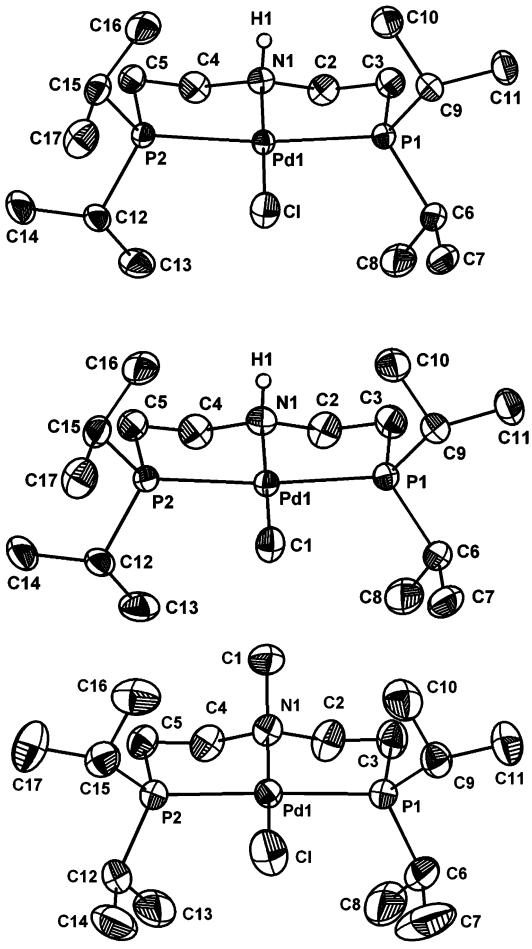


Figure 1. DIAMOND plot of the cations of $\mathbf{1}^{\mathbf{Cl}}$ (above), $\mathbf{1}^{\mathbf{Me}}$ (middle), and **5** (below) in the crystal with thermal ellipsoids drawn at the 50% ($\mathbf{1}^{\mathbf{Cl}}$ and $\mathbf{1}^{\mathbf{Me}}$) and 40% (**5**) probability levels, respectively. Hydrogen atoms other than amino protons are omitted for clarity.

Deprotonation of the amino ligand results in shorter covalent Pd−N bonds ($\Delta D_{\mathrm{Pd-N}}(\mathbf{1}^{\mathbf{Cl}}/\mathbf{2}^{\mathbf{Cl}}) = 0.03$ Å; $\Delta D_{\mathrm{Pd-N}}(\mathbf{1}^{\mathbf{Me}}/\mathbf{2}^{\mathbf{Me}}) = 0.07$ Å), and the shortest Pd−N bond was found for cationic $\mathbf{3}^{\mathbf{CN}t\mathbf{Bu}}$. The Pd−N bond distances ($\mathbf{2}^{\mathbf{Cl}}$: 2.033(2) Å, $\mathbf{2}^{\mathbf{Me}}$: 2.075(2) Å, $\mathbf{3}^{\mathbf{CNtBu}}$: 2.019(3) Å) compare well with those reported for palladium(II) arylamido and silylamido complexes, which typically range around 2.03−2.09 Å.[10b,12,13a,56] Therefore, the Pd1−N1 distances in $\mathbf{2}^{\mathbf{Cl}}$, $\mathbf{2}^{\mathbf{Me}}$, and $\mathbf{3}^{\mathbf{CNtBu}}$ provide no evidence for a stronger N−Pd π-interaction because of the higher basicity of dialkylamines. Furthermore, amine deprotonation results in an elongation of the bond in *trans* position to the nitrogen atom ($\Delta D_{\mathrm{Pd-Cl}}(\mathbf{1}^{\mathbf{Cl}}/\mathbf{2}^{\mathbf{Cl}}) = 0.07$ Å; $\Delta D_{\mathrm{Pd-C}}(\mathbf{1}^{\mathbf{Me}}/\mathbf{2}^{\mathbf{Me}}) = 0.04$ Å), resulting from an increased amido ligand *trans*-influence.

Most significantly, upon deprotonation of the amino ligand the PNP pincer conformation is retained resulting in pyramidal amido nitrogen atoms, as evidenced by the sum of bond angles around N1 ($\mathbf{2}^{\mathbf{Cl}}$: 337.4°, $\mathbf{2}^{\mathbf{Me}}$: 345.7°, $\mathbf{3}^{\mathbf{CNtBu}}$: 343.2°). This observation contrasts sharply with molecular structures of palladium complexes bearing non-bridging aryl- or silylamido ligands, which generally feature planar amido donor atoms.[57,58] Amido complexes with pyramidal nitrogen atoms are particularly rare. Few examples of octahedral rhenium and ruthenium d^6 complexes have been reported.[59] Since in these complexes no empty orbital on the metal center

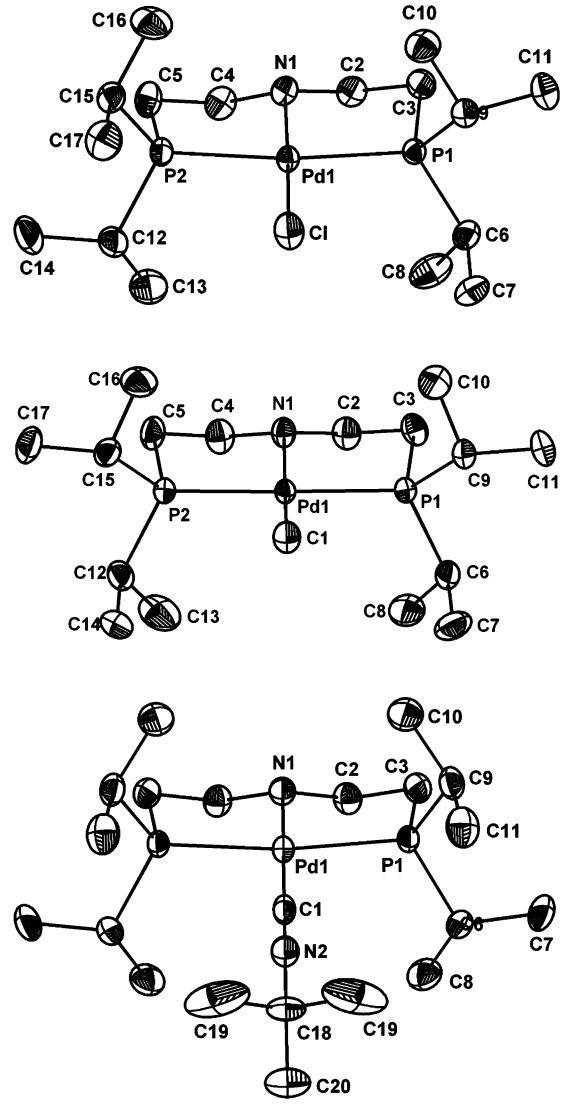


Figure 2. DIAMOND plot of $\mathbf{2}^{\mathbf{Cl}}$ (above), $\mathbf{2}^{\mathbf{Me}}$ (middle), and the cation of $\mathbf{3}^{\mathbf{CN}t\mathbf{Bu}}$ (below) in the crystal with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

(56) Examples:(a) Coleman, K. S.; Green, M. L. H.; Pascu, S. I.; Rees, N. H.; Cowley, A. R.; Rees, L. H. *J. Chem. Soc., Dalton Trans.* **2001**, *338*, 4–3395. (b) Santra, P. K.; Byabartta, P.; Chattopadhyay, S.; Falvello, L. R.; Sinha, C. *Eur. J. Inorg. Chem.* **2002**, *112*, 4–1131. (c) Hooper, M. W.; Hartwig, J. F. *Organometallics* **2003**, *22*, 3394–3403. (d) Huang, M.-H.; Liang, L.-C. *Organometallics* **2004**, *23*, 2813–2816. (e) Liang, L.-C.; Chien, P.-S.; Huang, M.-H. *Organometallics* **2005**, *24*, 353–357.

(57) Out of the structurally characterized palladium complexes L_nPd-NRR′ with terminal aryl- and silylamido ligands (total 311 hits on the CSD database), most complexes exhibit Pd−N−R−R′ torsional angles θ between 160°−180°, which is considerably higher as compared with $\mathbf{2}^{\mathbf{Cl}}$ (θ = 129.0°), $\mathbf{2}^{\mathbf{Me}}$ (θ = 138.9°), and $\mathbf{3}^{\mathbf{CNtBu}}$ (θ = 131.8°). Nine complexes were found with 150° < θ < 160°,[12,56c,58a−e] and only one with θ = 126.6°.[58f]

(58) (a) Kim, Y.-J.; Choi, J.-C.; Osakada, K. *J. Organomet. Chem.* **1995**, *491*, 97–102. (b) Braunstein, P.; Naud, F.; Rettig, S. J. *New J. Chem.* **2001**, *25*, 32–39. (c) Coleman, K. S.; Green, M. L. H.; Pascu, S. I.; Rees, N. H.; Cowley, A. R.; Rees, L. H. *J. Chem. Soc., Dalton Trans.* **2001**, 3384–3395. (d) Pascu, S. I.; Anderson, G. D. W.; Green, M. H. L.; Green, J. C.; Rees, N. H.; Cowley, A. R. *Inorg. Chim. Acta* **2006**, *359*, 3677–3692. (e) Michon, C.; Ellern, A.; Angelici, R. J. *Inorg. Chim. Acta* **2006**, *359*, 4549–4556. (f) Angurell, I.; Martínez-Ruiz, I.; Rossell, O.; Seco, M.; Gómez-Sal, P.; Martín, A.; Font-Bardia, M.; Solans, X. *J. Organomet. Chem.* **2007**, *692*, 3882–3891.

Table 2. Selected Bond Lengths and Angles of the Cations of $\mathbf{1}^{Cl}$, $\mathbf{1}^{Me}$, and **5** and of $\mathbf{2}^{Cl}$, $\mathbf{2}^{Me}$, $\mathbf{3}^{CNtBu}$ in the Crystal and of the $[PdCl(PNP^{H})]^{+}$ ($\mathbf{1}^{Cl}_{calc}$) and [PdCl(PNP)] ($\mathbf{2}^{Cl}_{calc}$) DFT models (PBE/6-31+G**)[a]

	$\mathbf{1}^{Cl}$	$\mathbf{1}^{Cl}_{calc}$	$\mathbf{1}^{Me}$	$\mathbf{2}^{Cl}$	$\mathbf{2}^{Cl}_{calc}$	$\mathbf{2}^{Me}$	$\mathbf{3}^{CNtBu}$	**5**
				Bond Lengths (Å)				
Pd−N1	2.064(2)	2.100	2.146(2)	2.033(2)	2.038	2.075(2)	2.019(3)	2.089(2)
Pd−P1	2.3045(6)	2.326	2.2960(7)	2.2927(7)	2.308	2.2711(6)	2.2923(6)	2.3108(7)
Pd−P2	2.2988(6)	2.334	2.2970(7)	2.2886(7)	2.310	2.2729(7)	2.2923(6)[d]	2.3060(7)
Pd-R	2.2898(8)[b]	2.296	2.075(3)[c]	2.3553(7)[b]	2.373	2.109(2)[c]	1.956(5)[e]	2.2925(8)[b]
				Bond Angles (deg)				
P1−Pd−P2	170.15(2)	170.7	169.23(3)	168.71(2)	168.0	165.82(2)	168.55(3)[f]	168.77(3)
N1−Pd-R	179.39(7)[b]	178.8	179.4(1)[c]	176.12(5)[b]	177.5	171.8(1)[c]	177.2(2)[e]	173.87(7)[b]
N1−Pd−P1	84.84(6)	85.3	84.73(7)	85.09(6)	84.5	83.82(6)	84.31(2)	85.92(6)
N1−Pd−P2	85.35(6)	85.8	84.52(7)	83.62(6)	83.7	83.73(6)	84.31(2)[g]	85.78(6)
C2−N1−C4	111.2(2)	112.8	112.2(2)	108.5(2)	109.9	109.8(2)	108.2(3)[h]	107.8(2)
C2−N1−Pd	113.4(2)	111.6	111.9(2)	114.7(2)	115.6	118.2(2)	115.7(2)	111.3(2)
C4−N1−Pd	113.5(2)	113.1	112.5(2)	114.1(2)	114.3	117.7(2)	115.7(2)[i]	110.6(2)

[a] $\mathbf{3}^{CNtBu}$ is sited on a crystallographic mirror plane with a symmetry code for equivalent atoms _a: *x*, *y*, 1/2 − *z*. [b] R = Cl. [c] R = CH_3. [d] Pd−P1_a; R = CN*t*Bu. [e] Pd−P1_a; R = CN*t*Bu. [f] P1−Pd−P1_a. [g] N1−Pd−P1_a. [h] C2−N1−C2_a. [i] C2_a −N1−Pd.

is available for N→M π-donation, pyramidalization of the amido moiety is a consequence of minimizing repulsive filled-filled p_π-d_π interactions, resulting in a M−N single bond.[15] A similar bonding picture should arise in square-planar d^8 and in d^{10} amido complexes, but higher bond orders can be expected in three-coordinate d^8 amido complexes because of N→M π-bonding with an empty in-plane metal d-orbital.[14d,60] While palladium(II) complexes with strongly π-basic dialkylamido ligands were not structurally characterized prior to this work, isoelectronic four-coordinate gold(III) dialkylamides in fact exhibit pyramidal nitrogen atoms.[61] The comparison with [IrL(PNP)] (L = CO, C_2H_4, PMe_3), reveals a much higher degree of planarization of the dialkylamido nitrogen atom bound to iridium(I) ($\Sigma_{angles\ around\ N}$ = 355.7° (L = CO); 356.7° (L = C_2H_4); 353.0° (L = PMe_3)).[19,45] This observation can be rationalized by delocalization of electron density into π*-orbitals of the strong (CO, C_2H_4) or moderate (PMe_3) π-acceptor ligands bound to iridium in *trans*-position to the amido moiety, resulting in a stabilizing *push*−*pull*-type π-interaction.[15] Although $\mathbf{3}^{CNtBu}$ bears a potentially strong π-acceptor in *trans*-position to the amido ligand, a pyramidal nitrogen atom is observed, comparable to the complexes with a pure σ-donor ($\mathbf{2}^{Me}$: CH_3) or a σ- and π-donor ligand ($\mathbf{2}^{Cl}$: Cl) in this position, respectively. Therefore, the molecular structures of $\mathbf{2}^{Cl}$, $\mathbf{2}^{Me}$, and $\mathbf{3}^{CNtBu}$ suggest that N−M π-interactions are generally strongly reduced for Pd^{II} amides as compared with isoelectronic group 9 metal centers.

DFT Calculations. DFT models of [PdCl(PNP)] and $[PdCl(PNP^{H})]^{+}$ were calculated to gain further insights into the nature of the Pd−N_{amido} bond. The calculated geometries are in good agreement with the experimentally derived molecular structures in the solid state (Table 2), including

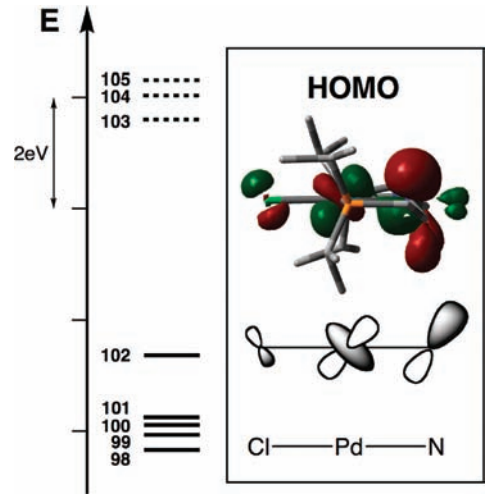


Figure 3. Relative frontier orbital energies of $\mathbf{2}^{Cl}$ from DFT calculations (PBE/6-31+G**) with occupied (solid lines) and unoccupied (dashed lines) orbitals. A contour plot of the HOMO and schematic representations of Cl, Pd, and N contributions are depicted in the box.

pyramidalization of the $\mathbf{2}^{Cl}$ nitrogen atom ($\Sigma_{angles\ around\ N}$ = 339.8 °). The frontier orbital scheme of complex $\mathbf{2}^{Cl}$ exhibits a particularly high lying highest occupied molecular orbital (HOMO, Figure 3, MO 102) with high nitrogen p_z character and small contributions from palladium ($4d_{z^2}$, 5s), chlorine (p_y), and the axial NCH_2 hydrogen atoms. Hirshfeld charges of the nitrogen (−0.21e), palladium (0.25e), and chlorine atoms (−0.43e) in $\mathbf{2}^{Cl}$ are reduced to −0.05e (N), 0.28e (Pd), and −0.33e (Cl) in $\mathbf{1}^{Cl}$ with a charge of 0.12e found for the amino proton. Consequently, protonation of the nitrogen atom results in overall charge transfer to the proton (Δq = −0.88e) from N (Δq = 0.16e) and Cl (Δq = 0.10e) rather than from palladium (Δq = 0.03e), confirming a high concentration of charge at the nitrogen atom in the amido complexes. Therefore, our results explain the nitrogen centered reactivity of $\mathbf{2}^{Cl}$, for example, with Brønstedt acids, nucleophiles, and oxidizing agents. While the repulsive π-interactions are avoided by *N*-pyramidalization it is evident that efficient charge transfer is accomplished via the σ-bonding framework between the two *trans*-ligands N and Cl. This picture strongly resembles the bonding model that was proposed by Pud-

(59) (a) Dewey, M. A.; Arif, A. M.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1991**, 712–714. (b) Dewey, M. A.; Stark, G. A.; Gladysz, J. A. *Organometallics* **1996**, *15*, 4798–4807. (c) Jayaprakash, K. N.; Gunnoe, T. B.; Boyle, P. D. *Inorg. Chem.* **2001**, *40*, 6481–6486.
(60) (a) Mindiola, D. J.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2001**, *123*, 4623–4624. (b) Blue, E. D.; Davis, A.; Conner, D.; Gunnoe, T. B.; Boyle, P. D.; White, P. S. *J. Am. Chem. Soc.* **2003**, *125*, 9435–9441.
(61) (a) Nardin, G.; Randaccio, L.; Annibale, G.; Natile, G.; Pitteri, B. *J. Chem. Soc., Dalton, Trans.* **1980**, 220–223. (b) Rossignoli, M.; Bernhardt, P. V.; Lawrance, G. A.; Maeder, M. *J. Chem. Soc., Dalton Trans.* **1997**, 323–327. (c) Cao, L.; Jennings, M. C.; Puddephatt, R. J. *Inorg. Chem.* **2007**, *46*, 1361–1368.

dephatt and co-workers for Au^{III} amido complex $[AuCl\{N(CH_2\text{-}o\text{-}C_5H_4N)\}]^+$.[61c]

Conclusions

We have reported the synthesis and first structural characterization of palladium(II) dialkylamido complexes. The stability of $\mathbf{2^R}$ and $\mathbf{3^L}$ toward β-hydrogen elimination can be attributed to the chelating effect of the PNP pincer ligand, preventing phosphine dissociation. The molecular structures of the amido complexes, which feature pyramidal nitrogen atoms, and the DFT calculations of $\mathbf{2^{Cl}}$ indicate repulsive $Pd-N^{amido}$ π-interactions, determining the nitrogen-centered reactivity with electrophiles and oxidizing agents. Unlike for isoelectronic iridium(I) amido complexes, even with a potentially strong π-acceptor in *trans*-position (CN^tBu) *N*-pyramidalization indicates a lack of stabilizing *push−pull* π-interactions in $\mathbf{3^{CN\textit{t}Bu}}$.

The pK_a values found for $\mathbf{2^R}$ (R = Me, Ph) do not disagree with Buchwald's proposal that the chemoselectivity of PhCl coupling with alkyl- versus arylamines can be related to pK_a arguments.[8] However, our results show that even dialkylamines are sufficiently acidified by coordination to palladium to be fully deprotonated by alkoxides in non-protic solvents, raising the question if further effects must be considered to explain the observed chemoselectivity, for example, alkoxide coordination to the metal center as proposed by Hartwig and co-workers.[62]

(62) (a) Alcazar-Roman, L. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 12905–12906. (b) Shekhar, S.; Hartwig, J. F. *Organometallics* **2007**, *26*, 340–351.

Available kinetic data reveal, that $N-C^{aryl}$ reductive elimination rates from palladium(II) are higher for electron-poor aryls and more basic nitrogen centers.[1,6,7] Hence, Hartwig proposed, that *although the reason for the observed effect is likely to be complex, one can consider that this trend could result from a favorable pairing of a nucleophilic nitrogen ligand and an electrophilic aryl group*.[1i] Regarding C−N reductive elimination as intramolecular nucleophilic attack of the amido ligand at the aryl *ipso* carbon suggests that a general reluctance of palladium(II) for π-bonding could be prerequisite for its predominant role in catalytic C−N coupling reactions.

Acknowledgment. The authors are grateful to Prof. W. A. Herrmann for generous support. We thank the DFG (Emmy-Noether Programm (SCHN950/2-1): S.S.), the Stifterverband für die deutsche Wissenschaft (Projekt-Nr. 11047 (ForschungsDozentur Molekulare Katalyse): J.E.), the Elitenetzwerk Bayern (graduate fellowship for A.N.M.), and the IDK NanoCat for funding. Dr. S. D. Hoffmann and Dr. F. Kraus are acknowledged for operating the Xcalibur diffractometer.

Supporting Information Available: Crystallographic information for $\mathbf{1^{Cl}}$, $\mathbf{1^{Me}}$, $\mathbf{2^{Cl}}$, $\mathbf{2^{Me}}$, $\mathbf{3^{CNtBu}}$, and **5** in CIF format. NMR spectra of $\mathbf{1^{Cl}}$, $\mathbf{1^{Me}}$, $\mathbf{1^{Ph}}$, $\mathbf{2^{Cl}}$, $\mathbf{2^{Me}}$, $\mathbf{2^{Ph}}$, $\mathbf{3^{CNtBu}}$, $\mathbf{3^{PMe3}}$, **4** and **5** and coordinates for the optimized geometries of $\mathbf{1^{Cl}}$ and $\mathbf{2^{Cl}}$ in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC802286U