J|A|C|S
ARTICLES
Published on Web 11/10/2004

Synthetic, Structural, and Mechanistic Aspects of an Amine Activation Process Mediated at a Zwitterionic Pd(II) Center

Connie C. Lu and Jonas C. Peters*

Contribution from the Division of Chemistry and Chemical Engineering, Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Received June 17, 2004; E-mail: jpeters@caltech.edu

Abstract: A zwitterionic palladium complex [[Ph_2BP_2]Pd(THF)$_2$][OTf] (**1**) (where [Ph_2BP_2] = [$Ph_2B(CH_2PPh_2)_2$]$^-$) reacts with trialkylamines to activate a C−H bond adjacent to the amine N atom, thereby producing iminium adduct complexes [Ph_2BP_2]Pd(N,C:η^2-NR_2CHR'). In all cases examined the amine activation process is selective for the secondary C−H bond position adjacent to the N atom. These palladacycles undergo facile β-hydride elimination/olefin reinsertion processes as evident from deuterium scrambling studies and chemical trap studies. The kinetics of the amine activation process was explored, and β-hydride elimination appears to be the rate-limiting step. A large kinetic deuterium isotope effect for the amine activation process is evident. The reaction profile in less polar solvents such as benzene and toluene is different at room temperature and leads to dimeric {[Ph_2BP_2]Pd}$_2$ (**4**) as the dominant palladium product. Low-temperature toluene-d_8 experiments proceed more cleanly, and intermediates assigned as [Ph_2BP_2]Pd(NEt_3)(OTf) and the iminium hydride species [[Ph_2BP_2]Pd(H)($Et_2N{=}CHCH_3$)][OTf] are directly observed. The complex (Ph_2SiP_2)Pd(OTf)$_2$ (**14**) was also studied for amine activation and generates dimeric [(Ph_2SiP_2)Pd]$_2$[OTf]$_2$ (**16**) as the dominant palladium product. These collective data are discussed with respect to the mechanism of the amine activation and, in particular, the influence that solvent polarity and charge have on the overall reaction profile.

Introduction

Exploiting transition metals to functionalize tertiary amines via initial C−H bond activation is a growing area of synthetic interest.[1] For instance, Murai and co-workers described a catalytic process for the carbonylation of tertiary amines at a position adjacent to an amine N atom using a rhodium(I) precursor.[2] This system requires amine substrates with pendant directing groups to chelate the metal catalyst. More recently, Murahashi et al. reported a ruthenium catalyst for the cyanation of tertiary amines without the requirement of directing groups.[3] Iminium adducts of ruthenium, while not observed, were proposed as key intermediates. Precedent for this type of reactivity had been previously demonstrated at osmium by the Harman group,[4] who provided spectroscopic data to support the generation of an Os(II) η^2-iminium hydride complex via β-hydride elimination upon reduction of an Os(III) amine complex. Murahashi also invoked η^2-iminium hydrides of Pd(II) as intermediates in trialkylamine exchange reactions catalyzed by palladium black at 200 °C ($NR^1{}_2R^2 \rightarrow NR^1{}_3 + NR^2{}_3 + NR^1{}_2R^2 + NR^1R^2{}_2$, where $R^1 \neq R^2$).[5] Another example of a catalytic transformation of tertiary amines comes from Goldman's group with the report that iridium(III) dihydride precursors can mediate the dehydrogenation of tertiary amines to produce enamines in the presence of a H_2-acceptor (i.e., NEt_3 + alkene → $Et_2NCH{=}CH_2$ + alkane).[6]

Previous work from our lab has concerned mechanistic aspects of aromatic C−H bond activations mediated by a zwitterionic platinum(II) center.[7] With an interest in extending this effort, we turned to developing a related palladium system. In this report a reactive Pd(II) complex is described, [[Ph_2BP_2]Pd(THF)$_2$][OTf] (**1**), where [Ph_2BP_2] represents the bis(phosphino)borate ligand [$Ph_2B(CH_2PPh_2)_2$]$^-$. This system stoichiometrically activates a variety of trialkylamines at a secondary

(1) (a) Murahashi, S.-I. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2443−2465. (b) Doye, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3351−3353.
(2) (a) Chatani, N.; Asaumi, T.; Ikeda, T.; Yorimitsu, S.; Ishii, Y.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **2000**, *122*, 12882−12283. For Rh-catalyzed carbenoid insertions into C−H bonds α to N, see: (b) Davies, H. M. L.; Hansen, T.; Hopper, D. W.; Panaro, S. A. *J. Am. Chem. Soc.* **1999**, *121*, 6509−6510. (c) Davies, H. M. L.; Venkataramani, C.; Hansen, T.; Hopper, D. W. *J. Am. Chem. Soc.* **2003**, *125*, 6462−6468. (d) Davies, H. M. L.; Venkataramani, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2197−2199. For a related example of imine activation, see: (e) Sakaguchi, S.; Kubo, T.; Ishii, Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 2534−2536.
(3) (a) Murahashi, S.-I.; Komiya, N.; Terai, H.; Nakae, T. *J. Am. Chem. Soc.* **2003**, *125*, 15312−15313. For other Ru examples, see: (b) Chatani, N.; Asaumi, T.; Yorimitsu, S.; Ikeda, T.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **2001**, *123*, 10935−10941. (c) Chatani, N.; Fukuyama, T.; Tatamidani, H.; Kakiuchi, F.; Murai, S. *J. Org. Chem.* **2000**, *65*, 4039−4047.
(4) (a) Barrera, J.; Orth, S. D.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 7316−7318. (b) Orth, S. D.; Barrera, J.; Rowe, S. M.; Helberg, L. E.; Harman, W. D. *Inorg. Chim. Acta* **1998**, *270*, 337−344.
(5) (a) Murahashi, S.-I.; Hirano, T.; Yano, T. *J. Am. Chem. Soc.* **1978**, *100*, 348−350. (b) Murahashi, S.-I.; Yoshimura, N.; Tsumiyama, T.; Kojima, T. *J. Am. Chem. Soc.* **1983**, *105*, 5002−5011.
(6) Zhang, X.; Fried, A.; Knapp, S.; Goldman, A. S. *Chem. Commun.* **2003**, 2060−2061.
(7) (a) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 5100−5101. (b) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 8870−8888.

10.1021/ja046415s CCC: $27.50

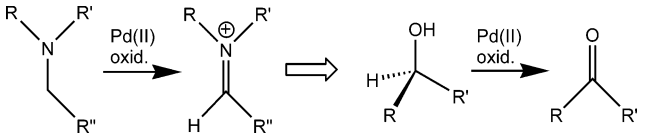


Figure 1. Relationship between amine-to-iminium ion and alcohol-to-ketone oxidation reactions.

C−H position adjacent to the amine N atom. Formal proton loss accompanies the activation process, and structurally unusual iminium adduct complexes of palladium are obtained.

This reaction system is particularly well suited to mechanistic examination, and we have therefore undertaken such a study. We attempt to address the reaction's overall selectivity and suggest a plausible operational mechanism. Our data indicate that the processes may be mechanistically germane to the mode of palladium-catalyzed alcohol oxidations[8] (Figure 1) and also to the in situ reduction of Pd(II) precursors by trialkyamines[9] in Pd(0)-catalyzed reactions, as, for example, in the Heck reaction.[10] These processes are also of potential relevance to β-hydride elimination processes of palladium amides[11] and to β-hydride eliminations that generate imines from secondary amines.[12]

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with N_2 gas, followed by passage through an activated alumina column. Diethyl ether, tetrahydrofuran, petroleum ether, and benzene were typically tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. The solvents were dried over activated 3 Å molecular sieves and degassed by freeze−pump−thaw cycles prior to use. The preparation of $Et_2NC(H)=CH_2$,[13] diisopropyl(2-propenyloxymethyl)amine,[14] $(COD)PdCl_2$,[15] Ph_2SiP_2,[7] and $[NBu_4][Ph_2BP_2]$[16] was carried out following literature procedures. Amines and *o*-phenylpyridine were purchased from Aldrich, dried over CaH_2, distilled or vacuum transferred, and stored over activated 3 Å molecular sieves. The reagents $(PhCN)_2PdCl_2$ and AgOTf were purchased from Strem; the latter was dried under vacuum with heating at 80 °C for 12 h, and the former was used without further purification. The reagent NaCN (99%) was dried under vacuum with heating at 80 °C. *tert*-Butyl isocyanide was dried over 3 Å molecular sieves and used without further purification. Elemental analyses were performed by Desert Analytics, Tucson, AZ. A Varian Mercury-300 NMR spectrometer and a Varian Inova-500 NMR spectrometer were used to record ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra unless otherwise stated. ^1H and ^{13}C NMR chemical shifts were referenced to residual solvent. Proton peaks were assigned based on TOCSY-1D and ^{31}P-decoupled ^1H NMR studies. ^{31}P NMR chemical shifts are reported relative to an external standard of 85% H_3PO_4. ^{19}F NMR chemical shifts are reported relative to an external standard of hexafluorobenzene. IR measurements were obtained with a KBr solution cell using a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Bio-Rad Merlin Software (v. 2.97) set at 4 cm^{-1} resolution. X-ray diffraction experiments were performed at the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer.

$[(Ph_2BP_2)Pd(THF)_2][OTf]$ (1). A THF solution of AgOTf (72.9 mg, 71 μmol) was added to a THF suspension of $\{[Ph_2BP_2]Pd(\mu\text{-}Cl)\}_2$ (0.200 g, 142 μmol). The reaction was stirred for 7 h and filtered through glass wool. The bright yellow filtrate was dried in vacuo for 9 h to give a yellow foam−powder (0.252 g, 92% yield). ^1H NMR (C_6D_6, 500 MHz) δ 7.41 (dd, J = 7.0 and 12.0 Hz, 8H, H_o of PPh_2), 7.23 (br d, J = 7.0 Hz, 4H, H_o of BPh_2), 7.09 (t, J = 7.5 Hz, 4H, H_m of BPh_2), 7.04 (tt, J = 1.0 and 7.5 Hz, 2H, H_p of BPh_2), 6.97 (dd, J = 6.5 and 8.0 Hz, H_p of PPh_2), 6.89 (app t, 8H, H_m of PPh_2), 3.44 (m, 8H, $O(CH_2CH_2)_2$), 1.95 (br dd, J = 5.0 and 14.5 Hz, 4H, CH_2PPh_2), 1.26 (m, 8H, $O(CH_2CH_2)_2$); ^{13}C NMR (d_6-benzene, 75 MHz) δ 160.3 (br, C_{ipso} of BPh_2), 133.1 (app t, J = 5.4 Hz, C_o of PPh_2), 132.6 (C_o of BPh_2), 131.9 (C_p of PPh_2), 129.8 (d, J = 55.8 Hz, C_{ipso} of PPh_2), 129.0 (app t, J = 5.4 Hz, C_m of PPh_2), 127.7 (C_m of BPh_2), 124.0 (C_p of BPh_2), 118.7 (d, J = 319 Hz, CF_3), 69.9 ($O(CH_2CH_2)_2$), 25.9 ($O(CH_2CH_2)_2$), 18.6 (br, CH_2PPh_2); ^{31}P NMR (C_6D_6, 121 MHz) δ 48.2; ^{19}F NMR (C_6H_6, 282 MHz) δ −73.5. Anal. Calcd for $C_{47}H_{50}BF_3O_5P_2PdS$: C, 58.61; H, 5.23; N, 0. Found: C, 58.66; H, 5.18; N, 0.08.

$[NBu_4][(Ph_2BP_2]PdCl_2]$ (2). A THF solution (10 mL) of $(COD)PdCl_2$ (0.600 g, 2.10 mmol) was added dropwise to a stirring suspension of $[NBu_4][Ph_2BP_2]$ (1.694 g, 2.10 mmol) in THF (13 mL). The reaction mixture immediately became homogeneous and turned burnt orange. After stirring for 30 min, all volatiles were removed in vacuo. The resulting orange oil was taken up in benzene to precipitate the product as a light yellow crystalline solid. The solids were collected on a frit and washed with benzene and petroleum ether to give light yellow **2** (0.410 g, 40% yield). ^1H NMR (d_6-acetone, 500 MHz) δ 7.56 (m, 8H, H_o of PPh_2), 7.24 (app t, J = 7.0 Hz, 4H, H_p of PPh_2), 7.11 (td, J = 1.5 and 7.5 Hz, 8H, H_m of PPh_2), 6.85 (br d, J = 6.5 Hz, 4H, H_o of BPh_2), 6.70 (app t, J = 7.5 Hz, 4H, H_m of BPh_2), 6.65 (tt, J = 1.5 and 7.5 Hz, 2H, H_p of BPh_2), 3.35 (m, 8H, $N(CH_2CH_2CH_2CH_3)_4$), 1.76 (br d, J = 10.5 Hz, 4H, CH_2PPh_2), 1.73 (m, 8H, $N(CH_2CH_2CH_2CH_3)_4$), 1.38 (sextet, J = 7.5 Hz, 8H, $N(CH_2CH_2CH_2CH_3)_4$), 0.95 (t, J = 7.5 Hz, 12H, $N(CH_2CH_2CH_2CH_3)_4$); ^{13}C NMR (d_6-acetone, 125 MHz) δ 163.3 (br, C_{ipso} of BPh_2), 135.5 (dd, J = 4.3 and 55.6 Hz, C_{ipso} of PPh_2), 134.5 (m, C_o of PPh_2), 132.7 (C_o of BPh_2), 129.8 (C_p of PPh_2), 127.7 (m, C_m of PPh_2), 126.7 (C_m of BPh_2), 122.6 (C_p of BPh_2), 59.3 (t, J = 2.4 Hz, $N(CH_2CH_2CH_2CH_3)_4$), 24.4 ($N(CH_2CH_2CH_2CH_3)_4$), 21.6 (br, CH_2PPh_2), 20.3 ($N(CH_2CH_2CH_2CH_3)_4$), 13.9 ($N(CH_2CH_2CH_2CH_3)_4$); ^{31}P NMR (d_6-acetone, 121 MHz) δ 35.46. Anal. Calcd for $C_{54}H_{70}BCl_2NP_2Pd$: C, 65.96; H, 7.18; N, 1.42. Found: C, 65.83; H, 7.60; N, 1.63.

$\{[Ph_2BP_2]Pd(\mu\text{-}Cl)\}_2$ (3). A THF solution of $PdCl_2(NCPh)_2$ (1.4856 g, 3.834 mmol) was added rapidly to a stirring THF solution of $[NBu_4][Ph_2BP_2]$ (3.0900 g, 3.834 mmol). The orange-yellow solution was filtered through Celite and dried in vacuo. The residue was washed thoroughly with Et_2O to give pale yellow solids, which by ^{31}P NMR was a mixture of compounds **2** and **3**. The solids were dissolved in THF (150 mL) in a 300 mL of RBF with a stir bar, and $NaBPh_4$ (1.3123 g, 3.834 mmol) was added in the dark. After stirring for 8 h in the

(8) For mechanistic considerations pertaining to these types of reactions, see: (a) Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1999**, *64*, 6750−6755. (b) Mueller, J. A.; Sigman, M. S. *J. Am. Chem. Soc.* **2003**, *125*, 7005−7013. (c) Jensen, D. R.; Schultz, M. J.; Mueller, J. A.; Sigman, M. S. *Angew. Chem., Int. Ed.* **2003**, *42*, 3810−3813. (d) Steinhoff, B. A.; Stahl, S. S. *Org. Lett.* **2002**, *4*, 4179−4181. (e) Steinhoff, B. A.; Fix, S. R.; Stahl, S. S. *J. Am. Chem. Soc.* **2002**, *124*, 766−767. (f) Mueller, J. A.; Jensen, D. R.; Sigman, M. S. *J. Am. Chem. Soc.* **2002**, *124*, 8202−8203. (g) ten Brink, G.-J.; Arends, I. W. C. E.; Sheldon, R. A. *Adv. Synth. Catal.* **2002**, *344*, 355−369. (h) Trend, R. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 4482−4483. (i) Noronha, G.; Henry, P. M. *J. Mol. Catal. A: Chem.* **1997**, *120*, 75−87. (j) For a review on this topic, see: Muzart, J. *Tetrahedron* **2003**, *59*, 5789−5816. (k) Steinhoff, B. A.; Guzei, I. A.; Stahl, S. S. *J. Am. Chem. Soc.* **2004**, *126*, 11268−11278.
(9) See: Trzeciak, A. M.; Ciunik, Z.; Ziółkowski, J. J. *Organometallics* **2002**, *21*, 132−137 and references therein.
(10) (a) Tsuji, J. *Palladium Reagents and Catalysts−Innovations in Organic Synthesis*; John Wiley & Sons: New York, 1995; pp 125−128. (b) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009−3066 and references therein.
(11) For a review, see: (a) Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046−2067. See also: (b) Hartwig, J. F.; Richards, S.; Barañano, D.; Paul, F. *J. Am. Chem. Soc.* **1996**, *118*, 3626−3633.
(12) (a) Strieter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 13978−13980. (b) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348−1350.
(13) Laban, G.; Mayer, R. *Z. Chem.* **1967**, *7*, 12−13.
(14) Arenz, T.; Frauenrath, H.; Raabe, G.; Zorn, M. *Liebigs Ann. Chem.* **1994**, 931−942.
(15) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1990**, *28*, 346−349.
(16) Peters, J. C.; Thomas, J. C. *Inorg. Synth.* **2004**, *34*, 8−14.

dark, yellow solids precipitated from the brown solution. The first crop of solids were collected and washed sparingly with THF and a 1:1 THF/Et_2O solution. To remove NaCl, the solids were dissolved in CH_2Cl_2 and filtered through Celite. The bright yellow solution was dried in vacuo to give yellow crystalline solids. A second crop of product was collected from the concentrated brown filtrate at −30 °C. The crops were combined to give 1.911 g of **3** (73% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30−7.18 (m, 12H, H_p and H_o of PPh_2), 7.07 (t, J = 7.8 Hz, 8H, H_m of PPh_2), 6.91−6.82 (m, 10H, aryl H's of BPh_2), 1.79 (br d, J = 10.5 Hz, 4H, C*H*$_2$PPh$_2$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.4 (br, C_{ipso} of BPh_2), 133.3 (m, C_o of PPh_2), 132.1 (C_o of BPh_2), 131.5 (d, J = 56.0 Hz, C_{ipso} of PPh_2), 130.7 (C_p of PPh_2), 128.1 (m, C_m of PPh_2), 126.8 (C_m of BPh_2), 123.0 (C_p of BPh_2), 17.7 (br, *C*H$_2$PPh$_2$); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ 43.07. Anal. Calcd for $C_{76}H_{68}B_2Cl_2P_4Pd$: C, 64.71; H, 4.86; N, 0.00. Found: C, 64.80; H, 4.83; N, <0.05.

[Ph$_2$BP$_2$]Pd(*o*-phenylpyridine)OTf (5). To a bright yellow THF solution of **1** (75.0 mg, 78.0 μmol) was added *o*-phenylpyridine (11.1 μL, 84.0 μmol). The solution immediately turned off-white and slightly turbid. Petroleum ether (5 mL) was added to precipitate solids. The white solids were collected and washed liberally with Et_2O. The solids were dried in vacuo to give 69 mg of a pale yellow powder (91% yield). Complex **5** is fluxional in solution at room temperature. ^{1}H NMR ($CDCl_3$, 300 MHz, −40 °C) δ 8.35 (d, J = 4.8 Hz, 1H, H_o of pyr), 7.69−7.52 (m, 12H, aryl), 7.32−7.07 (m, 10H, aryl), 6.84 (t, 2H, J = 6.4 Hz, H_p of BPh_2), 6.72−6.67 (m, 12H, aryl), 6.24 (br d, J = 7.5 Hz, 2H, aryl), 2.55 (d, J = 13.5 Hz, 1H, C*H*H′PPh$_2$), 1.93 (d, J = 14 Hz, 1H, CH*H*′PPh$_2$), 1.65 (d, J = 14 Hz, 1H, C*H*H′P′Ph$_2$), 1.53 (d, J = 13.8 Hz, 1H, CH*H*′P′Ph$_2$); ^{31}P NMR ($CDCl_3$, 121 MHz, −40 °C) δ 46.3 (d, J = 20 Hz), 35.3 (d, J = 20 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, −40 °C) δ −81.6. Anal. Calcd for $C_{50}H_{43}BF_3NO_3P_2PdS$: C, 61.65; H, 4.45; N, 1.44. Found: C, 61.80; H, 4.21; N, 1.54.

[Ph$_2$BP$_2$]Pd(N,C:η^2-N^{i}Pr$_2$CHCH$_3$) (6). Compound **6** was prepared with N^{i}Pr$_2$Et using a procedure identical to that used for compound **7** (68.0 mg, 82% yield). ^{1}H NMR (C_6D_6, 300 MHz) δ 7.32−7.50 (m, 14H, aryl H), 7.00−7.14 (m, 16H, aryl H), 3.38 (app quintet d, J = 1.8 and 6.9 Hz, 1H, PdNC*H*CH$_3$), 2.95 (septet, J = 6.0 Hz, 1H, N(C*H*Me$_2$)C′HMe$_2$), 2.74 (septet, J = 6.0 Hz, 1H, N(CHMe$_2$)C′*H*Me$_2$), 2.18−2.42 (m, 4H, C*H*$_2$PPh$_2$ and C′*H*$_2$P′Ph$_2$), 0.88 (d, J = 6.9 Hz, 3H, N(CHMe$_2$)C′H*Me*$_2$), 0.835 (d, J = 6.3 Hz, 3H, N(CH*Me*$_2$)C′HMe$_2$), 0.73 (td, J = 9.6 and 15.9 Hz, 3H, PdNCHC*H*$_3$), 0.50 (d, J = 5.4 Hz, 6H, N(CH*Me*$_2$)C′H*Me*$_2$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.8 (br, C_{ipso} and C'_{ipso} of BPh_2), 141.5 (d, J = 24.3 Hz, C_{ipso} of PPh_2), 139.1 (d, J = 35.4 Hz, C'_{ipso} of PPh_2), 137.9 (d, J = 29.3 Hz, C_{ipso} of P′Ph$_2$), 137.1 (d, J = 40.5 Hz, C'_{ipso} of P′Ph$_2$), 133.9 (d, J = 31.5 Hz, C_o of PPh_2), 133.3 (d, J = 12.7 Hz, $C_{o'}$ of PPh_2), 133.0 (C_o of BPh_2), 132.6 ($C_{o'}$ of BPh_2), 132.1 (d, J = 11.6 Hz, C_o of P′Ph$_2$), 132.0 (d, J = 10.8 Hz, $C_{o'}$ of P′Ph$_2$), 129.0 (d, J = 2.0 Hz, C_p of PPh_2), 128.9 (d, J = 1.9 Hz, $C_{p'}$ of PPh_2), 128.4 (d, J = 2.3 Hz, C_p of P′Ph$_2$), 128.1 (d, J = 1.5 Hz, $C_{p'}$ of P′Ph$_2$), 128.0 (d, J = 9.2 Hz, C_m of PPh_2), 127.7−127.9 (m, $C_{m'}$ of PPh_2, C_m and $C_{m'}$ of P′Ph$_2$), 126.2 (C_m of BPh_2), 126.1 ($C_{m'}$ of BPh_2), 122.3 (C_p of BPh_2), 122.2 ($C_{p'}$ of BPh_2), 62.6 (dd, J = 13.8 and 56.7 Hz, PdN(*C*HMe)), 54.6 (N(*C*HMe$_2$)$_2$), 50.4 (N(*C*′HMe$_2$)$_2$), 26.1 (N(CH*Me*$_2$)$_2$), 24.8 (N(CH*Me*′$_2$)$_2$), 23.4 (N(C′H*Me*$_2$)$_2$), 21.2 (N(C′H*Me*′$_2$)$_2$), 20.5−22 (br m, *C*H$_2$PPh$_2$ and *C*′H$_2$PPh$_2$), 15.9 (dd, J = 2 and 5.3 Hz, PdN(CH*Me*)); ^{31}P NMR ($CDCl_3$, 121 MHz) δ 32.1 (d, J = 32.0 Hz), 14.1 (d, J = 32.0 Hz). Anal. Calcd for $C_{46}H_{52}BNP_2Pd$: C, 69.23; H, 6.57; N, 1.76. Found: C, 68.62; H, 6.77; N, 1.77.

[Ph$_2$BP$_2$]Pd(N,C:η^2-NEt$_2$CHCH$_3$) (7). Compound **1** (100.0 mg, 103.9 μmol) and NEt_3 (290 μL, 2.081 mmol) were dissolved in 8 mL of THF. The reaction mixture turned from yellow to a burnt orange. After 3 h, all volatiles were removed in vacuo, and 10 mL of petroleum ether was added to precipitate a peach-colored powder and wash away the excess amine. The solids were dissolved in 15 mL of benzene and flashed through a silica plug. The pale pink filtrate was dried in vacuo to give light pink crystalline solids (78.0 mg, 98% yield). ^{1}H NMR (C_6D_6, 300 MHz) δ 7.62 (br d, J = 6.9 Hz, H_o of BPh_2), 7.11−7.41 (m, 14H, aryl H), 6.97−7.00 (m, 12H, aryl H), 2.97 (app hextet, J = 6.0 Hz, 1H, PdNC*H*CH$_3$), 2.46 (septet d, J = 3.6 and 6.9 Hz, 1H, N(C*H*H′Me)Et′, 2.17−2.45 (m, 7H, N(CH*H*′Me)C′*HH*′Me, C*H*$_2$PPh$_2$, and C′*H*$_2$P′Ph$_2$), 0.75 (td, J = 8.1 and 10.2 Hz, 3H, PdNCHC*H*$_3$), 0.47 (m, 6H, N(CH$_2$*Me*)C′H$_2$*Me*); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.4 (br, C_{ipso} and C'_{ipso} of BPh_2), 140.7 (d, J = 26.1 Hz, C_{ipso} of PPh_2), 139.2 (d, J = 34.3 Hz, C'_{ipso} of PPh_2), 139.1 (d, J = 28.0 Hz, C_{ipso} of P′Ph$_2$), 138.3 (d, J = 37.8 Hz, C'_{ipso} of P′Ph$_2$), 133.6 (C_o of BPh_2), 133.2 (d, J = 13.1 Hz, C_o of PPh_2), 133.1 ($C_{o'}$ of BPh_2), 132.8 (d, J = 12.7 Hz, $C_{o'}$ of PPh_2), 132.34 (d, J = 13.2 Hz, C_o of P′Ph$_2$), 132.31 (d, J = 11.6 Hz, $C_{o'}$ of P′Ph$_2$), 128.8 (d, J = 2.3 Hz, C_p of PPh_2), 128.62 (d, J = 1.9 Hz, $C_{p'}$ of PPh_2), 128.59 (d, J = 1.5 Hz, C_p of P′Ph$_2$), 128.2 (d, J = 2.0 Hz, $C_{p'}$ of P′Ph$_2$), 127.95 (d, J = 6.2 Hz, C_m of PPh_2), 127.8−127.9 (m, $C_{m'}$ of PPh_2, C_m and $C_{m'}$ of P′Ph$_2$), 126.4 (C_m of BPh_2), 126.1 ($C_{m'}$ of BPh_2), 122.73 (C_p of BPh_2), 122.66 ($C_{p'}$ of BPh_2), 64.3 (dd, J = 13.5 and 57.9 Hz, PdN(*C*HMe)), 52.2 (s, N(*C*H$_2$Me)), 45.6 (s, N(*C*′H$_2$Me)), 20.6 (br m, *C*H$_2$PPh$_2$ and *C*′H$_2$PPh$_2$), 16.1 (app t, J = 3.5 Hz, PdN(CH*Me*)), 13.1 (s, N(CH$_2$*Me*)), 12.5 (s, N(CH$_2$*Me*′)): ^{31}P NMR (C_6D_6, 121 MHz) δ 32.2 (d, J = 35.7 Hz), 15.7 (d, J = 35.7 Hz). Anal. Calcd for $C_{44}H_{48}BNP_2Pd$: C, 68.63; H, 6.28; N, 1.82. Found: C, 68.82; H, 5.99; N, 1.88.

[Ph$_2$BP$_2$]Pd(N,C:η^2-NCy$_2$CHCH$_3$) (8). Compound **1** (200.0 mg, 207.86 μmol) and NEtCy$_2$ (0.96 mL, 4.17 mmol) were dissolved in THF. After stirring for 3 h, the solution was dried in vacuo. The residue was washed with petroleum ether, benzene, and acetonitrile. The remaining pink powder was dissolved in CH_2Cl_2 and filtered through Celite (69 mg, 38% yield). Single crystals suitable for X-ray diffraction studies were grown from vapor diffusion of petroleum ether into a CH_2Cl_2 solution of **8** at −30°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.11−7.36 (m, 24H, aryl H), 6.80−6.93 (m, 6H, aryl H), 3.38 (app quintet d, J = 1.1 and 2.9 Hz, 1H, PdNC*H*CH$_3$), 2.79 (app q, J = 4.9 Hz, 1H, NC*H*(CH$_2$)$_5$), 1.08−2.07 (m, 25H, aliphatic *H*'s), 0.96 (td, J = 5.4 and 9.0 Hz, 3H, PdNCHC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.2 (br, C_{ipso} and C'_{ipso} of BPh_2), 141.6 (d, J = 23.9 Hz, C_{ipso} of PPh_2), 139.6 (d, J = 34.6 Hz, C'_{ipso} of PPh_2), 137.7 (d, J = 28.8 Hz, C_{ipso} of P′Ph$_2$), 137.2 (d, J = 38.2 Hz, C'_{ipso} of P′Ph$_2$), 133.96 (d, J = 13.4 Hz, C_o of PPh_2), 133.4 (d, J = 13.2 Hz, $C_{o'}$ of PPh_2), 133.1 (C_o of BPh_2), 132.7 ($C_{o'}$ of BPh_2), 131.88 (d, J = 10.7 Hz, C_o of P′Ph$_2$), 131.85 (d, J = 11.2 Hz, $C_{o'}$ of P′Ph$_2$), 129.0 (d, J = 2.0 Hz, C_p of PPh_2), 128.9 (d, J = 1.9 Hz, $C_{p'}$ of PPh_2), 128.4 (d, J = 2.4 Hz, C_p of P′Ph$_2$), 128.0 (d, J = 9.2 Hz, C_m of PPh_2), 127.9 (d, J = 1.5 Hz, $C_{p'}$ of P′Ph$_2$), 127.72 (d, J = 8.8 Hz, $C_{m'}$ of PPh_2), 127.70 (d, J = 10.1 Hz, C_m of P′Ph$_2$), 127.68 (d, J = 8.0 Hz, $C_{m'}$ of P′Ph$_2$), 126.2 (s, C_m of BPh_2), 126.1 (s, $C_{m'}$ of BPh_2), 122.3 (C_p of BPh_2), 122.2 ($C_{p'}$ of BPh_2), 64.5 (dd, J = 13.4 and 56.7 Hz, PdN(*C*HMe)), 63.8 (N(*C*H(CH$_2$)$_5$)), 59.9 (d, J = 3.1 Hz, N(*C*′H(C′H$_2$)$_5$)), 36.5 (Cy), 35.4 (Cy), 35.2 (Cy), 32.71 (Cy), 26.7 (Cy), 26.4 (Cy), 26.22 (Cy), 26.18 (Cy), 25.5 (2 overlapping s, Cy), 20.4−21.9 (br m, *C*H$_2$PPh$_2$ and *C*′H$_2$PPh$_2$), 15.7 (d, J = 4.3 Hz, PdN(CH*Me*)); ^{31}P NMR ($CDCl_3$, 121 MHz) δ 31.8 (d, J = 31.1 Hz), 13.2 (d, J = 31.1 Hz). Anal. Calcd for $C_{52}H_{60}BNP_2Pd$: C, 71.12; H, 6.89; N, 1.59. Found: C, 70.77; H, 6.65; N, 1.36.

[Ph$_2$BP$_2$]Pd(N,C:η^2-NCH$_3$CH(CH$_2$)$_3$) (9). Compound **9** was prepared with *N*-methylpyrrolidene using a procedure identical to that used for compound **7** (67 mg, 82% yield). Single crystals suitable for X-ray diffraction studies were grown from vapor diffusion of petroleum ether into a THF solution of **9** at −30 °C. ^{1}H NMR (C_6D_6, 300 MHz) δ 7.63 (br t, J = 6.3 Hz, 4H, aryl H), 7.38 (dd, J = 8.7 and 9.6 Hz, 2H, H_o of PPhPh′), 7.11−7.30 (m, 12H, aryl H's), 6.96−6.99 (m, 12 H, aryl H's), 2.86 (m, 1H, PdN(Me)C*H*(CH$_2$)$_3$), 2.75 (m, 1H, aliphatic H of pyrrolidene), 2.32−2.25 (m, 2H, C*HH*′PPh$_2$), 2.14−2.10 (m, 2H, C′*HH*′P′Ph$_2$), 2.07 (d, J = 3.3 Hz, 3H, N*Me*), 1.71−1.87 (m, 2H, aliphatic H's of pyrrolidene), 1.56 (m, 1H, aliphatic H of pyrrolidene), 1.21−1.37 (m, 2H, aliphatic H's of pyrrolidene); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.6 (br, C_{ipso} and C'_{ipso} of BPh_2), 140.2 (d, J = 26.0 Hz, C_{ipso} of PPh_2), 139.4−138.8 (m, C'_{ipso} of PPh_2, C_{ipso} and C'_{ipso} of P′Ph$_2$), 133.6 (C_o of BPh_2), 133.2 ($C_{o'}$ of BPh_2), 133.0 (d, J = 13.1 Hz, C_o of

PPh_2), 132.8 (d, J = 13.7 Hz, $C_{o'}$ of PPh_2), 132.2 (d, J = 13.1 Hz, C_o of $P'Ph_2$), 131.9 (d, J = 11.4 Hz, $C_{o'}$ of $P'Ph_2$), 128.9 (C_p of PPh_2), 128.6 ($C_{p'}$ of PPh_2), 128.5 (C_p of $P'Ph_2$), 128.3 ($C_{p'}$ of $P'Ph_2$), 128.0−127.9 (m, C_m and $C_{m'}$ of PPh_2, C_m and $C_{m'}$ of $P'Ph_2$), 126.3 (C_m of BPh_2), 126.2 ($C_{m'}$ of BPh_2), 122.8 (C_p and $C_{p'}$ of BPh_2), 69.5 (dd, J = 14.6 and 61.8 Hz, PdN(Me)*C*H), 60.3 (N(*C*H_2)), 45.5 (d, J = 3.8 Hz, N*Me*), 31.6 (*C*H_2 of pyrrolidene), 26.1 (*C*H_2 of pyrrolidene), 20.2 (br m, *C*H_2-PPh_2), 17.9 (br m, *C'*H_2PPh_2); ^{31}P NMR (C_6D_6, 121 MHz) δ 32.7 (d, J = 39.5 Hz), 16.9 (d, J = 39.5 Hz). Anal. Calcd for $C_{43}H_{44}BNP_2Pd$: C, 68.50; H, 5.88; N, 1.86. Found: C, 68.53; H, 5.96; N, 2.06.

[Ph_2BP_2]Pd(N,C:η^2-NCH$_3$CH(CH$_2$)$_4$) (10). Compound **10** was prepared with *N*-methylpiperidene using a procedure identical to that used for compound **7**. Yield 54.1 mg, 69%. ^{1}H NMR (C_6D_6, 300 MHz) δ 7.67 (br d, 2H, J = 6.9 Hz, H_o of BPhPh′), 7.61 (br d, 2H, J = 6.0 Hz, $H_{o'}$ of BPhPh′), 7.31−7.39 (m, 8H, H_o and $H_{o'}$ of PPhPh′ and P′PhPh′), 7.25 (t, J = 6.9 Hz, 2H, H_p and $H_{p'}$ of BPhPh′), 7.10−7.14 (m, 4H, H_m and $H_{m'}$ of BPhPh′), 6.95−6.98 (m, 12 H, H_m, $H_{m'}$, H_p, and $H_{p'}$ of PPhPh′ and P′PhPh′), 2.98 (m, 1H, PdN(Me)C*H*(CH$_2$)$_4$), 2.29−2.42 (m, 3H, C*HH*′PPh_2 and C*H*H′$P'Ph_2$), 2.11 (br d, J = 12.3 Hz, 1H, CH*H*′$P'Ph_2$), 2.04 (d, J = 3.3 Hz, 3H, N*Me*), 1.82 (app q, J = 12. 3 Hz, 1H, aliphatic H of piperidene), 1.71 (m, 1H, aliphatic H of piperidene), 1.07−1.15 (m, 4H, aliphatic H's of piperidene), 0.86−0.88 (m, 2H, aliphatic H's of piperidene); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.4 (br, C_{ipso} and C'_{ipso} of BPh_2), 140.7 (d, J = 25.9 Hz, C_{ipso} of PPh_2), 139.5 (d, J = 28.2 Hz, C'_{ipso} of PPh_2), 139.1−139.5 (m, C_{ipso} and C'_{ipso} of $P'Ph_2$), 133.7 (C_o of BPh_2), 133.1 ($C_{o'}$ of BPh_2), 132.9 (d, J = 13.1 Hz, C_o of PPh_2), 132.2 (m, $C_{o'}$ of PPh_2, C_o and $C_{o'}$of $P'Ph_2$), 128.8 (C_p of PPh_2), 128.6 ($C_{p'}$ of PPh_2), 128.5 (C_p of $P'Ph_2$), 128.3 ($C_{p'}$ of $P'Ph_2$), 127.9−128.0 (br m, C_m and $C_{m'}$ of PPh_2, C_m and $C_{m'}$ of $P'Ph_2$), 126.4 (C_m of BPh_2), 126.1 ($C_{m'}$ of BPh_2), 122.8 (C_p and $C_{p'}$ of BPh_2), 66.9 (dd, J = 13.8 and 60.4 Hz, PdN(Me)*C*H), 51.4 (N(*C*H_2)), 49.7 (N*Me*), 22.6 (*C*H_2 of piperidene), 22.4 (*C*H_2 of piperidene), 20.7 (br m, *C*H_2PPh_2), 17.8 (br m, *C'*H_2PPh_2), 16.6 (*C*H_2 of piperidene); ^{31}P NMR (C_6D_6, 121 MHz) δ 32.7 (d, J = 39.5 Hz), 16.9 (d, J = 39.5 Hz). Anal. Calcd for $C_{44}H_{46}BNP_2Pd$: C, 68.81; H, 6.04; N, 1.82. Found: C, 67.93; H, 6.39; N, 1.41.

[Ph_2BP_2]Pd(N,C:η^2-N^{i}Pr$_2$CH$_2$) (11). Compound **1** (100.4 mg, 104.4 μmol) and diisopropyl(2-propenyloxymethyl)amine (357.4 mg, 2.088 mmol) were dissolved in THF. The reaction mixture turned from yellow to orange-red immediately but faded to pale yellow after stirring for 5 min. After 1 h, all volatiles were removed in vacuo, and petroleum ether was added to precipitate the powder and wash away the excess amine. The solids were dissolved in benzene and flashed through a silica plug. The filtrate was dried in vacuo to give pale yellow solids (63.7 mg, 78% yield). ^{1}H NMR (C_6D_6, 300 MHz) δ 7.55 (br d, J = 6.9 Hz, H_o of BPh_2), 7.32−7.44 (m, 8H, aryl H's), 7.08−7.18 (m, 6H, aryl H's), 6.98−7.02 (m, 12H, aryl H's), 2.61 (m, 2H, N(C*H*Me$_2$)$_2$), 2.51 (app t, J = 5.1 Hz, 2H, PdNC*H*$_2$), 2.29 (m, 4 H, C*H*$_2PPh_2$), 0.70 (d, J = 6.9 Hz, 6H, N(CH*Me*Me′)$_2$), 0.59 (d, J = 6.0 Hz, 6H, N(CHMe*Me*′)$_2$); ^{13}C NMR (C_6D_6, 75 MHz) δ 163.8 (v br, C_{ipso} of BPh_2), 140.6 (d, J = 28.7 Hz, C_{ipso} of PPh_2), 139.8 (d, J = 38.3 Hz, C_{ipso} of $P'Ph_2$), 133.9 (C_o of BPh_2), 133.4 (d, J = 12.6 Hz, C_o of PPh_2), 133.0 (d, J = 12.0 Hz, C_o of $P'Ph_2$), 128.3−129.1 (m, C_p and C_m of PPh_2 and $P'Ph_2$), 127.0 (C_m of BPh_2), 123.2 (C_p of BPh_2), 54.5 (d, J = 2.0 Hz, PdN(*C*HMe$_2$)$_2$), 50.1 (dd, J = 56 and 13 Hz, NCH_2), 24.1 (N(CH-*Me*Me′)$_2$), 21.7 (N(CH*Me*Me′)$_2$), 20.3 (br m, *C*H_2PPh_2 and *C*$H_2P'Ph_2$); ^{31}P NMR (C_6D_6, 121 MHz) δ 31.5 (d, J = 39.3 Hz), 16.3 (d, J = 39.3 Hz). Anal. Calcd for $C_{45}H_{50}BNP_2Pd$: C, 68.93; H, 6.43; N, 1.79. Found: C, 68.66; H, 6.73; N, 1.64.

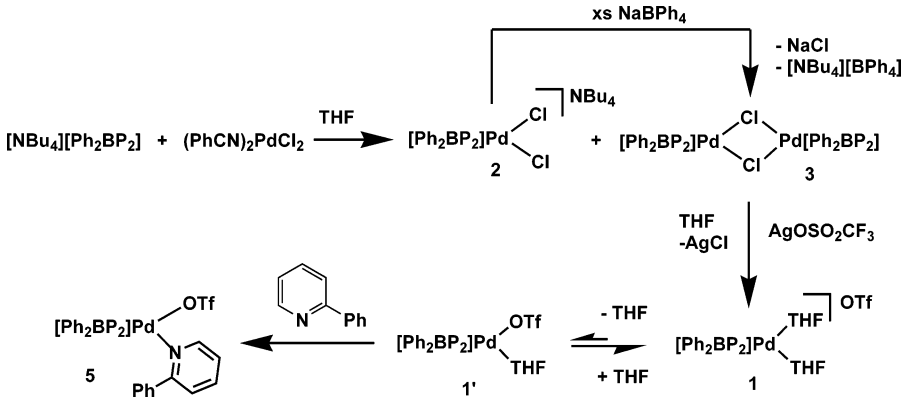
[Ph_2BP_2]Pd(N,C:η^2-N^{i}Pr$_2$CHCH$_2$CH$_3$) (12). Compound **12** was prepared with N^{i}Pr$_2$^{n}Pr using a procedure identical to that used for compound **7** (65.8 mg, 78% yield). ^{1}H NMR (C_6D_6, 500 MHz) δ 7.37−7.51 (m, 14H, aryl H), 6.96−7.19 (m, 16H, aryl H), 3.19 (m, 1H, PdNC*H*Et), 2.86 (d septet, J = 3.0 and 6.5 Hz, 1H, N(C*H*Me$_2$)C′HMe$_2$), 2.81 (septet, J = 6.5 Hz, 1H, N(CHMe$_2$)C′*H*Me$_2$), 2.19−2.38 (m, 4H, C*H*$_2PPh_2$ and C′*H*$_2P'Ph_2$), 1.28 (m, 2H, PdNCHC*H*$_2$Me), 1.00 (d, J = 6.5 Hz, 3H, N(CH*Me*$_2$)$_2$), 0.91 (d, J = 6.0 Hz, 3H, N(CH*Me*$_2$)$_2$), 0.57 (d, J = 6.5 Hz, 3H, N(CH*Me*$_2$)$_2$), 0.53 (d, J = 7.0 Hz, 3H, N(CH*Me*$_2$)$_2$), 0.47 (t, J = 7.0 Hz, 3H, PdNCHCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.1 (br, C_{ipso} and C'_{ipso} of BPh_2), 140.7 (d, J = 25.0 Hz, C_{ipso} of PPh_2), 139.1 (d, J = 28.0 Hz, C'_{ipso} of PPh_2), 138.3 (dd, J = 2.0 and 37.0 Hz, C_{ipso} of $P'Ph_2$), 138.1 (d, J = 36.2 Hz, C'_{ipso} of $P'Ph_2$), 133.5 (d, J = 12.8 Hz, C_o of PPh_2), 133.1 (C_o of BPh_2), 132.9 (d, J = 12.3 Hz, $C_{o'}$ of PPh_2), 132.7 ($C_{o'}$ of BPh_2), 132.63 (d, J = 11.1 Hz, C_o of $P'Ph_2$), 132.62 (d, J = 11.9 Hz, $C_{o'}$ of $P'Ph_2$), 128.8 (d, J = 2.3 Hz, C_p of PPh_2), 128.7 (d, J = 1.9 Hz, $C_{p'}$ of PPh_2), 128.6 (d, J = 1.5 Hz, C_p of $P'Ph_2$), 128.2 (d, J = 1.6 Hz, $C_{p'}$ of $P'Ph_2$), 128.0 (d, J = 9.3 Hz, C_m of PPh_2), 127.8−127.7 (m, $C_{m'}$ of PPh_2, C_m and $C_{m'}$ of $P'Ph_2$), 126.2 (C_m of BPh_2), 126.1 ($C_{m'}$ of BPh_2), 122.3 (C_p of BPh_2), 122.2 ($C_{p'}$ of BPh_2), 70.2 (dd, J = 14.1 and 56.5 Hz, PdN(*C*HEt)), 54.1 (N(*C*HMe$_2$)$_2$), 50.7 (N(*C'*HMe$_2$)$_2$), 26.1 (N(CH*Me*$_2$)$_2$), 26.0 (N(CH*Me'*$_2$)$_2$), 23.4 (N(C′H*Me*$_2$)$_2$), 23.1 (PdN(CH*C*H$_2$Me)), 22.0 (br q, *C*H$_2PPh_2$), 21.5 (N(C′H*Me'*$_2$)$_2$), 20.3 (br q, *C'*H_2PPh_2), 15.3 (dd, J = 7.8 and 8.5 Hz, PdN(CHCH$_2$*Me*)); ^{31}P NMR (C_6D_6, 121 MHz) δ 32.3 (d, J = 30.2 Hz), 13.7 (d, J = 30.2 Hz). Anal. Calcd for $C_{47}H_{54}BNP_2Pd$: C, 69.51; H, 6.70; N, 1.72. Found: C, 69.23; H, 6.67; N, 1.42.

[Ph_2BP_2]Pd(C(N^{t}Bu)H)(CN^{t}Bu) (13). Compound **7** (32.0 mg, 41.6 μmol) and *tert*-butylisocyanide (15 μL, 248.5 μmol) were dissolved in benzene. The reaction mixture turned bright yellow. After 1 h, all volatiles were removed in vacuo, and the residue was taken up in a benzene/petroleum ether solution. After storing at −30 °C, microcrystalline solids precipitated. The solids were collected and washed with petroleum ether and diethyl ether (27.9 mg, 80% yield). IR(CH_2Cl_2, KBr): ν(H*C*=*N*^{t}Bu) = 1608 cm^{-1}, ν(*C*≡*N*) = 2195 cm^{-1}; ^{1}H NMR (C_6D_6, 300 MHz) δ 8.75 (dd, J = 38.8 and 27.5 Hz, 1H, Pd(CN^{t}Bu)-*H*), 7.57−7.56 (m, 8H, aryl H's), 7.31 (t, J = 9.0 Hz, 4H, aryl H's), 7.21−7.08 (m, 6H, aryl H's), 6.95−6.87 (m, 12H, aryl H's), 2.28 (d, J = 14.7 Hz, 2H, C*H*$_2PPh_2$), 2.13 (d, J = 13.8 Hz, 2H, C*H'*$_2PPh_2$), 0.95 (s, 9H, Pd(CN^t*Bu*)H), 0.58 (s, 9H, Pd(CN^t*Bu*)); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 179.3 (dd, J = 8.6 and 131 Hz, Pd(*C*N^{t}Bu)H), 163.4 (v br, C_{ipso} of BPh_2), 137.4 (d, J = 35.6 Hz), 133.0 (dd, J = 10 and 25 Hz), 132.8, 132.4, 130.5, 129.0 (dd, J = 2 and 69 Hz), 127.8 (dd, J = 11 and 34 Hz), 126.7, 126.4, 123.0, 122.7, 29.9, 29.2, 19 (br m), 16 (br m); ^{31}P NMR (C_6D_6, 121 MHz) δ 23.6 (d, J = 55.8 Hz), 13.1 (d, J = 55.8 Hz). Anal. Calcd for $C_{48}H_{53}BNP_2Pd$: C, 68.87; H, 6.38; N, 3.35. Found: C, 69.19; H, 6.64; N, 3.06.

(Ph_2SiP_2)Pd(OTf)$_2$ (14). A THF solution of AgOTf (455.0 mg, 1.77 mmol) was added dropwise to a THF solution of $Ph_2Si(CH_2PPh_2)_2$-$PdCl_2$ (671.2 mg, 0.886 mmol). The reaction turned bright yellow and cloudy. The reaction mixture was filtered through Celite, and the filtrate was concentrated in vacuo to a thick yellow residue. Upon addition of petroleum ether and vigorous stirring, **14** was isolated as a yellow powder in 98% yield (854 mg). ^{1}H NMR (d_6-acetone, 300 MHz) δ 7.89 (dd, J = 7.5 and 12.9 Hz, 8H, H_o of PPh_2), 7.67 (br t, J = 7.5 Hz, 4H, H_p of PPh_2), (td, J = 2.1, 7.5 Hz, 8H, H_m of PPh_2), 7.38−7.33 (m, 6H, H_o and H_p of $SiPh_2$), 7.20 (t, J = 7.5 Hz, 4H, H_m of $SiPh_2$), 3.01 (dd, J = 6.9 and 17.0 Hz, 4H, C*H*$_2SiPh_2$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.0 (C_o of $SiPh_2$), 134.5 (m, C_o of PPh_2), 134.3 (C_p of PPh_2), 133.0 (m, C_{ipso} of PPh_2), 131.2 (C_p of $SiPh_2$), 130.4 (m, C_m of PPh_2), 129.0 (C_m of $SiPh_2$), 127.4 (d, J = 59.9 Hz, *C*F_3), 6.6 (m, *C*H_2PPh_2) (C_{ipso} of $SiPh_2$ was not clearly visible); ^{31}P NMR (d_6-acetone, 121 MHz) δ 36.4; ^{19}F NMR (d_6-acetone, 282 MHz) δ −74.3. Anal. Calcd for $C_{40}H_{34}F_6O_6P_2$-PdS_2Si: C, 48.76; H, 3.48; N, 0. Found: C, 48.36; H, 3.46; N, <0.05.

(Ph_2SiP_2)PdCl$_2$ (15). A THF solution of $PdCl_2(NCPh)_2$ (398.3 mg, 1.038 mmol) was added rapidly to a stirring THF solution of Ph_2Si-$(CH_2PPh_2)_2$ (603.0 mg, 1.038 mmol). After stirring for 1 h, the solution was filtered through Celite and dried in vacuo. The residue was washed thoroughly with Et_2O/CH_3CN and Et_2O/THF (>4:1) and dried under vacuum overnight to give a pale lime-yellow powder (768.3 mg, 89%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.62 (dd, J = 7.5 and 12.3 Hz, 8H, H_o of PPh_2), 7.39 (dd, J = 6.9 and 8.4 Hz, 4H, H_p of PPh_2), 7.34−7.25 (m, 10H, H_m of PPh_2 and H_p of $SiPh_2$), 7.12 (t, J = 7.5 Hz, 4H, H_m of

Scheme 1



$SiPh_2$), 7.20 (d, $J = 6.9$ Hz, 4H, H_o of $SiPh_2$), 2.11 (dd, $J = 5.4$ and 15.0 Hz, 4H, CH_2SiPh_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 133.8 (C_o of $SiPh_2$), 133.7 (app t, $J = 6.0$ Hz, C_o of PPh_2), 132.9 (m, C_{ipso} of PPh_2), 131.6 (C_{ipso} of $SiPh_2$), 131.5 (C_p of PPh_2), 130.2 (C_p of $SiPh_2$), 128.4 (app t, $J = 6.0$ Hz, C_m of PPh_2), 128.3 (C_m of $SiPh_2$), 9.4 (dd, $J = 13.1$ and 15.8 Hz, CH_2PPh_2); ^{31}P NMR ($CDCl_3$, 121 MHz) δ 22.66. Anal. Calcd for $C_{38}H_{34}Cl_2P_2PdSi$: C, 60.21; H, 4.52; N, 0. Found: C, 59.34; H, 4.52; N, <0.05.

[((Ph$_2$SiP$_2$)Pd)$_2$][OTf]$_2$ (16). Diisopropylethylamine (54 μL, 0.310 mmol) was added dropwise to a THF solution (8 mL) of **14** (100.5 mg, 0.102 mmol). Within 5 min the solution turned from yellow to burnt orange. The reaction was monitored by ^{31}P NMR. After 20 h all volatiles were removed in vacuo. After washing with Et_2O, the residue was redissolved in CH_3CN and filtered through Celite. Et_2O was added to the solution to precipitate orange crystalline solids. The solids were collected, washed with Et_2O/CH_3CN (9:1), and dried in vacuo to afford 59.3 mg of **16** (70% yield). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.8−7.6 (m, 8H, aryl H's), 7.4−7.0 (m, 44H, aryl H's), 6.9 (d, 8H, aryl H's), 2.6 (d, 4H, CH_2SiPh_2), 1.7 (d, 4H, $C'H_2Si'Ph_2$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 134.9 (C_p of PPh_2), 134.2−134.1 (m, C_o of PPh_2 and C_p of $P'Ph_2$), 133.3 (d, $J = 11$ Hz, C_m of PPh_2), 133.1 (m, C_{ipso} of PPh_2), 131.5 (C_{ipso} of $SiPh_2$), 130.6 (d, $J = 11$ Hz, C_m of $P'Ph_2$), 129.9 (C_p of $SiPh_2$), 129.3 (m, C_{ipso} of $P'Ph_2$), 128.8 (m, C_o of $P'Ph_2$), 128.3 (C_m of $SiPh_2$), 108.0 (br m, CF_3), 13.8 (CH_2SiPh_2), 12.5 ($C'H_2SiPh_2$); ^{19}F NMR ($CDCl_3$, 282 MHz) δ −74.7; ^{31}P NMR ($CDCl_3$, 121 MHz) δ 22.2 (d, $J = 50$ Hz), −0.2 (d, $J = 50$ Hz). Anal. Calcd for $C_{78}H_{68}F_6O_6P_4Pd_2S_2Si_2$: C, 56.02; H, 4.10; N, 0. Found: C, 55.93; H, 3.83; N, <0.05.

[(Ph$_2$SiP$_2$)Pd(2-phenylpyridine)OTf][OTf]. *o*-Phenylpyridine was added dropwise to a THF solution of **14**. This compound was generated in situ for the purpose of this experiment and has not been isolated in crystalline form. ^{31}P NMR (THF, 121 MHz) δ 37.1 (d, $J = 14.5$ Hz), 22.8 (d, $J = 14.5$ Hz); ^{19}F NMR (THF, 282 MHz) δ −75.3, −75.9.

Standard Kinetic Protocol: Measurement of Reaction Rates. Complex **1** (30.0 mg, 31.2 μmol) was dissolved in 0.6 mL of THF, transferred to a J-Young NMR tube, and chilled inside a glovebox cold-well below −50 °C. Diisopropylethylamine (109 μL, 626 μmol) was then added to the cold solution. The tube was inserted into an NMR probe at 23 °C, and the temperature was allowed to equilibrate for 10 min. The decay of complex **1** was monitored by $^{31}P\{^1H\}$ NMR spectroscopy against an internal integration standard, which consisted of a sealed capillary tube containing a 1.6 M solution of $Ph_3P{=}O$ in CH_2Cl_2. Spectra were taken at intervals of ca. 3 min for ca. 3.5 half-lives. Besides the integral standard, the only observable peaks were due to **1** and the palladacycle **6**. The data were satisfactorily fit to an exponential decay, and the first-order rate constant was obtained from the ln(**1**) versus time plot. The reaction was carried out in triplicate, giving $k_{obs} = 5.63$, 5.49, and 5.76×10^{-4} s^{-1}. This protocol was also used in determining KIE data, measuring the rate dependence on amine concentration and generating the Eyring plot.

KIE Studies. $N^iPr_2CD_2CH_3$ was prepared by reducing the amide $N^iPr_2C(O)CH_3$ with $LiAlD_4$ under standard conditions.[17] The amine was extracted with petroleum ether and filtered through a silica plug to give spectroscopically pure $N^iPr_2CD_2CH_3$. The reaction was carried out in triplicate, giving $k_{obs} = 9.36$, 9.65, and 10.57×10^{-5} s^{-1}.

Rate Dependence on Amine Concentration. Seven kinetic runs were conducted in which the concentration of N^iPr_2Et was varied from 0.16 to 1.56 M (3 to 30 equiv relative to **1**). The total volume of the samples was kept constant at 0.6 mL. The following values for k_{obs} ($\times 10^{-4}$ s^{-1}) were obtained: 1.21 (3 equiv of amine), 1.80 (5 equiv of amine), 3.03 (10 equiv of amine), 4.43 (15 equiv of amine), 5.49 (20 equiv of amine), 6.96 (25 equiv of amine), and 8.41 (30 equiv of amine).

Activation Parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) for the Overall Amine Activation. A series of reactions was conducted over a 35 °C temperature range (0− 35.3 °C). The NMR probe temperatures were measured using an anhydrous MeOH standard. The following values for $k_{obs}[THF]_i^2/[N^iPr_2Et]_i$ ($\times 10^{-2}$ s^{-1}) were obtained: 0.37 (0.0 °C), 0.94 (7.5 °C), 1.76 (13.3 °C), 1.82 (13.3 °C), 2.81 (17.1 °C), 5.41 (23.1 °C), 9.16 (28.4 °C), and 18.41 (35.3 °C). The data provided a satisfactory linear fit in the Eyring plot, from which the activation parameters were calculated, $\Delta H^{\ddagger} = 17.9 \pm 0.2$ kcal/mol, $\Delta S^{\ddagger} = -4 \pm 1$ eu. Regression analyses of the data were performed using Microsoft Excel, and the activation parameters are reported with 95% confidence.

VT-NMR Studies. Complex **1** (20.0 mg, 20.8 μmol) was dissolved in 0.6 mL of toluene-d_8, transferred to a J-Young NMR tube, and chilled inside a glovebox cold-well. Triethylamine (145 μL, 1.04 mmol) was then added to the cold solution. The tube was inserted into an NMR probe at −50 °C. As the temperature was slowly raised to 0 °C, the reaction was monitored by ^1H and ^{31}P NMR spectroscopy. Conversion to the palladacycle **7** was relatively clean (~80% crude yield by ^{31}P NMR spectroscopy).

Results

Synthesis and Structural Characterization of [[Ph$_2$BP$_2$]-Pd(THF)$_2$][OTf] (1) and [Ph$_2$BP$_2$]Pd(THF)(OTf) (1′). A reactive $[Ph_2BP_2]Pd(II)$ system was required to carry out the C−H bond activation studies described herein. A labile triflate derivative, $[Ph_2BP_2]Pd(OTf)(L)$, was targeted, and the following protocol (Scheme 1) afforded the species of interest. Mixing $[Ph_2BP_2][NBu_4]$ and $PdCl_2(NCPh)_2$ in THF afforded a mixture of two products, $[[Ph_2BP_2]PdCl_2][NBu_4]$ (**2**) and $\{[Ph_2BP_2]Pd(\mu\text{-}Cl)\}_2$ (**3**). The mixture of **2** and **3** was converted completely to $\{[Ph_2BP_2]Pd(\mu\text{-}Cl)\}_2$ (**3**) by addition of a slight excess of $NaBPh_4$ to the reaction mixture (Scheme 1). Crystals of **3** were grown from THF/CH_2Cl_2 solutions at −30 °C in 73% overall yield (based upon $PdCl_2(NCPh)_2$). Dimeric **3** was then converted to the more reactive species, $[[Ph_2BP_2]Pd(THF)_2][OTf]$ (**1**), by

(17) March, J. *Advanced Organic Chemistry—Reactions, Mechanisms, and Structure*; John Wiley & Sons: New York, 1992; p 448.

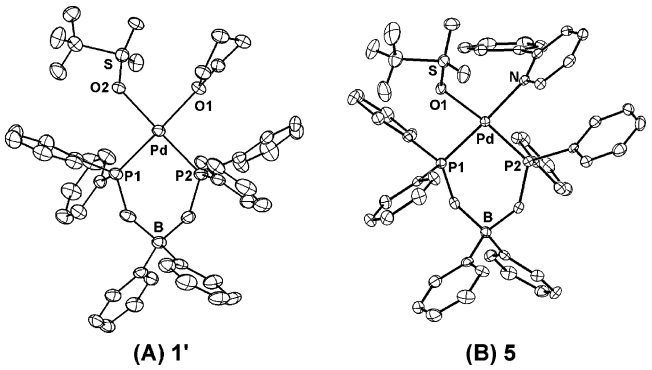
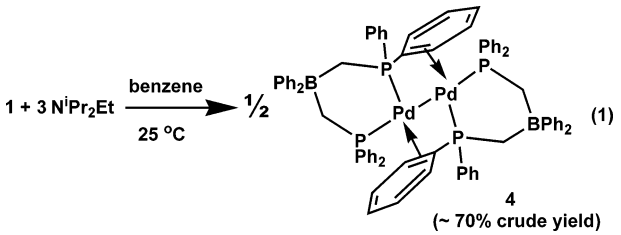


Figure 2. (A) Displacement ellipsoid representation (50%) of complex **1′**. Selected bond distances (Å) and angles (deg): Pd−O1, 2.157(2); Pd−O2, 2.155(2); Pd−P1, 2.2378(8); Pd−P2, 2.2309(9); O1−Pd−O2, 86.52(7); P1−Pd−P2, 89.16(3); O1−Pd−P2, 92.33(6); O2−Pd−P1, 91.90(5). (B) Displacement ellipsoid representation (50%) of complex **5**. Selected bond distances (Å) and angles (deg): Pd−O1, 2.195(2); Pd−N, 2.139(3); Pd−P1, 2.2718(9); Pd−P2, 2.2503(9); O1−Pd−N, 89.85(9); P1−Pd−P2, 88.43(3), O1−Pd−P1, 88.00(6); N−Pd−P2, 93.87(7). Hydrogen atoms and solvent molecules were omitted for clarity.

addition of AgOTf in THF. As indicated by its formula, complex **1** exists in THF solution predominantly as a bis(solvento) cation, which is consistent with the following: (a) a single resonance (s, δ = 48.2 ppm) at 23 °C in the ^{31}P NMR spectrum, (b) integrations consistent with 2 equiv of THF in the ^{1}H NMR spectrum, and (c) combustion analysis data. Nonetheless, an X-ray diffraction analysis of a single-crystal grown from a purified sample in THF at −30 °C revealed a zwitterionic, mono-THF adduct, ([Ph_2BP_2]Pd(THF)(OTf)) (**1′**) (Scheme 1, Figure 2A), and an unbound THF molecule. The THF coligands of **1** are appreciably labile and in rapid exchange with the competitive triflate ligand. This exchange process, **1** ⇌ **1′** + THF, was observed by ^{31}P VT-NMR spectroscopy in CD_2Cl_2 solution. A broad signal is evident at 47 ppm, indicative of fluxional behavior at ambient temperature. Upon cooling the sample to −85 °C, two signals become fully resolved with a peak separation of 916 Hz. These peaks coalesce at −42.3 °C, and a barrier of 16.2 kcal/mol can be calculated for the THF and triflate exchange at −42.3 °C.[18]

The crystal structure of **1′** shows an essentially square planar complex with bond angles that deviate only slightly from their ideal values. The O(1)−Pd−O(2) and O(1)−Pd−P(2) bond angles are 86.52(7)° and 92.33(6)°, respectively. The Pd−O bond distances for each of the oxygen donors are identical (2.157(2) and 2.155(2) Å for the THF and triflato donors, respectively). Complex **1′** has few structurally authenticated congeners in the palladium literature. The most comparable structures are those of the complexes [(dppp)Pd(H_2O)(X)][X] (where X = OTf and OTs) reported separately by Stang and Toniolo.[19] The Pd−O bond distances in **1′**, and also its Pd−P bond distances (2.2378(8) and 2.2309(9) Å), compare favorably with these examples.

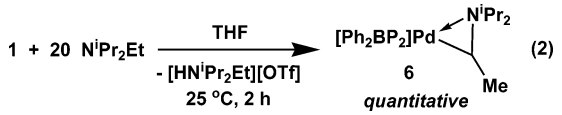
Reactivity of 1 with Arene Substrates. The possibility for complex **1** to mediate aryl C−H bond activation was briefly examined by dissolving **1** in benzene solution in the presence of the sterically encumbered amine base N^{i}Pr$_2$Et. Our lab had observed phenyl transfer from benzene to a platinum(II) triflate complex in the presence of N^{i}Pr$_2$Et, which served as a formal H^+ acceptor to produce [HN^{i}Pr$_2$Et][OTf].[20] In the present case, adding an excess of N^{i}Pr$_2$Et to a benzene solution of **1** at 25 °C indeed generated a stoichiometric equivalent of [HN^{i}Pr$_2$Et][OTf]. However, the major palladium-containing species generated (>70% of the mixture by ^{31}P NMR spectroscopy) was the previously reported palladium(I) dimer, {[Ph_2BP_2]Pd}$_2$ (**4**, eq 1).[21] A second diamagnetic species was also evident (^{31}P NMR), but none of the anticipated aryl transfer product, [Ph_2BP_2]Pd(Ph)(THF), was detected.[22] Several observations from the literature suggest that [Ph_2BP_2]Pd(Ph)(THF) may be unstable. For example, it is known that biphenyl and other biaryls can be liberated from palladium(II) aryl species.[23] Biphenyl has also been derived directly from a benzene C−H activation process mediated by palladium(II).[24] Related aryl coupling processes are known for phosphine-supported platinum(II) systems.[25,7b] In the present [Ph_2BP_2]Pd(II) system, however, benzene-derived biphenyl could not be identified (^{1}H NMR, GC−MS).



To further explore whether **1** might activate aryl C−H bonds, *o*-phenylpyridine was tested as a substrate, our explanation being that a favorable chelate stabilization might encourage metalation of the arene ring. Several platinum(II) and palladium(II) halide and pseudo-halide precursors are known to react with *o*-phenylpyridine in the presence of a sacrificial base to produce cyclometalated products.[26] Exposure of **1** to either stoichiometric or excess *o*-phenylpyridine afforded a single product, the adduct complex [Ph_2BP_2]Pd(*o*-phenylpyridine)(OTf) (**5**), which was verified by X-ray crystallography. Complex **5** is quite hindered, as can be gleaned from its solid-state crystal structure (Figure 2B). At room temperature in solution, its ^{1}H NMR resonances are broad, presumably due to hindered rotation about the Pd−N bond. These peaks sharpen upon cooling to −40 °C, and the expected four resonances for the ligand methylene protons become well resolved. Relative to **1′**, the Pd−OTf interaction of **5** is modestly elongated (2.195(2) versus 2.155(2) Å), also true of the Pd−P bond distances (2.25−2.27 versus 2.23−2.34 Å). These relative bond lengths reflect the steric congestion suffered by **5**, which nonetheless is unexpectedly robust. For example, no reaction occurred when **5** was incubated in THF at 80 °C in the presence of either excess *o*-phenylpyridine or excess K_2CO_3.

(18) Gasparro, F. P.; Kolodny, N. H. *J. Chem. Educ.* **1977**, *54*, 258−261.
(19) (a) Stang, P. J.; Cao, D. H.; Poulter, G. T.; Arif, A. M. *Organometallics* **1995**, *14*, 1110−1114. (b) Benetollo, F.; Bertani, R.; Bombieri, G.; Toniolo, L. *Inorg. Chim. Acta* **1995**, *233*, 5−9.
(20) Harkins, S. B.; Peters, J. C. *Organometallics* **2002**, *21*, 1753−1755.
(21) Lu, C. C.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 5272−5273.
(22) We note that [Ph_2BP_2]Pd(Ph)(CH_3CN) can be generated in solution and spectroscopically identified by reaction of {[Ph_2BP_2]Pd(μ-Cl)}$_2$ with PhMgBr in the presence of acetonitrile.
(23) Yagyu, T.; Hamada, M.; Osakada, K.; Yamamoto, T. *Organometallics* **2001**, *20*, 1087−1101.
(24) Ackerman, L. J.; Sadighi, J. P.; Kurtz, D. M.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2003**, *22*, 3884−3890.
(25) Konze, W. V.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **2002**, *124*, 12550−12556.
(26) (a) Constable, E. C.; Thompson, A. M. W. C.; Leese, T. A.; Reese, D. G. F.; Tocher, D. A. *Inorg. Chim. Acta* **1991**, *182*, 93−100. (b) Wong-Foy, A. G.; Henling, L. M.; Day, M.; Labinger, J. A.; Bercaw, J. E. *J. Mol. Catal. A: Chem.* **2002**, *189*, 3−16.

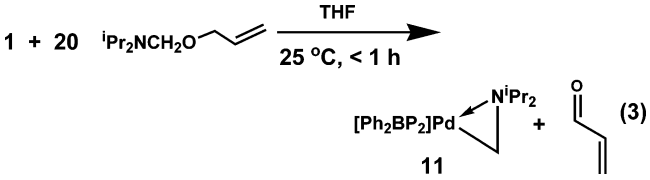
Activation of Trialkylamines by Complex 1. Treating **1** with 20 equiv of N^iPr_2Et in THF solution at ambient temperature resulted in the gradual consumption of starting material and the rise of a single new palladium product, along with a stoichiometric equivalent of $[HN^iPr_2Et][OTf]$. The new palladium species exhibited resonances in the ^{31}P NMR spectrum that compared well to a minor product that was observed when **1** was exposed to N^iPr_2Et in benzene solution (vide supra). Single crystals of this species were grown from a THF/petroleum ether solution, and an X-ray diffraction study revealed it to be the three-membered palladacycle $[Ph_2BP_2]Pd(N,C:\eta^2\text{-}N^iPr_2CHCH_3)$ (**6**, eq 2). This formulation is consistent with the complex's spectral data in solution. For example, the $^{13}C\{^1H\}$ NMR spectrum features a signature resonance at 62.6 ppm (dd, $^2J_{C-Pcis} = 13.8$ Hz, $^2J_{C-Ptrans} = 56.7$ Hz) due to the coupling of an organometallic carbon atom to two nonequivalent phosphorus nuclei.



The scope and selectivity of the amine activation process was explored (Scheme 2). In general, the activation process was found to proceed for trialkylamine substrates that feature secondary C−H bonds adjacent to the N atom. Palladacycle products that feature three-membered rings appear to be formed exclusively, with no apparent tendency to form larger metallacycles. To test the reaction's selectivity, the amine NCy_2Et was chosen as a substrate as it contains both tertiary and secondary C−H bonds that can undergo activation. Treatment of **1** with excess NCy_2Et in THF resulted in clean conversion to only one palladacycle, $[Ph_2BP_2]Pd(N,C:\eta^2\text{-}NCy_2CHMe)$ (**8**), derived from formal cleavage of a secondary C−H bond of the ethyl group. The substrates *N*-methylpyrrolidene and *N*-methylpiperidene were also examined to compare the reactivity of primary versus secondary C−H bonds. Again, activation at the secondary C−H position occurred exclusively, affording the bicyclic palladacycles $[Ph_2BP_2]Pd(N,C:\eta^2\text{-}NMeCH(CH_2)_3)$ (**9**) and $[Ph_2BP_2]Pd(N,C:\eta^2\text{-}NMeCH(CH_2)_4)$ (**10**), respectively.

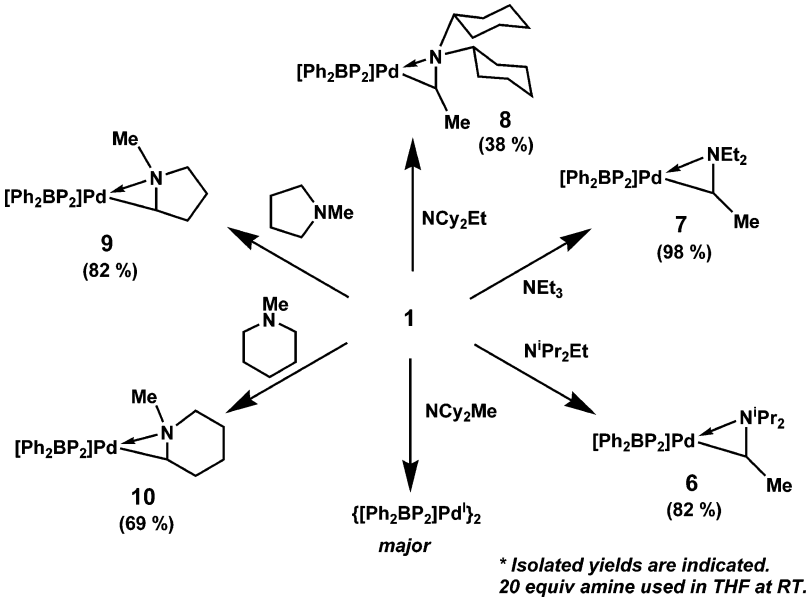
To induce reactivity of primary C−H bonds, the reactivity of **1** with NCy_2Me and N^iPr_2Me was examined. A steric bias might in these cases be expected to direct the palladium center toward the methyl position. However, the predominant byproduct (70−80%) for these substrates was the familiar palladium(I) dimer, $\{[Ph_2BP_2]Pd\}_2$ (**4**) (^{31}P NMR).

Addition of diisopropyl(2-propenyloxymethyl)amine to **1** effected formal C−O rather than C−H bond cleavage to generate $[Ph_2BP_2]Pd(N,C:\eta^2\text{-}N^iPr_2CH_2)$ (**11**, eq 3) in good yield. Allyl ethers are known to react with Pd(0) sources to generate palladium allyl products via formal C−O cleavage.[27] The high-yield isolation of **11** shows quite clearly that $[Ph_2BP_2]Pd(N,C:\eta^2\text{-}NR_2CH_2)$ are viable products of amine activation, and it is therefore puzzling that a similar product is not formed when **1** is treated with N^iPr_2Me (vide infra). To determine the fate of the allyl ether group, an NMR-scale reaction was monitored in THF-d_8 with 3 equiv of diisopropyl(2-propenyloxymethyl)amine. A ^1H NMR spectrum of the crude product mixture suggested the presence of an aldehyde byproduct which could be isolated by vacuum transfer and clearly identified as acrolein by comparison of its ^1H NMR spectrum to that of an authentic sample.



Molecular Structures of the Palladacycles 8 and 9. X-ray diffraction studies of the palladacycles were pursued to gain insight into the structural nature of the Pd−N−C core. Crystals of **6** and **11** suffered from disorder of the iminium group, $R_2C{=}N^iPr_2$, which sits in two orientations. Derivatives **8** and **9** provided more reliable structural parameters (Figure 3, Table 1). In each structure the bond angles around palladium are largely distorted from 90°, though all four atoms coordinated to palladium lie in a well-defined plane. Specifically, for **8** and **9**, the N−Pd−C_α angles are acute (39.7(1)° and 38.3(2)°,

Scheme 2



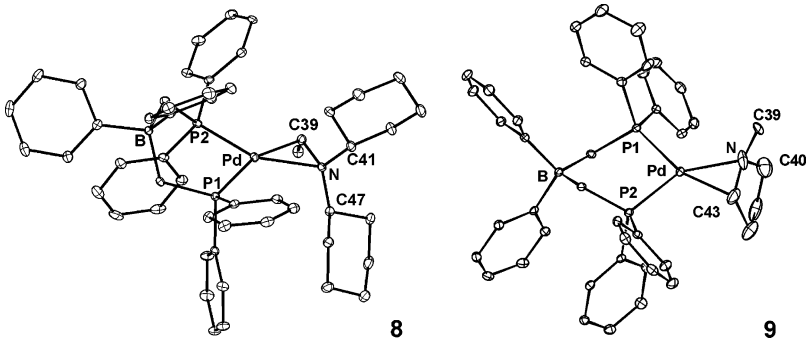


Figure 3. Displacement ellipsoid representations (50%) of $[Ph_2BP_2]Pd(N,C:\eta^2\text{-}NCy_2CHMe)$ (**8**) and $[Ph_2BP_2]Pd(N,C:\eta^2\text{-}NMeCH(CH_2)_3)$ (**9**). Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (°) for Complexes **8** and **9**

complex **8**		complex **9**	
Pd−C(39)	2.037(3)	Pd−C(43)	2.048(4)
Pd−N	2.180(3)	Pd−N	2.104(3)
Pd−P(1)	2.3641(9)	Pd−P(1)	2.3354(8)
Pd−P(2)	2.2549(9)	Pd−P(2)	2.2945(8)
N−C(39)	1.438(4)	N−C(43)	1.361(5)
N−C(41)	1.502(4)	N−C(39)	1.460(5)
N−C(47)	1.484(4)	N−C(40)	1.420(6)
P(1)−Pd−P(2)	93.60(3)	P(1)−Pd−(2)	93.49(3)
P(1)−Pd−N	122.31(7)	P(1)−Pd−N	120.9(1)
P(2)−Pd−C(39)	104.04(9)	P(2)−Pd−C(43)	107.6(2)
N−Pd−C(39)	39.7(1)	N−Pd−C(43)	38.3(2)
C(39)−N−C(41)	115.8(3)	C(43)−N−C(39)	117.4(4)
C(39)−N−C(47)	117.9(3)	C(43)−N−C(40)	108.0(4)
C(41)−N−C(47)	119.3(2)	C(39)−N−C(40)	117.0(4)

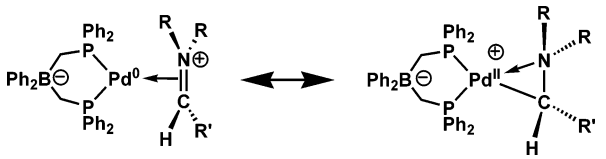


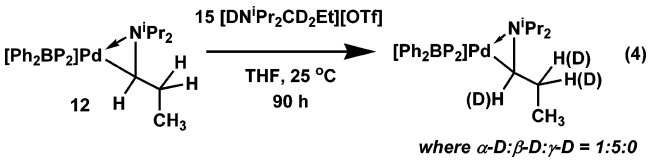
Figure 4. Limiting resonance forms for the palladacycles.

respectively) and the P(1)−Pd−N angles (122.3° and 120.9°) are significantly larger than the P(2)−Pd−C_α angles (104.0° and 107.6°).

Palladacycles akin to **8** and **9** have not to our knowledge been described. However, metallaaziridines featuring other transition metals are well established, though they are formed from different methods of preparation.[28] For example, a family of nickel aziridines $(PR_3)(X)Ni(N,C:\eta^2\text{-}CH_2NMe_2)$ that are structurally related to the palladacycles described here were first reported nearly three decades ago.[28d] Two limiting resonance forms are to be considered with respect to the Pd−N−C core (Figure 4).[28a,d] The first emphasizes a Pd(0) form of the complex with an anionic $\{[Ph_2BP_2]Pd\}^-$ fragment coordinated by an iminium cation ($RHC{=}NR_2^+$). This formulation is analogous to the many olefin complexes of palladium(0) that are known. The other limiting resonance form assigns the alkylamine functionality as a three-electron LX-type organometallic ligand. In this latter view a palladium(II) center is formally coordinated to an alkyl ligand with a β-amine donor occupying the fourth site.

Close examination of the structural parameters of **8** and **9** does not unambiguously distinguish between the two resonance forms. The Pd−C_α distances observed for **8** and **9** are unusually short for *cis*-bis(phosphine)Pd complexes. Their respective distances of 2.037(3) and 2.048(4) Å are just below both the minimum Pd−C(sp^3) and Pd−C(sp^2-alkene) bond distances reported for palladium supported by two phosphines in cis relation. The N−C_α bond lengths for complexes **8** and **9** are between those of free iminium cations (ca. 1.32 Å) and N−C single bonds (ca. 1.50 Å) but are also quite different from one another (1.438(4) Å for **8** and 1.361(5) Å for **9**). The latter N−C bond distance is the shortest thus far reported for mononuclear metallaaziridines of related structure (range 1.392−1.548 Å, mean of 1.440 Å, SD = 0.03 Å, Cambridge Structural Database[29]). The bond angles around the nitrogen atom are nearly 120° for complex **8**,[30] suggesting the nitrogen atom is perhaps better formulated as sp^2- rather than sp^3-hybridized.

Probing the Reversibility of Palladacycle Formation. To probe whether the formation of the palladacycles $[Ph_2BP_2]Pd(N,C:\eta^2\text{-}NR_2CHR')$ might be reversible, we examined whether deuterium would scramble into the palladacycle aliphatic positions upon incubation in the presence of a deuterated ammonium salt. Exposure of **1** to $^iPr_2NCH_2CH_2CH_3$ proceeded in similar fashion to provide the expected palladacycle $[Ph_2BP_2]Pd(N,C:\eta^2\text{-}^iPr_2NCHCH_2CH_3)$ (**12**). A homogeneous solution of complex **12** and 15 equiv of $[DN^iPr_2CD_2Et][OTf]$ was stirred at 25 °C for several days. Complex **12** was stable under these conditions: no degradation was evident in the ^{31}P NMR spectrum of the reaction solution. Upon examination of the ^2H NMR spectrum, however, it was evident that deuterium had scrambled into the α- and β-carbon positions of the iminium ligand in an approximate ratio of 1:5, respectively (eq 4).



In a related experiment we examined whether iminium ligand substitution would proceed in the presence of an ammonium

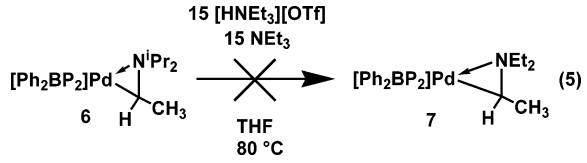
(27) See: Yamamoto, T.; Akimoto, M.; Saito, O.; Yamamoto, A. *Organometallics* **1986**, *5*, 1559−1567 and references therein.

(28) For pertinent examples, see: (a) Crawford, S. S.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 3201−3207. (b) Matsumoto, M.; Nakatsu, K.; Tani, K.; Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1974**, *96*, 6777−6778. (c) Abel, E. W.; Rowley, R. J.; Mason, R.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1974**, 72. (d) Sepelak, D. J.; Pierpont, C. G.; Barefield, E. K.; Budz, J. T.; Poffenberger, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 6178−6185.

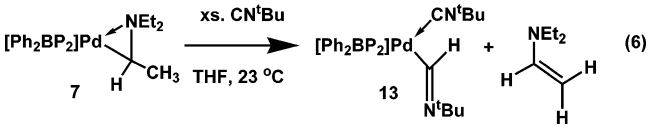
(29) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380−388.

(30) For complex **9**, the bond angles around nitrogen are also near 120° with the exception of the pyrrolidene ring angle, which is restrained by the ring.

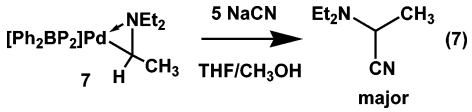
salt and a trialkylamine. The palladacycle $[Ph_2BP_2]Pd(N,C:\eta^2\text{-}N^iPr_2CHCH_3)$ **6** was incubated with 15 equiv of $[HNEt_3][OTf]$ and 15 equiv of NEt_3 in THF at 80 °C. Under these conditions, none of the palladacycle $[Ph_2BP_2]Pd(N,C:\eta^2\text{-}NEt_2CHCH_3)$ **7** could be detected after several days (eq 5). If **6** could undergo protonation to produce $[Ph_2BP_2]Pd(N^iPr_2Et_2)(OTf)$ at some reasonable rate, then we would expect a detectable degree of exchange to occur (i.e., $[Ph_2BP_2]Pd(N^iPr_2Et)(OTf) + NEt_3 \rightarrow [Ph_2BP_2]Pd(NEt_3)(OTf) + N^iPr_2Et$).



Addition of *tert*-Butyl Isocyanide and Sodium Cyanide to $[Ph_2BP_2]Pd(N,C:\eta^2\text{-}NEt_2CHCH_3)$ (7). The addition of excess *tert*-butyl isocyanide to **7** resulted in a single new palladium complex, $[Ph_2BP_2]Pd(C(H)=N^tBu)(CN^tBu)$ (**13**), and concomitant expulsion of the enamine $Et_2NC(H)=CH_2$ (eq 6). Complex **13** is characterized by two intense vibrations in its infrared spectrum ($\nu(HC=N^tBu) = 1608\ cm^{-1}$, $\nu(C\equiv N^tBu) = 2195\ cm^{-1}$; CH_2Cl_2/KBr) and a signature ^1H NMR resonance at 8.75 ppm for the iminoformyl proton $Pd(C(H)=N^tBu)$.[31] The release of the enamine $Et_2NC(H)=CH_2$ was confirmed by comparing the crude reaction spectrum with that of an independently prepared sample.



Addition of cyanide anion to **7** effected the release of the iminium ligand as a functionalized amine product via generation of a new C−C bond at the α position (eq 7). Treatment of **7** with 5 equiv of NaCN in methanol/THF produced $Et_2NCH(CN)CH_3$, confirmed by GC-MS and ^1H NMR analysis following workup. A ^1H NMR spectrum of the reaction solution immediately following the addition in CD_3OD/THF-d_8 established that the consumption of **7** is very rapid at room temperature and that the $Et_2NCH(CN)CH_3$ byproduct is released quantitatively. The palladium product(s) of the reaction have not been identified.



Kinetic Data. The decay of complex **1** (0.044 M) in the presence of 20 equiv of N^iPr_2Et was monitored by ^{31}P NMR spectroscopy and exhibited clean first-order decay in THF at 23 °C. The reaction rate was conveniently determined by integrating the ^{31}P NMR resonance of complex **1** versus an internal standard of $Ph_3P=O$, sealed as a CH_2Cl_2 solution within a capillary tube. During the reaction course the starting material

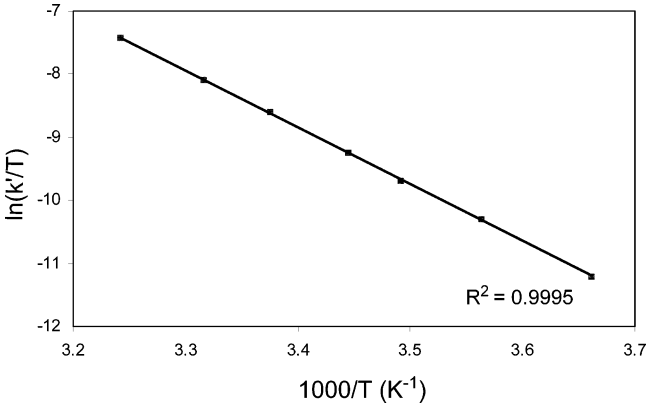


Figure 5. Eyring plot for the reaction of **1** with 20-fold N^iPr_2Et from 273.2 to 308.5 K, $\Delta H^‡ = 17.9 \pm 0.2$ kcal/mol, $\Delta S^‡ = -4 \pm 1$ eu, $\Delta G^‡ = 19.0 \pm 0.3$ kcal/mol at 23.1 °C.

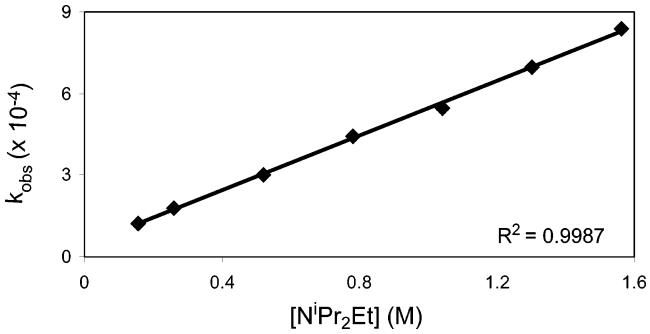


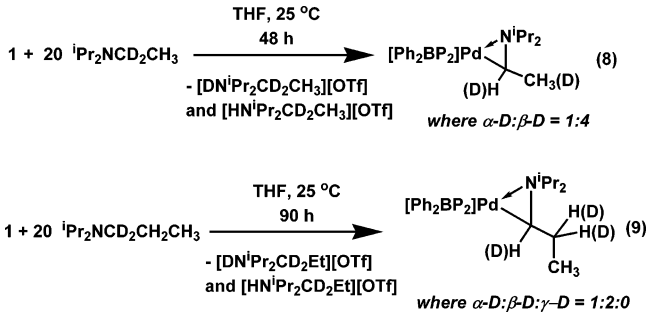
Figure 6. Rate dependence on $[N^iPr_2Et]$. Reaction conditions: $[\mathbf{1}] = 0.052$ M; $[N^iPr_2Et]$ is varied between 0.16 and 1.56 M at 296 K in THF (0.6 mL total solution volume).

1 and the product **6** were the only two species observed. The rate constant, $k_{obs} = 5.6(1) \times 10^{-4}\ s^{-1}$, was obtained as the average of three independent runs, and $\Delta G^‡$ was calculated to be 19.0 ± 0.3 kcal/mol at 23.1 °C. Perhaps a more meaningful constant is k', where $k_{obs} = k'[N^iPr_2Et]/[THF]^2$ (vide infra). By assuming constant concentrations of N^iPr_2Et and THF, a value of $k' = 5.6(1) \times 10^{-2}\ s^{-1}$ is obtained ($[N^iPr_2Et]_i = 0.88$ M and $[THF]_i = 9.33$ M). The temperature dependence of the reaction rate was explored between 0 and 35.3 °C. An Eyring plot of these data is provided in Figure 5, from which the activation parameters $\Delta H^‡ = 17.9 \pm 0.2$ kcal/mol and $\Delta S^‡ = -4 \pm 1$ eu can be extrapolated. The effect of the amine concentration $[N^iPr_2Et]$ on the reaction rate was also examined by monitoring the rate of decay of **1** in the presence of 3−30 equiv of N^iPr_2Et at 23 °C in THF. The rate data for consumption of **1** versus $[N^iPr_2Et]$ are plotted in Figure 6 and indicate a rate that is first order in $[N^iPr_2Et]$.

The relative rate of the reaction between **1** (0.044 M) and the substrate N^iPr_2Et or $N^iPr_2CD_2Me$ (0.88 M) was examined in THF. A dramatic attenuation in rate was observed for the deuterated amine substrate ($k_{obs} = 9.9(6) \times 10^{-5}\ s^{-1}$), providing a kinetic deuterium isotope effect (KDIE), $k_{rel}(k_H/k_D)$, of 5.9. For the case of $N^iPr_2CD_2Me$, a small amount of an intermediate species was detected in the ^{31}P NMR spectrum. This species featured a pair of doublets at 28.5 and 39.4 ppm with $^2J_{PP} = 62$ Hz and can be tentatively assigned as the amine adduct complex, $[Ph_2BP_2]Pd(N^iPr_2CD_2Me)(OTf)$, based upon the similarity of its chemical shift to $[Ph_2BP_2]Pd(o\text{-phenylpyridine})(OTf)$ (**5**). We presume that $[Ph_2BP_2]Pd(N^iPr_2CD_2Me)(OTf)$ accumulates due to the attenuated C−D activation rate.

(31) (a) Ciriano, M.; Green, M.; Gregson, D.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1979**, *8*, 1294−1300. (b) Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 917−927. (c) Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1994**, *13*, 441−450.

Inspection of the ^1H and ^2H NMR spectra of the reaction between **1** and $N^iPr_2CD_2Me$ after the complete consumption of **1** revealed that the palladacycle product **6** contained deuterium at the α- and β-carbon positions in a nearly statistical ratio of 1:4 (eq 8). The ammonium salt byproducts, $[DN^iPr_2CD_2CH_3]^+$ and $[HN^iPr_2CD_2CH_3]^+$, showed no evidence for deuterium scrambling into the β-carbon position. The extent of deuterium scrambling into the alkyl chain was next investigated using the *N*-propylamine substrate $^iPr_2NCD_2CH_2CH_3$. In this case deuterium incorporation occurred only at the α- and β-carbon positions and in a statistical ratio of 1:2. No scrambling into the γ-carbon position was detected (eq 9).



Observation of Intermediates by NMR Spectroscopy Using NEt_3 in Toluene. Intermediates during the amine activation reaction were difficult to study because of their low concentrations in THF. Unfortunately, THF is the only solvent that mediates the quantitative conversion of **1** and amine to the corresponding palladacycle product. A reasonable compromise was found by studying the activation reaction at low temperature in toluene. Recall that in benzene or toluene the treatment of **1** with N^iPr_2Et (or NEt_3) at room temperature generates $\{[Ph_2BP_2]Pd\}_2$ (**4**) as the major product and only a small amount of the palladacycle **6** (or **7**). At low temperature (toluene, −35 to 0 °C), however, the palladacycle products dominate. The case of NEt_3 was examined in detail because of its slightly simplified ^1H NMR spectrum in the aliphatic region. A toluene-d_8 solution of **1** in the presence of 50 equiv of NEt_3 was examined from −50 to 0 °C by both ^1H and ^{31}P NMR spectroscopy (see Figure 7). In the low-temperature regime (−50 °C), two broad resonances are observed in the ^{31}P NMR spectrum (42.7 ppm, 45.2 ppm) due to slow exchange between **1** and **1′**. As noted previously, a similar spectrum is observed for **1** in CD_2Cl_2 at −50 °C in the absence of amine. At −35 °C the two signals have coalesced into a single resonance that is centered at 45 ppm, indicating that **1** and **1′** are in fast exchange. As the sample is further warmed to −20 °C, precursor **1** decays and four new doublets arise that represent two independent species. The more downfield pair of doublets (45.0 and 29.5 ppm, $J_{PP} = 25.9$ Hz) is relatively similar in chemical shift to the resonances observed for the *o*-phenylpyridine adduct complex **5** (46.3 and 35.3 ppm). By analogy, this intermediate is proposed to be the amine adduct complex $[Ph_2BP_2]Pd(NEt_3)(OTf)$. An alternative and perhaps equally reasonable formulation for this intermediate would be to suggest that an agostic C−H bond from the amine ligand fills the fourth site and that the triflate anion is outer sphere. However, examination of the ^1H NMR spectrum between −60 and −20 °C provided no evidence for an agostic C−H proton.

The other pair of doublets (32.5 and 18.0 ppm, $^2J_{PP} = 36.0$ Hz), which corresponds to another intermediate, is more complex in the proton-coupled ^{31}P NMR spectrum (Figure 7, inset a). The doublet centered at 18 ppm splits into a doublet of doublets with a rather large secondary coupling constant of ∼200 Hz. The ^1H NMR spectrum shows a doublet of doublets centered at −8.62 ppm ($^3J_{HP}$ (*cis*) = 30.5 Hz and $^3J_{HP}$ (*trans*)

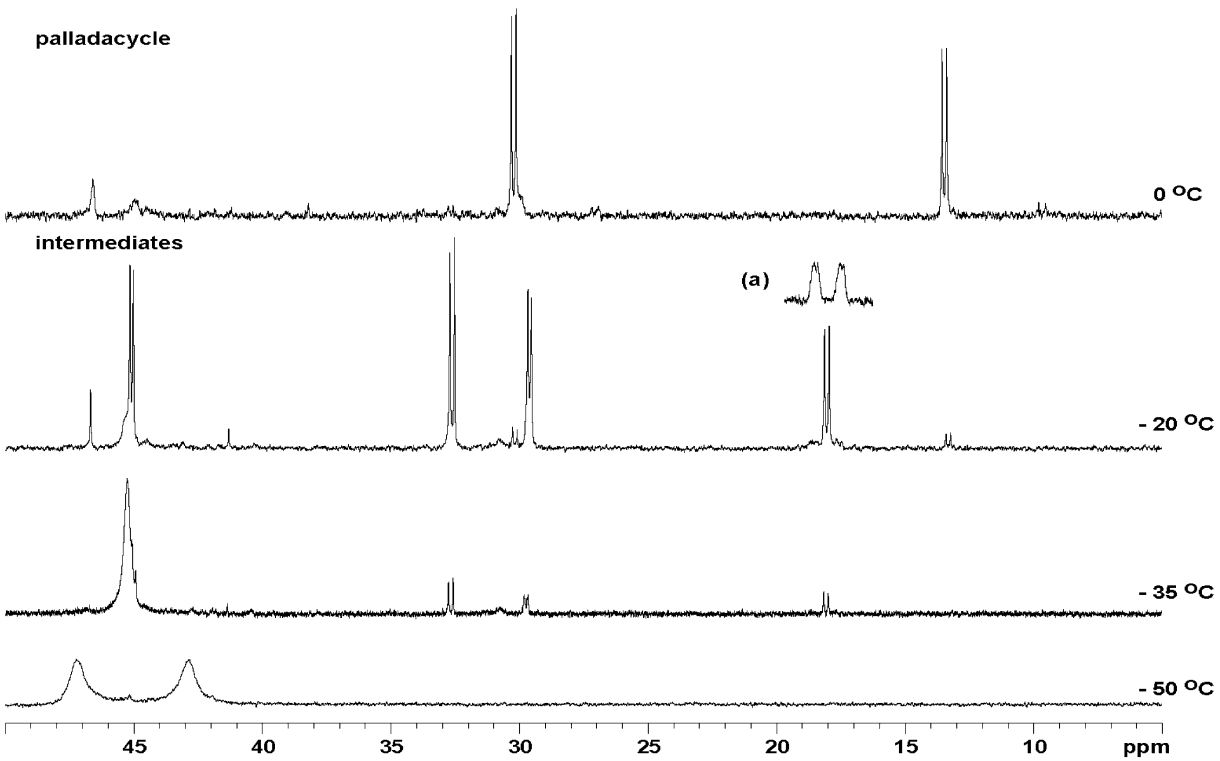


Figure 7. Reaction profile followed by $^{31}P\{^1H\}$ NMR spectroscopy of **1** and 50 equiv of NEt_3 in d_8-toluene. The temperature was gradually warmed from −50 to 0 °C. (a) Inset shows splitting of peak upon removing proton decoupling. Spectra and inset correspond to the scale shown at the bottom.

= 200.4 Hz). This resonance simplifies to a singlet when the ^{31}P nuclei are decoupled. These data collectively intimate a square planar "[Ph_2BP_2]Pd(H)(L)" hydride intermediate. As discussed below, this intermediate is proposed to be the hydride iminium adduct [[Ph_2BP_2]Pd(H)($Et_2N{=}CHCH_3$)][OTf].

The two detectable intermediates decayed as the concentration of palladacycle **7** increased. As the reaction proceeded at −20 °C, the intermediates maintained a ∼1:1 ratio until they were consumed. Integration of the final ^{31}P NMR spectrum acquired at 0 °C established that **7** had been generated in ∼80% yield. As shown in Figure 7, the palladium dimer {[Ph_2BP_2]Pd}$_2$ **4** was present in only trace quantity (doublets at ∼10 and 27 ppm). The majority of the impurities comprise the resonances between 44 and 47 ppm and are not readily assigned.

Comparison to the System [(Ph_2SiP_2)Pd($THF)_2$][$OTf]_2$. The lack of precedent for the palladaziridines described herein was surprising given their thermal stability and the fact that five- and six-membered palladacycles are rather common.[32] To inquire as to whether the choice of the anionic [Ph_2BP_2] phosphine ligand was serendipitous, a palladium system supported by the neutral bis(phosphine) ligand $Ph_2Si(CH_2PPh_2)_2$ (abbreviated as Ph_2SiP_2) was studied. The ligand Ph_2SiP_2 is a structurally faithful, neutral analogue of [Ph_2BP_2] that gives rise to reaction profiles very similar to the more familiar bis(diphenylphosphino)propane (dppp) ligand.[7] The desired precursor complex, (Ph_2SiP_2)Pd($OTf)_2$ (**14**), was conveniently prepared in two steps in 87% overall yield by reaction of Ph_2SiP_2 with $PdCl_2(NCPh)_2$ to generate (Ph_2SiP_2)$PdCl_2$ (**15**), followed by treatment with 2 equiv of AgOTf to give **14**.

Similar to [[Ph_2BP_2]Pd($THF)_2$][OTf] (**1**), (Ph_2SiP_2)Pd($OTf)_2$ (**14**) coordinated *o*-phenylpyridine in THF but did not effect arylmetalation in the temperature range between 25 and 80 °C. Moreover, like **1**, complex **14** is quite reactive toward trialkylamine substrates. Indeed, complex **14** was fully consumed in less than 1 h at room temperature, releasing a stoichiometric equivalent of [HN^iPr_2Et][OTf] when exposed to just 3 equiv of N^iPr_2Et in THF. Complete consumption of **1** on a similar time scale requires 20 equiv of N^iPr_2Et. Despite these promising signs, the major palladium-containing product in the case of **14** is the dimeric palladium(I) complex [{(Ph_2SiP_2)Pd}$_2$][$OTf]_2$ (**16**) (eq 10). A second set of NMR signals (^{31}P and ^{13}C NMR) was also present, albeit in much lower concentration relative to **16**, that may be attributed to [(Ph_2SiP_2)Pd(N,C:η^2-$N^iPr_2CHCH_3$)][OTf]. The ^{13}C NMR spectrum showed a characteristic resonance at 47 ppm, roughly the chemical shift expected for the Pd-bound carbon atom of the iminium ligand. Other tertiary amines provided similar results, but in no case were the secondary reaction products isolated or more thoroughly characterized due to their low concentrations and the difficulty in separating them from dimeric **16**. Gentle warming of a solution that presumably contains [(Ph_2SiP_2)Pd(N,C:η^2-$N^iPr_2CHCH_3$)][OTf] does not lead to its conversion to **16**.

Discussion

Access to the chemistry described herein required a synthetic route to [NBu_4][Ph_2BP_2]Pd($THF)_2$][OTf] (**1**). Starting with [Ph_2BP_2] and commercially available $(PhCN)_2PdCl_2$, complex **1** is readily prepared in three steps and in an overall isolated yield of 67%. The THF and triflate ligands of **1** are highly labile. Consequently, complex **1** reacts as an unsaturated Pd(II) center with two open cis sites. The reactivity of **1** with trialkylamines is marked in its rapidity at room temperature. Moreover, the reaction conditions and workup are fairly general for the various amine substrates examined. The palladacycles are produced cleanly and isolable in high yields (typically 80%). Extremely bulky amines, however, result in lower isolated yields (e.g., 38% yield for [Ph_2BP_2]Pd(N,C:η^2-NCy_2CHMe) (**8**)). The decreased yields are likely the result of the difficulty in separating the palladacycles from the ammonium salt byproduct due to the decreased solubility associated with the increased rigidity of the more encumbered palladacycles.

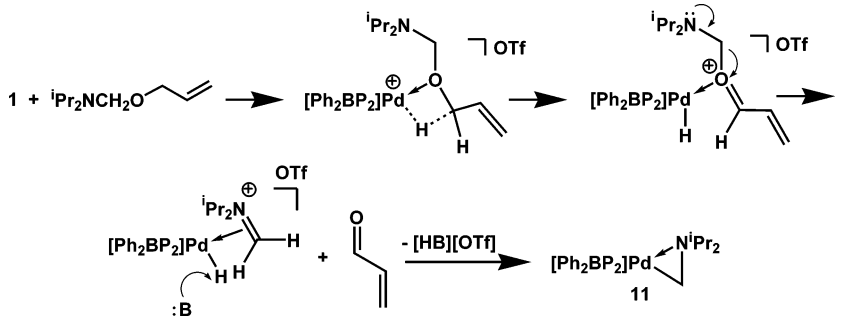
The amine activation process is selective for secondary C−H bonds. The bias against tertiary C−H bonds is presumably of steric origin, while the bias against primary C−H bonds is consistent with C−H bond dissociation energies (methylene CH_2 < primary CH_3). While the focus of this paper centers on amine activation exclusively, the transformations described may prove to be more general. One clue that this might be the case comes from the curious reaction that converts **1** to **11** upon addition of diisopropyl(2-propenyloxymethyl)amine (eq 3). A mechanistic sequence that would account for this transformation invokes coordination of an O-atom lone pair to Pd(II) followed by a β-hydride elimination step. The oxonium intermediate formed could then rearrange to **11** along with the release of acrolein (Scheme 3). Comparing C−H bond dissociation energies, the allylic C−H bond is expected to be weaker and thus is preferentially cleaved. The proposed scheme is consistent with the observation that acrolein is a byproduct of the reaction.

Reactivity of the Palladacycles. The observation that deuterium can scramble from a deuterated ammonium salt into the aliphatic positions of the neutral palladacycles (see eq 4) suggests that the palladacycles are not static species in solution but are perhaps capable of dynamic β-hydride elimination/olefin reinsertion processes akin to those of cationic palladium alkyl species such as Brookhart's (α-diimine)Pd(alkyl)$^+$ systems.[33] As shown in Scheme 4, facile chain walking would allow deuterium to wash into the α- and β-carbon positions, though we must stress that the direct observation of these intermediates has not been realized. Curiously, deuterium does not wash into the γ-carbon position. This discrepancy may arise from differences in the stability of the palladium hydride intermediates

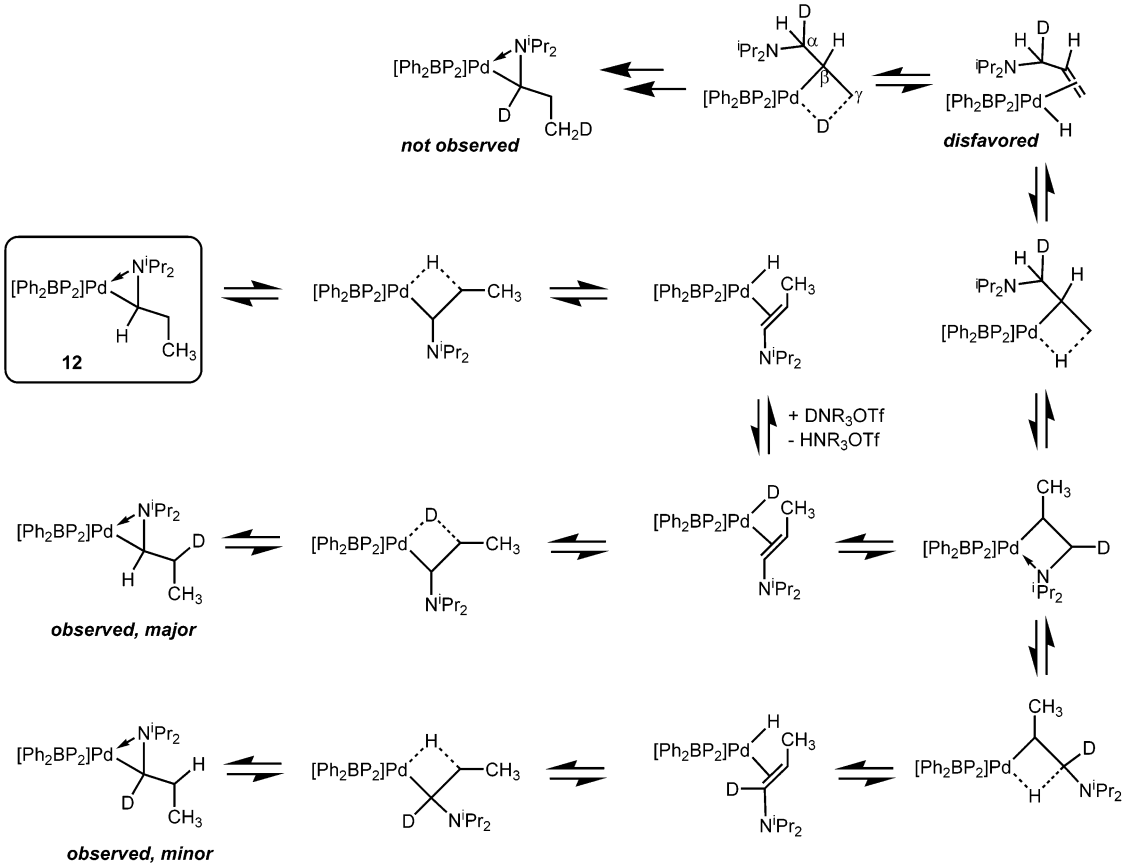
(32) (a) Canty, A. J.; Patel, J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2000**, *607*, 194−202. (b) Dunina, V. V.; Gorunova, O. N.; Averina, E. B.; Grishin, Y. K.; Kuz'mina, L. G.; Howard, J. A. K. *J. Organomet. Chem.* **2000**, *603*, 138−151. (c) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403−424.

(33) (a) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686−6700. (b) Shultz, L. H.; Tempel, D. J.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 11539−11555.

Scheme 3



Scheme 4



that lie along the path leading to deuterium incorporation (Scheme 4). Incorporation of deuterium at the α and *β* positions is expected to proceed via a palladium enamine hydride species,[34] whereas incorporation at the *γ* position is expected to proceed through a palladium allylamine hydride species. It may be that this latter species is conformationally disfavored, and hence deuterium scrambling traverses exclusively along the lower three paths shown in Scheme 4. It is also plausible to suggest that electronic factors would play a role in destabilizing a Pd allylamine hydride species. In the Pd enamine hydride, the N-atom lone pair should increase the *π*-basicity of the olefin ligand. This would not be true of an allylamine hydride species.

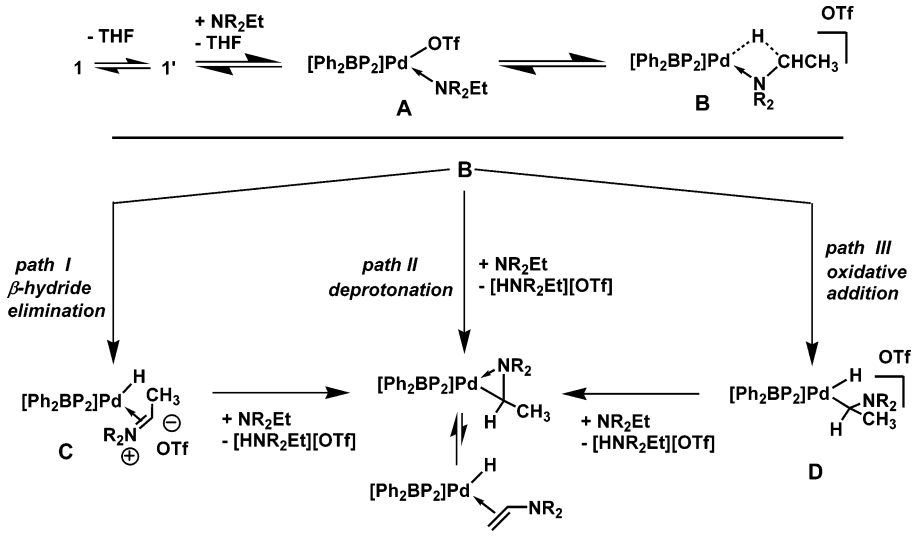
Although palladium enamine hydride complexes are invoked as plausible intermediates in Scheme 4, they cannot be directly observed. It appears, however, that they can be trapped. For instance, addition of excess *tert*-butylisocyanide to $[Ph_2BP_2]$-Pd(N,C:η^2-NEt_2CH_2) (**7**) liberates enamine and traps the inferred hydride to generate the complex $[Ph_2BP_2]Pd(C(H)=N^tBu)(CN^tBu)$ (**13**) (eq 6).

The reactivity of **7** with NaCN to generate a new C−C bond is consistent with nucleophilic attack of cyanide at an electrophilic iminium ion bound to Pd(0) (eq 7). Though we have not thoroughly explored the reactivity of these palladacycles, it is apparent that the Pd−N−C core shows reactivity consistent with both of its limiting resonance forms: as a Pd(0) iminium adduct (NaCN) and as a Pd(II) alkyl complex with an amine donor (*β*-hydride elimination, deuterium scrambling).

Mechanism. Three limiting mechanisms for the amine C−H activation process are presented in Scheme 5. Common to each path is an amine adduct of **1**. The amine adduct **A** is designated with a triflate ligand coordinated to palladium, though THF and triflate are likely in rapid exchange in THF solvent. Intermediate **A** presumably rearranges to species **B**, whereby an intramolecular C_α−H bond replaces the donor ligand (OTf or THF)

(34) A Pd enamine hydride intermediate has been previously proposed, see: Murahashi, S.-I.; Watanabe, T. *J. Am. Chem. Soc.* **1979**, *101*, 7429−7430.

Scheme 5



in the site adjacent to the amine donor. At the formal C−H bond-breaking step, the proposed paths diverge. Path I invokes β-hydride elimination to generate the palladium iminium hydride complex **C**, which is then deprotonated by an exogenous base to give the palladacycle product. Another possibility, path II, suggests that the agostic proton in **B** is directly deprotonated. Alternatively, the agostic C−H bond may undergo oxidative addition to a Pd(IV) alkyl hydride complex **D**, which like **C** is subsequently deprotonated (path III).

Proposed intermediate **B** is common to each of the three paths. While no direct spectroscopic evidence for **B** has been obtained, its intermediacy to either a β-hydride elimination process (path I) or an oxidative addition step (path III) seems reasonable to infer. Moreover, an agostic C−H proton coordinated to a positively charged palladium center should have markedly increased acidity, which would facilitate its direct deprotonation by a Brønsted base (path II). A wealth of mechanistic information has been collected for cationic $P_2Pd(II)$ alkyl complexes by Brookhart and co-workers. In some favorable cases an agostic C−H proton coordinated to a cationic palladium(II) center can be directly observed (e.g., (dippp)Pd(CH_2CH_2-μ-H)$^+$).[35] The topological analogy between inferred **B** and $P_2Pd(R)^+$ systems is apparent (Figure 8).

The spectroscopic observation of an intermediate palladium hydride species at low temperature in d_8-toluene solution is evidence against path II. A possible counterargument to this assertion is that this intermediate lies along a nonproductive path and is in equilibrium with **B**. If path II is operative, however, then the deprotonation step would have to be rate determining to give rise to the large KDIE observed. The rate law of the reaction would then be expected to show a second-order dependence on amine concentration, assuming exogenous amine to be the base. Observation of a first-order dependence of rate on amine concentration therefore appears to be inconsistent with path II. Moreover, the small magnitude of $\Delta S^{\ddagger}$ is inconsistent with a bimolecular rate-limiting step and therefore appears to be incompatible with path II.

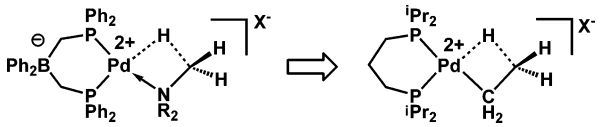


Figure 8. Comparison of proposed intermediate **B** and (dippp)Pd(CH_2-CH_2-μ-H)$^+$.

Experimentally discriminating between paths I and III is less straightforward. Both paths invoke palladium hydride intermediates, both are expected to exhibit a primary KDIE, and both could exhibit a first-order dependence on amine. The prevalence of β-hydride elimination processes in Pd(II) complexes of similar structure to **B** favors path I. Given the lack of a well-defined Pd(II/IV) redox couple associated with a C−H bond cleavage step, there is no compelling reason to invoke such a scenario here (i.e., path III).[36]

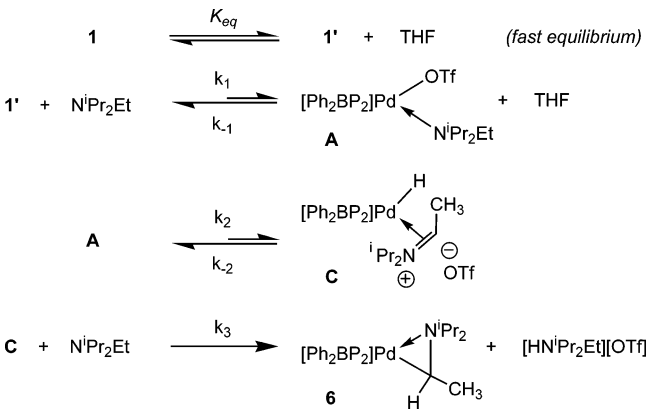
In the context of path I, the work of Murahashi et al. is relevant. These authors proposed the intermediacy of an η^2-iminium hydride of Pd(II), Pd(H)(RHC=NR^1R^2)$^+$, in trialkylamine redistribution reactions catalyzed by palladium black at 200 °C.[5] Formal oxidative insertion of Pd(0) into a secondary C−H bond adjacent to an amine N atom was invoked as the key bond-breaking step. In the present system, we suggest β-hydride elimination from Pd(II) to be the C−H bond-cleaving step. An additional system that appears to be mechanistically related to the present case comes from Harman and co-workers, who provided spectroscopic data to suggest that one-electron reduction of an Os(III) amine complex induces β-hydride elimination to generate an Os(II) η^2-iminium hydride complex.[4]

The mechanistic data presented here is interesting to compare with that available for Pd-catalyzed alcohol oxidation systems. The KDIE value we report for the amine activation process (5.9) is large by comparison to KDIE's that have been reported elsewhere for catalytic alcohol oxidation (values range between 1.3 and 2.5).[8b,d,f,g,i] Sigman's group reported a notable exception in which the KDIE for an N-heterocyclic carbene-supported Pd(II) system was reported to be quite large in magnitude (6.8),[8c]

(35) (a) Ledford, J.; Schultz, C. S.; Gates, D. P.; White, P. S.; DeSimone, J. M.; Brookhart, M. *Organometallics* **2001**, *20*, 5266−5276. (b) Shultz, L. H.; Brookhart, M. *Organometallics* **2001**, *20*, 3975−3982.

(36) For examples of Pt(II/IV) redox couples associated with C−H bond cleavage, see: (a) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235. (b) Jensen, M. P.; Wick, D. D.; Reinartz, S.; White, P. S.; Templeton, J. L.; Goldberg, K. I. *J. Am. Chem. Soc.* **2003**, *125*, 8614−8624. (c) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180. (d) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507−514.

Scheme 6



and Goldman reported a large KDIE (7) for the catalytic dehydrogenation of tertiary amines by an iridium system.[6] At present it is difficult to say what isotope-dependent factors collectively contribute to the magnitudes of the various kinetic isotope effects that have been recorded, though this is an interesting topic for further study. While few activation parameters are available for Pd-catalyzed alcohol oxidation, Sigman reported values of $\Delta H^{\ddagger} = 20.25 \pm 0.89$ kcal/mol and $\Delta S^{\ddagger} = -5.4 \pm 2.7$ eu for a sparteine-supported system under conditions where β-hydride elimination is rate determining. These parameters compare favorably with those we report here ($\Delta H^{\ddagger} = 17.9 \pm 0.2$ kcal/mol and $\Delta S^{\ddagger} = -4 \pm 1$ eu).

Rate Law in THF. The proposed mechanism for the amine activation process in THF is represented in Scheme 6 as elementary steps. All steps are drawn as reversible except for the deprotonation step, which appears to be irreversible based upon the lack of overall iminium exchange in the palladacycles (eq 5). Inclusion of intermediate **B** would not alter the rate law and has therefore been excluded.

The following rate law is derived by treating **1** ⇌ **1′** as a fast equilibrium with a constant K_{eq} and applying the steady-state approximation to intermediates **A** and **C**:

$$\text{rate} = \frac{K_{eq}k_1k_2k_3[\mathbf{1}][\text{N}^i\text{Pr}_2\text{Et}]^2}{k_{-1}k_3[\text{THF}]^2[\text{N}^i\text{Pr}_2\text{Et}] + k_{-1}k_{-2}[\text{THF}]^2 + k_2k_3[\text{N}^i\text{Pr}_2\text{Et}][\text{THF}]} \quad (11)$$

In the limit where THF is in vast excess and $k_3[\text{N}^i\text{Pr}_2\text{Et}] \gg k_{-2}$, the rate equation simplifies to

$$\text{rate} = \frac{K_{eq}k_1k_2[\mathbf{1}][\text{N}^i\text{Pr}_2\text{Et}]}{k_{-1}[\text{THF}]^2} \quad \text{and} \quad k_{obs} = \frac{K_{eq}k_1k_2[\text{N}^i\text{Pr}_2\text{Et}]}{k_{-1}[\text{THF}]^2} \quad (12)$$

The reduced rate law is in agreement with the experimental data wherein the reaction rate is first order in both [N^{i}Pr$_2$Et] and [**1**]. Moreover, the rate law can be applied to the kinetic studies performed in THF with 20-fold amine for which k_{obs} was measured. The rate constant k' ($k' = K_{eq}k_1k_2/k_{-1}$) comprises two equilibrium constants and the rate of the β-hydride elimination step (k_2). Future studies would be needed to ascertain K_{eq} and k_1/k_{-1} and to obtain a value for k_2. Reports of the isolated rate constants for β-hydride elimination steps are few in number. The most related case is Harman's osmium system, which is reported to undergo β-hydride elimination at a rate of 6×10^{-2} s^{-1} at 25 °C.[4] The rate constant k' reported here ($k' = 5.6(1) \times 10^{-2}$ s^{-1}) is of similar magnitude.

Table 2. Summary of Observations for Various Reaction Conditions

	intermediates		crude product distribution[a]	
	A	C	palladacycle	{[PhBP$_2$]Pd}$_2$ (**4**)
THF, 23 °C			quantitative	
toluene/benzene, 23 °C			minor	major
toluene, −20 °C	observed	observed	major	trace

[a] On the basis of ^{31}P NMR spectroscopy.

Reaction Profile as a Function of Solvent and Temperature. The reaction profile changes dramatically upon varying the solvent and temperature (Table 2). The variation in product distribution between low and ambient temperatures in toluene may suggest that {[PhBP$_2$]Pd}$_2$ (**4**) is the thermodynamic product and that the palladacycles are the kinetic products. Nonetheless, the palladacycles are thermally quite stable. They show no proclivity to convert to **4** at high temperatures upon isolation (up to 90 °C). We presume that complex **4**, like the palladacycles, is formed from the Pd iminium hydride intermediate (**C**). Owing to the low polarity of toluene, the transition state for deprotonation of **C** must be sufficiently raised that the competitive loss of iminium triflate dominates the reaction profile. Such a step would generate "[Ph$_2$BP$_2$]PdH", which in the absence of a strong donor is known to be quite unstable and leads to the generation of {[Ph$_2$BP$_2$]Pd}$_2$ (**4**).[21] For the case of the more polar solvent THF, the barrier to deprotonation is presumably very low relative to the barrier for iminium dissociation. Consequently, complex **1** funnels cleanly into the palladacycle product in THF. In toluene, intermediates **A** and **C** appear to be in equilibrium. In this case, β-hydride elimination *cannot* be rate limiting.[37] Instead, deprotonation becomes both rate limiting and product determining in toluene.

Reaction Profile as a Function of Charge on Palladium. Solvent is not the only factor contributing to the observed product distribution. The electrophilicity of the palladium species also seems to play a role in determining how competitive iminium release from intermediate **C** will be relative to deprotonation. For example, when (Ph$_2$SiP$_2$)Pd(OTf)$_2$ **14**, the (Ph$_2$SiP$_2$)-supported analogue of **1**, is exposed to N^{i}Pr$_2$Et, an analogous Pd iminium hydride intermediate may be invoked, but the iminium ligand is presumably more labile in this case. Thus, a pathway leading to a dimeric Pd(I) product, [(Ph$_2$SiP$_2$)-Pd]$_2$[OTf]$_2$ **16**, would be favored. Several previous studies have shown that the anionic [Ph$_2$BP$_2$] ligand is appreciably more electron releasing than (Ph$_2$SiP$_2$).[7,21] It is therefore reasonable to anticipate that a π-bonded iminium ligand in the adduct complex, [(Ph$_2$SiP$_2$)Pd(H)(R$_2$N═CHCH$_3$)]$^{2+}$, would be more labile than such a ligand in the complex [[Ph$_2$BP$_2$]Pd(H)(R$_2$N═CHCH$_3$)]$^+$ (**C**). The anionic charge of the [Ph$_2$BP$_2$] chelate thus appears to play an important role with respect to the generation of these unusual palladacycle species.

(37) We studied the product distribution for the reaction of **1** and Et$_2$NCD$_2$CD$_3$ in toluene to obtain a KIE of 2.0. This primary KIE does not help to establish whether β-hydride elimination is rate determining in toluene. For instance, a primary KIE would also be consistent with deprotonation of the Pd−H as the rate-limiting step.

In summary, iminium adducts of palladium supported by a bis(phosphino)borate ligand are readily generated from β-hydride elimination of amines at a coordinatively unsaturated Pd(II) center. It is rare to isolate or even observe intermediates relevant to the in situ reduction of Pd(II) by amines or the Pd(II)-catalyzed oxidation of alcohols. Thus, the isolable Pd(0)−iminium adducts and the mechanistic observations accompanying this study may provide important mechanistic information regarding the nature of these processes. Moreover, this study also alludes to an attractive opportunity for incorporating Pd(II) species in the presence of an oxidant within the broader synthetic context of new methods for the catalytic functionalization of tertiary amines.

Acknowledgment. This work was supported by the NSF (CHE-0132216), the ACS Petroleum Research Fund, and the Dreyfus Foundation. The authors thank Theodore Betley, Larry Henling, and Dr. Michael Day for crystallographic assistance. C.C.L. thanks the Department of Defense for a Graduate Research Fellowship.

Supporting Information Available: Complete crystallographic details for **1′**, **5**, **8**, and **9** (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA046415S