Processes Involved in the Reduction of a Cyclometalated Palladium(II) Complex

Christian M. Frech,*,† Gregory Leitus,‡ and David Milstein*,§

Department of Inorganic Chemistry, University of Zurich, 8057 Zurich, Switzerland, and Department of Organic Chemistry and Department of Chemical Services, The Weizmann Institute of Science, Rehovot 76100, Israel

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Reaction of $[Pd(TFA)_2]$ (**1**; TFA = trifluoroacetate) with 2 equiv of benzyldiisopropylphosphine resulted in formation of the metalated complex $[Pd\{C_6H_4(CH_2P^iPr_2)\}\{(C_6H_5CH_2)P^iPr_2\}(TFA)]$ (**2**). The dinuclear trifluoroacetate complex $[Pd\{C_6H_4(CH_2P^iPr_2)\}(TFA)]_2$ (**3**) was formed when the reaction was performed with an equimolar amount of the phosphine. Both complexes were structurally characterized. Reduction of the cyclometalated palladium complex **2** with sodium metal in THF gave a mixture of cis and trans isomers of the dimetalated bis(*o*-benzyldiisopropylphosphine)palladium(II) (**6a**,**b**) and bis(benzyldiisopropylphosphine)palladium(0) (**7**). A mechanism for the reduction process is presented. Treatment of the reaction mixture of **6a**,**b** and **7** with an equimolar amount of hydrochloric acid led to a mixture of **7**, $[Pd\{C_6H_4(CH_2P^iPr_2)\}\{(C_6H_5CH_2)P^iPr_2\}(Cl)]$ (**9**), $[Pd\{(C_6H_5CH_2)P^iPr_2\}_2(H)(Cl)]$ (**8**), $[Pd\{(C_6H_5CH_2)P^iPr_2\}_2(Cl)_2]$ (**4**), and both isomeric forms of $[Pd\{C_6H_4(CH_2P^iPr_2)\}_2]$ (**6a**,**b**). All complexes were independently prepared and fully characterized. The addition of another 1 equiv of hydrochloric acid to this reaction mixture resulted in the exclusive formation of **4**. Reduction of **4** with sodium metal in THF cleanly yielded the Pd^0 complex **7** in high yields, offering a new, facile, and high-yield route toward the synthesis of dicoordinated bis(phosphine) Pd^0 complexes. Reaction of **7** with an equimolar amount of HCl led to the clean formation of $[Pd\{(C_6H_5CH_2)P^iPr_2\}_2(H)(Cl)]$ (**8**). The addition of another 1 equiv of HCl led to the quantitative formation of **2** and H_2. Reactions of **9** and an equimolar amount of $NaBHEt_3$ cleanly yielded complex **7**, which was also exclusively formed by treatment of **4** with 2 equiv of $NaBHEt_3$. Mixtures of the cis and trans isomers **6a**,**b** were formed by the addition of 2 equiv of (*o*-lithiobenzyl)diisopropylphosphine to benzene solutions of bis(diethyl sulfide)palladium dichloride (**5**) at room temperature.

Introduction

Palladacyclic compounds are among of the most active precatalysts for C−C and C−heteroatom bond formation.[1] They are generally believed to undergo a reduction process which leads to a catalytically active Pd^0 species.[2] For instance, reactions of the dinuclear Pd^{II} complex $[Pd\{C_7H_6P(o\text{-tol})_2\}(OAc)]_2$ with $HNEt_2$ yielded the amine adduct, which was deprotonated in the presence of $NaOC(CH_3)_3$ to give the bis(tri-*o*-tolylphosphine) Pd^0 complex $[Pd\{P(o\text{-tol})_3\}_2]$ via β-elimination of the amide ligand. When β-elimination was not possible, i.e. when diphenylamine was used as a base, no catalytic activity was observed, whereas preformed $[Pd\{P(o\text{-tol})_3\}_2]$ was active.[3] We have previously observed that reduction of the pincer-type palladium complexes $[Pd\{C_6H_3(CH_2P^iPr_2)_2\}(X)]$ (X = TFA, Cl)[2a] results in collapse of the pincer framework, leading to a novel binuclear Pd^0/Pd^{II} complex incorporating a 14e linear Pd^0 center and a *nonplanar*, "butterfly"-type Pd^{II} 16e center.[4]

We report here the reactivity pattern of a cyclopalladated Pd(II) complex under strongly reducing conditions in the absence of substrate molecules that could stabilize the formed products or induce further transformations.

Results and Discussion

When $[Pd(TFA)_2]$ (**1**; TFA = trifluoroacetate) was treated with 2 equiv of benzyldiisopropylphosphine in THF at 70 °C overnight, cyclometalation took place, leading to the bis(phosphine) trifluoroacetate complex $[Pd\{C_6H_4(CH_2P^iPr_2)\}\{(C_6H_5CH_2)P^iPr_2\}(TFA)]$ (**2**) in high yields (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits two sets of doublet resonances (AX) centered at δ 74.91 and 32.13 ppm with coupling constants of $^2J_{PP} = 371.8$ Hz. The ^1H NMR spectrum displays all the signals due to the phosphine units, suggesting a "free" and an ortho-metalated benzyl unit. The $^{13}C\{^1H\}$ NMR

* To whom correspondence should be addressed. E-mail: chfrech@aci.uzh.ch (C.M.F.); david.milstein@weizmann.ac.il (D.M.).
† University of Zurich.
‡ Department of Chemical Services, The Weizmann Institute of Science.
§ Department of Organic Chemistry, The Weizmann Institute of Science.

(1) See, for example: (a) Bedford, R. B. *Chem. Commun.* **2003**, 1787. (b) Herrmann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C.-P.; Priermeier, T.; Beller, M.; Fischer, H. *Angew. Chem., Int. Ed.* **1995**, *34*, 1844. (c) Ohff, M.; Ohff, A.; Milstein, D. *Chem. Commun.* **1999**, 357. (d) Weissmann, H.; Milstein, D. *Chem. Commun.* **1999**, 1901. (e) Alonso, D. A.; Najera, C.; Pacheco, M. C. *Adv. Synth. Catal.* **2002**, *344*, 172.

(2) (a) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009. (b) Herrman, W. A.; Böhm, V. P. W.; Reisinger, C.-P. *J. Organomet. Chem.* **1999**, *576*, 23. (c) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (d) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917. (e) Bedford, R. B. *Chem. Commun.* **2003**, 1787. (f) Nowotny, M.; Hanefeld, U.; van Koningsveld, H.; Maschmeyer, T. *Chem. Commun.* **2000**, 1877.

(3) Louie, J.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **1996**, *35*, 2359.

(4) Frech, C. M.; Shimon, L. J. W.; Milstein, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 2.

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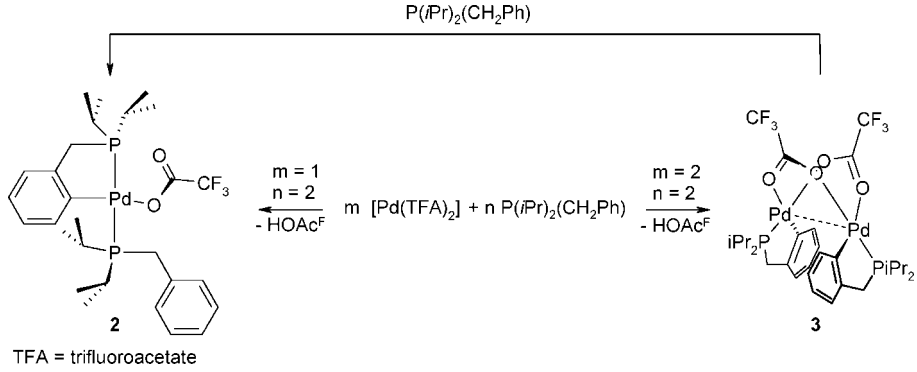
Scheme 1. Syntheses of Complexes 2 and 3



spectrum exhibits a signal centered at δ 147.87 ppm with a dd pattern ($^2J_{PC}$ = 18.9 Hz and $^2J_{PC}$ = 6.1 Hz) attributable to a σ-bound Pd−C_{ipso} carbon atom. In addition, two quartet signals at δ 160.56 ppm ($^2J_{FC}$ = 34.4 Hz) and at δ 117.32 ($^1J_{FC}$ = 291.8 Hz) due to the trifluoroacetate ligand were detected. The presence of the trifluoroacetate ligand was further confirmed by $^{19}F\{^1H\}$ NMR spectroscopy, giving rise to a sharp singlet at δ –74.11 ppm.

The molecular structure of **2** was determined by an X-ray diffraction study (see Figure 1). Well-diffracting crystals were grown by slow evaporation of a concentrated diethyl ether solution of **2** at −30 °C.

Interestingly, when **1** was treated with an equimolar amount of benzyldiisopropylphosphine, formation of the dinuclear trifluoroacetate complex $[Pd\{C_6H_4(CH_2P^iPr_2)\}(TFA)]_2$ (**3**) was observed, which was isolated as a colorless solid in 72% yield.[5] Addition of another 1 equiv of benzyldiisopropylphosphine to THF solutions of **3** led to the immediate, quantitative formation of **2**. The $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits a singlet resonance at δ 83.00 ppm. Cyclopalladation was confirmed by NMR spectroscopy. For instance, the ^1H NMR spectrum exhibits in the aromatic region signals corresponding to eight hydrogen atoms. In addition, the $^{13}C\{^1H\}$ NMR spectrum exhibits a well-defined doublet resonance at δ 148.14 ppm ($^2J_{PC}$ = 15.4 Hz), which is assigned to the Pd−C carbon. The doublet pattern of that signal indicates coordination of only one phosphine ligand to the metal center. Quartet resonances centered at δ 160.56 ($^2J_{CF}$ = 34.4 Hz) and at δ 117.32 ppm ($^1J_{CF}$ = 291.8 Hz) are attributed to the trifluoroacetate anions. Single crystals of **3** were grown by slow evaporation of a concentrated THF solution at –30 °C. The X-ray structure of **3** is shown in Figure 2.

The solid-state structure of **3** exhibits two cyclometalated square-planar palladium centers, bridged by two cis-arranged trifluoroacetate ligands. The distance between the metal centers of 3.066(8) Å seems too long for Pd···Pd interactions, although there are instances where Pd···Pd separations of 3.0 Å are treated as bonding.[6] Nevertheless, weak interactions of the palladium centers may be the reason for the line broadening in the NMR spectra. On the other hand, no spectroscopic evidence for Pd···Pd interactions was observed in a recently reported

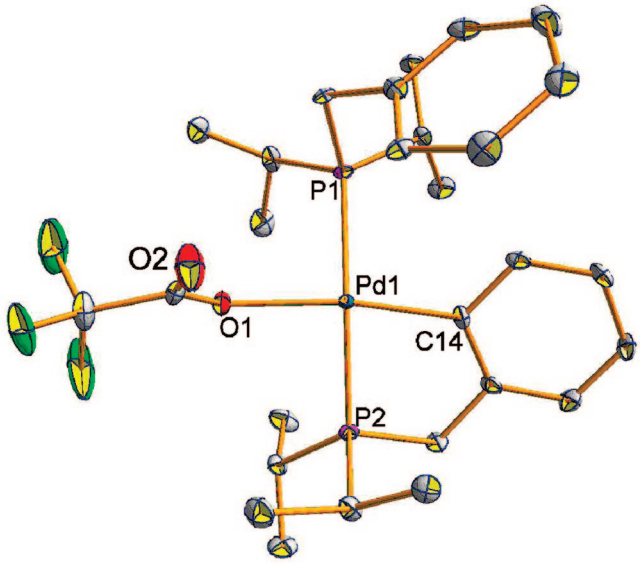


Figure 1. ORTEP diagram of a molecule of **2**, showing the atom-labeling scheme (50% probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1−P1 = 2.3783(19), Pd1−P2 = 2.2702(19), Pd1−O1 = 2.148(5), Pd1−C14 = 2.015(7); P1−Pd1−C14 = 99.0(2), C14−Pd1−P2 = 81.1(2), P2−Pd1−O1 = 90.37(15), O1−Pd1−P1 = 90.21(15).

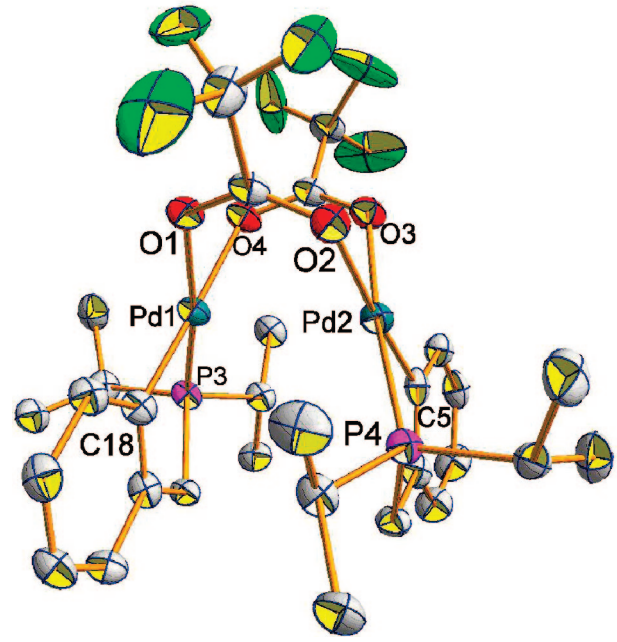
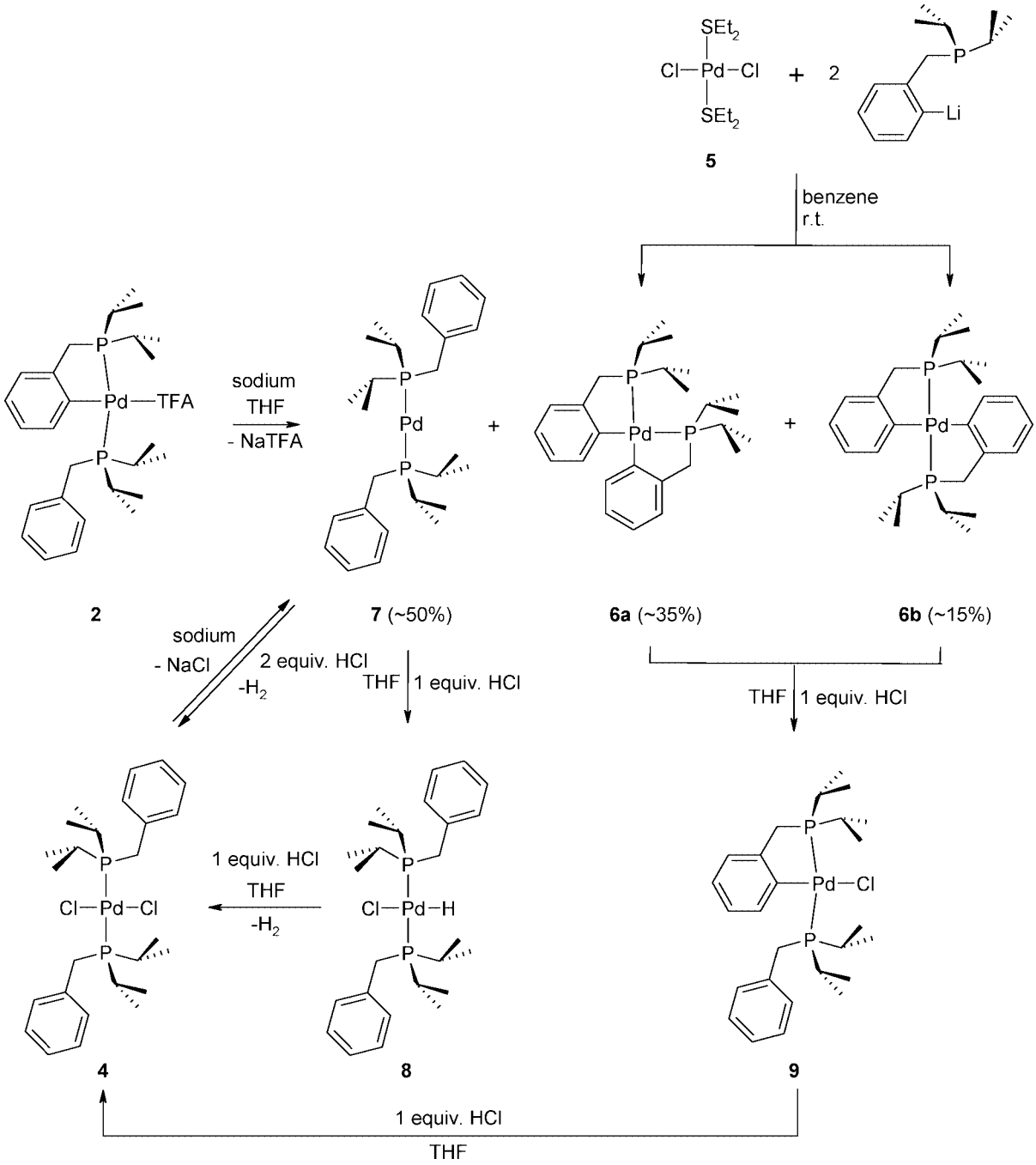


Figure 2. ORTEP diagram of a molecule of **3**, showing the atom-labeling scheme (50% probability). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1···Pd2 = 3.066(8), Pd1−P3 = 2.2169(13), Pd1−O1 = 2.170(3), Pd1−O4 = 2.143(4), Pd1−C18 = 1.983(5), Pd2−P4 = 2.2208(15), Pd2−O2 = 2.143(4), Pd2−O3 = 2.157(4), Pd2−C5 = 1.996(5); C18−Pd1−O1 = 95.49(17), O1−Pd1−O4 = 83.18(14), O4−Pd1−P3 = 100.24(10), P3−Pd1−C18 = 80.99(14), C5−Pd2−O3 = 93.75(19), O3−Pd2−O2 = 83.69(15), O2−Pd2−P4 = 100.91(11).

Scheme 2. Reduction of 2 and Related Reactions



dinuclear palladium pincer complex bearing a Pd···Pd separation of 3.0389(11) Å.[4]

Reduction of the Pd^{II} complex **2** with a large excess (~100 equiv) of sodium metal in THF under N_2 at room temperature overnight led to an inseparable mixture of three phosphorus-containing compounds. None of the formed complexes contained a trifluoroacetate ligand, as indicated by $^{19}F\{^1H\}$ NMR spectroscopy, and no hydride signals were detected in the ^1H NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum of this reaction mixture displayed two sharp singlets at δ 70.28 and 65.95 ppm and a broad signal at δ 33.18 ppm, the latter corresponding to approximately 50% of the products (by NMR). Since all the resonance signals showed different intensities, the formation of dinuclear compounds is unlikely. The generation of monophosphine complexes can be excluded, since no signals attributable to free phosphines were spectroscopically detected. The presence of cyclopalladated bis(phosphine) complexes in the reaction mixture of reduced **2** was indicated by $^{13}C\{^1H\}$ NMR spectroscopy, where signals with triplet and doublet of doublets patterns in the chemical shift range characteristic of Pd−C σ-bonds were detected. In order to elucidate the identity of the products formed, an equimolar amount (based on **2**) of hydrochloric acid (~4 M in dioxane) was added to a THF solution of the reaction mixture of reduced **2** (see Scheme 2). Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy showed

(5) For the synthesis of strongly related palladacycles, see for example: (a) Abicht, H. P.; Issleib, K. *Z. Antimicrob. Antineoplast. Chemother.* **1983**, *500*, 31. (b) Hiraki, K.; Fuchita, Y.; Uchiyama, T. *Inorg. Chim. Acta* **1983**, *69*, 187. (c) Ryabov, A. D.; Yatsimirskii, A. K.; Abicht, H. P. *Polyhedron* **1987**, *6*, 1619. (d) Pereira, M. M.; Muller, G.; Ordinas, J. I.; Azenha, M. E.; Arnaut, L. G. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1583.

(6) (a) Murahashi, T.; Kurosawa, H. *Coord. Chem. Rev.* **2002**, *231*, 207. (b) Yamamoto, Y.; Ohno, T.; Itoh, K. *Organometallics* **2003**, *22*, 2267.

formation of several compounds. The growth of two new singlets at δ 47.26 and 29.43 ppm was observed, with a concomitant decrease in the intensity of the signals at δ 70.28, 65.95, and 33.18 ppm. In addition, two sets of doublet resonances (AX) with the centers of the signals at δ 76.86 and 30.77 ppm ($^2J_{PP}$ = 376.3 Hz), similar to the chemical shifts of complex **2**, were detected. The ^{1}H NMR spectrum of this mixture displayed one sharp triplet at δ –14.01 ppm with a coupling constant of $^3J_{PH}$ = 9.3 Hz, suggesting the formation of a palladium hydride complex.[7] Remarkably, when another 1 equiv of hydrochloric acid was added, evolution of dihydrogen gas (detected by ^{1}H NMR spectroscopy and GC equipped with a TCD detector) and exclusive formation of [Pd{($C_6H_5CH_2$)P^{i}Pr$_2$}$_2$(Cl)$_2$] (**4**) within 1 h was observed. Complex **4** was isolated in almost quantitative yield (based on **2**). The ^{31}P{^{1}H} NMR spectrum of **4** displays a sharp singlet at δ 29.43 ppm. The ^{1}H NMR spectrum exhibits a doublet corresponding to four hydrogen atoms centered at δ 7.45 ppm ($^3J_{HH}$ = 7.3 Hz) and a multiplet due to six protons at δ 7.04 ppm. The ^{13}C{^{1}H} NMR spectrum exhibits all the signals due to the phosphine ligands, but none in the chemical shift range characteristic of Pd–C bonds. The structure of **4** was additionally confirmed by its independent synthesis.[8] Further information about the identity of the products formed upon reduction of **2** was obtained by the independent synthesis of both isomeric forms of bis(*o*-benzyldiisopropylphosphine)palladium complexes. The addition of 2 equiv of (*o*-lithiobenzyl)diisopropylphosphine to benzene solutions of bis(diethyl sulfide)palladium dichloride (**5**) at room temperature led to a mixture of cis and trans isomers of bis(*o*-benzyldiisopropylphosphine)palladium (**6a**,**b**) in a ratio of approximately 2:1.[9–11] Importantly, their chemical shifts in the ^{31}P{^{1}H} NMR and ^{13}C{^{1}H} NMR spectra were identical with those found in the reaction mixtures of reduced **2**, proving their formation in the reduction process.

The signal at δ 33.18 ppm in the ^{31}P{^{1}H} NMR of the reaction mixture of reduced **2** is broad, indicating dynamic behavior that may be caused by weak interactions of the metal center with the solvent or the π-system of the benzyl units of the bis(benzyldiisopropylphosphine) ligands. Changing the NMR solvent from THF to benzene did not have any influence on the line broadening, indicating that interactions of the metal center with the solvent can be excluded. Comparing the IR spectra of **2** and of reduced **2** suggests the formation of a palladium complex with "free" benzyl groups, such as [Pd{($C_6H_5CH_2$)P^{i}Pr$_2$}$_2$] (**7**), since in both cases an intense absorption band at 700 cm^{-1} was detected, which is characteristic for C–H out-of-plane bending vibrations of unsubstituted benzyl groups. Further evidence regarding the identity of the product formed was gained from treatment of THF solutions of **4** with sodium metal overnight. Remarkably, the bis(benzyldiisopropylphosphine)palladium complex **7** was exclusively formed, offering a facile and high-yield route toward the synthesis of dicoordinated bis(phosphine) Pd^0 complexes. Complex **7** was isolated in 87% yield.[12,13] The ^{31}P{^{1}H} NMR spectrum of **7** exhibits a broad singlet at δ 33.18 ppm, which is identical with one of the signals detected in the reaction mixture of reduced **2**. The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra display all the signals due to the phosphine ligands. No carbon resonances were found in the chemical shift range characteristic of Pd–C atoms, in line with the proposed structure. Further information about the identity of **7** was obtained from reactions with hydrochloric acid. The addition of an equimolar amount of hydrochloric acid (~4 M in dioxane) to THF solutions of **7** led to the clean and quantitative formation of [Pd{($C_6H_5CH_2$)P^{i}Pr$_2$}$_2$(H)(Cl)] (**8**). The ^{31}P{^{1}H} NMR spectrum of **8** shows a sharp singlet at δ 47.26 ppm. The ^{1}H NMR spectrum exhibits, in addition to all the signals due to the phosphine ligands, a sharp triplet at δ –14.01 ppm with a coupling constant of $^2J_{PH}$ = 9.3 Hz, which is characteristic for a bis(phosphine) hydrido Pd^{II} complex. When another 1 equiv of hydrochloric acid was added, evolution of H_2 gas (detected by ^{1}H NMR spectroscopy and by GC equipped with a TCD detector) and quantitative formation of **4** were observed.

A possible scenario leading to the products formed in the reduction process includes single electron transfer from sodium to the Pd^{II} centers with precipitation of NaTFA and formation of a tricoordinate Pd^I intermediate which is likely to undergo dimerization,[14,15] followed by disproportionation to the cationic Pd^{II} and anionic Pd^0 intermediates. The Pd^0 system can undergo intramolecular C–H activation[16] followed by a hydride transfer to the cationic Pd^{II} complex to yield complexes **6a**,**b** together

(7) It finally turned out that this reaction mixture contained bis(benzyldiisopropylphosphine)palladium, (benzyldiisopropylphosphine)(*o*-benzyldiisopropylphosphine)chloropalladium, bis(benzyldiisopropylphosphine)-chlorohydridopalladium, bis(benzyldiisopropylphosphine)dichloropalladium, and both isomeric forms of bis(*o*-benzyldiisopropylphosphine)palladium.

(8) See the Experimental Section.

(9) (a) For examples of bis-cyclopalladated complexes containing phosphine ligands see: Longoni, G.; Fantucci, P.; Chini, P.; Canziani, F. *J. Organomet. Chem.* **1972**, *39*, 413. (b) Fantucci, P.; Chini, P.; Canziani, F. *Gazz. Chim. Ital.* **1974**, *104*, 249. (c) Abicht, H. P.; Issleib, K. *Z. Antimicrob. Antineoplast. Chemother.* **1976**, *422*, 237. (d) Abicht, H. P.; Issleib, K. *J. Organomet. Chem.* **1978**, *149*, 209. (e) Abicht, H. P.; Issleib, K. *J. Organomet. Chem.* **1980**, *185*, 265. (f) Abicht, H. P.; Lehniger, P.; Issleib, K. *J. Organomet. Chem.* **1983**, *250*, 609.

(10) For examples of bis-cyclopalladated complexes containing amine ligands, see: (a) Kasahara, A.; Izumi, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1765. (b) Trofimenko, S. *Inorg. Chem.* **1973**, *12*, 1215. (c) Garber, A. R.; Garrou, P. E.; Hartwell, G. E.; Smas, M. J.; Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1975**, *86*, 219. (d) Murahashi, S.; Tamba, Y.; Yamamura, M.; Yoshimura, N. *J. Org. Chem.* **1978**, *43*, 4099. (e) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *222*, 155. (f) Van der Ploeg, A. F. M. J.; van Koten, G.; Schmitz, J. E. J.; Van der Linden, J. G. M. *Inorg. Chim. Acta* **1982**, *58*, 53. (g) Arlen, C.; Pfeffer, M.; Bars, O.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1983**, *8*, 1535. (h) Janecki, T.; Jeffreys, J. A. D.; Pauson, P. L.; Pietrzykowski, A.; McCullough, K. J. *Organometallics* **1987**, *6*, 1553. (i) lsters, P. L.; Teunissen, H. T.; Boersma, J.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 4691. (j) Valk, J.-M.; Maassarani, F.; van der Sluis, P.; Spek, A. L.; Boersma, J.; van Koten, G. *Organometallics* **1994**, *13*, 2320. (k) Valk, J.-M.; Boersma, J.; van Koten, G. *Organometallics* **1996**, *15*, 4366. (l) Fuchita, Y.; Yoshinaga, K.; Hanaki, T.; Kawano, H.; Kinoshita-Nagaoka, J. *J. Organomet. Chem.* **1999**, *580*, 273. (m) Berger, A.; Djukic, J.-P.; Pfeffer, M.; Lacour, J.; Vial, L.; De Cian, A.; Kyritsakas-Gruber, N. *Organometallics* **2003**, *22*, 5243.

(11) Mixtures of **6a** and **6b** were synthesized in analogy to related derivatives (see ref 9c).

(12) It was reported that attempts to form [Pd^0(PR$_3$)$_2$] (R = bulky tertiary phosphine) by direct reduction of the corresponding dichlorides with Na/Hg were not successful, palladium metal being formed: Otsuka, S. *J. Organomet. Chem.* **1980**, *200*, 191.

(13) (a) Burrows, A. D.; Mahon, M. F.; Varrone, M. *Dalton Trans.* **2004**, 3321. (b) Grotjahn, D. B.; Gong, Y.; Zakharov, L.; Golen, J. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **2006**, *128*, 438. (c) Littke, A. F.; Fu, G. C. *Org. Synth.* **2005**, *81*, 63. (d) Weng, Z.; Teo, S.; Koh, L. L.; Hor, T. S. A. *Organometallics* **2004**, *23*, 4342. (e) Netherton, M. R.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 3910. (f) Kirchhoff, J. H.; Netherton, M. R.; Hills, I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 13662. (g) Bohm, V. P. W.; Herrmann, W. A. *Chem. Eur. J.* **2001**, *7*, 4191. (h) Holzhey, N.; Pitter, S. *J. Mol. Catal. A: Chem.* **1999**, *146*, 25. (I) Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030. (j) Mann, G.; Shelby, Q.; Roy, A. H.; Hartwig, J. F. *Organometallics* **2003**, *22*, 2775 and ref 14b.

(14) For examples of Pd^I dimer formation upon reduction of Pd^{II}, see: (a) Portnoy, M.; Milstein, D. *Organometallics* **1994**, *13*, 600. (b) Weissman, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2004**, *23*, 3931.

(15) For Pd^I dimer formation by reactions between 2 equiv of [Pd(NCCH$_3$)$_4$]$^{2+}$ and [Pd$_2$. (dba)$_3$], see for example: Han, X.; Weng, Z.; Hor, T. S. A. *J. Organomet. Chem.* **2007**, *692*, 5690.

(16) A theoretical study showing that C–H activation by Pd(0) is possible: Diefenbach, A.; Bickelhaupt, F. M. *J. Phys. Chem.* **2004**, *108*, 8460.

with the neutral (benzyldiisopropylphosphine)(*o*-benzyldiisopropylphosphine)hydridopalladium(II) complex, which subsequently can undergo reductive elimination of the benzyl unit to give **7**.[17] Significantly, according to the proposed mechanism an overall yield of 50% of **7** was expected, which was experimentally confirmed. Furthermore, treatment of THF solutions of [Pd{$C_6H_4(CH_2P^iPr_2)$}{$(C_6H_5CH_2)P^iPr_2$}(Cl)] (**9**) with an equimolar amount of $NaBHEt_3$ (~1.0 M in toluene) cleanly yielded **7**, further supporting the proposed reaction mechanism. Similarly, treatment of THF solutions of **4** with 2 equiv or an excess (~5 equiv) of $NaBHEt_3$ (~1.0 M in toluene) quantitatively yielded complex **7** within a few hours.

In summary, reduction of [Pd{$C_6H_4(CH_2P^iPr_2)$}{$(C_6H_5CH_2)P^iPr_2$}(TFA)] (**2**) leads to an inseparable mixture of bis(*o*-benzyldiisopropylphosphine) Pd^{II} complexes (**6a**,**b**) and the Pd^0 complex [Pd{$(C_6H_5CH_2)P^iPr_2$}$_2$] (**7**). Thus, although cyclopalladated compounds of the general type of κ^2L,C (L = donor) are thermally very stable, they can undergo reduction to bis(phosphine) Pd^0 complexes, which are known to catalyze various C−C and C−heteroatom coupling reactions, following the traditional Pd^0/Pd^{II} cycles. Reduction of [Pd{$(C_6H_5CH_2)P^iPr_2$}$_2$(Cl)$_2$] (**4**) with sodium metal results in the bis(phosphine)palladium(0) complex **7** in high yield, offering a facile, high-yield route that may be applicable to various other bulky [$Pd(PR_3)_2$] complexes. A plausible mechanism was proposed and supported by experimental observations.

Experimental Section

General Procedures. All synthetic operations were carried out in oven-dried glassware using a combination of glovebox (M. Braun 150B-G-II) and Schlenk techniques under a dinitrogen atmosphere. Solvents were reagent grade or better, freshly distilled under an N_2 atmosphere by standard procedures, and were degassed by freeze–thaw cycles before use. Deuterated solvents were purchased from Armar, stored in a Schlenk tube (Teflon tap) over P_4O_{10}, distilled, and degassed prior to use. All the chemicals were purchased from Aldrich Chemical Co. or Fluka and used as received.

Analysis. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, and ^{19}F{^{1}H} NMR data were recorded at 500.13, 125.76, 202.46, and 235.40 MHz, respectively, on a Bruker AMX-500 and a Bruker DRX-500 spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm), and coupling constants (J) are in Hz. The ^{1}H and ^{13}C NMR chemical shifts are relative to tetramethylsilane; the resonances of the residual protons of the solvents were used as internal standards for ^{1}H (δ 7.15 benzene; δ 3.58 and 1.73 tetrahydrofuran) and *all-d* solvent peaks for ^{13}C (δ 128.0 benzene; δ 67.4 and 25.2 tetrahydrofuran). ^{31}P NMR chemical shifts are reported downfield relative to external 85% H_3PO_4 at in D_2O at δ 0.0 ppm. ^{19}F NMR chemical shifts were referenced to C_6F_6 (δ −163 ppm). All measurements were carried out at 298 K. Abbreviations used in the description of NMR data are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; v, virtual. Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium (Germany) and at the University of Zurich.

Preparation of [Pd{$C_6H_4(CH_2P^iPr_2)$}{$(C_6H_5CH_2)P^iPr_2$}(TFA)] (2). To a THF solution of [$Pd(TFA)_2$] (100 mg, 0.301 mmol) was added 2 equiv of $(C_6H_5CH_2)P^iPr_2$ (125.4 mg, 0.605 mmol), and the solution was refluxed overnight. The reaction mixture was filtered through a cotton pad at room temperature, and the solvent was removed under reduced pressure. The colorless solid was extracted with diethyl ether (3 × 10 mL) and dried. Crystallization from a concentrated diethyl ether solution at −30 °C gave the complex as a colorless solid (148.6 mg, 0.234 mmol, 78% yield).

^{31}P{^{1}H} NMR (C_6D_6; δ, ppm): 74.91 (d (left part of an AX system), J = 371.8 Hz, $C_6H_4(CH_2P^iPr_2)$), 32.13 (d (right part of an AX system), J = 371.8 Hz, $(C_6H_5CH_2)P^iPr_2$). ^{1}H NMR (δ, ppm): 7.72 (d, J = 7.2 Hz, 2H, *Ar*), 7.27 (t, J = 7.3 Hz, 2H, *Ar*), 7.14 (t, J = 7.3 Hz, 1H, *Ar*), 7.01 (broad t, J = 7.3 Hz, 2H, *Ar*), 6.84 (broad s, 2H, *Ar*), 3.24 (d, J = 9.8 Hz, 2H, CH_2P), 2.82 (d, J = 9.8 Hz, 2H, CH_2P), 2.18 (m, 2H, PCH(CH_3)$_2$), 2.10 (m, 2H, PCH(CH_3)$_2$), 1.37 (dist q, J = 4.9 Hz, 6H, PCH(CH_3)$_2$), 1.07 (m, 12H, PCH(CH_3)$_2$), 0.88 (dist q, J = 4.9 Hz, 6H, PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (δ, ppm): 160.56 (q, J = 34.4 Hz, OC(=O)CF_3), 147.87 (dd, J = 18.9 Hz, J = 6.1 Hz, C_{ipso}), 138.93 (dd, J = 11.2 Hz, J = 1.3 Hz, *Ar*), 135.90 (d, J = 2.3, *Ar*), 130.47 (d, J = 4.6, *Ar*), 128.45 (d, J = 4.6, *Ar*), 128.06 (s, *Ar*), 126.54 (d, J = 2.3, *Ar*), 124.76 (s, *Ar*), 124.49 (s, *Ar*), 124.10 (d, J = 17.6 Hz, *Ar*), 117.32 (q, J = 291.8 Hz, OC(=O)CF_3), 32.77 (d, J = 13.8 Hz, CH$_2$P), 27.49 (d, J = 11.3 Hz, CH$_2$P), 25.04 (dd, J = 17.6 Hz, J = 3.7 Hz, PCH(CH_3)$_2$), 22.79 (dd, J = 15.1 Hz, J = 1.3 Hz, PCH(CH_3)$_2$), 19.44 (s, PCH(CH$_3$)$_2$), 18.88 (s, PCH(CH$_3$)$_2$), 18.30 (s, PCH(CH$_3$)$_2$), 17.82 (s, PCH(CH$_3$)$_2$). ^{19}F{^{1}H} NMR (δ, ppm): −74.11 (OC(=O)CF_3). IR (ATR; cm^{-1}): 700 (C−H_{arom} of 1,2-disubstituted phenyl groups). Anal. Calcd for $C_{28}H_{41}F_3O_2P_2Pd$: C, 52.96; H, 6.51. Found: C, 52.93; H, 6.56.

Preparation of [Pd{$C_6H_4(CH_2P^iPr_2)$}(TFA)]$_2$ (3). To a THF solution of [$Pd(TFA)_2$] (100 mg, 0.301 mmol) was added 1 equiv of $(C_6H_5CH_2)P^iPr_2$ (62.7 mg, 0.301 mmol), and the solution was refluxed overnight. After filtration of the reaction mixture through a cotton pad at room temperature the solvent was removed under reduced pressure. Complex **3** was washed with diethyl ether (3 × 5 mL) and dried again under reduced pressure. The product was crystallized from THF at −30 °C and obtained as a colorless solid (92.2 mg, 0.108 mmol, 72%).

^{31}P{^{1}H} NMR (THF-d_8; δ, ppm): 83.00 (s, $C_6H_4(CH_2P^iPr_2)$). ^{1}H NMR (δ, ppm): 7.35 (broad s, 2H, *Ar*), 7.08 (d, J = 7.3 Hz, 2H, *Ar*), 7.00 (t, J = 7.3 Hz, 2H, *Ar*), 6.93 (t, J = 7.3 Hz, 2H, *Ar*), 3.00 (broad s, 4H, CH_2P), 2.09 (m, 2H, PCH(CH_3)$_2$), 1.67 (m, 2H, PCH(CH_3)$_2$), 1.34 (m, 6H, PCH(CH_3)$_2$), 0.98 (m, 12H, PCH(CH_3)$_2$), 0.92 (m, 6H, PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (δ, ppm): 160.56 (q, J = 34.4 Hz, OC(=O)CF_3), 148.14 (d, J = 15.4 Hz, C_{ipso}), 146.88 (s, *Ar*), 135.78 (broad s, *Ar*), 126.27 (d, J = 17.4 Hz, *Ar*), 124.39 (d, J = 2.3 Hz, *Ar*), 117.32 (q, J = 291.8 Hz, OC(=O)CF_3), 35.34 (d, J = 33.9 Hz, CH$_2$P), 26.38 (broad s, PCH(CH_3)$_2$), 21.56 (broad s, PCH(CH$_3$)$_2$), 19.56 (broad s, PCH(CH$_3$)$_2$), 17.98 (broad s, PCH(CH$_3$)$_2$). ^{19}F{^{1}H} NMR (δ, ppm): –75.32 (OC(=O)CF_3). Anal. Calcd for $C_{30}H_{40}F_6O_4P_2Pd_2$: C, 42.22; H, 4.72. Found: C, 42.31; H, 4.79.

Preparation of [Pd{$(C_6H_5CH_2)P^iPr_2$}$_2$(Cl)$_2$] (4). To a THF solution of [Pd(COD)(Cl)$_2$] (50 mg, 0.175 mmol) was added 2 equiv of $(C_6H_5CH_2)P^iPr_2$ (36.5 mg, 0.301 mmol), and the solution was stirred for 5 min at room temperature. After filtration of the reaction mixture through a cotton pad the solvent was removed under reduced pressure. Complex **4** was washed with pentane (2 × 5 mL) and dried again under reduced pressure. The product was obtained as a bright yellow solid in quantitative yield (103.8 mg, 0.174 mmol).

^{31}P{^{1}H} NMR (THF-d_8; δ, ppm): 29.43 (s, $(C_6H_5CH_2)P^iPr_2$)). ^{1}H NMR (δ, ppm): 7.45 (d, J = 7.3 Hz, 4H, *Ar*), 7.04 (m, 6H, *Ar*), 3.60 (t, J = 4.2 Hz, 4H, CH_2P), 2.05 (m, 4H, PCH(CH_3)$_2$), 1.25 (m, 24H, PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (δ, ppm): 137.10 (s, *Ar*), 131.52 (s, *Ar*), 129.31 (s, *Ar*), 127.23 (s, *Ar*), 32.12 (d, J = 33.9 Hz, CH$_2$P), 24.74 (s, PCH(CH_3)$_2$), 20.06 (s, PCH(CH$_3$)$_2$), 18.96 (s, PCH(CH$_3$)$_2$). Anal. Calcd for $C_{26}H_{42}Cl_2P_2Pd$: C, 52.58; H, 7.13. Found: C, 52.39; H, 7.08.

Preparation of [Pd{$C_6H_4(CH_2P^iPr_2)$}$_2$] (6a,b). A diethyl ether solution of 2 equiv of (*o*-lithiobenzyl)diisopropylphosphine was added dropwise at room temperature to a benzene solution of **5**

(17) The involvement of the solvent in this process can be excluded, since no deuterium was incorporated in complex **7** when the reaction was performed in THF-d_8, as shown by ^{1}H and ^{2}D NMR spectroscopy.

(50 mg, 0.140 mmol), and the mixture was stirred at room temperature for 3 h. After filtration of the reaction mixture through a cotton pad the solvent was removed under reduced pressure. The residue was washed with cold pentane (2 × 5 mL); extraction with benzene gave a mixture of **6a** (∼65%) and **6b** (∼35%) in a yield of 62% (45.2 mg, 0.086 mmol) as an off-white solid.

Data for **6a** are as follows. $^{31}P\{^1H\}$ NMR (C_6D_6; δ, ppm): 65.95 (s, $C_6H_4(CH_2P^iPr_2)$). ^1H NMR (δ, ppm): 7.76 (d overlapped with signals of **6b**, J = 11.6 Hz, 2H, *Ar*), 7.24 (m overlapped with signals of **6b**, 3H, *Ar*), 2.89 (s, 4H, CH_2P), 1.93 (m, 4H, PCH(CH$_3$)$_2$), 1.16 (m overlapped with signals of **6b**, 24H, PCH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (δ, ppm): 173.94 (dd, J_{PC} = 119.54 Hz, J_{PC} = 13.1 Hz, C_{ipso}), 148.06 (vt, J_{PC} = 11.1 Hz, *Ar*), 142.74 (vt, J_{PC} = 5.2 Hz, *Ar*), 133.21 (s, *Ar*), 132.84 (s, *Ar*), 128.08 (s, *Ar*), 127.91 (s, *Ar*), 125.59 (s, *Ar*), 124.58 (s, *Ar*), 124.44 (s, *Ar*), 36.43 (dd, J_{PC} = 12.4 Hz, J_{PC} = 4.1 Hz, *C*H$_2$P), 24.58 (vt, J_{PC} = 10.4 Hz, P*C*H(CH$_3$)$_2$), 22.43 (vt, J_{PC} = 10.3 Hz, P*C*H(CH$_3$)$_2$), 20.51 (vt, J_{PC} = 2.6 Hz, PCH(*C*H$_3$)$_2$), 20.38 (vt, J_{PC} = 3.3 Hz, PCH(*C*H$_3$)$_2$), 18.41 (broad s, PCH(*C*H$_3$)$_2$), 16.05 (broad s, PCH(*C*H$_3$)$_2$). Data for **6b** are as follows. $^{31}P\{^1H\}$ NMR (C_6D_6; δ, ppm): 70.28 (s, $C_6H_4(CH_2P^iPr_2)$). ^1H NMR (δ, ppm): 7.74 (d overlapped with signals of **6a**, J = 11.4 Hz, 2H, *Ar*), 7.24 (m overlapped with signals of **6a**, 3H, *Ar*), 2.93 (s, 4H, CH_2P), 1.89 (m, 4H, PCH(CH$_3$)$_2$), 1.16 (m overlapped with signals of **6a**, 24H, PCH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (δ, ppm): 167.80 (vt, $^2J_{PC}$ = 7.2 Hz, C_{ipso}), 149.61 (vt, $^2J_{PC}$ = 9.2 Hz, *Ar*), 131.03 (s, *Ar*), 128.58 (s, *Ar*), 126.04 (s, *Ar*), 124.01 (s, *Ar*), 34.82 (vt, J_{PC} = 12.4 Hz, *C*H$_2$P), 31.82 (d, J_{PC} = 5.2 Hz, P*C*H(CH$_3$)$_2$), 20.09 (s, PCH(*C*H$_3$)$_2$), 18.96 (s, PCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{26}H_{40}P_2Pd$: C, 59.95; H, 7.74. Found: C, 60.07; H, 7.88.

Preparation of [Pd{(C$_6$H$_5$CH$_2$)P^{i}Pr$_2$}$_2$] (7). A THF solution of **4** (50 mg, 0.084 mmol) and a large excess of sodium metal (∼500 equiv) was stirred at room temperature overnight. After filtration of the reaction mixture through a cotton pad the solvent was removed under reduced pressure. **7** was extracted with pentane (15 mL), filtered, and dried again under reduced pressure. The product was obtained in 87% yield (34.3 mg, 0.066 mmol) as an oily substance, which solidified within a few days.

$^{31}P\{^1H\}$ NMR (THF-d_8; δ, ppm): 33.18 (broad s, $(C_6H_5CH_2)P^iPr_2$)). ^1H NMR (δ, ppm): 7.70 (broad d, J = 11.7 Hz, 2H, *Ar*), 7.12 (m, 3H, *Ar*), 2.95 (broad s, 4H, CH_2P), 1.81 (m, 4H, PCH(CH$_3$)$_2$), 1.16 (broad s, 24H, PCH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (δ, ppm): 139.96 (s, *Ar*), 131.25 (s, *Ar*), 128.62 (s, *Ar*), 126.36 (s, *Ar*), 32.16 (broad s, *C*H$_2$P), 26.14 (broad s, P*C*H(CH$_3$)$_2$), 20.64 (s, PCH(*C*H$_3$)$_2$), 20.28 (s, PCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{26}H_{42}P_2Pd$: C, 59.71; H, 8.09. Found: C, 59.62; H, 8.02.

Preparation of [Pd{(C$_6$H$_5$CH$_2$)P^{i}Pr$_2$}$_2$(Cl)(H)] (8). To a THF solution of **7** (20 mg, 0.038 mmol) was added an equimolar amount of hydrochloric acid (∼4 M in dioxane) at room temperature, and the mixture was stirred for a few minutes. After filtration of the reaction mixture through a cotton pad the solvent was removed under reduced pressure. Complex **8** was extracted with pentane (15 mL), filtered, and dried again under reduced pressure. The product was obtained as an orange powder in almost quantitative yield (20.1 mg, 0.036 mmol).

$^{31}P\{^1H\}$ NMR (C_6D_6; δ, ppm): 47.26 (s, $(C_6H_5CH_2)P^iPr_2$). ^1H NMR (δ, ppm): 7.72 (d, J = 7.2 Hz, 4H, *Ar*), 7.17 (m, 4H, *Ar*), 7.05 (t, J = 7.2 Hz, 2H, *Ar*), 3.37 (t, J = 3.6 Hz, 4H, CH_2P), 1.91 (m, 4H, PCH(CH$_3$)$_2$), 1.02 (dist q, J = 7.2 Hz, 24H, PCH(CH_3)$_2$), –14.01 (t, J = 9.3 Hz, 1H, Pd−*H*). $^{13}C\{^1H\}$ NMR (δ, ppm): 137.11 (s, *Ar*), 130.78 (broad s, *Ar*), 128.49 (s, *Ar*), 126.49 (s, *Ar*), 29.61 (vt, J = 9.0 Hz, *C*H$_2$P), 25.47 (t, J = 11.3 Hz, P*C*H(CH$_3$)$_2$), 19.52 (s, PCH(*C*H$_3$)$_2$), 19.38 (s, PCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{26}H_{43}ClP_2Pd$: C, 55.82; H, 7.75. Found: C, 55.96; H, 7.79.

Preparation of [Pd{C$_6$H$_4$(CH$_2$P^{i}Pr$_2$)}{(C$_6$H$_5$CH$_2$)P^{i}Pr$_2$}(Cl)] (9). To a THF solution of a mixture of **6a** and **6b** (30 mg, 0.057 mmol) was added an equimolar amount of hydrochloric acid (∼4 M in dioxane), and the solution was stirred for 1 h. After filtration of the reaction mixture through a cotton pad the solvent was removed under reduced pressure. The colorless solid was extracted with pentane (10 mL), filtered, and dried under reduced pressure. Complex **9** was obtained in almost quantitative yield (29.3 mg, 0.052 mmol, 92%).

$^{31}P\{^1H\}$ NMR (C_6D_6; δ, ppm): 76.86 (d (left part of an AX system), J = 376.3 Hz, $C_6H_4(CH_2P^iPr_2)$), 30.77 (d (right part of an AX system), J = 376.3 Hz, $(C_6H_5CH_2)P^iPr_2$)). ^1H NMR (δ, ppm): 7.69 (d, J = 7.2 Hz, 2H, *Ar*), 7.21 (t, J = 7.2 Hz, 2H, *Ar*), 7.09 (t, J = 7.3 Hz, 1H, *Ar*), 6.93 (broad t, J = 7.3 Hz, 2H, *Ar*), 6.82 (broad s, 2H, *Ar*), 3.19 (d, J = 9.7 Hz, 2H, CH_2P), 2.82 (d, J = 9.8 Hz, 2H, CH_2P), 2.11 (m, 2H, PCH(CH$_3$)$_2$), 2.04 (m, 2H, PCH(CH$_3$)$_2$), 1.33 (dist q, J = 4.8 Hz, 6H, PCH(CH_3)$_2$), 1.07 (m, 12H, PCH(CH_3)$_2$), 0.85 (dist q, J = 4.7 Hz, 6H, PCH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (δ, ppm): 147.66 (dd, J = 18.6 Hz, J = 6.2 Hz, C_{ipso}), 138.76 (dd, J = 11.0 Hz, J = 1.2 Hz, *Ar*), 135.79 (s, *Ar*), 130.32 (s, *Ar*), 128.36 (s, *Ar*), 128.07 (s, *Ar*), 126.53 (s, *Ar*), 124.68 (s, *Ar*), 124.54 (s, *Ar*), 124.13 (d, J = 17.4 Hz, *Ar*), 32.64 (d, J = 13.8 Hz, *C*H$_2$P), 27.54 (d, J = 11.0 Hz, *C*H$_2$P), 24.97 (dd, J = 17.8 Hz, J = 3.8 Hz, P*C*H(CH$_3$)$_2$), 22.74 (dd, J = 15.0 Hz, J = 1.2 Hz, P*C*H(CH$_3$)$_2$), 19.54 (s, PCH(*C*H$_3$)$_2$), 18.93 (s, PCH(*C*H$_3$)$_2$), 18.27 (s, PCH(*C*H$_3$)$_2$), 17.80 (s, PCH(*C*H$_3$)$_2$). IR (ATR; cm^{-1}): 701 (C−H$_{arom}$ of 1,2-disubstituted phenyl groups). Anal. Calcd for $C_{26}H_{41}ClP_2Pd$: C, 56.02; H, 7.41. Found: C, 55.93; H, 7.56.

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Supporting Information Available: CIF files containing X-ray crystallographic data for complexes **2** (CCDC-637692) and **3** (CCDC-637693). This material is available free of charge via the Internet at http://pubs.acs.org. This material is also available free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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