Synthesis and Solution Structure of Palladium Tris(*o*-tolyl)phosphine Mono(amine) Complexes

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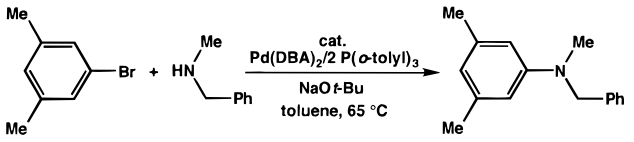
The complex(es) resulting from a 1:4 mixture of $Pd_2(DBA)_3$ and P(*o*-tol)$_3$ react with aryl bromides or aryl iodides *p*-XC_6H_4R (X = Br, I; R = Me, *t*-Bu, OMe) to generate the corresponding halide dimers {Pd[P(*o*-tol)$_3$](*p*-C_6H_4R)(μ-X)}$_2$ (X = Br, R = *t*-Bu (**1**), Me (**2**), OMe (**3**); X = I, R = *t*-Bu (**4**), Me (**5**), OMe (**6**)) in 46−76% yield. Iodide dimer **5** reacts with AgOTf in acetonitrile to form the cationic bis(acetonitrile) complex {Pd[P(*o*-tol)$_3$](*p*-C_6H_4-Me)(CH_3CN)$_2$]}$^+$OTf$^-$ (**8**) which was treated in situ with LiCl to form the chloride dimer {Pd[P(*o*-tol)$_3$](*p*-C_6H_4Me)(μ-Cl)}$_2$ (**9**) in 93% yield. The *p*-tolyl halide dimers **2**, **5**, and **9** react with *N*-benzylmethylamine to generate the corresponding 1:1 palladium amine adducts Pd[P(*o*-tol)$_3$](*p*-C_6H_4Me)[HN(Me)Bn]X (X = Cl (**12**), 85%; X = Br (**13**), 72%; X = I (**14**), 77%). Reaction of a mixture of $Pd_2(DBA)_3$ and P(*o*-tol)$_3$ with the haloamines 2-$IC_6H_4(CH_2)_2N(H)Bn$, 2-$BrC_6H_4CH_2N(H)$(*p*-tolyl), and 2-$BrC_6H_4(CH_2)_3N(H)Bn$ gave the chelated palladium amine complexes Pd[P(*o*-tol)$_3$](2-$C_6H_4(CH_2)_2$N(H)Bn]I (**18**, 71%), Pd[P(*o*-tol)$_3$][2-$C_6H_4CH_2$N(H)(*p*-tolyl)]Br (**19**, 77%), and Pd[P(*o*-tol)$_3$](2-$C_6H_4(CH_2)_3$N(H)Bn]Br (**21**, 24%), respectively. Variable-temperature ^{1}H and ^{31}P NMR analysis of **12**−**14** and related complexes was consistent with hindered rotation about the P−C bonds, with predominant formation of the *exo*$_2$-P(*o*-tol) conformer, and hindered rotation about the Pd−P bond with formation of three unequally populated rotamers.

Introduction

In 1983 Migita reported that Pd[P(*o*-tol)$_3$]$_2$Cl$_2$ (*o*-tol = *o*-tolyl) served as an effective catalyst for the cross-coupling of aryl bromides with (diethylamino)stannane in toluene at 100 °C.[1] Despite the importance of aromatic amines in areas such as pharmaceuticals[2] and conductive polymers,[3] and due to limitations in traditional methods for the synthesis of anilines,[4] Pd-catalyzed C−N bond formation remained undeveloped for over a decade. However, recent work[5] has led to the development of a tin-free Pd-catalyzed procedure for the conversion of aryl bromides[6] to the corresponding anilines via reaction with free amine and sodium *tert*-butoxide. For example, reaction of 5-bromo-*m*-xylene, *N*-benzylmethylamine (1.2 equiv), and sodium *tert*-butoxide (1.4 equiv) with 2 mol % of Pd(DBA)$_2$ (DBA = dibenzylideneacetone) and 4 mol % of P(*o*-tol)$_3$ in toluene at 65 °C formed *N*-benzyl-*N*-methyl-3,5-xylidine in 84% yield (Scheme 1).[6a] The corresponding reaction of aryl iodides[7] and amines required higher temperatures and produced slightly lower yields of cross-coupled product than did aryl bromides.

Scheme 1



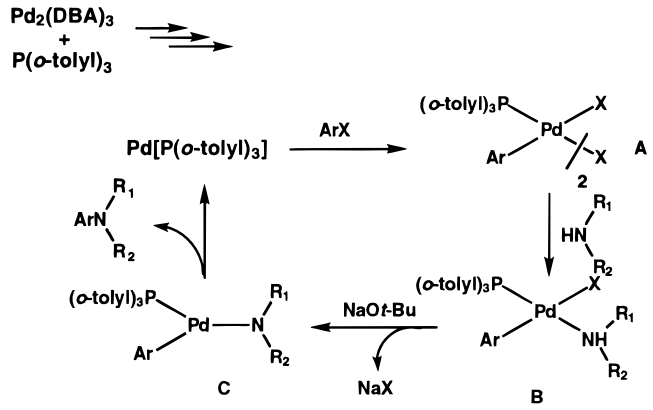
The proposed catalytic cycle for the palladium-catalyzed amination of aryl halides, based on Hartwig's mechanism for the cross-coupling of aminostannanes with aryl bromides,[5b,c] is shown in Scheme 2. The key steps include the cleavage of the aryl halide dimer **A** (X = Br, I) by free amine to form the corresponding palladium amine monomer **B** followed by deprotonation to generate the requisite three-coordinate palladium amide complex **C**. Due to the central role of the 1:1 palladium amine adducts **B** in the overall catalytic cycle, we have been interested in the factors which influence both the formation and reactivity of these complexes. Here we report on the synthesis and solution structure of a series of cyclic and acyclic palladium tris(*o*-tolyl)-phosphine mono(amine) complexes.[8]

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

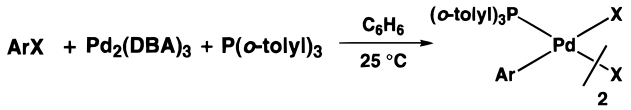
(1) Kosugi, M.; Kameyama, M.; Migita, T. *Chem. Lett.* **1983**, 927.
(2) Negwer, M. *Organic-Chemical Drugs and Their Synonyms (an International Survey)*, 7th ed.; Akademie Verlag: Berlin, 1994.
(3) D'Aproano, G.; Schiavon, G.; Zotti, G.; Leclerc, M. *Chem. Mater.* **1995**, *7*, 33.
(4) (a) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; pp 641−676. (b) Mitchell, H.; Leblanc, Y. *J. Org. Chem.* **1994**, *59*, 682. (c) ten Hoeve, W.; Kruse, C. G.; Luteyn, J. M.; Thiecke, J. R. G.; Wynberg, H. *J. Org. Chem.* **1993,** *58*, 5101. (d) Banfi, A.; Bartoletti, M.; Bellora, E.; Bignotti, M.; Turconi, M. *Synthesis* **1994**, 777. (e) Finet, J. P.; Khamsi, J.; Barton, D. H. R. *Tetrahedron Lett.* **1986**, *27*, 3615.
(5) (a) Guram, A. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 7901. (b) Paul, F.; Patt, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 5969. (c) Hartwig, J. F.; Paul, F. *J. Am. Chem. Soc.* **1995**, *117*, 5373.
(6) (a) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348. (b) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609.
(7) Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **1996**, *61*, 1133.
(8) While this work was in progress, Hartwig and co-workers reported the syntheses of some palladium tris(*o*-tolyl)phosphine amine adducts: Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030.

S0276-7333(95)00959-9 CCC: $12.00

Scheme 2



Scheme 3



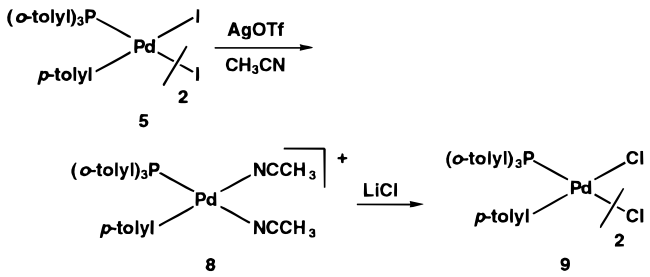
Cmpd	X	Ar	isolated yield
1	Br	*p*-*t*-BuC$_6$H$_4$	69
2	Br	*p*-MeC$_6$H$_4$	76
3	Br	*p*-MeOC$_6$H$_4$	46
4	I	*p*-*t*-BuC$_6$H$_4$	52
5	I	*p*-MeC$_6$H$_4$	60
6	I	*p*-MeOC$_6$H$_4$	51

Results and Discussion

Synthesis of the Palladium Aryl Bromide and Iodide Dimers {Pd[P(*o*-tol)$_3$](Ar)(μ-X)}$_2$. Hartwig has previously reported the synthesis of the aryl bromide dimers {Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$R)(μ-Br)}$_2$ (R = *t*-Bu (**1**), Me (**2**), *n*-Bu) from the reaction of Pd[P(*o*-tol)$_3$]$_2$ with the corresponding aryl bromide.[5b,c,8] However, we sought a synthesis of the aryl bromide dimers which did not require isolation of the bis(phosphine) complex Pd[P(*o*-tol)$_3$]$_2$. To this end, reaction of Pd$_2$(DBA)$_3$, P(*o*-tol)$_3$ (8 equiv), and 1-bromo-4-*tert*-butylbenzene (10 equiv) in benzene for 1 h led to the isolation of the palladium bromide dimer **1** in 69% yield (Scheme 3). A similar procedure was employed to synthesize the bromide dimers **2**·$^1/_4$OEt$_2$ (76%) and {Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$OMe)(μ-Br)}$_2$ (**3**; 46%) and also the aryl iodide dimers {Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$CMe$_3$)(μ-I)}$_2$ (**4**; 52%), {Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)(μ-I)}$_2$ (**5**; 60%), and {Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$OMe)(μ-I)}$_2$ (**6**; 51%).

In the syntheses of palladium bromide dimers **1**−**3**, reaction times of >1 h led to contamination of the desired aryl bromide dimer with the bis(phosphine) dibromide complex Pd[P(*o*-tol)$_3$]$_2$Br$_2$ (**7**),[9] although the extent of contamination was dependent on the aryl bromide. For example, reaction of Pd$_2$(DBA)$_3$, P(*o*-tol)$_3$, and 1-bromo-4-*tert*-butylbenzene in benzene for 48 h formed only a trace (≤5%) of **7**, as determined by ^{1}H and ^{31}P NMR analysis of the crude reaction mixtures. The analogous reaction of Pd$_2$(DBA)$_3$, P(*o*-tol)$_3$, and *p*-bromotoluene for 24 h gave a ~5:1 ratio of **1**:**7**, while reaction of Pd$_2$(DBA)$_3$, P(*o*-tol)$_3$, and *p*-bromoanisole for 24 h produced a ~1:1 mixture of **3**:**7**.[10] ^{31}P NMR analysis of the crude reaction mixtures in the syntheses of aryl iodide dimers **4**−**6** showed no evidence for formation of the diiodide mono(phosphine) dimer {Pd[P(*o*-tol)$_3$]I(μ-I)}$_2$.[11]

Scheme 4



Synthesis of Palladium Aryl Chloride Dimers. Due to the low cost and wide availability of aryl chlorides, the palladium-catalyzed cross-coupling of amines with aryl chlorides represents a significant and as yet unrealized transformation.[12] Because the palladium aryl chloride dimers {Pd[P(*o*-tol)$_3$](Ar)(μ-Cl)}$_2$ are the potential intermediates in these transformations, we have also investigated their coordination chemistry. However, because the direct oxidative addition of aryl chlorides to Pd$_2$(DBA)$_3$/P(*o*-tol)$_3$-derived catalysts has not yet been demonstrated, palladium chloride dimers were generated via silver-mediated halide exchange from the corresponding bromide or iodide dimers. For example, when a suspension of iodide dimer **5** and AgOTf in CH$_3$CN was stirred for 2 min, a yellow solution of Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)(CH$_3$CN)$_2$]$^+$OTf$^-$ (**8**) was formed and treated with LiCl without isolation (Scheme 4). The resulting cream-colored suspension was evaporated, extracted with toluene, and precipitated with hexane to give the aryl chloride dimer {Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)(μ-Cl)}$_2$ (**9**) in 93% yield. Dimer **9** was characterized by ^{1}H NMR, ^{31}P NMR, and elemental analysis. By a similar procedure, the chloride dimer {Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$CMe$_3$)(μ-Cl)}$_2$ (**10**) was formed from bromide dimer **1** via the bis(acetonitrile) adduct Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$CMe$_3$)(CH$_3$CN)$_2$]$^+$OTf$^-$ (**11**).

Attempts to isolate the bis(acetonitrile) adducts **8** and **11** by concentration of solvent or by precipitation with ether led to rapid decomposition. However, the corresponding cations Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)(CD$_3$CN)$_2$]$^+$OTf$^-$ (**8**-(CD$_3$CN)$_2$) and Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$CMe$_3$)(CD$_3$CN)$_2$]$^+$-

(9) Bennett, M. A.; Longstaff, P. A. *J. Am. Chem. Soc.* **1969**, *91*, 6266.

(10) The origin of dibromide complex **7** is not clear. The reaction of *p*-bromoanisole with Pd$_2$(DBA)$_3$ and P(*o*-tol)$_3$ in C$_6$D$_6$ did not produce detectable quantities of the palladium bis(*p*-anisole) complex Pd[P(*o*-tol)$_3$]$_2$(*p*-anisole)$_2$ (as determined by ^{1}H NMR) or its reductive-elimination product 4,4′-dimethoxybiphenyl (as determined by GCMS analysis), which suggests that **7** is not formed by disproportionation of **3**. Similarly, products derived from insertion of DBA into a palladium−anisyl bond followed by β-hydrogen elimination, such as PhCHCHC(O)C(*p*-anisyl)CHPh or PhCHCHC(O)CHC(*p*-anisyl)Ph, were not detected. Such a process would presumably lead to the formation of free HBr via reductive elimination from the initially formed palladium bromide hydride complex. However, GC−MS analysis of the reaction mixture indicated the presence of significant quantities of anisole, which may suggest the presence of an electron transfer process. We thank a reviewer for suggesting this mechanism.

$$ArBr + L_2Pd^{(0)} \longrightarrow Pd^{(I)}Br(L)_2 + Ar^{\cdot}$$

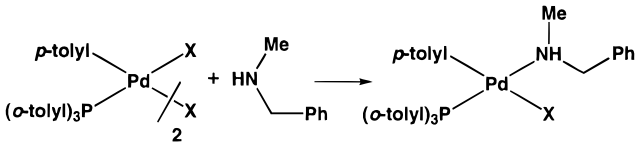
$$2Pd^{(I)}Br(L)_2 \longrightarrow 2Pd^{(II)}Br_2(L)_2 + L_2Pd^{(0)}$$

$$Ar^{\cdot} \longrightarrow ArH$$

(11) Reaction of PdI$_2$ and excess P(*o*-tol)$_3$ (2 equiv) forms only the mono(phosphine) diiodide complex {Pd[P(*o*-tol)$_3$]I(μ-I)}$_2$ and none of the corresponding bis(phosphine) monomer (see Experimental Section).

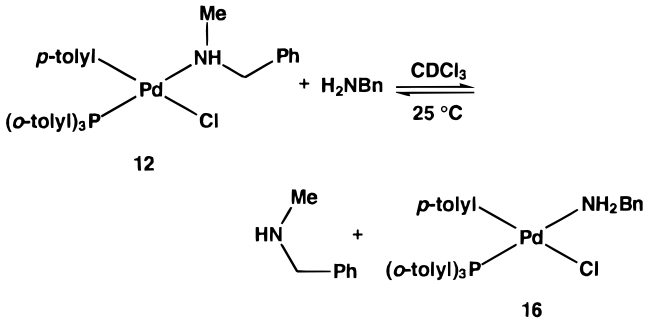
(12) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047.

Scheme 5



X	halide dimer	amine adduct	isolated yield
Cl	**9**	**12**	85
Br	**2**	**13**	83
I	**5**	**14**	71

Scheme 6



OTf^- (**11**-$(CD_3CN)_2$) were generated in CD_3CN and were analyzed without isolation by ^1H, ^{31}P, and ^{19}F NMR spectroscopy. The ^1H NMR spectrum of **8**-$(CD_3CN)_2$ at 75 °C displayed a singlet at δ 2.25 for the time-averaged P(*o*-tol)$_3$ methyl groups and a peak at δ 2.09 for the *p*-tolyl methyl group. As the temperature was lowered, the signals for the P(*o*-tol)$_3$ methyl groups broadened and split into three resonances at δ 3.11, 2.13, and 1.53 at −47 °C. In the ^{19}F NMR spectrum of **8**-$(CD_3CN)_2$ no resonances were observed which could be assigned to coordinated OTf. Similar bis(acetonitrile) or bis(solvent) palladium complexes have been generated via reaction of palladium halide complexes with silver salts.[13]

Synthesis of Palladium Amine Complexes. Amines reacted rapidly (<1 min) with palladium halide dimers via cleavage of the halide bridge to produce monomeric palladium amine complexes (Scheme 5).[8] For example, addition of *N*-benzylmethylamine (5 equiv) to a yellow benzene solution of the chloride dimer **9** gave a clear solution from which the 1:1 palladium amine adduct Pd[P(*o*-tol)$_3$](*p*-C_6H_4Me)[HN(Me)Bn]Cl (**12**) precipitated in 85% yield as a white microcrystalline solid. Amine adduct **12** was characterized by spectroscopy and by elemental analysis, and a *trans* orientation of the amine and phosphine ligands is inferred by analogy to the corresponding benzylamine derivative (see below). The ^1H NMR spectrum of **12** ($CDCl_3$, 55 °C) displayed a resonance at δ 2.07 for the methyl group of the *p*-tolyl ligand and a broad peak at δ 2.3 ($\omega_{1/2}$ = 70 Hz) for the methyl groups of the P(*o*-tol)$_3$ ligand. Coordination of amine to palladium was confirmed by resonances for the diastereotopic benzyl protons at δ 4.39 (br t, J = 12.4 Hz) and 3.47 (dd, J = 7.0, 12.5 Hz). The presence of an NH proton was confirmed by a ^1H NMR resonance at δ 3.22, which diminished in intensity upon addition of D_2O.

The related 1:1 palladium bromide and iodide *N*-benzylmethylamine adducts were more soluble than complex **12** and were synthesized by a modified procedure. Addition of *N*-benzylmethylamine to a yellow methylene chloride solution of bromide dimer **2** gave a clear solution. Concentration of the solution and addition of hexane gave the 1:1 palladium amine adduct Pd[P(*o*-tol)$_3$](*p*-C_6H_4Me)[HN(Me)Bn]Br (**13**) in 83% yield. Likewise, reaction of *N*-benzylmethylamine with the palladium iodide dimer led to the isolation of the amine adduct Pd[P(*o*-tol)$_3$](*p*-C_6H_4Me)[HN(Me)Bn]I (**14**) in 71% yield. Unlike the corresponding chloride (**12**) and bromide adducts (**13**), the room-temperature ^1H NMR spectrum of **14** revealed an equilibrium mixture of **14** and **5** (~80:20) and HN(Me)Bn.[14] An excess of *N*-benzylmethylamine (0.03 M) was required to effect complete conversion (>95% by ^1H NMR) of **5** to **14** in solution at room temperature.

Palladium amine adducts **13** and **14** were also formed as the exclusive products in the reaction of *N*-benzylmethylamine, $Pd_2(DBA)_3$, P(*o*-tol)$_3$, and *p*-bromotoluene or *p*-iodotoluene, respectively, in C_6D_6. Isolation of **13** or **14** from the corresponding preparative-scale reactions was complicated by the comparable solubility of free DBA. However, the related amine adduct Pd[P(*o*-tol)$_3$](*p*-C_6H_4OMe)[HN(CH_3)Bn]Br (**15**) was isolated in 51% yield from reaction of *p*-bromoanisole, *N*-benzylmethylamine, $Pd_2(DBA)_3$, and P(*o*-tol)$_3$. The formation of the 1:1 palladium amine adducts **13**−**15** from mixtures of $Pd_2(DBA)_3$ and P(*o*-tol)$_3$ is consistent with the intermediacy of the 1:1 amine adducts in the $Pd_2(DBA)_3$/P(*o*-tol)$_3$-catalyzed cross-coupling of aryl halides and amines.

Although the chloride adduct **12** was thermodynamically stable, the coordinated *N*-benzylmethylamine was kinetically labile and was readily displaced by free amine. For example, addition of benzylamine to a solution of **12** in $CDCl_3$ revealed resonances in the ^1H NMR spectrum after <1 min corresponding to benzylamine, *N*-benzylmethylamine, **12**, and Pd[P(*o*-tol)$_3$](*p*-C_6H_4Me)[H_2NBn]Cl (**16**), where K = [**16**][HN(Me)Bn]/[**12**][benzylamine] ≈ 4 at 25 °C (Scheme 6).[14] The ^1H NMR spectrum obtained after 15 min was identical with that obtained directly after addition of benzylamine, consistent with rapid approach to equilibrium. Likewise, addition of HN(Me)Bn to a $CDCl_3$ solution of **16** generated an equilibrium mixture of **12**, **16**, HN(Me)Bn, and benzylamine. Pure **16** was isolated in 70% yield from reaction of benzylamine with **9**, although the synthesis was complicated by formation of the bis(benzylamine) complex Pd(*p*-C_6H_4Me)[H_2NBn]$_2$Cl.[15]

The stereochemistry of the 1:1 palladium amine adducts was determined from the ^{31}P NMR spectra of the ^{15}N-labeled benzylamine adducts Pd[P(*o*-tol)$_3$](*p*-C_6H_4Me)[$H_2{}^{15}$NBn]Cl (**16**-^{15}N) and Pd[P(*o*-tol)$_3$](*p*-C_6H_4Me)[$H_2{}^{15}$NBn]Br (**17**-^{15}N). **16**-^{15}N displayed a doublet in the $^{31}P\{^1H\}$ NMR spectrum at δ 28.3 (J_{PN} = 40.0 Hz), while the bromide derivative **17**-^{15}N displayed a doublet at δ 27.7 (J_{PN} = 40.1 Hz). The J_{PN} values observed for **16**-^{15}N and **17**-^{15}N are consistent with *trans*-phosphine

(13) (a) Valk, J. M.; Maassarani, F.; van der Sluis, P.; Spek, A. L.; Boersma, J.; van Koten, G. *Organometallics* **1994**, *13*, 2320. (b) Vicente, J.; Saura-Llamas, I.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1993**, 3619.

(14) The equilibrium constant for the formation of palladium amine adducts from the corresponding halide dimers is dependent on both the halide ligand and the amine: Widenhoefer, R. A.; Buchwald, S. L. *Organometallics* **1996**, *15*, 2755.

(15) The rate and extent of formation of bis(amine) complexes was dependent on both the amine and the halide ligand. We are currently investigating the formation of palladium bis(amine) complexes in detail as a potential chain-limiting step in the catalytic cross-coupling of aryl bromides and primary amines.

and amine ligands.[16] For example, in a series of rhodium complexes containing amine and phosphine ligands, *trans*-J_{PN} ranged from 35 to 45 Hz, while *cis*-J_{PN} was consistently <5 Hz.[16a]

Conformations and Interchange Mechanisms of M[P(*o*-tol)$_3$] Complexes. In his initial report, Migita noted that the P(*o*-tol)$_3$ ligand was crucial to the success of the palladium-catalyzed cross-coupling of aryl bromides and aminostannanes.[1] The use of P(*o*-tol)$_3$ has also been shown to produce higher reaction rates than PPh_3 in both the palladium-catalyzed Heck arylation reaction[17] and Stille reaction.[18] The enhanced activity of P(*o*-tol)$_3$ has typically been attributed to the steric bulk of the P(*o*-tol)$_3$ ligand, which promotes both phosphine lability and coordinative unsaturation of the metal.[18] In addition, P(*o*-tol)$_3$ can also undergo cyclometalation of the *o*-methyl group with electrophilic transition metals[17,19] to generate catalysts of unusually high activity. For example, Herrmann and Beller have recently shown that P(*o*-tol)$_3$ reacts with $Pd(OAc)_2$ to form the acetate-bridged cyclometalated dimer {Pd[P(*o*-tol)$_2$-*o*-$C_6H_4CH_2$](μ-OAc)}$_2$, which was an extremely active catalyst for both the Heck arylation reaction[20] and the Suzuki cross-coupling reaction.[21]

Of the potential conformations available to rotationally restricted triaryl systems,[22] two conformations of P(*o*-tol)$_3$ are accessible and have been observed in structurally characterized metal complexes. The *exo*$_3$ conformation[23] orients the three *o*-methyl groups toward the metal atom (*exo*), with each *o*-tolyl ring rotated approximately 60° off the M−P−*ipso*-C plane (Figure 1). The *exo*$_2$ conformation[24] possesses two *exo* *o*-tolyl groups in an orientation similar to those in the *exo*$_3$ conformer, while the third *o*-methyl group is directed away from the metal atom (*endo*) with the *o*-tolyl ring rotated only slightly off the M−P−*ipso*-C plane (~15°). The *exo*$_2$ conformation decreases the phosphine cone angle ~35° relative to the *exo*$_3$ conformation at the expense of approximately 9 kcal mol^{-1} increased strain energy between the *o*-tolyl groups.[25] For example, Tolman calculated a cone angle for *exo*$_3$-P(*o*-tol)$_3$ of 195° from space-filling CPK models with a M−P bond distance of 2.28 Å,[26] while a cone angle of 198° was determined from the crystal structure of the mercury perchlorate dimer {Hg[ClO_4][P(*o*-tol)$_3$](μ-Cl)}$_2$.[27] Conversely, a cone angle of 160° was calculated from the crystal structure of the *exo*$_2$-P(*o*-tol)$_3$ chromium dicarbonyl complex (*p*-xylene)Cr(CO)$_2$P(*o*-tol)$_3$.[28] Both the *exo*$_3$ and *exo*$_2$ P(*o*-tol)$_3$ conformers are chiral due to the screw axis generated by the propeller-like arrangement of the *o*-tolyl rings.

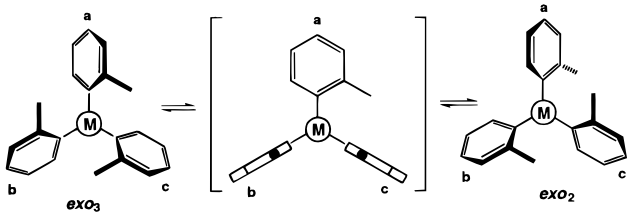


Figure 1. The two-ring-flip mechanism for interconversion of the *exo*$_3$ and *exo*$_2$ conformations of the P(*o*-tol)$_3$ ligand, as viewed down the M−P axis.

Because of the steric congestion about the *o*-tolyl rings, rotation about a single P−*ipso*-C bond requires correlated rotation about the other two P−*ipso*-C bonds. These rotations are often of sufficient energy to generate configurationally stable conformers and enantiomers on the NMR time scale. The mechanisms for the correlated rotation of sterically hindered triaryl systems were originally proposed by Kruland.[29] The lowest energy process for P−C bond rotation in P(*o*-tol)$_3$ complexes involves rotation of one ring (Figure 1, ring a) through the plane perpendicular to the M−P−*ipso*-C plane with correlated rotation of the other two rings (Figure 1, rings b and c) through the corresponding M−P−*ipso*-C planes.[30] This two-ring-flip mechanism[29] interconverts the *exo*$_2$ and *exo*$_3$ isomers and necessarily inverts the helicity of the phosphine; consecutive two-ring flips then leads to complete interchange of the *o*-tolyl rings.

Fluxional Behavior and Solution Structure of 13. The ^{1}H NMR spectrum of bromide adduct **13** in CD_2Cl_2 at −42 °C displayed a 1:1:1 ratio of three sets of P(*o*-tol)$_3$ methyl resonances at δ 3.30, 3.50, 3.27 (~8:2:1), δ 2.39, 2.14, 2.26 (~8:2:1), and δ 1.54, 1.61, 1.58

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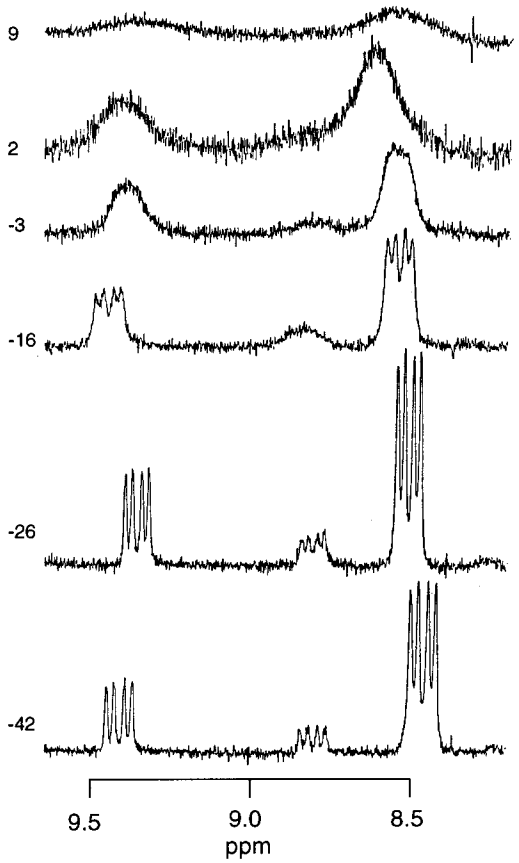

Figure 2. Variable-temperature ^{1}H NMR spectrum of the H-6 resonance of the *endo*-P(*o*-tol)$_3$ ring of **13** in CD_2Cl_2. Temperatures are given in °C.

(~8:2:1).[31] As the temperature was raised, the P(*o*-tol)$_3$ methyl resonances broadened and coalesced at 24 °C, forming a single broad resonance at δ 2.30 ($\omega_{1/2}$ = 95 Hz) at 55 °C ($CDCl_3$). In addition, the −42 °C spectrum displayed a ~2:1:8 ratio of high-frequency peaks at δ 9.36 (dd, J = 7.33, 18.7 Hz), 8.71 (dd, J = 8.2, 18.1 Hz), and 8.36 (dd, J = 8.0, 17.6 Hz) (Figure 2), which integrated to one proton. As the temperature was raised, these resonances broadened and coalesced at ~15 °C (Figure 2), eventually forming a broad three-proton resonance at δ 7.5−8.0 at 55 °C ($CDCl_3$). The *p*-tolyl methyl resonance, which was observed as a sharp singlet at δ 2.05 at 55 °C in $CDCl_3$, broadened slightly but did not split upon cooling to −50 °C (CD_2Cl_2). Resonances corresponding to the coordinated amine were broadened and uninformative at low temperatures.

The ^{1}H NMR spectrum of **13** at −42 °C is consistent with two processes: (1) hindered rotation about the P−*ipso*-C bonds with predominant formation of the *exo*$_2$-P(*o*-tol)$_3$ conformer and (2) hindered rotation about the Pd−P bond with formation of three unequally populated rotamers (see below). The high-frequency resonance at δ 8.36 (dd, J = 8.0, 17.6 Hz, major isomer) is indicative of the *exo*$_2$-P(*o*-tol)$_3$ conformation as the H-6 proton of the *endo*-P(*o*-tol)$_3$ ring is forced into close proximity to the palladium d_{z^2} orbital. The H-6 proton then experiences a downfield shift due to the paramagnetic anisotropy of the palladium atom.[32] A similar chemical shift and J_{PH} value (δ 9.27 (d, J_{PH} = 16 Hz)) was

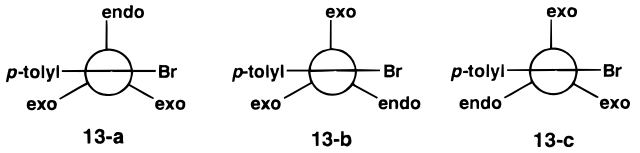

Figure 3. Pd−P bond rotamers of the *exo*$_2$-P(*o*-tol)$_3$ ligand in **13** relative to the *p*-tolyl and bromide ligands, as viewed down the N−Pd−P axis (amine not shown).

observed for the H-6 proton of the *endo*-P(*o*-tol)$_3$ ring in the ^{1}H NMR spectrum of the palladium complex Pd[P(*o*-tol)$_3$][hfac]$_2$ (hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate).[33] Similarly, the bis(phosphine)palladium complex Pd[P(*t*-Bu$_2$Ph)]$_2$ displayed a resonance at δ 9.33 for the deshielded *ortho* phenyl protons.[34]

The formation of a 1:1:1 ratio of P(*o*-tol)$_3$ methyl resonances at δ 3.30, 2.39, and 1.54 (major isomer) is expected for a static *exo*$_2$-P(*o*-tol)$_3$ ligand. One *o*-methyl group is distinguished by its *endo* orientation; the two *exo*-*o*-methyl groups are inequivalent due to the helicity of the phosphine, which orients one *o*-methyl group toward an *endo*-*o*-tolyl ring and one *o*-methyl group toward an *exo*-*o*-tolyl ring (Figure 1). The failure to detect *p*-tolyl or P(*o*-tol)$_3$ methyl resonances which did not correlate with a high-field resonance indicates that the concentration of the *exo*$_3$ isomer (which would display *p*-tolyl and P(*o*-tol)$_3$ methyl resonances but no high-field resonance) must be small (<10%).

The 2:1:8 multiplicity of both the 1:1:1 P(*o*-tol)$_3$ methyl groups and the high-field H-6 *endo*-*o*-tolyl resonance of **13** in the ^{1}H NMR spectrum at −42 °C is consistent with hindered rotation about the Pd−P bond with the formation of three unequally populated rotamers. Three gauche rotamers of the P(*o*-tol)$_3$ ligand which differ in the relative orientation of the *endo*-P(*o*-tol)$_3$ ring to the *cis*-bromide and *p*-tolyl ligands are depicted in Figure 3. Presumably, the highest frequency H-6 *endo*-P(*o*-tol)$_3$ resonance (δ 9.36) corresponds to rotamer **13a**, in which the *endo* ring is in closest proximity to the d_{z^2} orbital. However, halide ligands have also been shown to induce downfield shifts in proximal aromatic resonances.[35] Hindered rotation of M−P bonds with formation of rotamers in metal complexes possessing bulky phosphine ligands has been observed. For example, the bis(phosphine) carbonyl chloride complexes M[P(*t*-Bu)$_2$Et]$_2$(CO)Cl (M = Ir,[36] Rh[37]) displayed resonances corresponding to three rotamers in the low-temperature ^{31}P NMR spectrum.

The presence of a single P(*o*-tol)$_3$ resonance at δ 2.33 in the ^{1}H NMR spectrum of **13** at 55 °C is consistent with rapid rotation about both the Pd−C and Pd−P bonds. Although P−C rotation in P(*o*-tol)$_3$ complexes is typically of higher energy than M−P rotation, the

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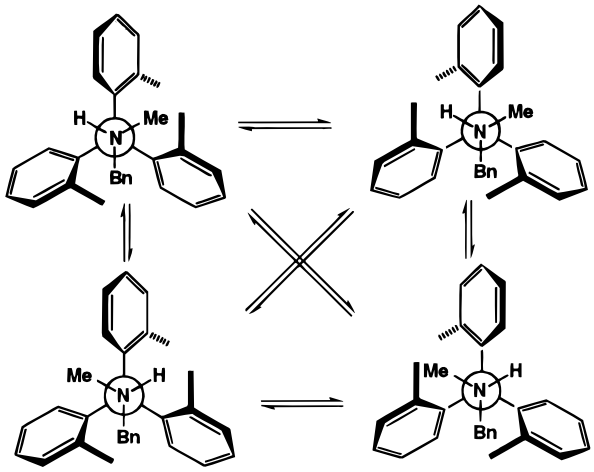

Figure 4. Potential diastereomers of **13** as viewed down the N−Pd−P bond. Diastereomers are related horizontally by inversion of phosphine helicity and vertically by amine inversion; enantiomers are related diagonally.

simultaneous coalescence of all nine P(*o*-tol)$_3$ methyl resonances indicates that the two processes possess comparable rotational barriers. The simultaneous coalescence of the P(*o*-tol)$_3$ methyl resonances may result from correlated P−C and Pd−P rotation due to intermeshing of the phosphine *o*-tolyl rings with the *p*-tolyl ligand. The presence of diastereotopic benzyl protons of the coordinated HN(Me)Bn ligand at 55 °C requires that chirality of the amine be static on the NMR time scale.

Although hindered Pd−P bond rotation has precedence and adequately accounts for the 2:1:8 isomer ratio observed in the low-temperature ^{1}H NMR spectrum of **13**, hindered Pd−P bond rotation is not required to produce the observed isomers. For example, because both the phosphine and the amine are chiral on the NMR time scale, two sets of diastereomers of **13** are possible (Figure 4). In addition, three geometric isomers, two of which possess *cis*-amine and phosphine ligands, are also possible (Figure 5). As a result, a combination of diastereomers and geometric isomers could account for the observed 2:1:8 ratio of isomers in **13**. In an effort to probe for the presence of these potential isomers, we investigated the variable-temperature ^{31}P{^{1}H} NMR spectrum of **16**-^{15}N, which possesses an achiral, ^{15}N-labeled amine.

The ^{31}P{^{1}H} NMR spectrum of **16**-^{15}N at −42 °C displayed a ∼2:1.3:1 ratio of doublets at δ 27.6 (J_{PN} = 36.8 Hz), 26.9 (J_{PN} = 35.6 Hz), and 23.9 (J_{PN} = 37.4 Hz), consistent with *trans* phosphine and amine ligands (Figure 6). As the temperature was raised, these doublets collapsed and eventually formed a doublet at δ 26.4 (J_{PN} = 40.1 Hz) at 35 °C. In addition, a small doublet at δ 27.1 (J_{PN} = 36.6 Hz) was observed at −33 °C which accounted for <10% of the total isomers and may correspond to a small amount of an *exo*$_3$-P(*o*-tol)$_3$ isomer. The presence of multiple isomers which all possess *trans*-phosphine and amine ligands in the low-temperature ^{31}P NMR spectrum of **16**-^{15}N suggests that the low-temperature isomers of **13** also correspond to neither geometric isomers nor diastereomers. The failure to observe diastereomers in **13** as a result of amine chirality indicates that either one set of diastereomers is highly favored relative to the second set or that chirality at nitrogen does not significantly perturb the chemical shifts of the P(*o*-tol)$_3$ proton resonances.

Amine adducts **12** and **14** displayed temperature-dependent ^{1}H NMR behavior analogous to that displayed by bromide derivative **13**; at −42 °C, each complex displayed three high-frequency H-6 *endo*-P(*o*-tol)$_3$ resonances (Table 1) along with the corresponding P(*o*-tol)$_3$ methyl resonances. Because the chemical shifts for the P(*o*-tol)$_3$ methyl groups were similar for each complex, the coalescence temperature (T_c; Table 1) is directly related to the rotational barrier for each complex. Comparison of T_c values (Table 1) reveals that T_c increased in the order **12** < **13** < **14**, which corresponds to the van der Waals radius of the *cis*-halide ligand (Cl (1.75 Å) < Br (1.85 Å) < I (1.96 Å)],[38] presumably due to increased steric interaction of the P(*o*-tol)$_3$ ligand with increasing halide size. The steric bulk of ancillary ligands has been shown to increase the rotational barriers of P−C and M−P bonds of PPh$_3$ and P(*o*-tol)$_3$ complexes.[39]

Chelated Palladium Amine Complexes. Palladacyclic amine complexes are of interest as potential intermediates in the Pd-catalyzed intramolecular amination of haloamines.[40] A series of chelating palladium amine complexes was synthesized in a one-pot procedure analogous to that employed in the synthesis of **17**. For example, reaction of Pd$_2$(DBA)$_3$, P(*o*-tol)$_3$, and *N*-benzyl-*o*-iodophenethylamine in benzene for 24 h at room temperature led to the isolation of the six-membered palladacycle Pd[P(*o*-tol)$_3$][2-C$_6$H$_4$(CH$_2$)N(H)Bn]I (**18**) in 71% yield. By a similar procedure, the five-membered palladacyles Pd[P(*o*-tol)$_3$][2-C$_6$H$_4$(CH$_2$)N(H)*p*-tolyl]Br (**19**) and Pd[P(*o*-tol)$_3$][2-C$_6$H$_4$(CH$_2$)^{15}N(H)Ph]Br (**20**) and the seven-membered palladacycle Pd[P(*o*-tol)$_3$][2-C$_6$H$_4$(CH$_2$)$_3$-N(H)Bn]Br (**21**) were also isolated.

The ^{1}H NMR spectra of the five-membered palladacycles were similar to those of the corresponding acyclic derivatives. For example, **20** displayed a 1:2.6:2.6 ratio of high-field resonances at δ 9.54 (br d, J = 17.2 Hz), 8.78 (dd, J = 7.05, 15.5 Hz), and 8.28 (dd J = 8.6, 17.5 Hz) in the low-temperature ^{1}H NMR spectrum (Figure 7, Table 1), and a 2.6:2.6:1 ratio of doublets at δ 36.8 (J_{PN} = 36.3 Hz), 34.1 (J_{PN} = 37.0 Hz), and 28.7 (J_{PN} = 36.3 Hz) in the low-temperature ^{31}P{^{1}H} NMR spectrum (Figure 7, Table 1). Complexes **18** and **21** were somewhat unusual, as only a single isomer was detected by low-temperature ^{1}H and ^{31}P NMR spectroscopy. As was anticipated, chelation promotes coordination of amine to the palladium atom. For example, the ^{1}H NMR spectrum of iodide complex **18** at 55 °C showed no evidence for amine dissociation and formation of a palladium iodide dimer, in contrast to the acyclic iodide derivative **14**, which was ∼35% dissociated at room temperature.

The chelated amine complexes **18**−**20** displayed higher coalescence temperatures (T_c) for the P(*o*-tol)$_3$ methyl resonances than did the corresponding acyclic derivatives (Table 1). In the chelated amine complexes, the

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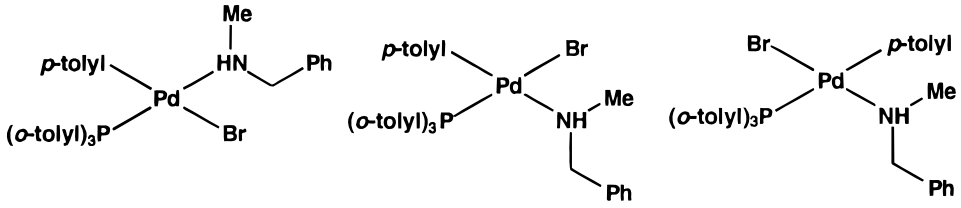

Figure 5. Potential geometric isomers of **13**.

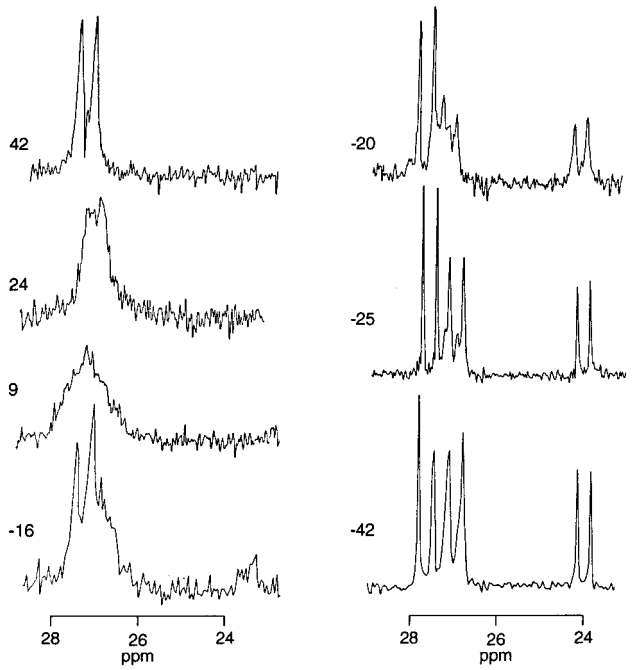

Figure 6. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **16**-^{15}N in $CDCl_3$. Temperatures are given in °C.

aryl ring is forced to lie in or near the coordination plane.[41] Although this orientation may not produce excessive ground-state interaction between the H-6 proton of the palladium-bound aryl ligand and the phosphine-bound *o*-tolyl groups due to potential intermeshing, rotation about the Pd−P or P−C bonds will clearly produce a high-energy interaction. Conversely, the palladium: bound *p*-tolyl ligand of the corresponding acyclic amine complexes is able to rotate about the P−C bond and adopt an orientation perpendicular to the coordination plane either in the ground state or as a transition state for Pd−P and/or P−C rotation.[42] The very high coalescence temperature (85 °C) of **18** apparently results from the combination of the large iodide ligand and the chelated aryl ring.

Conclusions

Reaction of aryl bromides or aryl iodides with a mixture of $Pd_2(DBA)_3$ and P(*o*-tol)$_3$ can be employed to generate gram quantities of the corresponding palladium halide dimers in a single step as pure material. These halide dimers undergo a rapid bridge cleavage reaction with amines to form the corresponding 1:1 palladium amine adducts which possess *trans* phosphine and amine ligands. The amine complexes are also formed as the exclusive product in the reaction of $Pd_2(DBA)_3$ and P(*o*-tol)$_3$ with aryl halide and amine. Variable-temperature ^1H and ^{31}P NMR analysis of the palladium amine adducts was consistent with hindered rotation about the P−C bonds, with predominant formation of the *exo*$_2$-P(*o*-tol)$_3$ conformer and hindered rotation about the Pd−P bond. The barriers for rotation about the P−C and Pd−P bonds were sensitive to the steric bulk of the ligands *cis* to the phosphine ligand. We are currently investigating the effect of both the halide ligand and the amine on the equilibrium formation and reactivity of the 1:1 palladium amine adducts and the relevance of these processes on the Pd-catalyzed cross-coupling of amines and aryl halides. In addition, we are investigating the formation of palladium bis(amine) complexes as a potential chain-limiting step in the catalytic process.

Experimental Section

General Methods. Palladium halides, $Pd_2(DBA)_3$, aryl halides, amines, and phosphines were manipulated in air. All other manipulations and all reactions were performed under an atmosphere of nitrogen or argon in an inert-atmosphere glovebox or by standard Schlenk techniques. Preparative-scale reactions were performed in flame or oven-dried Schlenk tubes equipped with a stirbar, side-arm joint, and a septum. NMR spectra were obtained on a Varian XL−300 spectrometer in $CDCl_3$ at ambient temperature unless otherwise noted. ^1H and $^{13}C\{^1H\}$ (75.6 MHz) spectra were referenced relative to the residual solvent peak. Room-temperature ^{31}P NMR (96 MHz) spectra were referenced relative to external 85% H_3PO_4; low-temperature ^{31}P NMR spectra were referenced relative to external PPh_3 in $CDCl_3$ (δ −4.69). Probe temperatures were calibrated with a 0.3% solution of HCl in methanol. IR spectra were recorded on a Perkin-Elmer Model 6000 FTIR spectrometer. Elemental analyses were performed by E+R Analytical Laboratories (Corona, NY).

Diethyl ether, hexane, pentane, benzene, and benzene-d_6 were distilled from purple solutions of sodium and benzophenone under argon or nitrogen. THF-d_8 and dioxane-d_8 were distilled from Na/K alloy, methylene chloride and methylene chloride-d_2 were distilled from CaH_2, and $CDCl_3$ was distilled from P_2O_5. $Pd_2(DBA)_3$ (Strem),[43] P(*o*-tol)$_3$ (Strem), 1-bromo-4-*tert*-butylbenzene (Fluka), 1-iodo-4-*tert*-butylbenzene (Lancaster), *p*-bromotoluene (Aldrich), *p*-iodotoluene (Lancaster), *p*-bromoanisole (Aldrich), and *p*-iodoanisole (Aldrich) were used as received. LiI (Aldrich), LiCl (Mallinckrodt), and LiBr (Aldrich) were dried at 80 °C under vacuum prior to use. *N*-Benzylmethylamine and benzylamine were purchased from Aldrich and were distilled from CaH_2 under N_2 prior to use.

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(43) The stoichiometry and purity of $Pd_2(DBA)_3$ was confirmed by elemental analysis. Anal. Calcd (found) for $C_{51}H_{42}O_3Pd$: C, 66.9 (67.16); H, 4.6 (4.75); Pd, 23.2 (23.08).

Table 1. Low−Temperature ^{1}H NMR Data for Complexes 12−14 and 18−21

cmpd	temp (°C)	H-6 *endo*-P(*o*-tol)$_3$ resonance (δ)	P(*o*-tol)$_3$ methyl resonances (δ)	isomer ratio	T_c (±5 °C)[a]
12	−42[b]	9.33 (dd, J = 8.3, 17.6 Hz)	3.35, 2.00, 1.42	1.5	0[b]
		8.71 (dd, J = 7.8, 18.0 Hz)	3.12, 2.11, 1.41	1	
		8.34 (dd, J = 7.9, 17.0 Hz)	3.15, 2.24, 1.43	10	
13	−42[b]	9.36 (dd, J = 7.2, 18.6 Hz)	3.50, 2.14, 1.61	2.5	25[b]
		8.71 (dd, J = 7.1, 18.1 Hz)	3.27, 2.26, 1.58	1	
		8.36 (dd, J = 7.8, 17.6 Hz)	3.30, 2.39, 1.54	8.4	
14	−16[b]	9.46 (dd, J = 8, 18 Hz)	3.32, 1.93, 1.37	5	55[c]
		8.7 br		1	
		8.42 (dd, J = 8, 18 Hz)	3.48, 2.03, 1.48	5	
18	−42[b]	9.49 (dd, J = 8.2, 18.1 Hz)	3.17, 1.51, 0.83		65[d]
19	−42[b]	9.54 (br d, J = 18 Hz)	2.85, 1.32, 1.53	1	65[d]
		8.78 (dd, J = 8.4, 17.7 Hz)	3.12, 1.82, 1.58	2.6	
		8.38 (dd, J = 7.8, 17.7 Hz)	2.73, 1.94, 1.55	2.6	
20	8[c]	9.54 (br d, J = 17.2 Hz)	2.82, 1.30, 1.52	1	85[d]
		8.73 (dd, J = 7.1, 15.5 Hz)	3.11, 1.92, 1.57	2.6	
		8.28 (dd, J = 8.6, 17.5 Hz)	2.66, 1.79, 1.55	2.6	
21	8[c]	9.50 (dd, J = 7.8, 16.5 Hz)	3.18, 1.98, 0.92		

[a] Coalescence temperature for P(*o*-tol)$_3$ methyl resonances. [b] CD_2Cl_2. [c] $CDCl_3$. [d] Toluene-d_8.

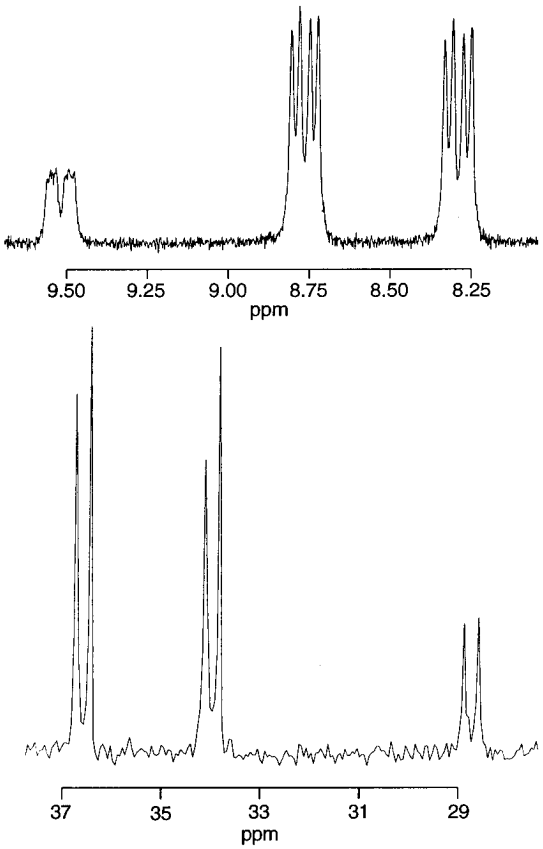
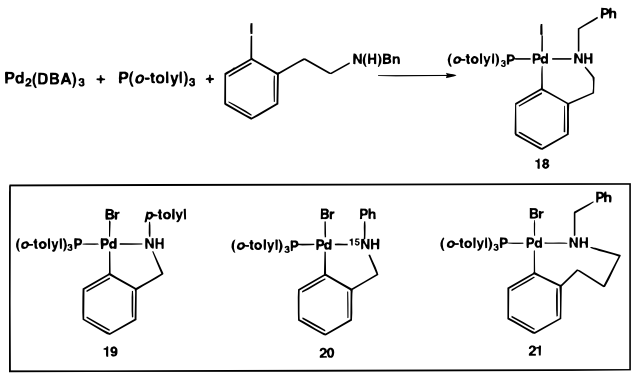


Figure 7. H-6 resonance of the *endo*-P(*o*-tol)$_3$ ring in the ^{1}H NMR spectrum (top) and ^{31}P{^{1}H} NMR spectrum (bottom) of **20** at −42 °C in CD_2Cl_2.

Benzylamine-^{15}N (Isotech) and aniline-^{15}N (Cambridge Isotope Laboratories) were used as received. *N*-benzyl-*o*-iodophenethylamine and *N*-benzyl-3-(*o*-bromophenyl)propylamine were synthesized by published procedures.[7a]

{**Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$CMe$_3$)(*μ*-Br)**}$_2$ **(1).**[8] A purple solution of $Pd_2(DBA)_3$ (1.5 g, 1.6 mmol), P(*o*-tol)$_3$ (2.0 g, 6.6 mmol), and *p*-*tert*-butyl bromobenzene (3.2 g, 14.7 mmol) in 80 mL of benzene was stirred at room temperature for 1 h. The resulting green-brown solution was filtered through Celite, and benzene was evaporated under vacuum. Addition of Et_2O (100 mL) to the oily residue formed a precipitate over 4 h, which was filtered, washed with Et_2O, and dried under vacuum to give **1** (1.4 g, 69%) as a yellow powder. ^{1}H NMR (55 °C): δ 7.24, 7.11, 7.03, 6.68, 6.48 (d, J = 8.2 Hz), 2.14 [br, 9 H, P(*o*-tol)$_3$], 1.08 (C$_6$H$_4$C*Me*$_3$). ^{31}P{^{1}H} NMR: δ 28.7 (br). Anal. Calcd (found) for $C_{62}H_{68}Br_2P_2Pd_2$: C, 59.68 (59.78); H, 5.49 (5.51); Br, 12.81 (12.62).

Scheme 7



{**Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)(*μ*-Br)**}$_2$ **(2).**[8] Reaction of $Pd_2(DBA)_3$ (500 mg, 0.55 mmol), P(*o*-tol)$_3$ (700 mg, 2.3 mmol), and 4-bromotoluene (1.4 g, 8.2 mmol) using a procedure analogous to that used to prepare **1** led to the isolation of **2** (480 mg, 76%) as a bright yellow powder which contained 0.4 Et_2O/Pd by ^{1}H NMR analysis. ^{1}H NMR (55 °C): δ 7.65 (br), 7.26 (m), 7.07 (br), 6.58 (br), 6.30 (d, J = 7.71 Hz), 2.18 [br, 9 H, P(*o*-tol)$_3$], 1.98 (C$_6$H$_4$*Me*). ^{31}P{^{1}H} NMR: δ 28.4 (br).

{**Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$OMe)(*μ*-Br)**}$_2$ **(3).** Reaction of $Pd_2(DBA)_3$ (250 mg, 0.27 mmol), P(*o*-tol)$_3$ (330 mg, 1.1 mmol), and 4-bromoanisole (510 mg, 2.7 mmol) using a procedure analogous to that used to prepare **1** led to the isolation of **3** (152 mg, 46%) as a bright yellow powder which contained traces (<5%) of Et_2O by ^{1}H NMR analysis. ^{1}H NMR (55 °C): δ 7.55 (br), 7.29 (m), 7.06 (br), 6.59 (br), 6.15 (d, J = 7.95 Hz), 3.53 (C$_6$H$_4$*OMe*), 2.19 [br, 9 H, P(*o*-tol)$_3$]. ^{31}P{^{1}H} NMR: δ 28.2. Anal. Calcd (found) for $C_{56}H_{56}Br_2O_2P_2Pd_2$: C, 56.26 (56.53); H, 4.72 (4.96); Br, 13.37 (13.58).

{**Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$CMe$_3$)(*μ*-I)**}$_2$ **(4).** A solution of $Pd_2(DBA)_3$ (250 mg, 0.27 mmol), P(*o*-tol)$_3$ (330 mg, 1.1 mmol), and *p*-*tert*-butyliodobenzene (700 mg, 2.7 mmol) in 15 mL of benzene was stirred at room temperature for 30 min. The resulting green-brown solution was filtered through Celite, and the solution was concentrated to 10 mL under vacuum. Addition of Et_2O (50 mL) formed an orange precipitate over 4 h, which was collected, washed with Et_2O, and dried under vacuum to give **4** (190 mg, 52%) as a pale orange powder. ^{1}H NMR (55 °C): δ 7.24, 7.10 (br), 6.88 (br), 6.50 (d, J = 8.33 Hz), 2.10 [br, 9 H, P(*o*-tol)$_3$], 1.08 (C$_6$H$_4$C*Me*$_3$). ^{31}P{^{1}H} NMR: δ 25.8 (br). Anal. Calcd (found) for $C_{62}H_{68}I_2P_2Pd_2$: C, 55.50 (55.32); H, 5.11 (5.14); I, 18.92 (19.08).

{**Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)(*μ*-I)**}$_2$ **(5).**[8] Reaction of $Pd_2(DBA)_3$ (250 mg, 0.27 mmol), P(*o*-tol)$_3$ (330 mg, 1.1 mmol), and

p-iodotoluene (0.6 g, 2.7 mmol) using a procedure analogous to that used to prepare **4** led to the isolation of **5** (207 mg, 60%) as a pale orange powder which contained traces (<5%) of Et_2O by ^1H NMR analysis. ^1H NMR (55 °C): δ 7.34, 7.07 (br), 6.73 (br), 6.32 (d, J = 6.38 Hz), 2.11 [br, 9 H, P(*o*-tol)$_3$], 1.98 (C_6H_4Me). $^{31}P\{^1H\}$ NMR: δ 25.5 (br). Anal. Calcd (found) for $C_{56}H_{56}I_2P_2Pd_2$: C, 53.48 (53.45); H, 4.49 (4.65); I, 20.18 (20.19).

{Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$OMe)(*μ*-I)}$_2$ (6). Reaction of $Pd_2(DBA)_3$ (250 mg, 0.27 mmol), P(*o*-tol)$_3$ (330 mg, 1.1 mmol), and *p*-iodoanisole (900 mg, 3.8 mmol) using a procedure analogous to that used to prepare **4** led to the isolation of **6** (180 mg, 51%) as a pale orange powder which contained traces (<5%) of Et_2O by ^1H NMR analysis. ^1H NMR (55 °C): δ 7.25 (m), 7.08 (br), 6.75 (br), 6.17 (d, J = 7.46 Hz), 3.53 (s, 3 H, C_6H_4OMe), 2.14 [br, 9 H, P(*o*-tol)$_3$]. $^{31}P\{^1H\}$ NMR: δ 25 (br). Anal. Calcd (found) for $C_{56}H_{56}I_2O_2P_2Pd_2$: C, 52.16 (52.01); H, 4.38 (4.54); I, 19.68 (19.97).

{Pd[P(*o*-tol)$_3$]I(*μ*-I)}$_2$. A solution of PdI_2 (200 mg, 0.55 mmol), LiI (162 mg, 1.21 mmol), and P(*o*-tol)$_3$ (380 mg, 1.25 mmol) in MeOH (7 mL) was heated at reflux for 30 min. The resulting brown suspension was cooled to room temperature, filtered in air, washed with methanol (20 mL) and Et_2O (20 mL), and dried under vacuum to give {Pd[P(*o*-tol)$_3$]I$_2$}$_2$ (357 mg, 97%) as a dark brown powder. ^1H NMR: δ 9.21, 7.47, 7.14, 3.26, 1.90, 1.55. $^{31}P\{^1H\}$ NMR: δ 30.6 (br). Anal. Calcd (found) for $C_{42}H_{42}I_4P_2Pd_2$: C, 37.95 (37.65); H, 3.26 (3.11); I, 38.19 (38.09).

Pd[P(*o*-tol)$_3$]$_2$Br$_2$ (7).[9] Reaction of $PdBr_2$ (200 mg, 0.75 mmol), LiBr (140 mg, 1.61 mmol), and P(*o*-tol)$_3$ (514 mg, 1.70 mmol) using a procedure analogous to that used to prepare {Pd[P(*o*-tol)$_3$]I$_2$}$_2$ led to the isolation of **7** (623 mg, 100%) as an orange powder. ^1H NMR: δ 9.21, 8.85, 7.22, 7.10, 2.97 (br), 1.95 (br), 1.60. $^{31}P\{^1H\}$ NMR: δ 20.2, 19.4 (~1:1).

{Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)[CD$_3$CN]$_2$}$^+$OTf$^-$ (8-(CD$_3$CN)$_2$). Silver triflate (3 mg, 1×10^{-2} mmol) was added to a suspension of **5** (5 mg, 4×10^{-3} mmol) in CD_3CN (0.75 mL), and the mixture was shaken for 1 min. The resulting yellow solution of **8**-$(CD_3CN)_2$ was filtered into an NMR tube and analyzed without isolation. ^1H NMR (CD_3CN, 75 °C): δ 7.68 (m), 7.48 (t, J = 7.5 Hz), 7.33 (t, J = 7.5 Hz), 7.28 (t, J = 7.5 Hz), 6.56 (t, J = 7.5 Hz), 2.34 [br s, 9 H, P(*o*-tol)$_3$], 2.10 (s, 3 H, C_6H_4Me). $^{31}P\{^1H\}$ NMR (CD_3CN, 50 °C): δ 25.2.

{Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)(*μ*-Cl)}$_2$ (9). A suspension of **5** (220 mg, 0.17 mmol) and AgOTf (94 mg, 0.37 mmol) in 5 mL of CH_3CN was stirred at room temperature for 5 min. The resulting yellow solution was decanted from the gray precipitate, which was extracted with an additional 5 mL of CH_3CN. LiCl (500 mg, 12.7 mmol) was added to the combined extracts, and the resulting suspension was stirred at room temperature for 2 days. Acetonitrile was evaporated under vacuum, and the residue was extracted with toluene and filtered through Celite. Evaporation of toluene and addition of Et_2O (5 mL) gave a pale yellow solution. Dropwise addition of pentane (10 mL) formed a yellow precipitate, which was washed with Et_2O and pentane and dried under vacuum to give **9** (175 mg, 93%) as a pale yellow powder. ^1H NMR: δ 7.68 (br, 3 H), 7.27 (t, J = 7.05 Hz, 3 H), 7.08 (m, 6 H), 6.48 (br, 2 H), 6.30 (d, J = 7.72 Hz, 2 H), 2.22 [s, 9 H, P(*o*-tol)$_3$], 1.98 (s, 3 H, C_6H_4Me). $^{31}P\{^1H\}$ NMR: δ 28.8. Anal. Calcd (found) for $C_{56}H_{56}Cl_2P_2Pd_2$: C, 62.59 (62.34); H, 5.25 (5.53); Cl, 6.60 (6.71).

{Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$CMe$_3$)(*μ*-Cl)}$_2$ (10). Reaction of **1** (410 mg, 0.33 mmol) and AgOTf (169 mg, 0.66 mmol), followed by treatment with LiCl (750 mg, 17.8 mmol) using a procedure analogous to that used to prepare **9**, led to the isolation of **10** (216 mg, 57%) as a yellow powder. ^1H NMR (55 °C): δ 7.70 (br, 3 H), 7.25 (m, 3 H), 7.08 (br, 6 H), 6.59 (br), 6.47 (d, J = 7.76 Hz), 2.17 [br, 9 H, P(*o*-tol)$_3$], 1.07 ($C_6H_4CMe_3$). $^{31}P\{^1H\}$ NMR: δ 28.2. Anal. Calcd (found) for $C_{62}H_{68}Cl_2P_2Pd_2$: C, 64.26 (64.48); H, 5.91 (6.17); Cl, 6.12 (6.11).

{Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$CMe$_3$)[CD$_3$CN]$_2$}$^+$OTf$^-$ (11-(CD$_3$CN)$_2$). Reaction of silver triflate (5 mg, 2×10^{-2} mmol) and **1** (7 mg, 6×10^{-3} mmol) in CD_3CN (0.80 mL) using a procedure analogous to that used to generate **8**-$(CD_3CN)_2$ formed **11**-$(CD_3CN)_2$, which was analyzed without isolation by NMR. ^1H NMR (CD_3CN, 50 °C): δ 7.64 (m), 7.49 (t, J = 7.5 Hz), 7.28 (m), 6.75, 6.72, 6.67 (m), 2.16 [br s, 9 H, P(*o*-tol)$_3$], 1.32 (s, 3 H, $C_6H_4CMe_3$). $^{31}P\{^1H\}$ NMR (CD_3CN, 50 °C): δ 25.2.

Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)[HN(CH$_3$)Bn]Cl (12). *N*-Benzylmethylamine (263 mg, 2.2 mmol) was added to a yellow solution of **9** (200 mg, 0.19 mmol) in 10 mL of C_6H_6 and stirred at room temperature for 15 min, and the resulting clear solution was allowed to stand at room temperature. A white precipitate formed over 2 h, which was filtered, washed with ether, and dried under vacuum to give **12** (207 mg, 85%) as a white microcrystalline solid. ^1H NMR (55 °C): δ 7.63 (br), 7.51 (d, J = 3.4 Hz), 7.38 (m), 7.34, 7.29 (t, J = 7.5 Hz), 7.09 (m), 6.36 (m), 4.39 [br t, J = 12.4 Hz, 1 H, HN(CH$_3$)CH_2Ph], 3.47 [dt, J = 12.5, 7 Hz, HN(CH$_3$)CH_2Ph], 3.22 [br s, 1 H, *H*N(CH$_3$)Bn], 2.46 [d, J = 6.0 Hz, 3 H, HN(CH_3)Bn], 2.22 [br, 9 H, P(*o*-tol)$_3$], 2.03 (s, C_6H_4Me). $^{31}P\{^1H\}$ NMR: δ 27.9. IR (Nujol): 3261 cm^{-1}. Anal. Calcd (found) for $C_{36}H_{39}ClNPPd$: C, 65.66 (65.92); H, 5.97 (6.07); N, 2.13 (2.10).

Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)[HN(CH$_3$)Bn]Br (13). *N*-Benzylmethylamine (160 mg, 1.32 mmol) was added to a yellow solution of **2** (150 mg, 0.13 mmol) in 5 mL of CH_2Cl_2 and stirred at room temperature for 10 min. The resulting colorless solution was concentrated to 1 mL under vacuum and diluted with 20 mL of hexane. Cooling the solution via concentration to 10 mL under vacuum formed a white precipitate, which was filtered, washed with hexane, and dried under vacuum to give **13** (148 mg, 83%) as a pale yellow microcrystalline solid. ^1H NMR (55 °C): δ 7.84, 7.37, 7.29 (t, J = 7 Hz), 7.10, 6.38, 4.40 [br s, 1 H, HN(CH$_3$)CH_2Ph], 4.35 [br s, 1 H, *H*N(CH$_3$)Bn], 3.42 [br s, 1 H, HN(CH$_3$)CH_2Ph], 2.46 [br s, 3 H, HN(CH_3)Bn], 2.18 [br, 9 H, P(*o*-tol)$_3$], 2.05 (s, 3 H, C_6H_4Me). $^{31}P\{^1H\}$ NMR: δ 27.9. IR (Nujol): 3257 cm^{-1}. Anal. Calcd (found) for $C_{36}H_{39}BrNPPd$: C, 61.51 (61.63); H, 5.59 (5.83); N, 1.99 (2.06).

Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)[HN(CH$_3$)Bn]I (14). Reaction of **5** (220 mg, 0.18 mmol), and *N*-benzylmethylamine (212 mg, 1.75 mmol) using a procedure analogous to that used to prepare **13** led to the isolation of **14** (186 mg, 71%) as a pale yellow microcrystalline solid. ^1H NMR (~80:20 ratio of **14**:**5**): δ 7.37, 7.29, 7.05, 6.4, 4.48 [br, 1 H, HN(CH$_3$)CH_2Ph], 3.47 [br, 1 H, HN(CH$_3$)CH_2Ph], 3.22, [br, 6 H, P(*o*-tol)$_3$], 2.48 [br, 3 H, HN(CH_3)Bn], 2.04 (s, 3 H, C_6H_4Me), 1.50 [br s, 3 H, P(*o*-tol)$_3$], *H*N(CH$_3$)Bn not observed. $^{31}P\{^1H\}$ NMR {$CDCl_3$ [0.05 M HN(Me)Bn]}: δ 28.1. IR (Nujol): 3253 cm^{-1}. Anal. Calcd (found) for $C_{36}H_{39}ClNPPd$: C, 57.65 (57.53); H, 5.24 (5.48); N, 1.87 (2.14).

Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$OMe)[HN(CH$_3$)Bn]Br (15). A purple solution of $Pd_2(DBA)_3$ (150 mg, 0.16 mmol), P(*o*-tol)$_3$ (250 mg, 0.82 mmol), *p*-bromoanisole (313.1 mg, 1.6 mmol), and benzyl(methyl)amine (235 mg, 1.9 mmol) in 5 mL of benzene was stirred at room temperature for 2 days. The resulting green-brown suspension was filtered through Celite, and the residue was extracted with CH_2Cl_2 (50 mL) and evaporated under vacuum. Addition of Et_2O (20 mL) to the resulting oily residue formed a yellow precipitate, which was filtered, washed with Et_2O and pentane, and dried under vacuum to give **15** (120 mg, 51%) as a pale yellow powder. ^1H NMR (C_6D_6, 75 °C): δ 7.80, 7.20, 7.05, 6.88, 6.36, 4.55 [br, HN(Me)CH_2Ph], 3.50 [br, HN(Me)CH_2Ph], 3.29 (s, C_6H_4OMe), 3.18 [br, *H*N(Me)CH$_2$Ph], 2.33 [br, P(*o*-tol)$_3$], 2.25 [br, HN(*Me*)Bn]. $^{31}P\{^1H\}$ NMR: δ 27.9 (br). IR (Nujol): 3258 cm^{-1}. Anal. Calcd (found) for $C_{36}H_{39}BrNOPPd$: C, 60.14 (60.35); H, 5.47 (5.79); N, 1.95 (1.95).

Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)[H$_2$NBn]Cl (16). Reaction of **9** (150 mg, 0.14 mmol) and benzylamine (74 mg, 0.7 mmol) using a procedure analogous to that used to prepare **13** led to the isolation of **16** (127 mg, 70%) as a pale yellow microcrystalline solid, which contained traces (≤5%) of hexane by ^1H NMR analysis. ^1H NMR (50 °C): δ 7.74 (br, 3 H), 7.28 (t, J = 6.4 Hz, 3 H) 7.21 (m, 3 H), 7.11 (m, 7 H), 6.58 (br s, 2 H), 6.46 (d, J = 7.3 Hz, 2 H), 3.75 (br, 2 H, H$_2$NCH_2Ph), 2.91 (br, 2 H, H_2NCH$_2$Ph), 2.21 [br s, 9 H, P(*o*-tol)$_3$], 2.07 (s, 3 H, C_6H_4Me).

$^{31}P\{^{1}H\}$ NMR: δ 28.3. Anal. Calcd (found) for $C_{35}H_{37}ClNPPd$: C, 65.23 (65.03); H, 5.78 (5.93); N, 2.17 (2.31).

Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)[H$_2$^{15}NBn]Cl (16-^{15}N). Small amounts (<0.5 mL) of benzylamine-^{15}N were added via syringe to a solution of **9** (7 mg, 6×10^{-3} mmol) in $CDCl_3$ (0.75 mL) and monitored after each addition by ^{1}H NMR spectroscopy. Addition of 1.4 mL of benzylamine-^{15}N generated **16**-^{15}N, which contained ~5% **9** by ^{1}H NMR analysis. $^{31}P\{^{1}H\}$ NMR (50 °C): δ 28.1 (d, $J_{PN} = 40.0$ Hz).

Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)[H$_2$NBn]Br (17). Reaction of **2** (100 mg, 0.09 mmol), and benzylamine (19 mg, 0.18 mmol) using a procedure analogous to that used to prepare **13** led to the isolation of **17** (82 mg, 69%) as a pale yellow microcrystalline solid which contained traces (≤5%) of hexane by ^{1}H NMR analysis. ^{1}H NMR (50 °C): δ 7.80 (br s, 3 H), 7.31 (t, J = 7.9 Hz, 3 H), 7.24 (s, 5 H), 7.12 (br s, 6 H), 6.63 (br s, 2 H), 6.51 (br s, 2 H), 3.79 (br, 2 H, H_2NCH_2Ph), 2.98 (br, 2 H, H_2NCH_2Ph), 2.20 [br s, 9 H, P(*o*-tol)$_3$], 2.09 (s, 3 H, C_6H_4Me). $^{31}P\{^{1}H\}$ NMR: δ 28.9. Anal. Calcd (found) for $C_{35}H_{37}BrNPPd$: C, 61.02 (61.25); H, 5.41 (5.32).

Pd[P(*o*-tol)$_3$](*p*-C$_6$H$_4$Me)[H$_2$^{15}NBn]Br (17-^{15}N). Reaction of benzylamine-^{15}N and **2** (7 mg, 6×10^{-3} mmol) in $CDCl_3$ (0.75 mL) using the procedure employed in the synthesis of **16**-^{15}N formed **17**-^{15}N. $^{31}P\{^{1}H\}$ NMR: δ 28.9 (d, $J_{PN} = 40.1$ Hz).

Pd[P(*o*-tol)$_3$][2-C$_6$H$_4$(CH$_2$)$_2$N(H)Bn]I (18). A purple suspension of $Pd_2(DBA)_3$ (200 mg, 0.21 mmol), P(*o*-tol)$_3$ (370 mg, 1.1 mmol), and 2-IC$_6$H$_4$(CH$_2$)$_2$N(H)Bn (535 mg, 0.57 mmol) in 20 mL of benzene was stirred at room temperature for 24 h. The resulting green-brown suspension was filtered through Celite, and benzene was evaporated under vacuum. Addition of Et_2O (10 mL) to the oily residue formed a white precipitate, which was filtered, washed with Et_2O, and dried under vacuum to give **18** (368 mg, 71%) as a yellow powder which was ≥95% pure by ^{1}H NMR analysis. **18** was further purified by recrystallization from CH_2Cl_2/hexane. ^{1}H NMR (0 °C): 9.49 (dd, J = 8.2, 18.1 Hz), 7.4−6.3 (m, aromatic), 5.49 (br s, 1 H, NH, identified by D_2O exchange), 3.93 (dd, 1 H, J = 4.2, 13.8 Hz), 3.53 (dt, 1 H, J = 6.4, 13.2 Hz), 3.17 [s, 3 H, P(*o*-tol)$_3$], 2.81 (m, 2 H), 2.05 (br t, J = 9.3 Hz), 1.51 [s, 3 H, P(*o*-tol)$_3$], 0.83 [s, 3 H, P(*o*-tol)$_3$]. ^{31}P NMR: δ 29.1. IR (Nujol): 3241 cm^{-1}. Anal. Calcd (found) for $C_{36}H_{37}INPPd$: C, 57.81 (57.63); H, 4.99 (4.84); N, 1.87 (1.80).

N-(*p*-tolyl)-*o*-bromobenzylamine. A suspension of 2-bromobenzyl bromide (5 g, 20.1 mmol), *p*-toluidine (10.7 g, 100 mmol), and K_2CO_3 (14 g, 100 mmol) in 20 mL of THF was refluxed for 18 h. After the suspension was cooled to room temperature, water (50 mL) and Et_2O were added and the layers were separated. The aqueous layer was extracted with Et_2O (3 × 75 mL), and the combined Et_2O fractions were dried ($MgSO_4$) and concentrated using a rotary evaporator. The residue was chromatographed (SiO_2, hexane/ethylacetate, (2/1) with 1% Et_3N), and the first band to elute was collected to give *N*-(*p*-tolyl)-*o*-bromobenzylamine (4.7 g, 85%) as a yellow oil which solidified upon standing. ^{1}H NMR: δ 7.55 (dd, J = 2.2, 8.2 Hz, 1 H), 7.39 (dd, J = 2.0, 7.7 Hz, 1 H), 7.23 (dt, J = 2.0, 7.7 Hz, 1 H), 7.10 (dt, J = 1.8, 7.4 Hz, 1 H), 6.97 (d, J = 8.3 Hz, 2 H), 6.52 (d, J = 8.2 Hz, 2 H), 4.36 (s, 2 H), 4.05 (br s, 1 H), 2.22 (s, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 145.6, 138.5, 132.9, 129.9, 129.3, 128.7, 127.6, 127.0, 123.4, 113.2, 48.8, 20.5. Anal. Calcd (found) for $C_{14}H_{14}BrN$: C, 60.89 (60.98); H, 5.11 (5.21).

Pd[P(*o*-tol)$_3$][2-C$_6$H$_4$CH$_2$N(H)(*p*-tolyl)]Br (19). Reaction of $Pd_2(DBA)_3$ (200 mg, 0.44 mmol), P(*o*-tol)$_3$ (290 mg, 0.95 mmol), and 2-Br-C$_6$H$_4$CH$_2$N(H)(*p*-tolyl) (345 mg, 1.25 mmol) using a procedure analogous to that used to prepare **18** gave **19** (260 mg, 77%). ^{1}H NMR (−42 °C): δ 9.54 (br d, J = 17 Hz), 8.78 (dd, J = 7.92, 17.6 Hz), and 8.38 (dd, J = 7.72, 17.6 Hz) (1:2.6:2.6, 1 H), 7.50−6.80 (m, 17 H), 6.2−6.5 (m, 3 H), 5.26 (dd, J = 6.3, 15.0 Hz), 5.16 (dd, J = 5.6, 14.6 Hz), and 4.94 (dd, J = 6.6, 15.3 Hz) (1:2.6:2.6, 1 H), 4.20 (br d, J = 15.3 Hz, 1 H), 3.12, 2.85, and 2.73 [2.6:1:2.6, 3 H, P(*o*-tol)$_3$], 2.26, 2.20, and 2.17 [2.6:2.6:1, 3 H, *p*-tolyl], 1.94, 1.82, and 1.32 [2.6:2.6:1, 3 H, P(*o*-tol)$_3$], 1.58, 1.55, 1.53 [2.6:2.6:1, 3 H, P(*o*-tol)$_3$]. IR (Nujol): 3187 cm^{-1}. $^{31}P\{^{1}H\}$ NMR (96 MHz, $CDCl_3$, −42 °C): δ 37.3, 35.1, and 29.4 (2.6:2.6:1). Anal. Calcd (found) for $C_{35}H_{35}BrNPPd$: C, 61.20 (61.22); H, 5.14 (5.37); N, 2.04 (1.95).

Pd[P(*o*-tol)$_3$][2-C$_6$H$_4$(CH$_2$)^{15}N(H)Ph]Br (20). A suspension of 2-bromobenzyl bromide (0.6 g, 2.4 mmol), aniline-^{15}N (1 g, 11 mmol), and K_2CO_3 (1.4 g, 10 mmol) in 5 mL of THF was refluxed for 2 h. After the suspension was cooled to room temperature, water (5 mL) and Et_2O (5 mL) were added and the layers were separated. The aqueous layer was extracted with Et_2O (3 × 5 mL), and the combined Et_2O fractions were dried ($MgSO_4$) and concentrated under vacuum to give a mixture of ^{15}N-phenyl-*o*-bromobenzylamine-^{15}N[44] and aniline-^{15}N. The resulting oil was diluted to 5 mL with C_6H_6, and 1.5 mL of this solution was added via syringe to a solution of $Pd_2(DBA)_3$ (150 mg, 0.16 mmol) and P(*o*-tol)$_3$ (200 mg, 0.66 mmol) in C_6H_6 (10 mL). The resulting mixture was stirred for 2 h to form a brown solution, which was filtered through Celite and concentrated to 1 mL under vacuum. Addition of Et_2O (20 mL) formed a tan precipitate over 4 h, which was filtered, washed with Et_2O, and dried under vacuum to give **20** (113 mg, 51% based on Pd) as a yellow powder which contained ~5% Et_2O by ^{1}H NMR analysis. ^{1}H NMR (0 °C): δ 9.54 (dd, J = 6.8, 17.2 Hz), 8.73 (dd, J = 7.05, 15.5 Hz), and 8.28 (dd J = 8.6, 17.5 Hz) (1:2.6:2.6, 1 H), 7.5−6.8 (m, 12 H), 6.6−5.8 (m, HN + aromatic, 3 H), 5.26 (dd, J = 7.2, 13.8 Hz), 5.17 (dd, J = 7.1, 14.2 Hz), and 4.95 (dd, J = 7.4, 13.7 Hz) (1:2.6:2.6, 1 H), 4.25 (d, J = 13.9 Hz, 1 H), 3.11, 2.82, and 2.66 [2.6:1:2.6, 3 H, P(*o*-tol)$_3$], 1.92, 1.79, and 1.30 [2.6:2.6:1, 3 H, P(*o*-tol)$_3$], 1.57, 1.55, and 1.52 [2.6:2.6:1, 3 H, P(*o*-tol)$_3$]. $^{31}P\{^{1}H\}$ NMR (−42 °C): δ 36.8 (d, $J_{PN} = 36.3$ Hz), 34.1 (d, $J_{PN} = 37.0$ Hz), and 28.7 (d, $J_{PN} = 36.3$ Hz) (2.6:2.6:1).

Pd[P(*o*-tol)$_3$](2-C$_6$H$_4$(CH$_2$)$_3$N(H)Bn]Br (21). Reaction of $Pd_2(DBA)_3$ (410 mg, 0.88 mmol), P(*o*-tol)$_3$ (530 mg, 1.74 mmol), and 2-BrC$_6$H$_4$(CH$_2$)$_3$N(H)Bn (570 mg, 1.90 mmol) using a procedure analogous to that used to prepare **18** led to the isolation of **21** (150 mg, 24%) as a white powder. ^{1}H NMR: δ 9.6 (br, 1 H), 7.6−7.0, 6.8−6.2 (m, 8 H), 4.14 (s, 1 H), 4.01 (s, 2 H), 3.18 (s, 3 H), 3.10 (s, 2 H), 2.96 (s, 1 H), 3.36 (s, 1 H), 1.98 (s, 1 H), 1.77 (s, 1 H), 1.53 (s, 1 H), 0.92 (s, 3 H). $^{31}P\{^{1}H\}$ NMR (50 °C): δ 28.5 (br). IR (Nujol): 3227 cm^{-1}. Anal. Calcd (found) for $C_{37}H_{39}BrNPPd$: C, 62.15 (61.87); H, 5.50 (5.43); N, 1.96 (2.13).

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