Syntheses and Properties of Palladium Complexes Containing Phosphorus−Nitrogen−Phosphorus Ligands with a Tunable Hemilabile Site

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Received December 3, 1998

A series of phosphorus−nitrogen−phosphorus (PNP) ligands of the type R−N(CH_2CH_2-PPh_2)$_2$ (R = C(=O)(C_6H_4OMe-*p*), ^{t}Bu, Ph, C_6H_4OMe-*p*) have been prepared. Their coordination chemistry to palladium(II) and palladium(0) complexes was examined using a combination of X-ray crystallography, NMR, and electrochemical techniques. The palladium(0) complexes undergo reactions with aryl iodides to give the palladium(II) complexes [Pd(Ar){R−N(CH_2-CH_2PPh_2)$_2$}]$^+I^-$, where the rate of oxidative addition was found to be dependent on the nature of the aryl group, as well as the substitution on nitrogen.

Introduction

Ligands with mixed donor atoms have been the subject of many studies in recent years.[1] Particularly interesting are the hemilabile ligands, in which "soft" and "hard" donor atoms are combined to give flexible coordination modes. This behavior has been exploited to maximize the stability of a metal complex and has been implicated in a number of catalytic reactions.[2] The majority of hemilabile ligands used in metal-mediated catalysis are bidentate,[3] although ter-[4] and tetradentate[5] ligands have also been employed.

The first synthesis of ligands containing phosphorus−nitrogen−phosphorus donors (PNP ligands) was reported as early as the 1960s.[6] Although the coordination chemistry of these ligands to transition metals has been widely reported,[7,8] their application to catalysis is fairly recent, where in most cases the nitrogen is used either as a means of tethering the ligand to solid supports,[9] and chiral[10] or hydrophilic groups.[11]

This paper describes the preparation of a new class of terdentate PNP ligands, R−N($CH_2CH_2PPh_2$)$_2$, containing tunable, hemilabile nitrogen and phosphorus donors. As nitrogen is inherently a weaker donor toward later transition metals than phosphines, it is conceivable that the complex could isomerize between *cis* and *trans* configurations as the ligand alters between the bi- and terdentate modes (Scheme 1). As this isomerization process does not necessarily entail a cleavage of the M−P bond, it is envisaged that ligand dissociation and decomposition during a catalytic reaction should be minimized. By changing the steric and electronic requirements of the R substituent at nitrogen, we hope to control metal−nitrogen bond dissociation and association, such that this behavior could be exploited in

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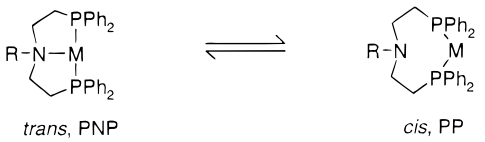
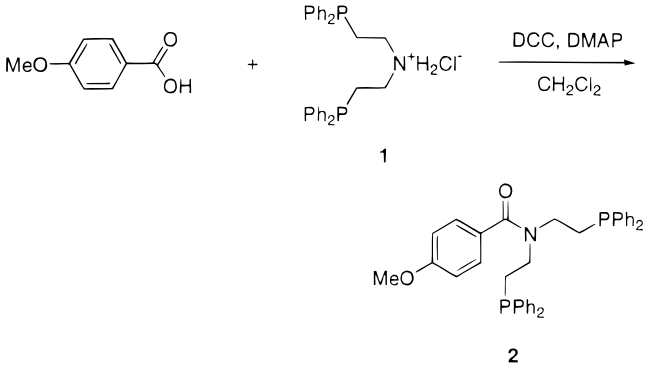
10.1021/om980978t CCC: $18.00
Publication on Web 04/24/1999

Scheme 1. Modes of *cis*/*trans* Isomerization of PNP Ligands



Scheme 2. Synthesis of Amido Diphosphine 2



improving the catalytic efficiency of conventional transition-metal-catalyzed reactions.

The present work demonstrates for the first time that the coordination behavior of PNP ligands with respect to palladium is dependent on the nature of the nitrogen donor. This has also been found to dramatically alter the reactivity of their palladium(0) complexes in oxidative addition reactions toward aryl halides—an important first step in many palladium-catalyzed reactions.

Results and Discussion

Preparation of Amido Diphosphines. These have been previously synthesized by the reaction between the salt bis[2-(diphenylphosphino)ethyl]amine−HCl (**1**) and acyl halides or acyl anhydrides in the presence of base. Although the reactions work well, side products incurred during the reactions are often difficult to remove.[11−13]

The reaction of carboxylic acids with bis[2-(diphenylphosphino)ethyl]amine (**1**), in the presence of dicyclohexylcarbodiimide (DCC) and *N*,*N*-(dimethylamino)-pyridine (DMAP), afforded a cleaner synthesis (Scheme 2). As the insoluble side product is easily removed from the reaction mixture, analytically pure amido diphosphine **2** is obtained after only one recrystallization from methanol.

Formation of the amide bond was confirmed by the observation of a characteristic carbonyl absorption peak at 1635 cm^{-1} in the infrared spectrum. A solution of **2** showed dynamic NMR behavior—two singlets were observed in the $^{31}P\{^1H\}$ NMR spectrum which coalesce at elevated temperatures to a sharp singlet. In the corresponding ^1H NMR spectrum, the methylene protons were observed as four sets of resonances at −20 °C, which in turn coalesce to two sets of multiplets at higher temperatures. This process appears to be intramolecular and has been attributed to restricted rotation about the C−N amide bond.[11]

Table 1. Interatomic Distances (Å) with Esds in Parentheses

Pd(1)−Cl(1)	2.2971(5)	Pd(1)−Cl(2)	2.3086(5)
Pd(1)−P(2*)	2.3126(5)	Pd(1)−P(1)	2.3207(5)
P(1)−C(121)	1.818(2)	P(1)−C(111)	1.823(2)
P(1)−C(1)	1.835(2)	C(111)−C(116)	1.387(3)
C(111)−C(112)	1.387(3)	C(112)−C(113)	1.387(4)
C(113)−C(114)	1.370(4)	C(114)−C(115)	1.380(4)
C(115)−C(116)	1.390(3)	C(121)−C(126)	1.391(3)
C(121)−C(122)	1.395(3)	C(122)−C(123)	1.388(3)
C(123)−C(124)	1.382(4)	C(124)−C(125)	1.384(4)
C(125)−C(126)	1.388(3)		
P(2)−C(221)	1.809(2)	P(2)−C(211)	1.827(2)
P(2)−C(4)	1.833(2)	C(211)−C(216)	1.389(3)
C(211)−C(212)	1.393(3)	C(212)−C(213)	1.381(3)
C(213)−C(214)	1.382(3)	C(214)−C(215)	1.375(4)
C(215)−C(216)	1.400(3)	C(221)−C(222)	1.389(3)
C(221)−C(226)	1.392(3)	C(222)−C(223)	1.392(3)
C(223)−C(224)	1.368(3)	C(224)−C(225)	1.381(3)
C(225)−C(226)	1.384(3)		
C(1)−C(2)	1.528(3)	C(2)−N(2)	1.468(2)
N(2)−C(5)	1.359(3)	N(2)−C(3)	1.470(2)
C(3)−C(4)	1.531(3)	O(5)−C(5)	1.234(3)
C(5)−C(51)	1.501(3)	C(51)−C(52)	1.388(3)
C(51)−C(56)	1.390(3)	C(52)−C(53)	1.382(3)
C(53)−C(54)	1.384(3)	C(54)−O(54)	1.360(3)
C(54)−C(55)	1.387(3)	C(55)−C(56)	1.377(3)
O(54)−C(57)	1.413(3)		

Preparation of Dichloropalladium(II) Complex 3. When a solution of $[PdCl_2(NCMe)_2]$ was added to amido diphosphine **2** in dichloromethane, a yellow product was obtained which showed a dimeric $[L_2Pd_2Cl_3]^+$ mass ion (*m*/*z* 1469) in its FAB mass spectrum.

Crystals of $[Pd_2Cl_4\{(4\text{-}MeOC_6H_4CO)N(CH_2CH_2PPh_2)_2\}_2]$ (**3**) were obtained by slow recrystallization from dichloromethane/hexane. The ORTEP drawing is shown in Figure 1. Selected bond distances and bond angles are collected in Tables 1 and 2. The molecule possesses a crystallographic inversion center with the amido diphosphine ligands **2** bridging two palladium metal centers, forming a 16-membered macrocycle. The chloride anions adopt a mutually *trans* configuration at each palladium atom, with each Cl(1)−Pd(1)−Cl(2) vector tilted at an angle of 23.1° from the P(1)−P(2)−P(1′)−P(2′) plane.

The solution NMR spectra of complex **3** exhibited dynamic behavior. A broad signal was observed in the $^{31}P\{^1H\}$ NMR spectrum at room temperature, which resolved into an AB pattern ($\delta(P_A)$ 10.0 ppm, $\delta(P_B)$ 13.2 ppm, $J_{PP} = 553$ Hz) and two singlets (δ(P) 10.6 and 12.8 ppm) at −20 °C (Figure 2).[14] This fluxionality is ascribed to restricted rotation around the C−N bond leading to *syn* and *anti* conformations (Scheme 3). No other fluxional processes were observed down to −60 °C. The complex is surprisingly stable, even in refluxing chloroform (65 °C) for 3 days. Attempts to synthesize the monomeric palladium chloride complex by the reaction of amido diphosphine **2** with *cis*-$[PdCl_2(COD)]$ under high dilution conditions only led to the formation of **3**—demonstrating the remarkable kinetic and thermodynamic stability of the 16-membered-ring structure.

The reluctance of the amido diphosphine ligands to behave as chelating ligands toward palladium is partly ascribed to the electron-deficient, planar nature of the

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(14) In the ^1H NMR spectrum, the proton signals corresponding to H_{ortho}(anisole) and H_{meta}(anisole) were found as two sets of AB patterns at −30 °C, which coalesce to a single set at 50 °C.

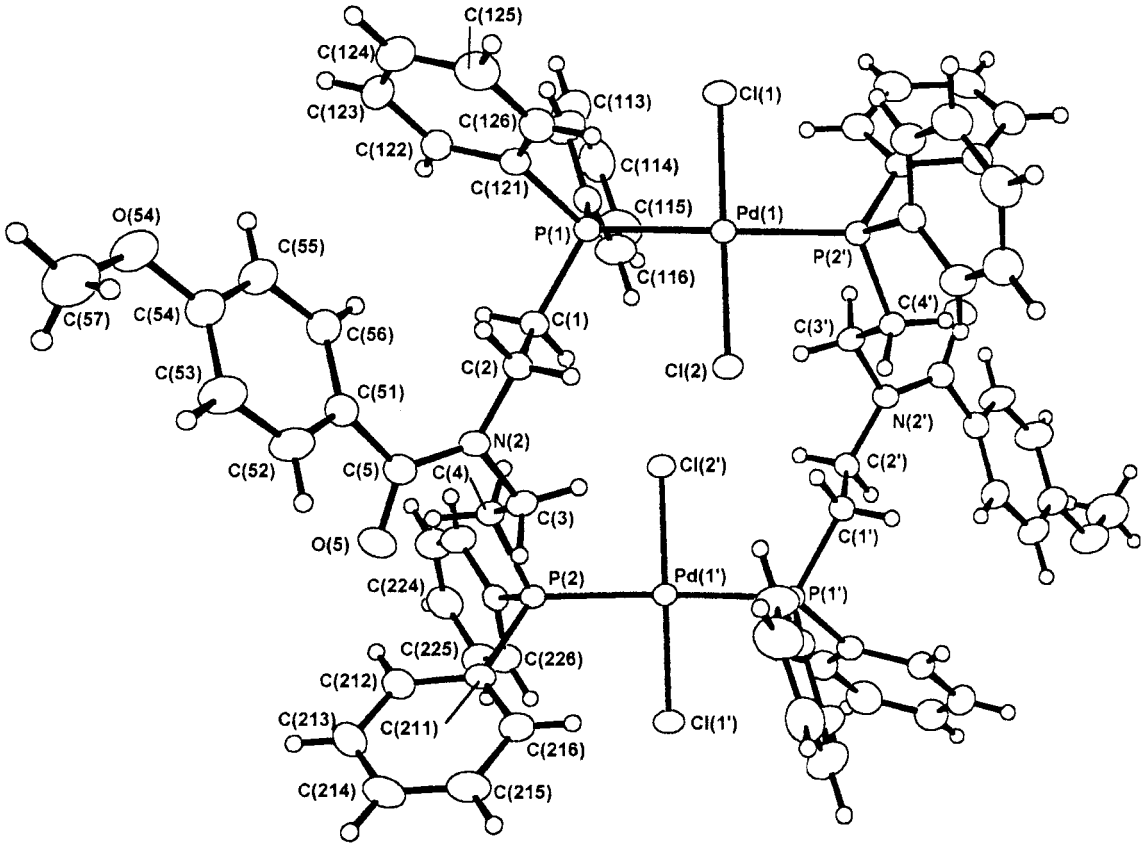


Figure 1. ORTEP drawing of complex **3** with thermal ellipsoids shown at the 40% probability level.

Table 2. Angles between Interatomic Vectors (deg) with Esds in Parentheses

Cl(1)−Pd(1)−Cl(2)	169.18(2)	Cl(1)−Pd(1)−P(2*)	91.60(2)
Cl(2)−Pd(1)-P(2*)	88.84(2)	Cl(1)−Pd(1)−P(1)	88.08(2)
Cl(2)−Pd(1)−P(1)	94.13(2)	P(2*)−Pd(1)−P(1)	165.78(2)
C(121)−P(1)−C(111)	107.92(10)	C(121)−P(1)−C(1)	103.74(9)
C(111)−P(1)−C(1)	101.86(9)	C(121)−P(1)−Pd(1)	120.11(7)
C(111)−P(1)−Pd(1)	102.93(7)	C(1)−P(1)−Pd(1)	118.44(7)
C(116)−C(111)−C(112)	118.9(2)	C(116)−C(111)−P(1)	118.7(2)
C(112)−C(111)−P(1)	122.2(2)	C(113)−C(112)−C(111)	120.1(3)
C(114)−C(113)−C(112)	120.9(3)	C(113)−C(114)−C(115)	119.5(2)
C(114)−C(115)−C(116)	120.2(3)	C(111)−C(116)−C(115)	120.4(2)
C(126)−C(121)−C(122)	119.3(2)	C(126)−C(121)−P(1)	119.4(2)
C(122)−C(121)−P(1)	121.3(2)	C(123)−C(122)−C(121)	120.4(2)
C(124)−C(123)−C(122)	119.7(2)	C(123)−C(124)−C(125)	120.4(2)
C(124)−C(125)−C(126)	120.0(2)	C(125)−C(126)−C(121)	120.2(2)
C(221)−P(2)−C(211)	104.07(9)	C(221)−P(2)−C(4)	106.58(9)
C(211)−P(2)−C(4)	100.32(9)	C(221)−P(2)−Pd(1*)	112.82(6)
C(211)−P(2)−Pd(1*)	118.91(7)	C(4)−P(2)−Pd(1*)	112.73(6)
C(216)−C(211)−C(212)	119.4(2)	C(216)−C(211)−P(2)	122.1(2)
C(212)−C(211)−P(2)	118.2(2)	C(213)−C(212)−C(211)	120.9(2)
C(212)−C(213)−C(214)	119.6(2)	C(215)−C(214)−C(213)	120.2(2)
C(214)−C(215)−C(216)	120.6(2)	C(211)−C(216)−C(215)	119.3(2)
C(222)−C(221)−C(226)	119.6(2)	C(222)−C(221)−P(2)	122.1(2)
C(226)−C(221)−P(2)	118.4(2)	C(221)−C(222)−C(223)	119.7(2)
C(224)−C(223)−C(222)	120.5(2)	C(223)−C(224)−C(225)	120.1(2)
C(224)−C(225)−C(226)	120.3(2)	C(225)−C(226)−C(221)	119.9(2)
C(2)−C(1)−P(1)	113.41(13)	N(2)−C(2)−C(1)	110.9(2)
C(5)−N(2)−C(2)	126.4(2)	C(5)−N(2)−C(3)	116.4(2)
C(2)−N(2)−C(3)	116.1(2)	N(2)−C(3)−C(4)	112.3(2)
C(3)−C(4)−P(2)	110.30(13)	O(5)−C(5)−N(2)	119.8(2)
O(5)−C(5)−C(51)	119.0(2)	N(2)−C(5)−C(51)	121.2(2)
C(52)−C(51)−C(56)	117.9(2)	C(52)−C(51)−C(5)	116.7(2)
C(56)−C(51)−C(5)	125.0(2)	C(53)−C(52)−C(51)	121.9(2)
C(52)−C(53)−C(54)	119.3(2)	O(54)−C(54)−C(53)	124.3(2)
O(54)−C(54)−C(55)	116.1(2)	C(53)−C(54)−C(55)	119.6(2)
C(56)−C(55)−C(54)	120.4(2)	C(55)−C(56)−C(51)	120.9(2)
C(54)−O(54)−C(57)	118.2(2)		

amido bond, which seems to prohibit coordination of the nitrogen donor and discourage any chelate formation.

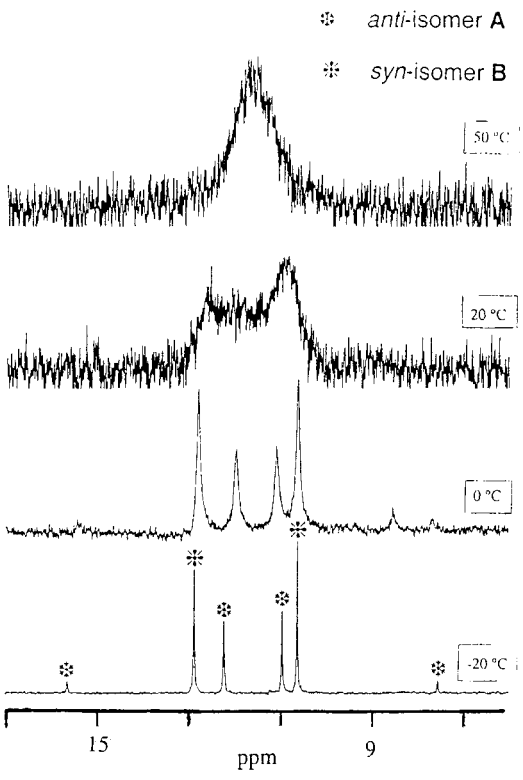
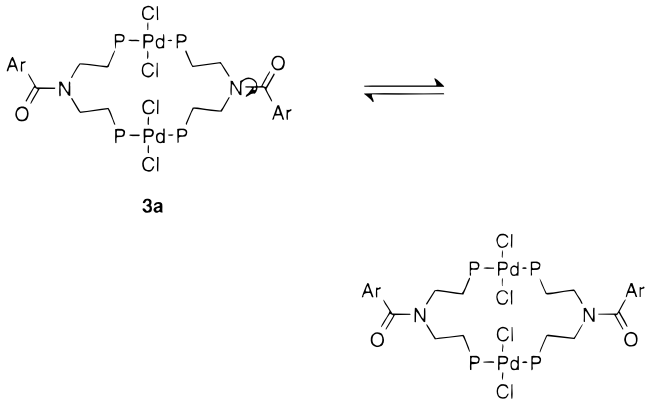


Figure 2. $^{31}P\{^{1}H\}$ NMR spectra of complex **3** in thf/acetone-d_6 at different temperatures (202 MHz).

This result led us to the synthesis of PNP ligands containing sp^3 nitrogen donors, i.e. amino diphosphine ligands $R-N(CH_2CH_2PPh_2)_2$, where R = alkyl or aryl groups.

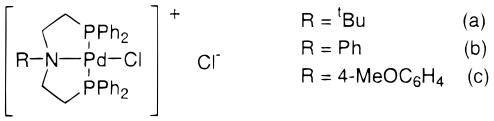
Scheme 3. Restricted Rotation in 3, Giving Rise to (a) *anti* and (b) *syn* Rotamers



3a **3b**

Synthesis of the Amino Diphosphine Ligands 7a−c. This was carried out in good yields from readily available reagents in four simple synthetic steps (Scheme 4): Amino diesters **4** were obtained by the condensation between a primary amine and ethyl bromoacetate. Subsequent reduction to the diol **5** took place,[15] followed by chlorination/tosylation of the ethyl group at the 2-position, and finally, introduction of the phosphine moiety via potassium diphenylphosphide. The amino diphosphines **7a−c** were obtained as white solids, and the methodology was found to be especially useful for the synthesis of amino diphosphines $R-N(CH_2CH_2-PPh_2)_2$, where R = aryl groups.

Reaction of the Amino Diphosphines 7a−c with Palladium Dichloride. At room temperature, **7a** initially reacts with $[PdCl_2(COD)]$ to give a mixture of compounds, indicated by the observation of several peaks in the $^{31}P\{^1H\}$ NMR spectrum, signifying the presence of several different coordination modes of the PNP ligand. However, at the end of several hours' reflux, a single species was obtained, which produced a sharp, singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum, implying the formation of the $[(PNP)PdCl]^+Cl^-$ salt **8a**.

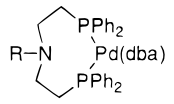


8

R = ^{t}Bu (a)
R = Ph (b)
R = 4-MeOC$_6$H$_4$ (c)

This was supported by the observation of virtual triplet patterns for the methylene ^{13}C resonance signals α to phosphorus, indicating the presence of two equivalent, *trans* phosphorus nuclei. The phenyl-substituted analogue **8b** was synthesized in a similar manner by heating the reaction mixture to obtain the thermodynamic product. In contrast, no heating was required for the formation of **8c**, which has been found to form the cationic monochloro salt at ambient temperature ($\Lambda_m = 2.23 \times 10^{-2}$ S M^{-1} cm^{-1} in DMSO).

Synthesis of Palladium(0) Complexes. The ligands were also found to be capable of coordinating in a P,P-bidentate mode. Reaction of **7a−c** with $[Pd_2(dba)_3 \cdot CHCl_3]$ (dba = dibenzylideneacetone) in toluene gave the complexes **9a−c** as yellow solids. The isolated



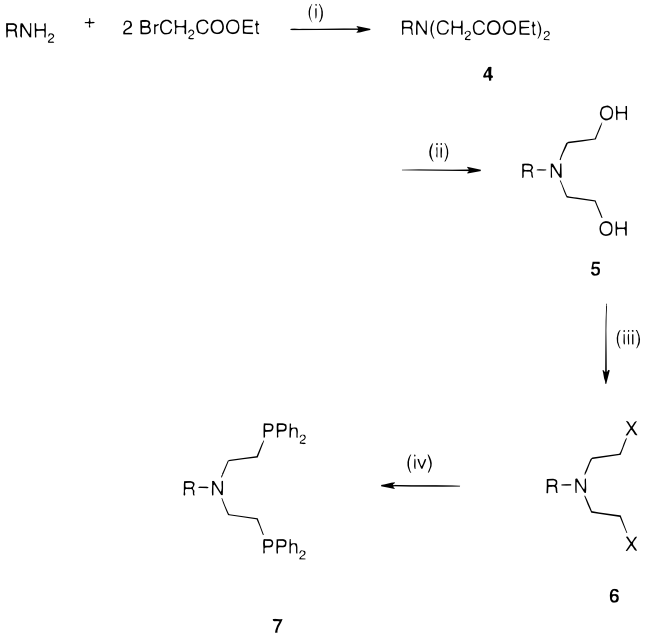
9

R = ^{t}Bu (a)
R = Ph (b)
R = 4-MeOC$_6$H$_4$ (c)

complexes are fairly stable in the solid state, but rapidly decompose in chlorinated solvents at room temperature. Moreover, they are only slightly soluble in toluene, acetone and methanol, thereby making purification by recrystallization very difficult. The observation of the $[PNP+Pd]^+$ ion (and the absence of higher aggregates) in the FAB mass spectra suggests that these complexes are monomeric.

These complexes displayed two ^{31}P NMR resonance signals which are characteristic of complexes of the type [(diphosphine)Pd(dba)].[16,19c] However, the resonances appeared to be broad. The dynamic process must be due partly to the rapid dissociation/association of the dba

Scheme 4. Synthesis of Amino Diphosphines[a]



4 **5** **6** **7**

R = ^{t}Bu (a)
R = Ph (b)
R = 4-MeOC$_6$H$_4$ (c)

[a] Legend: (i) Na_2CO_3, Δ, 16 h; (ii) $LiAlH_4$, THF, 16 h; (iii) TsCl, pyridine, 0 °C (X = OTs) or $SOCl_2$ (X = Cl); (iv) 2 $KPPh_2$, room temperature, 4 h.

(15) Schultz, R. A.; White, B. D.; Dishong, D. M.; Arnold, K. A.; Gokel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6659.

(16) Herrmann, W. A.; Thiel, W. R.; Brossmer, C.; Öfele, K.; Priermeier, T.; Scherer, W. *J. Organomet. Chem*., **1993**, *461*, 51.

(17) For a detailed investigation of electrochemical studies on palladium(0) species generated from diphosphines and $Pd(dba)_2$, see: Amatore, C.; Broeker, G.; Jutand, A.; Khalil, F. *J. Am. Chem. Soc.* **1997**, *119*, 5176 and references therein.

(18) The unligated [(PNP)Pd] should also be released in 8% yield during its oxidation in the diffusion layer. However, its oxidation peak is not observed (Figure 3a). This is probably due to the much smaller diffusion coefficient of [(PNP)Pd], which is a much larger molecule than dba ($i \propto nCD^{1/2}$, n = number of electrons; C = concentration; D = diffusion coefficient). At the same concentration, the monoelectronic reduction peak of dba always appears much higher than the bielectronic oxidation peak of the palladium(0) complexes due to important differences in the diffusion coefficients.[17,19c] This difference makes 8% of dba observable but not 8% of [(PNP)Pd].

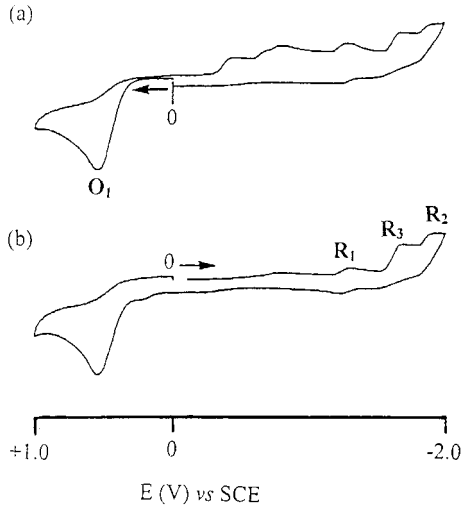
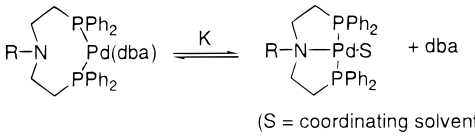


Figure 3. Cyclic voltammogram of **9b**, 2 mM in DMF/*n*-Bu_4NBF_4 (0.3 M) at a stationary gold-disk electrode (i.d. 2 mm) with a scan rate of 0.2 V s^{-1}: (a) oxidation; (b) reduction.

Scheme 5. Equilibrium Mixture of Ligated and Unligated Complexes



ligand. Evidence of this is provided by the cyclic voltammograms of complexes **9a**−**c** recorded in DMF. All three complexes gave rise to irreversible oxidation peaks, O_1 (Figure 3a). Of the three, the oxidation potential of complex **9a** (E^p = +0.35 V vs SCE) is remarkably different from the other two (**9b**, E^p = +0.53 V; **9c**, E^p = +0.57 V). More significantly, three peaks are observed in the voltammogram performed in reduction. Two of them correspond to the dissociated dba ligand, at −1.27 V (R_1, reversible) and −1.8 V (R_2, irreversible), confirmed by the increased intensity of these peaks with addition of the dba ligand to the solution. The third reduction peak at −1.7 V (R_3) is assigned to the reduction potential of the palladium(0) complex [(PNP)Pd(dba)].[17] The observation of the reduction peaks of dba suggests the presence of an equilibrium between the ligated [(PNP)Pd(dba)], unligated [(PNP)Pd], and dba in solution at room temperature (Scheme 5). The equilibrium is shifted to the right by the continuous reduction of dba in the diffusion layer during the voltammetric scan. Consequently, the reduction peak current of dba is a useful measure of the dynamic concentration of dba. Comparison of the reduction peak current of the released dba to that of an authentic sample of dba at the concentration of 1 mM showed that 8% of dba is released during the recording of the voltammagram at 0.2 V s^{-1}, which implies that the equilibrium is not totally labile at this time scale.[18]

(19) (a) Amatore, C.; Jutand, A.; Meyer, G.; Atmani, H.; Khalil, F.; Chahdi, F. O. *Organometallics* **1998**, *17*, 2958. (b) Amatore, C.; Jutand, A.; Medeiros, M. J. *New J. Chem.* **1996**, *20*, 1143 (c) Amatore, C.; Carre, E.; Jutand, A.; M'Barki, M. A. *Organometallics* **1995**, *14*, 1818. (d) Jutand, A.; Mosleh, A. *Organometallics* **1995**, *14*, 1810. (e) Amatore, C.; Jutand, A.; Khalil, F.; M'Barki, M. A.; Mottier, L. *Organometallics* **1993**, *12*, 3168.

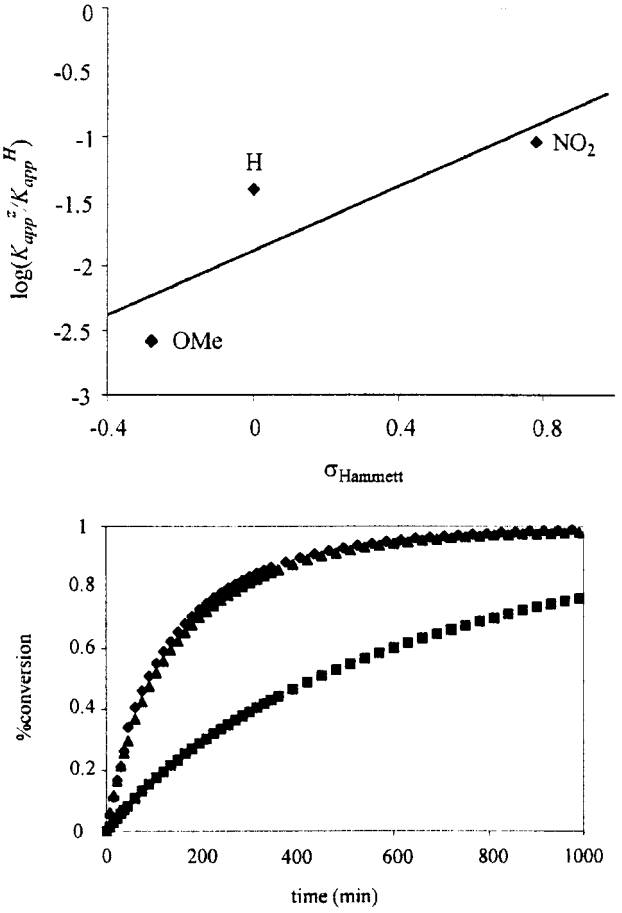


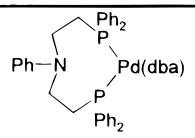
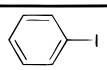
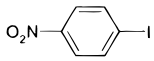
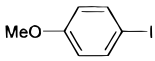
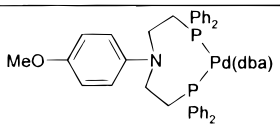
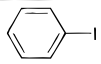
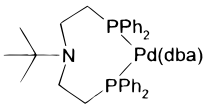
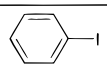
Figure 4. (a, top) Hammett plot for the oxidative addition of **9b**, to *para*-substituted aryl iodides *p*-Z-C_6H_4-I in DMSO at 20 °C. (b, bottom) Percentage formation (Ω/Ω_{lim}) of the cationic arylpalladium(II) iodide complexes **10a, 11**, and **12** as a function of time.

Although the dissociation of the dba ligand is detected by electrochemical methods, the precise coordination mode of the amino diphosphine ligand on the unligated complex [(PNP)Pd] complex is not known. However, it is not unreasonable to propose that the nitrogen donor is involved in the stabilization of the coordinatively unsaturated complex (Scheme 5).

Formation of [(PNP)Pd(Ar)]$^+$I$^-$ Complexes. Since oxidative addition of an aryl halide to palladium(0) constitutes a common first step in many palladium-catalyzed reactions,[19] the reactivity of the complexes **9a**−**c** with aryl iodides was tested. The addition of aryl iodides to **9a**−**c** furnished single species at room temperature, which were found to be 1:1 electrolytes in solution. This, combined with the observation of single $^{31}P\{^1H\}$ resonances, suggests the formation of cationic arylpalladium(II) iodide complexes, in which the PNP ligands are coordinated via all three donors (Table 3).

Rate of Oxidative Addition of Aryl Iodides. The rates of formation of complexes **10**−**12** were followed by the evolution of solution conductivity as a function of time, after addition of an excess (25 equiv) of aryl halide to solutions of **9a**−**c** at 20 °C. The measurements were carried out in a highly polar solution (DMSO) to minimize formation of ion pairs. Straight lines result from plots of $\ln[(\Omega_{lim} - \Omega_t)/\Omega_{lim}]$ vs time (Ω_{lim} = conductance at time = ∞; Ω_t = conductance at time *t*),

Table 3. ^{31}P NMR,[a] Conductivity,[b] and Rate[c] Data for the Oxidative Addition of Aryl Iodides to 9

Palladium(0) complex	Aryl iodide	Product	δP/ppm	Λ_m/S M^{-1}cm^{-1}	k_{app}/M^{-1}s^{-1}
 **9b**		**11a**	+23.8	1.34×10^{-2}	0.045
		**11b**	+26.2	1.45×10^{-2}	0.105
		**11c**	+23.7	1.38×10^{-2}	0.003
 **9c**		**12**	+23.9	1.55×10^{-2}	0.042
 **9a**		**10**	+25.3	1.65×10^{-2}	0.007

[a] Solution in DMSO with D_2O as external lock. [b] 5 mM solution in DMSO. [c] Addition of 25 equiv of aryl iodide to 5 mM of **9** in DMSO at 20 °C.[19d]

which indicates that the formation of the cationic arylpalladium(II) complex is first order in palladium(0).

The reaction of **9b** with different *para*-substituted aryl iodides was found to be fastest in the presence of electron-withdrawing substituents (Table 3); i.e., formation is faster in the order **11b** > **11a** > **11c**. A linear relationship was found to exist between $\log(k_{app}^{z}/k_{app}^{H})$ and Hammett σ constants (Figure 4a).

Since palladium(0) complexes **9a**−**c** dissociate in solution to form a mixture of dba-ligated and unligated species, the existence of such a pre-equilibrium needs to be taken into account. Of the two palladium precursors, the less-ligated palladium(0) species is expected to be more reactive toward oxidative addition.[17] This was confirmed when the rate of oxidative addition of iodobenzene to complex **9b** was dramatically reduced in the presence of added dba.

Likewise, the presence of a more electron-rich nitrogen donor, e.g. **9a**, is predicted to drive the equilibrium (Scheme 5) to the left. To probe this, the rates of formation of cationic phenylpalladium(II) iodide complex resulting from the reaction of **9a**−**c** with iodobenzene were also measured. We demonstrate that the rate of the reaction is indeed dependent on the nature of the nitrogen substituent (Figure 4b). The reaction with more electron-rich nitrogen donors are slower, i.e. rate of formation of **11a** > **12** ≫ **10**. This result is perhaps not surprising, since it is generally known that electron-rich palladium(0) metal centers generally disfavor the coordination of electron-rich (hard) nitrogen donor groups. This might favor the formation of the [(PNP)-Pd(dba)] complex, thus decreasing reactivity of the subsequent oxidative addition.

Summary and Conclusion

General routes for the synthesis of a number of PNP ligands of the general formula $R-N(CH_2CH_2PPh_2)_2$ (R = acyl, alkyl, aryl) have been developed. Their coordination chemistry with palladium has been explored and was found to be capable of PP-dimeric, PNP-monomeric, and PP-monomeric modes of coordination, depending on the substituents on palladium, as well as the nature of the R group on the nitrogen donor. It was also demonstrated for the first time that different substitutions on nitrogen have an appreciative effect on the rates of the oxidative addition reaction on palladium(0). This work has led to the preparation of a variety of other PNP type ligands incorporating different substitutions at nitrogen as well as on the backbone. The catalytic chemistry of these palladium complexes is currently under investigation.

Experimental Section

General Comments. All reactions and manipulations involving phosphine ligands were carried out under a dry nitrogen atmosphere by using standard Schlenk line techniques. Solvents such as THF (sodium/benzophenone), petroleum ether (sodium), and dichloromethane (CaH_2) were distilled before use. Diphenylphosphine,[20] $[PdCl_2(COD)]$,[21] $[Pd_2(dba)_3{\cdot}CHCl_3]$,[22] and bis[2-(diphenylphosphino)ethyl]amine−HCl[5] were prepared according to published procedures. All other reagents and chemicals were obtained commercially and used as received. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker ARX250 spectrometer (operating at 250.1, 62.9, and 101.2 MHz, respectively) or a Bruker AM400 MHz spectrometer (operating at 400.1, 100.6, and 161.9 MHz, respectively). ^{1}H and ^{13}C chemical shifts were reported relative to residual proton signals in the NMR solvent. ^{31}P NMR spectra were reported relative to external 85% H_3PO_4. Mass spectra and elemental analyses were carried out by the relevant Services within the School of Chemistry, University

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(21) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 52.
(22) (a) Takahashi, Y.; Ito, T.; Sakai, S.; Ishii, Y. *J. Chem. Soc. D* **1970**, 1065. (b) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1977**, *17*, 134.

Table 4. Crystallographic Data for 3

empirical formula	$C_{72}H_{70}Cl_4N_2O_4P_4Pd_2$
M_r	1505.78
size (mm)	0.42 × 0.23 × 0.1
temp (K)	180
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimensions	
a (Å)	9.63010(10)
b (Å)	13.6921(2)
c (Å)	14.2581(2)
α (deg)	71.6240(6)
β (deg)	72.7190(7)
γ (deg)	87.7460(7)
V (Å^3)	1700.55(4)
Z	1
ρ_{calcd} (Mg m^{-3})	1.470
μ (mm^{-1})	0.830
max, min transmissn	0.922, 0.722
F(000)	768
θ range (deg)	1.47−26.0
no. of rflns collected	42 066
no. of indep rflns	6656
R_{int}	0.0172
no. of params	399
goodness of fit on F^2	1.041
R1 ($F^2 > 2\sigma F^2$)	0.0262
wR2 (all data, F^2)	0.0727
largest peak/hole (e Å^{-3})	0.306, −0.672

of Leeds. Conductivity measurements were carried out in DMSO solutions using an EDT Series 3 BA380 conductivity meter with platinum electrodes (cell constant 1). Cyclic voltammetry was performed with a homemade potentiostat and a waveform generator, Tacussel Model GSTP4. The voltammograms were recorded on a Nicolet 3091 digital oscilloscope. Experiments were carried out in a three-electrode thermostated cell connected to a Schlenk line, under argon. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface area; the reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge (3 mL) filled with a 0.3 M *n*-Bu_4NBF_4 solution in THF. A 20 mL portion of THF containing 0.3 M *n*-Bu_4NBF_4 was introduced into the cell. The cyclic voltammetry was performed on a 2 mM solution of the palladium(0) complex with a stationary gold-disk electrode (i.d. 2 mm) with a scan rate of 0.2 V s^{-1}.

X-ray Structural Analysis of 3. Single yellow prismatic crystals were obtained by diffusion of *n*-hexane into a CH_2Cl_2 solution at room temperature. Crystal data and details of data collection and refinement are summarized in Table 4. All crystallographic measurements were carried out at 180 K on a Nonius KappaCCD area-detector diffractometer using Mo Kα radiation (λ = 0.710 73 Å). The detector was positioned 25 mm from the crystal, and data were collected as follows: "head-on" data (χ = 0°) as 360 oscillation frames of 60 s exposure time with 1° rotation in ϕ; "cusp" data (χ = 90°) as 35 frames of 60 s exposure time, and 1° ω rotations, collected at each of four different ϕ settings. The package DENZO-SMN[23] was used for indexing, unit cell refinement, and data integration and scaling. The data were corrected for Lorentz and polarization effects using Scalepack.[23] Subsequently an empirical absorption correction based on redundant and symmetry-equivalent data was applied using the program SORTAV.[24] The structure was solved by direct methods (SHELXS-97)[25] and was developed by alternating cycles of least-squares refinement (on F^2) and Fourier difference syntheses (SHELXL-97).[26] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were constrained to idealized positions (using a riding model with free rotation for methyl groups and fixed isotropic displacement parameters).

Preparation of Amino Diesters. *t*-$C_4H_9N(CH_2CO_2Et)_2$ (4a). Ethyl bromoacetate (2.1 equiv) was added to a stirred solution of the *tert*-butylamine in ethanol (50 mL). The solution was stirred at room temperature for 30 min. Sodium carbonate (1.5 equiv) was added, and the reaction mixture was subsequently refluxed for 16 h. The solution was filtered and the residue washed successively with dichloromethane. The combined filtrates were evaporated and the residue dissolved in 2 N HCl. The acidic solution was washed with diethyl ether to remove excess ethyl bromoacetate. The aqueous solution was then rendered basic (pH >10) by the addition of sodium hydroxide and extracted with dichloromethane. The combined organic layers were subsequently dried (Na_2SO_4), evaporated, and distilled in a Kugelröhr apparatus. The diester was obtained as a colorless oil (60%): bp 75 °C, 1.0 mmHg. Anal. Calcd for $C_{12}H_{23}NO_4$: C, 58.75; H, 9.45; N, 5.7. Found: C, 58.75; H, 9.35; N, 5.8. IR spectrum (thin film): ν(C=O) 1749 cm^{-1}. ^{1}H NMR ($CDCl_3$, 20 °C, 250 MHz; δ): 1.07 ppm, 9H, s, $(CH_3)_3C$; 1.19 ppm, 6H, t, J = 7.1 Hz, CH_3CH_2; 3.47 ppm, 4H, s, CH_2CO_2Et; 4.07 ppm, 4H, q, J = 7.1 Hz, CH_2CH_3. ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, 62.9 MHz, δ): 14.1 ppm, CH_2CH_3; 27.3 ppm, $(CH_3)_3C$; 51.2 ppm, CH_2CH_3; 54.9 ppm, $C(CH_3)_3$; 60.3 ppm, CH_2CO_2Et; 172.8 ppm, C=O.

$PhN(CH_2CO_2Et)_2$ (**4b**)[27] was obtained as a pale yellow oil (64%): bp 218−220 °C, 12 mmHg (lit.[27] bp 201 °C, 15 mmHg). IR spectrum (thin film): ν(C=O) 1746 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 20 °C, 400 MHz; δ): 1.26 ppm, 6H, t, J = 7.1 Hz, CH_3-CH_2; 4.13 ppm, 4H, s, CH_2CO_2Et; 4.23 ppm, 4H, q, J = 7.1 Hz, CH_3CH_2; 6.62 ppm, 2H, dd, J = 2.2, 7.4 Hz, H_{ortho}; 6.76 ppm, 1H, t, J = 7.3 Hz, H_{para}; 7.20 ppm, 2H, dd, J = 2.2, 7.4 Hz, H_{meta}.

$(4\text{-}MeOC_6H_4)N(CH_2CO_2Et)_2$ (**4c**)[15] was obtained as a pale yellow oil in 61% yield: bp 80 °C, 0.5 mmHg. The product slowly decomposes in air to a dark colored oil. IR spectrum (thin film): ν(C=O) 1746 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 20 °C, 400 MHz; δ): 1.27 ppm, 6H, t, J = 7.0 Hz, CH_3CH_2; 3.72 ppm, 3H, s, O*Me*; 4.10 ppm, 4H, s, CH_2CO_2Et; 4.19 ppm, 4H, q, J = 7.0 Hz, CH_3CH_2; 6.61 ppm, 2H, dm, H_{meta}(anisole); 6.80 ppm, 2H, dm, H_{ortho}(anisole). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, 62.9 MHz, δ): 14.2 ppm, CH_3CH_2; 54.0 ppm, CH_2CH_3; 55.6 ppm, O*Me*; 60.9 ppm, CH_2CO_2Et; 114.5 ppm, C_{ortho} *or* C_{meta}(anisole); 114.7 ppm, C_{ortho}- or C_{meta}(anisole); 142.4 ppm, C_{ipso}(anisole); 152.6 ppm, C_{para}(anisole); 171.1 ppm, C=O.

Preparation of Amino Diols. *t*-$C_4H_9N(CH_2CH_2OH)_2$ (5a).[28] The diester **4a** (10 g, 40.7 mmol) was added dropwise to a stirred suspension of lithium aluminum hydride (5.4 g, 142 mmol) in THF (80 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h, before it was refluxed for a further 16 h. The solution was cooled to 0 °C, and excess reducing agent was destroyed by the careful addition of water. The solid was removed via filtration, and the residue was washed with diethyl ether (2 × 100 mL). The combined filtrates were dried ($MgSO_4$) and evaporated to give a pale yellow oil (76%). ^{1}H NMR ($CDCl_3$, 20 °C, 250 MHz; δ): 0.91 ppm, 9H, s, $(CH_3)_3C$; 2.50 ppm, 4H, t, J = 6.0 Hz, CH_2N; 3.37 ppm, 4H, t, J = 6.0 Hz, CH_2O; 3.89 ppm, 2H. br.s, *OH*. ^{13}C-{^{1}H} NMR ($CDCl_3$, 20 °C, 62.9 MHz, δ): 26.9 ppm, $(CH_3)_3C$; 52.1 ppm, CH_2N; 55.0 ppm, $(CH_3)_3C$; 61.6 ppm, CH_2O.

$(4\text{-}MeOC_6H_4)N(CH_2CH_2OH)_2$ (5c).[15] A solution of the amine diester (5.03 g, 17 mmol) in THF (3 mL) was added dropwise to a cooled suspension of lithium aluminum hydride (2.5 g, 65.9 mmol) in THF (30 mL) at 0 °C. The solution was refluxed for 16 h. The reaction mixture was cooled (ice−water), and

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(24) Blessing, R. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.
(25) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
(26) Sheldrick, G. M. SHELXL-97, Program for Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.
(27) Thorpe, J. F.; Wood, A. S. *J. Chem. Soc.* **1913**, *103*, 1607.
(28) Imbach, J.-L.; Katritzky, A. R.; Kolinski, R. A. *J. Chem. Soc. B* **1966**, 556.

water was added carefully to destroy excess reducing agent, before filtering through a sintered-glass funnel. The residue and the filtrate were extracted successively with diethyl ether (100 mL) and dichloromethane (50 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and evaporated to give a yellow solid, which was recrystallized from methanol to give the product as colorless plates (84%). ^{1}H NMR ($CDCl_3$, 20 °C, 250 MHz; δ): 3.33 ppm, 2H, br s, O*H*; 3.44 ppm, 4H, t, $J = 5$ Hz, CH_2N; 3.74 ppm, 4H, t, $J = 5$ Hz, CH_2O; 3.75 ppm, 3H, s, O*Me*; 6.73 ppm, 2H, dm, H_{meta}(anisole); 6.82 ppm, 2H, dm, H_{ortho}(anisole). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, 62.9 MHz, δ): 55.8 ppm, O*Me*; 55.9 ppm, CH_2N; 60.6 ppm, CH_2O; 114.8 ppm, C_{ortho}(anisole); 115.8 ppm, C_{meta}(anisole); 142.6 ppm, C_{ipso}-(anisole); 152.4 ppm, C_{para}(anisole).

PhN(CH$_2$CH$_2$OH)$_2$ (5b)[29] was similarly obtained as a white solid, which was recrystallized from petroleum ether (82%).^{1}H NMR ($CDCl_3$, 20 °C, 250 MHz; δ): 3.32 ppm, 2H, br s, O*H*; 3.55 ppm, 4H, t, $J = 5$ Hz, CH_2N; 3.82 ppm, 4H, t, $J = 5$ Hz, CH_2O; 6.72 ppm, 1H, t, $J = 7.1$ Hz, H_{para}(Ph); 6.69 ppm, 2H, d, $J = 8.8$ Hz, H_{ortho}(Ph); 7.21 ppm, 2H, dd, $J = 7.1$, 8.8 Hz, H_{meta}(Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, 62.9 MHz, δ): 55.3 ppm, CH_2N; 60.81 ppm, CH_2O; 112.66 ppm, C_{ortho}(Ph); 116.98 ppm, C_{para}(Ph); 129.3 ppm, C_{meta}(Ph); 147.85 ppm, C_{ipso}(Ph).

Preparation of Alkylamine Dichlorides. ***t*-C$_4$H$_9$N(CH$_2$CH$_2$Cl)$_2$·HCl (6a, X = Cl)**.[28] A solution of the amino alcohol *t*-$C_4H_9N(CH_2CH_2OH)_2$ (2 g, 12.4 mmol) in chloroform (10 mL) was added to a stirred solution of thionyl chloride (15 cm^3, 205 mmol) in chloroform (10 mL) at 0 °C. The solution was warmed to room temperature, and stirring was continued for 3 days. Evaporation of excess thionyl chloride gave the product as a white solid (92%). ^{1}H NMR ($CDCl_3$, 20 °C, 250 MHz; δ): 1.50 ppm, 9H, s, C(CH_3)$_3$; 3.40 ppm, 4H, br m, CH_2N; 4.1 ppm, br t, CH_2Cl. ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, 62.9 MHz, δ): 24.7 ppm, C(CH_3)$_3$; 38.1 ppm, CH_2Cl; 52.1 ppm, CH_2N; 66.2 ppm, $C(CH_3)_3$.

Preparation of Arylamine Ditosylates. **PhN(CH$_2$CH$_2$OTs)$_2$ (6b; X = OTs)**.[30] Toluenesulfonyl chloride (8.2 g, 36.2 mmol.) was added portionwise to stirred pyridine (20 mL) at 0 °C. The mixture was stirred and warmed to room temperature, where it was allowed to stand for 30 min. Stirring was reactivated, and the solution was recooled to 0 °C, whereupon the amine diol (3 g, 15.3 mmol) was added very slowly over 15 min. White precipitate started to form at this stage. The reaction mixture was then stirred at room temperature for 4 h and poured into ice−water. The aqueous solution was extracted with dichloromethane (4 × 25 mL), and the combined organic extracts were washed with 1 M HCl (2 × 25 mL), brine (30 mL), and saturated Na_2HCO_3 solution (25 mL). The colorless solution was dried over $MgSO_4$, filtered, and evaporated to give a white solid, which was recrystallized from dichloromethane/diethyl ether. The product was obtained as white needles (85%). ^{1}H NMR ($CDCl_3$, 20 °C, 250 MHz; δ): 2.41 ppm, 6H, s, *Me*; 3.54 ppm, 4H, t, $J = 6.0$ Hz, CH_2N; 4.09 ppm, 4H, t, $J = 6.0$ Hz, CH_2O; 6.43 ppm, 2H, d, $J = 8.7$ Hz, H_{ortho}-(Ph); 6.70 ppm, 1H, t, $J = 7.3$ Hz, H_{para}(Ph); 7.12 ppm, 2H, d, $J = 7.3$, 8.7 Hz; H_{meta}(Ph); 7.27 ppm, 4H, d, $J = 8.3$ Hz, H_{meta}-(tosylate); 7.71 ppm, 4H, d, $J = 8.3$ Hz, H_{ortho}(tosylate).

***p*-MeOC$_6$H$_4$N(CH$_2$CH$_2$OTs)$_2$ (6c; X = OTs)** was prepared in a similar manner from the ditosylate (62%). ^{1}H NMR ($CDCl_3$, 20 °C, 250 MHz; δ): 2.42 ppm, 6H, *Me*; 3.46 ppm, 4H, t, $J = 6.0$ Hz, CH_2N; 3.73 ppm, 3H, s, O*Me*; 4.04 ppm, 4H, t, $J = 6.0$ Hz, CH_2O; 6.46 ppm, 2H, dm, H_{meta}(anisole); 6.73 ppm, 2H, dm, H_{ortho}(anisole); 7.28 ppm, 4H, dm, H_{meta}(tosylate); 7.72 ppm, 4H, dm, H_{ortho}(tosylate).

Preparation of (4-methoxyphenyl)bis[2-(diphenylphosphino)ethyl]amide (2). A solution of *p*-anisic acid (96 mg, 0.63 mmol), *N*,*N*-bis(dimethylamino)pyridine (95 mg, 0.78 mmol), and diphosphine **1** in dry dichloromethane (3 mL) was stirred and cooled to 0 °C. A solution of dicyclohexylcarbodiimide (130 mg, 0.63 mmol) in dichloromethane (3 mL) was added dropwise. The resultant reaction mixture was stirred at room temperature for 16 h, whereupon a white precipitate formed. The reaction mixture was filtered through Celite, and the filtrate was evaporated to dryness. The residue was recrystallized from methanol, giving the analytically pure amido diphosphine as a white solid. Yield: 246 mg (70%). Anal. Calcd for $C_{36}H_{35}NO_2P_2$: C, 75.10; H, 6.1; N, 2.4. Found: C, 74.95; H, 6.1; N, 2.35. IR spectrum (KBr disk): ν(C≡O) 1635 (s) cm^{-1}; ν(C═C) 1606 (m), 1507 (m) cm^{-1}. MS (EI): *m*/*z* 575 (M$^+$), 498 (M$^+$ − Ph), 390 (M$^+$ − PPh$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, −20 °C, 101.2 MHz, δ): −19.9, −20.6 ppm. ^{1}H NMR ($CDCl_3$, −20 °C, 400 MHz; δ): 2.15 ppm, 2H, m, CH_2P; 2.45 ppm, 2H, m, CH_2P; 3.35 ppm, 2H, m, CH_2N; 3.58 ppm, 2H, m, CH_2N; 6.78 ppm, 2H, dm, H_{meta}(anisole); 7.17 ppm, 2H, dm, H_{ortho}-(anisole); 7.23−7.35 ppm, 20H, m, P*Ph*.

Preparation of *tert*-Butylbis[2-(diphenylphosphino)-ethyl]amine (7a). Potassium hydride (20% in oil, 3.4 g, 17.0 mmol) was placed in a Schlenk tube, washed with pentane (3 × 5 mL), and dried. Dry THF (20 mL) was added, and the suspension was stirred at room temperature while diphenylphosphine (2.96 mL, 17 mmol) was added slowly, dropwise, via a syringe. The resultant red solution was stirred at room temperature for 2 h and then cooled to 0 °C (ice−water). The dichloro compound was added slowly dropwise, and the orange slurry was stirred at room temperature for another 3 h. Methanol (2 mL) was added to destroy any excess base, and the solvents were removed under vacuum. The residue was then extracted with diethyl ether (100 mL) and filtered. The filtrate was evaporated to give a dense white oil, which crystallized when left at room temperature overnight. This was washed with *n*-pentane, water, and a small amount of cold methanol. Yield: 2.69 g, 75%. Anal. Calcd for $C_{32}H_{37}NP_2$: C, 77.25; H, 7.5; N, 2.8. Found: C, 77.25; H, 7.6; N, 2.8. ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C, 101.2 MHz, δ): −19.3 ppm. ^{1}H NMR ($CDCl_3$, 20 °C, 250 MHz; δ): 0.99 ppm, 9H, s, (CH_3)$_3$C; 2.15 ppm, 4H, m, CH_2P; 2.36 ppm, 4H, m, CH_2N; 7.28−7.69 ppm, 20H, m, P*Ph*. ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, 62.9 MHz, δ): 27.4 ppm, s, (CH_3)$_3$C; 29.9 ppm, d, $J_{C,P} = 12.5$ Hz, CH_2P; 46.4 ppm, d, $J_{C,P} = 26.0$ Hz, CH_2N; 55.3 ppm, s, $C(CH_3)_3$; 128.4 ppm, d, $J_{C,P} = 12.0$ Hz, C_{meta}(PPh); 128.4 ppm, s, C_{para}(PPh); 132.8 ppm, d, $J_{C,P} = 18.5$ Hz, C_{ortho}(PPh); 138.6 ppm, d, $J_{C,P} = 12.5$ Hz, C_{ipso}(PPh).

Preparation of Phenylbis[2-(diphenylphosphino)ethyl]amine (7b). This compound was prepared similarly from the corresponding ditosylate **6b** (87%). Anal. Calcd for $C_{34}H_{33}NP_2$: C, 78.90; H, 6.4; N, 2.7. Found: C, 78.95; H, 6.6; N, 2.8. MS (EI) *m*/*z* 517 (M$^+$), 440 (M$^+$ − Ph), 332 (M$^+$ − PPh$_2$), 318 (M$^+$ − CH$_2$PPh$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C, 101.2 MHz, δ): −20.5 ppm. ^{1}H NMR ($CDCl_3$, 20 °C, 250 MHz; δ): 2.24 ppm, 4H, m, CH_2P; 3.31 ppm, 4H, m, CH_2N; 6.32 ppm, 2H, d, $J = 8.3$ Hz, H_{ortho}(NPh); 6.59 ppm, 1H, t, $J = 7.0$ Hz, H_{para}(NPh); 7.05 ppm, 2H, dd, $J = 7.0$, 8.3 Hz, H_{meta}(NPh); 7.21−7.37 ppm, 20H, m, P*Ph*.^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, 62.9 MHz, δ): 26.0 ppm, d, $J_{C,P} = 14.5$ Hz, CH_2P; 47.7 ppm, d, $J_{C,P} = 25$ Hz, CH_2N; 112.4 ppm, s, C_{ortho}(NPh); 116.2 ppm, s, C_{para}(NPh), 128.5 ppm, d, $J_{C,P} = 12.0$ Hz, C_{meta}(PPh); 128.5 ppm, s, C_{para}(PPh); 128.6 ppm, d, $J_{C,P} = 13.0$ Hz, C_{meta}(PPh); 129.2 ppm, s, C_{meta}(NPh); 132.8 ppm, d, $J_{C,P} = 19$ Hz, C_{ortho}(PPh); 138.0 ppm, d, $J_{C,P} = 12.2$ Hz, C_{ipso}(PPh); 146.8 ppm, s, C_{ipso}(NPh).

Preparation of (4-Methoxyphenyl)bis[2-(diphenylphosphino)ethyl]amine (7c). This compound was prepared similarly from the corresponding ditosylate (60%). A sample recrystallized from methanol was found to contain 0.5 mol of water (^{1}H NMR). Anal. Calcd for $C_{35}H_{35}NOP_2 \cdot 0.5H_2O$: C, 77.5; H, 6.5; N, 2.5. Found: C, 75.35; H, 6.3; N, 2.35.MS (EI) *m*/*z* 547 (M$^+$), 470 (M$^+$ − Ph), 362 (M$^+$ − PPh$_2$), 348 (M$^+$ − CH$_2$-PPh$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C, 101.2 MHz, δ): −20.2 ppm. ^{1}H NMR ($CDCl_3$, 20 °C, 250 MHz; δ): 2.14−2.20 ppm, 4H, m,

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CH$_2$P; 3.18−3.26 ppm, 4H, m, *CH*$_2$N; 3.69 ppm, 3H, s, O*Me*; 6.37 ppm, 2H, dm, H_{meta}(anisole); 6.67 ppm, 2H, dm H_{ortho}-(anisole); 7.21−7.71 ppm, 20H, m, P*Ph*. ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, 62.9 MHz, δ): 25.9 ppm, d, $J_{C,P}$ = 14 Hz, *CH*$_2$P; 48.6 ppm, d, $J_{C,P}$ = 25 Hz, *CH*$_2$N; 55.7 ppm, s, O*Me*; 114.8 ppm, C_{para}(PPh); 115.6 ppm, C_{para}(PPh); 128.5 ppm, d, $J_{C,P}$ = 11 Hz, C_{meta}(PPh); 128.6 ppm, d, $J_{C,P}$ = 7.0 Hz, C_{meta}(PPh); 132.7 ppm, d, $J_{C,P}$ = 12.5 Hz, C_{ortho}(PPh); 138.2 ppm, d, $J_{C,P}$ = 12.5 Hz, C_{ipso}(PPh); 141.8 ppm, s, C_{ipso}(anisole); 151.9 ppm, s, C_{para}-(anisole).

Palladium Complexes. [{4-MeOC$_6$H$_4$CON(CH$_2$CH$_2$PPh$_2$)$_2$}-PdCl$_2$]$_2$ (3). Method A (Concentrated). [$PdCl_2$(NCMe)$_2$] (18 mg, 0.07 mmol) and amido diphosphine **2** (40 mg, 0.07 mmol) were mixed in dichloromethane (2 mL). The yellow solution was stirred for 1 h and then filtered through Celite. The filtrate was evaporated to dryness, and the addition of methanol to the residue gave the required palladium complex as a yellow solid. Yield: 33 mg, 63%. Anal. Calcd for $C_{36}H_{35}NO_2P_2PdCl_2$: C, 57.4; H, 4.7; N, 1.85; Cl, 9.4. Found: C, 57.0; H, 4.6; N, 1.75; Cl, 9.8. MS (FAB): *m*/*z* 1469 (L_2 + Pd_2 + Cl_3), 716 (L + Pd + Cl). ^{31}P{^{1}H} NMR ($CDCl_3$, −20 °C, 161 MHz, δ): **3a**, P_A-10.0 ppm, d; **3a**, P_B 13.2 ppm; $J_{P,P}$ = 553 Hz; **3b**, P_C 10.6 ppm, s; **3b**, P_D 12.8 ppm, s. ^{1}H NMR ($CDCl_3$, −20 °C, 400 MHz; δ, two geometrical isomers): 2.54 ppm, 2H, br m, C*H*$_2$N; 3.0 ppm, 4H, br m, C*H*$_2$N; 3.25 ppm, 2H, br m, C*H*$_2$N; 3.45 ppm, 2H, br m, C*H*$_2$P; 3.6 ppm, 2H, br m, C*H*$_2$P; 3.80 ppm, 3H, s, O*Me*; 3.85 ppm, 3H, s, O*Me*; 3.95 ppm, 4H, br m., C*H*$_2$P; 6.58 ppm, 2H, dm, H_{meta}(anisole); 6.68 ppm, 2H, dm, H_{meta}(anisole); 6.95 ppm, 2H, dm, H_{ortho}(anisole); 7.07 ppm, 2H, dm, H_{ortho}(anisole); 7.23−7.9 ppm, 40H, P*Ph*.

Method B (Dilute). A solution of [$PdCl_2$(COD)] (25 mg, 0.09 mmol) in dichloromethane (5 mL) was added very slowly to a stirred solution of the amido diphosphine **2** (50 mg, 0.09 mmol) in dichloromethane (12 mL). The reaction mixture was stirred for 4 h. The solvent was then removed, and the product was precipitated with diethyl ether. The product was then collected by filtration, washed (diethyl ether), and dried. Yield: 54 mg, 82%. The product was found to be identical with that prepared using the previous method.

[{*t*-C$_4$H$_9$N(CH$_2$CH$_2$PPh$_2$)$_2$}PdCl]$^+$Cl$^-$ (8a). A solution of [$PdCl_2$(COD)] (55 mg, 0.19 mmol) in toluene (2 mL) was added to a refluxing solution of bis[2-(diphenylphosphino)ethyl]-*tert*-butylamine (**7a**; 100 mg, 0.2 mmol) in toluene (2 mL). The reaction mixture was subjected to reflux for a further 2 h. The cooled reaction mixture was then evaporated. Addition of diethyl ether to the residue yielded the product as a buff solid. Yield: 99 mg, 72%. A sample was recrystallized from methanol for microanalysis; the presence of one molecule of solvent was confirmed by the ^{1}H NMR spectrum. Anal. Calcd for $C_{32}H_{35}$-NOP_2PdCl_2·MeOH: C, 54.95; H, 5.45; N, 1.95; Cl, 9.85. Found: C, 54.75; H, 5.6; N, 1.75, Cl, 10.0. ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C, 101.2 MHz, δ): 20.3 ppm. ^{1}H NMR ($CDCl_3$, 20 °C, 250 MHz; δ): 1.00 ppm, 9H, s, C*Me*$_3$; 2.51 ppm, 4H, m, C*H*$_2$N; 2.99 ppm, 4H, dm, J = 21 Hz, C*H*$_2$P; 7.18−7.64 ppm, 20H, m, P*Ph*. ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, 62.9 MHz, δ): 26.5 ppm, s, C*Me*$_3$; 29.1 ppm, d, $J_{C,P}$ = 33 Hz, *CH*$_2$N; 46.7 ppm, virtual triplet, *CH*$_2$P; 56.8 ppm, s, *C*Me$_3$; 128.2 ppm, d, $J_{C,P}$ = 11 Hz, C_{meta}(PPh); 130.5 ppm, s, C_{para}(PPh); 132.2 ppm, $J_{P,C}$ = 54 Hz, C_{ipso}(PPh); 133.2 ppm, d, $J_{C,P}$ = 10 Hz, C_{ortho}(PPh).

[{Ph(CH$_2$CH$_2$PPh$_2$)$_2$}PdCl]$^+$Cl$^-$ (8b). A solution of palladium dichloride (50 mg, 0.28 mmol) and the amino diphosphine (146 mg, 0.28 mmol) in dimethyl sulfoxide (1.5 mL) was stirred and heated until a clear orange solution was obtained. The reaction mixture was then poured into water to give **8b** as a yellow solid, which was filtered off, washed with methanol, and dried in *vacuo*. Yield: 111 mg, 57%. MS (FAB): *m*/*z* 658 (M$^+$− Cl), 623 (M$^+$− 2Cl). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C, 101.2 MHz, δ): 32.6 ppm. ^{1}H NMR ($CDCl_3$, 20 °C, 250 MHz; δ): 2.03 ppm, 1H, m, C*H*$_2$N; 2.27 ppm, 1H, m, C*H*$_2$N; 2.69 ppm, 1H, m, C*H*$_2$N; 3.25 ppm, 1H, m, C*H*$_2$P; 3.44 ppm, 2H, m, C*H*$_2$P; 4.00 ppm, 1H, m, C*H*$_2$P; 4.60 ppm, 1H, m, C*H*$_2$P; 7.30−8.42 ppm, 25H, m, *Ph*.

[{*p*-MeOC$_6$H$_4$N(CH$_2$CH$_2$PPh$_2$)$_2$}PdCl]$^+$Cl$^-$ (8c). A solution of [$PdCl_2$(COD)] (54 mg, 0.19 mmol) in dichloromethane (4 mL) was added slowly to a stirred solution of the amino diphosphine (104 mg, 0.19 mmol) in dichloromethane (3 mL). Stirring was continued at room temperature for 16 h. Solvent was evaporated, and the addition of diethyl ether to the residue gave the product as a yellow solid. Yield: 129 mg, 94%. Λ_m (DMSO) = 2.23 × 10^{-2} S M^{-1} cm^{-1}. IR (Nujol mull): ν(Pd−Cl) 352 cm^{-1}. MS (FAB): *m*/*z* (FAB) 690 (M$^+$− Cl), 653 (M$^+$− 2Cl). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C, 161.9 MHz, δ): 32.7 ppm. ^{1}H NMR ($CDCl_3$, 20 °C, 400 MHz; δ): 2.32 ppm, 2H, m, C*H*$_2$N; 2.71 ppm, 2H, m, C*H*$_2$N; 3.70 ppm, 2H, m, C*H*$_2$P; 3.78 ppm, 3H, s, O*Me*; 4.87 ppm, 2H, m, C*H*$_2$P; 7.30−7.65 ppm, 15H, *Ph*; 7.93 ppm, 2H, m, P*Ph*; 8.57 ppm, 2H, m, P*Ph*. ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C, 100.6 MHz, δ): 29.7 ppm, virtual triplet, C*H*$_2$P; 55.6 ppm, 2, O*Me*; 66.2 ppm, s, C*H*$_2$N; 126.9 ppm, virtual triplet, C_{ipso}(PPh); 128.0 ppm, virtual triplet, C_{ipso}(PPh); 129.3−133.6 ppm, *Ar*; 138.5 ppm, s, C_{ipso}(anisole); 160.3 ppm, s, C_{para}-(anisole).

[{*t*-C$_4$H$_9$N(CH$_2$CH$_2$PPh$_2$)$_2$}Pd(η^2-PhCH=CHCOCH=CHPh)] (9a). $Pd_2(dba)_3$·$CHCl_3$ (290 mg, 0.28 mmol) was added to a stirred solution of the amino diphosphine in toluene (3 mL). The reaction mixture was stirred for 1 h, whereupon the product precipitated as an orange solid, which was filtered off, washed (Et_2O), and dried. Yield: 308 mg, 65%. MS (FAB): *m*/*z* 603 (M$^+$− dba), 546 (M$^+$− dba − ^{t}Bu). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C, 101.2 MHz, δ): 10.9 ppm, br s; 12.3 ppm, br s. E^p (vs SCE, DMF): +0.35 V.

[{PhN(CH$_2$CH$_2$PPh$_2$)$_2$}Pd(η^2-PhCH=CHCOCH=CHPh)] (9b) was prepared similarly in 60% yield. Anal. Calcd for $C_{51}H_{47}NOP_2Pd$·H_2O: C, 69.9; H, 5.6; N, 1.6. Found: C, 69.4; H, 5.6; N, 1.5. MS (FAB): *m*/*z* 858 (M$^+$), 623 (M$^+$− dba). ^{31}P-{^{1}H} NMR ($CDCl_3$, 20 °C, 101.2 MHz, δ): 17.0 ppm, br s, 18.7 ppm, br s. E^p (vs SCE, DMF): +0.53 V.

[{*p*-MeOC$_6$H$_4$N(CH$_2$CH$_2$PPh$_2$)$_2$}Pd(η^2-PhCH=CHCOCH=CHPh)] (9c) was prepared in a similar manner in 64% yield. MS (FAB): *m*/*z* 653 (M$^+$− dba).^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C, 101.2 MHz, δ): 16.9 br s; 18.2 ppm, br s. E^p (vs SCE, DMF): +0.57 V.

[{PhN(CH$_2$CH$_2$PPh$_2$)$_2$}Pd(Ph)]$^+$I$^-$ (11a). Iodobenzene (70 μL) was added to a solution of palladium(0) complex **9b** in dichloromethane (1 mL). The solution turned pale yellow at room temperature over 10 min, whereupon the solvent was removed under reduced pressure and diethyl ether added to the residue to precipitate the required iodide salt as a beige solid. ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C, 101.2 MHz, δ): 24.2 ppm. ^{1}H NMR (CD_2Cl_2, 20 °C, 250 MHz; δ): 2.34 ppm, 2H, m, C*H*$_2$N; 2.89 ppm, 1H, m, C*H*$_2$N; 3.76−3.91 ppm, 2H, m, C*H*$_2$P; 4.52−4.75 ppm, 1H, m, C*H*$_2$P; 6.85 ppm, 2H, m, H_{meta}(NPh); 7.09 ppm, 2H, m, H_{ortho}(NPh); 7.127.97 ppm, 20H, m, P*Ph*; 8.39 ppm, 1H, d, J = 8.1 Hz, H_{para}(NPh).

[{PhN(CH$_2$CH$_2$PPh$_2$)$_2$}Pd(4-O$_2$NC$_6$H$_4$)]$^+$I$^-$ (11b) was isolated as a deep purple solid. MS (FAB): *m*/*z* 745 (M$^+$). ^{31}P-{^{1}H} NMR ($CDCl_3$, 20 °C, 101.2 MHz, δ): 26.6 ppm. ^{1}H NMR ($CDCl_3$, 20 °C, 250 MHz; δ): 2.45 ppm, 2H, m, C*H*$_2$N; 3.10 ppm, 2H, m, C*H*$_2$N; 4.15 ppm, 2H, m, C*H*$_2$P; 4.70 ppm, 2H, m, C*H*$_2$P; 7.09−7.89 ppm, 29H, aryl H's.

Measurement of the Rate of Oxidative Reaction of Aryl Halides to Palladium(0) Complexes. The palladium-(0) complex (0.025 mmol) was dissolved in DMSO (5 mL). Residual conductivity was checked. The aryl iodides were dissolved in 1 cm^3 of DMSO and added quickly to the palladium complex solution, and the rise in conductivity of the reaction mixture was monitored during regular time intervals. The end point was taken when there was no change in conductivity. A sample of the reaction mixture was then removed and the ^{31}P{^{1}H} NMR spectrum of it recorded, using D_2O as an external lock.

Acknowledgment. This work was carried out in the School of Chemistry, University of Leeds, as part of the Ramsay Memorial Fellowship project, supported by the Ramsay Memorial Fellowship Trust and ICI Strategic Research Fund. K.K.H. thanks Johnson Matthey for the loan of precious metals and Dr. Duncan Carmichael for his generous donations of diphenylphosphine. She also acknowledges Dr. T. P. Kee for the loan of conductivity equipment and Dr. P. C. McGowan for useful discussions.

Supporting Information Available: X-ray crystallographic files for **3**, in CIF format, are available. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980978T