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Effect of Ligand Steric Properties and Halide Identity on the Mechanism for Oxidative Addition of Haloarenes to Trialkylphosphine Pd(0) Complexes

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Abstract: The oxidative addition of PhX (X = I, Br, Cl) to the complexes $Pd(P^tBu_3)_2$ (**1**), $Pd(1\text{-}AdP^tBu_2)_2$ (**2**), $Pd(CyP^tBu_2)_2$ (**3**), and $Pd(PCy_3)_2$ (**4**) (1-Ad = 1-adamantyl, Cy = cyclohexyl) was studied to determine the effect of steric properties on the coordination number of the species that undergoes oxidative addition and to determine whether the type of halide affects the identity of this species. The kinetic data imply that the number of phosphines coordinated to the complex that reacts in the irreversible step of the oxidative addition process for complexes **1**−**4** depends more on the halide than on the steric properties of the ligands. The rate-limiting step of the oxidative addition of PhI occurred with $L_2Pd(0)$ in all cases, as determined by the lack of dependence of k_{obs} on $[P^tBu_3]$, $[1\text{-}AdP^tBu_2]$, or $[CyP^tBu_2]$ and the inverse dependence of the rate constant on $[PCy_3]$ when the reaction was initiated with $Pd(PCy_3)_3$. The irreversible step of the oxidative addition of PhCl occurred with a monophosphine species in each case, as signaled by an inverse dependence of the rate constant on the concentration of ligand. The irreversible step of the oxidative addition of PhBr occurred with a bisphosphine species, as signaled by the zeroth-order or small dependence of the rate constant on the concentration of phosphine. Thus, the additions of the less reactive chloroarenes occur through lower-coordinate intermediates than additions of the more reactive haloarenes.

Introduction

The oxidative addition of haloarenes to Pd(0) complexes is a fundamental organometallic reaction.[1] It constitutes the first step in palladium-catalyzed reactions of haloarenes, such as aromatic amination[2−4] and Heck,[5,6] Suzuki,[7−10] and Stille[11,12] couplings. Many of these oxidative additions involve phosphine-ligated Pd(0) species. Some of the most active catalysts for these reactions involve hindered alkylphosphine ligands that form bisphosphine complexes of Pd(0).[13−17] Because of the high activity of these catalysts, the mechanism of the oxidative addition to the bisphosphine Pd(0) complexes is important to determine. Moreover, it would be valuable to reveal the relationships between the reactivity of the isolated $L_2Pd(0)$ species in which L is a hindered trialkylphosphine and the well-known Pd(0) reactive intermediate in which L is PPh_3.[18,19]

The oxidative addition of haloarenes to $L_2Pd(0)$ complexes in which L is a trialkylphosphine could occur directly to the bisphosphine starting complex to form a four-coordinate product, or it could occur to a monophosphine intermediate[20,21] that would form a three-coordinate arylpalladium halide complex[22,23] as the immediate product. Previous studies have shown that the coordination number of the palladium species that undergoes oxidative addition and the structure of the complexes produced

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by oxidative addition are different for reactions of complexes containing various ligands.[18,19,24−36]

A majority of these studies have been conducted on complexes containing monophosphine ligands.[18,19,24−29] The mechanism appears to depend on the steric and electronic properties of the ligand. For example, classic studies of the addition of ArI to $Pd(PPh_3)_4$ showed that this reaction occurs through the 14-electron intermediate $Pd(PPh_3)_2$ to produce a four-coordinate arylpalladium halide complex.[18,19] In contrast, more recent studies of the oxidative addition of PhBr to $Pd(P(o\text{-}Tol)_3)_2$ implied that this reaction occurred by addition of the aryl halide to a monophosphine intermediate to form a dimeric arylpalladium bromide complex containing a single phosphine per metal center.[20] Addition of ArI to a series of trialkylphosphine palladium complexes having the general formula $Pd(Cy_n\text{-}P^tBu_{3-n})_2$ ($n = 0-3$; Cy = cyclohexyl) has also been conducted. The authors of this work concluded that complexes containing the bulkier phosphines ($n = 0$, 1) underwent addition of ArI after dissociation of ligand to form a monophosphine intermediate and that complexes containing the smaller phosphines ($n =$ 2, 3) reacted through an associative pathway.[27] The results of studies of reactions of PPh_3 complexes in the presence of anions have also been published. For example, the 16-electron anion $[Pd(PPh_3)_2(OAc)]^-$ generated in situ from $Pd(OAc)_2$ and PPh_3 has been proposed as the species that adds haloarenes when the reaction is conducted in the presence of acetate.[25,26]

Studies of oxidative addition to complexes of bidentate ligands have also been conducted. The oxidative addition of aryl bromides to $[Pd(bisphosphine)_2]$ [bisphosphine = 1,1′-bis(diphenylphosphino)ferrocene (DPPF), 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP)] occurred predominantly to Pd(bisphosphine), with a second pathway appearing to involve reaction of the aryl halide with $[Pd(\kappa^2\text{-bisphosphine})(\kappa^1\text{-bisphosphine})]$.[31,32] Prior studies of the oxidative addition of ArCl to $Pd(dippp)_2$ [dippp =bis(diisopropylphosphino)propane] showed that this reaction involved addition to the 14-electron Pd(dippp) intermediate to form *cis*-(dippp)Pd(Ph)(Cl) as the main product. In the presence of free phosphine, this complex equilibrates with *trans*-$(\kappa^1\text{-dippp})_2Pd(Ph)(Cl)$.[28]

The identity of the halide in the haloarene could affect the mechanism of oxidative addition for a given ligand. In a recent communication, we reported that the oxidative additions of iodo-, bromo-, and chlorobenzene to Pd(0) complexes of Q-phos (Q-phos = pentaphenylferrocenyldi-*tert*-butylphosphine) occur with three different kinetic behaviors.[21] Addition of PhI occurs by irreversible associative displacement of a phosphine, addition of PhBr by rate-limiting dissociation of phosphine, and addition of PhCl by reversible dissociation of phosphine followed by rate-limiting oxidative addition.[21]

The diversity of these results from reactions of several classes of complexes with various haloarenes under different reaction conditions illustrates the need for a systematic study of the factors that control the coordination number of the Pd(0) species that adds the haloarene. Thus, we have conducted such a study of the oxidative addition of iodo-, bromo-, and chlorobenzene to complexes of alkyl phosphines of various sizes. This study has produced data that begin to clarify the effects of the halide in the haloarene and the effects of the size of the alkyl phosphine on the reaction mechanism. In brief, the number of phosphines coordinated to the complex that reacts in the irreversible step is more dependent on the identity of the halide than on the size of the phosphine ligands in this study, which contain cyclohexyl, *tert*-butyl, and 1-adamantyl (1-Ad) groups.

Results

1. Oxidative Additions Included in this Study and Characterization of Reaction Products. The oxidative addition of PhX (X = I, Br, Cl) to PdL_2 complexes **1−4** containing as L the trialkylphosphines P^tBu_3, 1-AdP^tBu_2, CyP^tBu_2, and PCy_3, respectively, were studied. Scheme 1 summarizes the Pd(0) complexes **1−4** and their reactions to form the arylpalladium halide products **5−19**. Although kinetic studies of the oxidative addition reactions showed that the mechanism depends predominantly on the identity of the halide, the identity of the reaction products depended most strongly on the steric properties of the ligand. Thus, this section describing the reactions and characterization of the products is organized by ligand type.

1.1. Additions of ArX to Complexes of P^tBu_3 and 1-AdP^tBu_2. The reactions of PhI and PhBr with the Pd(0) complexes $Pd(P^tBu_3)_2$ (**1**) and $Pd(1\text{-}AdP^tBu_2)_2$ (**2**) has been shown to produce the known three-coordinate complexes **5−8** (Scheme 1) in 50−87% yield.[22,23] These complexes have previously been shown to be stabilized by a weak agostic interaction of the metal with a phosphine C−H bond positioned at the open coordination site.

In the current work, the reaction of **1** with 1-chloro-2-trifluoromethylbenzene at 80 °C for 1 h produced the stable complex $[(P^tBu_3)Pd(2\text{-}CF_3C_6H_4)(Cl)]_2$ (**10**) in 59% isolated yield (Scheme 1). Reaction of **2** with 1-chloro-2-trifluoromethylbenzene at 80 °C for 1 h produced $[(1\text{-}AdP^tBu_2)Pd(2\text{-}CF_3C_6H_4)(Cl)]_2$ (**12**) in 85% yield as determined by ^{31}P NMR spectroscopy. Complex **12** was isolated in 39% yield after reaction for 20 min at 100 °C and subsequent recrystallization. The reactions of **1** and **2** in neat PhCl at 80 °C formed $[LPd(Ph)(Cl)]_2$ [L = P^tBu_3 (**9**), 1-AdP^tBu_2 (**11**)], but the yields of the oxidative addition products at full conversion were low because of decomposition of these products. The yields of the oxidative addition products at 50% conversion were high [∼80% with respect to the amount of reacted Pd(0) species], but at higher conversions, the arylpalladium halide products decayed.

Thus, phenylpalladium chloride complexes **9** and **11** were characterized after they were prepared independently (Scheme 2). P^tBu_3-ligated complex **9** was isolated in 42% yield from the reaction of $(Py)_2Pd(Ph)(Cl)$ (**20**) with P^tBu_3 in toluene solvent under dynamic vacuum to evaporate the liberated pyridine.

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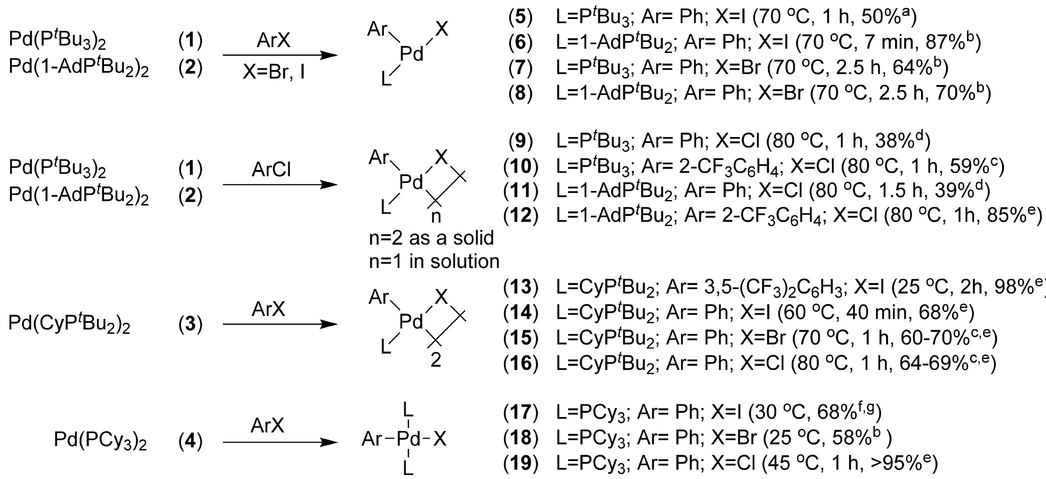
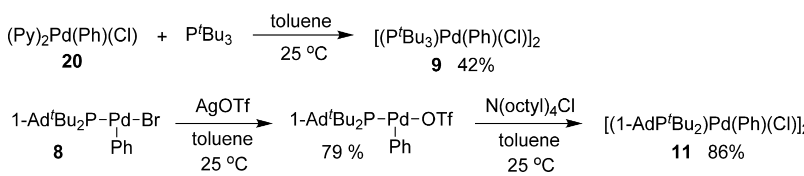
Scheme 1. Complexes Formed by Oxidative Addition of Different ArX to $L_2Pd(0)$



[a] See ref 22. [b] See ref 23. [c] See the Supporting Information. [d] Yield of product formed in situ, as determined by ^{31}P NMR spectroscopy, at 50% conversion. The yield decreased at longer reaction times. [e] Yield of product formed in situ, as determined by ^{31}P NMR spectroscopy. [f] See ref 27. [g] See ref 39.

Scheme 2. Routes for the Synthesis of Chloride Complexes [(P^{t}Bu$_3$)Pd(Ph)(Cl)]$_2$ (**9**) and [(1-AdP^{t}Bu$_2$)Pd(Ph)(Cl)]$_2$ (**11**)



1-AdP^{t}Bu$_2$-ligated **11** was isolated in 86% yield from the reaction of N(octyl)$_4$Cl with the known complex (1-AdP^{t}Bu$_2$)Pd(Ph)(CF_3SO_3),[37] which was obtained by the previously reported reaction of (1-AdP^{t}Bu$_2$)Pd(Ph)(Br) (**8**) with AgOTf.[23]

The nuclearity of the arylpalladium chloride complexes **10** and **11** depended on the phase. Our data indicate that both complexes are dimeric in the solid state and contain two bridging chlorides but are predominantly monomeric in solution. The solid-state structures of the P^{t}Bu$_3$-ligated 2-$CF_3C_6H_4$ complex **10** and the 1-AdP^{t}Bu$_2$-ligated phenyl complex **11** are shown in Figure 1. In this state, complex **10** contains two palladium atoms that are bridged nearly symmetrically by two μ^2-chloride ligands. The two aryl groups are located anti to each other. The Pd−Cl bond distances range from 2.39 to 2.49 Å, and the two palladium atoms are separated by 3.61 Å. The Pd coordination planes intersect at an angle of 145.6°. The structure of **11** also contains two palladium atoms bridged by two μ^2-chloride ligands, but the two aryl groups are syn to each other. In this case, the Pd−Cl(1) distances are shorter than the Pd−Cl(2) distances by ~0.1 Å, possibly as a result of the steric demands of the phosphines and the larger trans influence of the aryl groups located trans to Cl(2) than of the phosphines located trans to Cl(1). The two palladium atoms are separated by a longer distance of 3.78 Å, and the two coordination planes intersect at an angle of 166.3°.

Solution molecular weight and NMR spectroscopic data indicate that the tri-*tert*-alkylphosphine-ligated arylpalladium chloride complexes **9-11** are monomeric in solution. The molecular weight measurements by the Signer method[38] on the more stable complex **10** provided values of 530 g/mol in THF and 505 g/mol in benzene. These values are closer to the calculated molecular weight of the monomer (489 g/mol) than to that of the dimer (978 g/mol). The ^{31}P NMR chemical shifts of the arylpalladium chloride complexes **9**−**11** were similar and ranged from 69 to 73 ppm. These chemical shifts are expected for a monomeric species on the basis of the chemical shifts of the monomeric arylpalladium bromide (60−65 ppm) and iodide (55−60 ppm) complexes. Thus, the spectroscopic and solution molecular weight data together provide evidence that **9** and **11** possess the same monomeric structure shown clearly for **10** in solution. The nuclearity of these species, however, does not affect our conclusions about the mechanism of oxidative addition because the steps that control a monomer−dimer equilibrium occur after the rate-limiting steps.

1.2. Additions of ArX to Complexes of the Less Hindered Ligands CyP^{t}Bu$_2$ and PCy$_3$. The reactions of Pd(CyP^{t}Bu$_2$)$_2$ (**3**) with 3,5-$(CF_3)_2C_6H_3I$ and PhI at 25 and 60 °C, respectively, produced the dimeric arylpalladium halide complexes [(CyP^{t}Bu$_2$)Pd(Ar)(I)]$_2$ [Ar = 3,5-$(CF_3)_2C_6H_3$ (**13**), Ph (**14**)][27] in 98 and 68% yield, respectively, as determined by ^{31}P NMR spectroscopy. Reaction of complex **3** with PhBr and PhCl for 1 h at 70 and 80 °C produced the analogous bromide (**15**) and chloride (**16**) dimers in 70 and 64% yield, respectively. The complex Pd(PCy$_3$)$_2$ (**4**) reacted with PhI, PhBr, and PhCl at 25−45 °C to produce the known stable trans four-coordinate complexes **17**,[27,39] **18**,[23] and **19**, respectively.[40,41] These reactions occurred in high yield, as determined by ^{31}P NMR spectroscopy; the isolated yields depended on the solubility and crystallinity of the products.

The nuclearity of CyP^{t}Bu$_2$-ligated **15** was determined by X-ray crystallography (Figure 2) and Signer solution molecular weight analysis. In the solid state, the complex contains two bridging μ^2-bromide ligands and syn aryl groups. The core contains acute Br−Pd−Br angles of 82.79 and 82.53°, and the

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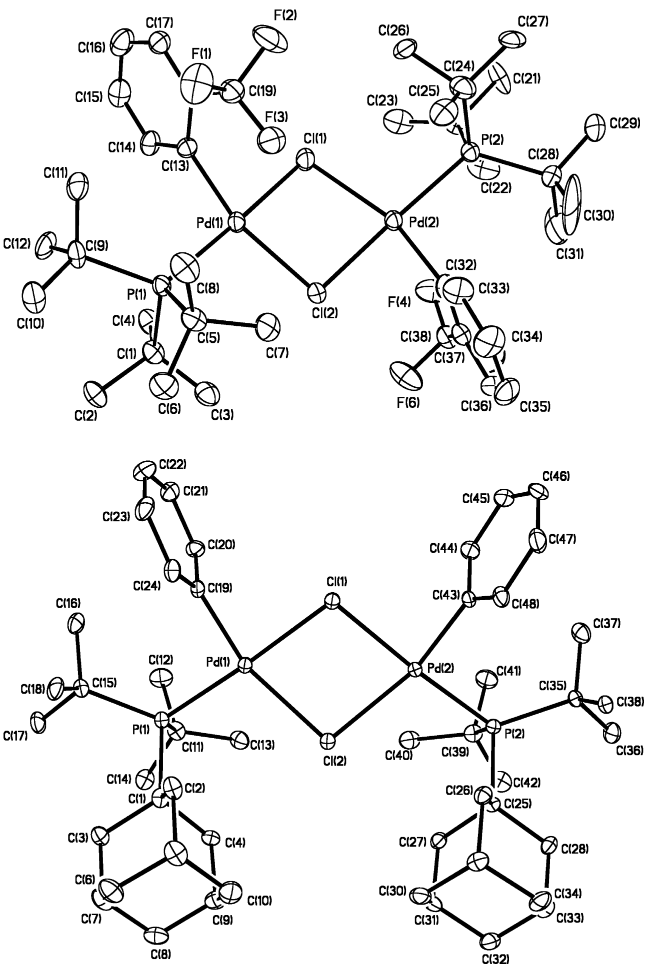

Figure 1. ORTEP diagrams of the complexes $[(P^tBu_3)Pd(2\text{-}CF_3C_6H_4)(Cl)]_2$ (**10**) and $[(1\text{-}AdP^tBu_2)Pd(Ph)(Cl)]_2$ (**11**).

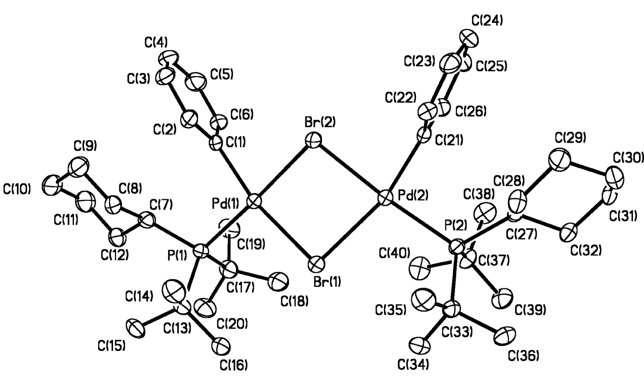

Figure 2. ORTEP diagram of the complex $[(CyP^tBu_2)Pd(Ph)(Br)]_2$ (**15**).

Pd coordination planes intersect at an angle of 20.7°. The Pd−Br(1) distances are longer than the Pd−Br(2) distances by ~0.1 Å, possibly because of the steric bulk the phosphines and the large trans influence of the aryl moiety.

Complex **15** appears to dissociate predominantly to a monomeric species in solution. The molecular weight in THF as determined by the Signer method was 523 g/mol. This value is close to the molecular weight of 491 g/mol for the monomer. Since the nuclearity of $(1\text{-}AdP^tBu_2)$ complex **10** was the same in THF and benzene by the Signer molecular weight measurement, neither THF nor benzene coordinates to the metal center in either structure, and the ^{31}P NMR chemical shifts in these two solvents for this class of compound have generally been nearly identical, we are confident that complex **15** is predominantly monomeric in solution.

2. Kinetic Studies. 2.1. General Considerations. The rates of oxidative addition of PhX (X = I, Br, Cl) to $Pd(0)L_2$ complexes were measured for complexes containing the bulky trialkylphosphines P^tBu_3, $1\text{-}AdP^tBu_2$, CyP^tBu_2, and PCy_3. The mechanism of the oxidative addition depended largely on the identity of the halide. For this reason, the kinetic data are presented according to the type of haloarene undergoing the reaction with the Pd(0) complexes. The data on the oxidative additions of iodoarenes and chloroarenes are simplest to interpret and are presented first. Our kinetic data on these reactions are plotted as the reciprocals of the rate constants to fit with the typical linear equations corresponding to reactions occurring through a pre-equilibrium followed by an irreversible step. The data on the additions of bromoarenes are more complex. These data were treated in several ways and suggest that the additions occur in some cases by a combination of mechanisms.

The LPd(Ph)(X) products from oxidative addition of PhBr and PhCl to $Pd(P^tBu_3)_2$ (**1**) and $Pd(1\text{-}AdP^tBu_2)_2$ (**2**) were unstable at the temperatures of the oxidative addition, leading to decomposition by cyclometalation at the phosphine to form L·HX as side product. This phosphonium salt has been shown to accelerate the rate of oxidative addition of aryl bromides.[42] Because this autocatalysis has been shown to be suppressed by conducting the reactions in the presence of the hindered phosphazene base *tert*-butyliminotris(pyrrolidino)phosphorane (**BTPP**),[42] the rate constants for oxidative addition of PhBr and PhCl to **2** were obtained from reactions containing 30 to 60 mol % of phosphazene base. Because the addition of PhI to **1** and **2** occurred at lower temperatures than those leading to the cyclometalation process, the oxidative addition of PhI exhibited an exponential decay of the starting Pd(0) complexes, without autocatalysis, in either the presence or absence of phosphazene base.

Before the data on the kinetics of oxidative addition to PCy_3 complex **4** are presented, some comments on the coordination chemistry of this Pd(0) species are warranted. Spectroscopic studies have shown that the combination of PCy_3 and **4** generates an equilibrium mixture of **4**, free ligand, and the trisphosphine complex $Pd(PCy_3)_3$.[43−45] The ^{31}P NMR spectra of a solution consisting of **4** and 2 equiv of PCy_3 obtained between 20 and −40 °C contained two broad signals (at 39 and 10 ppm) that corresponded to **4** and free PCy_3. At lower temperatures (−60 to −80 °C), a sharp signal for $Pd(PCy_3)_3$ at 26 ppm and a sharp signal for the remaining PCy_3 were observed. Thus, the $Pd(PCy_3)_2$ complex coordinates a third phosphine at low temperatures.

2.2. Kinetic Studies of the Oxidative Addition of Iodobenzene. Kinetic studies were conducted on the oxidative addition of iodobenzene to Pd(0) complexes **1**−**4**. In all cases, the rate constants were measured by ^{31}P NMR spectroscopy. The rate constants for the reactions of complexes **1**−**3** were obtained from the decay of the starting Pd(0) species. Because the signals for PCy_3-ligated **4** were broad in the presence of added PCy_3, the rate constants for the reaction of this complex

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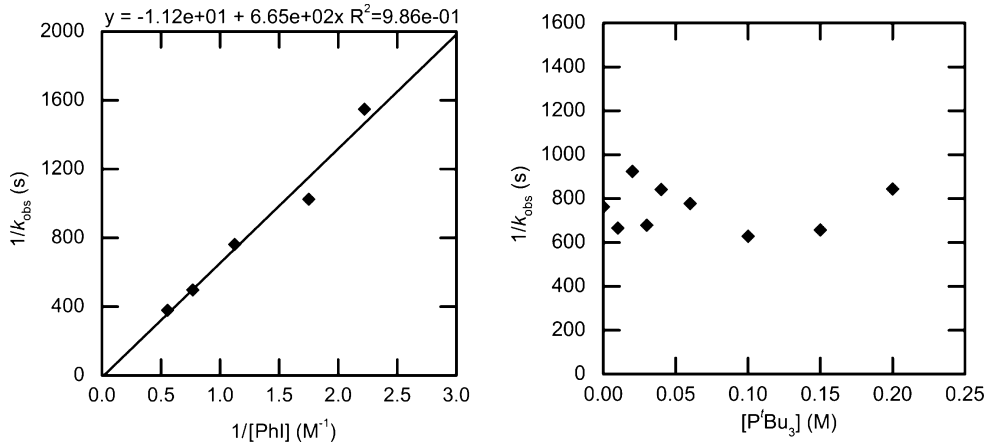


Figure 3. Dependence of the observed rate constant (k_{obs}) on the concentration of PhI (0.45−1.8 M) with no added P^tBu_3 (left) and on the concentration of P^tBu_3 (0−0.20 M) with [PhI] = 0.90 M (right) for the oxidative addition of PhI to $Pd(P^tBu_3)_2$ (**1**) (0.040 M) in chlorobenzene at 70 °C.

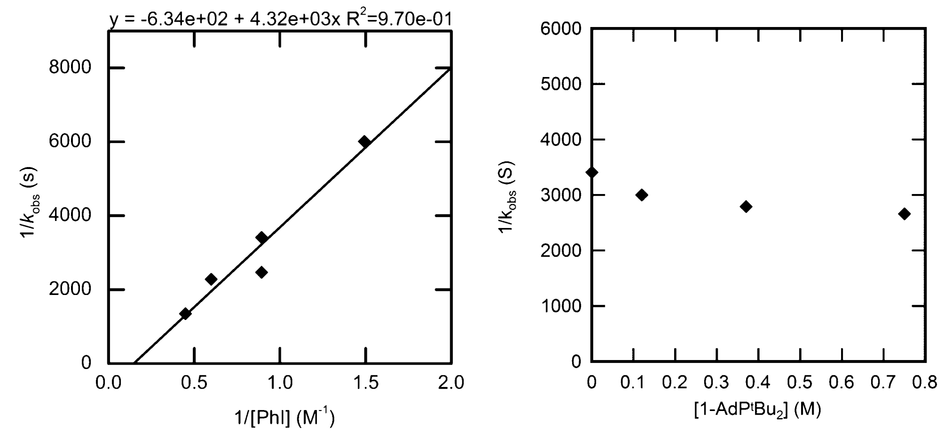


Figure 4. Dependence of k_{obs} on the concentration of PhI (0.67−2.2 M) with no added $1\text{-}AdP^tBu_2$ (left) and on the concentration of $1\text{-}AdP^tBu_2$ (0−0.75 M) with [PhI] = 1.1 M (right) for the oxidative addition of PhI to $Pd(1\text{-}AdP^tBu_2)_2$ (**2**) (0.025 M) in chlorobenzene at 50 °C.

were determined from the appearance of the oxidative addition product. The decay of complexes **1**−**3** and the appearance of product from reaction of **4** were clearly exponential with time, and the products were stable, except for the product ligated by P^tBu_3. Some of the arylpalladium iodide complex ligated by P^tBu_3 decomposed to form the iodo-bridged Pd(I) dimer $[(P^tBu_3)Pd(\mu\text{-}I)]_2$,[27] but this subsequent process did not affect the decay of P^tBu_3 complex **1**. Although autocatalysis was not observed for reactions of iodoarenes, the reaction of $1\text{-}AdP^tBu_2$ complex **2** with PhI was carried out in the presence of 30 mol % phosphazene to be consistent with the reactions of **2** with PhBr and ArCl.

2.2.1. Kinetic Studies of the Oxidative Addition of Iodobenzene to P^tBu_3 Complex 1. The rate constants for oxidative addition of PhI to P^tBu_3-ligated **1** to produce complex **5** were measured on reactions in chlorobenzene solvent at 70 °C. The plot of $1/k_{obs}$ versus 1/[PhI] for various concentrations of PhI (Figure 3, left) indicates that the reaction is first-order in PhI. However, the observed rate constant did not change significantly as a function of $[P^tBu_3]$ (Figure 3, right); the average value of k_{obs} over this phosphine concentration range was $(1.3 \pm 0.2) \times 10^{-3}$ s^{-1}.

2.2.2. Kinetic Studies of the Oxidative Addition of Iodobenzene to $1\text{-}AdP^tBu_2$-Ligated 2. The rate constants for the oxidative addition of PhI to $1\text{-}AdP^tBu_2$-ligated **2** to form arylpalladium iodide complex **6** were measured in chlorobenzene at 50 °C. The orders for this reaction were similar to those for the oxidative addition of PhI to **1**. The plot of $1/k_{obs}$ versus 1/[PhI] for various [PhI] (Figure 4, left) indicates that the reaction is first-order in PhI. Like those for the reaction of PhI with P^tBu_3-ligated **1**, the rate constants for addition to **2** did not change significantly when $[1\text{-}AdP^tBu_2]$ was varied (Figure 4, right); the average value of the observed rate constant for the reactions conducted with this phosphine concentration range was $(3.4 \pm 0.4) \times 10^{-4}$ s^{-1}.

2.2.3. Kinetic Studies of the Oxidative Addition of Iodoarenes to CyP^tBu_2-Ligated 3. The rate constants of the oxidative addition of PhI to CyP^tBu_2-ligated **3** to form phenylpalladium iodide complex **14** were measured in toluene at 50 °C. The plot of $1/k_{obs}$ versus 1/[PhI] (Figure 5, left) shows that the reaction is first-order in PhI. The reaction rate did not depend significantly on the concentration of ligand (Figure 5, right); the average value of k_{obs} for the reactions conducted over this phosphine concentration range was $(1.1 \pm 0.1) \times 10^{-3}$ s^{-1}. These data do not agree with the results of previously published work,[27] which stated that doubling the concentration of ligand decreased the rate of oxidative addition of 1-iodo-3,5-bis(trifluoromethyl)benzene by a factor of 2. Thus, we investigated the oxidative addition of haloarenes to CyP^tBu_2-ligated complex **3** more closely.

The rate constants for the oxidative addition of 1-iodo-3,5-bis(trifluoromethyl)benzene to CyP^tBu_2-ligated **3** to form arylpalladium iodide complex **13** were measured at 25 °C in benzene with [**3**] = 0.036 M, [ArI] = 0.36 M, and $[CyP^tBu_2]$ ranging

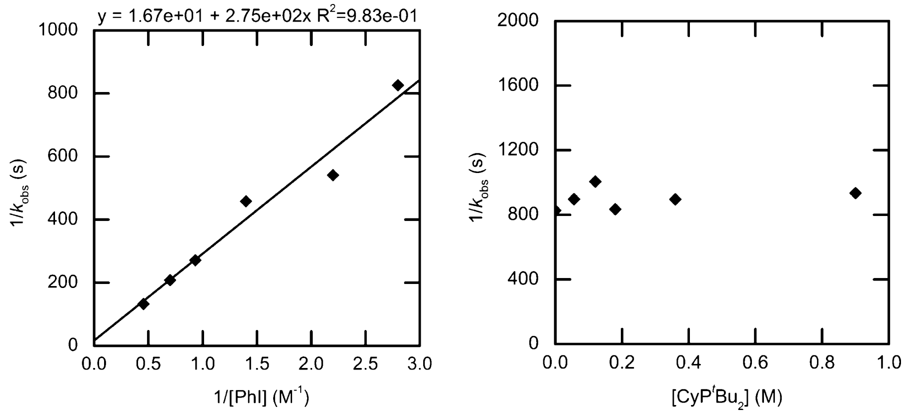


Figure 5. Dependence of k_{obs} on the concentration of PhI (0.36−1.4 M) with no added CyP^tBu_2 (left) and on the concentration of CyP^tBu_2 (0−0.90 M) with [PhI] = 0.36 M (right) for the oxidative addition of PhI to $Pd(CyP^tBu_2)_2$ (**3**) (0.036 M) in toluene at 50 °C.

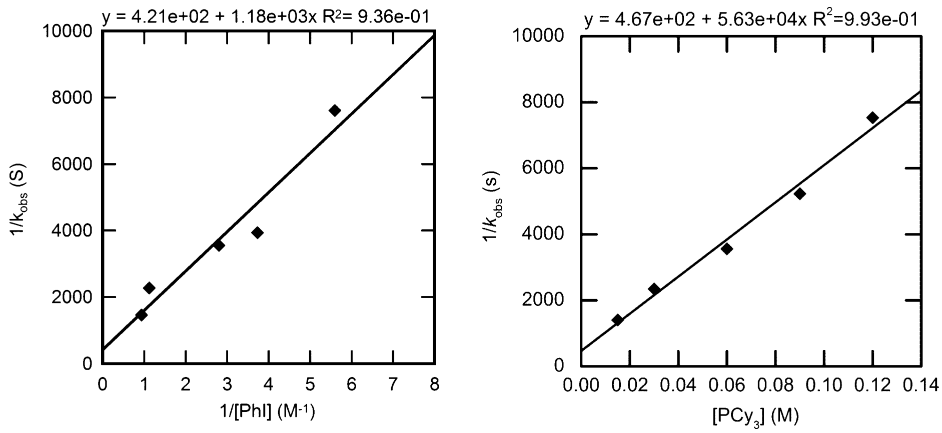


Figure 6. Dependence of k_{obs} on the concentration of PhI (0.18−1.1 M) with $[PCy_3]$ = 0.056 M (left) and on the concentration of PCy_3 (0.03−0.12 M) with [PhI] = 0.36 M (right) for the oxidative addition of PhI to $Pd(PCy_3)_3$ (**4**) (0.020 M) in toluene at −80 °C.

from 0 to 1.8 M. These substrates and conditions are identical to those reported previously.[27] In contrast to the published data, the rate of the reaction was only slightly affected by the presence of excess ligand; the average value of k_{obs} was $(6.1 \pm 0.6) \times 10^{-4}$ s^{-1}. We do not have an explanation for the difference between the previously published data and the data reported here; however, the previous reactions were monitored to only two half-lives, and reactions at only two different ligand concentrations were reported.

2.2.4. Kinetic Studies of the Oxidative Addition of Iodobenzene to PCy_3-Ligated 4. The reaction of PCy_3-ligated **4** with PhI formed phenylpalladium iodide complex **17** within minutes at room temperature. Thus, kinetic data on these oxidative additions were obtained on reactions conducted at −80 °C. Three series of reactions with iodobenzene were conducted, the first with varying [PhI], the second with $[PCy_3]$ ranging from 0.030 to 0.12 M, and the third with $[PCy_3]$ in the lower range 0.61−6.1 mM. The reciprocals of the rate constants for oxidative addition of PhI to the combination of **4** and PCy_3 at various [PhI] and $[PCy_3]$ are shown in Figure 6. These data indicate that the reaction is first-order in PhI and inverse-first-order in PCy_3 when the concentration of ligand is high. As noted in detail above in General Considerations, trisphosphine-ligated Pd(0) is the major species in the presence of more than 0.030 M added PCy_3 at −80 °C. Thus, Figure 6 corresponds to data and rate expressions when the starting complex is the $[Pd(PCy_3)_3]$ complex,[46] and the order of −1 with respect to PCy_3 indicates reversible dissociation of PCy_3 from $Pd(PCy_3)_3$ prior to carbon−halogen bond cleavage. At low concentrations of added ligand, the major species observed in solution at −80 °C is **4**. Under these conditions, the rate of the reaction was zeroth-order in added ligand, and the average value of k_{obs} was $(9.8 \pm 0.1) \times 10^{-4}$ s^{-1}.

2.3. Kinetic Studies of the Oxidative Addition of Chloroarenes. Kinetic studies of the oxidative addition of chloroarenes to $Pd(1\text{-}AdP^tBu_2)_2$ (**2**) were conducted with $2\text{-}CF_3C_6H_4Cl$ because it formed a more stable arylpalladium chloride complex than did PhCl. These reactions were conducted in the presence of added phosphazene base to avoid potential autocatalysis by the side products from decomposition of the arylpalladium chloride complex. They were also conducted with higher concentrations of haloarene than the reactions of bromoarenes and iodoarenes to improve the reaction yields, which are affected by product decomposition.[47] The decay of **2** was measured by ^{31}P NMR spectroscopy.

2.3.1. Kinetic Studies of the Oxidative Addition of $2\text{-}CF_3\text{-}C_6H_4Cl$ to $1\text{-}AdP^tBu_2$-Ligated 2. The rate constants for reactions of $2\text{-}CF_3C_6H_4Cl$ with $1\text{-}AdP^tBu_2$-ligated **2** to form arylpalladium

(46) As we treated the data here, the linear curve fit at low $[PCy_3]$ corresponds to the hypothetical case of reaction of $[Pd(PCy_3)_3]$ under these conditions. We did not fit the data to the full system, which would have included situations in which significant concentrations of both the $[Pd(PCy_3)_3]$ and $[Pd(PCy_3)_2]$ complexes were present.

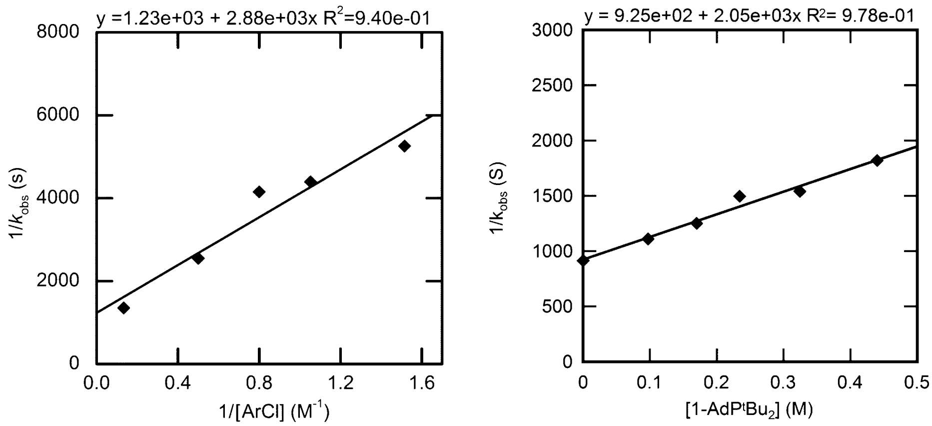


Figure 7. Dependence of k_{obs} on the concentration of 2-$CF_3C_6H_4Cl$ (0.54−7.2 M) with [1-AdP^{t}Bu$_2$] = 0.17 M (left) and on the concentration of 1-AdP^{t}Bu$_2$ (0−0.44 M) with [2-$CF_3C_6H_4Cl$] = 7.6 M (right) for the oxidative addition of 2-$CF_3C_6H_4Cl$ to Pd(1-AdP^{t}Bu$_2$)$_2$ (**2**) (0.025 M) in toluene at 100 °C.

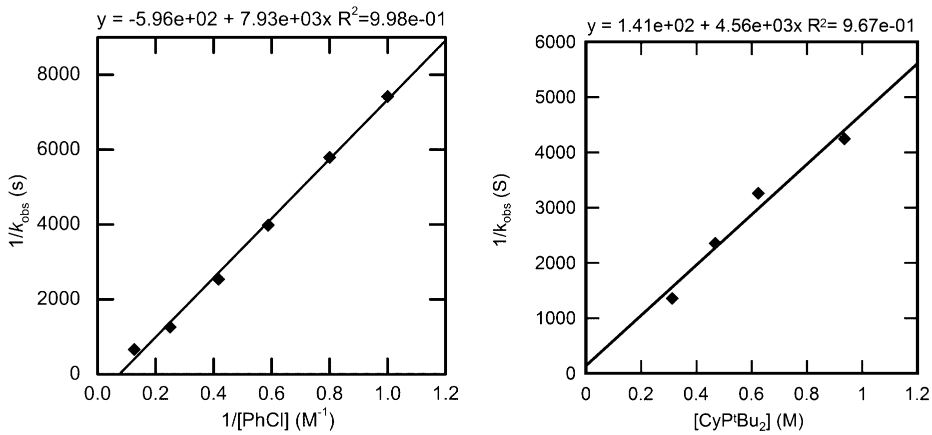


Figure 8. Dependence of k_{obs} on the concentration of chlorobenzene (1.0−7.9 M) with [CyP^{t}Bu$_2$] = 0.32 M (left) and on the concentration of CyP^{t}Bu$_2$ (0.32−0.94 M) with [PhCl] = 5.9 M (right) for the oxidative addition of chlorobenzene to Pd(CyP^{t}Bu$_2$)$_2$ (**3**) (0.036 M) in toluene at 100 °C.

chloride complex **12** were measured in toluene or neat ArCl at 100 °C in the presence of 0.015 M (60 mol %) phosphazene base (BTPP). The decay of **2** was exponential, showing that the additions of ArCl are first-order in the Pd(0) complex. The plots of 1/k_{obs} for varying [ArCl] and [1-AdP^{t}Bu$_2$] are shown in Figure 7. The plot of 1/k_{obs} versus 1/[ArCl] revealed a positive dependence of k_{obs} on chloroarene. The plot of 1/k_{obs} versus [1-AdP^{t}Bu$_2$] showed an inverse dependence of k_{obs} on [1-AdP^{t}Bu$_2$], although this dependence was not simply inverse-first-order.

2.3.2. Kinetic Studies of the Oxidative Addition of Chlorobenzene to CyP^{t}Bu$_2$-Ligated 3. The rate constants for the oxidative addition of PhCl to CyP^{t}Bu$_2$-ligated **3** to form phenylpalladium chloride complex **16** were measured in toluene at 100 °C in the absence of any added base. The plots of 1/k_{obs} measured for varying [PhCl] and [CyP^{t}Bu$_2$] are shown in Figure 8. The plot of 1/k_{obs} versus 1/[PhCl] revealed a positive dependence of k_{obs} on chlorobenzene. The plot of 1/k_{obs} versus [CyP^{t}Bu$_2$] revealed an inverse dependence of k_{obs} on the concentration of ligand.

2.3.3. Kinetic Studies of the Oxidative Addition of Chlorobenzene to PCy$_3$-Ligated 4. The rate constants for reactions of PCy$_3$-ligated **4** with chlorobenzene to form complex **19** were measured in toluene at 70 °C. At the concentrations of [PCy$_3$] investigated and the 70 °C temperature of the reaction, the starting Pd(0) species was the two-coordinate complex **4**. The plots of 1/k_{obs} obtained for varying [PhCl] and [PCy$_3$] (Figure 9) are similar to the analogous plots for the additions of PhCl to 1-AdP^{t}Bu$_2$-ligated **2** and CyP^{t}Bu$_2$-ligated **3**. The plot of 1/k_{obs} versus 1/[PhCl] revealed a positive dependence of k_{obs} on chloroarene; the plot of 1/k_{obs} versus [PCy$_3$] revealed an inverse dependence of k_{obs} on the concentration of ligand.

2.4. Kinetic Studies of the Oxidative Addition of Bromobenzene. As noted above in General Considerations and in previously published work,[42] the arylpalladium bromide product from oxidative addition of bromobenzene to P^{t}Bu$_3$-ligated **1** is unstable at elevated temperatures for extended times and undergoes cyclometalation to generate L·HBr. To avoid the problems associated with the generation of the phosphonium salt, the rate constants for oxidative additions of PhBr to **1** and **2** were measured in the presence of phosphazene base. Moreover, we focused on the oxidative addition of PhBr to 1-AdP^{t}Bu$_2$-ligated **2** because the oxidative addition product (1-AdP^{t}Bu$_2$)Pd(Ph)(Br) (**8**) was sufficiently stable to form in >90% yield in the presence of the phosphazene base. In contrast, the reactions of CyP^{t}Bu$_2$-ligated **3** and PCy$_3$-ligated **4** occurred in high yield and with an exponential decay of the Pd(0) complex in the absence of any added base. Thus, the additions of PhBr to **3** and **4** were conducted in the absence of base.

2.4.1. Kinetic Studies of the Oxidative Addition of Bromobenzene to 1-AdP^{t}Bu$_2$-Ligated 2. The reaction of PhBr with

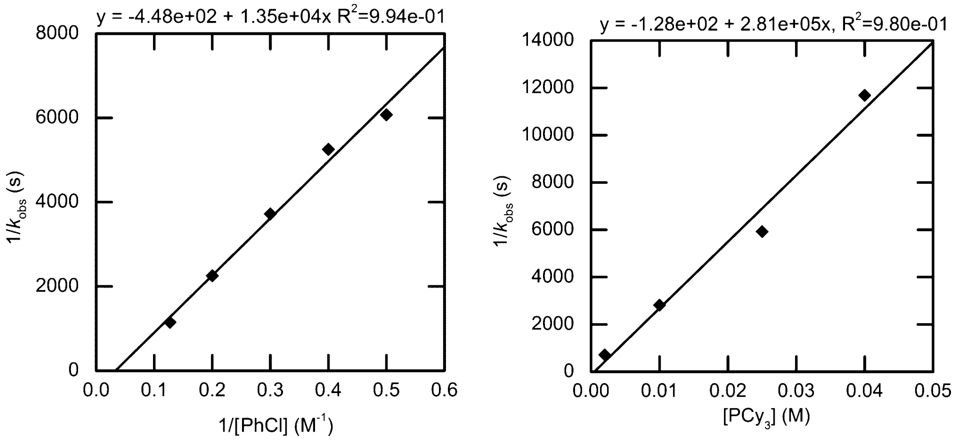


Figure 9. Dependence of k_{obs} on the concentration of chlorobenzene (2.0−7.9 M) with $[PCy_3]$ = 0.010 M (left) and on the concentration of PCy_3 (0.0020−0.040 M) with [PhCl] = 3.9 M (right) for the oxidative addition of chlorobenzene to $Pd(PCy_3)_2$ (**4**) (0.019 M) in toluene at 70 °C. In the left panel, the data for [PhCl] = 2.5 and 3.3 M are average values from 2−3 runs.

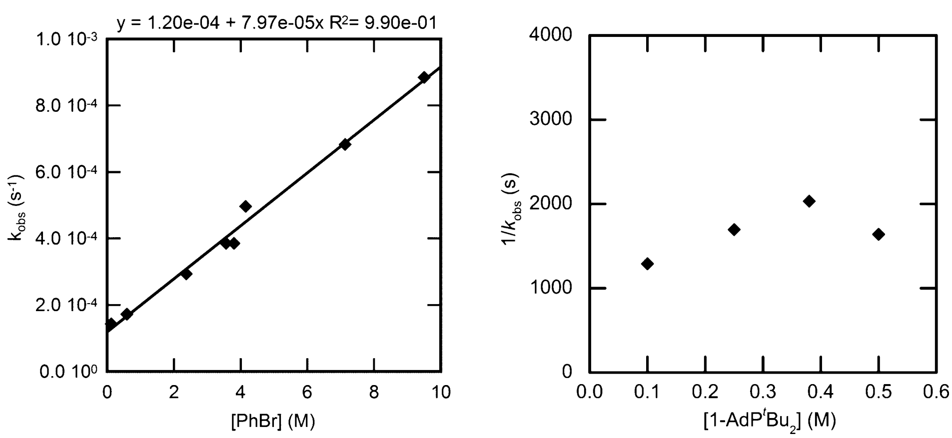


Figure 10. Dependence of k_{obs} on the concentration of PhBr (0.12−9.5 M) with no added 1-AdP^{t}Bu$_2$ (left) and on the concentration of 1-AdP^{t}Bu$_2$ (0.10−0.50 M) for [PhBr] = 8.5 M (right) for the oxidative addition of PhBr to Pd(1-AdP^{t}Bu$_2$)$_2$ (**2**) (0.025 M) in toluene at 90 °C.

1-AdP^{t}Bu$_2$-ligated **2** to form phenylpalladium bromide complex **8** was studied at 90 °C. The reactions were conducted in the presence of 0.015 M (60 mol %) added phosphazene. A clear exponential decay of **2** was observed under these conditions. Thus, the additions of PhBr are first-order in the Pd(0) complex. The kinetic data on the effect of the concentration of arene on the rate constant for oxidative addition of PhBr are plotted as k_{obs} versus [PhBr]. This plot allows us to assess the potential that two mechanisms contribute to the observed rate constant. When such a plot is linear with a nonzero *y*-intercept, the double-reciprocal plot analogous to those shown for data on the oxidative addition of ArCl and ArI is nonlinear. Conversely, when the double-reciprocal plot has a distinct nonzero *y*-intercept, the direct plot is curved.

The plot of k_{obs} versus [PhBr] (Figure 10, left) was linear with a positive slope and nonzero *y*-intercept. Moreover, the rate constant for this oxidative addition to 1-AdP^{t}Bu$_2$-ligated **2** did not depend on the concentration of ligand at high or low concentrations of bromobenzene. The plot of the dependence of $1/k_{obs}$ on [1-AdP^{t}Bu$_2$] (Figure 10, right) shows that the observed rate constant was independent of the concentration of added ligand [average $k_{obs} = (6.2 \pm 1.2) \times 10^{-4}\ s^{-1}$]. The data at high PhBr concentration contained some deviation, yet a change in [1-AdP^{t}Bu$_2$] by a factor of 4 led to a variation in rate by less than a factor of 2. Additionally, when [PhBr] = 2.5 M and [1-AdP^{t}Bu$_2$] ranged from 0.10 to 0.50 M, the value of k_{obs} varied by only 10−15% [$(2.5 \pm 0.3) \times 10^{-4}\ s^{-1}$]. As described in the Discussion, these data suggest that two mechanisms for oxidative addition of bromoarenes occur simultaneously.

2.4.2. Kinetic Studies of the Oxidative Addition of Bromobenzene to CyP^{t}Bu$_2$-Ligated 3. The rate constants for the reaction of CyP^{t}Bu$_2$-ligated **3** with PhBr to form phenylpalladium bromide complex **15** were measured in toluene at 70 °C. The plots of these data are shown in Figure 11. The observed rate constant depended positively on the concentration of bromoarene. Again, the plot of k_{obs} versus [PhBr] contained a nonzero *y*-intercept. In contrast, the observed rate constant was independent of the concentration of added ligand; the average value of k_{obs} was $(7.1 \pm 0.7) \times 10^{-4}\ s^{-1}$.

2.4.3. Kinetic Studies of the Oxidative Addition of Bromobenzene to PCy$_3$-Ligated 4. The rate constants for reactions of PCy_3-ligated **4** with bromobenzene to form arylpalladium bromide complex **18** were measured in toluene at 10 °C. The plots of these data are shown in Figure 12. These plots reveal a positive dependence of k_{obs} on [ArBr] and a nearly zeroth-order dependence on $[PCy_3]$. A change in the concentration of

(47) Some reactions contained almost neat haloarene. However, the rates of these reactions are not strongly affected by solvent polarity (as indicated by ref 18 and qualitative measurements with compound **2**), and the dielectric constant of chlorobenzene is between those of benzene and THF. Thus, a high concentration of ArCl should not give rise to a large medium effect.

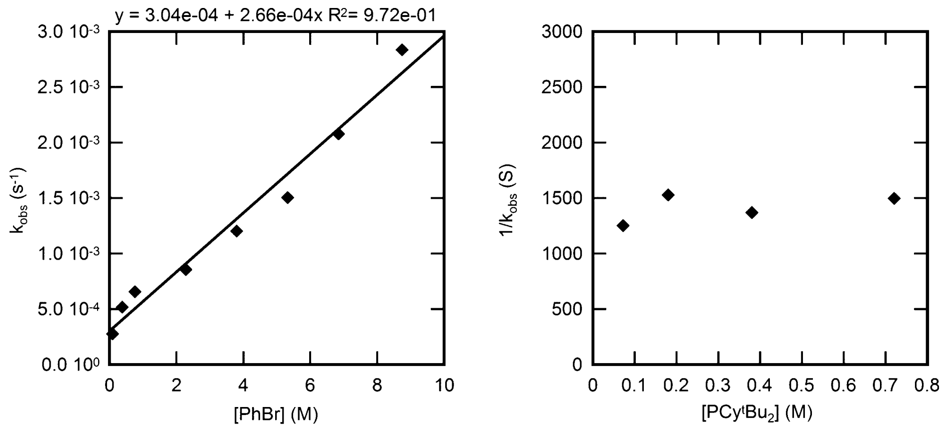


Figure 11. Dependence of k_{obs} on the concentration of PhBr (0.09−8.7 M) with $[CyP^tBu_2]$ = 0.32 M (left) and on the concentration of CyP^tBu_2 (0.07−0.72 M) with [PhBr] = 1.5 M (right) for the oxidative addition of PhBr to $Pd(CyP^tBu_2)_2$ (**3**) (0.036 M) in toluene at 70 °C.

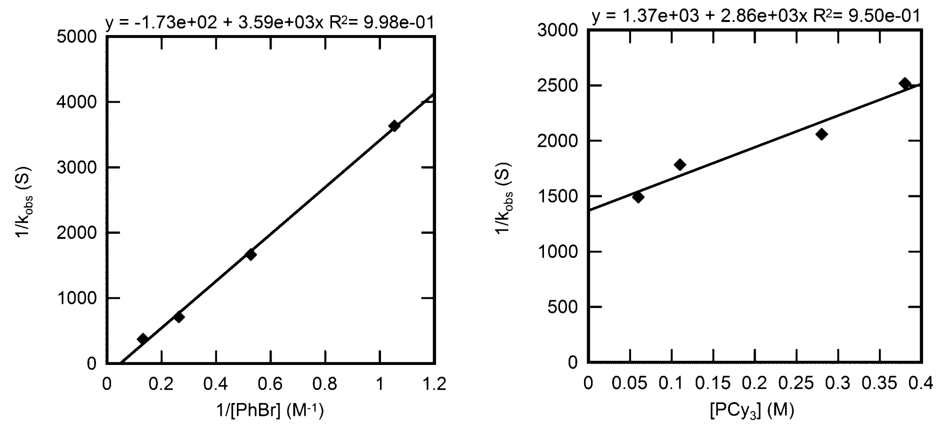


Figure 12. Dependence of k_{obs} on the concentration of PhBr (0.95−7.6 M) with $[PCy_3]$ = 0.19 M (left) and on the concentration of PCy_3 (0.060−0.38 M) with [PhBr] = 1.9 M (right) for the oxidative addition of PhBr to $Pd(PCy_3)_3$ (**4**) (0.019 M) in toluene at 10 °C.

PCy_3 by a factor of 6 led to a decrease in rate constant by less than a factor of 2.

Discussion

1. Structures of the Palladium and Arylpalladium Halide Reactants and Products. The most stable Pd(0) complexes of the bulky phosphines P^tBu_3,[48] $1\text{-}AdP^tBu_2$,[22] and CyP^tBu_2[27] are the bisphosphine complexes PdL_2.[49] In contrast, the most stable Pd(0) complex of PCy_3 depended on the temperature and the concentration of added PCy_3. At temperatures below −70 °C with $[PCy_3] < 0.03$ M, the complexes $Pd(PCy_3)_3$ and bis-ligated $Pd(PCy_3)_2$ were observed by ^{31}P NMR spectroscopy.[18] At the same temperature with $[PCy_3] > 0.03$ M, the trisphosphine complex $Pd(PCy_3)_3$ was the only Pd(0) complex observed. At room temperature or above, the signals due to the free and coordinated ligand are broad because of exchange on the NMR time scale, but the bisphosphine complex $Pd(PCy_3)_2$ was the major Pd(0) species present.

The identities of some of the oxidative addition products have been published. The products from addition of PhX (X= Cl, Br, I) to the Pd(0) complex of PCy_3 are four-coordinate bisphosphine species,[23,27,39−41] but the products from addition of ArX to complexes of the more hindered ligands contain a single ligand and are either dimeric with bridging halides[27] or monomeric.[22,23] Furthermore, the structures of the arylpalladium halide complexes in some cases depend on the identity of the halide.[21] For example, the arylpalladium bromide and iodide complexes containing the ligands P^tBu_3 and $1\text{-}AdP^tBu_2$ are monomeric three-coordinate complexes in solution and in the solid state, but the arylpalladium chloride complexes are mainly monomers in solution and dimers in the solid state. The kinetic data analyzed in the following sections show that the reactant and product structures do not correlate with either the coordination number of the species undergoing oxidative addition or the initial product formed by oxidative addition in many cases.

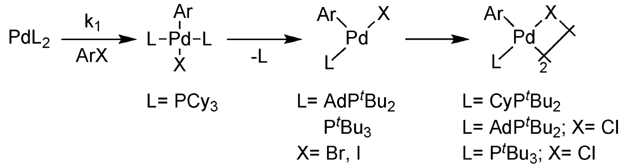
2. Potential Mechanisms of Oxidative Addition. Three possible mechanisms for the oxidative addition of ArX to the palladium complexes $L_2Pd(0)$ were considered. In the first mechanism, oxidative addition would take place by direct reaction of ArX with the starting bisphosphine complex $L_2Pd(0)$ to form a four-coordinate arylpalladium halide complex. This addition would be followed in some cases by dissociation of ligand and subsequent dimerization, depending on the phosphine or haloarene used. The reaction by this pathway would be first-order in the concentration of haloarene and independent of the concentration of ligand (Scheme 3).

Alternatively, the reaction could occur by reversible or irreversible associative displacement of the phosphine in PdL_2 by the haloarene, as shown in Scheme 4. This first step would

(48) Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 113.
(49) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850.

(50) The derivation of the rate expression is included in the Supporting Information.

Scheme 3. Oxidative Addition of ArX by Direct Reaction with PdL_2[50]



$$rate = [PdL_2]k_{obs} \qquad k_{obs} = k_1[ArX]$$

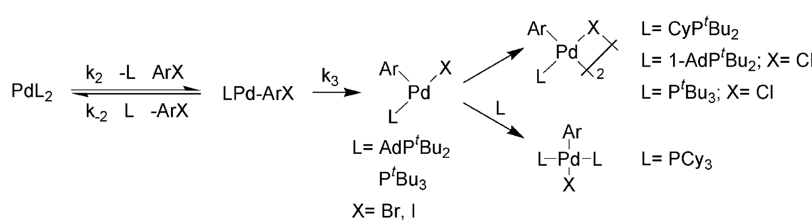
form a monophosphine intermediate coordinated by a haloarene that contains an intact C−X bond. Carbon−halogen bond cleavage would then form a three-coordinate arylpalladium halide complex. This three-coordinate complex could be the final product or could undergo dimerization or recoordination of ligand to form the final reaction product. If the initial associative displacement of phosphine is reversible, then the reaction rate will depend on the concentration of both the haloarene and the ligand. If the initial associative displacement of phosphine is irreversible ($k_3 \gg k_{-2}$[L]), then the reaction rate will be independent of the concentration of ligand. Thus, the orders of the reaction in haloarene and ligand alone cannot distinguish between irreversible, direct C−X bond cleavage by the L_2Pd complex (Scheme 3) and irreversible displacement of ligand by the haloarene followed by C−X bond cleavage by a monophosphine intermediate (Scheme 4). However, both mechanisms occur by reaction of the aryl halide with a bis-ligated Pd(0) species. In some cases, we were able to distinguish between these two mechanisms by the kinetic behavior of the reverse reaction.

Finally, the oxidative addition could occur by dissociation of a phosphine, followed by oxidative addition of ArX to the resulting LPd intermediate to form a three-coordinate arylpalladium halide complex (Scheme 5). This dissociation of phosphine could be reversible or effectively irreversible (i.e., k_5[ArX] $\gg k_{-4}$[L]) under the reaction conditions. If the ligand dissociation is fully reversible, then the reaction will depend on the concentration of both the haloarene and the ligand. If dissociation of ligand is effectively irreversible, then the rate of the reaction will be independent of the concentration of the haloarene and added ligand. In the latter case, the observed rate constant will be equal to k_4. After the addition, dimerization of the three-coordinate complex or coordination of a second ligand to form a square-planar complex could occur, depending on the identity of the phosphine or the halide (Scheme 5).

All of these mechanisms considered predict a positive dependence of k_{obs} on [ArX], which is consistent with the observations. However, the predicted differences in the dependence on [L] can be used to differentiate the mechanisms. Direct oxidative addition to PdL_2 (Scheme 3) is excluded if there is an inverse dependence of k_{obs} on [L]. Oxidative addition to PdL (Scheme 5) is excluded if there is no dependence on [L] but a positive dependence on [ArX]. Associative displacement of L by ArX (Scheme 4) is excluded if the plot of $1/k_{obs}$ versus 1/[ArX] has a significant y-intercept, but such an analysis requires extremely accurate data, and we could not use this y-intercept to distinguish between the mechanisms in Schemes 4 and 5 in most cases. These predictions apply to systems in which the $L_2Pd(0)$ complex is the starting complex. The palladium complex of PCy_3 adopts an L_3Pd structure with added phosphine at low temperature. Thus, reactions under these conditions are analyzed separately. Most generally, the analysis of our data shows that the identity of the halide rather than the identity of the ligand in this study has a larger effect on whether the irreversible step of the mechanism involves a bisphosphine or monophosphine complex.

3. Mechanism of Oxidative Addition of Iodoarenes. 3.1. Overview. The kinetic data for addition of iodobenzene to each of the four Pd(0) complexes **1**−**4** imply that the irreversible ("rate-determining") step involves reaction of the iodoarene with a palladium complex ligated by two phosphines. The reactions of iodobenzene with complexes **1**−**3** were zeroth-order in ligand and first-order in iodobenzene. The rate of the reaction of iodobenzene with complex **4** depended inversely on the concentration of added ligand when the concentration of the added ligand was high, but this kinetic behavior was observed

Scheme 4. Oxidative Addition of ArX after Associative Displacement of Ligand from PdL_2[50]



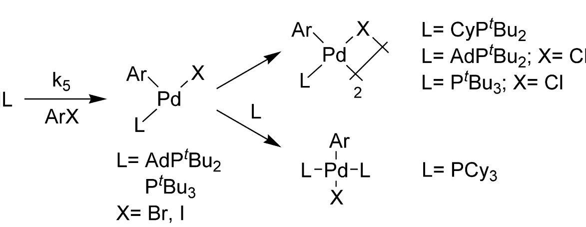
$$rate = [PdL_2]k_{obs} \qquad k_{obs} = \frac{k_2k_3[ArX]}{k_3 + k_{-2}[L]}$$

$$1/k_{obs} = \frac{1}{k_2[ArX]} + \frac{[L]}{K_2k_3[ArX]}$$

$$1/k_{obs} = \left(\frac{1}{k_2} + \frac{[L]}{K_2k_3}\right)\frac{1}{[ArX]}$$

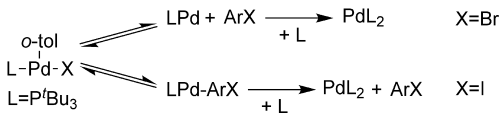
$$\text{If } k_3 >> k_{-2}[L] \qquad k_{obs} = k_2[ArX]$$

Scheme 5. Oxidative Addition of ArX after Dissociation of Ligand from PdL_2[50]



$$rate = k_{obs}\,[PdL_2]$$

Scheme 6. Mechanisms for the Reductive Elimination of ArX from Three-Coordinate Aryl Palladium(II) Halide Complexes



because the starting complex **4** was converted to the trisphosphine complex in the presence of this amount of added ligand.

3.2. Addition of PhI to L_2Pd Complexes 1−3 Ligated by P^tBu_3, 1-AdP^tBu_2, and CyP^tBu_2. Our kinetic data indicate that the "rate-determining" or first irreversible step in the reactions of iodobenzene with bisphosphine complexes **1**−**3** ligated by P^tBu_3, 1-AdP^tBu_2, and CyP^tBu_2, respectively, involves the starting bisphosphine species. This step can occur either by direct oxidative addition to the starting Pd(0) species, as shown in Scheme 3, or by irreversible displacement of the coordinated phosphine by iodoarene, as shown in Scheme 4 ($k_3 \gg k_{-2}$[L]). Both rate equations are zeroth-order in the concentration of added ligand and first-order in the concentration of iodoarene. Although the two pathways cannot be distinguished by the reaction orders of the forward process, we were able to distinguish between these two mechanisms for reaction of complexes **1** and **2** by the kinetic behavior of the reverse reaction, reductive elimination of iodoarene from the arylpalladium halide products **5** and **6**, which we studied previously.[21]

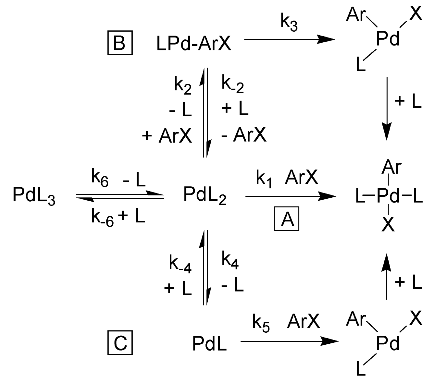
If the carbon−halogen bond cleavage occurs via direct oxidative addition to the PdL_2 complex (Scheme 3), then the principle of microscopic reversibility would dictate that the elimination of ArI must also occur from a bisphosphine palladium complex. In that case, reductive elimination from the LPd(Ar)(I) complex would be first-order in the concentration of ligand. In contrast, if C−X bond cleavage during the oxidative addition process involves a monophosphine species generated via associative displacement of the ligand by the iodoarene (Scheme 4), then microscopic reversibility would dictate that the elimination of ArI must occur from a monophosphine palladium complex, and reductive elimination from the LPd(Ar)(I) complex would be zeroth-order in added ligand.

We previously showed that the rate of reductive elimination of 2-iodotoluene from (P^tBu_3)Pd(*o*-tol)(I) was independent of the concentration of added ligand (Scheme 6).[21] Thus, we conclude that the oxidative addition of PhI to **1** and **2** occur by irreversible, associative displacement of a phosphine followed by cleavage of the C−X bond by the resulting haloarene complex (Scheme 4). This mechanism is the same as that proposed for oxidative addition of iodobenzene to the Pd(0) complex ligated by the hindered ferrocenylphosphine ligand Q-phos.[21]

The mechanism of reductive elimination of haloarene did not provide clear information on the mechanism of the oxidative addition of iodoarenes to CyP^tBu_2-ligated **3** because reductive elimination of ArI from complexes ligated by CyP^tBu_2 occurred in low yield.[51] The smaller size of the CyP^tBu_2 ligand in complex **3** provides the potential for the oxidative addition of iodobenzene to **3** to occur directly, but the presence of a single phosphine in the product argues against this pathway. Thus, we favor a pathway involving irreversible displacement of the phosphine by the iodoarene. However, in either case, the kinetic data show that *the rate-determining step during the reaction of PhI with CyP^tBu_2-ligated **3** involves a bisphosphine complex*.

(51) Roy, A. H.; Hartwig, J. F. *Organometallics* **2004**, *23*, 1533.

Scheme 7. Possible Mechanisms for the Oxidative Addition of ArI to PdL_3 (L = PCy_3)[50]



$$rate = [PdL_3]k_{obs}$$

A. Direct reaction to L_2Pd

$$k_{obs} = \frac{k_6 k_1[\mathrm{ArX}]}{k_1[\mathrm{ArX}] + k_{-6}[\mathrm{L}]}$$

$$1/k_{obs} = \frac{1}{k_6} + \frac{[\mathrm{L}]}{K_6 k_1[\mathrm{ArX}]}$$

B. Associative displacement of the ligand in L_2Pd

$$k_{obs} = \frac{k_6 k_2 k_3[\mathrm{ArX}]}{k_2 k_3[\mathrm{ArX}] + k_3 k_{-6}[\mathrm{L}] + k_{-6} k_{-2}[\mathrm{L}]^2}$$

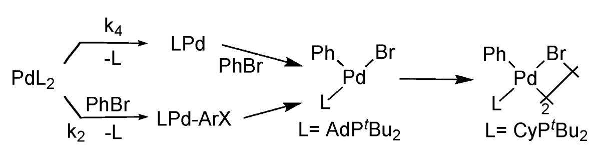
$$1/k_{obs} = \frac{1}{k_6} + \frac{[\mathrm{L}]}{K_6 k_2[\mathrm{ArX}]} + \frac{[\mathrm{L}]^2}{K_6 K_2 k_3[\mathrm{ArX}]}$$

C. Dissociation of ligand from L_2Pd

$$k_{obs} = \frac{k_6 k_4 k_5[\mathrm{ArX}]}{k_4 k_5[\mathrm{ArX}] + k_5 k_{-6}[\mathrm{ArX}][\mathrm{L}] + k_{-6} k_{-4}[\mathrm{L}]^2}$$

$$1/k_{obs} = \frac{1}{k_6} + \frac{[\mathrm{L}]}{K_6 k_4} + \frac{[\mathrm{L}]^2}{K_6 K_4 k_5[\mathrm{ArX}]}$$

Scheme 8. Two Concurrent Mechanisms for the Oxidative Addition of PhBr to **2** and **3**



$$rate = k_{obs}[PdL_2];\ k_{obs} = k_4 + k_2[PhBr]$$

This conclusion contrasts with the dissociative mechanism deduced previously by others for reactions of CyP^tBu_2-ligated **3** with iodoarenes.[27]

3.3. Mechanism of the Oxidative Addition of PhI to $Pd(PCy_3)_3$. Because the trisphosphine complex $Pd(PCy_3)_3$ is the major Pd(0) complex at the −80 °C temperature of the oxidative addition process, interpretation of the kinetic data for oxidative addition of iodobenzene to the PCy_3-ligated Pd(0) complex is slightly different from that for oxidative addition of iodobenzene to the other two complexes. Scheme 7 shows the possible mechanisms for oxidative addition of PhI to the trisphosphine species $Pd(PCy_3)_3$.

The observed inverse dependence on added ligand shows that the oxidative addition process occurs after loss of one ligand (Path A) or two ligands (Path B) to generate $Pd(PCy_3)_2$ or $Pd(PCy_3)$, respectively. Data over a wide enough range of

Table 1. Summary of the Experimental Observations and Suggested Mechanisms for the Oxidative Addition of ArX to Complexes **2**−**4**

		$Pd(1\text{-}AdP^tBu_2)_2$	$Pd(CyP^tBu_2)_2$	$Pd(PCy_3)_n$ (n = 2, 3)	general conclusion
ArI	order in ArI	1	1	1	ArI reacts with the PdL_2 species
	order in L	0	0	−1 for n = 3, 0 for n = 2	
	conclusion	irreversible associative displacement of L by ArI		reaction of ArI with L_2Pd	
ArCl	order ArCl	1	1	1	the C−X bond cleavage step occurs after reversible dissociation or displacement of one phosphine from PdL_2 to form PdL or LPd(ArX)
	order in L	−1	−1	−1	
	conclusion	reversible exchange of L with PhCl prior to C−X bond cleavage			
ArBr	order in ArBr	1	1	1	the C−X bond cleavage step appears to occur by two pathways of similar energy: one major pathway clearly involves reaction of ArBr with the $L_2Pd(0)$ species, which could occur by irreversible displacement of one L to form LPdArX or by irreversible direct C−X bond cleavage; the second, less defined pathway is zeroth-order in ArBr and appears to occur by irreversible dissociation of L to form LPd
	y-intercept of k_{obs} vs [ArBr]	nonzero	nonzero	0	
	order in L	0	0	nearly 0	
	conclusion	one pathway involves reaction of ArBr with L_2Pd, most likely by associative displacement of L to form LPdArX; a second competing pathway that is zeroth-order in ArBr most likely occurs by initial dissociation of L, followed by rapid reaction with ArBr.		reaction of ArBr with the bisphosphine complex L_2Pd as the major pathway (by nearly irreversible associative displacement of L by PhBr prior to C−X bond cleavage or by nearly irreversible direct oxidative addition)	

concentrations could not be obtained with sufficient accuracy to distinguish between the inverse-first-order and inverse-second-order dependence on the concentration of added ligand corresponding to reaction of the iodoarene with $Pd(PCy_3)_2$ and $Pd(PCy_3)$, respectively. However, we were able to distinguish between addition to $Pd(PCy_3)_2$ and addition to $Pd(PCy_3)$ by conducting the oxidative addition with low enough concentrations of added ligand at −80 °C that PdL_2 was the major species in solution. Under these conditions, the reaction was independent of the concentration of added ligand. Therefore, we conclude that the dependence on the concentration of ligand observed at high concentrations of added phosphine resulted from the reversible dissociation of one phosphine from $Pd(PCy_3)_3$ to form $Pd(PCy_3)_2$. We then conclude that $Pd(PCy_3)_2$ reacts with PhI by irreversible reaction between PhI and the bisphosphine complex. This irreversible reaction could occur by Path A in Scheme 7, which involves irreversible oxidative addition to $Pd(PCy_3)_2$, or by a version of Path B in which the ArI irreversibly displaces a phosphine from $Pd(PCy_3)_2$.

4. Mechanism of Oxidative Addition of Chloroarenes. The data on the oxidative addition of chloroarenes to $Pd(0)L_2$ complexes **2**−**4** containing the ligands $1\text{-}AdP^tBu_2$, CyP^tBu_2, and PCy_3, respectively, imply that the irreversible step in these processes involves a monophosphine Pd(0) complex. Each of the reactions depended positively on the concentration of chlorobenzene and inversely on the concentration of added ligand. Thus, the number of phosphines in the complex involved in the rate-determining step for addition of chloroarenes is the same for complexes of each of the ligands studied and differs from the number of phosphines contained in the complex involved in the rate-determining step for addition of iodoarenes.

More specifically, the rate data for the addition of PhCl to complexes **2**−**4** were consistent with the rate equations for the mechanisms in Schemes 4 and 5 involving reversible loss of a ligand. These rate data include linear plots of $1/k_{obs}$ versus 1/[ArCl] and $1/k_{obs}$ versus [L] for reactions of PhCl with each of the three Pd(0) complexes.

The pathway in Scheme 4 involves reversible associative displacement of ligand by the haloarene, and the pathway in Scheme 5 involves a reversible sequence of ligand dissociation and haloarene association. In principle, these two pathways can be distinguished by the y-intercepts of the plots of $1/k_{obs}$ versus 1/[ArCl] and $1/k_{obs}$ versus [L]. Reaction by either mechanism predicts that a plot of $1/k_{obs}$ versus [L] will have a nonzero y-intercept. However, the mechanism in Scheme 4 predicts that a plot of $1/k_{obs}$ versus 1/[ArCl] will have a y-intercept of zero, while the mechanism in Scheme 5 predicts that the same plot would have a nonzero y-intercept. Moreover, the mechanism in Scheme 5 predicts that the y-intercept of the plot of $1/k_{obs}$ versus 1/[ArCl] would be identical to the y-intercept of the plot of $1/k_{obs}$ versus [L]. For the reactions of $1\text{-}AdP^tBu_2$ complex **2**, the kinetic behavior predicted for the reaction by initial dissociation of ligand was clearly observed. As shown in Figure 7, the plot of $1/k_{obs}$ versus [L] has a distinct nonzero y-intercept. Moreover, the y-intercepts of the plots of $1/k_{obs}$ versus [L] and $1/k_{obs}$ versus 1/[ArCl] are within experimental error of each other (925 and 1230 s). Finally, the values of K_4k_5 deduced from these plots (5.9×10^{-5} s^{-1} and 6.4×10^{-5} s^{-1}) are within experimental error of each other. We could not distinguish between these two mechanisms as confidently for reactions of the CyP^tBu_2 and PCy_3 complexes by this analysis because the y-intercepts of their plots of $1/k_{obs}$ versus 1/[ArCl] were close to zero. However, the values of K_4k_5 calculated from Figures 8 and 9 were similar to each other in both cases. This equivalence of the values of K_4k_5 and the clear finding of a dissociative mechanism for reaction of **2** suggest that complexes **3** and **4** also react with aryl chlorides by a dissociative mechanism.

Most generally, our data show unambiguously that the irreversible step in the addition of chloroarenes involves a monophosphine species and that the number of phosphine ligands in the Pd(0) species involved in the irreversible step of the oxidative addition of chloroarenes is identical for each of the Pd(0) complexes in this study. Moreover, these data show that the number of phosphines in the Pd(0) species in the irreversible step of the oxidative additions of chloroarenes is different than that in the Pd(0) species that reacts in the irreversible step of the oxidative additions of iodoarenes.

5. Mechanism of Oxidative Addition of Bromoarenes. Like the rate data on the oxidative addition of PhCl and PhI, the rate data on the oxidative addition of PhBr to each of the $L_2Pd(0)$ complexes **2**−**4** were closely related to each other. The oxidative addition of bromoarenes to each of these three complexes depended positively on the concentration of bromoarene, and each reaction occurred with little (L = PCy_3) or no (L = 1-AdP^{t}Bu$_2$, CyP^{t}Bu$_2$) dependence on the concentration of ligand. This lack of dependence of k_{obs} on [L] is similar to that for oxidative addition of PhI and is distinct from the strong dependence of k_{obs} on [L] for oxidative addition of PhCl. As shown below, a detailed assessment of the dependence of the rate constant on the concentration of bromoarene implies that two pathways for the oxidative addition of bromoarenes occur concurrently. One of these pathways clearly is the irreversible dissociation of ligand, as was deduced for reaction of the chloroarene, and the second pathway could be irreversible associative displacement of ligand by the bromoarene, as was deduced for the reactions of iodobenzene.

The dependence of k_{obs} on [L] was nearly zeroth-order for the addition of PhBr to each of three complexes. Thus, the irreversible step of these oxidative addition processes involves a bisphosphine Pd(0) species. Again, the coordination number of the species involved in the irreversible step of the oxidative addition of bromoarenes was identical for all of the Pd(0) species in this study.

Although this conclusion is the most concrete one and the major conclusion we wish to draw from our studies on the oxidative addition of bromoarenes is the coordination number of the species reacting in the rate-limiting step of the major pathway, we can draw some additional conclusions about the mechanism of the oxidative addition of bromoarenes. The presence of a nonzero *y*-intercept implies that the reaction likely occurs by two competing mechanisms involving bisphosphine species. For reactions of complexes **2** and **3**, plots of k_{obs} versus [PhBr] were linear, but they also contained nonzero *y*-intercepts, suggesting that two pathways involving bisphosphine complexes in the rate-determining step compete: one dependent on the bromoarene concentration and one independent of this concentration. Of the mechanisms considered, only the mechanism involving initial irreversible dissociation of ligand (Scheme 5) is independent of the concentration of ligand and haloarene ($k_{obs} = k_4$). Thus, we conclude that the value of the *y*-intercept roughly corresponds to the rate constant for reaction by this path.[52]

Two other paths predict rate constants that are independent of the concentration of ligand and positively dependent on the concentration of haloarene: direct C−X bond cleavage to form a four-coordinate intermediate (Scheme 3) and irreversible associative displacement of ligand followed by C−X bond cleavage (Scheme 4). We consider the pathway involving direct C−X bond cleavage to form a four-coordinate intermediate the least likely. Besides the formation of a crowded intermediate, microscopic reversibility implies that the elimination of ArBr from LPd(Ar)(Br) would occur through a four-coordinate intermediate. Previous studies on reductive elimination of ArBr from (P^{t}Bu$_3$)Pd(*o*-tol)Br implied that the elimination involves a three-coordinate intermediate (Scheme 6).[53] Although reductive elimination of ArBr from aryl Pd(II) halide complexes of AdP^{t}Bu$_2$ and CyP^{t}Bu$_2$ have not been reported, the steric properties of these phosphines make the formation of a bisphosphine intermediate L_2Pd(Ar)(X) and a change in mechanism from that of the reactions of P^{t}Bu$_3$ complex **1** unlikely.

Therefore, on the basis of the nonzero *y*-intercepts, we conclude that the addition of PhBr to complexes **2** and **3** most likely occurs by two competitive paths involving rate-determining reactions of bisphosphine complexes to give rise to monophosphine intermediates. One pathway could occur by irreversible dissociation of ligand and the second by irreversible associative displacement of ligand prior to the C−X bond cleavage step (Scheme 8).

In contrast, the oxidative addition of PhBr to PCy_3-ligated **4** appears to occur by a single mechanism involving associative displacement of the ligand or oxidative addition to the two-coordinate species. The rate of the oxidative addition of PhBr to PCy_3-ligated **4** was measured at a temperature at which the major Pd(0) species was the L_2Pd complex. The data in Figure 12 showed that this oxidative addition occurred with a positive dependence on the concentration of bromobenzene and only a weak dependence on the concentration of added ligand. The small slope and large *y*-intercept of the plot of $1/k_{obs}$ versus [L] is consistent with the rate equations corresponding to nearly irreversible associative substitution of PCy_3 by PhBr (Scheme 4) or nearly irreversible oxidative addition to the two-coordinate species to generate a four-coordinate product (Scheme 3). The small slope implies that the product of the equilibrium and rate constants in the second term of the equation (K_2k_3) is large relative to the rate constant in the first term (k_2). Because both processes would be favorable with the smaller PCy_3 ligand, we cannot distinguish between these two mechanisms. However, we can conclude in general that a major pathway for reactions of bromoarenes with the $L_2Pd(0)$ complexes **2**−**4** occurs by irreversible reaction of the bromoarene with the bisphosphine complex. This irreversible reaction could occur either by

(52) Unimolecular decomposition of the Pd(0) complex can be excluded as a significant contributor to the value of the *y*-intercept because **2** was stable in toluene at 100 °C. Our values for the *y*-intercepts of the plots of k_{obs} versus [PhBr] in Figures 10 and 11 are similar. If these correspond to the rate constants for oxidative addition by irreversible dissociation of ligand, one might expect the value of the *y*-intercept to be larger for the reaction of the complex containing the more sterically bulky 1-AdP^{t}Bu$_2$ than for that containing CyP^{t}Bu$_2$. However, comparison of these *y*-intercept values is complicated because they represent only an approximate value for the rate of ligand dissociation. A quantitative value for the rate constant for ligand dissociation (k_4) cannot be obtained from a simple extrapolation of the plot of k_{obs} versus [ArBr] over the linear range investigated because the plots become nonlinear as [ArBr] approaches zero.

(53) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 13944.

associative displacement of ligand followed by oxidative addition or by direct oxidative addition.

Conclusions

The observed kinetic data are summarized in Table 1, which shows that the rate constants depend on the identity of the halide more than on the steric bulk of the ligand. The reactions of iodobenzene were all zeroth-order in added ligand, the reactions of bromobenzene were all zeroth- or nearly zeroth-order in added ligand, and the reactions of chlorobenzene were all inverse-first-order in added ligand. Moreover, all of the reactions depended positively on the concentration of haloarene. Thus, all of the reactions of the iodoarenes occur by rate-determining reaction with a bisphosphine complex, whereas all of the reactions of the chloroarene occur by rate-determining reaction with a monophosphine complex. The reactions of the bromoarenes occur by rate-determining reaction of a bisphosphine complex. Our data imply that the reactions of chloroarenes occur by reversible formation of a monophosphine intermediate, while the reactions of iodobenzene occur by an irreversible reaction of the starting bisphosphine species. The oxidative additions of bromoarenes appear to occur by a combination of irreversible reaction of the bromoarene with the two-coordinate Pd(0) species and dissociation of phosphine prior to reaction with the bromoarene. In particular, the reactions of bromoarenes with Pd(1-AdP^{t}Bu$_2$)$_2$ (**2**) appeared to occur by a combination of both associative and dissociative substitution of the ligand by haloarene, and this result reveals the fine balance between these two mechanisms for generation of the monophosphine intermediates.

We propose that the iodoarenes react with the bisphosphine species via an irreversible process because they are softer and more reactive than the other haloarenes, while addition of chloroarenes requires generation of the more reactive monophosphine species because they are poorer ligands and require a more reactive intermediate to cleave the less reactive C−Cl bond. These conclusions are supported by the low barriers for oxidative addition of chloroarenes to monophosphine palladium(0) species and high barriers for oxidative addition of chloroarenes to bisphosphine palladium(0) species recently calculated using density functional theory.[34,36]

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Supporting Information Available: Crystallographic data for **10**, **11**, and **15** (CIF), experimental procedures, representative decays, and characterization of palladium complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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