Influences on the Relative Rates for C−N Bond-Forming Reductive Elimination and β-Hydrogen Elimination of Amides. A Case Study on the Origins of Competing Reduction in the Palladium-Catalyzed Amination of Aryl Halides

John F. Hartwig,* Steven Richards, David Barañano, and Frédéric Paul

Contribution from the Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107

Received December 7, 1995[⊗]

Abstract: Typical decomposition by β-hydrogen elimination has limited the productive catalytic organometallic chemistry of late transition metal amido complexes. However, one reaction that has been shown to involve a late metal amido complex with β-hydrogens and elude extensive β-hydrogen elimination is the palladium-catalyzed amination of aryl bromides to give arylamines. The primary side products formed in these catalytic aminations are arenes, the products of aryl halide reduction. It would seem reasonable that both arylamine and arene products result from competitive reductive elimination of amine and β-hydrogen elimination from a common amido aryl intermediate. Our results do substantiate competitive β-hydrogen elimination and reductive elimination involving an amido group, but also reveal a second pathway to reduction that occurs when employing Pd(II) precursors. This second pathway for aryl halide reduction was shown principally by the observations that (1) stoichiometric reactions of aryl halide complexes or catalytic reactions employing $[P(o\text{-tolyl})_3]_2Pd(0)$ showed less arene side product than did catalytic reactions employing Pd(II) precursors, (2) increasing amounts of Pd(II) catalyst gave increasing amounts of arene product, and (3) reactions catalyzed by Pd(II) precursors showed amine:arene ratios at early reaction times that were lower than ratios after complete reaction. In addition to data concerning arene formation during Pd(II) reduction, we report data that demonstrate how electronic and steric factors control the relative rates for amine vs arene formation. The relative amounts of reduction product and amination product depend on the size of the phosphine and substitution pattern of the amide ligands. Systematic variation of phosphine size demonstrated that increasing the size of this ligand gave increasing amounts of arylamine product, increasing size of the amido group gave increasing amounts of arylamine product, while decreased nucleophilicity of the amide gave decreased amounts of arylamine product. Further, the presence of electron withdrawing groups on the palladium-bound aryl ring accelerated the reductive elimination reaction, relative to β-hydrogen elimination, and this result is consistent with previously observed acceleration of carbon−heteroatom bond-forming reductive eliminations with isolable palladium complexes.

Introduction

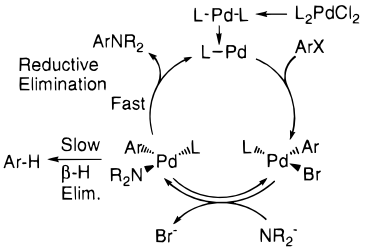
The reaction of an amide source—either a tin amide, a boron amide with base, or an amine in the presence of base—with aryl bromides catalyzed by tri-*o*-tolylphosphine palladium complexes leads to the formation of arylamines as shown in eq 1.[1−9] The dominant reaction that competes with amination is

$$ArBr + \text{"}R_2N^-\text{"} \xrightarrow[L=P(o\text{-Tolyl})_3]{L_2PdCl_2 \text{ or } L_2Pd} ArNR_2 \quad (1)$$

$$\text{"}R_2N^-\text{"} = Bu_3SnNR_2,\ B(NR_2)_3 + \text{base},\ HNR_2 + \text{base}$$

reduction of the aryl halide to the corresponding arene. We have recently provided strong evidence for a reaction pathway[10] in Scheme 1 that involves oxidative addition of aryl halide to a monophosphine Pd(0) complex,[5] and subsequent generation

Scheme 1



of an amido aryl intermediate by either reversible, endothermic[6] transfer of the amide from the tin reagent[11] or coordination of an amine to the aryl halide complex and deprotonation of the amine N−H.[7]

The formation of a palladium dialkylamido complex is unusual, and productive catalytic chemistry of such intermediates is rare. Indeed the dialkylamido complex involved in the catalytic amination chemistry is unstable at room temperature. Experiments directed at generating the complex at low temperatures by methods that were independent of the catalytic reactions showed that such complexes provided arylamine products below room temperature.[10] Further, it is remarkable that this intermediate would undergo the rare reductive elimination of amine, since β-hydrogen elimination of alkylamido

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

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0002-7863/96/1518-3626$12.00/0

complexes has been thought to be a rapid route to their decomposition.[12,13]

The most concise mechanism that accounts for both arylamine and arene products includes a palladium−amido intermediate that would competitively form amine by C−N bond-forming reductive elimination and arene after initial β-hydrogen elimination. Few data are known concerning factors that would control the relative rates for C−N bond-forming reductive elimination of amines and for β-hydrogen elimination from transition metal amides. Only a handful of papers report reductive elimination of amines.[6,14,15] Although imine insertions into hydrides, the reverse of β-hydrogen elimination from amides, are presumably crucial to imine hydrogenation reactions,[16] little is known about factors that control either direction of this transformation.[17]

Since the selectivity of reactive intermediates typically controls product composition in both catalytic and stoichiometric processes, information on factors controlling the chemistry of the organometallic palladium−amide reactive intermediate would be important for understanding the capability of late metal amido complexes to serve as intermediates in productive catalytic chemistry despite, or as a result of, their instability. In this paper, we provide strong evidence for a reaction mechanism that accounts for amine and arene product formation by reaction of an amido group with a palladium aryl halide complex, and our results are consistent with divergent reactivity of a palladium amido complex. However, we also provide strong evidence for a separate reaction pathway that forms arenes during the early stages of reactions initiated by Pd(II) catalyst precursors. We have drawn these conclusions by analyzing product ratios formed during stoichiometric reactions involving either Pd(0) complexes or Pd(II) aryl halide complexes and catalytic reactions involving either Pd(0) complexes, Pd(II) aryl halide complexes, Pd(II) dichloride catalyst precursors, and Pd(II) diacetate catalytst precursors. Further, we have delineated the steric and electronic effects on product selectivity in both stoichiometric and catalytic reactions to reveal their effects on the relative rates for β-hydrogen elimination and reductive elimination. As a side light, these studies have also revealed several advantages of the tri-*o*-tolylphosphine ligand for such catalytic chemistry.

Results and Discussion

I. Comparison of Product Selectivities between Stoichiometric and Catalytic Reactions. The aryl halide complexes $\{[(o\text{-tolyl})_3P]Pd(p\text{-}C_6H_4\text{-}t\text{-Bu})(Br)\}_2$ clearly lie on the palladium-catalyzed amination reaction pathway in either their monomeric or dimeric forms.[3,10] Thus, stoichiometric reactions of tin amides with these compounds allow observation of the products resulting from amide generation and amide reactivity during a single turnover of the catalysis. In order to understand the selectivity of the amido intermediate, reaction of the aryl halide complex $\{[(o\text{-tolyl})_3P]Pd(p\text{-}C_6H_4\text{-}t\text{-Bu})(Br)\}_2$ (**1**)[4] with tin amides (eq 2) was conducted and the ratio of *tert*-butylbenzene vs *N*,*N*-dialkylaniline product was determined by gas chromatography after correcting for response factors. The stoichiometric reaction of **1** at 80 °C in benzene in the presence of 6 equiv of $(o\text{-tolyl})_3P$ to trap the Pd(0) as L_2Pd gave the dialkylaniline products in greater than 85% yields. No $p\text{-Bu}C_6H_4\text{-}t\text{-Bu}$ was formed that could result from transfer of the alkyl rather than the amido group.

$$[LPd(Ar)(Br)]_2 + Bu_3SnNR_2 \xrightarrow[L=P(o\text{-Tolyl})_3]{L} ArNR_2 + L_2Pd \quad (2)$$

Amido tin reagents were employed as the source of the amide group, since their reaction is likely to be milder than generating the amide by reaction of amine in the presence of base. Further, reactions with tin reagents allowed for comparisons to be made between reactions involving different Pd−phosphine systems. Phosphines smaller than tri-*o*-tolylphosphine are not displaced by secondary amines, precluding catalytic activity in the tin-free system.[7,9]

In addition to stoichiometric experiments, catalytic reactions (eq 1) between $p\text{-Br}C_6H_4\text{-}t\text{-Bu}$ and tin amides were conducted using either **1**, $[(o\text{-tolyl})_3P]_2Pd$ (**2**),[4] $Pd(OAc)_2$ with 3 equiv of $P(o\text{-tolyl})_3$ (**3**: catalyst mixture), or $[(o\text{-tolyl})_3P]_2PdCl_2$ (**4**)[1] as catalyst, and the ratios of arene and arylamine products were again determined by GC. Unless otherwise state, 5 mol % catalyst was employed and reactions were conducted with 0.13 mmol of aryl bromide, 1.5 equiv of tin amide, and 0.5 mL of benzene solvent. In all cases, arene and arylamine were the only products observed in substantial quantities. Other products were formed in less than 5% yields. Again, no $p\text{-Bu}C_6H_4\text{-}t\text{-Bu}$ was formed that could result from transfer of the alkyl rather than the amido group.

The ratios of amine to arene products formed from the catalytic and stoichiometric experiments involving complexes of the $P(o\text{-tolyl})_3$ ligand are provided in Table 1. The stoichiometric reations gave amine:arene product ratios of 11:1 for tin dimethylamide and 15:1 for tin diethylamide. Ratios of amine: arene that were comparable to those formed during stoichiometric reactions of **1** were observed during reactions of the aryl bromide with tin amide catalyzed by either Pd(0) complex **2** or aryl bromide complex **1**.[10] Reactions catalyzed by **1** or **2** gave ratios between 9:1 and 10:1 in favor of amine product. In the case of **1** or **2**, varying the amount of catalyst from 0.5 mol % to 5 mol % had no measurable effect on selectivity. Further, product ratios remained constant throughout the course of the reaction.

Reactions involving Pd(II) catalyst precursors **3** and **4** gave more arene product than those catalyzed by **1** and **2**. For example, reactions catalyzed by the mixture **3** gave a 5:1 ratio of amine to arene, while the Pd(II) complex **4** gave a 6:1 ratio. The amount of reduction product was greater for reactions that used a higher mole percent of Pd(II) catalyst precursors. For example, the use of 0.5 mol % **4** in reactions of Me_3SnNMe_2 led to greater than 90% conversion of aryl bromide and gave a 10:1, rather than 6:1, ratio of amine to arene. The use of 25 mol % catalyst gave a 4:1 ratio of amine to arene. Similar results were observed with Bu_3SnNEt_2. The ratio of 9:1 with 5 mol % catalyst was reduced to 5:1 in reactions employing 25 mol % catalyst.

As one might expect from this result, the observed ratios of amine to arene products varied with time when employing the Pd(II) precursors, and improved over the course of the reaction. For example, the reaction of $p\text{-Br}C_6H_4\text{-}t\text{-Bu}$ with Bu_3SnNMe_2 catalyzed by 5 mol % **4** showed a 4:1 ratio of amine to arene after roughly 50% conversion. The reaction was stopped at this point since all of the insoluble dichloride catalyst had reacted to provide soluble materials. A product ratio near the 9:1 selectivity for the Pd(0) complex would be required for the remainder of the reaction in order to obtain a final ratio of 6:1.

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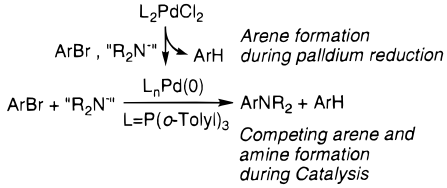
Table 1. Ratios of Amine:Arene under Different Stoichiometric and Catalytic Conditions for Reactions Involving the Aryl Group *p*-C_6H_4-*t*-Bu

expt no.	description	Pd complex	tin amide Bu_3SnX, X =	ratio of amine:arene
1	stoichiometric	**1**	NMe_2	11:1
2	stoichiomeric	**1**	NMe_2-d_6	25:1
2	stoichiometric	**1**	NEt_2	15:1
3	catalytic	**1** (5%)	NMe_2	10:1
4	catalytic	**2** (5%)	NMe_2	9:1
5	catalytic	**3** (5%)	NMe_2	5:1
6	catalytic	**4** (5%)	NMe_2	6:1
7	catalytic	**4** (25%)	NMe_2	4:1
8	catalytic	**4** (0.5%)	NMe_2	9:1
9	catalytic	**4** (5%)	NEt_2	9:1
10	catalytic	**4** (25%)	NEt_2	5:1

Scheme 2



Although these data are approximate, the required selectivity is clearly similar if not identical to the 9:1 selectivity observed with **1** or **2** or with 0.5 mol % of **4**.

These data are consistent with at least two independent reaction pathways to form arene as depicted simply in Scheme 2. The arene product does not arise from competitive transfer of a butyl and an amido group, because no *p*-BuC_6H_4-*t*-Bu is formed as reaction product. Carbon−carbon bond-forming reductive elimination is known to be faster than β-hydrogen elimination with these systems, since alkyl groups can be employed in coupling reactions with aryl halides. Thus, any arene formed by butyl group transfer must be accompanied by *p*-BuC_6H_4-*t*-Bu. Instead, one pathway for arene formation appears to involve the aryl bromide complexes, is a direct result of the catalytic cycle, and produces both amine and arene product. Competitive reductive elimination and β-hydrogen elimination is the simplest mechanism that accounts for both amine and arene products during the stoichiometric reaction. Steric and electronic effects on the product selectivity presented below are further consistent with such competitive reactions that most likely diverge at a common amido intermediate.

However, a second pathway occurs during the reduction process and leads to additional formation of arene. This conclusion is clearly indicated by (1) the similarity between selectivities observed for stoichiometric reactions involving **1** and for catalytic reactions involving either **1** or **2**, (2) the increased amount of arene formed in catalytic reactions involving either **3** or **4**, (3) the increased amount of arene product with increasing amounts of Pd(II) catalyst, and (4) similar selectivity with variable amounts of Pd(0) catalyst. More subtly, the increasing ratio of amine:arene over the course of time with reactions catalyzed by Pd(II), but not Pd(0), indicates that additional arene is formed early in the reaction, presumably when the Pd(II) precursor is being reduced to Pd(0). It is unclear how the arene is produced as a result of Pd(II) reduction, but one possibility is the formation of arene by reaction of a portion of the aryl halide complex with HCl that may form as a byproduct of palladium reduction.

II. Source of Hydrogen on the Arene Reduction Product. In order to demonstrate conclusively that the reduction product arises from β-hydrogen elimination from the amido group we conducted reactions with $Bu_3SnN(CD_3)_2$. Two predictions can be made for reactions involving this substrate. First, arene product would contain a single deuterium. Second, the ratio of amine:arene would increase since the β-hydrogen elimination would be slower for $N(CD_3)_2$ as a result of a primary isotope effect. The experimental data were consistent with these predictions. The labeled reagent was prepared using $LiN(CD_3)_2$, generated from commercially available $(CD_3)_2NH_2Cl$.

As expected for stoichiometric reactions, the arene product consisted of predominantly deuterated material. For example, reaction of **1** with $Bu_3SnN(CD_3)_2$ under identical conditions to the stoichiometric reaction of Bu_3SnNMe_2 gave arene and amine products, with the arene showing 70% monodeuterated material.[18] The amount of deuterium incorporation was unaffected by using protiated or deuterated solvent. Further, the ratio of amine:arene was altered as a result of using deuterated amide. The ratio of amine:arene was 25:1 rather than 11:1, as was observed with protiated amide. Assuming that the rate of reductive elimination of amine is identical for deuterated and protiated amides, the value of k_H/k_D is on the order of 2 for the β-hydrogen elimination process, and this value is consistent with a primary isotope effect. Of course, this value is approximate since the arene is not completely deuterated and the reductive elimination may show a significant secondary isotope effect resulting from the six deuteria on the amide group. The deuterated amide reagent was also employed in reactions catalyzed by **4**. In this case, the arene product was roughly 50% protiated and 50% deuterated. Thus, the additional arene product formed when using Pd(II) catalysts may be formed by a process other than that involving amide β-hydrogen elmination. Alternatively, generation of small amounts of HCl in the reduction process may lead to scrambling with trace amounts of water. Again, protons or deuterons from solvent were not incorporated into the arene product; arene product formed during reactions conducted in benzene-d_6 showed identical isotope patterns to those formed during reactions in protiated benzene. In the catalytic reactions, the majority of arene is formed during reduction of Pd(II) to Pd(0), and the ratio of amine:arene was not altered enough to allow quantitative conclusions in this more complex catalytic case.

Table 2. Electronic Effects on Amination vs Reduction Selectivity for reactions Involving Bu_3SnNMe_2

expt no.	aryl group	stoichiometric amine:arene	catalytic L_2PdCl_2 amine:arene
1	$C_6H_4C(O)Me$	30:1	15:1
2	C_6H_4-*t*-Bu	9:1	6:1
3	C_6H_4-*p*-NMe_2	5:1	3:1

III. Effect of Palladium-Bound Aryl Group Electronic Properties. Table 2 shows the effect of aryl group electronic properties on the ratio of amine:arene. Reaction of Bu_3SnNMe_2 with $\{Pd[P(o\text{-tolyl})_3][C_6H_4\text{-}p\text{-}C(O)Me](Br)\}_2$ gave significantly higher ratios of amine:arene than did reactions with $\{Pd[P(o\text{-tolyl})_3](p\text{-}C_6H_4\text{-}t\text{-Bu})(Br)\}_2$, while reaction of $\{Pd[P(o\text{-tolyl})_3](C_6H_4\text{-}p\text{-}NMe_2)(Br)\}_2$ gave significantly lower ratios of amine:arene. Once again, the reactions of *p*-$BrC_6H_4C(O)Me$ and *p*-$BrC_6H_4NMe_2$ catalyzed by **4** showed lower amine to arene ratios than the stoichiometric reactions of the corresponding aryl

(18) The amine product is fully d_6. It is, therefore, unlikely that the residual protiated arene results from preliminary scrambling of the amide β-hydrogens. Alternatively, the hydrogen of the arene may result from scrambling of the intermediate palladium hydride, a small amount of competing transfer of the butyl group, reaction with a small amount of tin hydride, or reversible metallation of the phosphine. In any case, these are clearly minor pathways.

Table 3. Effect of Amino Group on Amination vs Reduction Selectivity for Reactions Involving the Aryl Group *p*-C_6H_4-*t*-Bu

expt no.	amido group	stoichiometric amine:arene
1	NMe_2	11:1
2	NEt_2	15:1
3	NMePh	5:1

halide complexes. However, the relative effects of aryl substitution were the same for stoichiometric reactions with analogs of **1** and for catalytic reactions involving **4**.

These results are consistent with a previous result from our group concerning electronic effects on the rates for reductive eliminations that form carbon−heteroatom bonds.[19] We have shown that the rates of carbon−heteroatom bond-forming reductive eliminations involving aryl groups are accelerated by the presence of electron withdrawing groups attached to the palladium-bound aromatic system. Although little is known about β-hydrogen elimination of amido groups, it is reasonable to expect that the properties of the palladium-bound aryl group would have less effect on this reaction than on reductive elimination, since the β-hydrogen elimination step does not directly involve the aryl system. Thus, the change in amination:reduction ratios as a function of arene electronics is consistent with acceleration of the reductive elimination and substantiates the proposal of competitive reductive elimination and β-hydrogen elimination by divergent reactivity with a common intermediate.

IV. Effect of Amide Group on Selectivity. We investigated the effect of amide size, amide electronic properties, and the prsence of primary vs secondary C−H bonds in the amide β-position by comparing selectivities of Bu_3SnNMe_2 with Bu_3SnNEt_2 and $Bu_3SnNMePh$. These results are presented in Table 3. Larger tin amides such as $Bu_3SnN(i\text{-}Bu)_2$ reacted very slowly with **1**, suggesting that the amido group was too large to undergo transmetalation. In both catalytic and stoichiometric reactions, the ratio of amine:arene was slightly greater for reaction with Bu_3SnNEt_2 than for the reaction with Bu_3SnNMe_2. In contrast, stoichiometric reaction of the larger, but less nucleophilic $Bu_3SnNMePh$ with **1** gave a 5:1 ratio of amine: arene, markedly reduced from ratios obtained from $SnNMe_2$. The data for NMe_2 vs NEt_2 are consistent with slightly slower β-hydrogen elimination involving secondary hydrogens than that involving primary hydrogens and/or faster reductive elimination with the slightly larger diethylamido group. The lower amine: arene ratio with NMePh is clearly consistent with the electronic effects in the previous section. The aromatic ring acts as an electrophile, the amide as a nucleophile, and reductive elimination is faster with more nucleophilic amides. Alternatively, β-hydrogen elimination may be faster with aryl-substituted amides because a conjugated imine would be formed. In either case, these results again support divergent reactivity with a common intermediate.

V. Phosphine Steric Effects on Catalytic and Stoichiometric Reactions. In order to determine the selectivities for complexes containing phosphines with systematically varied steric requirements, aryl halide complexes of P(*o*-tolyl)$_2$Ph, {Pd[P(*o*-tolyl)$_2$Ph]$_2$(*p*-C_6H_4-*t*-Bu)(Br)} (**5**), and of P(*o*-tolyl)Ph_2, {Pd[P(*o*-tolyl)Ph_2]$_2$(*p*-C_6H_4-*t*-Bu)(Br)} (**6**), were prepared. The simplest method we found for preparing these compounds was exchange of the smaller phosphines for P(*o*-tolyl)$_3$ in **1**. Reaction of the dimeric aryl halide complex {Pd[P(*o*-tolyl)$_3$](*p*-C_6H_4-*t*-Bu)(Br)}$_2$ or {Pd[P(*o*-tolyl)$_3$](C_6H_4-*p*-Me)(Br)}$_2$ with P(*o*-tolyl)$_2$Ph or P(*o*-tolyl)Ph_2 quantitatively displaced P(*o*-tolyl)$_3$. Solutions of isolated aryl halide complexes containing the P(*o*-tolyl)$_2$Ph ligand displayed an equilibrium in solution between two species. One complex displayed a resonance at δ 21.9 and the other one at δ 25.4 in the $^{31}P\{^1H\}$ NMR spectrum. A resonance for free P(*o*-tolyl)$_2$Ph that was equal in intensity to the resonance at δ 25.4 was also observed. Treatment of the solution with additional free phosphine provided solutions displaying $^{31}P\{^1H\}$ NMR spectra with a single resonance at δ 21 accompanying the signal for free phosphine. We, therefore, assign the resonance at δ 21 to the monomeric aryl bromide complex **5** with two phosphine ligands and the resonance at δ 25.4 to a dimeric species {Pd[P(*o*-tolyl)$_2$Ph](*p*-C_6H_4-*t*-Bu)(Br)}$_2$ with a structure analogous to that for {Pd[P(*o*-tolyl)$_3$](Ar)(Br)}$_2$, which we have reported previously.[4] Solid product obtained from the exchange reactions analyzed satisfactorily for the monomeric bis-phosphine complex and an X-ray diffraction study was performed on the analogous four-coordinate, monomeric *p*-tolyl analog {Pd[P(*o*-tolyl)$_2$Ph]$_2$(*p*-C_6H_4-*t*-Bu)(Br)} (**5′**) (*vide infra*).

Table 4. Effect of Phosphine Size on Product Selectivity for Reactions Involving Bu_3SnNMe_2

expt no.	phosphine	stoichiometric {$L_nPd(C_6H_4$-*t*-Bu)(Br)}$_m$ *n*, *m*; Amine:Arene	catalytic Pd(OAc) + 3L amine:arene	catalytic L_2PdCl_2 amine:arene
1	P(*o*-tolyl)$_3$	$n = 1$, $m = 2$; 9:1	5:1	6:1
2	P(*o*-tolyl)$_2$Ph	$n = 2$, $m = 1$; 8:1	3:1	4:1
3	P(*o*-tolyl)Ph_2	$n = 2$, $m = 1$; 3:1	1:1.2	2:1
4	PPh_3	$n = 2$, $m = 1$; 1:1.2	−	−

The ratios of amine:arene obtained from stoichiometric and catalytic amination reactions catalyzed by palladium complexes of phosphine ligands with systematically varied steric requirements are given in Table 4. It should be noted that reaction rates and total yields of amine and arene decreased significantly with decreasing phosphine size. Yields of amine in stoichiometric and catalytic reactions were on the order of 60% for P(*o*-tolyl)$_2$Ph, 30% for P(*o*-tolyl)Ph_2, and less than 10% for PPh_3. $L_nPd(0)$ complexes were the dominant metal-containing product. Besides the arene and amine products, multiple organic side products were observed by ^1H NMR spectroscopy and GC, but were not identified. Nevertheless, the four ligands show the same characteristic of higher amination:reduction ratios for stoichiometric reactions than for catalytic reactions. Again, these results are consistent with a pathway for reduction that is separate from the pathway that forms arylamine.

Experiments with the different phosphines demonstrated that amination:reduction ratios decreased with decreasing ligand size. These results were observed for both stoichiometric and catalytic reactions. The ratios for stoichiometric reactions of the aryl bromide complexes containing P(*o*-tolyl)$_3$ and P(*o*-tolyl)$_2$Ph were measurably different, but increases in reduction product were more dramatic as the ligand was changed from P(*o*-tolyl)$_2$Ph to P(*o*-tolyl)Ph_2.

The combination of data from catalytic and stoichiometric reactions revealed a second factor that led to increasing amounts of reduction product with the mixed aryl phosphines. Reactions involving complexes that contained a mixture of *o*-tolyl and phenyl groups rapidly gave phosphines resulting from scrambling of the phosphine aryl groups. Thus, reactions involving complexes of P(*o*-tolyl)$_2$Ph produced P(*o*-tolyl)Ph_2 and P(*o*-tolyl)$_3$. Surprisingly, little scrambling with the palladium-bound aryl group occurred.[19−22] Exchange of aryl groups between

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phosphines was clearly faster than exchange between the palladium-bound and phosphine aryl groups. Since the smaller ligands coordinate in preference to the larger ligands, the observed selectivities should approach those of the smaller ligands as the reactions proceed. Of course, this effect will be more pronounced for the catalytic reactions than the stoichiometric reactions, since the stoichiometric reactions gave less ligand group scrambling. In a similar fashion, reactions containing P(*o*-tolyl)Ph_2 produced P(*o*-tolyl)$_2$Ph and PPh_3.

One can rationalize the generally favorable selectivity for reductive elimination over β-hydrogen elimination from complexes bearing larger ligands in terms of changes in coordination number for the two competing reactions. A reaction that decreases the coordination number should be favored over one that increases or maintains the same coordination number when larger ligands are present. Reductive elimination reduces the metal coordination number. β-Hydrogen elimination either maintains the same coordination number or increases it before subsequent reactions, such as reductive elimination, occur that ultimately decrease coordination number. It is reasonable to expect that a single amide ligand would generate a hydride and coordinated imine since it is believed that β-hydrogen elimination from alkyl groups gives rise to a hydride and a coordinated alkene.[23] Further, Blum and Milstein have recently provided mechanistic data on β-hydrogen elimination with an iridium methoxide complex and their data suggest that a hydride and a coordinated aldehyde initially forms during this process.[24] An alternative pathway for the β-hydrogen elimination in our studies, direct transfer of a β-hydrogen from the tin amide to palladium, would also increase or maintain the coordination number of the aryl halide complex. Thus, one would expect that the amine:arene ratio resulting from competitive reductive elimination and β-hydrogen elimination would increase with increasing size of the phosphine ligand, as we have observed experimentally.

VI. X-ray Structural Studies of Ligand Conformations. We have previously reported X-ray diffraction data for a dimeric tri-*o*-tolylphosphine palladium aryl bromide complex and for the monomeric two-coordinate Pd(0) complex **2**.[4] The structure of the aryl halide complex showed two *o*-tolyl methyl groups pointing toward the metal center and the third *o*-tolyl methyl group pointing toward the region of space between the three aryl groups. In contrast, all three *o*-tolyl groups within the phosphines of **2** were pointed toward the metal. It would, therefore, be possible that the P(*o*-tolyl)$_2$Ph ligand could create a similar steric environment to P(*o*-tolyl)$_3$ if both *o*-tolyl groups pointed toward the metal or a smaller steric environment than P(*o*-tolyl)$_3$ if one tolyl group pointed toward the metal and the other between the three aryl groups. Solution NMR spectroscopic data presented above suggested that P(*o*-tolyl)$_2$Ph was smaller than P(*o*-tolyl)$_3$ since monomeric, rather than dimeric, complexes predominated in solution.

The P(*o*-tolyl)$_2$Ph-ligated *p*-tolyl bromide complex **5′** provided single crystals suitable for an X-ray diffraction study after addition of pentane to the toluene reaction solution. An ORTEP drawing of **5′** is given in Figure 1. Crystal and data collection parameters are given in Table 5, and bond distances and angles are given in Tables 6 and 7. Compound **5′** crystallized in space group *P*2/*n*, and the structure was solved by Patterson methods.

Consistent with the solution data, P(*o*-tolyl)$_2$Ph was shown in the solid state to be smaller than P(*o*-tolyl)$_3$, since one methyl group pointed at the metal and the other pointed toward the space between the three aryl groups. Both phosphine groups showed this conformation. In fact, the molecule lay on a crystallographic 2-fold axis containing the bromide, the palladium center, and the palladium-bound tolyl group. The molecule showed nearly perfect 90° angles in the pseudo-square-planar geometry. The Pd−P (2.354(3) Å) distance was measurably longer than that in {Pd[P(*o*-tolyl)$_3$](C$_6$H$_4$-*p*-Bu)(Br)}$_2$ (2.288(3) Å). This difference in distance must result from the trans effect of phosphine in **5′** vs bridging bromide in the *p*-Bu analogs of **1**, since the trend opposes that expected for steric effects. Consistent with the distances controlled by trans effects rather than steric effects, the Pd−C distances in the two compounds are essentially identical. Both aryl groups are trans to a bromide, although one is a bridging and one a terminal bromide.

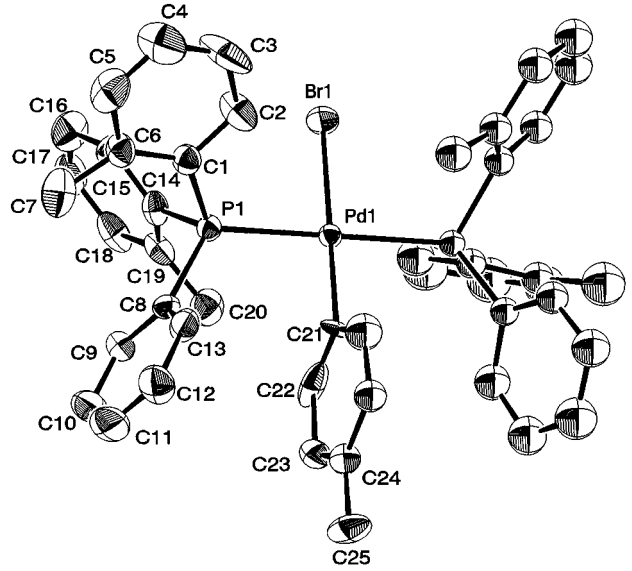
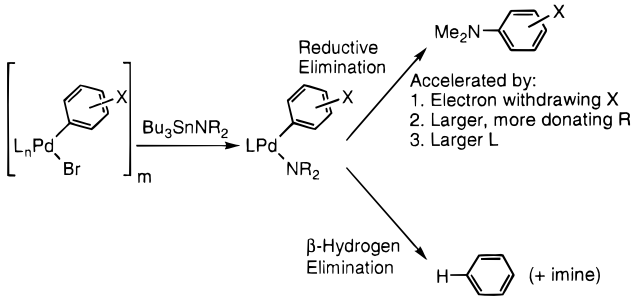
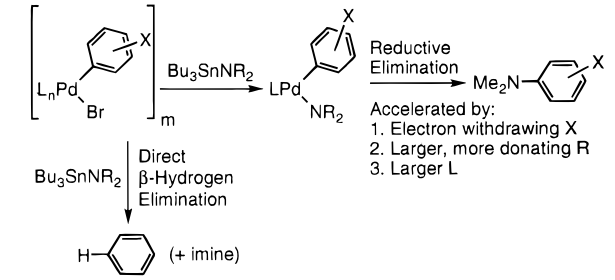


Figure 1. ORTEP Drawing of **5′**.

Scheme 3



Scheme 4



(23) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, 1987.

(24) Blum, O.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 4582.

VII. Potential Divergent Pathways for Formation of Amine and Arene. Although formation of amine and arene from the same amido intermediate during stoichiometric reactions and catalytic reactions involving **1** or **2**, as shown in Scheme 3, is the most concise explanation for both products, it

Table 5. Experimental Details

A. Crystal Data	
empirical formula	$C_{23.5}H_{21}PBr_{0.5}Pd_{0.5}$
formula weight	427.55
crystal color/habit	pale yellow prism
crystal dimensions (mm)	0.10 X 0.15 X 0.17
crystal system	monoclinic
no. of reflcns used for unit cell determination (2θ range)	17 (8.8−18.0°)
lattice parameters	
	a = 12.506(2) Å
	b = 12.572(2) Å
	c = 12.825(2) Å
	β = 97.35(1)°
	V = 1999.8(9) Å^3
space group	$P2/n$ (No. 13)
Z value	4
D_{calc}	1.420 g/cm^3
F000	870
ν(MoKα)	15.56 cm^{-1}
B. Intensity Measurements	
diffractometer	Enraf-Nonius CAD-4
radiation	Mo Kα (λ = 0.71069 Å)
temperature	23 °C
attenuator	Zr foil (factor = 20.4)
take-off angle	2.8°
detector aperture	2.0−2.5mm hor./2.0mm vert.
crystal-to-detector distance	21 cm
scan type	ω-2θ
scan rate	1.0 − 16.5°/min (in omega)
scan width	(0.94 + 0.61 tanθ)°
$2\theta_{max}$	52.6°
no. of reflcns meas	total 4436
unique	4249 (R_{int} = 0.073)
corrections	Lorentz−polarization absorption (trans 0.90−1.00)
C. Structure Solution and Refinement	
structure solution	Patterson method
refinement	full-matrix least-squares
function minimized least-squares weights	$\sum w(\|F_o\| - \|F_c\|)^2$ $4F_o^2/\sigma^2(F_o^2)$
p-factor	0.03
anomalous dispersion	all non-hydrogen atoms
no. of observations ($I > 3.00\sigma(I)$)	1777
no. of variables	232
reflcn/parameter ratio	7.66
residuals	R, R_w: 0.057, 0.062
goodness of fit indicator	1.81
max shift/error in final cycle	0.00
max peak in final diff map	1.00 e$^-$/Å^3
min peak in final diff map	−0.53 e$^-$/Å^3

Table 6. Intramolecular Distances Involving the Non-Hydrogen Atoms[a]

atom−atom	distance	atom−atom	distance
Pd1−Br1	2.516(2)	C9−C10	1.38(2)
Pd1−P1	2.354(3)	C10−C11	1.41(2)
C11−C12	1.36(2)	Pd1−C21	2.04(1)
C12−C13	1.37(2)	P1−C1	1.83(1)
C14−C15	1.39(2)	P1−C8	1.85(1)
C14−C19	1.38(2)	P1−C14	1.83(1)
C15−C16	1.36(2)	C1−C2	1.37(1)
C16−C17	1.35(2)	C1−C6	1.39(1)
C17−C18	1.37(2)	C2−C3	1.40(2)
C18−C19	1.43(2)	C3−C4	1.32(2)
C19−C20	1.44(2)	C4−C5	1.35(2)
C21−C22	1.25(2)	C5−C6	1.40(2)
C6−C7	1.44(2)	C22−C23	1.46(2)
C8−C9	1.31(2)	C23−C24	1.38(1)
C8−C13	1.40(2)	C24−C25	1.52(2)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 7. Intramolecular Bond Angles Involving the Non-Hydrogen Atoms

atom−atom−atom	angle	atom−atom−atom	angle
Br1−Pd1−P1	89.92(9)	C9−C8−C13	118(1)
C8−C9−C10	125(1)	Br1−Pd1−C21	180.00
C9−C10−C11	115(1)	P1−Pd1−P1	179.8(2)
C10−C11−C12	122(1)	P1−Pd1−C21	90.08(9)
C11−C12−C13	119(2)	C8−C13−C12	121(1)
Pd1−P1−C1	114.1(4)	P1−C14−C15	119.3(9)
Pd1−P1−C8	117.5(4)	P1−C14−C19	122(1)
Pd1−P1−C14	112.3(3)	C15−C14−C19	119(1)
C1−P1−C8	101.8(5)	C14−C15−C16	123(1)
C1−P1−C14	105.8(5)	C15−C16−C17	118(1)
C8−P1−C14	103.9(6)	C16−C17−C18	124(1)
P1−C1−C2	116.5(9)	C17−C18−C19	118(1)
P1−C1−C6	124.9(9)	C14−C19−C18	119(1)
C2−C1−C6	118(1)	C14−C19−C20	125(1)
C1−C2−C3	121(1)	C18−C19−C20	117(1)
C2−C3−C4	120(1)	Pd1−C21−C22	121.3(9)
C3−C4−C5	119(2)	C4−C5−C6	123(1)
C22−C21−C22	117(2)	C1−C6−C5	118(1)
C21−C22−C23	126(1)	C1−C6−C7	128(1)
C22−C23−C24	118(1)	C5−C6−C7	115(1)
C23−C24−C23	116(2)	P1−C8−C9	124(1)
C23−C24−C25	122.2(9)	P1−C8−C13	118(1)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

is possible that arene is produced by a β-hydrogen elimination process that does not involve transfer of the amide from tin to palladium. Specifically, the arene can form by a β-hydrogen elimination pathway that competes with amide formation and involves direct transfer of the β-hydrogen from the amido group to palladium as shown in Scheme 4. Since a combination of transmetalation and reductive elimination, not simply transmetalation, determines the reaction rate of the aryl halide complex, we have not been able to find a way to distinguish between competitive reactivity of the amido intermediate and direct transfer of the β-hydrogen by a path that is separate from the one involving the palladium amide. Of course, the labeling study simply demonstrates the origin of the hydrogen necessary for the reduction and does not discriminate between the mechanisms in Schemes 3 and 4. However, none of our data contradict the simplest mechanism, competitive reductive elimination and β-hydrogen elimination from the same amido intermediate. Moreover, the arene clearly forms by a β-hydrogen elimination pathway involving the amido group, and this pathway competes with reductive elimination of amine from the palladium amido complex. Our studies reveal the factors that accelerate or decelerate the relative rates for reductive elimination vs β-hydrogen elimination.

VIII. Conclusions. The factors that control product selectivity in metal-catalyzed chemistry are often subtle, and those controlling amine vs arene selectivity in the palladium-catalyzed amination of aryl halides are no exception. Our results have shown that the dominant reaction pathway is a combination of aryl halide oxidative addition, production of an aryl amido species from the aryl halide complex, and reductive elimination of arylamine that competes, albeit effectively, with β-hydrogen elimination. The results of this paper show that a second pathway exists for formation of additional arene product for reactions run with Pd(II) catalyst precursors. The increasing amounts of arene observed for reactions conducted with increasing quantities of Pd(II) catalyst suggest strongly that some arene is formed either directly or indirectly from reduction to Pd(0) from Pd(II). The similarity of amine:arene product ratios formed from stoichiometric reactions to those formed from catalytic reactions involving either the tri-*o*-tolylphosphine Pd(0) phosphine complex or the Pd(II) aryl bromide intermediate

confirm this conclusion. However, some arene appears to be formed by a β-hydrogen elimination that competes with reductive elimination. This arene is not formed as a result of competing alkyl and amido group transfer, since no *p*-BuC_6H_4-*t*-Bu is formed that would also result from alkyl group transfer. The rates for reductive elimination and β-hydrogen elimination are modulated by the combination of steric and electronic factors summarized in Schemes 3 and 4. Reactions catalyzed by complexes containing phosphines with increasing steic demands, involving amides with increasing nucleophilicity and steric demands, and involving palladium-bound aryl groups with decreasing electron density led to higher ratios of arylamine to arene product.

Experimental Section

General. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. *n*-Pentane (tech grade) was distilled under nitrogen from purple sodium/benzophenone ketyl made soluble by addition of tetraglyme to the still. Diethyl ether, THF, benzene, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Deuterated solvents for use in NMR experiments were dried as their protiated analogs, but were vacuum transferred from the drying agent. {Pd[P(*o*-Tol)$_3$]$_2$Cl$_2$}, {Pd[P(*o*-Tol)$_2$Ph]$_2$Cl$_2$}, {Pd[P(*o*-Tol)Ph$_2$]$_2$Cl$_2$}, and [Pd(PPh$_3$)$_2$Cl$_2$] were prepared by standard addition of phosphine to $(CH_3CN)_2PdCl_2$ formed by refluxing $PdCl_2$ in CH_3CN. Pd[P(*o*-Tol)$_3$]$_2$,[4] {Pd[P(*o*-tolyl)$_3$][*p*-C_6H_4-*t*-Bu](Br)}$_2$, {Pd[P(*o*-tolyl)$_3$](C$_6$H$_4$-*p*-Me)(Br)}$_2$,[4] and P(*o*-tolyl)$_2$Ph[25] were prepared by literature methods. {Pd[P(*o*-tolyl)$_3$](C$_6$H$_4$-*p*-NMe$_2$)-(Br)}$_2$ and {Pd[P(*o*-tolyl)$_3$](C$_6$H$_4$-*p*-C(O)Me)(Br)}$_2$ were prepared and isolated in a fashion identical to {Pd[P(*o*-tolyl)$_3$][*p*-C_6H_4-*t*-Bu](Br)}$_2$.

Unless otherwise noted, all manipulations were carried out in an inert atmosphere glovebox or by using standard Schlenk or vacuum line techniques. ^{1}H NMR spectra were obtained on a GE QE 300 MHz or Ω 300 MHz Fourier Transform spectrometer. ^{31}P NMR spectra were obtained on the Ω 300 operating a 121.65 MHz. ^{1}H NMR spectra were recorded relative to residual protiated solvent and ^{31}P{^{1}H} chemical shifts are reported in units of parts per million realtive to 85% H_3PO_4. A positive value of the chemical shift denotes a resonance downfield from the reference. Samples for elemental analysis were submitted to Atlantic Microlab, Inc. GC analyses were conducted on a Hewlett Packard 5890 instrument connected to a 3395 integrator. Response factors were determined by injection of samples containing known quantities of authentic materials.

Pd[P(*o*-tolyl)$_2$Ph]$_2$[*p*-C_6H_4-*t*-Bu](Br). The aryl bromide complex [Pd[P(*o*-tolyl)$_3$][C$_6$H$_4$-*p*-(*t*-Bu)](Br)}$_2$ (250 mg, 0.201 mmol) was suspended in 5 mL of ether and to this suspension was added 2.2 equiv (129 mg, 0.442 mmol) of P(*o*-tolyl)$_2$Ph. The solution was stirred for 1 h, after which time the solid product was isolated by filtration and was washed several times with ether. This procedure gave 340 mg (84%) of product as a pale yellow powder that analyzed satisfactorily for the monomeric bis-phosphine complex. ^{1}H NMR (300 MHz, C_6D_6, 2 equiv of P(*o*-tolyl)$_2$Ph added) δ 8.29 (broad s, 4H), 7.26 (broad s, 4H), 6.90−7.15 (m, 16H), 6.79 (t, J = 7.3 Hz, 4H), 6.24 (d, J = 7.6 Hz, 2H), 2.41 (s, 12 H), 1.10 (s, 9H); ^{31}P{^{1}H} NMR δ 21.9. Anal. Calcd for $C_{50}H_{51}BrP_2Pd$: C, 66.71; H, 5.71. Found: C, 67.26; H, 5.80.

Pd[P(*o*-tolyl)$_2$Ph]$_2$(C$_6$H$_4$-*p*-Me)(Br). The aryl bromide complex {Pd[P(*o*-tolyl)$_3$][C$_6$H$_4$-*p*-Me](Br)}$_2$ (132 mg, 0.106 mmol) was dissolved in 5 mL of toluene and to this solution was added 2.2 equiv (68 mg, 0.233 mmol) of P(*o*-tolyl)$_2$Ph. The solution was allowed to stand for 1 h, after which time 15 mL of pentane was added and the solution was mixed. Over the course of 24 h, 181 mg (36%) of product formed pale yellow crystals suitable for X-ray diffraction that were pure as determined by NMR spectroscopy. ^{1}H NMR (300 MHz, C_6D_6, 2 equiv of P(*o*-tolyl)$_2$Ph added) δ 8.16 (broad s, 4H), 7.28 (broad s, 4H), 6.95−7.1 (m, 8H), 6.92 (m, 8H), 6.80 (m, 4H), 6.24 (d, J = 7.6 Hz, 2H), 2.45 (broad s, 12 H), 1.95 (s, 3H); ^{31}P{^{1}H} NMR δ 21.9.

(25) Segall, Y.; Granoth, I. *J. Am. Chem. Soc.* **1978**, *100*, 5130.

Pd[P(*o*-tolyl)Ph$_2$]$_2$(*p*-C_6H_4-*t*-Bu)(Br). The aryl bromide complex {Pd[P(*o*-tolyl)$_3$](*p*-C_6H_4-*t*-Bu)(Br)}$_2$ (182 mg, 0.146 mmol) was suspended in 5 mL of ether and to this suspension was added 2.2 equiv (89 mg, 0.321 mmol) of P(*o*-tolyl)Ph$_2$. The suspension was stirred for 1 h, after which time the solid product was isolated by filtration and was washed several times with ether. This procedure gave 255 mg (72%) of product as a white powder that was pure by NMR spectroscopy. Samples that were analytically pure were obtained by dissolving the compound in a large amount of toluene followed by precipitation with pentane. ^{1}H NMR (300 MHz, C_6D_6) δ 7.58 (q, J = 5.3 Hz, 8H), 7.05 (m, 6H), 6.93 (m, 12H), 6.48 (d, J = 8.2 Hz, 2H), 3.09 (s, 6H), 1.16 (s, 9H); ^{31}P{^{1}H} NMR δ 17.9. Anal. Calcd for $C_{48}H_{47}BrP_2Pd$: C, 66.10; H, 5.43. Found: C, 65.93; H, 5.52.

General Procedure for Stoichiometric Reactions. The appropriate aryl bromide complex (0.008 mmol, ca. 5 mg) and 15 mg of phosphine were dissolved in 0.5 mL of benzene. This solution was added to a vial that contained 10 mg (0.03 mmol) of tin amide. The sample was placed in a vial equipped with a Teflon-lined septum and was heated at 90 °C. Samples for GC analysis were removed by syringe.

General Procedure for Catalytic Reactions. The appropriate catalyst or catalyst precursor (0.004 mmol, ca. 3 mg) and 5 mg of phosphine were dissolved in 0.5 mL of benzene. This solution was added to a vial that contained 55 mg (0.16 mmol) of tin amide and 28 mg (0.13 mmol) of aryl bromide. The sample was placed in a vial equipped with a Teflon-lined septum and was heated at 90 °C. Samples for GC analysis were removed by syringe.

X-ray Diffraction Study of 5′. Crystals of **5′** were obtained by adding pentane to the reaction solution and rapidly mixing. A pale yellow prism having approximate dimensions of 0.10 × 0.15 × 0.17 mm was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation.

Cell constants and orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 17 carefully centered reflections in the range $8.80 < 2\theta < 18.05°$ corresponding to a monoclinic cell. Based on the systematic absences of $h0l$ ($h + 1 = 2n + 1$), packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P2/n$ (No. 13). In this space group, the molecule is situated on a crystallographic 2-fold axis. Refinement of the molecule in the space group Pn (No. 7) was also attempted, but was not successful.

The data were collected at a temperature of 23 ± 1 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 52.6°. Scans of (0.94 + 0.61 tan θ)° were made at speeds ranging from 1.0 to 16.5 deg/min (in Ω). Moving-crystal moving-counter-background measurements were made by scanning an additional 25% above and below the scan range. The counter aperture consisted of a variable horizontal slit with a width ranging from 2.0 to 2.5 mm and a vertical slit set to 2.0 mm. The diameter of the incident beam collimator was 0.8 mm and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatrically inserted in front of the detector.

Of the 4436 reflections which were collected, 4249 were unique (R_{int} = 0.073). The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo Kα was 15.6 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.90 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by the Patterson method, which revealed the location of the Pd and Br atoms. The remaining atoms were located in subsequent electron density maps. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions. The hydrogen atoms were omitted from the C25 methyl group since it was located on the crystallographic 2-fold axis. The final cycle of full-marix least-squares refinement was based on 1777 observed reflections ($I > 3.00\sigma(I)$) and 232 variable parameters and

(26) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, 1974; Vol. IV.

converged (the largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.057$$

$$R_w = [(\sum w(|F_o| - |F_c|)^2/\sum|F_o|)]^{1/2} = 0.062$$

The standard deviation of an observation of unit weight was 1.81. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/l$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.00 and -0.53 e$^-$/Å^3. Neutral atom scattering factors were taken from Cromer and Waber.[25] Anomalous dispersion effects were included in F_{calc}; the values for $\Delta f'$ and $\Delta f''$ were also those of Cromer and Waber. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp.

Acknowledgment. We are grateful for an NSF Young Investigator Award, a Dreyfus Foundation New Faculty Award, a Union Carbide Innovative Recognition Award, a DuPont Young Faculty Award, and a Yale University Junior Faculty Fellowship that supported this work. We are also grateful to Johnson Matthey/Alpha/Aesar for a generous loan of palladium dichloride.

Supporting Information Available: Positional parameters and *B*(eq), *U* values, Cartesian coordinates, and torsion or conformational angles for **5′** (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and internet access instructions.

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