

A Rare, Low-Valent Alkylamido Complex, a Diphenylamido Complex, and Their Reductive Elimination of Amines by Three-Coordinate Intermediates

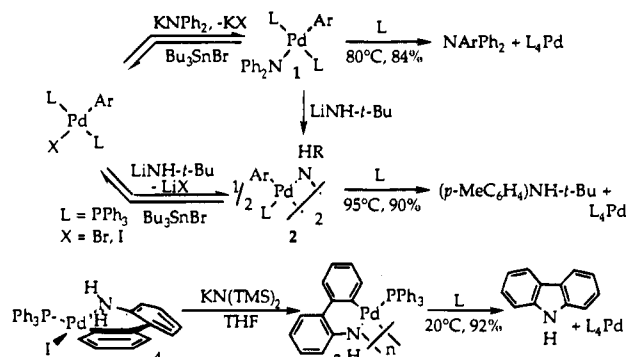
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Low-valent transition metal amido complexes comprise a group of highly reactive molecules due to the mismatch between a soft metal center and hard amido ligand.¹ Presently, arylamido,^{2,3} silylamido,^{2,4} and parent amido^{2,5} (NH₂) ligands bound to low-valent metal centers have been characterized. Alkylamido complexes, however, remain rare.⁶ Arylamido compounds have displayed insertion chemistry^{2,3} and exchanges with even mildly acidic HX bonds,^{2,3,7} and in some cases they have undergone N-H bond forming reactions.^{2,3g,i,j,6c} Yet, amido complexes which undergo reductive eliminations to form the carbon-nitrogen bond in amines, a crucial reaction for developing the organometallic chemistry of these species, have been elusive.^{8,9} We report the preparation and isolation of monomeric arylamido and dimeric alkylamido complexes of palladium that produce arylamines through such carbon-nitrogen bond forming reductive elimination. Preliminary mechanistic results indicate that these reactions involve three-coordinate intermediates formed by dissociative processes. These studies provide the strongest evidence for reductive elimination as the key C-N bond forming step in the palladium-catalyzed production of arylamines from tin amides and aryl halides.¹⁰

Scheme 1



Our synthetic chemistry is summarized in Scheme 1. The palladium(II) arylamido compound *trans*-[P(C₆H₅)₃]₂Pd(C₆H₅)-[N(C₆H₅)₂] (**1**) was prepared by reaction of *trans*-[P(C₆H₅)₃]₂Pd(Ar)I¹¹ with KN(C₆H₅)₂.¹² Generation of **1** in THF, followed by filtration and addition of ether, gave analytically pure red crystals in 86% yield. Alkylamido compound {[P(C₆H₅)₃]Pd-(C₆H₄-*p*-Me)(μ-NH-*t*-Bu)}₂ (**2**) was prepared from *trans*-[P(C₆H₅)₃]Pd(Ar)I and LiNH-*t*-Bu. The ³¹P chemical shift of dimeric **2** (δ 25.7 ppm) was located downfield of monomeric **1** (δ 21.4 ppm). Low-valent alkylamido complexes are rare, and their preparation from alkali metal amides is particularly unusual.^{6c} On a small scale, addition of the lithium amide in THF generated **2** in 60–80% yields by ³¹P NMR spectroscopy (P(*o*-tolyl)₃ as internal standard). However, the solubility of the reduced side product (PPh₃)₄Pd was similar to that of **2**, complicating isolation of the alkylamido complex. Our method for isolation of pure **2** involved addition of 4-iodotoluene after generating preparative amounts of **2** as a suspension in ether. This addition converted (PPh₃)₄Pd to [P(C₆H₅)₃]Pd(C₆H₄-*p*-Me)I, which is much less soluble than **2**. Subsequent filtration, extraction of the resulting solid with toluene, concentration of the extract, and addition of pentane led to pure samples of **2** in 20% yield.

The amido complexes underwent exchanges with main group amides and tin halides that revealed unexpected thermodynamic properties of these compounds. Addition of LiNH-*t*-Bu to diphenylamido complex **1** led to formation of the dimeric phenyl, rather than *p*-tolyl, derivative of **2** in 63% yield. We expected the less basic, delocalized arylamido ligand to favor the low-valent transition metal rather than the alkali metal. We, therefore, believe that the direction of this exchange is controlled by a combination of stabilization of the alkylamido group as a bridging ligand, increased entropy from ligand dissociation, and destabilization of the diphenylamido group by steric factors. Both palladium amido species **1** and **2** reverted to aryl halide complexes upon addition of trialkyltin halides. The reaction completely consumed the palladium amide complexes and gave the bis-phosphine aryl bromide complexes in yields of 73% from **1** and 54% from **2**. Since the exchange produces a number of molecules equal to that in the starting solution, ΔS will be small and ΔH is very likely to be the thermodynamic driving force. These data indicate that the reverse transmetalation reaction that forms palladium amides from tin amides^{10c} is endoergic and almost certainly endothermic.

In the presence of triphenylphosphine, which acts to trap the Pd(0) product, both complexes **1** and **2** underwent reductive elimination of arylamine at elevated temperatures. By ¹H and ³¹P NMR, the only palladium species observable at the end of

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the reaction was Pd(PPh₃)₄. As pure material in THF solution, complex **1** formed triphenylamine in 84% yield at 80 °C after 5–12 h. Toluene solutions of pure compound **2** formed (*p*-MeC₆H₄)NH-*t*-Bu in 90% yield after 8 h at 95 °C. In the absence of added phosphine, yields of arylamine upon thermolysis of **1** or **2** were below 20%. We have not fully investigated the reaction under these conditions, but amine and biaryls are the major organic products. Thermolysis of the *p*-tolyl analog of **1**, *trans*-[P(C₆H₅)₃]₂Pd(C₆H₄-*p*-Me)[N(C₆H₅)₂], gave both Ph₂N(C₆H₄-*p*-Me) and Ph₃N, reflecting exchange of the palladium-bound aryl group and phosphine aryl group on the time scale of the reductive elimination process.^{13,14}

Intramolecular reductive elimination reactions from strained metallacycles occurred rapidly to form heterocyclic products (Scheme 1, bottom). Azametallacycle **3** was generated from the amine complex **4**, and it underwent conversion to Pd(0) and carbazole at room temperature. Amine precursor **4** was prepared by oxidative addition of 2'-amino-2-iodobiphenyl to Pd(PPh₃)₄. The amino protons of **4** appeared as a broad signal at δ = 5.1 ppm in the ¹H NMR spectrum at 50 °C, but below 10 °C, resonances for the individual N–H protons at δ = 5.26 and 5.00 ppm were resolved, presumably due to slow inversion of the ring pucker shown in Scheme 1. Azametallacycle **3** was formed by addition of KN(TMS)₂ to **4** in THF or toluene. A single new ³¹P NMR resonance at δ = 31.9 ppm, an upfield shift of the NH proton to δ = 2.00 ppm (d; *J* = 7.8 Hz), and a new NH band in the infrared spectrum at 3289 cm⁻¹ signaled formation of **3**. The similarity of this N–H vibration to that of a bridging palladium arylamide⁸ and the reduced frequency from terminal arylamides,¹⁵ along with the rarity of three-coordinate Pd(II) species, suggest that the observed complex is dimeric. Azametallacycle **3** produced carbazole in 92% yield after standing for 1 h at room temperature.

Pathways for reductive elimination from **1** and **2** involving ligand dissociation, dimerization, ligand association, and direct reaction are shown in Scheme 2. These pathways can all be distinguished by the order of reaction in palladium amide and the effect of phosphine concentration on the reaction rate. Initially the mechanism for amine formation from **1** was studied. This compound has an absorption at λ_{max} = 489.6 nm (ε = 800 cm⁻¹ M⁻¹), which was used to monitor reaction rates by UV–vis spectroscopy. The products of the reaction did not show any absorption bands above 300 nm. The reactions were conducted with 2.3 mM **1** at 80 °C with concentrations of phosphine ranging from 22 to 68 mM, which created pseudo-first-order conditions.¹⁶ Plots of ln(absorbance) vs time yielded excellent linearity (*R* = 0.999) over 3 half-lives, indicating a first-order dependence on palladium amide **1** and reductive elimination from a monomeric species. By monitoring the reductive elimination at varied phosphine concentrations and graphing ln(*k*_{obs}) vs ln[P(C₆H₅)₃], to determine reaction order (Scheme 2),¹⁷ an inverse first-order dependence of rate on phosphine concentration (slope = -1.1 ± 0.2) was determined. These kinetic data were consistent with pathway c and its corresponding rate equation (Scheme 2) for reductive elimination from a three-coordinate monomer that is slower than recombination with phosphine (*k*₂ ≪ *k*₋₁).

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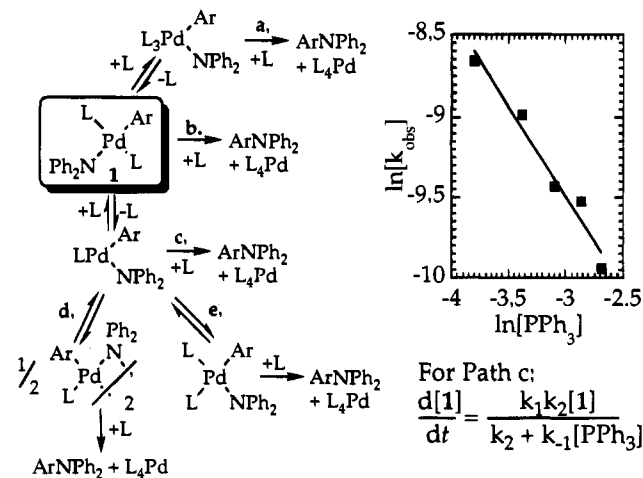
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Scheme 2



The reductive elimination of dimeric **2** was monitored at 95 °C to determine whether the rate-determining step of the elimination reaction involved a dimeric species or a three-coordinate intermediate formed by dimer cleavage. Reaction rates were clearly first order over 3 half-lives and were identical when initial concentrations of **2** were 4.3 or 10.3 mM. Moreover, the reaction rates were independent of phosphine concentration (17–76 mM), although added phosphine was necessary to form arylamine in high yield. Even in the presence of high phosphine concentrations, **2** and Pd(PPh₃)₄ were the only palladium species observed throughout the course of the reaction. In order to probe for reversible dimer dissociation that may precede reductive elimination, reactions were conducted with a mixture of **2** and [(PPh₃)(Ph)Pd(μ-NH-*t*-Bu)]₂. No evidence for formation of the mixed dimer [(PPh₃)(Ph)Pd(μ-NH-*t*-Bu)₂Pd(C₆H₄-*p*-Me)(PPh₃)] was obtained over the course of the reaction.¹⁸ We, therefore, propose that the reductive elimination process from dimeric **2** is initiated by irreversible dimer dissociation to form three-coordinate monomers that are analogous to those generated by phosphine dissociation from **1**.

In conclusion, we have presented a rare example of carbon–nitrogen bond forming reductive eliminations which are crucial steps in the hetero-cross-coupling reactions catalyzed by palladium compounds and are important fundamental organometallic reactions. The mechanistic information presented here strongly suggests that the reductive eliminations proceed by dissociative processes to form three-coordinate intermediates.

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Supplementary Material Available: Spectroscopic and analytical data for compounds **1**, **2**, **4**, and **5** (2 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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(18) A sample of the mixed dimer was prepared by the reaction of (PPh₃)₂Pd(tol)I and (PPh₃)₂Pd(Ph)I with LiNH-*t*-Bu in THF, and it was analyzed by ³¹P and ¹H NMR spectroscopy in C₆D₆. The ³¹P NMR signals for the three compounds were not resolvable, but the ¹H NMR signals for the *t*-Bu peaks were distinguishable at 50 °C: **2** δ 1.237 ppm; **5** δ 1.218 ppm; **6** δ 1.228 and 1.226 ppm.