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Synthesis, Characterization, and Reactivity of Monomeric, Arylpalladium Halide Complexes with a Hindered Phosphine as the Only Dative Ligand

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Most organometallic reactions occur through intermediates that possess an open coordination site.[1] Such unsaturated intermediates are generally detected by kinetic studies and are rarely observed directly or isolated. For example, oxidative addition[2,3] and reductive elimination[4,5] are often preceded by dissociation of a dative ligand, and migratory insertion requires an open coordination site for binding of a substrate.[6] As a result, palladium-catalyzed cross coupling is commonly proposed to involve 14-electron, three-coordinate complexes.[7−9] Three-coordinate, 14-electron palladium(II) complexes have not been isolated, but are believed to be favored when the catalysts possess sterically hindered ligands.[10−13] Three-coordinate 14-electron nickel $[Ni(mes)_3]^{-}$[14] and rhodium $[Rh(PPh_3)]^{+}$[15] complexes have been isolated, but these unsaturated species are not intermediates in catalytic chemistry. We report the isolation of a series of monomeric arylpalladium(II) halide complexes with a single dative ligand. These complexes are likely intermediates in metal-catalyzed cross-coupling reactions.

The monophosphine, arylpalladium halide complexes were synthesized as shown in Scheme 1. The combination of $Pd(dba)_2$, phosphine, and aryl halide in THF solvent formed arylpalladium halide complexes **1**−**3b**, as shown in Scheme 1.[16] The monophosphine-ligated arylpalladium halides were also prepared by dissolution of $Pd(dba)_2$ and the appropriate ligand in neat aryl halide. The products were isolated by precipitation from THF after concentration of the reaction solution or from the neat aryl halide by addition of pentane. Formation of dimeric Pd(I) halides $[LPdX]_2$[17] accompanied the generation of the oxidative addition product, but the formation of this dimeric material was suppressed by conducting reactions with concentrations of palladium below 0.1 M in THF solvent or below 0.5 M in neat aryl halide.

These complexes were also obtained by direct oxidative addition of aryl halides to the $L_2Pd(0)$ precursors.[18] Addition of 40 equiv of PhBr to Pd[P(*t*-Bu)$_2$(1-adamantyl)]$_2$ formed **1** in 50% yield. Addition of 40 equiv of PhI to Pd[P(*t*-Bu)$_3$]$_2$[19] formed **3a** in 50% yield along with 36% of the Pd(I) dimer. Reaction of Pd[P(*t*-Bu)$_3$]$_2$ with 40 equiv of PhBr formed small amounts of the oxidative addition product after 12 h, but many side products were formed at longer reaction times. These results are consistent with reductive elimination of aryl bromides and chlorides and ortho-substituted aryl iodides reported recently.[20] These oxidative additions to isolated L_2Pd complexes were slower than additions to the 1:1 mixture of $Pd(dba)_2$ and ligand.

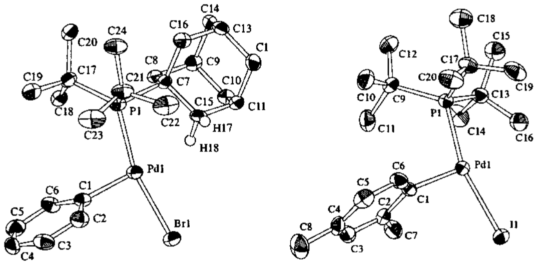
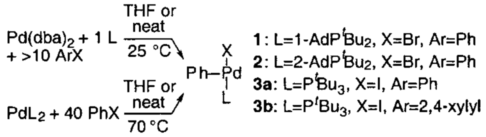


Figure 1. X-ray structure of **1** is shown on the left, and **3b** is shown on the right.

Scheme 1



Previous arylpalladium halide complexes with a single hindered ligand, such as P(*o*-tol)$_3$, have been dimeric,[21,22] but X-ray diffraction of **1** and **3b** showed that the complexes described here are monomeric. Small, light orange crystals of complex **1** were grown from a cold solution of pentane and THF (95/5), and its X-ray structure was obtained (Figure 1). Complex **1** is a T-shaped monomer. The phenyl group is located trans to the open coordination site of the metal. This geometry allows the ligand with the greatest steric demand to bind in the least hindered position and the covalent ligand with the largest trans effect[23] to bind trans to the open site. The angles about the palladium are 100.9°, 91.3°, and 162.6°. Hydrogens H17 and H18 were refined isotropically, and the distance between the palladium and the closest hydrogen (H18) is 2.27(3) Å, which is within the distance of an agostic interaction.[24] Crystals of P(*t*-Bu)$_3$-ligated 2-*m*-xylyl complex **3b** were suitable for X-ray diffraction (Figure 1). Again, the geometry was T-shaped. The angles about palladium were 100.9°, 94.0°, and 164.6°. The calculated distance between the metal and H27 bound to C16 was 2.33 Å, which could, again, reflect an agostic reaction.

^{31}P and ^{13}C NMR spectroscopy suggested that similar structures were present in solution. The unusual coordination number was indicated by an upfield, rather than downfield, change in chemical shift upon oxidative addition to the L_2Pd complex. Typical arylpalladium halide complexes display ^{31}P NMR chemical shifts that are located downfield of the corresponding Pd(0) complex.[21] A cis disposition of aryl and phosphine groups was shown by a small J_{P-C} for the ipso carbon.

Infrared spectroscopy of complexes **1** and **3** in KBr did not provide evidence for agostic interactions. However, infrared spectra of complex **2** contained a medium-strong band at 2710 cm^{-1}. This stretching frequency is reduced from the C−H stretches of the free ligand and indicates a stronger agostic interaction between the metal and the ligand C−H bond in compound **2** than of compounds **1** or **3a**,**b**.

^{1}H NMR spectra of complexes **1** and **2** obtained at −115 °C were broad, poorly resolved, and difficult to interpret with the large number of adamantyl resonances. Low-temperature NMR spectra

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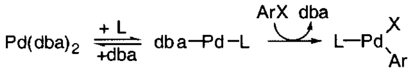
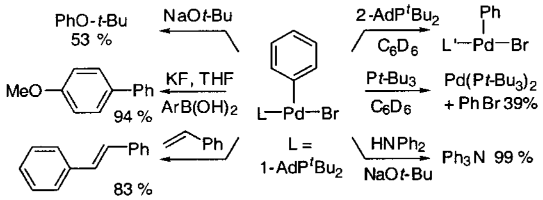
Scheme 2



Scheme 3



of P(t-Bu)$_3$-complex **3** were better resolved, but the ^{1}H NMR spectrum at −115 °C did not contain any upfield signal that would definitively demonstrate an agostic interaction.

Thus, we computed geometries and harmonic vibrational frequencies at the BP86/ECP1 level;[25] a gradient-corrected density functional, effective core potentials on Pd, Br, and I,[26] and polarized split-valence basis sets were used to provide information on the presence or absence of an agostic interaction in these complexes. The calculations showed low-energy C−H vibrations decreasing in the order **3a** (2919 cm^{-1}) > **1** (2812 cm^{-1}) > **2** (2750 cm^{-1}). The optimized Pd−H distances decrease in the same sequence, 2.46 > 2.28 > 2.15 Å, while the concomitant Wiberg bond indices (WBIs)[27] that probe for covalent interactions increase in the same order 0.015 < 0.023 < 0.041. For comparison, the WBI for the Pd−Br bond in **2** was 0.42. Thus, we conclude from the static calculations that the strength of the M−H interaction in **1**−**3** follows the trend **3** < **1** < **2**, and this trend parallels the stability of the arylpalladium halide derivatives.

Calculations of ^{1}H NMR chemical shifts[28] using a hybrid density functional and a large all-electron basis set of approximately polarized triple-ζ quality on all atoms in C_1 symmetric **1** and **2** predicted resonances for the C−H closest to the metal of $\delta = +0.6$ and −0.4, respectively. Averaging of chemically equivalent hydrogens creates unremarkable $\delta(^1H)$ values that are consistent with the experimental spectra.

The formation of **1**−**3** from the Pd(dba)$_2$ precursor most likely occurs by displacement of one coordinated dba by phosphine and oxidative addition of the aryl halide to either of the monophosphine intermediates LPd or LPd(dba). This mechanism is depicted in Scheme 2. Because aryl halides reacted with L$_2$Pd(0) complexes more slowly than with Pd(dba)$_2$ and ligand, the reactions initiated by Pd(dba)$_2$ and ligand cannot occur through L$_2$Pd(0). This difference in the rate of formation of **1** parallels the differences between the rate of catalytic reactions initiated by a 1:1 ratio of Pd(dba)$_2$ to phosphine and by isolated L$_2$Pd(0).[9,29,30]

Preliminary reactivity of the three-coordinate arylpalladium halide complexes is summarized in Scheme 3. Reaction between **1** and 2-adamantyl-di-*tert*-butylphosphine formed **2** quantitatively. Conversely, treatment of **2** with 1-adamantyl-di-*tert*-butylphosphine produced only trace amounts of **1**. Reaction between tri-*tert*-butylphosphine and **1** consumed **1** completely and formed Pd(P-t-Bu$_3$)$_2$ in 25% yield and bromobenzene in 39% yield.

Addition of diphenylamine and sodium *tert*-butoxide to **1** gave triphenylamine in 99% yield, while addition of sodium *tert*-butoxide to **1** gave *tert*-butyl phenyl ether in 53% yield. Reaction of 4-methoxyphenylboronic acid with **1** in the presence of KF in THF formed 4-methoxybiphenyl in 94% yield at room temperature.

Complex **1** also reacted with styrene to form 83% yield of stilbene and the hydridopalladium halide complex. Despite the open coordination site present in complex **1**, the formation of stilbene was inhibited by added phosphine. Values of k_{obs} at varying concentrations of added ligand showed clean, inverse first-order rate behavior. No adduct between **1** and the added ligand was detected by ^{31}P NMR spectroscopy. Thus, the transition state of the rate-determining step lacks any coordinated phosphine. Dissociation of the large phosphine may be necessary to allow binding of the olefin or to allow binding of the olefin cis to the aryl group.

Complex **1** is kinetically competent to be an intermediate in the palladium-catalyzed amination of aryl halides.[8,31] The reaction of bromobenzene with diphenylamine occurred in 45 min at room temperature in 98% yield. This rate is comparable to the rate of reaction catalyzed by complexes of P(1-Ad)(t-Bu)$_2$ generated in situ.

In summary, we have isolated a set of structurally unique arylpalladium halide complexes that are intermediates in cross-coupling reactions induced by recently studied, highly active catalysts. These complexes should allow detailed mechanistic studies of a variety of palladium-catalyzed processes.

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Supporting Information Available: Experimental procedures and spectroscopic data of new complexes; X-ray structural data for **1** and **3b** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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