Oxidative Addition of Aryl Bromide after Dissociation of Phosphine from a Two-Coordinate Palladium(0) Complex, Bis(tri-*o*-tolylphosphine)palladium(0)

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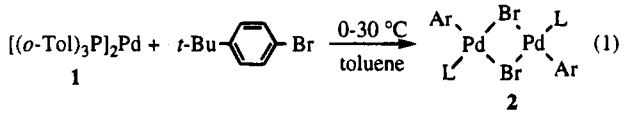
The oxidative addition of aryl halides to low-valent metal centers is a common method for generating compounds with σ-bound aryl groups that participate in stoichiometric or catalytic transformations such as carbonylation, cross-coupling, and Heck chemistry.[1] Oxidative addition of aryl halides to Pt(0), Pd(0), and Ni(0) complexes has been studied particularly intensively.[2] The mechanisms appear to depend on the metal−ligand system involved, and radical chain or radical cage processes,[3] aromatic substitutions, and concerted additions have all been proposed.[4] Regardless of the intimate mechanism of the carbon−halogen bond cleavage step, addition invariably occurs to two- or three-coordinate M(0) intermediates.

We have prepared the two-coordinate Pd(0) compound [(*o*-Tol)$_3$P]$_2$Pd (**1**) and have observed rapid oxidative addition reactions with aryl halides to form the dimeric complex **2** (eq 1).[5] This rapid reaction contrasts the 80 °C reaction conditions

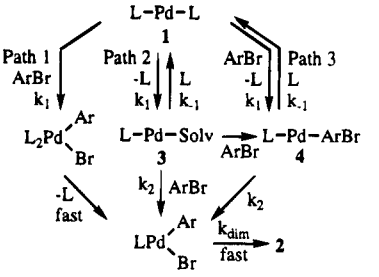


(1)

necessary for addition to the common triarylphosphine complex (PPh$_3$)$_4$Pd at similar rates. Moreover, the dimeric product **2** is different from essentially all other products of aryl halide oxidative addition to Pt(0), Pd(0), and Ni(0) phosphine complexes, which are monomers. Considering previous mechanistic information concerning oxidative addition to M(0) compounds, one would expect that reaction of aryl bromide would occur directly to **1**, and subsequent dissociation of phosphine from the initially formed bis-phosphine aryl bromide complex would then precede dimerization. We have obtained firm kinetic data that demonstrates this mechanism is not operating and that oxidative addition occurs to a highly unsaturated intermediate possessing a single phosphine ligand. Oxidative addition to **1** is dissociative.

Potential mechanisms for oxidative addition to **1** are shown in Scheme 1. Pathway 1 involves direct, irreversible oxidative addition to **1** or an aryl bromide adduct of it. This pathway will show a simple first-order dependence in both **1** and aryl bromide, but no dependence on phosphine concentration. Pathway 2 invokes reversible dissociation of phosphine to form a 12-electron Pd species or its solvent adduct **3**, which either forms aryl bromide complex **4** or undergoes oxidative addition without aryl bromide coordination. Pathway 3 involves exchange of one phosphine with aryl bromide by an associative or interchange mechanism to form intermediate **4**, which subsequently undergoes the irreversible addition. The

Scheme 1



rate expressions for pathways 2 (eq 2) and 3 (eq 3) under steady state conditions simplify to the same equation in the inevitable

$$\frac{d[\mathbf{1}]}{dt} = -\frac{k_1 k_2 [\mathbf{1}][\mathrm{ArBr}]}{k_{-1}[\mathrm{L}] + k_2[\mathrm{ArBr}]} \quad (2)$$

$$\frac{d[\mathbf{1}]}{dt} = -\frac{k_1 k_2 [\mathbf{1}][\mathrm{ArBr}]}{k_{-1}[\mathrm{L}] + k_2} \quad (3)$$

case that ligand association (k_{-1}) is faster than the bond cleaving oxidative addition (k_2).

Our rate data are shown in Figures 1 and 2. Reactions were conducted in NMR sample tubes at 30 °C in an NMR spectrometer probe. Rates were measured by monitoring the disappearance of the *o*-tolyl resonance at δ 2.92 in the ^{1}H NMR spectrum as a function of time. All reactions were conducted with a saturated solution (~6 mM) of the sparingly soluble L$_2$-Pd complex in 0.62 mL of aromatic solvent that contained either 8.5 or 17 μL of *p*-(*t*-Bu)C$_6$H$_4$Br (64 or 128 mM). Phosphine concentrations ranged from 76 to 300 mM. In no case was any evidence for a stable L$_3$Pd complex obtained. ^{31}P NMR spectra of these solutions before addition of ArBr showed only a resonance for free phosphine and a resonance for L$_2$Pd. The ^{1}H NMR resonance of the *o*-tolyl group broadened slightly at high concentrations of phosphine, indicating that exchange of free and coordinated phosphine began to occur on the NMR time scale. The exchange of free and coordinated phosphine in **1** was confirmed by a spin saturation transfer experiment. Thus, no observable amounts of L$_3$Pd existed in solution, although the fastest ligand exchange process appears to be associative since the line width of **1** depended on the concentration of free ligand.

Linear first-, but not second-, order plots for the decay of **1** under the reaction conditions of excess phosphine and aryl bromide ruled out any mechanism involving reversible addition of aryl bromide and rate-determining dimerization (k_{dim}). Most striking is the inverse first-order behavior in phosphine concentration shown in Figure 2 that rules out pathway 1. Instead, the inverse order behavior in phosphine ligand is consistent with pathways 2 and 3. As expected for conditions in which the k_{-1} step is faster than the k_2 step, the reaction was first order in aryl bromide. Increasing concentrations by a factor of 2, from 64 to 128 mM, led to doubling of the reaction rates. The absence of a measurable intercept for a k_{obs} vs 1/[L] plot (data not shown) shows that little reaction occurred by a nondissociative mechanism. Reaction rates in the presence of 10 equiv of dihydroanthracene ($(1.5 \pm 0.2) \times 10^{-3}$ s^{-1}) were identical to that in its absence ($(1.4 \pm 0.2) \times 10^{-3}$ s^{-1}). Moreover, reactions showed no initiation period, and rate constants for reactions conducted in different samples of degassed solvent were reproducible to within 5−10%, suggesting that a radical chain process was not operating.

In principle, eqs 2 and 3 predict that the two pathways involving monophosphine intermediates can be distinguished

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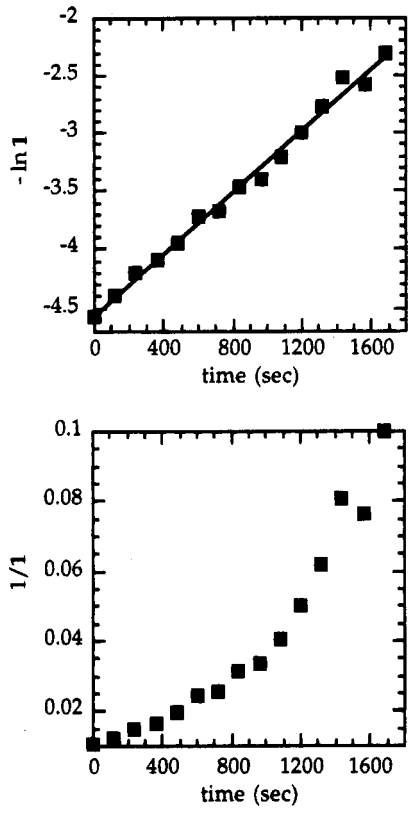

Figure 1. First- and second-order plots of the decay of **1**. The values for **1** are raw relative integrations and are not corrected for initial concentration.

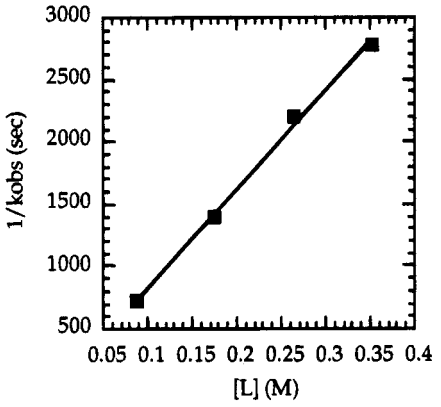

Figure 2. Plot showing inverse first-order dependence of observed rate constants on phosphine concentration.

by the dependence of the intercept of a $1/k_{obs}$ vs [L] plot on [ArBr]. In practice, this intercept cannot be determined accurately enough to discriminate between k_{obs} values that are different by less than several orders of magnitude. The intercept value is small, and the rate constant for the ligand substitution step is inversely related to the intercept value. Thus, even small variations in the slope of the plot that would arise from the 5−10% error in the observed rate constants would lead to rates of ligand loss that vary by at least an order of magnitude.

However, the structures of **3** and **4** in Scheme 1 suggest that probes for inner sphere solvent coordination may distinguish between pathways 2 and 3. It is known that oxidative addition of aryl iodides to the intermediate $(PPh_3)_2Pd$ is slightly slower in THF than in toluene.[4] Rather than dramatically change the class of solvent, we conducted the aryl bromide addition in three different aromatic media, *p*-xylene-d_{10}, toluene-d_8, and benzene-d_6. These solvents have similar dielectric constants but would form different intermediates **3** that would be likely to display different equilibria with starting **1** and different oxidative addition rates. It is likely that an intermediate **3** formed in xylene solvent would be less stable, since is has no C=C bond that is as unhindered as those in benzene or the C3−C4 bond in toluene and would produce slower overall reaction rates. However, the reaction rates in all three solvents were essentially identical (C_6D_6, $(1.3 \pm 0.1) \times 10^{-3}$ s^{-1}; C_7D_7, $(1.4 \pm 0.1) \times 10^{-3}$ s^{-1}; C_8D_{10}, $(1.0 \pm 0.2) \times 10^{-3}$ s^{-1}). Thus, direct coordination of solvent does not play a substantial role in controlling the energetics of the unsaturated intermediate. Our data in aromatic solvents are, therefore, most consistent with either pathway 3, in which the arylbromide coordinates reversibly, or a modified pathway 2, which involves a 12-electron monophosphine intermediate that is perhaps stabilized by coordination of a ligand *o*-C−H bond rather than by coordination of solvent.

Although we were initially surprised to find that the reversible oxidative addition step occurred after ligand dissociation, well-established mechanisms for reductive elimination provide precedent for a low-coordinate intermediate. For example, reductive elimination of ethane from $(PPh_3)_2PdMe_2$[6] and our recently discovered reductive elimination from $(PPh_3)_2PdPh(NPh_2)$[7] that forms the carbon−heteroatom bond in triphenylamine occur after dissociation of phosphine to form a three-coordinate intermediate. Similarly, elimination of alkanes from $(PR_3)AuR'_3$ and $[(PR_3)_2AuR'_2]^+$ complexes is known to follow phosphine dissociation.[8,9] Theoretical studies have provided orbital energy arguments to explain the importance of phosphine dissociation for concerted carbon−carbon bond forming reductive elimination.[10] These three-coordinate intermediates generate a transition metal product that possesses only one ligand after reductive elimination. The ethane and amine products may be coordinated, albeit weakly, to this LPd, $[(PR_3)Au]^+$, or RAu center in an intermediate that is analogous to **4**. Displacement of the potentially coordinated organic product by trapping ligands would be the reverse of the formation of **4** from **1** and could occur by the same dissociative, associative, or interchange mechanisms.

Although the oxidative addition of aryl bromide is not precisely the reverse of these reductive elimination reactions, similar orbital symmetries and energies may be involved. Well-demonstrated mechanisms for elimination from Pd(II) suggest that addition to form Pd(II) products from the unsaturated LPd intermediate is a pathway that is likely to be faster than addition to L_2Pd. However, higher concentrations of L_2Pd than monophosphine species typically lead to oxidative addition chemistry that occurs through the bis-phosphine intermediate. Steric effects that inhibit reaction through L_2Pd when L = (*o*-tolyl)$_3$P and increase concentrations of monophosphine species channel the oxidative addition chemistry through a monophosphine intermediate in our case.

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