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Organometallic Chemistry of Amidate Complexes. Accelerating Effect of Bidentate Ligands on the Reductive Elimination of *N*-Aryl Amidates from Palladium(II)

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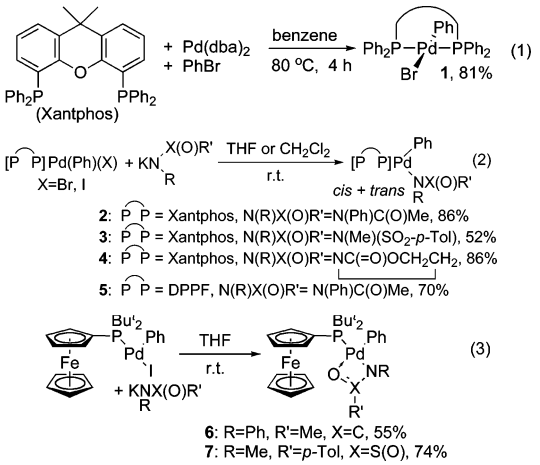
Organometallic reactions of isolated transition metal amides, such as reductive elimination[1] and migratory insertion,[2] have begun to develop during the past decade, but the organometallic reactions of transition metal amidates (deprotonated amides or sulfonamides) have not. Several properties of amidate ligands are likely to limit their reactivity. First, an amidate ligand should be less nucleophilic than an amide ligand due to the electron-withdrawing carbonyl group. Second, the M−N bond of an amidate complex would contain more ionic character than that of an amide complex, and this ionic character should increase the strength of the M−N bond.[3] Third, amidates can bind in a κ^2-fashion,[4] and the additional metal−ligand bond in a κ^2-binding mode would be expected to inhibit reactions that occur through a κ^1-structure.

To determine how to overcome these limitations, we have begun to study organometallic reactions of metal amidate complexes. We have focused first on the isolation, structural characterization, and reaction chemistry of arylpalladium amidate complexes possessing both monodentate and bidentate ligands. We report the first results of this work, which include the direct observation of reductive elimination to form *N*-aryl amides. In contrast to reductive eliminations that form the C−N bond in amines and C−C bonds in alkanes and alkylarenes,[5−8] these reductive eliminations that form the C−N bond in *N*-aryl amides occurred faster from the complexes containing bidentate ligands than from complexes containing a single hindered, monodentate ligand. Structural data imply that this opposing trend results from the distinct bonding modes of the amidate ligands in compounds containing the two classes of ligand.

To study the rates of reductive elimination of *N*-aryl amides, we prepared arylpalladium amidate complexes containing the bidentate ligand Xantphos (eq 1), the bidentate ligand 1,1-bis-(diphenylphosphino)ferrocene (DPPF), and the hindered monodentate ligand FcPBu$^t_2$ (Fc = ferrocenyl). Complexes of these ligands were studied because catalysts containing Xantphos are particularly reactive for the coupling of amides and sulfonamides with bromoarenes,[9,10] complexes of DPPF would allow a comparison of the rates of reaction of amidate complexes with those of amido complexes reported previously,[6] and the FcPBu$^t_2$ ligand is a representative hindered monophosphine that has previously induced reductive elimination from typically unreactive malonate complexes and electron-poor diarylamido complexes.[11] The preparation of arylpalladium amidate complexes ligated by these phosphines is shown in eq 1−3.

The phenylpalladium bromide complex **1** ligated by Xantphos was prepared by heating Pd(dba)$_2$, Xantphos, and bromobenzene at 80 °C for 4 h in benzene solvent (eq 1).[10,12,13] The ^{31}P NMR spectrum of the arylpalladium bromide complex **1** displayed one singlet (9.6 ppm) at room temperature that broadened below room temperature and resolved at −95 °C into signals corresponding to a 98.5:1.5 ratio of trans-to-cis isomers. The ^{1}H NMR spectrum at −95 °C also contained resonances corresponding to cis and trans isomers (see Supporting Information).



Addition of potassium *N*-phenylacetamidate, potassium *N*-methylsulfonamidate, and the potassium salt of 2-oxazolidinone to Xantphos complex **1** generated the corresponding arylpalladium amidate, sulfonamidate, and carbamate complexes **2**−**4** (eq 2). Formation of the palladium sulfonamidate required excess of the potassium salt and methylene chloride, instead of THF, as solvent, but the sulfonamidate **3** was isolated in acceptable yield.

The Xantphos-ligated amidate complexes were mixtures of cis and trans isomers, with the cis isomers of **2** and **3** predominating. The ^{31}P NMR resonance of **2** at room temperature was a singlet that proved to correspond to a rapidly interconverting mixture of isomers. The singlet broadened at 0 °C and resolved at −80 °C into signals consistent with a 65:35 ratio of the cis isomer and the combination of two trans isomers from slow rotation about the M−N bond. The ^{31}P NMR resonance of **3** at room temperature was also a broad resonance that corresponded to a rapidly interconverting mixture of cis and trans isomers. The cis:trans ratio was 75:25 in this case at −95 °C. The ^{31}P NMR spectrum of carbamate **4** at room temperature contained signals for both isomers, but was broad. The resonances sharpened at 0 °C, and a cis:trans ratio of 20:80 was measured. Complex **3** crystallized as the trans isomer. The structure determined by X-ray diffraction (Figure 1) confirmed that the sulfonamidate ligand is bound in a κ^1-mode.

Arylpalladium amidate **5** ligated by DPPF was prepared in 70% yield by similar procedures (eq 2). The NMR and IR spectra of this complex indicated that the structure contains a standard square-planar cis geometry with a κ^1-amidate ligand.

Analogous compounds ligated by the hindered monodentate phosphine FcPBu$^t_2$ were prepared as summarized in eq 3. The FcPBu$^t_2$-ligated arylpalladium iodide was converted to the *N*-phenylacetamidate **6** and *N*-methylsulfonamidate **7** by addition of potassium *N*-phenylacetamidate and *N*-methylsulfonamidate. These two complexes were isolated in 55 and 74% yield, respectively. X-ray diffraction of **6** and **7** (see Figure 1 for the structure of **6**

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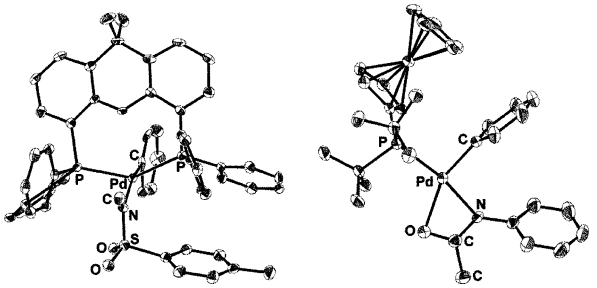
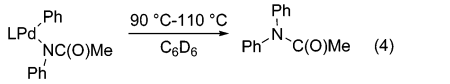


Figure 1. ORTEP diagrams of **3** and **6** illustrating the κ^1- and κ^2-binding modes. The Pd−O distances for **3**, **6**, and **7** (see Supporting Information) are 2.798(2), 2.2678(17), and 2.303(2) Å, and the Pd−N distances are 2.139(3), 2.098(2), and 2.085(3) Å. The P−Pd−P angle in **3** is 143.93(3)°.

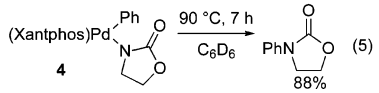
and Supporting Information for the structure of **7**) revealed that they are four-coordinate complexes with the acetamidate and sulfonamidate ligands coordinated in κ^2-binding modes.

The reductive elimination chemistry of the amidate complexes is shown in eq 4. Heating of DPPF-ligated **5** at 110 °C in the presence of additional DPPF (2 equiv) induced reductive elimination to give *N*,*N*-diphenylacetamide, but this reaction required 29 h to reach >90% conversion, and the yield of the reductive elimination product was only 34%. This reductive elimination is, thus, much slower and occurs in lower yield than reductive elimination from DPPF-ligated arylpalladium amides.[6] This comparison is consistent with the trend of decreasing rate of reductive eliminations from complexes containing ligands that are less basic, less nucleophilic, and bound to the metal by more ionic M−N bonds.[1,6]



(4)

5: L=DPPF, κ^1-amidate 110 °C 29 h, 34%
6: L=FcPBu$^t_2$, κ^2-amidate 110 °C 2 h, <2% $Ph_2NC(O)Me$
2: L=Xantphos, κ^1-amidate 90 °C 7 h, 93%



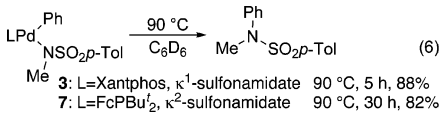
(5)

The analogous arylpalladium amidate complex **6** containing the hindered FcPBu$^t_2$ ligand was stable for hours below 110 °C and decomposed over 2 h without formation of $Ph_2NC(O)Me$ at 110 °C. This high stability contrasts with the facile reductive elimination of triarylamine below room temperature from a closely related arylpalladium ditolylamido complex.[7]

In contrast to these slow reactions, heating of the Xantphos complexes **2** and **4** containing the anions of *N*-phenylacetamide (eq 4) and oxazolidinone (eq 5) with 2 equiv of added Xantphos for 7 h at 90 °C formed the *N*,*N*-diphenylacetamide and *N*-phenyl-2-oxazolidinone in 93 and 88% yield, respectively, along with the palladium product $Pd(Xantphos)_2$.[14] The amount of added Xantphos did not affect the rate of the reductive elimination, implying that reductive elimination occurs directly from the starting **2** and **4** (see Supporting Information).

The faster reductive elimination from Xantphos complexes **2** and **4** than from DPPF and FcPBu$^t_2$ complexes **5** and **6** leads to two conclusions. First, the differences in rates of reaction of Xantphos complex **1** and DPPF complex **5** imply that a large bite angle[15] helps promote reductive elimination from amidate complexes, which are more stable than the analogous amide complexes.[6] Second, the faster reactions of the amidate complexes containing bidentate ligands imply that the binding mode of the amidate ligand in the ground state affects the reaction rate. Assuming reductive elimination occurs from a κ^1-structure, then the cleavage of the M−O interaction in the κ^2-amidate structure of the complex containing a monodentate ligand adds to an already considerable barrier for reductive elimination.

Finally, the *N*-methylsulfonamidate complexes underwent reductive elimination faster than the corresponding *N*-phenylacetamidate complexes (eq 6). Heating of the Xantphos-ligated *N*-methylsulfonamidate complex **3** in C_6D_6 with 2 equiv of added Xantphos at 90 °C for 5 h induced reductive elimination of *N*-methyl *N*-phenylsulfonamide in 88% yield, even though the *N*-methylsulfonamido group contains β-hydrogens. The rate constant for this process at 90 °C was $(4.7 \pm 0.2) \times 10^{-4}$ s^{-1}, whereas the rate constant for elimination from amidate **2** at this temperature was $(2.5 \pm 0.2) \times 10^{-4}$ s^{-1}. The sulfonamidate complex **7** ligated by the ferrocenyl ligand underwent reductive elimination in 82% yield, but this reaction required 30 h at 90 °C. This difference in rate of reaction of Xantphos complex **3** and FcPBu$^t_2$ is further consistent with slower eliminations from κ^2-amidate complexes containing monodentate ligands than from κ^1-amidate complexes containing bidentate ligands.



(6)

3: L=Xantphos, κ^1-sulfonamidate 90 °C, 5 h, 88%
7: L=FcPBu$^t_2$, κ^2-sulfonamidate 90 °C, 30 h, 82%

In general, these first direct observations of reductive eliminations to form the C−N bonds in *N*-aryl amides and sulfonamides illustrate that reductive elimination of *N*-aryl amides and sulfonamides from complexes with bidentate ligands can be faster than those from complexes with monodentate ligands. This trend is consistent with the difference in ground state binding modes of the amidate ligands in complexes of monodentate and bidentate phosphines. These results also suggest that a large bite angle in the ancillary ligand helps promote reductive elimination from complexes with weakly nucleophilic amidate ligands bound to palladium by relatively strong and ionic M−N bonds.

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Supporting Information Available: Experimental procedures and characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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