

Synthesis, Structure, and Reductive Elimination Chemistry of Three-Coordinate Arylpalladium Amido Complexes

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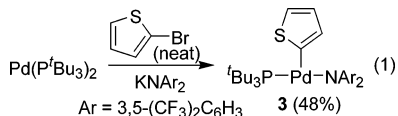
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Three-coordinate organopalladium(II) complexes are often claimed to be the species that forms the carbon–carbon or carbon–heteroatom bond in the product during reductive eliminations of palladium complexes with monodentate ligands.^{1–3} The intermediacy of such complexes has been deduced primarily from kinetic and computational studies. Three-coordinate organopalladium alkyl, aryl, alkoxo, or amido complexes have never been isolated or observed directly. The existence of true three-coordinate palladium(II) compounds without a donor in the open coordination site has even been called into question.⁴ We recently isolated arylpalladium halide complexes with a single phosphine,⁵ but each of these complexes contained an agostic interaction at the open site of a T-shaped geometry.

We now report the generation, isolation, structural characterization, and reductive elimination of three-coordinate arylpalladium amido complexes that form the arylamine in catalytic C–N couplings.^{6–8} These amido complexes are monomeric, with a single phosphine ligand, and several display true T-shaped structures. All of the complexes undergo direct reductive elimination. These reductive eliminations allow a direct comparison of the rates of elimination from three- and four-coordinate arylpalladium amido complexes and the rates and mechanism for elimination from arylpalladium halide⁹ and amide complexes with the same dative ligand.

To isolate three-coordinate arylpalladium amido complexes, we focused on the preparation of complexes with an electron-donating substituent on the palladium-bound aryl group and electron-withdrawing substituents on the amide. These groups on the respective anionic ligands retard reductive elimination.^{3a,10} Anisylpalladium bromide complexes **1a–1c** were synthesized from Pd(dba)₂, anisyl bromide and the hindered alkylphosphines P(*t*-Bu)₃, FcP(*t*-Bu)₂ (Fc = ferrocenyl) and Ph₅FcP(*t*-Bu)₂ (Ph₅Fc = 1',2',3',4',5'-pentaphenyl-1-ferrocenyl) by methods related to those published recently.¹¹ Treatment of these complexes with potassium bis(3,5-bis(trifluoromethyl)phenyl)amide in ether or THF generated three-coordinate arylpalladium amides **2a–2c** (see Scheme 1) that were stable at room temperature and were isolated as crystalline solids, albeit in modest yields due to their high solubility.

The palladium amido complex **3** containing a heteroaromatic thienyl group was isolated by a modified method (eq 1) because



[(P^{*t*}Bu₃)Pd(2-thienyl)(Br)] is unstable toward formation of the Pd(I) dimer (P^{*t*}Bu₃)₂PdBr₂.¹² Reaction of 2-thienyl bromide with Pd(P^{*t*}Bu₃)₂ in the presence of potassium diarylamide to trap the transient thienylpalladium bromide formed the heteroaryl palladium amide **3**. Complex **3** was isolated as red crystals.

Single-crystal X-ray diffraction of **2a–2c** and **3** showed the complexes to possess three-coordinate T-shaped structures. Table 1 provides a comparison of structural parameters of these complexes

Scheme 1. Syntheses of Three-Coordinate Arylpalladium Amides **2a–2c**

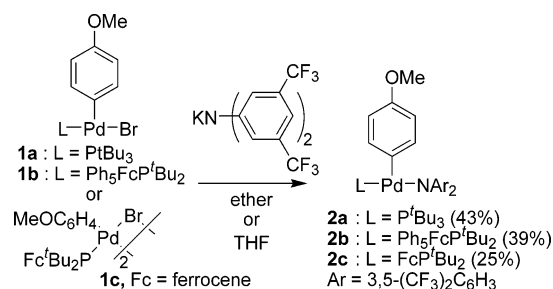


Table 1. Selected Bond Lengths (Å) and Angles (deg) of Three-Coordinate and Four-Coordinate Arylpalladium Amido Complexes **2a–2c**, **3**, and **4a**

amide	Pd–P(1) (Å)	Pd–N (Å)	Pd–C (Å)	P(1)–Pd–N (deg)	C–Pd–N (deg)
2a	2.2809(11)	2.078(3)	1.987(4)	168.23(10)	89.09(15)
2a'	2.2849(12)	2.080(3)	1.984(4)	166.00(9)	93.60(14)
2b	2.2965(10)	2.070(3)	1.965(3)	167.23(7)	93.46(22)
2c	2.2637(10)	2.091(2)	1.988(3)	168.52(7)	91.12(22)
3	2.2741(12)	2.073(2)	1.970(3)	170.66(7)	88.75(11)
4a	2.2786(12)	2.107(3)	2.041(4)	168.32(8)	83.86(13)

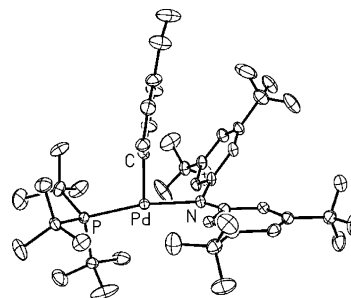
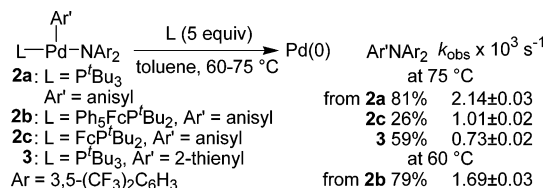


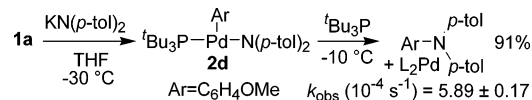
Figure 1. ORTEP drawing of one of two independent molecules of **2a** (30% thermal ellipsoid, hydrogen atoms are omitted for clarity).

to those of the corresponding four-coordinate (DPPF)Pd(anisyl)-[N(3,5-(CF₃)₂C₆H₃)₂] (**4a**). An ORTEP diagram of P(*t*-Bu)₃-complex **2a** is shown in Figure 1; ORTEP diagrams of **2b**, **2c**, **3**, and **4a** are provided as Supporting Information. The phosphine was located trans to the amido group, which has a weaker trans influence than an aryl group,¹³ in all the complexes with monodentate phosphines. The Pd–N and Pd–P bond distances in **2a–2c** and **3** were similar to those in DPPF-ligated **4a**. However, the absence of a ligand trans to the aryl group in three-coordinate **2a–2c** and **3** causes the Pd–C bonds in **2a–2c** and **3** to be shorter than that in **4a**.

Complex **2a** crystallized with two independent molecules in the asymmetric unit. One of these molecules and thienyl complex **3**

Scheme 2. Reductive Elimination of Amine from **2a–2c** and **3**

Scheme 3



possessed Pd–H distances of 2.09 and 2.14 Å that suggest the presence of agostic interactions and four-coordinate palladium centers.¹⁴

However, the other independent molecule of **2a** and complexes **2b** and **2c** were three-coordinate. The hydrogen atoms nearest the metal in the second independent molecule in **2a**, of **2b**, and in **2c** were 2.44, 2.65, and 2.52 Å, respectively, and these hydrogen atoms lay out of the palladium square plane by 0.792, 1.410 and 1.683 Å. Moreover, the Pd–Fe distances in **2b** and **2c** of 4.47 and 3.54 Å are well beyond the sum of atomic radii (2.617 Å),¹⁵ and are beyond the longest Pd–Fe distance (3.228 Å)¹⁶ for a Pd–Fe bond in the Cambridge Crystallographic database. Thus, three-coordinate, T-shaped *d*⁸ palladium(II) complexes can exist and can be observed directly.

The three-coordinate arylpalladium amido complexes **2a–2c** and complex **3** underwent reductive elimination upon heating in toluene. The yields of amine from **2a** and **2b** exceeded 81 and 79%, respectively; the yields of amine from the less hindered **2c** and heteroaryl **3** were lower. The major side product from reaction of **2c** and **3** was diarylamine by protonolysis. The DPPF complex **4a** with an electron-poor diarylamide did not undergo reductive elimination. Diarylamine was the major product containing nitrogen that was identified by GC/MS.

The rates of reaction of **2a–c** and **3** at 75 °C were monitored by ¹⁹F NMR spectroscopy (Scheme 2). The values of *k*_{obs} for reaction of **2a** (see Supporting Information for data) were indistinguishable in the presence of 0 mM, 1 mM, or 5 mM of added P(*t*-Bu)₃. These data show that the reductive elimination of amine occurs without association or reversible dissociation of phosphine and suggest strongly that reductive elimination occurs directly and irreversibly from the observed three-coordinate complex.¹⁷

The irreversibility of the C–N reductive elimination contrasts with reductive elimination of aryl halide from LPd(Ar)(X) (L = P(*t*-Bu)₃) complexes. Reactions of LPd(Ar)(X) occurred by reversible formation of free aryl halide and LPd, followed by trapping of the LPd intermediate with free ligand.⁹ Yet, the overall rates for C–N reductive elimination of triarylamine from the complex of the electron-poor amide are remarkably similar to those for elimination of aryl halide from LPd(Ar)(X) (see Scheme 3).

The rate constants for decomposition of **2b**, **2c**, and **3** were also measured. Complexes **2c** and **3** reacted about one-half and one-third as fast as **2a**, most likely because of the smaller size of the ferrocenyl ligand in **2c**¹⁸ and the greater electron density of the 2-thienyl ring in **3**.¹⁹ Complex **2b** reacted faster than complex **2a**; the rate constant for reaction of **2b** at 60 °C was similar to that for reaction of **2a** at 75 °C.

To quantify the difference in rate of reductive elimination from a three-coordinate amide and a well-studied, four-coordinate amide, the rate constant for reductive elimination from P(*t*-Bu)₃-ligated ditolylamide **2d** was compared to that for elimination from (DPPF)-Pd(anisyl)N(*p*-tol)₂ (**4b**). Anisylpalladium bromide **1a** was treated

with potassium di-*p*-tolylamide at –30 °C in THF to generate (t-Bu₃P)Pd(anisyl)N(*p*-tol)₂ (**2d**). The trans relationship between phosphorus and nitrogen atoms was confirmed by a large ³¹P–¹⁵N coupling (²*J*_{PN} = 40 Hz) in the analogous complex that was generated from K¹⁵NPh₂.

P(*t*-Bu)₃-ligated **2d** underwent reductive elimination at –10 °C to form the triarylamine product in 91% yield based on the starting arylpalladium bromide **1a**. The first-order decay of this complex corresponded to a half-life of 20 min at –10 °C. This rate is much faster than the rate of reaction of DPPF complex **4b**, which was shown previously to eliminate with a half-life of 55 min at the much higher temperature of 75 °C.^{3c}

In summary, arylpalladium amido complexes with a single hindered phosphine have been isolated, and several of these complexes display true three-coordinate, T-shaped geometries. Kinetic data are consistent with irreversible reductive elimination directly from the three-coordinate species. Even complexes with highly deactivating groups on both the palladium-bound aryl ring and the nitrogen undergo reductive elimination, and a comparison of the rates of reaction of the three-coordinate complexes to the rates of reaction of well-studied four-coordinate complexes show much faster rates for elimination from the three-coordinate species.²⁰

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Supporting Information Available: All experimental procedures and spectroscopic data of new complexes; X-ray structural data for **2a–2c**, **3**, and **4a** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, 1987; p 279.
- (a) Ozawa, F.; Ito, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 6457. (b) Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182. (c) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.
- (a) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 4708–4709. (b) Mann, G.; Shelby, Q.; Roy, A. H.; Hartwig, J. F. *Organometallics* **2003**, *22*, 2775.
- Casares, J. A.; Espinet, P.; Salas, G. *Chem. Eur. J.* **2002**, *8*, 4843.
- Stambuli, J. P.; Incarvito, C. D.; Buhl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 1184.
- Hartwig, J. F. In *Modern Arene Chemistry*; Astruc, C., Ed.; Wiley-VCH: Weinheim, 2002; p 107.
- Hartwig, J. F. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E. I., Ed.; Wiley-Interscience: New York, 2002; Vol. 1, p 1051.
- Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2001**, *219*, 131.
- Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 13944.
- (a) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217. (b) Mann, G.; Baranano, D.; Hartwig, J. F.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 9205. (c) Widenhoefer, R. A.; Zhong, H. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6787. (d) Widenhoefer, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 6504.
- Stambuli, J. P.; Buhl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9346.
- Hooper, M. W.; Utsunomiya, M.; Hartwig, J. F. *J. Org. Chem.* **2003**, *68*, 2861.
- Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. The DPPF-ligated arylpalladium amido complex **4a** contains a shorter Pd–P distance trans to the amide than trans to the aryl group.
- Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.
- Emsley, J. *The Elements*, 3rd ed.; Oxford University Press: New York, 1998.
- Sato, M.; Asano, H.; Akabori, S. *J. Organomet. Chem.* **1993**, *452*, 105.
- Our data do not distinguish between elimination from **2a** and elimination from an isomer of **2a** with the aryl group trans to the phosphine: Yamashita, M.; Cuevas Vicario, J. V.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 16347.
- Mann, G.; Incarvito, C.; Rheingold, A. L.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 3224.
- Hooper, M. W.; Hartwig, J. F. *Organometallics* **2003**, *22*, 3394.
- For a theoretical basis for this observation, see ref 2c.

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