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Xenon Difluoride Induced Aryl Iodide Reductive Elimination: a Simple Access to Difluoropalladium(II) Complexes

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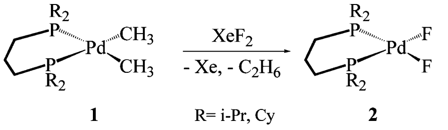
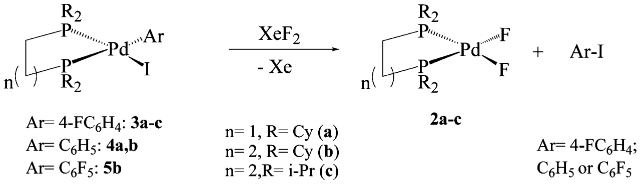
Palladium(II) aryliodo complexes bearing chelating diphosphine ligands react with XeF_2, giving iodoarene and rare palladium(II) difluoro complexes. The reaction is general with regard to the aryl group, with even C_6F_5–I undergoing facile reductive elimination from a Pd center.

Late-transition-metal oxidative addition of aryl−halide bonds is the key step in a variety of important catalytic organic transformations.[1] Today, there are dozens of metal complexes that are capable of rapid insertion into even the least active carbon−halogen bonds, and the requirements for such reaction are generally well-understood.[2] Precisely against this background, remarkably little is known about the reverse reaction: aryl halide reductive elimination. Although a related $C(sp^2)-X$ reductive elimination reaction was found to be an important step in the Monsanto methanol carbonylation process,[3] very few examples of Ar−X (X = halide) were reported. In 1969, Ettorre showed that heating $(Et_3P)_2Pt_2Ph_2$ in methanol gave iodobenzene and $(Et_3P)_2PtPh$.[4] Many years later, Hartwig et al. demonstrated the Ar−X (X = Cl, Br, I) reductive elimination in a sterically crowded Pd^{II} system.[5] We recently reported evidence for an Ar−Br and Ar−I reductive elimination reaction in a series of Pt^{IV} complexes.[6] Herein we present a highly efficient and selective Ar−I reductive elimination reaction from a Pd center triggered by reaction with xenon difluoride.

Scheme 1



Scheme 2



In the quest for synthetic routes toward diphosphine difluoropalladium(II) complexes, we recently reported that the reaction of the corresponding palladium(II) dimethyl complex with XeF_2 cleanly produces such products for complexes bearing chelating alkylphosphine ligands (Scheme 1).[7] The advantage of this reaction is that no laborious workup is required because the byproducts remain in the gas phase. In a continuation of our studies of XeF_2 reactivity with organometallic group 10 complexes, we found that upon its reaction with the palladium(II) aryliodo complexes **3a**−**c**, clean formation of the difluoro complexes **2** and free iodoarene was observed. Although Ar−X reductive elimination can generally be influenced by the chelate size,[6] no such effect was observed in this case, with both five- and six-membered chelates undergoing clean Ar−I reductive elimination (Scheme 2). Only ligands bearing electron-donating alkyl groups gave stable difluoro complexes. When the less electron-rich rigid o-$C_6H_4(Ph_2P)_2$ ligand (dppbz) was used, the resulting palladium difluoride could be observed at room temperature immediately after the addition of two compounds. It, however, decomposed within several minutes at 25 °C to form several P−F-bond-containing products.[8] The less rigid (dppp)PdF_2 complex could only be observed at

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(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Sausalito, CA, 1987. (b) Tsuji, J. *Palladium in Organic Synthesis (Topics in Organometallic Chemistry)*; Springer: Berlin, 2005.

(2) (a) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176. (b) Bedford, R. B.; Cazin, C. S. J.; Holder, D. *Coord. Chem. Rev.* **2004**, *248*, 2283.

(3) Dekleva, T. W.; Forster, D. *Adv. Catal.* **1986**, *34*, 81.

(4) (a) Ettorre, R. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 45. (b) In our hands, the reaction appeared to be more complex, giving large amounts of a byproduct.

(5) (a) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 13944. (b) Roy, A. H.; Hartwig, J. F. *Organometallics* **2004**, *23*, 1533.

(6) Yahav-Levi, A.; Goldberg, I.; Vigalok, A. *J. Am. Chem. Soc.* **2006**, *128*, 8710.

(7) Yahav, A.; Goldberg, I.; Vigalok, A. *J. Am. Chem. Soc.* **2003**, *125*, 13634.

(8) Fluoride migration to the coordinated phosphine ligand is the most common decomposition pathway for late-transition-metal fluoro complexes: (a) Grushin, V. V. *Organometallics* **2000**, *19*, 1888. (b) Marshall, W. J.; Grushin, V. V. *Organometallics* **2003**, *22*, 555.

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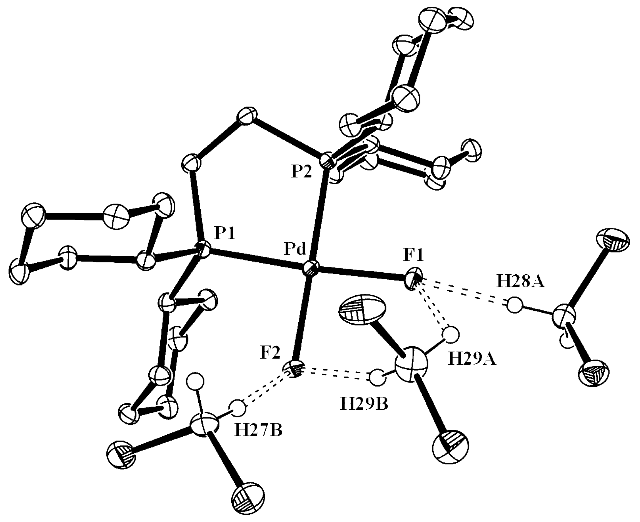

Figure 1. Single-crystal ORTEP (thermal ellipsoids drawn at 50% probability) structure of **2a**. H atoms, with the exception of the atoms of CH_2Cl_2, are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd−F1 2.0401(13), Pd−F2 2.058(13), Pd−P1 2.2061(6), Pd−P2 2.2177(6), F1−H28A 2.14, F1−H29A 2.23, F2−H27B 2.04, F2−H29B 2.42, F1−Pd−F2 90.62(5), P1−Pd−P2 87.37(2), F1−Pd−P2 92.87(4), F1−Pd−P1 174.90(4).

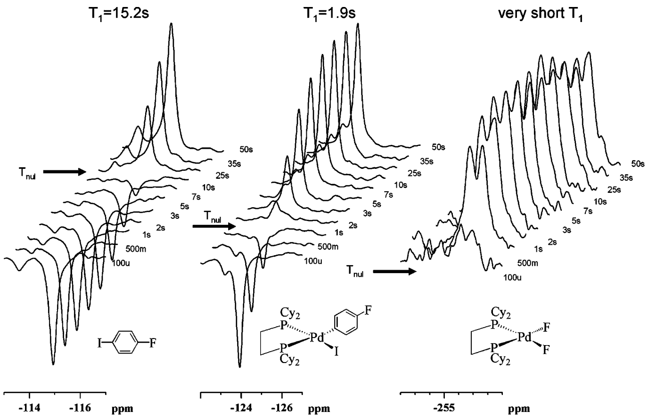

Figure 2. T_1 measurement graphs for the ^{19}F NMR signals of fluorine-containing complexes and 4-fluoroiodobenzene.

low temperatures.[7] The reaction appears to be quite general with regard to the aryl group involved in the reductive elimination. Pd^{II} complexes **4** and **5** also underwent smooth Ar−I reductive elimination upon treatment with XeF_2. Importantly, even the strong C_6F_5−Pd bond was readily cleaved under these conditions and C_6F_5−I was quantitively formed together with **2**. To our knowledge, the C_6F_5−X reductive elimination is unprecedented.[9]

We were able to obtain transparent colorless prisms of dcpePdF_2 from a CH_2Cl_2/pentane solvent mixture at −30 °C.[10] This crystal structure of **2a** is only the second reported for monomeric palladium(II) difluoro complexes.[7] The X-ray structure of **2a** shows a square-planar arrangement at the metal center, with two fluoro ligands involved in strong hydrogen-bond interactions with three dichloromethane molecules (Figure 1). No such interactions, however, were observed in the crystal structure of the previously reported **2c**, also crystallized from CH_2Cl_2. Coordination of three CH_2Cl_2 molecules to fluoro ligands in a *dimeric* Pd^{II} system has been described.[11] The "terminal" solvent molecules show relatively strong hydrogen-bond interactions with the fluoro ligands (2.04 and 2.14 Å) compared with the bridging CH_2Cl_2 (2.23 and 2.42 Å). The hydrogen bonding was proposed to alleviate the strong π-donation properties of the fluorides in their late-transition-metal complexes.[11] The Pd−F distances in **2a** of 2.040(13) and 2.058(13) Å are only slightly shorter than that in **2c** [2.065(3) Å].[7] There are also relatively short distances between the fluoro ligands and the cyclohexyl H atoms of the phosphine ligand. The P1−Pd−P2 angle is expectedly smaller than that in **2c** [87.37(2) vs 96.22(8)°].

Although the Pd−Ph complexes **4a** and **4b** easily undergo the Ph−I reductive elimination with XeF_2, using the 4-FC_6H_4 group instead of an unsubstituted phenyl group was found to be helpful in a number of transformations at a metal center due to the presence of a fluorine tag in the ^{19}F NMR spectra.[12] Surprisingly, the ratio between the 4-FC_6H_4I signal in the ^{19}F NMR spectrum and the signal of **2** was found to be less than 30% when **1** was reacted with XeF_2 in a CH_2Cl_2 solution. Because no other product was detected in the reaction mixture, we investigated the relaxation times of the fluorine signal in **2** and aromatic aryl fluorides. We found that the fluorine signal relaxation times in **2** were significantly faster (several orders of magnitude) than those in 4-FC_6H_4I (Figure 2). Increasing the delay time between the scans to 20 s gave the spectra with a correct integration ratio between the products. Significant differences in the relaxation times were also observed for the starting materials **3** and organic fluorides, in both the ^{19}F and ^{1}H NMR spectra. Thus, the NMR relaxation times of certain Pd^{II} complexes can be by several orders of magnitude shorter than those of simple aromatic molecules, and caution should be exercised when assigning the product ratio based on the integration of the NMR signals, even in the presence of an internal reference compound.

It was proposed that XeF_2 reacts with square-planar d^8 metal complexes in an S_N2-type mechanism, giving the trans oxidative addition product.[13] Organometallic palladium(IV) phosphine complexes have so far eluded isolation; however,

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(9) In fact, only a few Pd-catalyzed reactions involving the electron-accepting C_6F_5 group are known: (a) Albeniz, A. C.; Espinet, P.; Martin-Ruiz, B.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 11504. (b) Korenaga, T.; Kosaki, T.; Fukumura, R.; Ema, T.; Sakai, T. *Org. Lett.* **2005**, *7*, 4915. (c) Frohn, H.-J.; Adonin, N. Y.; Bardin, V. V.; Starichenko, V. F. *Tetrahedron Lett.* **2002**, *43*, 8111.

(10) X-ray structure data for **2a**: $C_{26}H_{48}F_2P_2Pd\cdot 3CH_2Cl_2$, M = 821.76, 0.4 × 0.3 × 0.25 mm^3, monoclinic, space group $P2_1/c$, a = 12.34840(10) Å, b = 14.20860(10) Å, c = 21.0151(3) Å, β = 103.3032(4)°, V = 3588.23(6) Å^3, Z = 4, Nonius Kappa CCD, Mo Kα radiation (λ = 0.710 73 Å), graphite monochromator, T = 110(2) K, 8587 collected reflections, 7142 unique reflections (R_{int} = 0.0360). The structure was determined by direct methods (*SIR-97*) and refined anisotropically by least squares on F^2 data (*SHELXL-97*; 361 parameters with no restraints). R1 = 0.0356, wR2 = 0.0466 for 11 587 data with $I > 2\sigma(I)$ and R1 = 0.0902, wR2 = 0.0978 for all unique data.

(11) Grushin, V. V.; Marshall, W. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4476.

(12) (a) Yahav, A.; Goldberg, I.; Vigalok, A. *Inorg. Chem.* **2005**, *44*, 1547. (b) Yahav, A.; Goldberg, I.; Vigalok, A. *Organometallics* **2005**, *24*, 5654.

(13) Cockman, R. W.; Ebsworth, E. A. V.; Holloway, J. H.; Murdoch, H.; Robertson, N.; Watson, P. G. In *Fluorine Chemistry (Toward the 21st Century)*; Thrasher, J. S., Strauss, S. H., Eds.; American Chemical Society: Washington, DC, 1994; Chapter 20, p 327.

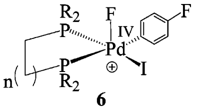

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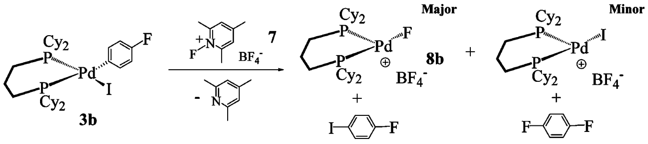
Figure 3.

Scheme 3



their participation in various transformations as reactive transients cannot be discounted.[14] XeF_2 reacts with related platinum(II) phosphine aryl complexes, resulting in platinum(IV) difluorides, although only cis positioning of the fluoro ligands in the final product was observed.[12a] In the S_N2-type mechanism, formation of the cationic Pd^{IV} complex **6** can be expected (Figure 3). Such a cationic intermediate can also be formed with "electrophilic fluorination" reagents other than XeF_2. Interestingly, while no reaction was obtained upon treatment of **3** with *p*-(difluoroiodo)toluene, the reaction between **3** and 1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate (**7**) also resulted in the Ar−I reductive elimination. With dcpp as the ligand, the cationic monofluoropalladium(II) complex **8b** (or its BF_4^- adduct) was observed and remained stable for several hours in solution (Scheme 3). The overall reaction was not as clean as the reaction with XeF_2. In addition to Ar−I, significant amounts of Ar−F (ca. 10%) were also observed.

While these observations may indicate the Ar−F reductive elimination pathway from **6**,[15] we must also consider the possibility that the electrophilic Pd−Ar bond cleavage with the N−F reagent might be responsible for the formation of the fluoroarene.[16,17]

The reaction of **3a** with **7** also gave mixtures of Ar−I and Ar−F; however, no stable palladium fluoro complexes were isolated. When (dcpp)Pd(C_6F_5)I was reacted with **7**, the formation of C_6F_5−I as the organic product was observed. No **8b** was observed in this reaction, and significant amounts of P−F-bond-containing products were detected in the ^{19}F NMR spectra.

We also studied the reactivity of the Pd(Ar)I complexes with other reagents capable of influencing the Ar−I reductive elimination. The reaction of **3** with Br_2 resulted in the simultaneous formation of the products of Ar−I (major) and Ar−Br (minor) bond formation. Thus, the reaction of **3** with XeF_2 appears to be the most selective in terms of the reductive elimination of iodoarene. To test the possibility of Ar−I formation by oxidation, we reacted complexes **3** with Fc^+ BF_4^-. No aryl iodide reductive elimination was observed in this reaction. However, the reaction between **3** and cerium ammonium nitrate did produce some 4-FC_6H_4I along with a number of unidentified products. These results demonstrate that the reductive elimination can be, to a certain extent, oxidatively induced. Yet, the difference in the reactivity of XeF_2 and **7** might indicate that the Ar−I formation mechanism is more complex than the oxidative addition−reductive elimination or oxidation−reductive elimination sequences. Although the reactions between late-transition-metal complexes and XeF_2 or its derivatives have previously been studied,[18] little is known about such chemistry involving complexes with alkyl− or aryl−metal bonds. Attempts to observe the reductive elimination of Ar−Br from the corresponding arylbromo complexes were, thus far, unsuccessful. A complex mixture of products was observed upon the reaction of palladium(II) arylbromo complexes and XeF_2.

In summary, the reaction of a series of chelating palladium(II) aryl iodide complexes with XeF_2 results in the remarkably mild and selective reductive elimination of iodoarene and the formation of the rare palladium(II) difluorodiphosphine complexes. We are presently investigating the mechanism of this reaction in detail. Given that Xe derivatives do not generate unwanted byproducts, their wider use in synthetic organometallic chemistry should be considered.

Acknowledgment. This work is dedicated to Prof. David Milstein on the occasion of his 60th birthday. It was supported by the German−Israel Science Foundation and Tel Aviv University internal grant.

Supporting Information Available: Experimental details (PDF) and X-ray data for complex **2a** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) An organometallic Pd^{IV} compound was recently characterized at low temperature: Canty, A. J.; Rodemann, T.; Skelton, B. W.; White, A. H. *Organometallics* **2006**, *25*, 3996.

(15) We recently a proposed similar intermediate in Ar−I and Ar−Br reductive elimination reactions from the chelating platinum complexes.[6]

(16) Ar−F reductive elimination reactions remain a significant synthetic challenge. A recently reported mechanism of Ar−F reductive elimination from a Pd^{II} center for the aryl ligand bearing a strong electron-accepting nitro group [(a) Yandulov, D. V.; Tran, N. T. *J. Am. Chem. Soc*. **2007**, *129*, 1342] has been contested: (b) Grushin, V. V.; Marshall, W. J. *Organometallics* **2007**, *26*, 4997.

(17) For the ligand-assisted synthesis of fluoroarenes using the electrophilic N−F reagents, see: Hull, K. L.; Anani, W. Q.; Sanford, M. S. *J. Am. Chem. Soc*. **2006**, *128*, 7134.

(18) Seppelt, K. *Z. Anorg. Allg. Chem*. **2003**, *629*, 2427.