Synthesis of the Elusive (R₃P)₂MF₂ (M = Pd, Pt) Complexes

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There has recently been considerable interest in transition metal fluorine chemistry.[1] Transition metal fluoride complexes are important intermediates in selective C−F bond activation processes[2] and in catalysis.[3] While much progress has been achieved in the synthesis of various transition metal fluorides, preparation of the palladium(II) and platinum(II) fluoride complexes remains a significant challenge. Such complexes are generally considered inaccessible, to a large extent due to the weak interactions between the "soft" late transition metal center and the hardest anion F⁻.[1,4] Only recently were the first unambiguously characterized Pd(II) monofluoride complexes of formula *trans*-(Ph₃P)₂Pd(R)F (R = Ar, Me) reported,[5,6] while (R₃P)₂MF₂ (M = Pd, Pt) complexes are still unprecedented.[7] The latter complexes lack the strong push−pull interactions provided by alkyl or aryl ligands, assumed to be essential for their stabilization.[8] Herein, we report the high-yield synthesis of stable Pd(II) and Pt(II) difluorides.

Pd(II) and Pt(II) monofluoride complexes are commonly prepared by the metathesis reaction with silver(I) fluoride.[5,6b−d,f] This approach, however, fails to furnish the desired (Ph₃P)₂PdF₂ when the dichloro- or diiodo-precursor was treated with AgF in various solvents. Only decomposition took place, generating Pd black and a Pd(0) complex, which was trapped by adding iodobenzene to the reaction mixture. Since the nucleophilic fluoride anion is known to cause the reductive decomposition of several Pd(II) phosphine complexes,[9] we were interested in developing a different strategy to achieve the fluorination process. When the dimethyl complexes **1** were treated with an equivalent amount of XeF₂ in dry dichloromethane, the quantitative formation of the difluoro complexes **2** was observed with the di(*i*-propylphosphino)propane (dippp) and di(cyclohexylphosphino)propane (dcpp) ligands (eq 1). As the byproducts are released in the gaseous phase, simple triturating of the concentrated CH₂Cl₂ solution with pentane afforded pure **2** as a white solid with a nearly 100% yield. Compounds **2** slowly decomposed at room temperature both in solution and in the solid state when stored in a drybox. However, at 0 °C, a CDCl₃ sample of **2a** showed no decomposition after several weeks. It was important to adhere to exact stoichiometry in eq 1 because an excess of XeF₂ led to partial decomposition, giving fluorinated phosphorus(V) products, metal black, and **2**-HF adducts.[10]

$$L_2Pd(CH_3)_2 + XeF_2 \xrightarrow[- Xe, - C_2H_6]{CH_2Cl_2, -30° - RT} L_2PdF_2 \qquad (1)$$

1

2 (a, b)
but not c, d or e

L₂= dippp (a); dcpp (b)
dppe (c); dppp (d); 2 Ph₃P (e)

The ³¹P{¹H} and ¹⁹F{¹H} NMR spectra of **2** show an AA′XX′ pattern with ²J_PF(trans) ≈ 180 Hz.[11] The gNMR simulations for **2a** were in excellent agreement with the observed spectra.[11] The ¹⁹F signals for the difluoride complexes are in the area expected for the Pd(II) complexes (cf. −248 ppm in **2a** with −274 ppm in (Ph₃P)₂Pd(Ph)F). In some instances, the ³¹P and ¹⁹F NMR signals

Figure 1. Single-crystal ORTEP (thermal ellipsoids drawn at 50% probability) structure of **2a**. Selected bond distances (Å) and angles (deg): Pd−F(1) 2.065(3), Pd−P(1) 2.2241(15), F(1)−Pd−F(1′) 89.99(19), P(1)−Pd−P(1′) 96.22(8), F(1)−Pd−P(1) 86.84(8), F(1)−Pd−P(1′) 175.90(12).

were broadened, presumably due to the presence of small amounts of moisture.[5] Performing the measurements at low temperatures restored the original AA′XX′ signal structure.

Colorless crystals of **2a** were obtained by slow pentane diffusion into its CH₂Cl₂ solution at −30 °C. The molecules adopt a perfect C_s symmetry in the crystal, being positioned on crystallographic mirror planes. The X-ray crystal structure of **2a** (Figure 1) shows the palladium center located in an almost perfect square-planar environment with the P(1′)−Pd−F(1) bond angle being 175.90(12)°.[12] The Pd−F bond length of 2.065(3) Å is within the range reported for inorganic palladium fluoride salts (1.991−2.178 Å).[13] It is slightly shorter than the Pd−F bond in *trans*-(Ph₃P)₂Pd(Ph)F (2.085(3) Å),[5a] which is due to a weaker *trans*-influence of the phosphine group than that of the phenyl, but longer than the same bond in the *trans*-(Ph₃P)₂Pd(*p*-NO₂Ar)F (2.049(2) Å)[5c] where the fluorine atom might be involved in conjugation with the *p*-nitrophenyl group. The Pd−F bonds in **2a** are significantly longer than the Pd−O bond in terminal Pd hydroxide complexes with nitrogen ligands (1.966−2.025 A).[14]

Xenon(II) difluoride was used in the oxidative fluorination of transition metal complexes, providing the corresponding metal fluorides in the high oxidation state.[15] In our case, no change in the oxidation state occurs as the addition of two fluorine atoms is coupled with the reductive elimination process. This method was also applied toward the synthesis of the Pt(II) fluoro complexes. When (R₃P)₂Pt(Ph)₂ (**3**) was reacted with XeF₂ in CH₂Cl₂, complexes **4a−c** were obtained in quantitative yields and biphenyl was identified as the organic byproduct (eq 2). The ³¹P{¹H} and ¹⁹F{¹H} NMR spectra for these complexes exhibit an AA′MXX′ splitting pattern (²J_PF(trans) ≈ 170 Hz, ¹J_PtP ≈ 3660 Hz), except for **4c** which has the *trans*-configuration. We believe that the initial oxidation of the metal center by XeF₂ triggers the C−C reductive elimination followed by the addition of two fluorine atoms. In
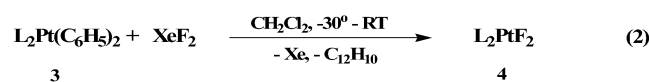
support of this mechanism, the Pd(0) complex (dippp)$_2$Pd[16] reacts with XeF$_2$, giving **2a** as the major metal-containing product in the reaction mixture. An alternative route toward **2** involves an initial oxidative addition step to form the M(IV) difluoride complex with concomitant ethane reductive elimination. Low-temperature experiments provided no evidence for such an intermediate.

$$L_2Pt(C_6H_5)_2 + XeF_2 \xrightarrow[\text{- Xe, - C}_{12}H_{10}]{\text{CH}_2\text{Cl}_2,\ -30^\circ - \text{RT}} L_2PtF_2 \quad (2)$$

$$\underset{\textbf{3}}{} \qquad\qquad \underset{\textbf{4}}{}$$

L$_2$= **dippp (a)**; **dppp (b)**; **2 Ph$_3$P (c)**

While stable in solution, the palladium difluoride complexes are reactive toward strong electrophiles, giving the corresponding fluorination products.[17] For example, treatment of **2a** with 2 equiv of RCOCl (R = Me or Ph) immediately results in formation of the known[18] dipppPdCl$_2$ and an acyl fluoride.

In light of the predicted instability of the Pd(II) difluoride complexes, the isolation of complexes **2a** and **b** is somewhat unexpected.[5a,9] These complexes are not stabilized via the typical push−pull interactions, nor does the metal center appear to be electron-deficient, allowing for strong electrostatic interactions.[8] Importantly, reactions of XeF$_2$ with (Ph$_3$P)$_2$PdMe$_2$ or (dppp)PdMe$_2$ resulted in decomposition, and no corresponding palladium difluoride was isolated. In the latter case, the transient (dppp)PdF$_2$ (**2c**) was observed in the ^{19}F NMR spectrum of the reaction mixture (AA′XX′ multiplet at −238.69 ppm, −30 °C) along with various P−F bond-containing decomposition products. The mixture consequently turned black with the signal attributed to the Pd−F bond disappearing. As steric differences between the *cis*-chelating phosphine ligands are unlikely to play a role when small fluoride atoms are involved, the electron-donating dippp and dcpp ligands are essential for the difluoride stabilization. Reacting *trans*-(*t*-Bu$_3$P)$_2$-PdMe$_2$ or (*t*-Bu$_3$P)$_2$Pd(0) with XeF$_2$ did not lead to (*t*-Bu$_3$P)$_2$PdF$_2$ but rather resulted in several unidentified products. Although *t*-Bu$_3$P is an electron-donating ligand similar to dippp, it is expected to impart the *trans*-arrangement around the palladium center. Thus, the stability of the Pd(II) complexes of formula (R$_3$P)$_2$PdF$_2$ *is strictly limited to alkyl phosphine ligands that can adopt the mutual cis-orientation.* The platinum analogs are more stable, giving isolable difluoride complexes with both alkyl and aryl phosphine ligands. The observed stability trend led us to reinvestigate the halide metathesis pathway toward the Pd(II) and Pt(II) fluorides. Simple stirring of the dipppPdI$_2$ complex with 2.5 equiv of AgF in dichloromethane for 2−3 h in the dark resulted in the clean formation of **2a**, while, as expected, under the same reaction conditions, dpppPdI$_2$ gave only decomposition products. To our surprise, reacting (Ph$_3$P)$_2$Pd(Ph)I with 1.5 equiv of AgF in CH$_2$Cl$_2$ for 3 h gave the known (Ph$_3$P)$_2$Pd(Ph)F[5] in a quantitative yield, indicating that no sonication is required. The platinum(II) diiodo complexes reacted similarly with 2.5 equiv of AgF, providing the corresponding (R$_3$P)$_2$PtF$_2$ in excellent yields. While generally not innocent in transition metal fluoride chemistry,[17] CH$_2$Cl$_2$ appears to be the solvent of choice in the synthesis of palladium and platinum fluorides.

In summary, we demonstrated that the difluoro Pd(II) phosphine complexes are significantly more robust than was commonly believed, provided *cis*-alkyl phosphine ligands are used. The new oxidative fluorination−reductive elimination sequence using XeF$_2$ has been developed and can be used alongside the traditional halide metathesis reaction. As XeF$_2$ provides 2 equiv of F$^-$ and essentially no workup is required, this method has certain advantages over the AgF fluorination. The mechanistic aspects of this process are currently under investigation.

Supporting Information Available: Experimental procedures for complexes **2** and **4** (PDF). X-ray crystallographic file (CIF) for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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