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trans-Difluoro Complexes of Palladium(II)

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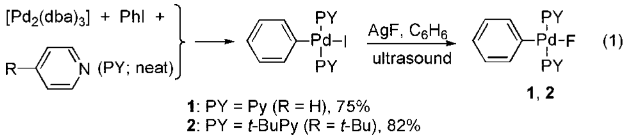
Known for nearly 200 years, molecular d^8 square-planar complexes of the type *trans*-$[(L)(L')M(X)_2]$, where X = Cl, Br, I, are numerous and widely used. In contrast, their isolable difluoro analogues (X = F) have not been reported, even though the variety of types of isolated and fully characterized late transition metal fluorides has broadened significantly due to recent rapid progress in the area.[1] The lack of this key class of fluoro complexes might be unsurprising: filled/filled $d_\pi-p_\pi$ repulsion[2,3] considerations suggest that mutually trans M−F bonds in square-planar complexes should be destabilized (see below), conceivably to the extent of nonexistence. Against all expectations, however, we have now synthesized the first striking examples of such compounds which are not only stable, but their trans−F−Pd−F bonds are by far the shortest ever reported for soluble fluoro complexes of Pd(II).

In continuation of our studies toward the highly sought Ar−F reductive elimination from Pd(II),[1d,4] we have now synthesized $[(Py)_2Pd(Ph)(F)]$ (**1**; Py = pyridine) and $[(t\text{-BuPy})_2Pd(Ph)(F)]$ (**2**; *t*-BuPy = 4-*tert*-butylpyridine). Reacting $[Pd_2(dba)_3]$ with iodobenzene in neat Py or *t*-BuPy afforded $[(Py)_2Pd(Ph)(I)]$ and $[(t\text{-BuPy})_2Pd(Ph)(I)]$, respectively. These iodides were then converted to **1** and **2** upon treatment with AgF under sonication, using our original method (eq 1).[5] Both **1** and **2** were isolated and found to be trans in solution and in the solid state (Figure 1).



The formation of **1** and **2** was unexpected. These complexes are the first examples of aryl palladium fluorides devoid of tertiary phosphine ligands which seem to play an important role in M−F bond stabilization.[6] Furthermore, our previous attempts to synthesize isolable aryl palladium fluorides stabilized by *N*,*N*- and *S*,*S*-chelates were unsuccessful.[4f] Surprisingly, the Pd−F bond distances in **1** (2.077(4) and 2.080(2) Å for two polymorphs) and **2** (2.079(2) Å) are almost identical to that found in *trans*-$[(Ph_3P)_2Pd(Ph)(F)]$ (2.085(3) Å).[5] This is also true for the Pd−C bond distances in **1** (1.982(3) and 1.979(6) Å), **2** (1.978(2) Å), and $[(Ph_3P)_2Pd(Ph)(F)]$ (1.998(5) Å).[5] These values indicate that the geometry parameters along the Ph−Pd−F axis remain virtually the same regardless of the other two ligands being Py, *t*-BuPy, or PPh_3. The ^{19}F NMR signals from **1** (−219.2 ppm) and **2** (−220.5 ppm) are noticeably downfield from the resonance reported for $[(Ph_3P)_2Pd(Ph)(F)]$ (−274 ppm).[5]

Thermal decomposition of **1** and **2** in anhydrous benzene at 80 °C did not result in C−F bond formation. Pd black and Ph_2 (GC−MS) were produced instead, along with new Pd−F species resonating as sharp singlets at −386.0 and −392.9 ppm (^{19}F NMR), for the reactions of **1** and **2**, respectively. Isolation of the new fluorides appeared impossible: after the first 2 h at 80 °C (ca. 20% conversion) the reaction proceeded with deceleration and could be driven to full conversion only after 2−4 days, during which time the newly formed fluorides were also decomposing. The identified products of the reactions after 2 h (Pd and Ph_2) along with stoichiometry considerations suggested that the fluorides formed on decomposition of **1** and **2** might be simple species containing only Py (or *t*-BuPy) and F ligands. We therefore attempted independent synthesis of these new Pd−F compounds.

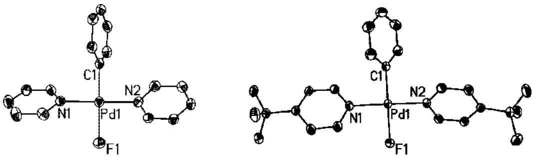


Figure 1. ORTEP drawings of **1** (left) and **2** (right).

We found that $[(Py)_2Pd(I)_2]$ and $[(t\text{-BuPy})_2Pd(I)_2]$ reacted with AgF to give palladium fluorides that displayed ^{19}F NMR signals identical to those observed from the products of the thermolysis of **1** and **2**. Isolation and full characterization of the new fluorides revealed their composition $[(Py)_2Pd(F)_2]$ (**3**) and $[(t\text{-BuPy})_2Pd(F)_2]$ (**4**), unexpected *trans* geometry (Figure 2), and even more striking, uniquely short Pd−F bond distances.

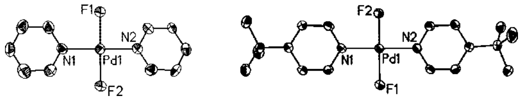


Figure 2. ORTEP drawings of **3** (left) and **4** (right).

Soluble difluoride complexes of Pd(II) and Pt(II) are extremely rare.[7] Only two Pd(II) difluorides[7a,c] and one Pt(II) difluoride[7b] have been structurally characterized, all three being cis. Importantly, treatment of *trans*-$[(R_3P)_2Pt(I)_2]$ (R = Ph, Et) with AgF produces *cis*-$[(R_3P)_2Pt(F)_2]$.[7b] Although evidence has been reported[7b] for the formation of *trans*-$[(i\text{-}Pr_3P)_2Pt(F)_2]$, the latter could not be isolated due to decomposition. All these and many other observations in the chemistry of square-planar late transition metal fluorides are rationalized in terms of destabilizing $d_\pi-p_\pi$ filled/filled repulsion between the filled *d* orbitals on the metal and fluoride's lone electron pair.[2,3] As interaction of the latter with the empty $d(x^2-y^2)$ orbital is symmetry forbidden,[3] the filled−filled repulsion may be alleviated via push−pull interactions of the p_π electrons on F with the π^* of the ligand trans to it through the filled *d* orbitals on the metal.[1a,d,3,8] In accord with this, enhanced π-acidity of the σ-aryl ligand trans to F stabilizes and shortens the Pd−F bond.[9] Furthermore, the formation of stable *trans*-$[(R_3P)_2Rh(F)(L)]$ upon treatment of $[(R_3P)_4Rh_2(\mu\text{-}F)_2]$ with L has been shown to occur for π-acidic L = CO, CNR, PhC≡CPh, $CH_2{=}CH_2$, and R_3P[10,11] but not for L = Py or MeCN, much weaker π-acids.[11] One would therefore expect the Pd−F bond in **1** and **2** (trans to π-acidic Ph) to be more

10.1021/ja808975a CCC: $40.75

stabilized than in **3** and **4** (trans to π-basic and non-π-acidic F). Very much on the contrary, however, the mutually trans Pd−F bonds in **3** and **4** are the shortest ever found in a molecular Pd(II) complex, being only 1.947(4)−1.958(4) Å long (Figure 3) and shorter than those in **1** and **2** by 0.12−0.13 Å![12]

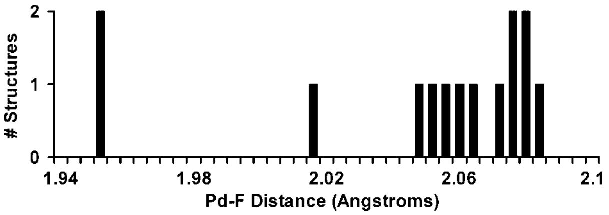


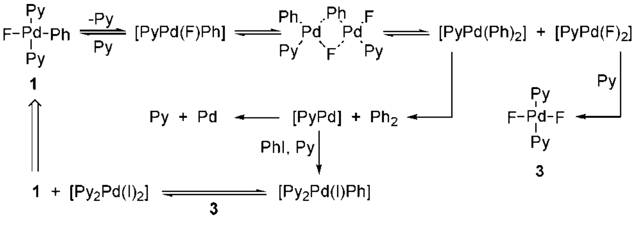
Figure 3. Terminal Pd−F bond distances (Å) in Pd(II) complexes.[13]

Figure 3 shows the bimodal distribution of the Pd−F bond lengths in all reported complexes and also **1**−**4** with the *trans*-difluorides **3** and **4** appearing on the far left.[13] The next shortest Pd−F bond distance of 2.016(2) Å has been reported by Perutz and co-workers[9b] for *trans*-[$(i\text{-}Pr_3P)_2Pd(F)(4\text{-}C_5F_4N)$] and aptly rationalized in terms of diminished filled/filled repulsion due to push−pull interaction with the π^* of the highly electron-deficient 4-tetrafluoropyridyl ligand.[14] Fluoride is not π-acidic and pyridine is a very weak π-acid,[15] which rules out the possibility of easing the filled/filled repulsion in **3** and **4** via metal-to-ligand π back-donation. Although fluoride is not necessarily always the strongest π-donating halide[16−18] and the destabilizing energy of the filled/filled repulsion may not exceed 1−2 kcal/mol,[19] this number might be considerably higher if the filled t_{2g} orbital interacts with *two* p_π orbitals on two mutually trans F ligands.

The stability of **3** and **4** and their exceptionally short Pd−F bond lengths are accounted for by the widely used (in both organic[20] and inorganic[21] chemistry) models of donor−acceptor interactions as combinations of electrostatic and covalent contributions. Coordination of the first F^- to "$[Py_2Pd]^{2+}$" changes the tendency of the metal center to bind the second fluoride.[22] The field effects of the two *trans*-fluoro ligands strengthen the Pd−F bonds by increasing their ionicity[23] that enhances charge control (in Klopman's terms)[20] or the electrostatic component (in Drago's terms)[21] of the bonding.[24] Apparently this stabilization is much stronger than the destabilizing filled/filled $d_\pi-p_\pi$ repulsion effects.

Regarding the formation of **3** from **1** (and **4** from **2**; see above), the reaction was found to be inhibited by extra pyridine. In the presence of PhI, however, 100% conversion of **1** was quickly reached in a reaction that gave rise to *trans*-[$(Py)_2Pd(I)_2$], **3**, Ph_2, and no Pd metal. In accord with these observations, the proposed mechanism shown in Scheme 1 involves Py predissociation, followed by transmetalation and Ph−Ph reductive elimination. In the absence of PhI, the resultant Py-stabilized Pd(0) species decompose to give Pd metal and free pyridine that slows down the reaction by shifting the predissociation equilibrium toward **1**. In the presence of PhI, the formation of [$(Py)_2Pd(Ph)(I)$] via C−I oxidative addition prevents the release of Pd black and free pyridine that inhibits the reaction. Halide exchange between [$(Py)_2Pd(Ph)(I)$] and **3** (0.5 equiv) produces [$(Py)_2Pd(I)_2$] (0.5 equiv) and **1**, with the overall stoichiometry being $2[(Py)_2Pd(Ph)(F)] + 2PhI = [(Py)_2Pd(I)_2] + [(Py)_2Pd(F)_2] + 2Ph_2$.

Scheme 1. Formation of **3** from **1**



Acknowledgment. This is DuPont CRD Contribution No. 8898. We thank Professor Stuart A. Macgregor and Dr. David L. Thorn for discussions.

Supporting Information Available: Experimental details, NMR data (PDF), and X-ray analysis data (CIF) for **1**−**4** and two polymorphs of *trans*-[$(Py)_2Pd(I)_2$]. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) For the same X (X = Cl, Br, I), Pd−X bonds are shorter when trans to X then when trans to Ph, a much stronger trans-influencing ligand.[13]
(13) See Supporting Information for details.
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(24) In terms of the HSAB principle, the hard-soft mismatch is diminished.[18]

JA808975A