Journal of Fluorine Chemistry 131 (2010) 1100–1102

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis and reactivity of unsymmetrical difluoro Pt(IV) complexes

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ARTICLE INFO

Article history:
Received 17 February 2010
Received in revised form 27 April 2010
Accepted 3 May 2010
Available online 15 May 2010

Dedicated to Russell Hughes
on the occasion of his 2010
ACS award for creative work
in fluorine chemistry.

Keywords:
Platinum
Fluoro ligand
Phosphine complexes

ABSTRACT

Difluoro Pt(IV) complexes (P–P)Pt(Ar)$_2$F$_2$ were prepared and characterized. One of the fluoro ligands can be selectively removed from the Pt coordination sphere giving the cationic product with the phosphine ligand trans to the empty coordination site.

1. Introduction

In the last decade, a great variety of stable late transition metal fluoro complexes have been prepared, defying the myth of the incompatibility of late transition metals with the hardest anion, F$^-$ [1,2]. To date, the molecular fluoro complexes of each of the platinum group metals are known and their reactivity was thoroughly investigated [3]. In nearly all of these complexes, the metal is bound to a single fluoro ligand which often acts as a center of reactivity in organometallic transformations. Only a few platinum group metal complexes bearing two fluoro ligands are known [4]. When two fluorine atoms are bound to a metal center in a non-symmetrical fashion, their reactivity might be different and depends on the ligand environment in the complex. Considering the unique properties of the fluoro ligand in organometallic chemistry we were interested in the preparation of such complexes and of studying their structural properties and reactivity.

Oxidative addition of two fluoro ligands to a Pt(II) center using XeF$_2$ [5] is the shortest pathway toward the difluoro Pt(IV) complexes. While it works satisfactorily with complexes bearing monodentate phosphines giving the symmetrically substituted products (Scheme 1a), applying the same strategy to systems with bidentate phosphine ligands results in the concomitant C–C reductive elimination reaction (Scheme 1b) [6]. Herein, we report the preparation and reactivity studies on Pt(IV) difluoro complexes bearing non-equivalent fluoro ligands.

2. Results and discussion

We recently showed that addition of Br$_2$ to complexes (P–P)Pt(Ar)$_2$ (Ar = 4-fluorophenyl) gives the Pt(IV) oxidative addition products **1** with the cis-orientation of the halide ligands [7]. The initial formation of the trans oxidative addition intermediate was also observed [7,8]. Upon the reaction with slight excess of AgF in CH$_2$Cl$_2$, complexes **1** gave the corresponding difluoro complexes **2** (Scheme 2). Complex **2a** was obtained as a single compound while **2b** and **2c** contained significant amounts of the Pt(II) difluoro complexes both because of the presence of Pt(II) in the reaction mixture and partial reductive elimination of the diaryl during the fluorination with AgF. The fluoro ligands in **2** preserve the mutual cis-orientation, as evident from the ^{19}F NMR spectra of these complexes which show two singlets for the inequivalent 4-FC$_6$H$_4$ groups. Overall, the presence of several inequivalent NMR-active nuclei makes the overall ligand assignments quite straightforward. The fluoro ligands show the two multiplets in the area of -250 ppm. Considering the large spectral window of the ^{19}F NMR spectrometry it was unexpected to observe both fluorine ligands giving very close resonance signals as the ^{19}F chemical shift is generally highly sensitive to the electronic effects.

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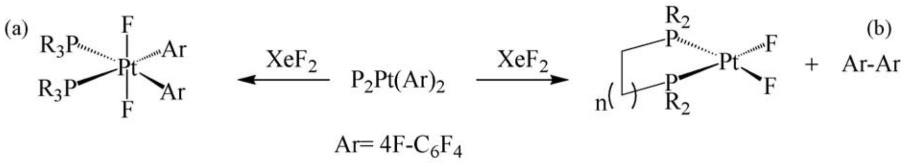
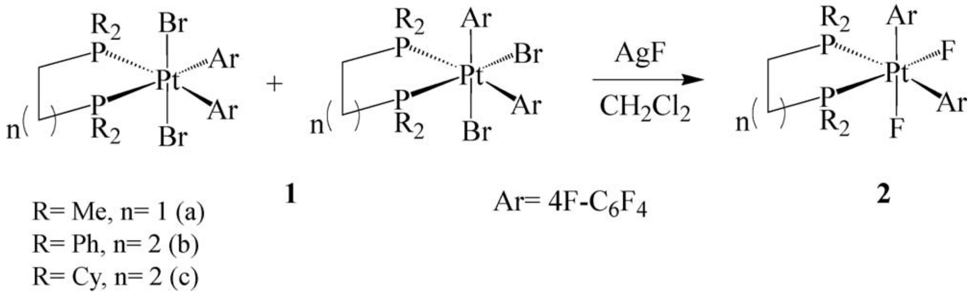
doi:10.1016/j.jfluchem.2010.05.001



Scheme 1. Reactivity of monodentate (a) and bidentate (b) phosphine $Pt^{II}(Ar)_2$ complexes toward XeF_2.



Scheme 2. Synthesis of the bidentate phosphine Pt^{IV} difluoro complexes.

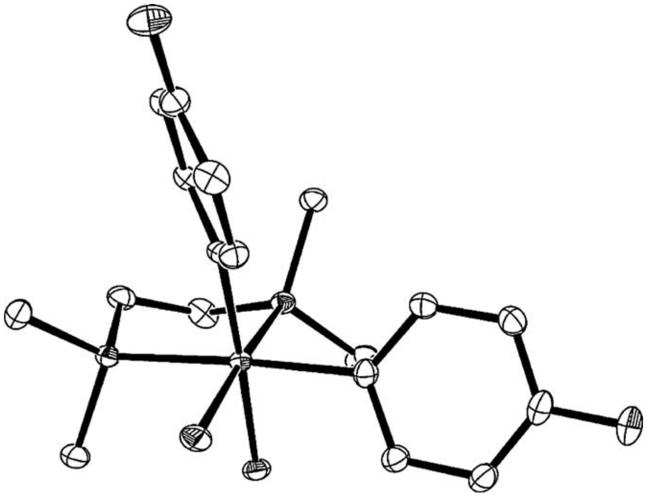
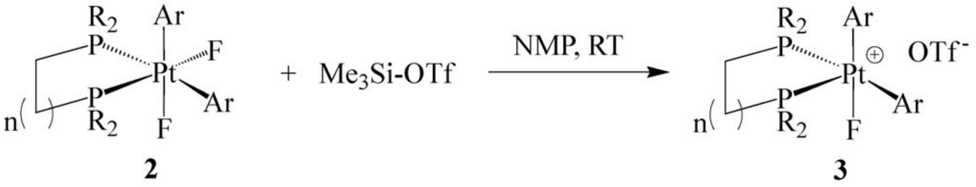


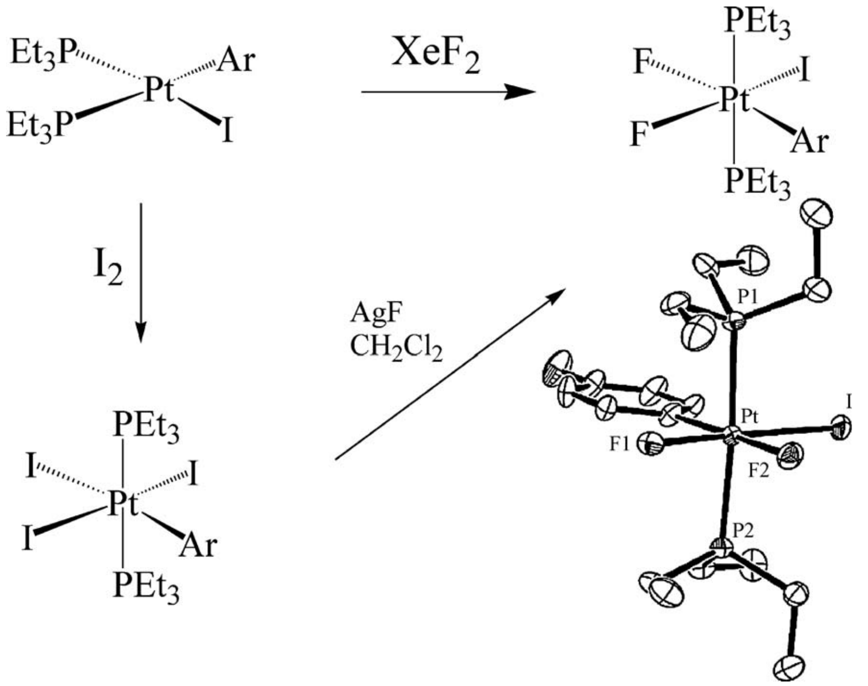
Fig. 1. X-ray structure of **2a**.

Upon standing at −30 °C, colorless crystals of complex **2a** deposited from its CH_2Cl_2–pentane solution. The crystals were subjected to the X-ray structure analysis which revealed that the platinum atom is located in the center of an octahedron, with the identical ligands occupying mutual cis-positions (Fig. 1). Interestingly, despite the presence of substantively different ligands in the trans-positions, the distances between the fluorine ligands and platinum center are fairly similar: 2.0423(18) Å vs. 2.0935(18) Å. The small changes in the Pt–F distances in unsymmetrically substituted difluoro complexes contrast the substantial differences in bond lengths in the difluoro Pd(IV) complexes [4b,9] bearing imine and aryl ligands underlying some important dissimilarity between the two metals. Just as the Pt–F bonds, the Pt–Carbon bond lengths of 2.032(3) and 2.077(3) Å in **2a** are also quite similar. The most significant difference in bond distances is observed for the Pt–P bonds, with lengths being 2.2404(8) and 2.3486(8) Å. Noteworthy, a similar trend was observed in the analogous diiodo complex of Pt(IV) [7], where the Pt–P distances were the most influenced by the ligand in the trans-position. In all cases, within the pair, the longer Pt distance in **2a** is to the ligand that has a stronger ligand in the trans-position. Because of the small size of the dmpe ligand, the corresponding bond angles are practically undistorted being close to those in an octahedron. Significantly larger deviations were observed for the diiodo analog[8] likely as a result of more pronounced steric interactions.

As organometallic fluorides are extremely reactive toward electrophiles, we were interested in studying the reactivity of **2** to determine the regioselectivity of the substitution reaction. Trimethylsilyl triflate (TMS-OTf) was used as the electrophile to ensure the irreversible nature of the substitution. We found that the reaction of **2a** with 1 equiv. of TMS-OTf gave the product of single fluorine substitution at the Pt(IV) center (Scheme 3). The ^{19}F NMR spectra of new complex **3a** showed a signal at −250.4 ppm (dd, J_{PF} = 46 and 12 Hz) as well as two singlets for the aromatic fluorine atoms at −119.1 and −117.8 ppm. The $^{31}P\{H^1\}$ NMR spectrum of **3a** gave rise to two signals at 36.8 ppm (d, J_{PtP} = 3107 Hz, J_{FP} = 12 Hz) and 33.8 ppm (d, J_{PtP} = 1396 Hz, J_{FP} = 46 Hz). For comparison, the $^{31}P\{H^1\}$ NMR spectrum of **2a** shows two signals at 13.0 ppm (dd, J_{PtP} = 3016 Hz, J_{FP} = 180 Hz, J_{FP} = 18 Hz) and 28.4 ppm (m, J_{PtP} = 1321 Hz, J_{FP} = 52 Hz, J_{FP} = 38 Hz), the former corresponding to the phosphine group trans to the fluoro ligand. Thus, based on the NMR data, it appears that *the selective replacement of the fluoro ligand trans to the phosphine ligand takes place*. This unusually high selectivity appears to be in contrast with the expected greater trans-effect of the aryl vs. phosphine ligands. However, it is also possible that no, or low, selectivity in the fluoride abstraction is compensated by



Scheme 3. Reactivity of the difluoro Pt^{IV} complexes toward TMS-OTf.



Scheme 4. Synthesis of the difluoro complex **5**.

a rapid equilibration to give the more stable isomer of **3a**. We plan to address this possibility in our ongoing work. Complex **3a** was unstable at room temperature and underwent C–C reductive elimination within several hours in solution thus precluding characterization by X-ray crystallography. In the absence of an X-ray structure, it is difficult to assess whether **3a** is a true cationic species or anion (or solvent) serves as the sixth ligand. Reacting **2a** with 1 equiv. of BF_3–Me_2O, instead of TMS-OTf, gave a complex which showed NMR signals nearly identical to those of **3a**. The ^{19}F NMR spectrum showed a single resonance due to BF_4^-, suggesting that, in this case, there is no strong anion coordination at room temperature.

Finally, we were interested in addressing the possibility of preparing organometallic Pt(IV) complexes bearing three fluoro ligands. A similar palladium complex has recently been reported, however, with only two “real” fluoro ligands and one end-on bound HF_2^- [9]. Toward this end, we prepared a triiodo complex $(Et_3P)_2Pt(4\text{-}FC_6H_4)I_3$, **4**, and reacted it with AgF in CH_2Cl_2. Interestingly, although the replacement of two of the iodo ligands proceeded smoothly giving the difluoro complex **5** (Scheme 4), no replacement of the third iodo ligand took place even after prolonged stirring with a large excess of AgF. The X-ray structure of **5** (Fig. 2) shows that the two Pt–F bonds are different in length, with the one trans to the remaining iodo ligand being shorter (1.992(3) Å vs 2.072(3) Å). The Pt–I bond of 2.6225(4) Å is shorter than Pt–I bonds in **1a** (2.7077(5) Å and 2.7848(5) Å) but is of similar length compared with the trans I–Pt–I bond of ca. 2.66 Å found in the trans-isomer of **1a** [8]. Thus, there is no obvious explanation for the reluctance of the remaining iodo ligand to undergo halogen exchange with AgF.

In summary, we prepared previously unknown unsymmetrical organometallic difluoro complexes of Pt(IV) and elucidated their structural parameters. Against expectations, the product of the formal replacement of the shorter Pt–F bond is obtained preferentially in the nucleophilic exchange reaction. We are presently investigating other reactivity patterns of these and similar organometallic fluoro complexes.

Acknowledgements

This research was supported by the US – Israel Binational Science Foundation and Levi Eshkol Fellowship from the Israel Ministry of Science to A.Y.-L.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.05.001.

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