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Difluoro Complexes of Platinum(II) and -(IV) with Monodentate Phosphine Ligands: An Exceptional Stability of d^6 Octahedral Organometallic Fluorides

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Complexes $(R_3P)_2PtF_2$ were prepared by reaction of the corresponding diiodo precursors with AgF in dichloromethane. The intermediate formation of *trans*- and *cis*-$(R_3P)_2Pt(I)F$ was also observed. All fluoro complexes demonstrate a strong preference for the cis-configuration (R = Ph or Et) unless a bulky phosphine ligand is used (R = *i*-Pr), in which case the trans complex was observed. The Pt(IV) difluoro compounds $(R_3P)_2Ar_2PtF_2$ were obtained by reacting the Pt(II) diaryl precursors with XeF_2. The fluoro ligands are located in the trans-position relative to the aryl groups in the overall octahedral environment. The representative Pt(II) and Pt(IV) difluoro complexes were characterized by X-ray crystallography. All fluoro compounds react rapidly with chlorotrimethylsilane to give the corresponding chloro complexes. The Pt(IV) difluorides are remarkably stable in the C–C reductive elimination reaction, relative to their dichloro analogs which reductively eliminate diaryl within several hours at 45 °C in *N*-methylpyrrolidone. It was found that phosphine dissociation from the octahedral Pt(IV) complex is essential for the reductive elimination reaction to take place, the difluoro complex being kinetically stable even at 60 °C.

Introduction

Palladium and platinum phosphine complexes are of great interest to organometallic chemistry and catalysis.[1] Many important textbook examples of oxidative addition, reductive elimination, and ligand exchange reactions have been performed on such complexes.[2] In most of these transformations the participation of a metal halide complex is involved, with chloride, bromide, or iodide being the natural ligands of choice. In contrast, little is known about palladium and platinum phosphine complexes containing a fluoro ligand.[3–5] Only recently did adequately characterized fluoro complexes, which show high reactivity in nucleophilic substitution reactions, start to appear in the literature.[6,7] Still, palladium and platinum phosphine complexes with more than one fluoro ligand were believed to be too unstable to be isolated in their pure form.[6a,8] The reasons for the limited stability of late transition metal complexes with the fluoride ligand

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are hard to evaluate conclusively, and it is often attributed to incompatibility of a "soft" transition metal acid with a very "hard" fluoride base.[3,9] Recently, Mezzetti and coworkers revisited the "hardening" the metal center, via either coordinative unsaturation or electrostatic interactions, as an essential requirement for metal−fluoride stabilization.[10] Unfavorable $p\pi-d\pi$ four electron repulsions may also be operative in late transition metal fluoro complexes.[11,12] The π-donation properties of the fluoride ion are strongest among the halide ligands, a notion supported by CO IR frequency analysis.[13] Due to the relative shortage of the late transition metal fluoro complexes, the experimental and theoretical comparative studies were often performed on different metal systems, which varied in the number and types of ligands, and their coordination geometries.[10,11]

We recently reported the first palladium(II) and platinum(II) complexes of the formula L_2MF_2, where L_2 is a cis-chelating diphosphine ligand (eq 1).[14] We hereby present the extension of our studies toward the synthesis and comparative reactivity of a series of Pt(II) and Pt(IV) difluoro complexes with *monodentate* phosphine ligands. Our results indicate that such complexes may be more common than previously believed and that the fluoro ligand can have a stabilizing effect on its metal complexes.

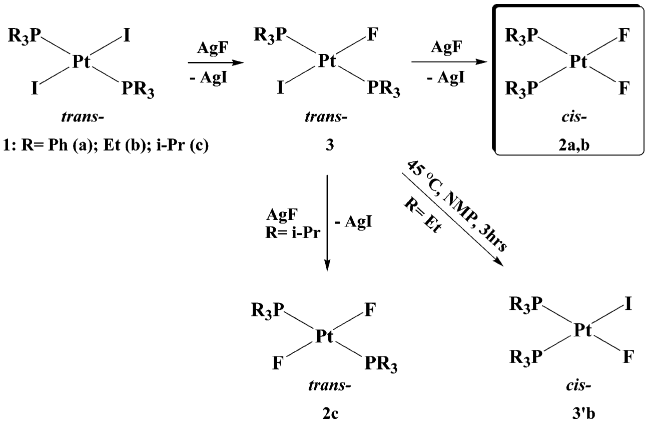
$$L_2M(R)_2 + XeF_2 \xrightarrow[-\ Xe,\ -\ R\text{-}R]{CH_2Cl_2,\ -30^o\ -\ RT} \boxed{L_2MF_2} \xleftarrow[-\ 2\ AgI]{CH_2Cl_2,\ RT} L_2MI_2 + 2\ AgF \qquad (1)$$

M= Pd, Pt; L_2= *cis*-chelating diphosphine ligand

Results and Discussion

1. Synthesis and Reactivity of Platinum(II) Difluoro Complexes. While palladium(II) and, especially, platinum(II) square planar complexes of the formula $(R_3P)_2MX_2$ (X = Cl, Br, I) have been extensively studied to evaluate kinetic and thermodynamic parameters of ligand exchange processes,[15] similar studies on fluorides have been hindered by the instability of such complexes. Several claims to have made the difluoro platinum complexes bearing phosphine ligands did not provide definitive characterization of the resulting products.[16] Only recently were the first fully characterized $(R_3P)_2MF_2$ (M = Pd, Pt) complexes reported by us.[14] While the analogous palladium(II) complexes could only be isolated with the cis-chelating tri*alkyl*phosphine ligands, the platinum complexes were also obtained with cis-chelating *aryl*phosphines as well as the monodentate triphenylphosphine. In the latter case, the formation of the *trans*-$(Ph_3P)_2PtF_2$ was mistakenly reported.[14]

Scheme 1



We found that *cis*-$(Ph_3P)_2PtF_2$ (**2a**) can be readily prepared by reacting $(Ph_3P)_2PtI_2$ (**1a**) with 3 equiv of AgF in CH_2Cl_2 for 3 h (Scheme 1). The ^{31}P (5.03 ppm) and ^{19}F NMR (−216.34 ppm) spectra of **2a** exhibit the characteristic AA′MXX′ pattern (for the ^{195}Pt isotope) with a calculated trans-J_{PF} of 180.0 Hz. Performing the reaction with 1 equiv of AgF in CH_2Cl_2 showed the formation of small amounts of *trans*-$(Ph_3P)_2Pt(I)F$ (**3a**) as an intermediate in the halide exchange reaction. Slowing the reaction, using benzene as a solvent, resulted in the formation of **3a** as a major reaction product. The ^{19}F NMR spectrum of **3a** showed a triplet at −310.38 ppm (J_{PF} = 19.1 Hz, J_{PtF} = 543.1 Hz), while the ^{31}P NMR spectrum showed the doublet at 13.61 ppm (J_{PtP} = 2747.1 Hz). Similarly, reacting *trans*-$(Et_3P)_2PtI_2$ with 3 equiv of AgF gave the *cis*-difluoro complex **2b** (^{19}F NMR, −225.31 ppm; AA′MXX′ for the ^{195}Pt isotope), and the corresponding trans-intermediate **3b** was observed during the reaction (triplet in ^{19}F NMR spectrum at −335.20 ppm, J_{PF} = 18.6 Hz, J_{PtF} = 494.4 Hz). Upon being warmed to 45 °C, *trans*-**3b** underwent clean conversion to *cis*-**3′b**. Thus, there is a strong thermodynamic preference for the overall cis-configuration in both mono- and difluoroplatinum(II) complexes. Interestingly, there is a dramatic difference (ca. 90 ppm) in the ^{19}F NMR chemical shifts upon moving from the *trans*-**3b** to *cis*-**3′b**, which exhibited a doublet of doublets in the ^{19}F NMR spectrum at −248.10 ppm ($J_{PtransF}$ = 166.9 Hz, J_{PcisF} = 22.3 Hz).[17]

When *trans*-$(i\text{-}Pr_3P)_2PtI_2$ was treated with an excess of AgF in CH_2Cl_2 for 3 h, the formation of *trans*-$(i\text{-}Pr_3P)_2Pt(I)F$ (**3c**) was observed as the major compound. Complex **3c** showed a triplet at −329.68 ppm (J_{PF} = 12.6 Hz, J_{PtF} = 520.6 Hz) in the ^{19}F NMR spectrum and a doublet at 31.09 ppm in the

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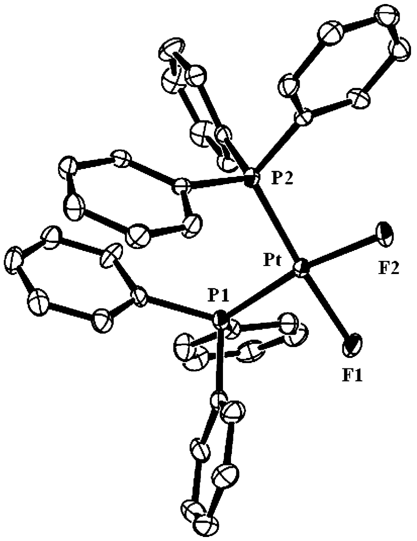
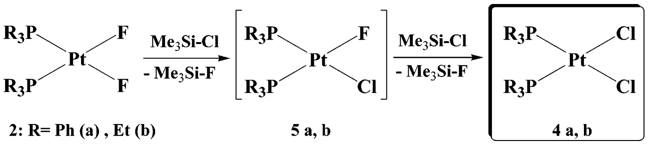


Figure 1. Selected bond distances (Å) and bond angles (deg) for a molecule of **2a**: Pt−F1 1.999(2), Pt−F2 2.016(2), Pt−P1 2.2198(9), Pt−P2 2.2304(10); F1−Pt−F2 84.81(9), F1−P−P1 91.05(7), F1−Pt−P2 169.92(7), F2−Pt−P1 175.74(7), F2−Pt−P2 85.27(7), P1−Pt−P2 98.89(3).

Scheme 2

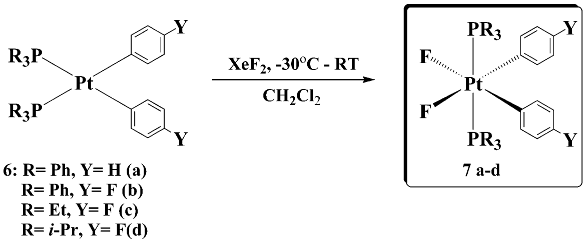


^{31}P NMR spectrum. Prolonged treatment (2 days) with an excess of AgF did not produce pure *trans*-(i-$Pr_3P)_2PtF_2$ (**2c**) although it was obtained as the major complex as indicated by a triplet at −455.90 ppm ($J_{PF} = 11.2$ Hz, $J_{PtF} = 973.6$ Hz) in the ^{19}F NMR spectrum and a triplet at 34.87 ppm ($J_{PtP} = 2822.4$ Hz) in the ^{31}P NMR spectrum. Large amounts of decomposition products were also observed in this case.

Colorless crystals of **2a** were obtained by slow pentane diffusion into the CH_2Cl_2 solution. The platinum center is located in the square planar arrangement (Figure 1) with the angle between the two fluoro ligands (84.81(9)°) being substantially smaller than that between the two phosphine ligands (98.89(3)°), indicating steric repulsions between the latter. The Pt−F1 and Pt−F2 distances of 1.999(2) and 2.016(2) Å, respectively, are significantly shorter than in *trans*-$(Ph_3P)_2Pt(Ph)F$ (2.117(3) Å).[7a] The fluoro ligands are also involved in intermolecular interactions with aromatic hydrogens of the phosphine ligands (2.276 and 2.376 Å). Shorter Pt−P bond distances in **2a** (2.2198(9) and 2.2304(10) Å) compared with those in *cis*-$(Ph_3P)_2PtCl_2$ (2.251(2) and 2.265(2) Å)[18] provide evidence of the weak trans-influence of the fluoride.

Complexes **2a**,**b** reacted rapidly with 2 equiv of chloro(trimethyl)silane (Me_3SiCl) to give Me_3SiF and the *cis*-dichloro complexes **4a**,**b** (Scheme 3). When less than 2 equiv of the organic chloride was used, a mixture of **2**, **4**, and the monosubstituted complex *cis*-$(R_3P)_2Pt(Cl)F$ (**5a**,**b**) was formed (Scheme 2). Complexes **5** show first-order patterns in their ^{19}F and ^{31}P NMR spectra (Experimental Section), in agreement with the proposed cis-orientation of the two phosphine ligands. Similarly, reacting **2** with <2 equiv of Me_3SiI gave a mixture of unreacted **2**, *cis*-diodo complexes **1**, and the monosubstituted complex *cis*- $(R_3P)_2Pt(I)F$ (**3′a**,**b**). Thus, the reactivity of the Pt(II) difluoro complexes **2** is similar to that observed for the Pd(II) and Pt(II) monofluoro complexes, which rapidly fluorinate strongly electrophilic organic reagents.[6,7]

Scheme 3



2. Synthesis and Reactivity of the Platinum(IV) Difluoro Complexes. A Pt(IV) difluoro complex was previously observed with only pyridine ligands, and no corresponding phosphine complexes were reported.[19] We prepared the bis(triphenylphosphine)platinum(IV) difluoro complex **7a** by reacting the diphenylplatinum(II) precursor (**6a**) with XeF_2 in CH_2Cl_2 (Scheme 3).[20] This reaction was previously reported to produce the *trans*-$(Ph_3P)_2PtF_2$.[14] The assignment was based on the ^{31}P and ^{19}F NMR spectra, which showed the expected pattern of two phosphine and two fluoro ligands being symmetrical and in the mutual cis-arrangement. While formation of biphenyl and the corresponding *cis*-$(R_3P)_2PtF_2$ complexes was observed with cis-chelating diphosphine ligands (eq 1), only trace amounts of carbon−carbon reductive elimination products were obtained in the reaction of **6a** with XeF_2. As monitoring the formation of biphenyl by ^1H NMR was obscured by triphenylphosphine aromatic signals, we also prepared the *para*-fluorophenyl analogs **6b** and **7b**, which would show the characteristic singlet in the ^{19}F NMR spectrum at −115.8 ppm if the formation of 4,4′-difluorobiphenyl occurred during the reaction.

The ^{19}F NMR spectrum of **7b** shows a broad singlet at −255.22 ppm, which resolves into a triplet ($J_{PtF} = 122.3$ Hz) in *N*-methylpyrrolidinone (NMP). Complex **7b** also shows a singlet at −119.83 ppm due to the *para*-fluoro substituent. The ^{31}P NMR spectrum of **7b** exhibits a triplet at 8.32 ppm with Pt−P satellite signals of 2070.4 Hz. Similar to the triphenylphosphine complexes, the corresponding Pt(IV) complexes **7c**,**d**, containing the trialkylphosphine ligands (Et_3P and i-Pr_3P), were also prepared using the same procedure (Scheme 1). Complex **7c** shows a triplet in the ^{31}P NMR spectrum at 7.03 ppm ($J_{FP} = 21.5$ Hz, $J_{PtP} = 1877.7$

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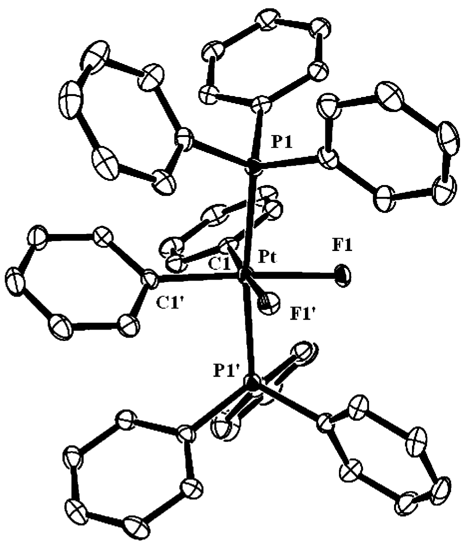
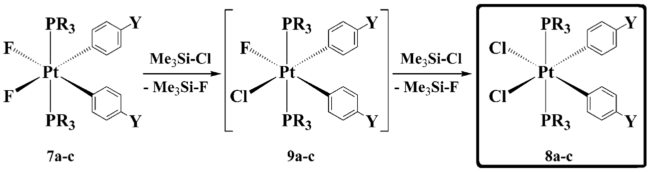


Figure 2. Selected bond distances (Å) and bond angles (deg) for a molecule of **7a**: Pt−F1 2.0892(14), Pt−C1 2.039(2), Pt−P1 2.3846(6); C1−Pt−C1′ 95.30(14), C1−Pt−F1 86.56(9), C1−Pt−F1′ 176.94(7), F1−Pt−F1′ 91.70(8), P1−Pt−P1′ 171.45(3).

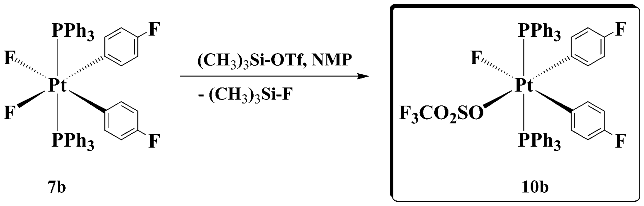
Hz) and a triplet in the ^{19}F NMR spectrum at −270.89 ppm (J_{PtF} = 104.3 Hz) in NMP. In the case of **7d** the resulting complex could not be purified due to its high solubility in hexane.

Crystals of **7a**, suitable for single-crystal X-ray analysis, were obtained by slow evaporation of its CH_2Cl_2 solution. The crystal structure of **7a** (Figure 2) shows the platinum atom in a distorted octahedral environment, with the phosphine ligands tilted toward the fluorides (P1−Pt−P1′ = 171.45(3)°). The platinum fluoride distances of 2.0892(14) Å are slightly shorter than those in *trans*-$(Ph_3P)_2Pt(Ph)F$ (2.117(3) Å),[7a] while the Pt1−C1 distance of 2.039(2) Å is longer than that in the Pt(II) case (1.978(5) Å). The Pt−F1 distance in **7a** also correlates well with Pt−F distances in Pt(II) complexes that have the fluoro ligand trans to the phosphine (2.043(7) and 2.03(1) Å in $(Et_3P)_3PtF^+$ and *cis*-$(Ph_3P)_2Pt(CH(CF_3)_2)F$, respectively).[7f,21] It is, however, significantly longer than the Pt−F bonds in the *trans*-$(py)_4PtF_2^{2+}$ complex (1.938(10) and 1.943(10) Å).[19] The C1−Pt−C1′ angle of 95.30(14)° is larger than C1−Pt−F1 (86.56(9)°) as a result of steric repulsions between the bulkier phenyl groups. These repulsions are further evident in the significant deviation (30.91°) of the two phenyl ligands from the equatorial plane.[22] There is a strong interaction between the fluoro ligands and one of the aromatic protons of each Ph_3P, manifested in the very short nonbonding distance of 2.059 Å.[23] The intramolecular and intermolecular nonbonding interactions between one of the aromatic hydrogens of the phenyl substituent and the fluoro ligands (2.491 and 2.367 Å, respectively) are also worth noting.

Scheme 4



Scheme 5



Reacting complexes **7a**−**c** with 2 equiv of Me_3SiCl resulted in the rapid formation of Me_3SiF and the Pt(IV) dichloro complexes **8a**−**c** (Scheme 4). Replacement of the fluoro ligand in **7b** with the chloride results in the upfield shift of the aromatic fluoro signal in the ^{19}F NMR spectrum, which appears at −121.03 ppm in **8b**. It also results in the decrease in J_{PtP} by ca. 100 Hz in the ^{31}P NMR spectrum—an indication of lower electron density at the metal center.[24] Similar to **2**, addition of less than 2 equiv of Me_3SiCl in CH_2Cl_2 or NMP gave a mixture of **7**, **8**, and the monosubstituted complex **9** (Scheme 4). Complexes **7** reacted with Me_3SiCl at significantly slower rates than complexes **2**. When a 10:1 mixture of **7b** and **2a** was treated with 1 equiv of Me_3SiCl (per **2a**), only **5a** was observed in the ^{19}F NMR spectrum along with the unreacted **2a** and **7b**. Formation of **5a** was also noted in the ^{31}P NMR spectrum. However, reaction of an NMP solution of **7b** with 2 equiv of Me_3SiOTf resulted in the monosubstituted complex **10b** as the only product (Scheme 5).

This compound could be isolated by performing the reaction in a toluene−NMP (9:1) mixture followed by the precipitation of **10b** with hexane. No formation of the disubstituted product was observed, even when an excess (3−5 equiv) of Me_3SiOTf was used. The ^{19}F NMR spectrum of **10b** showed a triplet at −274.52 ppm (J_{PtF} = 97.0 Hz) and two singlets, due to inequivalent fluorine atoms of the aromatic ligands, at 118.70 and 118.04 ppm. The ^{31}P NMR spectrum of **10b** exhibited a doublet at 4.27 ppm. The reaction with Me_3SiOTf is solvent dependent. A different reactivity pattern was observed in CH_2Cl_2, where substitution of both fluoro ligands occurs rapidly to give 2 equiv of Me_3SiF and the ditriflate complex. The latter could not be isolated at room temperature, and a number of decomposition products were observed. While the polarity of CH_2Cl_2 is significantly lower than that of NMP (ϵ = 9 vs 32.5, respectively),[25] it is inclined to form hydrogen bonds with the coordinated fluoride.[26] Thus, it is possible that, in a CH_2Cl_2 solution, formation of hydrogen bonds might be responsible for the higher lability and reactivity of the fluoro

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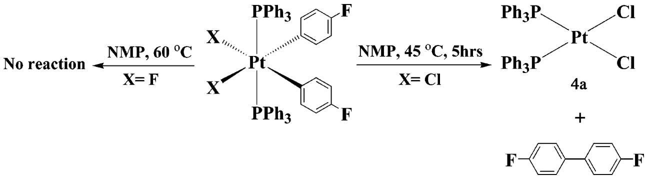
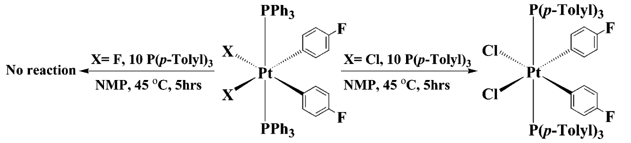
Scheme 6



Scheme 7



ligand compared with that in an NMP solution. This notion is supported by the broadening of the ^{19}F NMR signals in **7** in CH_2Cl_2 vs NMP. The addition of a 5−10-fold excess of methanol to solutions of **7b**,**c** in NMP caused no changes in their ^{19}F and ^{31}P NMR spectra over the period of 1 day.

While complex **7b** was stable when heated at 60 °C in NMP overnight, complex **8b** underwent a rapid reductive elimination to give **4** and 4,4′-difluorobiphenyl quantitatively within 5 h at 45 °C (Scheme 6). The formation of the latter was confirmed by ^{19}F NMR spectroscopy, EI-MS, and an authentic sample. The Pt(IV) Et_3P complexes were significantly more stable toward the reductive elimination, with both **2c** and **8c** unchanged after 12 h at 80 °C. Interestingly, **10b** is less reactive toward the C−C reductive elimination than **8b**, even though the platinum center is less electron rich and a highly labile ligand (OTf^-) is present.[27] The C−C reductive elimination from a Pt(IV) center is generally preceded by ligand dissociation[28] and, thus, could greatly benefit from the presence of a labile ligand, such as triflate.[29,30] Therefore, the presence of a *single* fluoro ligand in **10b** is sufficient to overcome both the electronic and (anionic) ligand lability factors (when compared with **8b**) that generally strongly facilitate the reductive elimination processes. When a 10-fold excess of Ph_3P was added to a solution of **8b** in NMP, very little C−C reductive elimination was observed after 5 h at 45 °C. Addition of a 10-fold excess of (p-Tolyl)$_3$P to a solution of **7b** in NMP showed no ligand exchange at 60 °C, while complex **8b** underwent a complete exchange reaction giving (p-Tolyl)$_3P_2Pt(Ar)_2Cl_2$ at 45 °C after 5 h (Scheme 7).

The reduced lability of the phosphine ligand in the difluoro complex **7b** can be attributed to lower electron density at the metal center bound to the most electronegative atom. Although ligand dissociation could provide partial relief of the filled-filled pπ−dπ repulsions present in the octahedral configuration,[11,31,32] this would only happen if the resulting unsaturated complex adapted a trigonal bipyramidal configuration. In our system, phosphine dissociation would only result in a square pyramidal structure due to the presence of two fluoro ligands trans to two aryl groups.

The overall stability of the Pt(IV) fluoro complexes in comparison with the corresponding chloro analogs is a rare example of a dramatic reactivity change upon replacing one halide with another.[33,34]

3. Summary. Platinum(II) square planar complexes $(R_3P)_2PtF_2$ were prepared and fully characterized. These compounds exhibit a strong preference for the cis-geometry, unless steric hindrance (R = i-Pr) exists. We also prepared octahedral Pt(IV) difluoro complexes $(R_3P)_2Ar_2PtF_2$ with the fluoro ligands in the trans position to the aryl groups. The platinum(II) and platinum(IV) difluoro complexes are stable at room temperature in both solution and the solid state, although they rapidly fluorinate strong organic electrophiles. Interestingly, the fluoro ligands stabilize Pt(IV) complexes which show greater stability in the C−C reductive elimination reaction than the analogous dichoro complexes. This stabilization is caused by stronger binding of the phosphine ligand in the Pt(IV) fluoro complexes, as phosphine dissociation from the octahedral complex was found to be essential for the reductive elimination process.

Experimental Section

General Methods. All operations with air- and moisture-sensitive compounds were performed in a nitrogen-filled Innovative Technology glovebox. All solvents were of reagent grade or better. Hexane, toluene, benzene, and THF were distilled over sodium/benzophenone ketyl. CH_2Cl_2 and NMP were refluxed over CaH_2 and distilled. All solvents were degassed and stored under high-purity nitrogen after distillation. All deuterated solvents (Aldrich) were stored under high-purity nitrogen on molecular sieves (3 Å). Commercially available reagents were used as received. Silver(I) fluoride and xenon difluoride were purchased from Matrix Scientific. **Caution:** *XeF_2 is a strong oxidant and may cause a fire upon contact with combustible materials.* $(R_3P)_2PtAr_2$ were prepared by ligand exchange with (1,5-cyclooctadiene)$PtAr_2$ as previously reported.[35] ^{1}H, ^{31}P, ^{19}F, and ^{13}C NMR spectra were recorded on Bruker AC 200 MHz and Bruker AMX 400 MHz spectrometers. ^{1}H and ^{13}C NMR signals are reported in ppm downfield from TMS. ^{1}H signals are referenced to the residual proton (7.26 ppm for $CDCl_3$) of a

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(27) Continued heating at higher temperatures gave a number of decomposition products, which could be the result of instability of $(Ph_3P)_2PtF(OTf)$, formed after the reductive elimination step. See: Thorn, D. L. *Organometallics* **1998**, *17*, 348 and ref 7b.

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Table 1. Selected ^{19}F NMR Signals of Complexes **2**−**10**

complex	^{19}F signal (ppm)^{a}	J_{PtF} (Hz)	J_{PF} (Hz)
2a	−216.34	108.0^{b}	180.0^{b} 18.0
2b	−225.31^{b}		
2c	−455.90^{c}	973.6	11.2
3a	−310.38^{d}	543.1	19.1
3′a	−246.99^{d}	68.8	181.9 28.6
3b	−335.20^{c}	494.4	18.6
3′b	−248.10^{d}		166.9 22.3
3c	−329.68^{c}	520.6	12.6
7a	−252.49	104.2^{d}	23.6
7b	−255.22 −119.83	122.3^{b}	21.5
7c	−270.89 −119.71	104.3^{d}	21.6
7d	−261.03^{c} −120.74		17.8
9b	−280.31^{c} −121.93, −121.86		19.9
9c	−281.92^{c} −120.99, −120.22		22.2
10b	−274.52^{d} −118.70, −118.04	97.0	18.8
10c	−263.81^{e} −117.69, −116.93	75.9	20.2

^{a} The signals are reported in $CDCl_3$, unless stated otherwise. ^{b} AA′MXX′ system (∼30%). ^{c} In CH_2Cl_2. ^{d} In NMP. ^{e} In C_6D_6.

Table 2. Crystal Structure Information for Complexes **7a** and **2a**

	7a	**2a**
empirical formula	$C_{48}H_{40}F_2P_2Pt$	$C_{36}H_{30}F_2P_2Pt$
fw	911.83	757.63
temp (K)	110(2)	110(2)
wavelength (å)	0.710 73	0.710 73
radiatn type	Mo Kα	Mo Kα
cryst system	monoclinic	monoclinic
space group	$C2/c$	$P2_1/c$
unit cell dimens		
a (Å)	20.5030(3)	9.7590(2)
b (Å)	9.85000(10)	33.2970(9)
c (Å)	19.2560(3)	10.0480(2)
α (deg)	90.00	90.00
β (deg)	102.0220(5)	116.1981(13)
γ (deg)	90.00	90.00
cell vol (Å^3)	3803.55(9)	2929.64(12)
Z	4	4
calcd density (g m^{-3})	1.592	1.718
cryst descriptn	colorless prisms	colorless prisms
cryst size (nm)	0.20 × 0.20 × 0.15	0.20 × 0.15 × 0.15
θ range for data collcn (deg)	2.45−27.86	2.34−28.24
index ranges	$0 \leq h \leq 26$ $0 \leq k \leq 12$ EnDash25 $\leq l \leq 24$	$0 \leq h \leq 12$ $0 \leq k \leq 43$ EnDash13 $\leq l \leq 12$
reflcns collcd/unique	4509/4288	6932/5681
refinement method	full-matrix F^2	full-matrix F^2
goodness-of-fit	1.054	1.026
data/restrains/params	4509/0/240	6932/0/370
R_1 ($I > 2\sigma(I)$)	0.0249	0.0450
wR_2 (all data)	0.0588^{a}	0.0736^{b}

^{a} $w = 1/[\sigma^2(F_o^2) + (0.0311P)^2 + 6.4988P]$, where $P = (F_o^2 + 2F_c^2)/3$. ^{b} $w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 3.2056P]$, where $P = (F_o^2 + 2F_c^2)/3$.

deuterated solvent, and for ^{13}C NMR spectra, the signal of $CDCl_3$ (77.00 ppm) was used as a reference. ^{31}P chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% phosphoric acid sample. ^{19}F chemical shifts are reported in ppm downfield from $CClF_3$ and referenced to an internal C_6F_6. Table 1 shows selected ^{19}F NMR signals of reported compounds. All measurements were performed at 22 °C in $CDCl_3$ unless stated otherwise. The second-order coupling constants were deduced using the gNMR simulation program. Table 2 shows crystal structure information for complexes **2a** and **7a**. Elemental analyses were performed in the laboratory for microanalysis at the Hebrew University of Jerusalem.

Synthesis of 2. In a typical procedure, **1a** or **1b** (0.02 mmol) in 2 mL of CH_2Cl_2 was vigorously stirred with 8 mg (0.063 mmol) of AgF for 3 h. The suspension was filtered through a cotton pad and Celite, the filtrate was concentrated in a vacuum, and 3 mL of hexane was added. The resulting white precipitate was collected and dried in a vacuum. Yield: 90−95%. In the case of **1c**, 10 equiv of AgF were used and the suspension was stirred for 2 days. After filtration, the solvent was evaporated and the product extracted with hexane (ca. 85% pure by NMR).

2a: ^{31}P{^{1}H} 5.03 (AA′MXX′, ∼30%, $J_{F(trans)P} = 180.0$ Hz, $J_{PtP} = 3966.4$ Hz, $J_{P(cis)P} = 21.0$ Hz); ^{19}F{^{1}H} −216.34 (A = A′MXX′, $J_{PtF} = 108.0$ Hz, $J_{P(cis)F} = 18.0$ Hz, $J_{F(cis)F} = 88.0$ Hz); ^{1}H 6.92−7.49 (m, Ar-*H*); FAB-MS M$^+$ (M$^+$ calcd for $C_{36}H_{30}F_2P_2Pt$): *m/z* 757 (*m/z* 757). Anal. Found (calcd) for $C_{36}H_{30}F_2P_2Pt$: C, 56.26 (57.07); H, 4.46 (3.99).

2b: ^{31}P{^{1}H} 3.18 (AA′MXX′, ∼30%, $J_{F(trans)P} = 181.0$ Hz, $J_{PtP} = 3748.1$ Hz); ^{19}F{^{1}H} −225.31 (AA′MXX′); ^{1}H 1.20 (m, CH_3, 18H), 1.86 (m, CH_2, 12H); ^{13}C{^{1}H} 7.85 (s, *C*H_3), 15.08 (br s, *C*H_2). Anal. Found (calcd) for $C_{12}H_{30}F_2P_2Pt$: C, 30.75 (30.71); H, 6.71 (6.44).

2c: ^{31}P{^{1}H} 34.87 (t, $J_{FP} = 11.2$ Hz, $J_{PtP} = 2822.4$ Hz); ^{19}F{^{1}H} −455.90 (t, $J_{PtF} = 973.6$ Hz). FAB-MS M$^+$ (M$^+$ calcd for $C_{18}H_{42}F_2P_2Pt$): *m/z* 553 (*m/z* 553).

Observations of 3 and 3′. 3a: A solution of **1a** (0.02 mmol) in C_6H_6 (2 mL) was treated with AgF (0.03 mmol). The resulting suspension was stirred vigorously for 15 h. Further stirring led to the corresponding difluoride complex. The C_6H_6 was concentrated, and 3 mL of hexane was added resulting in product precipitation as a yellow powder (95% pure by NMR). ^{31}P{^{1}H}: 13.61 (d, $J_{FP} = 19.1$ Hz, $J_{PtP} = 2747.1$ Hz). ^{19}F{^{1}H}: −310.38 (t, $J_{PtF} = 543.1$ Hz). Addition of 1 equiv of $(CH_3)_3SiI$ to a solution of **2a** in CH_2Cl_2 or NMP resulted in the formation of **3′**, together with **1a** and the unreacted **2a**. **3′**: ^{31}P{^{1}H} 11.88 (overlapped), 1.95 (dd, $J_{PaPb} = 13.8$ Hz, $J_{F(trans)Pb} = 181.9$ Hz, $J_{PtPb} = 2991.0$ Hz); ^{19}F{^{1}H} −246.99 (dd, $J_{F(cis)P} = 28.6$ Hz, $J_{PtF} = 68.8$ Hz).

3b: A solution of **1b** (0.02 mmol) in CH_2Cl_2 (2 mL) was treated with AgF (0.02 mmol). The resulting suspension was vigorously stirred for 30 min resulting in a mixture of **2b** (30%) and **3b** (70%). ^{31}P{^{1}H}: 12.07 (d, $J_{FP} = 18.6$ Hz, $J_{PtP} = 2473.8$ Hz). ^{19}F{^{1}H}: −335.20 (t, $J_{PtF} = 494.4$ Hz). Warming this mixture in NMP at 45 °C for 5 h showed complete conversion of **3b** into the **3′**. ^{31}P{^{1}H}: 16.93 (m, $J_{PtPa} = 3501.8$ Hz), −1.47 (dd, $J_{PtPb} = 4469.9$ Hz, $J_{PaPb} = 14.9$ Hz, $J_{F(trans)Pb} = 166.9$ Hz). ^{19}F{^{1}H}: −248.10 (dd, $J_{F(cis)P} = 22.3$ Hz). **3′** was also observed in the reaction mixture upon addition of 1 equiv of $(CH_3)_3SiI$ to a solution of **2b** in CH_2Cl_2 or NMP.

3c: A solution of **1c** (0.03 mmol) in CH_2Cl_2 (2 mL) was treated with AgF (0.06 mmol). The resulting suspension was stirred vigorously for 4 h and filtered. The CH_2Cl_2 solution was concentrated, and 3 mL of hexane was added resulting in the product precipitating as a yellow powder (95% pure by NMR). ^{31}P{^{1}H}: 31.09 (d, $J_{PF} = 12.6$ Hz, $J_{PtP} = 2485.3$ Hz). ^{19}F{^{1}H}: −329.68 (t, $J_{PtF} = 520.6$ Hz). ^{1}H NMR: 1.38 (m, CH_3, 36H), 2.88 (m, C-*H*, 6H). FAB-MS M$^+$ (M$^+$ calcd for $C_{18}H_{42}FIPt$): *m/z* 661 (*m/z* 661).

Synthesis of 7a−d. In a typical procedure, a cold (−30 °C) freshly prepared solution of XeF_2 (0.034 mmol in 1 mL) was quickly added to a solution of **1** (0.034 mmol) in CH_2Cl_2 (1 mL) at −30 °C. The reaction mixture was left at this temperature for 10 min and then slowly warmed to room temperature. The ^{31}P-{^{1}H} NMR spectrum showed the disappearance of the starting material and formation of the corresponding difluoride complex. The CH$_2$Cl$_2$ was concentrated, and 3 mL of hexane was added resulting in the product precipitating as white powder in high yields (92−97%). **7d** was too soluble in hexane to be isolated by precipitation and purified. The XeF$_2$ solution must be reacted within 15−30 min of preparation to avoid the formation of side products.

7a: ^{31}P{^{1}H} 8.30 (t, J_{FP} = 23.6 Hz, J_{PtP} = 2130.4 Hz); ^{19}F{^{1}H} −252.49 (br s, 2F) which appears as triplet in NMP (J_{PtF} = 104.2 Hz); ^{1}H 6.32 (m, Ar-*H*), 6.73 (m, Ar-*H*), 6.77−7.74 (m, Ar-*H*). Anal. Found (calcd) for C$_{48}$H$_{40}$F$_2$P$_2$Pt: C, 62.20 (63.20); H, 4.63 (4.42).

7b: ^{31}P{^{1}H} 8.32 (t, J_{FP} = 21.5 Hz, J_{PtP} = 2070.4 Hz); ^{19}F{^{1}H} −255.22 (br s, 2F) which appears as triplet in NMP (J_{PtF} = 122.3 Hz), −119.83 (s, Ar-*F*, 2F); ^{1}H 6.14 (br t, *J* = 8.7 Hz, Ar-*H*, 4H), 6.89 (br s, 4H), 7.04−7.43 (m, 30H); ^{13}C{^{1}H} 112.73 (m, Pt−*Ar*), 126.43 (m, Ar), 128.17 (t, *J* = 5.5 Hz, Ar), 131.02 (s, Ar), 134.84 (m, Ar), 135.55 (br s, Ar), 137.21 (br s, Ar), 161.10 (br d, F-*Ar*, $J_{\mathrm{F-C}}$ = 242.2 Hz). Anal. Found (calcd) for C$_{48}$H$_{38}$F$_4$P$_2$Pt: C, 61.63 (60.82); H, 4.39 (4.04).

7c: ^{31}P{^{1}H} 7.03 (t, J_{FP} = 21.6 Hz, J_{PtP} = 1877.7 Hz); ^{19}F{^{1}H} −270.89 (br-s, Pt−*F*, 2F) which appears as triplet in NMP (J_{PtF} = 104.3 Hz), −119.71 (s, Ar-*F*, 2F); ^{1}H NMR 0.79 (m, C*H*$_3$, 18H), 1.68 (m, C*H*$_2$, 12H), 6.91 (br t, *J* = 8.6 Hz, Ar-*H*, 4H), 7.76 (br s, Ar-*H*, 4H); ^{13}C{^{1}H} 7.66 (s, *C*H$_3$), 12.48 (m, *C*H$_2$), 114.57 (m, Pt−*Ar*), 116.39 (m, Ar), 136.95 (br s, Ar), 162.24 (d, F−*C*, $J_{\mathrm{F-C}}$ = 242.6 Hz). Anal. Found (calcd) for C$_{24}$H$_{38}$F$_4$P$_2$Pt·0.2CH$_2$Cl$_2$: C, 42.84 (42.61); H, 5.73 (5.66).

7d: ^{31}P{^{1}H} 14.27 (t, J_{FP} = 17.8 Hz, J_{PtP} = 1762.5 Hz); ^{19}F-{^{1}H} −261.03 (br s, Pt−*F*, 2F), −120.74 (s, Ar-*F*, 2F).

Synthesis of 8b,c. A solution of 0.02 mmol of **7b**,**c** in 1 mL of CH$_2$Cl$_2$ was treated with 2 equiv of (CH$_3$)$_3$SiCl. The ^{31}P{^{1}H} and ^{19}F{^{1}H} NMR spectra indicated the disappearance of the starting material and formation of the corresponding dichloride complex. The CH$_2$Cl$_2$ was concentrated, and 3 mL of hexane was added resulting in product precipitation as a white powder (90−94% isolated yields).

8a: ^{31}P{^{1}H} 1.94 (s, J_{PtP} = 2014.7 Hz); ^{1}H NMR 6.33−7.74 (m, Ar-*H*); ^{13}C{^{1}H} 114.53 (m, Pt−*Ar*), 127.56 (br s, *Ar*), 128.28 (m, *Ar*), 129.31 (br s, *Ar*), 130.94 (br s, *Ar*) 134.83 (br s, *Ar*), 135.29 (m, *Ar*) 139.49 (br s, *Ar*).

8b: ^{31}P{^{1}H} 1.59 (s, J_{PtP} = 1966.1 Hz); ^{19}F{^{1}H} −121.03 (s, Ar-*F*, 2F); ^{1}H NMR 6.15 (br s, Ar-*H*, 4H), 7.00−7.50 (m, Ar-*H*, 34H); ^{13}C{^{1}H} 112.79 (m, Pt−*Ar*), 127.65 (t, *J* = 5.5 Hz, *Ar*), 128.03 (m, *Ar*), 130.76 (br s, *Ar*), 134.99 (br m, *Ar*) 135.85 (br s, *Ar*), 140.19 (br s, *Ar*). Anal. Found (calcd) for C$_{48}$H$_{38}$Cl$_2$F$_2$P$_2$Pt: C, 58.45 (58.78); H, 4.19 (3.91).

8c: ^{31}P{^{1}H} −3.91 (s, J_{PtP} = 1784.1 Hz); ^{19}F{^{1}H} −120.33 (s, Ar-**F**, 2F); ^{1}H NMR 0.94 (m, C*H*$_3$, 18H), 1.98 (m, C*H*$_2$, 12H), 6.75 (br t, *J* = 8.5 Hz, Ar-*H*, 4H), 7.24 (br s, Ar-*H*, 4H); ^{13}C{^{1}H} 8.54 (s, *C*H$_3$), 14.24 (m, *C*H$_2$), 114.26 (m, Pt−*Ar*), 122.65 (br s, *Ar*), 138.87 (br s, *Ar*), 161.41 (d, F-*Ar*, J_{FC} = 244.5 Hz). Anal. Found (calcd) for C$_{24}$H$_{38}$Cl$_2$F$_2$P$_2$Pt: C, 41.90 (41.63); H, 5.65 (5.53).

Observations of 9b,c. To a solution of **7b**,**c** in NMP or CH$_2$Cl$_2$ (1 mL) was added 1 equiv of (CH$_3$)$_3$SiCl. Complexes **9b**,**c** were observed in the mixture with **8b**,**c** and unreacted **7b**,**c**.

9b (NMP): ^{31}P{^{1}H} 3.39 (d, J_{FP} = 19.9 Hz, J_{PtP} = 1939.0 Hz); ^{19}F{^{1}H} −280.31 (m, Pt−*F*, 1F), −121.93 (s, Ar-*F*, 1F), 121.86 (s, Ar-*F*, 1F).

9c (CH$_2$Cl$_2$): ^{31}P{^{1}H} 0.77 (d, J_{FP} = 22.2 Hz, J_{PtP} = 1832.3 Hz); ^{19}F{^{1}H} −281.92 (br s, Pt−*F*, 1F), −120.99 (s, Ar-*F*, 1F), 120.22 (s, Ar-*F*, 1F).

Synthesis of 10b,c. To a 9:1 toluene−NMP solution of **7b** (20 mg, 0.02 mmol in 1 mL) was added 4 μL (0.022 mmol) of (CH$_3$)$_3$-SiOTf. The ^{19}F{^{1}H} NMR spectrum revealed the formation of 1 equiv of (CH$_3$)$_3$SiF and **10b**. The latter was isolated as a white solid in 80% yield by concentration in a vacuum and addition of 3 mL of hexane. Under similar conditions, **10c** was also prepared in solution; however, we could not isolate it in pure form.

10b: ^{31}P{^{1}H} 4.27 (s, J_{FP} = 18.8 Hz, J_{PtP} = 1987.4 Hz); ^{19}F-{^{1}H} −274.52 (m, Pt−*F*, 1F), which appears as triplet in NMP (J_{PtF} = 97.0 Hz), −118.70 (s, Ar-*F*, 1F), −118.04 (s, Ar-*F*, 1F), −80.36 (s, C*F*$_3$, 3F); ^{1}H NMR 7.06 (br s, Ar-*H*, 4H), 7.14 (br t, *J* = 7.4 Hz Ar-*H*, 4H), 7.20−7.62 (m, Ar-*H*, 30H); FAB-MS M$^+$ (M$^+$ calcd for C$_{49}$H$_{38}$F$_6$O$_3$SPt): *m*/*z* 1075 (*m*/*z* 1075).

10c: ^{31}P{^{1}H} 12.87 (d, J_{FP} = 20.2 Hz, J_{PtP} = 1808.5 Hz); ^{19}F-{^{1}H} −263.81 (t, Pt−*F*, 1F, J_{PtF} = 75.9 Hz in toluene), −117.69 (s, Ar-*F*, 1F), −116.93 (s, Ar-*F*, 1F), −77.45 (br s, C*F*$_3$, 3F); ^{1}H NMR 0.55 (m, C*H*$_3$, 18H), 1.69 (br m, C*H*$_2$, 12H), 6.68 (br t, Ar-*H*, 4H, J_{HH} = 8.4 Hz), 6.79−7.61 (m, Ar-*H*, 4H); FAB-MS M$^+$ (M$^+$ calcd for C$_{25}$H$_{38}$F$_6$O$_3$SPt): *m*/*z* 789 (*m*/*z* 789).

Reductive Elimination in 8b. An NMP solution of **8b** (20 mg,0.02 mmol) in a sealed NMR tube was warmed at 45 °C in an oil bath, and the reaction progress was monitored by ^{19}F NMR (C$_6$F$_6$ as a reference). After 5 h, the complete disappearance of **8b** was observed with the concomitant formation of 4,4-difluorobiphenyl. The ^{31}P NMR spectrum showed the formation of (Ph$_3$P)$_2$PtCl$_2$, **4a**, as the only product.

Exchange Reaction with (*p*-tolyl)$_3$P. To a solution of **8b** in NMP (10 mg, 0.01 mmol) was added 30 mg (10 equiv) of (*p*-tolyl)$_3$P, and the mixture was warmed at 45 °C for 5 h in an NMR tube. The ^{31}P and ^{19}F NMR spectra showed the disappearance of **8b** and formation of the new complex ((*p*-tolyl)$_3$P)$_2$Pt(*p*-FC$_6$H$_4$)$_2$-Cl$_2$. An equivalent amount of free PPh$_3$ was also observed in the ^{31}P NMR spectrum: ^{31}P{^{1}H} 0.93 (s, J_{PtP} = 1952.4 Hz); ^{19}F{^{1}H} −120.90 (s, Ar-*F*, 2F).

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Supporting Information Available: X-ray crystallographic files (CIF) for **2a** and **7a** and NMR spectra of complexes **2a** and **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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