Swimming against the Stream? A Discussion of the Bonding in d^6 and d^8 Fluoro Complexes and Its Consequences for Catalytic Applications

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Fluoride has recently found increasing application as coligand both in complexes of late transition metals and as a reagent in asymmetric catalysis. In recent papers, this topic was reviewed, with emphasis on the role played by so-called 'push-pull interactions' between the fluoro ligand and a π acid in the stabilization of fluoro complexes with a d^6 or d^8 electron configuration. This picture has led to the concept that fluoride is the strongest π-donor in the halide series. Herein, the latter concept is discussed and criticized. In particular, the effect of the ionicity of the metal-fluoride bond is proposed as an alternative explanation to most of the observations that show a 'reversed' halide order. The ionic character of the M–F bond also accounts for its intrinsic reactivity and suggests some strategies for the stabilizatioin of fluoro complexes, including the use of coordinative unsaturation. The scope and limitations of the application of d^6 and d^8 fluoro complexes in catalysis are also discussed. The most promising application is the use of 16-electron fluoro complexes in the metal-promoted formation of the C–F bond.

Introduction. – The main motivation for this account is the increasing application that fluoride has recently found as ligand or cocatalyst in a number of homogeneous catalytic processes [1]. *Carreira* has pointed out that fluoride can play different roles in homogeneous catalysis. Thus, the fluoro ligand can increase the *Lewis* acidity of a titanium catalyst, as in the enantioselective addition reaction of silyl dienolates to aldehydes [2]. Alternatively, fluoride acts as labile ligand, as in *Buchwald*'s hydrogenation of encumbered olefins [3]. In other reactions, such as olefin hydroamination [4], allylic amination [5], and the copper-catalyzed addition of dienolates to aldehydes [6], a fluoride salt boosts the enantioselectivity, but it is not clear whether F^- coordinates to the metal. In the latter cases, late transition metals – Ir^I, Pd^{II}, and Cu^{II} – are involved. Finally, fluoro complexes are intermediates in the activation of C–F bonds [7]. The above-mentioned examples show that the role played by fluoride as a ligand for transition-metal catalysts is much better understood for early transition metals than for the late ones.

In recent review articles, the coordination chemistry of fluoride has been extensively discussed [8–12], and there seems to be a general consensus that *a*) fluoride is the strongest π-donor ligand among the halides, and *b*) the coordination of fluoride to a d^6 or d^8 metal is as facile as that of chloride, bromide, or iodide (the implicit conclusion being that only a few fluoro complexes of this kind exist because synthetic interest and/or the appropriate reagents are lacking). In this work, we would like to question both theses *a*) and *b*). As for point *a*), we will try to highlight substantial experimental and theoretical evidence (which has been so far largely ignored) indicating that the 'inverse' halide order observed in several instances is due to the *ionic character of the M–F bond* rather than to an exceptionally high π-donor ability of fluoride. As for point *b*), is should be appreciated that fluoride coordination to d^6 and d^8 transition metals is far from general and that, *in the absence of stabilizing interactions, fluoro complexes of the late transition metals are extremely labile and reactive towards electrophiles*, which severely hampers their synthesis and isolation.

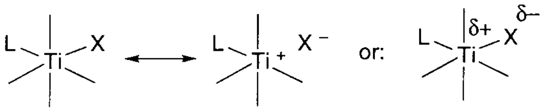
The latter point also explains why there are several catalytic reactions involving late transition metals for which a fluoride effect has been observed, but no fluoro complexes have been identified as intermediates. These include the asymmetric, iridium-catalyzed hydroamination of olefins [4], asymmetric palladium-catalyzed allylic amination [5], and the copper-catalyzed addition of dienolates to aldehydes [6] as mentioned above. Well-defined fluoro complexes of the late transition metals that have been used in organic transformations are exceedingly rare; those that have been developed mainly involve early transition metals [2][3]. In summary, one should recognize that the attempted preparation of fluoro complexes of low-valent transition metals is indeed like 'swimming against the stream', and that this is possible only under certain circumstances, which will be substantiated below.

Some Concepts of Basic Coordination Chemistry. – Traditionally, based on stability constants and the hard-soft-ligand theory [13], fluoride is considered a poor ligand for late transition metals. As fluoride is a hard ligand and late transition metal ions in low oxidation states are soft, their combination is unfavorable. Accordingly, fluoride as ligand is mainly found in combination with early transition metals, in complexes with an electron count between d^0 and d^4 [9].

Fluoride not only coordinates preferentially to hard *Lewis* acids, but also increases their 'hardness'. We can understand this effect by looking at the complexes of early transition metals. Indeed, fluoride is less hard than hydroxide, but much harder than the heavier halides [14]. In valence-bond theory, this means that the metal–fluoro bonds are much more ionic and less covalent than the M–X ones, where X is Cl, Br, or I. If we apply *Pauling*'s electroneutrality principle to a complex of the type $[MXL_5]^{n+}$ ($X =$ halide), then changing from iodide to fluoride will increase the ionic character of the M–X bond. The fluoro ligand is more negatively charged than iodide, meaning that the M–F bond is more ionic than the M–I bond. As this enhances the fractional positive charge on the metal, the M–L bond will be more covalent with fluoride as ancillary ligand. *Fig. 1* shows an application to a fluoro complex of titanium. Because of the increased charge on the metal when X is F, the covalent character of the M–L bond is enhanced [15]. In other words, the fluoro complex is the harder *Lewis* acid with respect to ligand L.

However, this is a very qualitative approach. If we want to understand the properties of a given complex, both the σ- and π-components of the metal–halide bond must be analyzed in the LCAO-MO approach. In an octahedral complex of the type $[MX_6]^{n-}$, the t_{2g} orbitals of the metal interact with the t_{2g} group orbitals of the X_6-donor set. If X has filled orbitals with π-symmetry, as it is the case with halides, this orbital overlap corresponds to the π-component of the M–X bond (*Fig. 2*). The π component is particularly interesting, as it normally involves the frontier orbitals (HOMO and LUMO) of the complex.

In a d^0 system, the π-component of the M–X bond stabilizes the complex, as partial electron transfer to the metal stabilizes the lone pairs on the halide. The metal t_{2g}



Ti–X	$\Delta\chi$	Ionic character
Ti–F	2.5	75 %
Ti–Cl	1.7	42 %

χ(Ti) = 1.5, χ(F) = 4.0, χ(Cl) = 3.2

Fig. 1. *Fluoro complexes and* Pauling's *electroneutrality principle.* The more ionic the M–X bond, the more covalent the M–L bond.

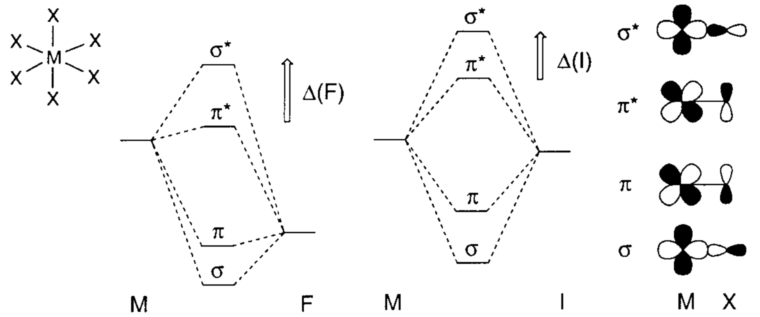
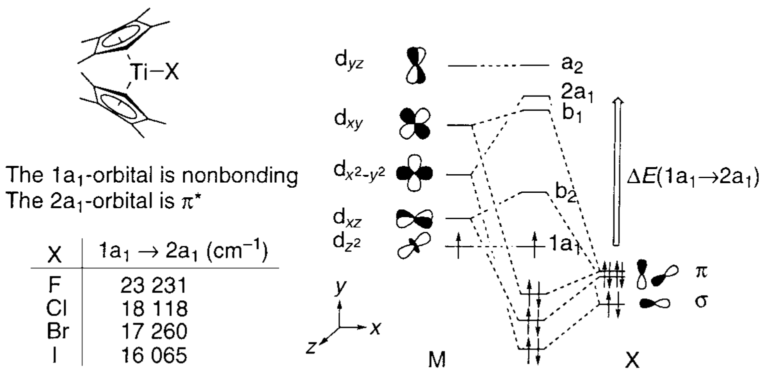


Fig. 2. *Schematic representation of σ- and π-effects in [MX$_6$]$^{n-}$*

orbitals, which have π-antibonding character, are empty. In an octahedral d^6 complex of the type [MX$_6$]$^{n-}$, however, the metal t_{2g} orbitals are filled and the π-π 4-electron interaction destabilizes the complex. As antibonding interactions are generally stronger than the corresponding bonding components, the overall π component destabilizes the complex. The latter issue is known as 'π-π 4-electron repulsion', as pointed out by *Mayer* [16] and *Caulton* [17]. For octahedral complexes, the d^6 configuration has the largest destabilization. However, as proposed by *Holland et al.*, the 'π-π 4-electron repulsion' argument can be reversed, in the sense that M–N, M–O, and M–F bonds are weak *both* in early *and* in late transition metal complexes, but are strengthened by constructive π-interactions with early transition metals [18]. However, both interpretations agree that the π-component stabilizes the fluoro complexes of the early transition metals with a d^0 – d^4 configuration with respect to the fluoro complexes having a d^6 or d^8 electron count. This is true both for octahedral d^6 systems and for square-planar d^8 species.

We ask now: which halide is the strongest π-donor, fluoride or iodide? Let us start our analysis from the traditional notions of inorganic spectroscopy, and, in particular, from the trends of the ligand-field parameter Δ. Extensive quantitative data for Δ have been derived for the homoleptic octahedral complexes [MX$_6$]$^{n-}$ (X = F, Cl, Br, or I) of Mn^{II}, Ni^{II}, Co^{II}, V^{II}, Fe^{III}, Cu^{III}, Cr^{III}, Co^{III}, Ru^{II}, Ag^{III}, Ni^{IV}, Mn^{IV}, Mo^{III}, Rh^{III}, Pd^{IV}, Tc^{IV}, Ir^{III}, and Pt^{IV} [19]. For all these complexes, the ligand-field parameter Δ has been factored into $\Delta = f(\text{ligands}) \cdot g(\text{central ion})$, and the values of g show that the field strength decreases on going from fluoride ($g = 0.9$) to chloride ($g = 0.78$) and to bromide ($g = 0.72$) [19]. This is known as the 'spectrochemical series', which orders the halides with increasing field strength Δ according to the sequence $\mathrm{I} < \mathrm{Br} < \mathrm{Cl} < \mathrm{F}$. As noted by *Jørgensen* for octahedral complexes having O_h-symmetry, Δ is the difference between the σ-antibonding and the π-antibonding effects on the five d-like orbitals distributed in the t_{2g} (π and π^*) and e_g (σ and σ^*) subsets (*Fig. 2*) [19]. That iodide has the weakest ligand field in these complexes is an indication that the π^*-effect becomes more important – with respect to the σ^*-interaction – on going from fluorine to iodine, which indicates that iodide is the strongest π-donor in the $[\mathrm{MX}_6]^-$ complexes, as qualitatively sketched in *Fig. 2*.

Contrary to these early results, however, the opposite ordering of halide π-donor ability has been suggested for an increasing number of complexes. A recent example is given by the electronic spectra of the titanium(III) complexes $[\mathrm{TiX(Cp^*)_2}]$ (a d^1 system) (X = F, Cl, Br, or I; $\mathrm{Cp^*} = \mathrm{C_5Me_5}$). On going from the iodo to the fluoro derivative, these complexes show an increase of the energy of the absorption maximum of the transition between the strictly nonbonding HOMO and the LUMO, which has π^*-character with respect to the titanium–halide bond [20] (*Fig. 3*). The trend can be explained on the assumption that the largest π-donation from the halide occurs in the fluoro derivative. This idea will be discussed and criticized in the following paragraphs.



The $1a_1$-orbital is nonbonding
The $2a_1$-orbital is π^*

X	$1a_1 \rightarrow 2a_1$ (cm^{-1})
F	23 231
Cl	18 118
Br	17 260
I	16 065

Fig. 3. *Orbital diagram of* $[\mathrm{TiX(Cp^*)_2}]$

We note that $[\mathrm{TiX(Cp^*)_2}]$ is, incidentally, a coordinatively unsaturated, 15-electron system. Indeed, most of the d^6 and d^8 fluoro complexes described in the literature are those *with fewer than 18 valence electrons*. Such complexes can be formed from 18-electron species by electrochemical oxidation [20], but also by dissociation of a ligand (introduction of coordinative unsaturation). As discussed later on, one should not overlook that coordinative unsaturation is often crucial in the stabilization of fluoro complexes of late transition metals. An alternative strategy for the stabilization of the M–F bond is the introduction of a strong π-acidic ligand in the position *trans* to the fluoro ligand. The role played by the X → M π-donation in the latter case is reviewed and discussed in the next paragraph.

Push-Pull Interactions and π-Donation. – Some of the first fluoro complexes having a d^6 configuration were (formally) obtained by reaction of a strongly *Lewis*-acidic fragment with a fluoride-containing anion [8]. An example is the d^6 complex $[ReF(CO)(PPh_3)_3(NO)]^+$, which is formed by fluoride abstraction from $[BF_4]^-$ upon protonation of $[ReH_2(PPh_3)_3(NO)]$ with HBF_4 under a CO atmosphere [21]. Although the mechanism of the reaction was not elucidated, one (or more) dihydrogen complexes are probably involved, which undergo dissociation of the (η^2-H_2) ligand and form a highly reactive, *Lewis* acid fragment of the type '$[Re(CO)(PPh_3)_3(NO)]^{2+}$'. On similar lines, the oxidation of carbonyl complexes with XeF_2 gave fluoro(carbonyl) complexes, such as $[MF_2(CO)_2(PPh_3)_2]$ (M = Ru or Os) [10] [22]. In both cases, the 18-electron fluoro complexes are stabilized by the presence of a π-acceptor (nitrosyl or carbonyl, but also phenyl) trans to the π-donor (the fluoride). This has been named a push-pull interaction by *Caulton* [17], who has prepared several 16-electron complexes of the type $[RuHX(CO)(P^tBu_2Me)_2]$, including the fluoro derivative [23]. According to *Caulton*, the mechanism of the push-pull interaction can be understood by analyzing the π-component of the bonding along the X–M–CO vector (*Fig. 4*). The π-orbitals of the halide push up the energy of the π-metal orbitals, which enhances the back bonding from the metal to the carbonyl ligand. Thus, the push-pull interaction relieves the π-π 4-electron destabilization.

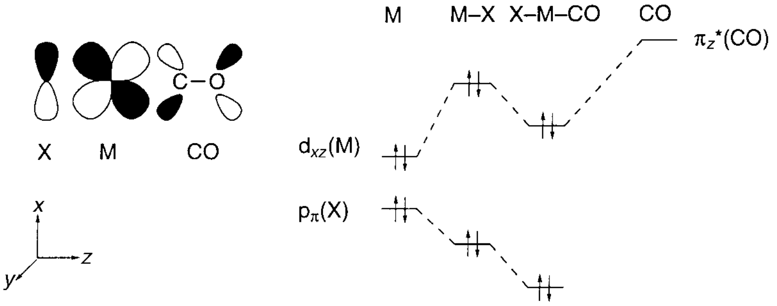
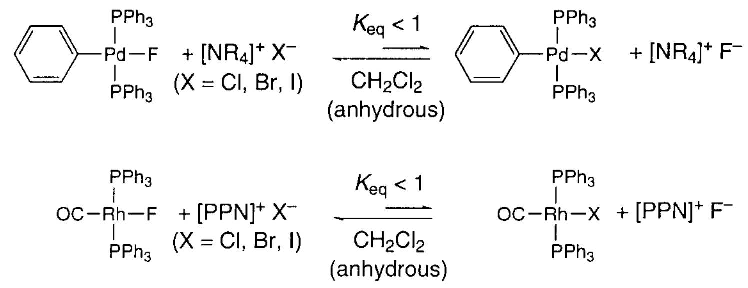


Fig. 4. *Push-pull interaction*

It is important to note here that *most fluoro complexes of the late transition metals are stabilized by π-acidic coligands by means of push-pull interactions* [8–12]. Push-pull interactions are not restricted to the d^6 systems mentioned above. In fact, the most representative complexes of this class are the fluoro derivatives of rhodium and palladium studied by *Hoffman* and co-workers [8] [24a] (a related 'push-pull-stabilized complex is $[RhF(cod)(PPh_3)]$ (cod = cycloocta-1,3,5-triene) [24b]) and *Grushin* and co-workers [12] [25] (other d^8 'push-pull-stabilized' complexes of the type $[MF(Ar)L_2]$ are related to the formation and cleavage of the C–F bond, which will be discussed together with the catalytic applications in a later paragraph). A very important result of these investigations is that the square-planar d^8 complexes *trans*-$[RhF(CO)(PPh_3)_2]$ and *trans*-$[PdF(Ph)(PPh_3)_2]$ are more stable than the analogues containing the heavier halides, as indicated by the halide-exchange equilibria that favor the fluoro derivatives (*Scheme 1*).

Scheme 1. *Halide-Exchange Equilibria of* trans-*[PdF(Ph)(PPh$_3$)$_2$] and* trans-*[RhF(CO)(PPh$_3$)$_2$]*



$[PPN]^+ = [Ph_3P{=}N{=}PPh_3]^+$

It is possible to apply the hard/soft argument to explain the preference of the palladium complex for fluoride if one considers that the 14-electron fragment $[ML(PPh_3)_2]^+$, where L is a π-acceptor, is a harder *Lewis* acid than d^8 complexes that do not contain a π-acid. However, the 'reversed' halide order in these complexes has been taken as evidence for fluoride being 'the strongest π donor' [8] [11][12].

Is Fluoride the Strongest π-Donor Halide? A Criticism. – Since publication of the review by *Hoffman* and *Doherty* [8], statements about fluoride being the strongest π-donor in the halide series have become increasingly common [11]. Much of the supporting evidence is based on push-pull-stabilized systems. Let us examine some of the arguments reported.

The $\tilde{\nu}$(CO) stretching frequency of *trans*-$[IrX(CO)(PR_3)_2]$ (X = F, Cl, Br, or I) decreases on going from the iodo to the fluoro ligand, which has been interpreted as supporting evidence for fluoride being the better π-donor in the push-pull interaction in *Fig. 4* [8]. However, this is disproved by a computational study of *trans*-$[IrF(CO)(PH_3)_2]$ by *Abu-Hasanayn et al.* who give an enlightening explanation of what 'strong π-donor' means in the case of a push-pull F–M–CO interaction [26]. Owing to the energy and form mismatch between the AOs of the F- and Ir-atoms, the M–F bond is largely ionic. Thus, the bonding π-orbital of the Ir–F bond has essentially F character, whereas the antibonding π^* orbital is mostly localized on IR and, thus, polarized towards CO (*Fig. 5*). The latter effect enhances the overlap between π^*(CO) and the π orbital on iridium that has π^* character with respect to the Ir–F bond (upper orbitals in *Fig. 5*). Therefore, the back donation is most efficient in the fluoro complex, *although the p_π orbital of the halide has a lower energy in the fluoro complex than in the iodo one.* In conclusion, the push-pull interaction is most efficient in the fluoro complex. However, this is not so because of the π-donation from the fluoro ligand, but because of the ionic character of the Ir–F bond. This conclusion was not reached by *Macgregor* and *MacQueen* in their investigation of CO dissociation from $[MX(CO)_5]^-$ (M = Cr, Mo, or W; X = NH_2, OH, halide, H, or Me), who state that the fluoro ligand is the strongest π-donor, although $[WF(CO)_5]^-$ shows the smallest $d_\pi(M)/p_\pi(X)$ mixing among the halogen derivatives [27]. In a related computational study on the 16-electron complex $[WF(CO)_4]^-$, *Kovacs* and *Frenking* found that the X → W π-donation is smaller for F than for Cl [28].

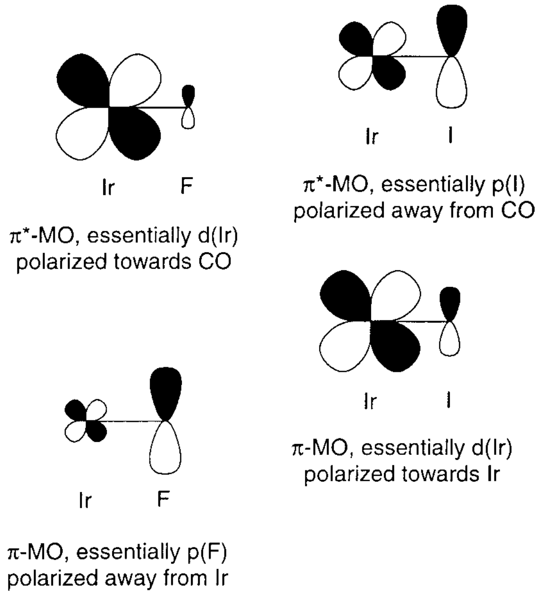


Fig. 5. *Schematic illustration of the difference in the halide–metal p–d π-type interaction in* trans-*[IrF(CO)(PR$_3$)$_2$] and* trans-*[IrI(CO)(PR$_3$)$_2$]*

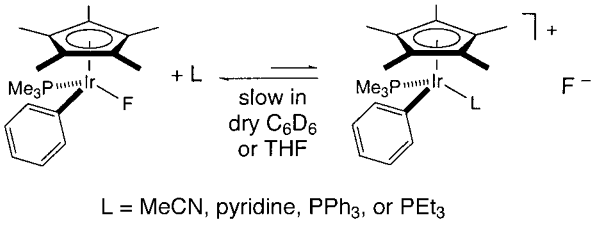
According to *Abu-Hasanayn et al.*, the ionic nature of the M–F bond also explains the trends observed in the redox potentials of the *Vaska* derivatives, in which the fluoro complex [IrF(CO)(PR$_3$)$_2$] is the most difficult to reduce, against expectations based on electronegativity arguments. In fact, the calculations show that corresponding metal-based orbitals (occupied and unoccupied) are always higher in energy when X = F than when X = I [26]. They attribute this observation to the smaller size of the F-atom, its closer proximity to the metal, and to its larger net negative charge in the complex. For all these factors, fluoride exerts a much stronger electrostatic field on the metal orbitals than does iodide. Thus, the greater 'electron richness' of the fluoro complex in the series [IrX(CO)(PPh$_3$)$_2$] claimed by *Hoffman* and *Doherty* [8] is actually a ligand-field effect caused by the ionicity of the M–F bond. Accordingly, the *Mulliken*'s net charge on iridium is +0.11 in [IrF(CO)(PH$_3$)$_2$] and −0.35 in the iodo analogue, in perfect agreement with the electronegativity trend of X.

The above interpretation also explains why the oxidative addition of H_2 to *Vaska*'s complex *trans*-[IrX(CO)(PR$_3$)$_2$] (X = F, Cl, Br, or I) is most exothermic with iodide and least exothermic with fluoride, *without invoking the argument of π-donation* as stated elsewhere [11]. In fact, the push-pull interaction, which is strongest for the fluoro complex, is lost on going from *trans*-[IrX(CO)(PR$_3$)$_2$] to [IrFH$_2$(CO)(Pr$_3$)$_2$], in which the halide is *trans* to one hydride and not to CO.

Finally, in the study of the push-pull-stabilized complexes [RuH(X)(CO)(PR$_3$)$_2$], *Eisenstein* and *Caulton* and co-workers have reached analogous conclusions, namely, that the $\tilde{\nu}$(CO) stretching frequency is not a reliable probe for the assessment of the π-bonding contribution to the Ru–X bond. They conclude that 'the increase of the ionicity of the Ru–X going up the periodic table dominates over the π-effect and lowers the CO frequency' [29]. Thus, the trends in the $\tilde{\nu}$(CO) stretching frequencies of [$MX(CO)(PPh_3)_2$] (M = Rh, Ir; X = F, Cl, Br, or I) and in the redox potentials are not the result of the 'π-donor strength' of the halide, but rather of the ionic nature of the metal–fluoro bond. *The term 'π-donation' in the context of fluoro complexes is inappropriate*, as the apparent 'electron richness' of the metal in the fluoro complex is an effect of the high electric field of the fluoro ligand, not of electron transfer from the F-atom to the metal. The dispute may be considered nominal, but we shall see later that it has very important practical consequences with regard to the reactivity of d^6 and d^8 fluoro complexes.

18-Electron, d^6 Complexes Lacking Push-Pull Interactions. – In the absence of π-acidic coligands, fluoride ligands are extremely labile, which can be ascribed to the significant ionic character of the M–F bond. The formation of strong H-bonds between the coordinated fluoride and sources of protons, such as adventitious H_2O, also enhances the lability of coordinated fluoride. Thus, traces of H_2O and other protic solvents affect dramatically both the rate and the position of the substitution equilibria of [$IrF(Ph)(PMe_3)(Cp^*)$] with L (L = MeCN, pyridine, PPh_3, or PEt_3) (*Scheme 2*) [30]. These equilibria, which are established slowly in dry aprotic solvents, are reached rapidly when traces of H_2O are added to the THF solvent. Also, they are shifted towards the formation of [$Ir(Ph)(L)(PMe_3)(Cp^*)$]$^+$ and fluoride, which is most probably involved in strong H-bonding to H_2O. The aqua complex [$Ir(Ph)(Cp^*)(H_2O)(PMe_3)$]F is formed rapidly even at low temperature and is the intermediate in the substitution reaction. Interestingly, removal of H_2O in vacuum restores the starting [$IrF(Ph)(Cp^*)(PMe_3)$]. The labilizing effect of H_2O has been observed also in [$RhF(CO)(PPh_3)_2$] [24].

Scheme 2. *Substitution Reactions of [$IrF(Ph)(Cp^*)(PMe_3)$]*



In contrast to the behavior of the fluoro analogue [$IrF(aryl)(Cp^*)(PMe_3)$], [$IrCl(aryl)(Cp^*)(PMe_3)$] does not react with L (L = MeCN, pyridine, PPh_3, or PEt_3) to give [$Ir(aryl)(Cp^*)(L)(PMe_3)$]Cl by chloride dissociation [30]. The latter observation implies that, *contrary to the trend observed in the push-pull-stabilized complexes* trans-*[$RhF(CO)(PPh_3)_2$]* [24] *and* trans-*[$PdF(Ph)(PPh_3)_2$]* [25], *the fluoro complex is less stable than the chloro derivative in the 18-electron species [$IrX(aryl)(Cp^*)(PMe_3)$].*

Rare examples of six-coordinate d^6 fluoro complexes devoid of π-acidic coligands are *cis*-[$IrF_2(dppe)_2$]$^+$ (dppe = 1,2-bis(diphenylphosphino)ethane = ethane-1,2-diylbis[diphenylphosphine]), prepared by reaction of [$Ir(dppe)_2$] with XeF_2, and *cis*-[$RuF(FHF)(dmpe)_2$] (dmpe = 1,2-bis(dimethylphosphino)ethane = ethane-1,2-diylbis[dimethylphosphine]), which is formed by reacting *cis*-[$RuH_2(dmpe)_2$] with

$(CF_3)_2C{=}C(F)CF_2CF_3$ [31]. A related species is *cis*-$[RuF_2(dppp)_2]$ (dppp = 1,3-bis(diphenylphosphino)propane = propane-1,3-diylbis[diphenylphosphine]), which is very hygroscopic and rapidly decomposes in the presence of traces of H_2O (even air moisture) [32]. This suggests that coordinated fluoride has a high affinity for acidic H-atoms and forms H···F H-bonds whose strength parallels that of the H–F bond itself (569.9 kJ mol^{-1}) [33].

Alternatively, the metal can be protonated instead of the fluoro ligand. The reactivity of 18-electron halo complexes towards protonation in $[MX(Cp)(PR_3)_2]$ (M = Ru or Os; R = Me or Ph; X = Cl, Br, or I) [34] has been attributed to the increase of the π-π 4-electron repulsion in the series I < Br < Cl [11]^1). Nevertheless, a thorough electrochemical, thermodynamic, and computational study of $[FeX(Cp^*)(dppe)]$ (X=F, Cl, Br, I, H, or Me) by *Tilset* and co-workers challenges this interpretation [35]. Again, the fluoro complex is the most easily oxidized in the halide series, which is accurately reproduced by the energy ordering of the HOMOs, with the fluoro complex having the most destabilized one. However, although the HOMO has π^*-antibonding character with respect to the Fe–X bond, the energy of the HOMO does not correlate with the extent of π-donation from the halide. In fact, the mixing of the atomic orbitals in the HOMO is least for the fluoro complex (67% Fe – 17% F) and largest for the iodo complex (55% Fe – 53% I), in perfect agreement with the expected π-donor order. As in the case of *trans*-$[IrX(CO)(PR_3)_2]$ [26], the bottom line is that fluoride acts as a negative point charge located close to the metal and destabilizes the metal orbitals, including those with π-symmetry [35].

In conclusion, *d^6 and d^8 fluoro complexes are generally labile and highly reactive towards nucleophiles in view of the significant ionic character of the M–F bond and of the hard/soft mismatch, unless some kind of stabilizing interaction is operative* (for instance, a push-pull interaction). *Push-pull interactions do stabilize the fluoro complexes, but fluoride remains labile*, as the solution behavior of $[PdF(Ph)(PPh_3)_2]$ in wet solvents shows [12]. From this viewpoint, one should appreciate that there is a substantial difference between a phenomenon that looks like π-donation and π-donation itself, which exclusively pertains to a covalent bond. In fact, although many properties of fluoro complexes can be explained by invoking strong π-donation from the fluoro ligand, it is clear that the high lability of fluoride in such complexes speaks against formation of a strong *covalent* M–F bond. *The stabilization of the M–F bond by push-pull effects is caused by electrostatic interactions and not by the formation of a strong covalent π-bond*. Let us consider now another circumstance that stabilizes the M–F bond, and possibly reduces its lability.

Five-Coordinate Complexes of d^6 Ions Devoid of π-Acidic Ligands. – We have mentioned above that coordinative unsaturation is one of the strategies for the stabilization of the M–F bond. It is well-established that five-coordinate complexes of d^6 metal ions can be either square pyramidal or (pseudo) trigonal-bipyramidal.

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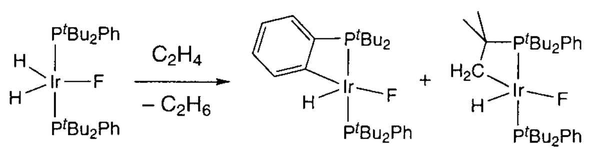
^{1}) In [11], the enthalpy of protonation of $[OsH(Cp)(PPh_3)_2]$ (– 37.3 kcal mol^{-1}) is erroneously attributed to $[OsF(Cp)(PPh_3)_2]$, which is not reported in the original paper [34]. On the basis of this attribution, the authors conclude that 'the basicity was found to be highest when X = F' and that 'fluoride is the best π-donor'.

However, it has been recognized only recently that strong σ-donors and π-acceptors (A) stabilize a square-pyramidal structure (with A in the apical position), whereas π-donors (X) favor a distorted ('Y-shaped') trigonal bipyramid (with X in the equatorial plane) [36]. *Caulton* and co-workers have extensively investigated the square-pyramidal species of the type $[MH(X)(CO)(PR_3)_2]$ ($M = d^6$ ion, $X = \pi$-donor) [23]. These coordinatively unsaturated complexes are stabilized by the joint effect of the hydride (as strong σ-donor) and of the push-pull interaction between X and CO. Much less is known about 16-electron complexes devoid of π-acids. *Caulton* and co-workers prepared the 16-electron iridium(III) complex $[IrFH_2(P^tBu_2Ph)_2]$, which does not contain a π-acidic ligand. This complex undergoes rapid hydrogenolysis under H_2 to give $[IrH_5(P^tBu_2Ph)_2]$, whereas no Ir–X cleavage occurs with the heavier halides. More interestingly, the presence of the fluoro ligand promotes unselective C–H activation at the sp^2 and sp^3 C-atoms of the ^{t}Bu and Ph groups to give a mixture of cyclometallated products (*Scheme 3*) [37].

Scheme 3. *C–H Activation by* $[IrFH_2(P^tBu_2Ph)_2]^+$



We have then investigated the fluoro derivatives of the 'Y-shaped' complexes $[RuX(P{-}P)_2]^+$ ($P{-}P$ = diphosphine) [38], whose stability relies, besides steric effects, only on the π-donation from X. To examine the latter case closer, let us start from the ideal trigonal-bipyramidal geometry. A trigonal-bipyramidal d^6 complex should be paramagnetic. However, it is *Jahn-Teller*-unstable, and some kind of distortion removes the degeneracy of the d_{xy} and $d_{x^2-y^2}$ orbitals [39]. As the d_{xy} orbital overlaps efficiently with a p_π orbital of the halide, the d^6 $[MXL_4]^{n+}$ complexes assume a 'Y-shaped' structure with an L–M–L angle of *ca.* 90° in the equatorial plane [36]. This gives π^* character to the d_{xy} orbital and maximizes the π-donation from the π-donor X (*Fig. 6*). It should be appreciated that this causes the electrons to pair in $d_{x^2-y^2}$, whereby d_{xy}, which is now antibonding, remains empty.

The stability of the 16-electron complexes $[MXL_4]^{n+}$ ($X = \pi$-donor) with respect to the corresponding six-coordinate, 18-electron complexes $[MX_2L_4]^{(n-1)+}$ derives from the π-π 4-electron repulsion being relieved upon dissociation of X^- [17]. Thus, the octahedral d^6 complexes $[MX_2L_4]$ are subject to dissociation despite their kinetic inertness. Indeed, hints of the labilizing effect of fluoride can be found in the literature. In *mer,trans*-$[ReX(CO)_3(PPh_3)_2]$ (X = F, Cl, Br, or I), the rate of exchange of ^{13}CO at the position *cis* to the fluoro ligand is roughly two orders of magnitude greater than in the chloro analogue, which has been explained by the stabilization of the five-coordinate transition state by the π-donor X [40]. Two recent theoretical (DFT) studies mentioned above similarly conclude that the *cis* destabilizing effect of π-donating ligands in $[MX(CO)_5]^-$ (M=Cr,Mo, or W; X=NH_2, OH, or halide) is caused by the stabilization of the 16-electron intermediate [27][28], which suggests that the push-pull interaction is enhanced in coordinatively unsaturated species.

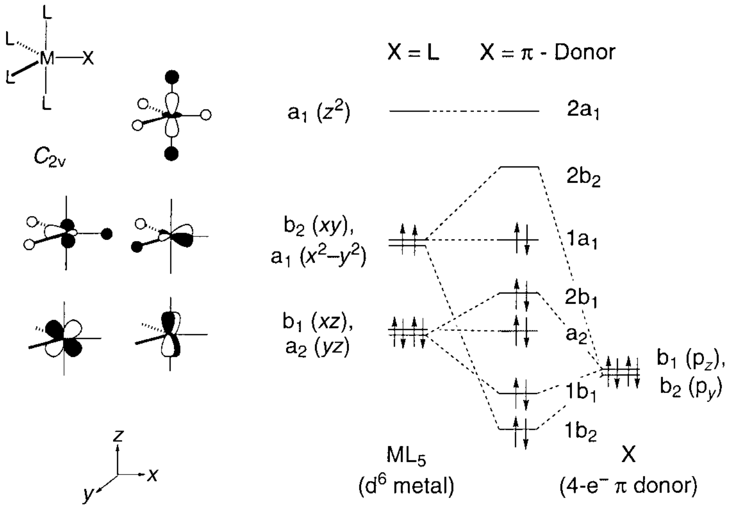
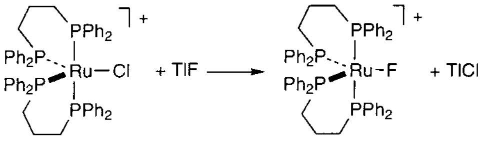


Fig. 6. *Qualitative MO diagram of* $[MXL_4]^{n+}$ ($M = d^6$ metal ion)

We reasoned that, if fluoride is a good π-donor, it should stabilize a 'Y-shaped' 16-electron complex. The main motivation for the synthesis of 16-electron complexes of a d^6 ion was that, contrary to square-planar d^8 systems, such complexes are *intrinsically* reactive and susceptible to nucleophilic attack. The latter reaction is disfavored with square-planar d^8 complexes since the orbital involved (p_z) has the same direction and energy similar to that of the doubly occupied d_{z^2} orbital. The d^6 $[MX(P-P)_2]^{n+}$ complexes are not only coordinatively unsaturated, but are also *Lewis* acids, and can react with very weak donors, including dihydrogen (for examples of reactions of $[MX(P-P)_2]^+$ (M = Ru or Os) with H_2, see [41]). In the case of d^6 fluoro complexes, this concept offers a handle to prepare five-coordinate species that are, at the same time, reactive but contain a relatively inert M–F bond. Compared to $[MH(X)(CO)(PR_3)_2]$, the $[MX(P-P)_2]^+$ species have the advantage of *not containing a hydride ligand* that could be too reactive for a number of applications. Thus, we have prepared the five-coordinate ruthenium(II) complex $[RuF(dppp)_2]^+$ [32], which completes the series $[RuX(dppp)_2]^+$ (X = Cl, Br, or I) (*Scheme 4*) [41b].

Scheme 4. *Synthesis of* $[RuF(dppp)_2]^+$



The 16-electron complex $[RuF(dppp)_2]^+$ can be handled and stored in air for longer periods of time. Thus, it is much less sensitive to moisture than the 18-electron difluoro analogue $[RuF_2(dppp)_2]$ mentioned above, which readily decomposes in moist air. Why is it so? We suggest that, on going from a neutral, 18-electron fluoro $[MF_2L_4]$ complex to a cationic, 16-electron $[MFL_4]^+$ species, the ionic character of the M–F bond decreases. Indeed, both the positive charge and the coordinative unsaturation increase the 'apparent electronegativity' of the metal (and, thus, decrease the electronegativity difference between M and F), which results in a more covalent M–F bond in $[MFL_4]^+$ than in $[MF_2L_4]$. It should be appreciated that the introduction of a π-acceptor ligand *trans* to the fluoro ligand – a push-pull arrangement – has the same overall effect.

On the lines of the above discussion for $[TiX(Cp^*)_2]$, we have measured the electronic spectra of the whole series $[RuX(dppp)_2]^+$ (X = F, Cl, Br, or I), whose bands have been attributed by analogy with the π-stabilized, Y-shaped Fe complex with C_{2v} symmetry $[FeX(P_4)]^+$ ($P_4 = Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$) and with the *Jahn-Teller*-distorted, d^7 system $[CoCl(QP)]^+$ ($QP = P(o\text{-}C_6H_4PPh_2)_3$) [42]. The HOMO-LUMO gap corresponds to the energy of the $a_1 \rightarrow 2b_2$ transition (*Fig. 6*), to which we attributed the low-energy band λ_1 (*Table*). The relatively intense λ_2 band probably corresponds to the $2b_1 \rightarrow 2b_2$ transition, which has charge-transfer character. Finally, the (not always observed) λ_3 shoulder should be related to $1a_1 \rightarrow 2a_1$, a pure d–d, and hence weak, transition. The energies of all three transitions decrease on going from fluoride to iodide. Thus, the electronic spectra of $[RuX(dppp)_2]^+$ unambiguously show that the fluoro derivative has the largest HOMO-LUMO gap and is, hence, *a harder Lewis acid* than $[RuI(dppp)_2]^+$ [43].

Table. *Electronic Spectra* (CH_2Cl_2) *of* $[RuX(dppp)_2]^+$ [a])

X	F	Cl	Br	I
λ_1 (ε)	511 (640)	547 (500)	560 (720)	604 (540)
λ_2 (ε)	413 (2480)	446 (1940)	453 (2320)	464 (2260)
λ_3 (ε)	330 (sh)	353 (sh)	370 (sh)	377 (3360)

[a]) λ in nm and ε in $dm^3\ mol^{-1}\ cm^{-1}$.

The actual order of the transition energies might be taken as an indication of decreasing π-donation in the same order. There are, however, alternative explanations of the spectroscopic trend, which are based on the ionic nature of the M–F bond, as discussed above for *trans*-$[IrX(CO)(PR_3)_2]$. In a ligand-field approach, fluoride can be thought to destabilize most metal d orbitals as it acts as a point charge close to the metal. Then, the energy mismatch between the p orbital of fluoride and the d orbital of ruthenium increases the metal character of the metal-based, antibonding $2b_2$ orbital (*Fig. 6*) with respect to the complexes of the heavier halogen ligands, and rehybridizes it away from X and towards the remaining equatorial ligands, which causes its further destabilization. Finally, discussing the σ-donor abilities of the halides in Cr^{III} complexes, *Burdett* [44] has noted that the halide donor strength derived by analysis of the energies of the d–d transitions are not reliable, since a large destabilization energy of an antibonding orbital is not always matched by a proportionally large stabilization of the bonding partner. Thus, whereas the stabilization energy of the bonding e_g orbitals in $[CrF_6]^{3-}$ is less than that in $[CrCl_6]^{3-}$, the opposite is true of the destabilization of the antibonding orbitals, which are responsible for the 'inverse' order of donor strength $F > Cl > Br > I$. In other words, the antibonding situation is not symmetrical to the bonding one, and the energies of the π^*-orbitals are not diagnostic of the degree of π-

donation from a series of ligands X *when the ionic character of the M–X bond varies significantly along the series*. Thus, care should be taken when drawing conclusions on the stability of the halo complexes from the relative energies of the π*-orbitals.

The reactivity of $[RuX(dppp)_2]^+$ (X = F, Cl, Br, or I) with H_2 gives further insight into the peculiarity of the M–F bond. Thus, the fluoro analogue $[RuF(dppp)_2]^+$ undergoes hydrogenolysis in the presence of H_2, and *trans*-$[RuH(\eta^2\text{-}H_2)(dppp)_2]^+$ is formed instead of *trans*-$[RuF(\eta^2\text{-}H_2)(dppp)_2]^+$, whereas the heavier halides give the dihydrogen complexes *trans*-$[RuX(\eta^2\text{-}H_2)(dppp)_2]^+$ (X = Cl, Br, or I) [41b][2]). Again, the reactivity of the fluoro complex is dominated by the lability of the Ru–F bond. The hydrogenolysis reaction is well explained taking into account the 'hardness' of fluoride, which probably deprotonates the (putative) acidic dihydrogen complex $[RuF(\eta^2\text{-}H_2)(dppp)_2]$ [45] to form HF.

Application of d^6 and d^8 Fluoro Complexes in Catalysis. – We have shown that push-pull interactions and coordinative unsaturation reduce the ionic character of the M–F bond (and, hence, its lability) in d^6 and d^8 complexes. Nonetheless, the inherent lability of the M–F bond poses severe limitations to the application of fluoro complexes of the late transition metals as homogeneous catalysts. In general, there are several catalytic reactions for which a fluoride effect has been observed, but no fluoro complexes have been identified as intermediates. These include the asymmetric, iridium-catalyzed hydroamination of olefins [4], asymmetric palladium-catalyzed allylic amination [5], and the copper-catalyzed addition of dienolates to aldehydes [6]. On the other hand, well-defined fluoro complexes of the late transition metals that have been used in organic transformations are exceedingly rare, and mainly involve early transition metals [2][3].

A major limitation is, for instance, the hydrogenolysis reaction mentioned above, which can be expected to take place when a 16-electron, five-coordinate fluoro complex adds H_2 to give an 18-electron species. The loss of the fluoro ligand as HF is a thermodynamic sink in view of the high stability of the H–F bond. Thus, there seems to be little chance of stabilizing a fluoro complex in a protic environment. Accordingly, *Caulton* and co-workers have found that the reactivity of $[RuHF(CO)(P^tBu_2Me)_2]$ is dominated by cleavage of the Ru–F bond [23b]. Despite this limitation, the fluoro ligand is compatible with hydride coligands. Thus, in a unique example of the use of fluoride as an ancillary ligand in a catalyst based on a late transition metal, *Cooper* and *Caulton* have used $[IrH_2X(P^tBu_2Ph)_2]$ (X = F, Cl, Br, or I) as catalysts for the isomerization of olefins [46]. The catalytically active species has been identified as the cyclometallated complex $[IrHX(\eta^2\text{-}C_6H_4P^tBu_2)(P^tBu_2Ph)]$ (*Scheme 3*). The M–F bond of the 16-electron, π-stabilized $[IrH_2F(P^tBu_2Ph)_2]$ is surprisingly inert, and fluoride is not eliminated even upon cyclometallation of the Ph or P–^{t}Bu groups 46].

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[2]) The minimum longitudinal relaxation time T_1 (which correlates with the H–H distance in the dihydrogen ligand) is a sensitive probe of the electronic properties of the ligand *trans* to the dihydrogen ligand in these complexes. In agreement with a computational study [45], the H–H distance in the homologous series $[RuX(\eta^2\text{-}H_2)(dppp)_2]^+$ and $[RuX(\eta^2\text{-}H_2)(dppe)_2]^+$ (X = Cl, Br, or I) remains constant on going from chloride to iodide [41b], which suggests that the donor properties of the halides are very similar. Therefore, the effective charge density on the metal is approximately constant in the Cl, Br, I series.

The observation that the fluoro analogue is the most active of these complexes was explained by invoking the strong π-donor ability of fluoride, which stabilizes the cyclometallated fluoro complex to the largest extent. However, if one appreciates that the cyclometallated complex is push-pull-stabilized (in view of the *trans* arrangement between the fluoro and the phenyl ligands), then we are back to the case of *trans*-$[IrX(CO)(PR_3)_2]$ and *trans*-$[PdX(Ph)(PPh_3)_2]$, whose relative stability can be explained by taking into account electrostatic arguments (see above) [26].

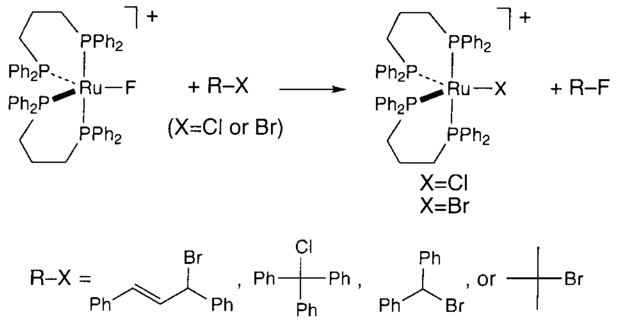
In most cases, however, the involvement of fluoro complexes in catalytic processes is, at best, only circumstantial [1][11]. This is the case for reactions in which fluoride is believed to act as a labile and weakly coordinating anion. Typical cases are palladium-catalyzed reactions that involve the intermediacy of allyl complexes. In such reactions, addition of halide to the reaction solution accelerates the isomerization of the allyl intermediates and establishes *Curtin-Hammett* conditions. The topic has been extensively reviewed recently [11] and will not be discussed further here. The only remark to this point is that the allyl ligand is a π-acceptor, and that, if the putative five-coordinate complex $[PdF(allyl)(P-P)]$ is formed, then it could be stabilized by a push-pull interaction.

The net conclusion to this point is that there seems to be little of importance involving fluoride as a ligand in catalysis. However, despite the limitations sketched above, there is, at least potentially, a catalytic application that is peculiar to fluoro complexes and is more exciting than its use as a good leaving group or *Brønsted* base.

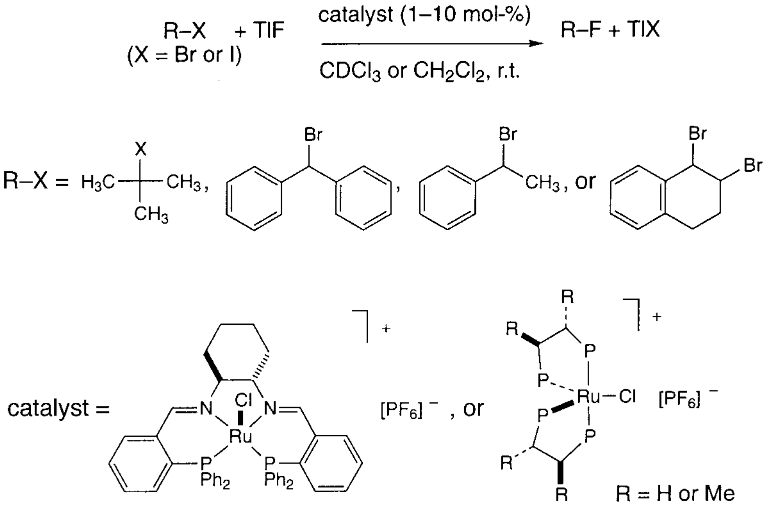
Strongly Bound Fluoro Ligands: Breaking and Making the C–F Bond. – Push-pull-stabilized complexes of the type $[MF(Ar)(PPh_3)_2]$ (M = Ni or Pd) are intermediates in both C–F bond-breaking and -forming *stoichiometric* reactions. Thus, $[NiF(Ar)(PEt_3)]$ complexes are formed by oxidative addition of a C–F bond of C_6F_6 or C_5NF_5 onto $[Ni(PEt_3)_4]$ [47a] (for a related reaction with *trans*-$[PtH_2(PCy_3)_2]$, see [47b]. The reverse reaction, that is, the reductive elimination from $[PdF(Ph)(PPh_3)_2]$ to give Ar–F and a Pd^0 complex, would afford an elegant way to produce fluoroarenes. Instead, $[PdF(Ph)(PPh_3)_2]$ decomposes thermally, giving a mixture of products that includes $[Pd(PPh_3)_3]$, Pd metal, biphenyl, Ph_3PF_2, and Ph_2P-PPh_2 [48]. Carbon monoxide, however, triggers reductive elimination from $[PdF(Ph)(PPh_3)_2]$ to give PhCOF and Pd^0 carbonyl complexes [49]. The interested reader should refer to a recent review for in-depth details of the reactivity of $[PdF(Ar)(PR_3)_2]$ [12]. A final note concerning the latter complex is that it reacts with [PPN]Cl (= $[Ph_3P{=}N{=}PPh_3]Cl$) to give $[PdCl(Ph)(PPh_3)]$ and 'naked' fluoride, which forms CH_2F_2 by reaction with the CH_2Cl_2 solvent [25]. Analogous X/F metathetic reactions have been observed for $[IrF(Ph)(PMe_3)(Cp^*)]$ [30] and $[RuH(FHF)(P-P)_2]$ [50], although their mechanisms have not been studied in detail.

Our approach also started from a stoichiometric reaction. We recently found that the 'Y-shaped' fluoro derivative $[RuF(dppp)_2]^+$ reacts with activated alkyl halides R–X (X = Cl, Br, or I), such as bromodiphenylmethane or *tert*-butyl bromide, to give the corresponding fluoroorganic R–F and $[RuX(dppp)_2]^+$ (*Scheme 5*) [32]. The reaction can be made catalytic with $[RuCl(dppe)_2]^+$ as the catalyst and TlF as the fluoride source (*Scheme 6*) [51]. The catalytic F/X metathesis is most efficient when the P_4 donor set is changed to P_2N_2, which increases the hardness of the *Lewis*-acidic 16-

Scheme 5. *Stoichiometric Fluorination of Activated Alkyl Halides with* $[RuF(dppp)_2]PF_6$



Scheme 6. *Catalytic Nucleophilic Fluorination of Activated Alkyl Halides*



electron complex. Thus, a catalytic amount (1 mol-%) of $[RuCl(PNNP)]^+$ (PNNP = (1*S*,2*S*)-*N*,*N'*-bis[2-(diphenylphosphino)benzylidene]cyclohexane-1,2-diamine) converts 1-bromo-1-phenylethane to the corresponding fluoride with 49% yield after 24 h of reaction time.

It is not yet evident which species is actually involved in the catalytic process, as the only species observed during catalysis with $[RuCl(dppe)_2]^+$ is the TlF adduct $[Tl(\mu\text{-}F)_2Ru(dppe)_2]PF_6$ (*Fig. 7*) [51]. The pattern of reactivity suggests that the mechanism has a S_N1 component. In fact, the only reactive substrates are those that form stabilized carbocations. The enhanced reactivity of $[RuCl(PNNP)]^+$, as compared with $[RuCl(P{-}P)_2]^+$, suggests a mechanism in which the *Lewis* acidic $[RuXL_4]^+$ ($L_4 = P_4$ or P_2N_2, *Scheme 6*) interacts with R–X and promotes the formation of an incipient carbocation. This would mean the C–Br bond starts to break before the formation of the C–F bond begins (*Fig. 7*).

Moreover, it is worth noting that nonracemic 1-fluoro-1-phenylethane (16% ee at 1% conversion) was formed in the reaction catalyzed by $[RuCl(PNNP)]^+$. The

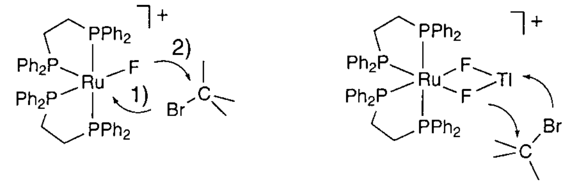
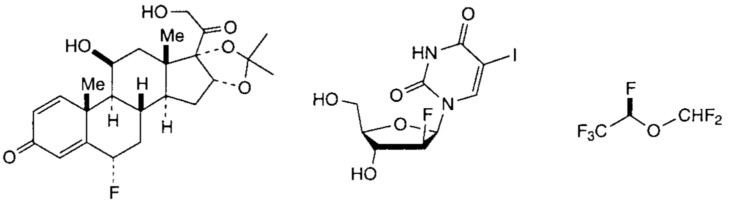


Fig. 7. *Possible mechanisms for the X/F exchange reaction*

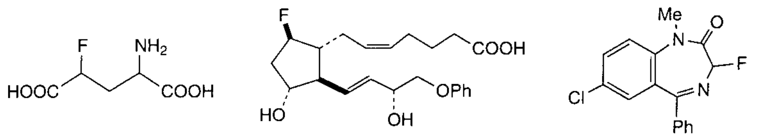
observation of 3% ee at quantitative conversion is a further indication that the mechanism is S_N1. The above observations indicate that the role played by the five-coordinate $[RuCl(PNNP)]^+$ in the catalytic cycle is more than the mere transport of TlF in the organic solvent. Also, although the (probable) S_N1 mechanism does not favor enantioselection, we have shown that nonracemic fluoroorganics are formed. We are trying to develop a practical catalytic protocol for catalytic nucleophilic fluorination, which would be the *pendant* to the asymmetric electrophilic fluorination of β-diketones recently reported by *Hintermann* and *Togni* [52]. Thus, the use of transition-metal catalysis based on fluoro complexes can potentially give access to several classes of organic molecules containing F-substituted stereogenic C-centers. *Fig. 8* provides examples of important fluoroorganic compounds that contain a single F-atom [53].



Flunisolide
(glucocorticoid, antiasthmatic)

Fialuridine
(antiviral agent)

(*R*)-Desfluran
(inhalation anesthetic)



4-Fluoroglutamic acid
(*erythro* and *threo*)
(antitumor, antiviral)

Flunoprost
(nasal decongestant)

Fluorodiazepam
(anxiolytic)

Fig. 8. *Important fluoroorganic compounds that contain a F-substituted stereogenic C-center*

Conclusions and Outlook. – Fluoro complexes of the late transition metals are intrinsically labile owing to the ionicity of the M–F bond. Most d^6 and d^8 fluoro complexes that have been reported either *a*) contain a π-acidic ligand that causes a push-pull interaction or *b*) are coordinatively unsaturated, as in the case of π-stabilized, cationic 16-electron complexes. Both the push-pull interaction and the coordinative unsaturation increase the 'hardness' of the metal atom and enhance the covalent character of the M–F bond. This effect attenuates the nucleophilic reactivity of the fluoro ligand and the lability of the M−F bond. However, the M−F bond remains very reactive (*e.g.*, it readily undergoes hydrogenolysis), which is consistent with an exceptionally highly ionic character.

Theoretical studies that estimate the orbital-mixing coefficients of the M−X bond in homologous series of halide complexes have come to the conclusion that fluoride is the *weakest* π-donor also in push-pull-stabilized complexes. The ionicity of the M−F bond accounts for the 'inverse halide order' that is generally found for such complexes. Therefore, *the generalization that 'fluoride is the strongest* π*-donor'*, which is repeatedly found in the literature [8][11][12][37], *is neither tenable nor necessary to explain the chemistry of* d^8 *and* d^6 *fluoro complexes.*

As to the question 'what can we make with fluoro complexes?', we must recognize that the lability of the M−F bond will hinder the use of well-defined fluoro complexes in stoichiometric and catalytic reactions. The most straightforward application of fluoro complexes remains the formation the C−F bond. *Grushin*'s investigations of $[PdF(Ar)(PPh_3)_2]$ indicate that the palladium-mediated formation of aromatic C−F bonds could be, in principle, feasible [12], provided that a method is found to favor the reductive elimination of Ar−F. We have shown that $[RuF(P-P)_2]^+$ are useful intermediates for the formation of aliphatic C−F bonds by halide metathesis, but a suitable source of fluoride must still be found. The breaking of the C−F bond is now mature. Making the C−F bond in a catalytic fashion is still a challenge.

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