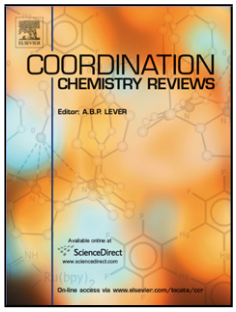

Title: Transition Metal Bifluorides

Author: Fady Nahra Marcel Brill Alberto Gómez-Herrera
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PII: S0010-8545(15)00281-7
DOI: http://dx.doi.org/doi:10.1016/j.ccr.2015.08.011
Reference: CCR 112133

To appear in: *Coordination Chemistry Reviews*

Received date: 13-5-2015
Revised date: 21-7-2015
Accepted date: 31-8-2015

Please cite this article as: F. Nahra, M. Brill, A. Gómez-Herrera, C.S.J. Cazin, S.P. Nolan, Transition Metal Bifluorides, *Coordination Chemistry Reviews* (2015), http://dx.doi.org/10.1016/j.ccr.2015.08.011

Highlights

Since their discovery four decades ago, transition metal bifluoride complexes have long been considered as unwanted byproducts, a necessary evil, on the route to access fluoride complexes. Until recently, reports on this chemistry almost always presented these complexes as a fluke discovery. However, with the recent increase in reports and applications involving such species, a renewed interest in these complexes has been observed. Most of the work done in this area, so far, has been directed toward the synthesis and quite challenging characterization of these complexes, yet mostly neglecting the behavior of such species and their influence on catalytic processes. The aim of this work is to present a summary of the various preparation methods, characterization techniques and applications of reported transition metal bifluoride complexes. It is our hope that by centralizing all information available on such species, future efforts aimed at exploiting the full potential of transition metal bifluoride species can be facilitated.

Transition Metal Bifluorides

Fady Nahra[a], Marcel Brill[a], Alberto Gómez-Herrera[a], Catherine S. J. Cazin[a]* and Steven P. Nolan[b]*

[a]*EaStCHEM, School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST. E-mail: cc111@st-andrews.ac.uk; stevenpnolan@gmail.com*

[b] *Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, (Saudi Arabia)*

Keywords: Phosphine; NHC; Transition metal; Bifluoride

Table of Contents

Abbreviations: FHF^- or HF_2^-, hydrogen(difluoride) anion or bifluoride; M, metal; F, fluoride; TM, transition metal; dmpe, 1,2-bis(dimethylphosphino)ethane; dcpe, bis(dicyclohexylphosphino)ethane; PMe_3, trimethylphosphine; ^{t}Bu-bpy, 4,4′-di-*tert*-butyl-2,2′-dipyridyl; NFSI, *N*-Fluorodibenzenesulfonimide; NBS, *N*-bromosuccinimide; NHC, *N*-heterocyclic carbene; IPr, [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]; IMes, [1,3-bis(2,4,6-trimethyl)phenyl)imidazol-2-ylidene]; DMPU, [1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone]; SIPr, [1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene]; cod, 1,5-cyclooctadiene; 6-^{i}Pr, [1,3-bis(*iso*-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene]; pipz, piperazine; OAc, acetate; NMR, nuclear magnetic resonance.

ABSTRACT: Since its initial discovery, four decades ago, transition metal bifluoride chemistry has exhibited a slow growth, mainly due to problems associated with synthesis and characterization. Until recently, reports on this chemistry almost always presented these complexes as a fluke discovery. However, with the recent increase in reports and applications involving such species, a renewed interest in these complexes has been observed. Most of the work done in this area, so far, has been directed toward the synthesis and quite challenging characterization of these complexes, yet mostly neglecting the behavior of such species and their influence on catalytic processes. The aim of this work is to present a summary of the various preparation methods, characterization techniques and applications of reported transition metal bifluoride complexes. It is our hope that by centralizing all information available on such species, future efforts aimed at exploiting the full potential of transition metal bifluoride species can be facilitated.

1. Introduction

The hydrogen(difluoride) anion, commonly known as the bifluoride anion, is a unique moiety as it features the strongest known hydrogen bond [1]. Hydrogen bond interactions are one of the most important intra- and intermolecular interactions in chemistry [1-7]. Understanding these interactions has been the driving force behind numerous studies, mostly revolving around non-metal systems. In recent years, in-depth studies of transition metal-based structures and reactions have shown that hydrogen bonding could also be found in these systems. As a result, interest has risen in understanding the characteristics of these interactions and the properties they confer upon the metal system. Leading reports by Crabtree [8] and Morris [9] on the unconventional hydrogen-hydrogen interaction between a metal hydride and common organic hydrogen bond donors, such as amines or alcohols, catalyzed the rapid development of this area of research [10-15].

In recent decades, significant progress has been made in the ever-growing field of transition metal fluorides. This type of complexes has shown a remarkable ability to promote various transformations [16-

26]. Furthermore, it is now known that the reactivity of these compounds can be further influenced by interactions of the M-F bond with hydrogen bond donors, such as -OH, -NH or -CH groups [27,28]. Other donor molecules, such as hydrogen chloride (M-F---H-Cl) have also been reported [29]. Considering that the M-F---H-F interaction should exhibit the strongest hydrogen bond, this would be the most interesting unit to explore. Consequently, new reports aimed at investigating the nature of hydrogen bonding between metal fluoride species and HF by studying transition metal bifluorides, are nowadays increasing.

Reports have shown that TM bifluorides can express the bifluoride moiety in various forms (coordinated, non-coordinated, symmetrical, unsymmetrical) with different dissociation patterns. Typically, these bifluorides are classified into two main categories; bifluoride complexes (where the bifluoride unit is coordinated to the metal) and bifluoride salts (where the bifluoride unit does not interact with the metal and is located outside the metal's coordination sphere). These manifestations could be especially important for catalytic fluorination processes, where catalysts, particularly metal fluorides, are exposed to an excess of a HF source [30-33]. However, the influence of the metal and/or the ligand on this moiety is still unclear.

To date, there are no comprehensive reviews combining all the valuable, scattered information on the synthesis, characterization and structural behavior of these species. Recent reports have started to present these species as possible reaction intermediates and/or feedstocks for fluoride release. In hopes of shedding more light on the properties of transition metal bifluorides, a summary of the various preparation methods, characterization techniques and applications of bifluoride complexes/salts is presented. A description and classification of the reported systems will most certainly ensure a better understanding and possibly will help guide future efforts towards fully exploiting their potential in *e.g.* TM-catalyzed reactions.

2. Phosphine-Based Transition Metal Bifluorides

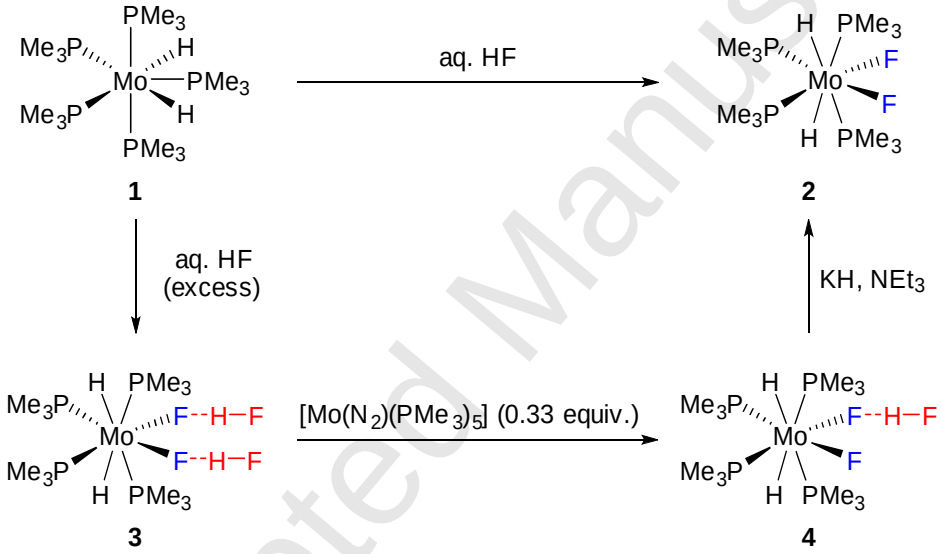
Since the initial report of a phosphine-based platinum bifluoride complex by Coulson [34], the use of phosphine ligands has been the main approach for the synthesis of these bifluoride complexes. The wide availability of these ligands with their wide range of tunable steric and electronic demands has enabled the isolation and characterization of several transition metal bifluorides.

2.1. Molybdenum and Tungsten

Bifluoride complexes based on group 6 transition metals (particularly, Mo and W) are the focus of the oldest reports in this field, and have contributed immensely to the advancement of this chemistry.

Twenty years after the first bifluoride was reported [34], Parkin and co-workers successfully synthesized a Mo-based bifluoride complex, $[MoF(H)_2(HF_2)(PMe_3)_4)]$ (**4**) [35]. The latter was obtained by reacting

$[Mo(H)_2(PMe_3)_5]$ (**1**) with aqueous hydrogen fluoride (HF) (Scheme 1). The use of substoichiometric amounts of aqueous HF afforded the conversion of **1** to the octacoordinate difluoride complex $[Mo(F)_2(H)_2(PMe_3)_4]$ (**2**) with concomitant loss of one equivalent of phosphine ligand. Unexpectedly, in the presence of further excess of HF, **1** afforded a mixture of the bis(bifluoride) $[Mo(H)_2(HF_2)_2(PMe_3)_4]$ (**3,** major compound) and the mono(bifluoride) complex $[MoF(H)_2(HF_2)(PMe_3)_4]$ (**4**). The procedure was further optimized in order to obtain full conversion to the bis(bifluoride) complex **3**. Selective formation of **4** was achieved by the subsequent reaction of **3** with 0.33 equivalents of $[Mo(N_2)(PMe_3)_5]$. Following this strategy, the complex was isolated and fully characterized. Consequently, it was revealed that the HF was involved in a hydrogen-bonding interaction with one of the Mo-F ligands (Figure 1).



Scheme 1. Synthesis of bis- and mono(bifluoride) molybdenum complexes 3 and 4 [35]

The X-ray structure of **4** highlights some fundamental features of the bifluoride complex. The complex presents an irregular dodecahedron structure, with the phosphine ligands occupying positions of the elongated tetrahedral subunit of the dodecahedron, while the anionic ligands form the flattened tetrahedral subunit. As shown in Figure 1, the F---H-F moiety is clearly not bound linearly to the molybdenum center, but depicts a Mo-F---F angle of 134º [36]. The Mo-FHF distance is longer than that of the Mo-F bond (2.124(3) Å *vs* 2.077(4) Å, respectively), and the distance between both fluorine atoms of the bifluoride unit (2.351(8) Å) permits the classification of the interaction as a "strong" hydrogen bond, although weaker than that present in bifluoride salts, such as KHF_2 (2.277 Å) [37]. Compared to that of a free bifluoride anion, this weakening is most likely due to a smaller polarity gap between the H and the F attached to the molybdenum center. These observations reveal that metal bifluorides and bifluoride salts are certainly based on different types of hydrogen bonding. Furthermore, a broad absorption at 2682 cm^{-1}

in the IR spectrum of complex **4** strongly contrasts with typical values observed for bifluoride salts (1284–1372 cm^{-1}) [38], thus reflecting their distinct character.

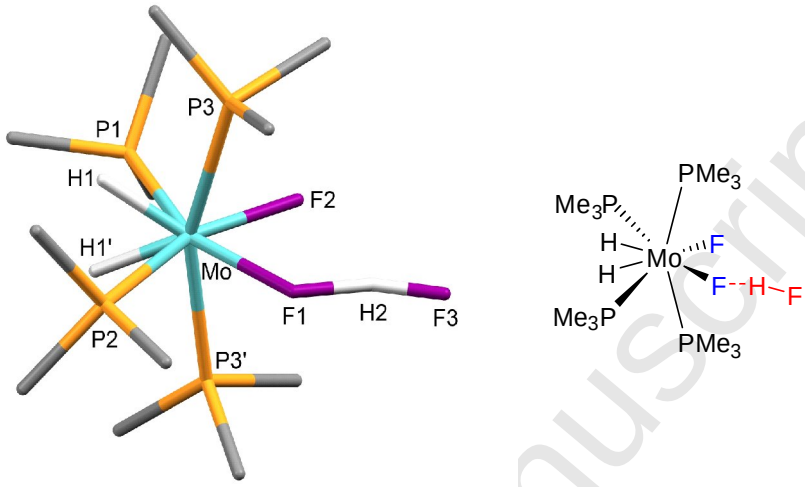


Figure 1. Solid-state structure of $[MoF(H)_2(HF_2)(PMe_3)_4]$ (4) [35]

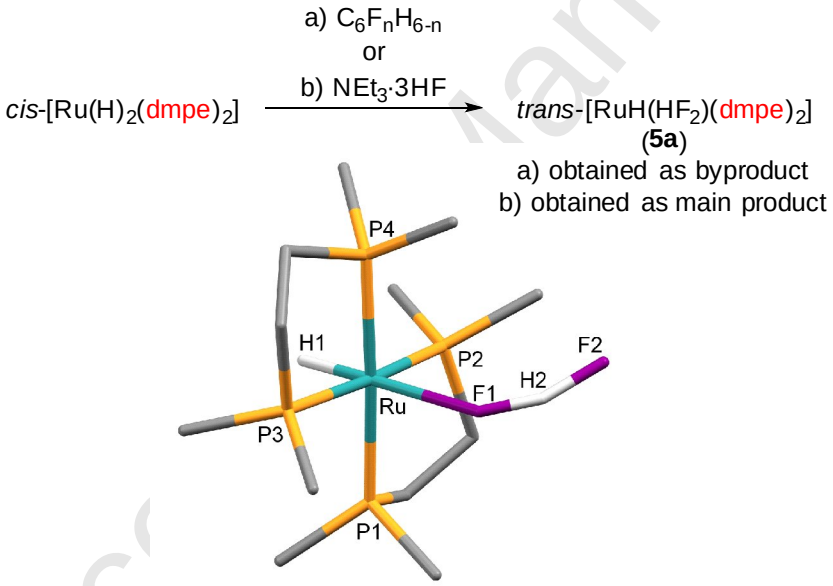
At the time, the reported NMR analyses were less informative about the spectroscopic properties of the bifluoride behavior in solution. ^1H NMR spectra of complex **4** exhibited a doublet at 12.5 ppm (C_6D_6, $^1J_{H\text{-}F}$ = 410 Hz), whereas the bifluoride anion in salts typically displayed a triplet ($^1J_{H\text{-}F}$ = 120 Hz) [39-40]. Based on these observations, it was suggested that the Mo-F---HF interaction was significantly weakened in solution with respect to that found in the solid state. A similar conclusion was drawn from the ^{19}F NMR analysis; complex **4** exhibited, in addition to the Mo-bound fluoride (proximal) signal at −230 ppm, a doublet at −182 ppm which was assigned to the distal fluoride of the FHF unit. The latter signal showed a coupling constant similar to that of a free HF molecule [41]. Later reports on similar complexes have helped to validate these notions.

The study of the aforementioned molybdenum complex was not only groundbreaking, but also initiated a re-evaluation of previously reported structures, now suspected to be bifluorides. For example, in 1984 Parkin and co-workers reported the reaction of the hydride complex $[WH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4]$ with aqueous HF, yielding a product which was initially assigned as the aqua complex $[WF(H)_2(OH_2)(PMe_3)_4][F]$ [42-44]. Driven by the isomorphism between molybdenum and tungsten, and considering the similarities of the reaction conditions and the obtained X-ray diffraction data with the Mo-FHF species described above, the complex formula was therefore re-examined. It was later shown that the experimental data were in excellent accord with the reformulation of the complex to the bifluoride species $[WF(H)_2(HF_2)(PMe_3)_4]$ [43,44,45].

2.2. Ruthenium

The discovery of ruthenium bifluoride complexes resulted from observations made from the application of ruthenium complexes in the activation of C-F bonds [46-49].

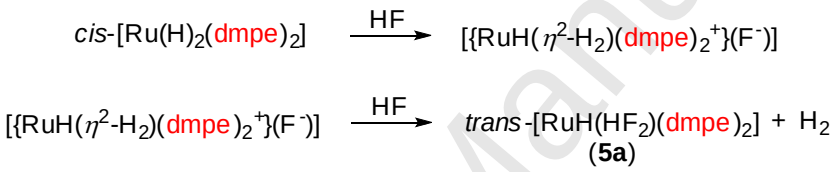
Perutz and co-workers, who were initially focused on the study of the C-F activation of fluoro-compounds [48] using ruthenium hydride complexes, pioneered the field of ruthenium bifluorides. In 1997, they reported the synthesis and structural study of the bifluoride species with formula *trans*-[RuH(HF_2)(dmpe)$_2$] (**5a**) [49]. This complex was obtained as a side-product in the reaction between *cis*-[Ru(H)$_2$(dmpe)$_2$] and hexafluorobenzene at −78 ºC, which mainly yielded *trans*-[RuH(C_6F_5)(dmpe)$_2$] *via* C-F bond activation (Scheme 2). The aromatic C-F activation promoted by metal complexes was a very active area of research at the time, and a precedent of this unexpected side-product was observed by the same group the previous year, although then, it had remained unidentified [48].



Scheme 2. Synthesis and solid-state structure of *trans*-[RuH(HF_2)(dmpe)$_2$] [49]

These studies showed that two equivalents of fluoroaryl compounds ($C_6F_nH_{6-n}$, n = 3,4,5,6) reacted with the dihydride ruthenium complex to afford an unknown compound in a 1:2 ratio with respect to the C-F activation product. ^{1}H NMR spectroscopy (d_8-THF, 293 K) of the former displayed two broad singlets at 13.8 and −25.8 ppm. ^{31}P{^{1}H} NMR experiments displayed a broad singlet, and ^{19}F NMR analysis showed no resonances. However, low-temperature ^{19}F NMR studies showed a pattern consistent with a bifluoride complex. Moreover, the presence of an excess of triethylamine completely suppressed the formation of this compound, whereas the addition of NEt_3·3HF (less than one equivalent in THF at room temperature), a mild source of HF, increased the yield of the desired product. According to these observations, bifluoride complex **5a** was proposed as the observed compound. IR studies were also conducted,

revealing a broad band at 1690 cm^{-1}, which is within the range of reported HF_2 salts. The structure of the bifluoride species was unambiguously determined by X-ray diffraction analysis and showed a Ru-bound bifluoride unit (FHF, with a Ru-F---F angle of 129.9(3)º) in a *trans* disposition relative to the hydride. Interestingly, the F---F distance of 2.276(8) Å found in complex **5a** is closer in range to that found in bifluoride salts [50,51] or pyridine·nHF [52], and considerably shorter than the F---F distance observed in the Parkin complex $[MoF(H_2)(HF_2)(PMe_3)_4]$ (**3**) (2.351(8) Å). The Ru-F bond length of 2.284(5) Å is significantly longer than that of Ru-F complexes (2.01-2.04 Å) known at the time [53-54]. The bifluoride complex was also highlighted as a very rare example of an octahedral complex containing a hydride and a fluoride ligand in a *trans* disposition [55]. The formation of the bifluoride species was suggested to proceed *via* the formation of a dihydrogen intermediate, followed by trapping of the excess HF to yield the desired compound **5a** (Scheme 3).

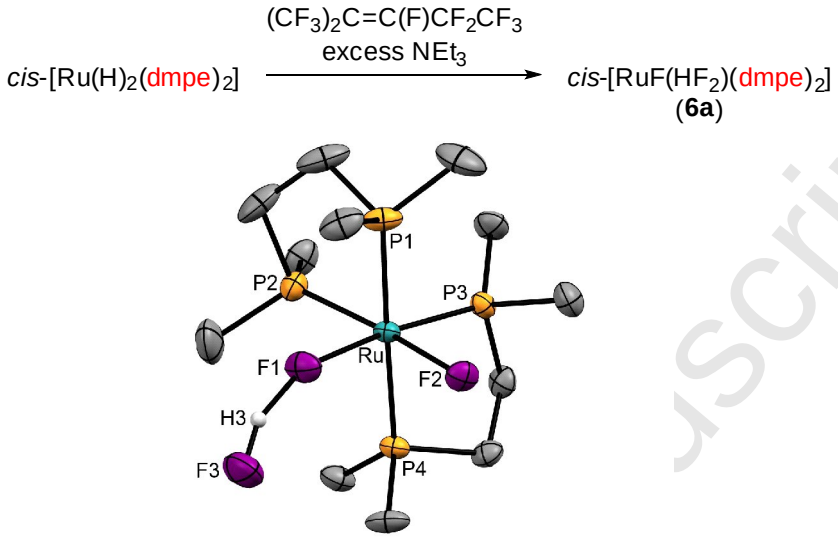


Scheme 3. Suggested reaction pathway for the synthesis of the ruthenium bifluoride complex 5a [49]

Furthermore, a second pattern of signals (belonging to a new species) was observed when NMR spectroscopy experiments were conducted at low temperatures. ^{1}H NMR and ^{19}F NMR analyses showed a triplet at 14.8 ppm (J = 145 Hz) and a broad doublet at −150.9 ppm, respectively. However, due to a lack of further data, an unambiguous identification of this species was not possible. Based on similarities with previously reported ruthenium complexes [56-59], it was tentatively assigned as $[\{RuH(dmpe)_2^+\}(HF_2^-)]$. In light of these results, the competition/equilibrium between free and coordinated bifluoride anions became the major interest of further studies.

In 2001, Whittlesey and co-workers showed that not only fluoroarenes, but also fluoroalkenes could be C-F activated with concomitant HF release and formation of new metal bifluoride species [60a]. In this example, perfluoroisohexene, $(CF_3)_2C{=}C(F)CF_2CF_3$, was used for the successful C-F cleavage/bifluoride synthesis, under similar conditions as before. However, the use of stoichiometric amounts of the *cis*-$[Ru(H)_2(dmpe)_2]$ and the fluoroalkene afforded a mixture of *trans*-$[RuH(HF_2)(dmpe)_2]$ (**5a**) and *cis*-$[RuF(HF_2)(dmpe)_2]$ (**6a**), in a 1:4 ratio. Addition of excess NEt_3 (10 equivalents) afforded full conversion towards the new *cis* complex (**6a**), which was isolated and characterized (Scheme 4). ^{1}H NMR spectroscopy showed a doublet at 14.2 ppm ($^1J_{H\text{-}F}$ = 328 Hz) indicating, once again, a weakening of the hydrogen bond in solution. ^{19}F NMR spectroscopy displayed a doublet at −174 ppm (attributed to the

distal fluoride, RuF-H-*F*) and two broad multiplets at −343 and −362 ppm (attributed to the two Ru-bound fluorides).

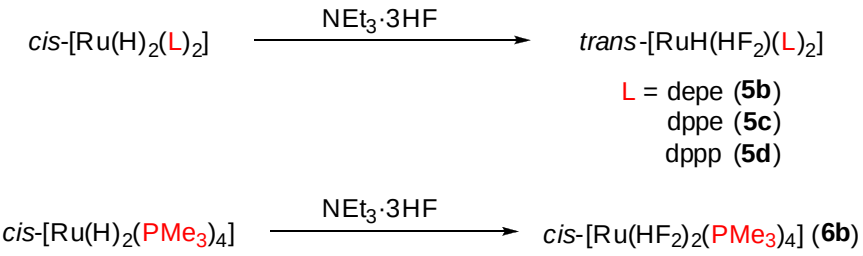


Scheme 4. Synthesis and solid-state structure of *cis*-[RuF(HF$_2$)(dmpe)$_2$] (6a) [60a]

X-ray analysis of **6a** shows a Ru-FHF bond length of 2.168(3) Å, which is longer than the other Ru-F bond (2.101(3) Å). The present bifluoride complex displays a longer F---F distance when compared to that of complex **5a** (2.292(8) Å *vs* 2.276(8) Å). The Ru-F---F angle of 142º is within the range observed for other transition metal bifluorides. Furthermore, IR measurements showed two bands at 2452 and 1915 cm^{-1} characteristic of two unsymmetrical H-F bonds.

Interestingly, the above methodology could not be extended to other ruthenium hydrides bearing different phosphine ligands. For example, the reaction of *cis*-[Ru(H)$_2$(dcpe)$_2$] with perfluoroisohexene afforded a 16-e$^-$ ruthenium complex, which was identified as a [{RuH(dcpe)$_2$}$^+$] bearing a perfluoro-enolate [(CF$_3$)$_2$C=C(O)CF$_2$CF$_3$] as counter-anion, in 31% yield. The origin of the enolate moiety presumably is promoted *via* hydrolysis by traces of water; the use of excess water afforded a quantitative yield of the cationic species, thus further supporting this hypothesis.

Perutz and co-workers were able to overcome the above limitation and extend the method, using NEt$_3$·3HF as a fluorinating reagent, to access new ruthenium bifluoride complexes bearing different phosphine ligands (Scheme 5) [60b]. Three new diphosphine-based ruthenium bifluorides (**5b-d**) were synthesized, of the formula *trans*-[Ru(H)(HF$_2$)(L)$_2$], in which the bifluoride ligand adopted a *trans* disposition to the hydride. A ruthenium bis-bifluoride complex (**6b**) was also successfully accessed, bearing trimethylphosphine as ligand. In contrast to the diphosphine analogs, the bifluoride moieties in *cis*-[Ru(HF$_2$)$_2$(PMe$_3$)$_2$] (**6b**) adopted a *cis* position relative to each other and each was located *trans* to a phosphine ligand.



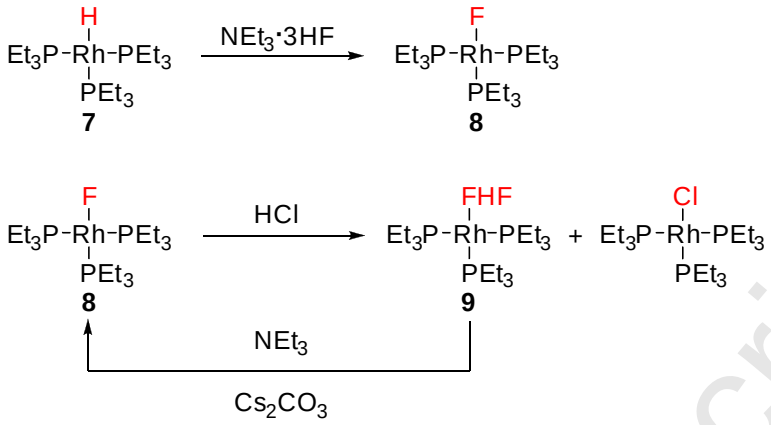
Scheme 5. Synthesis of new ruthenium bifluorides with different phosphine ligands [60b]

Exchange reactions and dynamic behavior studies, which were conducted in that report, showed that dissociation was more likely occurring at the Ru-F bond and as a consequence liberating free HF_2^- in solution and not HF.

2.3. Rhodium

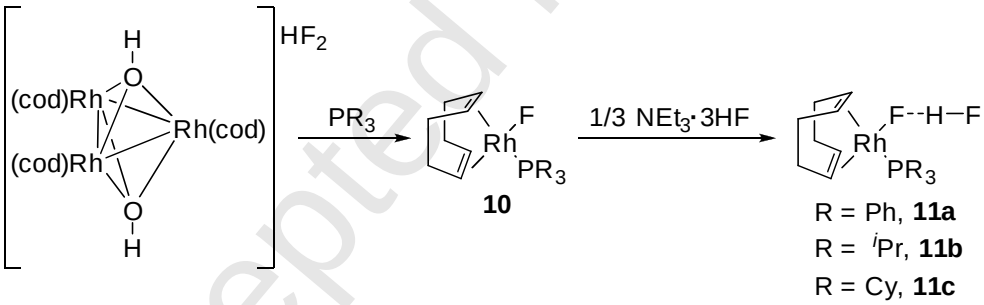
Rhodium fluoride complexes have attracted much attention in recent years, mostly due to the rapid growth of fluorination chemistry. These species were typically prepared by Cl/F exchange using AgF [17], or by C-F activation/hydrogenolysis of fluorinated alkenes [61]. Nowadays, the use of $NEt_3 \cdot 3HF$ is considered a more practical approach for metal fluoride synthesis [26,62]. However, since this reagent is also an excellent bifluoride promoter, various reports of Rh-FHF complexes have started to appear in the literature.

Braun and co-workers prepared $[RhF(PEt_3)_3]$ (**8**) by reacting $[RhH(PEt_3)_3]$ (**7**) with $NEt_3 \cdot 3HF$. Upon treatment of **8** with HCl in ether, the chloro analog $[RhCl(PEt_3)_3]$ was obtained (Scheme 6) [63]. However, it was found that the use of substoichiometric amounts of HCl affords the bifluoride complex, $[Rh(HF_2)(PEt_3)_3]$ (**9**), as the major compound. Tuning the amount of added HCl proved crucial for the selective formation of the bifluoride species. ^{31}P NMR analysis (223 K) shows a very similar pattern to that of the initial complex. However, the ^1H NMR spectrum (room temperature) displays a broad signal at 13.2 ppm, clearly indicating the presence of a bifluoride species. This signal can be further resolved at 223 K into a doublet of doublets ($^1J_{H\text{-}F}$ = 42 Hz with the Rh-bound proximal *F*, and $^1J_{H\text{-}F}$ = 382 Hz with the distal *F*). Furthermore, ^{19}F NMR spectroscopy clearly shows the two characteristic peaks at −176.4 ppm (distal *F*) and −278.3 ppm (proximal *F*). The proximal fluorine couples with a vicinal phosphorus nucleus ($^2J_{F\text{-}P}$ = 175 Hz, no $H\text{-}F_{proximal}$ coupling is observed), while the distal fluorine reveals a coupling with the proximal fluorine ($^2J_{F\text{-}F}$ = 116 Hz) and the H atom ($^1J_{F\text{-}H}$ = 386 Hz). The proposed reaction mechanism proceeds *via* protonation/chlorination of the starting complex with subsequent elimination of HF, which can be further trapped by the remaining Rh-F species.



Scheme 6. Synthesis of [Rh(HF$_2$)(PEt$_3$)$_3$] (9) [63]

During the same year, Vicente and co-workers reported the isolation and characterization of several rhodium bifluoride complexes. In a similar manner, fluoride complexes of the type [RhF(cod)(PR$_3$)] (**10**) were reacted with NEt$_3$·3HF to afford 3 new bifluorides, [Rh(HF$_2$)(cod)(PR$_3$)] (R = Ph, ^{i}Pr or Cy) [64]. [RhF(cod)(PR$_3$)] complexes were accessed by reacting the trinuclear bifluoride species [{Rh$_3$(μ_3-OH)$_2$(cod)$_3$}(HF$_2$)] with the corresponding phosphine. Under these conditions, the bifluoride complexes were obtained in 67-92% isolated yields (Scheme 7).



Scheme 7. Synthesis of [Rh(HF$_2$)(cod)(PR$_3$)$_3$] from the trinuclear [{Rh$_3$(μ_3-OH)$_2$(cod)$_3$}(HF$_2$)] [64]

X-ray analysis of [Rh(HF$_2$)(cod)(PPh$_3$)] (**11a**) confirmed the presence of the HF$_2$ ligand. The metal adopts a slightly distorted square-planar geometry. Being shorter than twice the van der Waals radius of fluorine (1.4 Å), the F---F distance (2.331(34) Å) is still within the range found for other metal bifluorides (2.276-2.400 Å). The Rh-F---F angle measured at 147.2º, was also within the observed range for other terminal metal bifluorides reported up to date (128.5º-156.7º). Similarly to other bifluorides, the Rh-F bond in the bifluoride species is weakened (2.083(2) Å) compared to the undisturbed Rh-F bond (2.0214(12) Å), as a consequence of the hydrogen bonding. Both fluoride and bifluoride complexes appear to possess similar *trans* effects, since the Rh-C distances for the olefin units in *trans* position with respect to the fluorine atoms were very similar. Expectedly, for both fluoride species this influence was lower in comparison to the phosphine ligands *trans* effect. IR measurements showed bands at 2630 and

1842 (**11a**), 2580 and 1866 (**11b**), and 2634 and 1842 cm^{-1} (**11c**), assigned to the stretching and bending $\nu(HF_2)$ modes. Since hydrogen bond interactions become stronger in bifluoride complexes, a decrease in the ν(FHF) relative to free HF (3960 cm^{-1}) is expected. However, all observed wavenumbers were much higher than those found in most common HF_2 salts (1284–1372 cm^{-1}). Furthermore, the bands at higher wavenumbers were closer to those observed in mixed XHF^- anions (X = Cl, 2491 cm^{-1}, or Br, 2803 cm^{-1}), thus indicating that these bifluoride ligands are highly unsymmetrical in nature. ^{19}F NMR spectroscopy (193 K) shows a characteristic doublet of doublets in the range of −176.2 to −190 ppm for all bifluoride complexes and an unresolved multiplet around ~ −260 ppm. ^{1}H NMR spectroscopy shows a broad signal at around 12 ppm, resolving into a doublet of doublets at low temperature. Once again, it is shown that the coupling constant for the distal fluoride is significantly higher than that of the rhodium-bound fluoride (360–375 Hz *vs* 32–41 Hz), both differing considerably from free HF_2^- anions (120 Hz) and free HF (476 Hz in CH_3CN). Again, the higher values are actually closer to those found in mixed anionic species, such as [$ClHF^-$] (404 Hz) [40].

In a later study, the fluoride analog of Wilkinson's catalyst, [$RhF(PPh_3)_3$], was synthesized and fully characterized. During this synthesis, a side-product was observed when reaction mixtures were filtered over cotton. The product was identified as the bifluoride complex, [$Rh(HF_2)(FPPh_2)(PPh_3)_2$] (Figure 2) [65a]. The latter displayed similar properties as previous bifluorides. The Rh-F bond length of 2.082(1) Å is again slightly longer than the value of the fluoride analog. Within a similar value range to other reported bifluoride species, the F---F distance has been measured as 2.329 Å, with a Rh-F---F angle of 135.6º.

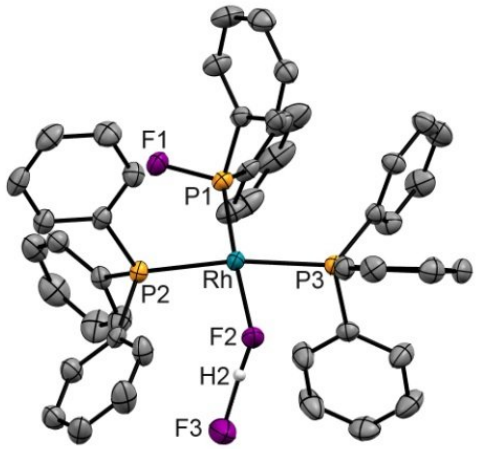


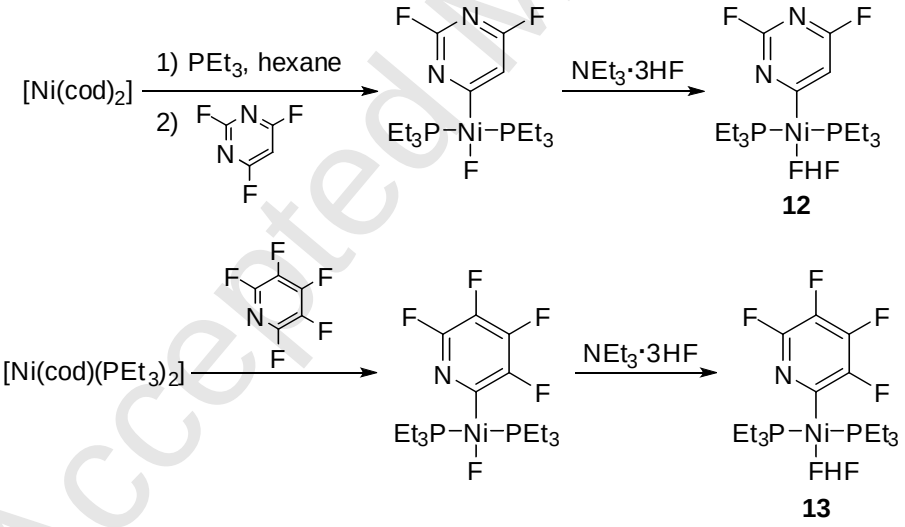
Figure 2. ORTEP representation of the solid-state structure of [$Rh(HF_2)(FPPh_2)(PPh_3)_2$] [65a]

Werner and co-workers observed the formation of a rhodium bifluoride as by-product and successfully identified this species; although only a mixture of products was observed and no complex was isolated

[65b]. The rhodium bifluoride was postulated as an intermediate in the reaction of fluoro(vinylidene)rhodium(I) complexes with acetic acid.

2.4. Nickel

Perutz and co-workers successfully isolated and characterized a nickel complex with the formula *trans*-[Ni(HF$_2$)(2-C$_4$HF$_2$N$_2$)(PEt$_3$)$_2$] (**12**) [66]. The reported synthesis involved the stepwise reaction of [Ni(cod)$_2$] with PEt$_3$, followed by oxidative addition of 2,4,6-trifluoropyrimidine, resulting in a tetra-coordinated nickel complex (Scheme 8). The subsequent reaction with NEt$_3$·3HF afforded the Ni-FHF complex. The structure was confirmed by the presence of two signals in the ^{19}F NMR spectrum at 233 K; a doublet at −180.35 ppm with a $^1J_{H\text{-}F}$ ~ 390 Hz for distal fluorine, and a broad singlet at −332.61 ppm for proximal fluorine. ^{1}H NMR spectroscopy showed a characteristic broad doublet at 11.36 ppm ($^1J_{H\text{-}F}$ ~ 430 Hz). The ^{31}P NMR spectrum reinforced the presence of the Ni-F unit, due to the observed F-P coupling (doublet at 13.2 ppm, $^2J_{P\text{-}F}$ = 43.2 Hz). Compared to the fluoride analog, the Ni-C bond length in the bifluoride complex is shorter (1.844 Å *vs* 1.856 Å), while the Ni-F bond is significantly longer (1.908 Å *vs* 1.869 Å) (Figure 3). These data are in agreement with previously described bifluorides.



Scheme 8. Synthesis of nickel bifluoride complexes [66,67]

In a later report by the same group, pentafluoropyridine was used instead of 2,4,6-trifluoropyrimidine for the oxidative addition reaction at the Ni(0) center. In a similar fashion as before, *trans*-[NiF(2-C$_5$NF$_4$)(PEt$_3$)$_2$] reacted with NEt$_3$·3HF to afford the desired bifluoride **13** (Scheme 8) [67]. ^{19}F NMR analysis at 190 K, showed a doublet of doublets at −179.37 ppm (distal fluorine H-*F*, $^1J_{F\text{-}H}$ = 422 Hz, $^2J_{F\text{-}F}$ = 85 Hz) and a broad singlet at −339.06 ppm (proximal fluorine, Ni-*F*). ^{1}H NMR analysis exhibited a broad doublet of doublets at 11.58 ppm ($^1J_{H\text{-}F}$ = 424 Hz, $^1J_{H\text{-}F}$ = 41 Hz). The presence of a Ni-F bond was

also confirmed by ^{31}P NMR spectroscopy, which showed a signal at 14.4 ppm with a P-F coupling ($^{2}J_{P\text{-}F}$ = 37.9 Hz). This is again in accordance with previous bifluoride reports.

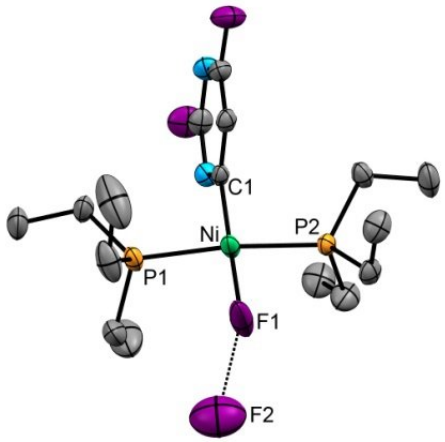


Figure 3. ORTEP representation of the solid-state structure of trans-[Ni(HF$_2$)(2-C$_4$HF$_2$N$_2$)(PEt$_3$)$_2$] (12) (A co-crystallized nickel complex is not shown) [66]

2.5. Palladium

In recent years, the use of palladium complexes as catalysts in fluorination chemistry has grown exponentially. For this reason, studies probing the behavior of the corresponding fluoro-derived intermediates have been the focus of investigation. This need propelled the investigation of Pd-fluoride complexes as well as their synthesis and characterization, which in turn led to the discovery and study of palladium bifluoride species.

The initial work of Grushin and co-workers on palladium fluoride complexes brought the bifluoride analogs into the spotlight [68-74]. They successfully prepared the bifluoride complexes *trans*-[Pd(HF$_2$)(Ph)(PPh$_3$)$_2$] (**14a**) and *trans*-[Pd(HF$_2$)(Me)(PPh$_3$)$_2$] (**14b**) (98% and 86% isolated yields, respectively) by treating the respective hydroxide precursor with excess NEt$_3$·3HF [75,76]. Coordination parameters of bifluoride **14a** were closer to those observed for the weakly π-donating monobromide or monoiodide analogs, and distinct from that of their monofluoride or monochloride counterparts (much stronger π-donors). This can be clearly seen in the X-ray structure of the bifluoride **14a** (Figure 4), since a twisted orientation of the phosphine is observed (typically found in the bromo and iodo analogs) and not an eclipsed conformation (found in the fluoro and chloro complexes). The Pd-F bond length (2.098(2) and 2.103(2) Å) is longer than that observed for the fluoride analogue (2.085(3) Å), and similar Pd-C bond lengths are observed in both cases (1.989(2) for C-Pd-FHF *vs* 1.994(2) Å for C-Pd-F). Infrared bands at 2578 and 1822 cm^{-1} for ν(HF) highlight the presence of strong hydrogen bonding within the complex. Based on the observed data, it was suggested that the bifluoride behaved more like a neutral [Pd-F---H-F] complex (unsymmetrical extreme) rather than a cationic [Pd---F-H-F] species (symmetrical extreme). The

Pd-F---F angle was measured as 153.6º and 153.4º in the two independent molecules found in the unit cell. The large value presumably arises from the existence of a push-pull system along the Ph-Pd-F axis. A similarly large angle (156.7º) is observed in *trans*-[Ni(HF_2)(2-$C_4HF_2N_2$)(PEt_3)$_2$] (**12**), for which push-pull considerations regarding the interaction between the fluoride and the pyrimidyl moiety are also conceivable [66].

^{1}H NMR and ^{31}P NMR spectroscopy of a sample of **14a** [CD_2Cl_2/toluene-d_8 (2/1, v/v), room temperature] displayed a broad singlet at 12.5 ppm (F-*H*-F) and at 22.9 ppm (*P*Ph_3), respectively. At this temperature, no clearly resolved resonances were observed in the ^{19}F NMR spectrum. However, at 213 K, the ^{19}F NMR spectrum displayed a doublet of doublets at −174 ppm (distal *F*, $^1J_{H\text{-}F}$ = 368 Hz, $^2J_{F\text{-}F}$ = 119 Hz) and a signal of ddt multiplicity at −254 ppm (proximal *F*, $^1J_{F\text{-}H}$ = 33 Hz, $^2J_{F\text{-}F}$ = 119 Hz, $^2J_{F\text{-}P}$ = 8 Hz). The proton resonance was also resolved as a doublet of doublets showing strongly differing coupling constant to the distal *F* atom ($^1J_{H\text{-}F}$ = 368 Hz) and the proximal *F* atom ($^1J_{H\text{-}F}$ = 33 Hz), thus reflecting the profound unsymmetrical nature of this bifluoride species.

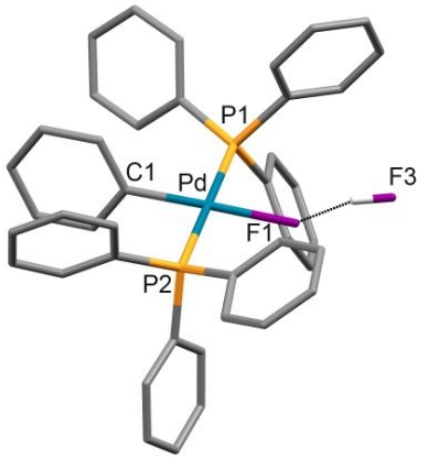
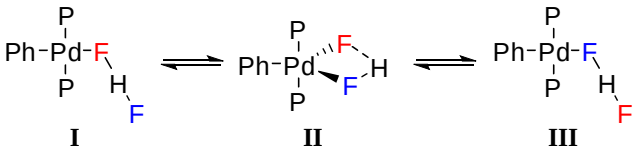


Figure 4. Solid-state structure of *trans*-[Pd(HF_2)(Ph)(PPh_3)$_2$] (14a) (Only one of the molecules of the unit cell is shown) [76]

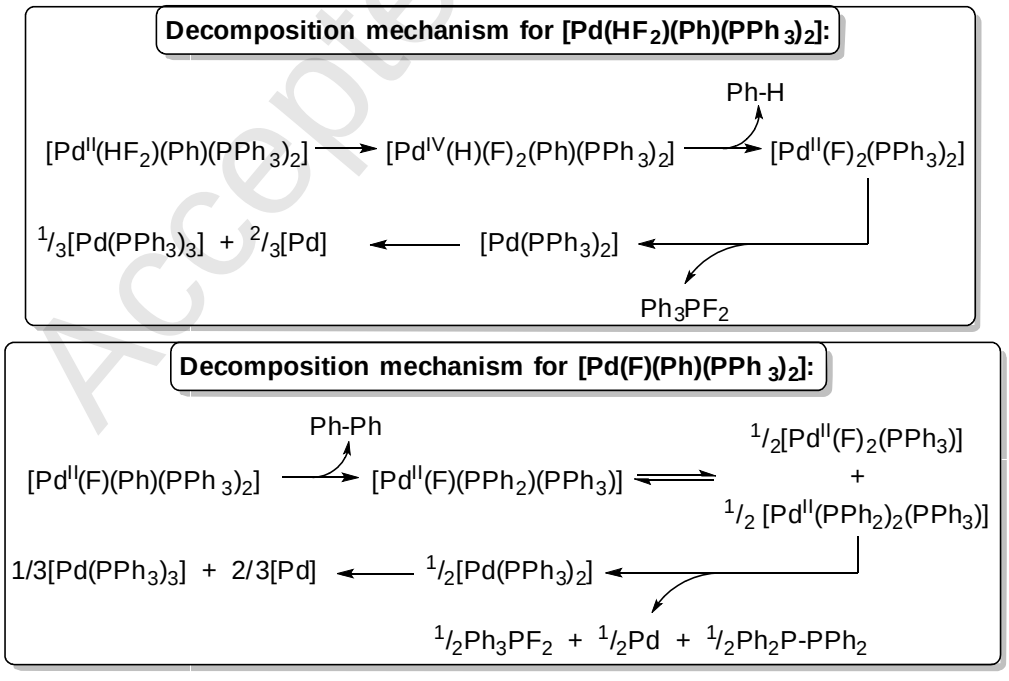
The same group went on to conduct a study on the behavior of complex **14a** in solution [76], which, at the time, was the first of its kind for bifluoride complexes. As was discussed previously, low temperatures are almost always needed in order to obtain clear data for the proper characterization of these species. This fact clearly underlines the importance of elucidating the solution behavior of these complexes.



Scheme 9. Proposed mechanism for the intramolecular exchange of the palladium bifluoride species in solution [76]

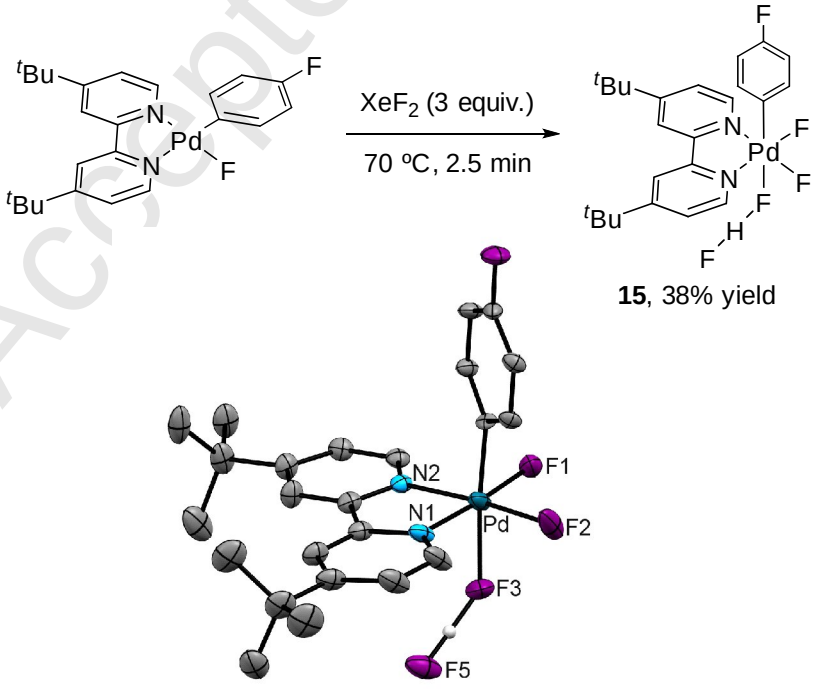
Evidence of HF dissociation and transfer were obtained if glass tubes were used for NMR spectroscopy experiments. Glass etching was detected and new signals were found in the ^{19}F NMR spectrum (assigned to Si-F species), whereas the use of Teflon liners completely inhibited this phenomenon. Magnetization transfer studies demonstrated that HF dissociation is a minor contributor to exchange processes in low polarity solvents. The exchange process depicted in Scheme 9 between **I** and **III** is fast and concentration independent, which points out to an intramolecular version of the known associative mechanism for ligand exchange in square-planar complexes of Pd(II) (*via* intermediate **II**) [77]. These observations ruled out mechanisms involving HF elimination or full ionization and dissociation of [FHF^-].

Decomposition studies were also performed and it was found that *trans*-[$Pd(HF_2)(Ph)(PPh_3)_2$] (**14a**) is significantly less thermally stable than its monofluoride analog. The bifluoride complex decomposed after 4 hours at 75 °C in toluene, whereas the fluoride species only decomposed after 16 hours at 110 °C [78]. A more detailed study of these reactions revealed different decomposition pathways for both complexes (Scheme 10).



Scheme 10. Proposed mechanism for the intramolecular exchange of the palladium bifluoride species in solution [78]

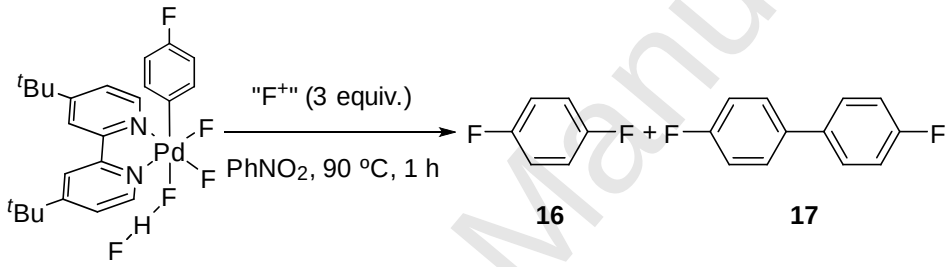
In an attempt to synthesize a [F-Pd^{IV}-Ar] species, Sanford and co-workers observed the formation of a Pd^{IV} bifluoride complex (Scheme 11) [79a]. This study was prompted by several reports suggesting that the Pd-catalyzed Ar-F bond formation, using electrophilic fluorinating reagents, involved a transient Pd^{IV} species. Moreover, evidence obtained by Ritter and co-workers gave prominence to this theory and spurred additional efforts to isolate such complexes [80]. For these reasons, [PdF(Ar)(^{t}Bu-bpy)] was prepared by reacting [PdI(Ar)(^{t}Bu-bpy)] with silver(I) fluoride (83% isolated yield). Upon addition of three equivalents of XeF_2 at 90 ^{o}C, the aryl-F reductive elimination product was observed. In an attempt to detect the palladium intermediate, the same reaction was repeated at a lower temperature (70 ^{o}C). After 2.5 minutes, a new complex was observed and isolated in 38% yield. X-ray diffraction analysis revealed a Pd^{IV} bifluoride complex, [Pd(F)$_2$(HF$_2$)(Ar)(^{t}Bu-bpy)] (**15**). ^{19}F NMR (298 K) spectroscopy showed three broad resonances at −117.2 ppm (Ar-*F*), −206.3 ppm (Pd-*F*) and −257.4 ppm (Pd-*F*), in a 1:1:2 ratio. At 203 K, the Pd-*F* signals appeared as a multiplet (−204.5 ppm) and a doublet (−256.9 ppm). Furthermore, a fourth signal appeared as a doublet of doublets at −177.6 ppm (distal fluoride, Pd-F-H-*F*). The corresponding group appeared in the low-temperature ^{1}H NMR spectrum as a doublet of doublets at 12.7 ppm ($^1J_{H\text{-}F}$ = 31 Hz with proximal *F*, $^1J_{H\text{-}F}$= 370 Hz with distal *F*). All spectroscopic data are in accord with the formulation of the product as a bifluoride complex. The source of the HF present in the final complex was suggested to originate from traces of H_2O present in the system, as noted in other reactive systems involving XeF_2 [81]. This complex is one of the first isolable monoaryl Pd^{IV} complexes with no stabilizing *ortho* substituent.

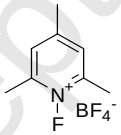


Scheme 11. Synthesis and solid-state structure of [Pd(F)$_2$(HF$_2$)(Ar)(^{t}Bu-bpy)] (15) [79a]

The reactivity of the palladium bifluoride species was also briefly analyzed in the same study (Table 1). While warming the complex did not afford a substantial amount of the aryl-F reductive elimination product (**16**), it did, however, yield significant quantities of the biaryl coupling product (**17**, 35%). This observation was discouraging, since Ritter and co-workers had previously shown that a Pd^{IV} complex bearing fluorides and aryl ligands could undergo reductive elimination upon thermolysis, to form the desired Ar-F bond [80]. However, it was discovered that the presence of additional XeF_2, greatly increased conversion, while changing the selectivity towards the fluorination product. The same reactivity was observed with two other electrophilic fluorination reagents, although in lower conversions.

Table 1. Synthesis and X-ray structure of [Pd(F)$_2$(HF$_2$)(Ar)(^{t}Bu-bpy)] (15) [79a]



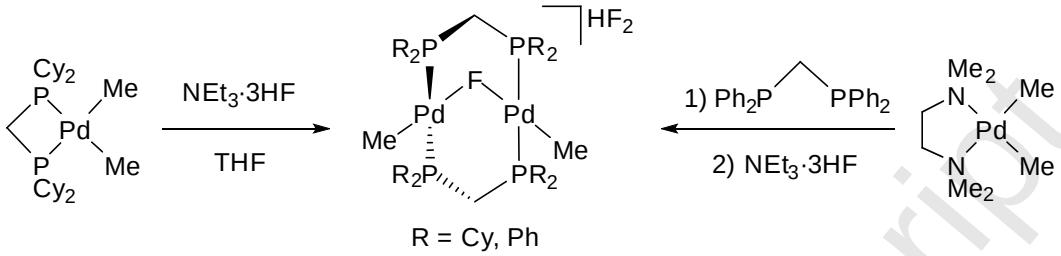
Entry	"F$^+$"	16[a]	17[a]
1	-	traces	35%
2	XeF_2	92%	4%
3	NFSI	83%	<1%
4		50%	2%
5	NBS	>95%	-

[a] Yields are determined by NMR spectroscopy, with hexafluorobenzene as internal standard.

These observations have confirmed the need for additional "F$^+$" in the reaction media to promote the formation of the fluorinated product. Interestingly, the reaction of *N*-bromosuccinimide with the bifluoride complex also afforded **16**, thus suggesting that the additional oxidant does not serve as a fluorine source. The authors reasoned that the oxidant could react with the bifluoride unit, thus allowing the reductive elimination, and consequently the Ar-F bond formation, to take place [82a].

Braun and co-workers reported two examples of palladium bifluoride salts by reacting [Pd(Me)$_2$(R$_2$PCH$_2$PR$_2$)] (R = Cy, Ph) with NEt$_3$·3HF in THF [79b]. The resulting A-frame palladium bifluorides were isolated and fully characterized (Scheme 12). X-ray structure analysis of one of the

compounds (R = Ph) confirmed the salt aspect by showing that the symmetrical HF_2 moiety was outside the coordination sphere of the metal, and having no interaction with the palladium metal center.



Scheme 12. Synthesis of nickel bifluoride complexes [79b]

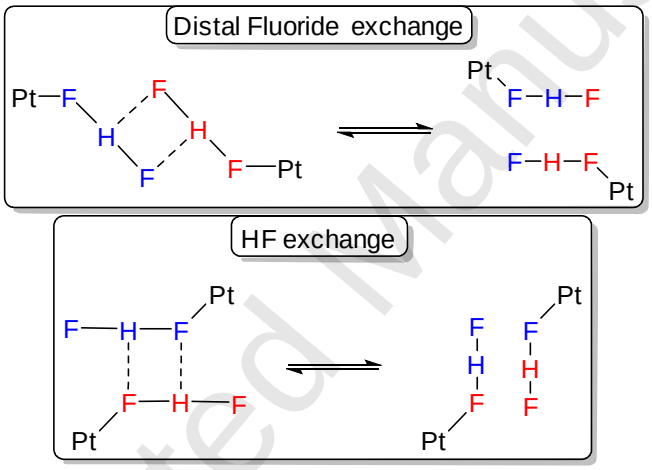
The remarkable results obtained in these reports showed the sensitive and complex nature of the Pd-catalyzed fluorination process towards oxidative and non-anhydrous conditions. Furthermore, the stability of the bifluoride complex, under mild conditions, suggested that the reductive elimination is probably the rate-limiting step in Pd^{II}/Pd^{IV}-catalyzed fluorination reactions.

2.6. Platinum

The first transition metal bifluoride complex to be observed was a Pt-based compound, formulated as *trans*-[$Pt(HF_2)(C_6H_5)(PEt_3)_2$], and was reported by Coulson in 1976. It was obtained as a by-product during attempts to prepare its fluoride analog, *trans*-[$PtF(C_6H_5)(PEt_3)_2$], from the reaction between *trans*-[$Pt(C_6H_5)_2(PEt_3)_2$] and gaseous HF [34]. However, as the above reports have come to show, metal fluorides will most certainly react with excess HF to generate the bifluoride species. Elemental analysis, as well as ^1H and ^{13}C NMR data indicated the formation of the suggested bifluoride complex. However, as the ^{13}C NMR spectroscopy cannot unambiguously distinguish between the fluoride and the bifluoride species, the only conclusive evidence for the bifluoride formation was the observation of a clear broad resonance at 10.7 ppm in the ^1H NMR spectrum, suggesting a strongly coupled and acidic hydrogen atom. The proton was assigned to the acidic proton in the HF_2 moiety, and the strong hydrogen bond interaction between free HF and the F ligand was put forth as a possible explanation for this observation. Unfortunately, no X-ray analysis was included in this report. Therefore the nature of this bifluoride complex remains uncertain.

In 1992, Hintermann and co-workers observed the formation of *trans*-[$PtH(HF_2)(PCy_3)_2$] in an electron-transfer reaction between *trans*-[$Pt(H)_2(PCy_3)_2$] and fluorinated benzonitrile [83]. However, attempts to isolate the complex were unsuccessful. Inspired by these findings, Perutz and co-workers succeeded in the isolation of this complex, by reacting the dihydride complex with $NEt_3 \cdot 3HF$ [82]. In this manner, two bifluoride complexes bearing different phosphine ligands were isolated and characterized; *trans*-[$PtH(HF_2)(PCy_3)_2$] and *trans*-[$PtH(HF_2)(P^iPr_3)_2$].

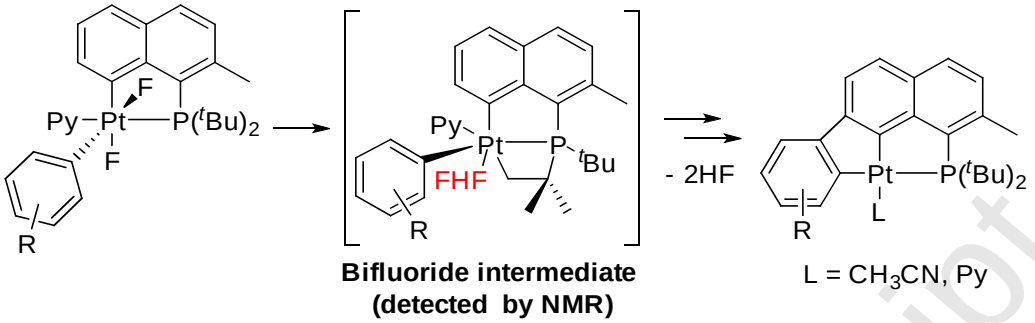
As expected, ^{19}F NMR analysis (room temperature) for each of the platinum bifluoride complexes shows two resonances: a doublet at −280 ppm (Pt-*F*) and a broad resonance at −180 ppm (distal *F*). The latter was resolved into a doublet of doublets at 193 K ($^{1}J_{H\text{-}F}$ = 400 Hz and $^{2}J_{F\text{-}F}$ = 103 Hz). The coupling constant $^{1}J_{Pt\text{-}F}$ between platinum and the proximal *F* (572 and 588 Hz, see Table 3), determined at 193 K, clearly highlights the bifluoride interaction with the metal center. ^{1}H NMR spectra (room temperature) showed that the acidic proton of each complex appears as a broad resonance at 11.5 ppm. At low temperature (193 K), this signal resolves into a doublet of doublets at 11.9 ppm (R = Cy, $^{1}J_{H\text{-}F}$ = 412 Hz with the distal *F*, and $^{1}J_{H\text{-}F}$ = 48 Hz with the proximal *F*) and at 11.3 ppm (R = ^{i}Pr, $^{1}J_{H\text{-}F}$ = 393 Hz and $^{1}J_{H\text{-}F}$ = 43 Hz). Dynamic NMR studies showed that two intermolecular exchange mechanisms were at play; distal fluoride exchange and/or HF exchange between two platinum centers (Scheme 13).



Scheme 13. Transition states for the intermolecular exchange of the distal fluoride and HF [82]

It was further demonstrated that the bifluoride ligand can easily be replaced by various anionic (*e.g.* OTf$^-$) and neutral ligands (*e.g.* PPh_3), or converted back to the monofluoride complex by reaction with CsOH in the presence of tetra-methylammonium fluoride.

Another example by Vigalok and co-workers proposed the formation of a Pt^{IV} bifluoride species while studying the migration of aryl ligands in aryl α-naphthyl Pt^{IV} difluorides (Scheme 14) [84]. This species was detected in most reaction mixtures during the investigation of the reaction scope. The reaction parameters were of importance, since the solvent, the reaction time and the nature of the aryl ligand affected the ratio of detected bifluoride intermediates considerably. However, these intermediates were never isolated.



Scheme 14. Aryl migration process and proposed bifluoride intermediate [84]

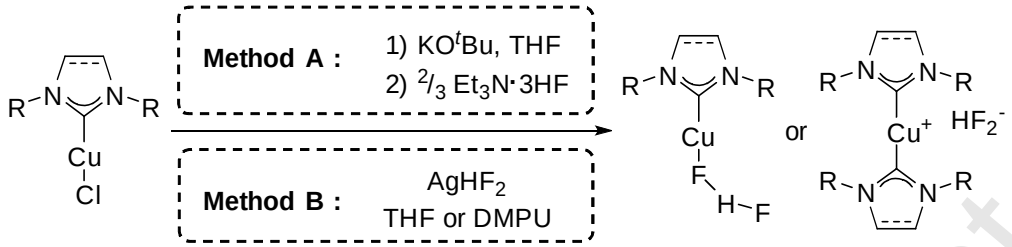
3. NHC-based Transition Metal Bifluorides

The most recent family of bifluorides consists of complexes bearing NHCs as ligands. Since the discovery of these stable carbenes, it has been of great interest to use their strong donating capabilities to coordinate and stabilize metal species which, otherwise, would have been difficult or impossible to obtain with other ligand classes [85]. For this reason, NHCs have appeared ideally suited to overcome difficulties related to the stabilization of metal fluoride complexes. The knowledge acquired during the synthesis of phosphine-based fluorides and bifluorides has been applied to related NHC-metal complexes. Despite the scarce number of reports compared to phosphine-based systems, a significantly greater number of complexes per report have been obtained. In this manner, a substantial amount of information on new metal bifluoride species has been gathered and discussed.

3.1. 5-membered NHCs

3.1.1 Copper

The first copper bifluorides to be synthesized were NHC-based species, and were reported by Riant and Leyssens [86]. In their report, four neutral and two cationic (salts) NHC copper bifluorides were synthesized (Scheme 15). The copper bifluorides were accessed using a modified synthesis of the monofluoride analogs [87-89]. In this fashion, the corresponding [CuCl(NHC)] was reacted with KO^{t}Bu, followed by addition of $NEt_3 \cdot 3HF$ in THF. The same species were also obtained by treating the copper chloride complexes with $AgHF_2$. X-ray diffraction data were obtained for the neutral complex [$Cu(HF_2)$(IPr)] (**18**) and the cationic [{$Cu(IMes)_2$}(HF_2)] (**19**).



Scheme 15. Synthesis of neutral and cationic NHC copper bifluoride complexes [86]

The preference for obtaining a mono- or a bis-(NHC) copper species was dependent on the nature of the *N*-substituents of the corresponding NHC. Steric rather than electronic factors were presumed as the major contributor to this phenomenon. The reaction outcome of the silver route proved highly solvent dependent, giving either the mono- or the bis-(NHC) copper in THF or DMPU, respectively. Two of the six reported bifluorides were based on a family of chiral NHC ligands developed by Tomioka and co-workers [90]. The latter constitute the first examples of metal bifluorides bearing a chiral ligand.

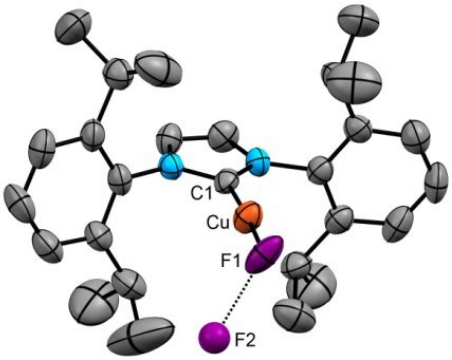


Figure 5. ORTEP representation of the solid-state structure of the neutral bifluoride complex [Cu(HF$_2$)(IPr)] (18) [86]

As expected, X-ray diffraction analysis of [Cu(HF$_2$)(IPr)] (**18**) revealed a longer Cu-F bond length (1.872 Å) compared to that of the monofluoride analog [CuF(IPr)] (1.820 Å) (Figure 5) [87]. The F---F distance, measured as 2.243 Å, was considerably smaller than the one observed for other bifluoride complexes (except in the case of ruthenium bifluorides). Surprisingly, the M-F---F angle of 108.87º was significantly more acute than in previously reported bifluorides (128º-156º). ^{19}F NMR spectroscopy in CD_3CN (room temperature) exhibited two broad signals at −138 ppm (distal *F*) and −220 ppm (Cu-*F*). The ^{1}H NMR spectrum (measured at room temperature) showed a broad singlet at 14.1 ppm, whereas at 193 K, a resolved triplet with J = 120 Hz was observed. Based on these data, the authors suggested that the HF_2 ligand ionization occurred at the Cu-F bond (Cu---F-H-F), instead of the usual F-H bond (Cu-F---H-F).

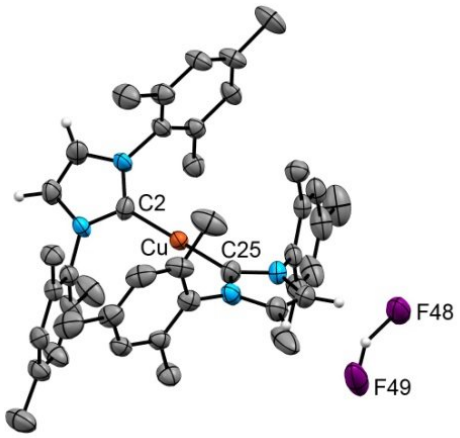


Figure 6. ORTEP representation of the solid-state structure of the bifluoride salt [{Cu(IMes)$_2$}(HF$_2$)] (19) [86]

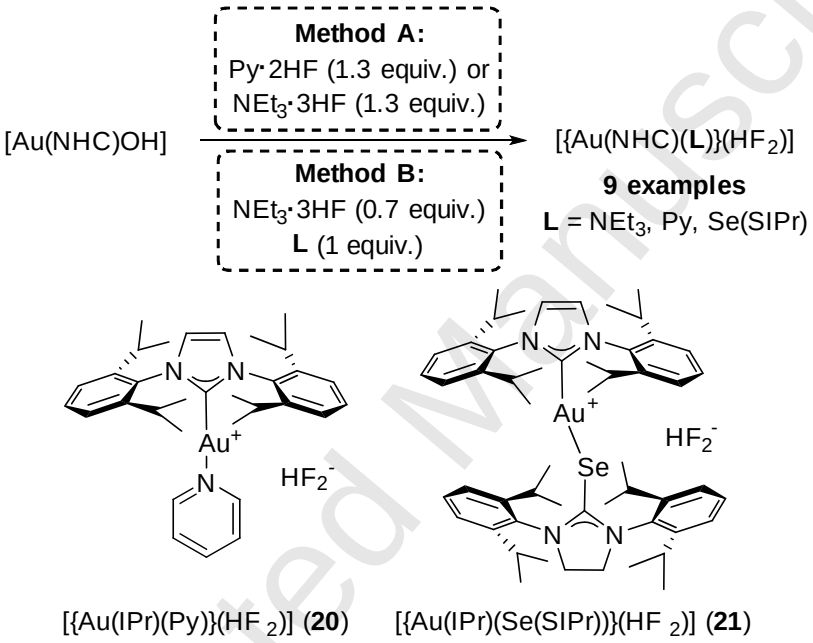
The crystal structure of [{Cu(IMes)$_2$}(HF$_2$)] (**19**) showed a Cu-C bond length of 2.182 Å, with a C-Cu-C angle of 180º and a torsion angle of 60.04º between the two NHC planes (in agreement with other bis-(NHC) salts, Figure 6). The HF$_2$ ligand was suggested to interact with the C-H bonds of the imidazole ring, since the shortest distance observed between both entities was 2.461 Å (smaller than the sum of the van der Waals radii (2.55 Å)). The ^{1}H NMR spectrum showed a resonance at 13.6 ppm in CD_2Cl_2, which was assigned to the acidic proton (F-*H*-F). Meanwhile, ^{19}F NMR data displayed a single signal at −170 ppm, thus highlighting the symmetrical nature of the HF$_2$ moiety.

The reactivity of the copper bifluorides was also investigated in the same report. It was shown that these complexes were highly active in a variety of reactions; mainly, reactions involving boron- or silicon-activation processes (*e.g.*, reduction of ketones, 1,4-borylation and 1,4-silylation of enones, allylation of aldehydes and aldimines). In contrast to similar copper-catalyzed procedures, bifluoride catalysts did not require *in situ* activation. In later reports by the same group, detailed studies on the generation of [CuH(IPr)] from [Cu(HF$_2$)(IPr)], using NMR and DFT analyses, greatly helped to elucidate the mechanism of the hydrosilylation of ketones [91-92].

3.1.2 Gold

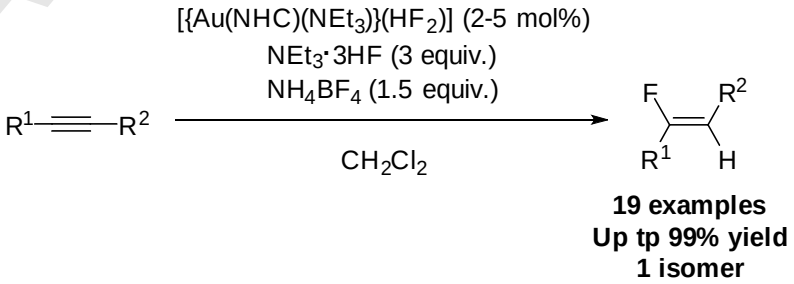
Following the above reports by Riant and Leyssens on the high stability and reactivity of bifluorides, of the type [Cu(HF$_2$)(NHC)$_n$] (n = 1, 2), the Nolan group applied the same strategy for the synthesis of NHC Au^I bifluorides. In this manner, nine gold bifluoride salts were obtained from the reaction of the corresponding [Au(OH)(NHC)] and NEt$_3$·3HF (Scheme 16) [93]. The high stability of gold hydroxides [94], compared to their *tert*-butoxide analogs, presented a more practical alternative. Under these conditions, only cationic gold bifluorides, formulated as [{Au(NHC)(NEt$_3$)}(HF$_2$)], were obtained. Controlling the amount and dilution of NEt$_3$·3HF proved crucial in achieving high product purity.

In the presence of additional stronger donating ligands than NEt_3 (such as pyridine (Py) or Se(SIPr) [95]), the same reaction afforded exclusively the desired [{Au(NHC)(L)}(HF_2)] (L = Py, Se(SIPr)) bifluoride salts. All gold bifluorides were air and moisture stable in the solid state, and in solution [96]. The ^{19}F NMR spectra displayed a broad singlet approximately −170 ppm, which is characteristic of a symmetric [FHF^-] anion. The acidic proton of the HF_2 moiety was observed in CD_2Cl_2 or CD_3CN (between 13.2 and 13.7 ppm). X-ray data for complexes **20** and **21** were obtained confirming the proposed structures.



Scheme 16. Synthesis of [{Au(NHC)(L)}(HF_2)] salts [93]

The relationship between the monofluoride and bifluoride congeners was also investigated. It was found that the former will react with NEt_3·3HF or traces of water to afford the gold bifluoride, whereas the latter delivers the gold fluoride under basic conditions. Furthermore, the gold bifluorides proved highly efficient and selective catalysts in the hydrofluorination of alkynes (Scheme 17).

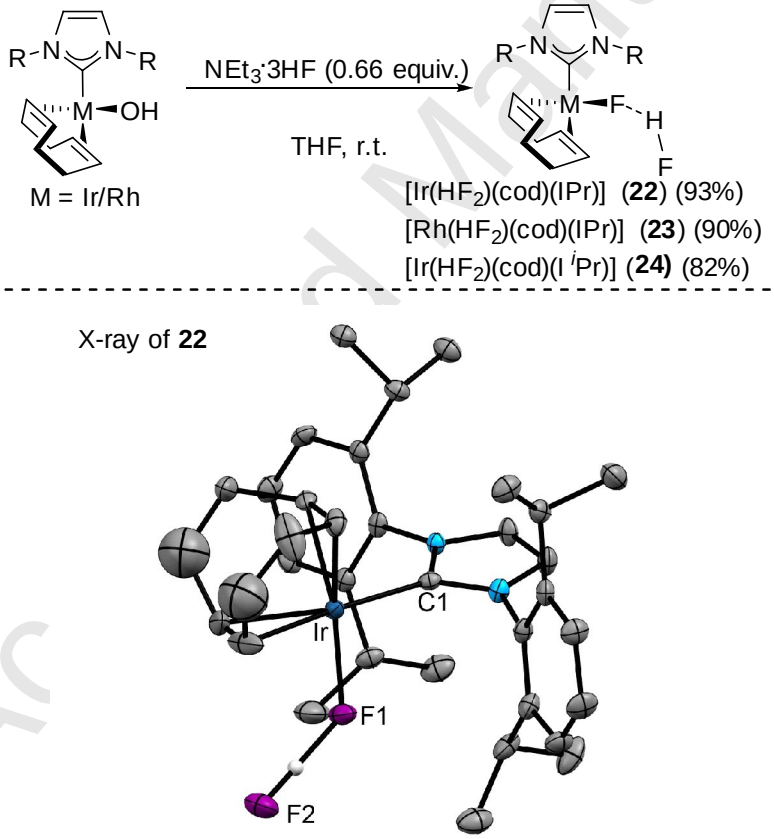


Scheme 17. Hydrofluorination of alkynes catalyzed by gold bifluorides [93]

3.1.3 Iridium and Rhodium

Recently, Nolan and co-workers also reported the synthesis of several NHC-based Ir^{I} and Rh^{I} fluoride and bifluoride complexes (Scheme 18) [97]. Using the same strategy described above, a metal hydroxide of the type [M(OH)(cod)(NHC)] (M = Rh, Ir) afforded the corresponding bifluorides **22**–**24** in good yields (93%, 90% and 82%, respectively).

NMR analyses of these new bifluoride complexes showed subtle differences compared to their fluoride counterparts. The ^{1}H NMR spectra (room temperature) showed a broad doublet (11.4 ppm, (**22**); 12.3 ppm, (**23**)) or a broad singlet (11.7 ppm (**24**)), assigned to the acidic proton. As in previous studies, at lower temperature (200 K), these signals resolved into doublets of doublets (for more details, see Table 3). ^{19}F NMR signals (at 200 K) for each compound appeared as distinct doublets of doublets (δ (ppm): −178 (**22**); −173 (**23**); −184.3 (**24**), distal *F*; and −253.6 (**22**); −239 (**23**); −246.5 (**24**), proximal *F*).



Scheme 18. Synthesis of NHC iridium and rhodium bifluoride complexes and ORTEP representation of the solid-state structure of 22 [97]

X-ray diffraction analysis of **22-24** revealed the expected square planar geometries (Scheme 18) and significantly elongated M-F bonds compared to the corresponding metal fluoride complexes. As seen previously, this weakening of the M-F bond is a consequence of the hydrogen bond to HF. The F---F

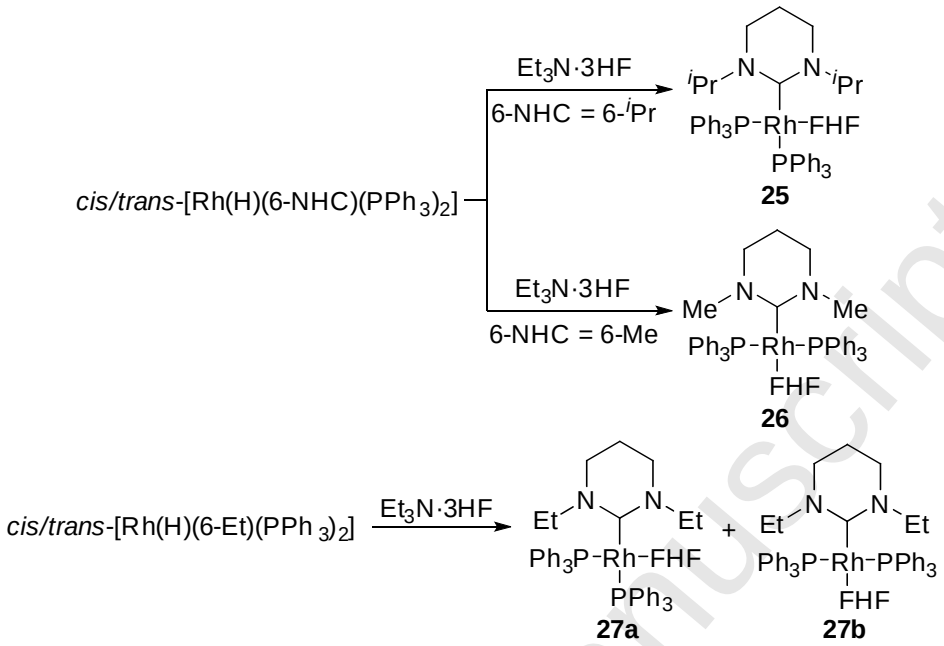
separation in **22** (2.35-2.39 Å) and **23** (2.32-2.33 Å) are indicative of strong hydrogen bonding, and are in agreement with previous reports. However, the solid-state structure of **24** showed an unusually large F---F separation (2.457(6), 2.587(6) Å). A higher stability was experienced for complexes **22** and **23** compared to **24**, which was attributed to interactions between the *iso*-propyl protons of the IPr ligand and the proximal fluoride (these interactions are not possible in complex **24**).

FT-IR analyses showed two broad bands for each compound ranging from 2530 to 2623 cm^{-1}, and from 1807 to 1869 cm^{-1}, corresponding to the two different types of H-F bonds. The spectroscopic data, together with the X-ray analysis, confirmed the unsymmetrical nature of the bifluoride unit in each complex (*i.e.* [M]-F---H-F rather than [M]---F-H-F).

3.2. 6-membered NHCs

In a recent report, Whittlesey and co-workers found that treatment of a *cis/trans* mixture of [RhH(6-^{i}Pr)$(PPh_3)_2$] with $NEt_3 \cdot 3HF$ afforded only one isomer of the corresponding bifluoride complex, *cis*-[$Rh(HF_2)$(6-^{i}Pr)$(PPh_3)_2$] (**25**) [98]. Later on, they extended the 6-NHC scope to include the methyl (6-NHC = 6-Me, **26**) and ethyl (6-NHC = 6-Et, **27**) derivatives (Scheme 19) [99].

While the *trans* bifluoride **26** was the only product obtained for 6-Me, a mixture of both isomers (**27a** and **27b**) was observed for 6-Et which isomerized into a 1:1 ratio after several hours in solution. Spectroscopic analyses helped differentiate between the two species: *e.g.*, *cis*-[$Rh(HF_2)$(6-Et)$(PPh_3)_2$] (**27a**) displayed a $^{31}P\{^{1}H\}$ NMR spectrum with two different doublet of doublet of doublets (indicating a dissimilar environment for each phosphines), whereas the *trans*-[$Rh(HF_2)$(6-Et)$(PPh_3)_2$] (**27b**) exhibited a single doublet of doublets. Based on these results, it was proposed that the decreasing bulk of the *N*-groups showed a preference towards the *trans* product.



Scheme 19. Synthesis of [Rh(HF$_2$)(6-NHC)(PPh$_3$)$_2$] [98,99]

Solid-state structures for both *trans* isomers (**26** and **27b**) were obtained (Figure 7). Interestingly, Rh-F---F angles (122.96(6)^o (**26**) and 121.41(9)^o (**27b**)) were significantly smaller than that found for the isopropyl derivative (127.44º), and were considered among the smallest M-F---F angles observed for bifluoride complexes.

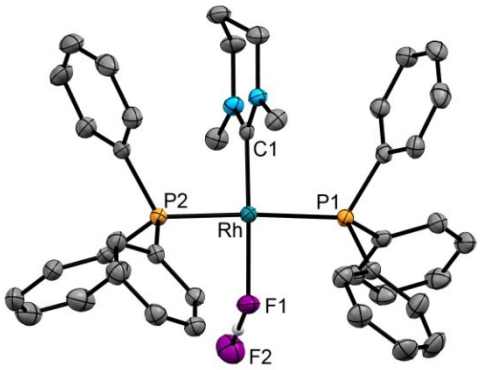


Figure 7. ORTEP representation of the solid-state structure of *trans*-[Rh(HF$_2$)(6-Me)(PPh$_3$)$_2$] (26) [99]

The solution behavior of *trans*-[Rh(HF$_2$)(6-Me)(PPh$_3$)$_2$] (**26**) was also investigated. A line broadening of the doublet at 13.2 ppm in the ^{1}H NMR spectrum (room temperature, C_6D_6, $^1J_{H\text{-}F} \approx 390$ Hz with the distal *F*) immediately revealed the fluxional nature of the FHF ligand. The coupling constant is comparable to the *iso*-propyl derivative and to the couplings observed in other bifluoride species, such as

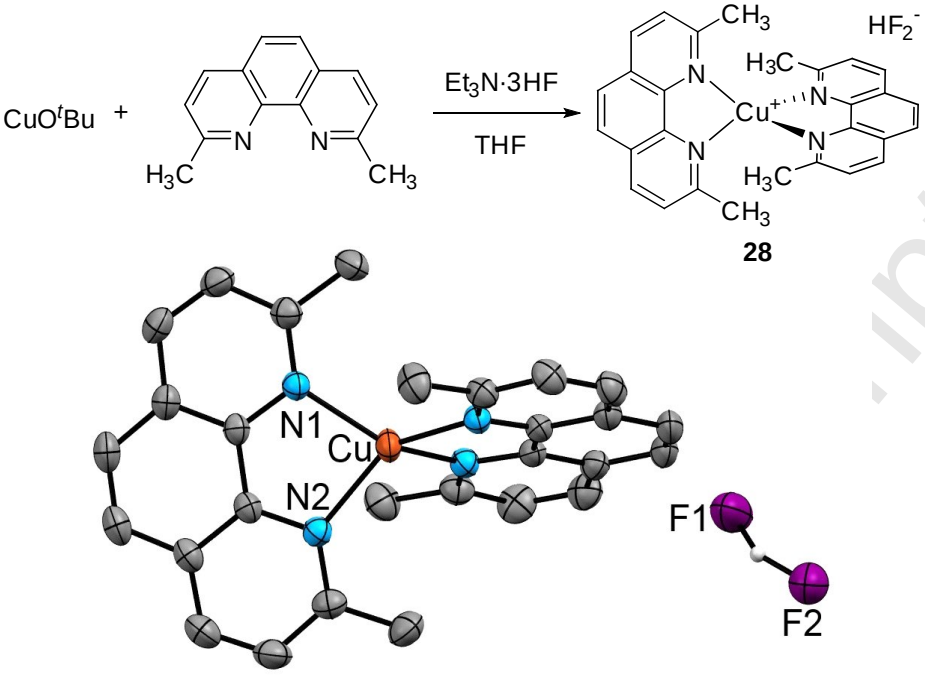
$[MoF(H)_2(HF_2)(PMe_3)_4]$ [35] or HF in solution [41], suggesting a Rh-F---H-F rather than a Rh---F-H-F interaction. IR measurements showed two broad bands at 2506 and 1896 cm^{-1} for **26**; the lower frequency band is similar to that of **25** (1923 cm^{-1}) and **27b** (1883 cm^{-1}), but the high frequency band differed significantly. ^{19}F NMR analysis of the complex at room temperature displayed a broadened doublet at −177 ppm ($^1J_{H\text{-}F}$ = 390 Hz, distal *F*) and a broad unresolved singlet at −312 ppm (proximal *F*). At low temperature (245 K), signals resolved into a doublet of doublets at −174 ppm ($^1J_{H\text{-}F} \approx$ 386 Hz, $^2J_{F\text{-}F}$ = 117 Hz) and a broad doublet at −311 ppm ($^2J_{F\text{-}F} \approx$ 114 Hz). At this temperature, only partial resolution occurred in the ^1H NMR spectrum affording an additional coupling constant with the proximal *F* ($^1J_{F\text{-}H} \approx$ 38 Hz).

Changing the NMR solvent to THF-d_8 severely lowered the resolution of all aforementioned signals. Interestingly, the removal of THF-d_8 under high vacuum and the reuse of C_6D_6 restored the previously observed resolution. These observations were attributed to the donor capability of the NMR solvent, based on similar reports [14]. Surprisingly, no evidence for the monofluoride species $[RhF(6\text{-}Me)(PPh_3)_2]$ was ever detected, even in the presence of excess base (NEt_3). Consequently, the remarkable stability of the bifluoride species is once again asserted. In line with this observation, no glassware etching was observed in any of the NMR experiments. In a similar fashion to other bifluoride species, magnetization transfer studies by ^{19}F NMR analysis revealed an intramolecular exchange process of the HF_2 moiety.

4. Other Transition Metal Bifluorides

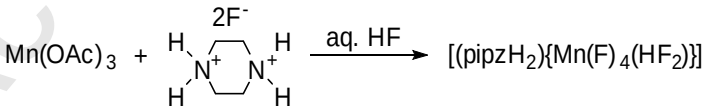
Recently, Weng and co-workers have reported the synthesis of a cationic Cu^I bifluoride salt (**28**), ligated by a phenantroline-derived ligand [100]. This compound was prepared in 92% yield by reacting Cu(O^{t}Bu) with the appropriate ligand and $NEt_3 \cdot 3HF$ in THF (Scheme 20). The bifluoride species was only obtained when small substituents (*i.e.* methyl) were used on the phenanthroline moiety (otherwise, a neutral monofluoride species was obtained). This is in correlation with previous observations reported by Riant and co-workers on NHC-copper bifluorides.

The structure, determined by single crystal X-ray diffraction analysis, shows a cationic Cu^I center with a tetrahedral arrangement of the phenanthroline ligands, and an outer-sphere HF_2^- anion. The ^1H NMR spectrum analysis displayed the typical F-*H*-F resonance at 13.6 ppm. ^{19}F NMR analysis revealed a singlet at −158.4 ppm, characteristic of a symmetrical bifluoride anion. The latter signal is significantly shifted compared to other cationic bifluorides, such as $[\{Cu(NHC)_2\}(HF_2)]$ and $[\{Au(NHC)(L)\}(HF_2)]$ (~ −170 ppm). Bifluoride **28** also proved highly efficient in the selective fluorination of primary and secondary alkyl bromides. The corresponding fluorides were obtained in good to excellent yields, hence further highlighting the importance and growing applicability of bifluoride catalysts in modern synthetic chemistry.



Scheme 20. Synthesis and X-ray structure of bifluoride complex 28 [100]

A manganese-based bifluoride was also prepared by Massa and co-workers in 2000 [101a]. The compound, with a reported formula $[(pipzH_2)\{Mn(F)_4(HF_2)\}]$, was obtained by reacting $Mn(OAc)_3{\cdot}2H_2O$ with a solution of piperaziniumfluoride in 20% aqueous HF (Scheme 21). The molecular structure was identified by single-crystal X-ray diffraction analysis. The structure contained anionic chains of MnF_4 bridged by HF_2 units. Piperazinium(+2) cations are located between the chain network. Alternatively, the chains can be viewed as distorted octahedral MnF_6 units with bridging H atoms. The manganese bifluoride features a narrow Mn-F---F angle of 111.7°.The bifluoride anions have a symmetry close to that of simple bifluoride salts, such as KHF_2, with H-F bond lengths of 1.14 Å.



Scheme 21. Synthesis of $[(pipzH_2)\{Mn(F)_4(HF_2)\}]$ [101a]

The work of Manson and co-workers has recently advanced this chemistry even further [101b-d]. The development of robust metal-organic frameworks containing a bifluoride bridge (M-F-H-F-M, with M = Cu, Ni) has introduced new properties to these compounds and highlighted the crucial role that the strong bonding in bifluorides could play.

An inorganic molybdenum bifluoride was reported by Mironov and co-workers [102]. The complex, with the formula $K_5[Mo_3S_4F_7(FHF)_2]{\cdot}2H_2O$, was prepared by mixing stoichiometric amounts of Mo, S

and Br_2 at 380 ºC, followed by the reaction with excess KHF_2 at 250-270 ºC. The desired compound was obtained in a 37% isolated yield. IR, X-ray and elemental analyses were also provided. A distance of 2.140 Å was determined for the Mo---FHF bond, with an $F_{proximal}$-H bond length of 1.3 Å, H-F_{distal} bond length of 1.1 Å and F---H-F angle of 170º. As expected, these data suggest a slightly unsymmetrical bifluoride unit. In recent ye

In 2004, Grushin and co-workers reported the synthesis and full characterization of a trinuclear rhodium bifluoride complex, [{$Rh_3(\mu_3$-OH)$_2$(cod)$_3$}(HF_2)] [103]. Later that year, Vicente and Gil-Rubio published a similar report, synthesizing the same compound from [Rh_2(μ-OH)$_2$(cod)$_2$] and stoichiometric amounts of HF [64]. X-ray diffraction analysis of the bifluoride species revealed a trigonal bipyramidal geometry, with the rhodium atoms forming the trigonal base and the OH units at the apical positions. O-H---F interactions between O-H bonds and F-H-F units of adjacent trimetallic cores were clearly observed in the crystal packing. It was shown that these hydrogen bond interactions persist in solution.

One of the earliest reports on modern bifluoride complexes was made by Roesky and co-workers describing the synthesis of a niobium-based complex, with the formula [{Nb(F)$_3$(HF_2)(η^5-C_5Me_5)}(AsF_3)]$_2$, containing bridging F---H-F units [104].

5. Analysis and Outlook

As shown in all previously described reports, bifluorides can be quite elusive and difficult to identify. Typically, low temperature NMR analysis is required to characterize such species. In some cases, acetonitrile-d_3 is used in order to observe the acidic proton (F-*H*-F) in the ^{1}H NMR spectroscopy [86,93]. Nevertheless, X-ray crystallography usually is the best way to unambiguously determine the true nature of metal bifluoride complexes. In order to centralize the bifluoride database, characteristic structural and NMR data of the HF_2 moiety for all reported compounds are assembled in Table 2 and 3. Furthermore, IR analyses of unsymmetrical bifluoride complexes typically show two bands; one ranging from 1690 to 1923 cm^{-1} and another ranging from 2422 to 2682 cm^{-1}. Since hydrogen bond interactions become stronger in bifluoride complexes, a decrease in the ν(FHF) relative to free HF (3960 cm^{-1}) is observed, as one might expect. However, all observed wavenumbers were much higher than those found in most common HF_2 salts (1284–1372 cm^{-1}); this is due to the unsymmetrical nature of the bifluoride moiety. It should be noted that all bifluoride salts reported here, which display a linear HF_2 geometry, exhibit one distinctive IR band in the same range of common HF_2 salts (1284–1372 cm^{-1}). These characteristics should provide a useful tool for future elucidation of new bifluoride complexes and their comparison with known analogues. Although too many variables would emerge from a strict analytical interpretation of the bifluorides reported here, an attempt is now presented to isolate and identify some of the key patterns.

^{1}H NMR data reveal a broad signal in the range of 11 to 14 ppm for both neutral (HF_2 is bound to the metal) and cationic (HF_2 in this case takes on the role of a weakly-coordinating anion) bifluorides, hence confirming the presence of the acidic proton. In the case of neutral complexes, one or both of the coupling constants (large $J_{H\text{-}F}$ with the distal *F* and a small $J_{H\text{-}F}$ with the proximal *F*) are observed for this proton due to the unsymmetrical nature of the HF_2 unit. A clear difference is observed in the ^{19}F NMR spectra when comparing neutral and cationic bifluoride complexes. Since the latter displayed a symmetrical HF_2 moiety, they are easily identified by a broad singlet at ~ −170 ppm. The only exception is the cationic Cu^{I}(phenanthroline)$_2$ salt **28** which shows a broad singlet at −158.4 ppm. This signal is significantly shifted downfield compared to other cationic bifluorides, and is closer to ammonium bifluorides (~ −150 ppm). This is probably due to the highly dissociative nature of this complex, indicating little or no interaction with the metal-ligand fragment.

The most interesting bifluorides are the neutral complexes. These species exhibit an unsymmetrical HF_2 unit, while the extent of dissymmetry is highly influenced by the metal-ligand fragment. For this reason, different dissociation and exchange patterns between metal bifluoride fragments can exist in solution. As stated earlier, understanding these processes would be especially important in catalytic fluorination reactions. For neutral bifluoride complexes, two fluorine signals are usually observed in the ^{19}F NMR spectra. The first signal, found in the range of −173 to −184 ppm (except for the copper complex **18** (−138 ppm)), belongs to the distal fluorine (M-FH*F*) and usually manifests as a doublet of doublets at low temperature. The second signal, typically found above −220 ppm, corresponds to the proximal fluorine (M-*F*HF) and has a chemical shift highly dependent on the metal center.

If the F---F separation of the solid-state is plotted as a function of the M-F distance, a rough pattern emerges (Figure 8). Most of the complexes behave as expected and exhibit an inverse relationship of the two distances. As the M-F bond increases in length, the F---F distance becomes shorter, hence indicating a shift towards the formation of a tight ion pair [(L-M$^+$)(HF_2^-)] bearing a symmetrical HF_2 unit. This is further demonstrated by the ruthenium bifluoride complex **5a** which is situated at the ionic limit of the correlation. After recrystallization of this complex, NMR analysis indicated the presence of another species (^{19}F NMR signal at −150 ppm) which was assigned to the cationic salt [{RuH(dmpe)$_2^+$}(HF_2^-)]. Furthermore, this complex exhibits the highest recorded F---F coupling constant (152 Hz) suggesting that the short F---F distance is similarly reflected in solution. These data indicate that this particular complex could be situated at the tipping point towards a complete dissociation of the HF_2 unit from the metal center. However, it should be kept in mind that the nature of the other ligands on the metal could drastically influence the HF_2 behavior, as demonstrated by the similar ruthenium complex **6a** (only the neutral character is observed in this case). The influence of the solvent on the nature of the bifluoride entity will also play an important role.

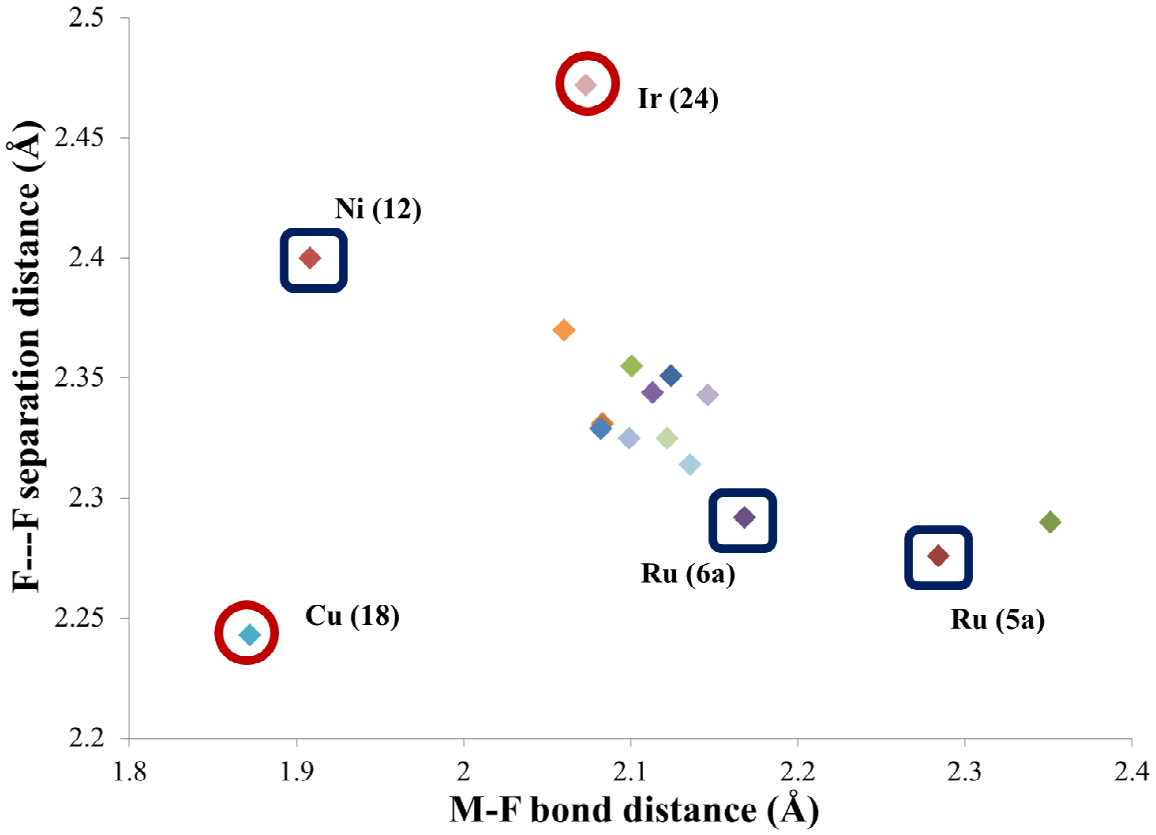


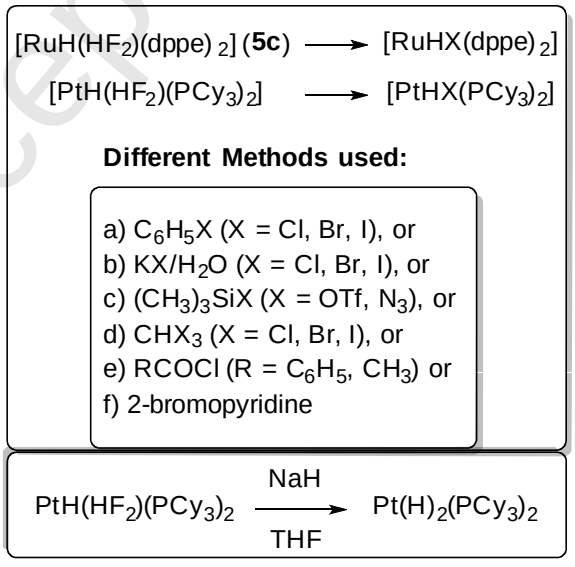
Figure 8. Plot of the F---F separation distance (Å) as a function of the M-F distance (Å) of all the bifluoride complexes reported in Table 2

A closer look at Figure 8 shows two distinct anomalies that are outside the correlation trend; NHC iridium complex **24** and NHC copper complex **18**. The former has an unusually long F---F separation which is apparent both in the solid state (2.457(6); 2.587(6)) and in solution ($^1J_{F\text{-}F}$ = 99 Hz). In their report, the authors attribute this phenomenon to a significant dissociation of the HF bond (M-F---HF), due to a lack of stabilization by the NHC ligand (I^iPr) compared to the IPr-based analog (**22**). The [Cu(HF_2)(IPr)] complex (**18**) is unique as it features; 1) the shortest M-F bond (1.872 Å), 2) the shortest F---F separation distance (2.243 Å), 3) and the smallest M-F---F angle (108°) of all reported bifluorides. However, when comparing the M-F bond of [Cu(HF_2)(IPr)] (**18**) to that of its monofluoride analog [CuF(IPr)] (1.820 Å), we realize that this bond is longer in the former. This indicates that the M-F bond contraction in this particular complex is most likely due to the nature of the Cu-F bond rather than an influence of the HF_2 moiety. If we disregard the M-F bond distance in this case and focus only on the F---F distance, we notice that the latter is in the same range as complex **5a**. Similarly to **5a**, **18** is also placed on a knife edge. And once again, the importance of ligand stabilization is highlighted when the IPr ligand is substituted by the smaller IMes ligand to afford the fully cationic species **19**. Finally, if the F---F

separation distance is plotted as a function of the M-F distance in phosphine-based complexes only, a better correlation is observed.

Unfortunately, since the NMR data for these compounds were recorded in different solvents and at different temperatures, no meaningful patterns could be extrapolated by an in-depth comparison. A proportional correlation between the H-F_{distal} coupling constant and the F---F separation distance is found when comparing complexes analyzed at similar temperatures and in the same solvent (CD_2Cl_2, complexes **11a**, **14a**, **15**, **22** and **23**). This could indicate a lengthening of the F---F distance and the concurrent contraction of the M-F bond (see above), is accompanied by a strengthening of the H-F_{distal} bond; as a result, this could identify a key feature for unraveling the extent of potential dissociation patterns between the M-F and H-F fragments. However, the data are far from conclusive as too many variables are at play and not enough data points are available. Future efforts should be directed towards reducing these variables in order to offer a more reliable comparison, especially on both ends of the correlation spectrum.

As it was shown in the previous sections, these bifluorides have started to appear in fluorination processes either as catalysts or intermediate species. Understanding the inner-workings of these species is an extremely important step forward, towards fully utilizing their reactivity. As already shown, the bifluoride species could be transformed, in most cases, back to the fluoride congener under basic conditions. Perutz and co-workers have shown in their reports that the bifluoride complexes of platinum and ruthenium can undergo ligand exchange with various reagents [82,60b]. A summary of the methods used is shown in Scheme 22. The Nolan group also applied the same strategy on NHC-based bifluoride complexes of Iridium and rhodium [97].



Scheme 22. Selected ligand exchange and HF_2 removal reactions used for Pt and Ru [82,60b]

In conclusion, an overview of the known transition metal bifluorides combining valuable data regarding their synthesis, characterization and structural behavior has been presented. A description and classification of the systems was carefully attempted in order to take initial steps towards obtaining a more comprehensive picture of these fascinating transition metal species. We hope this synthesis will assist further developments and full exploitation of the potential of this steadily growing field of research.

Table 2. X-ray and IR data for selected neutral bifluoride complexes

Complex formula	M-F (Å)	F---F (Å)	M-F---F angle	IR υ(FHF) (cm^{-1})	Reference
$[MoF(H)_2(HF_2)(PMe_3)_4)]$ (**4**)	2.124(3)	2.351(8)	133.8(1)º	2682	[35]
trans-$[RuH(HF_2)(dmpe)_2]$ (**5a**)	2.284(5)	2.276(8)	129.9(3)º	1690	[49]
trans-$[RuH(HF_2)(dppp)_2]$ (**5d**)	2.351(5)	2.290(8)	149.7(3)º	2310; 2450; 1889	[60b]
cis-$[RuF(HF_2)(dmpe)_2]$ (**6a**)	2.168(3)	2.292(8)	141.8(2)º	2452, 1915	[60a]
cis-$[Ru(HF_2)_2(PMe_3)_4]$ (**6b**)	2.150(5); 2.149(4)	2.323(8); 2.329(8)	128.5(3)º; 138.4(3)º	2290; 2399	[60b]
$[Rh(HF_2)(cod)(PPh_3)]$ (**11a**)	2.083(2)	2.331(34)	147.23(14)º	2630, 1842	[64]
$[Rh(HF_2)(FPPh_2)(PPh_3)_2]$	2.082(1)	2.329(2)	135.57(6)º	–	[65a]
trans-$[Ni(HF_2)(2\text{-}C_4HF_2N_2)(PEt_3)_2]$ (**12**)	1.908(3)	2.400(6)	156.7(2)º	–	[66]
trans-$[Pd(HF_2)(Ph)(PPh_3)_2]$ (**14a**)	2.098(2); 2.103(2)	2.359(3); 2.354(2)	153.5(1)º; 153.3(1)º	2578, 1822	[75,76]
$[Pd(F)_2(HF_2)(Ar)(^tBu\text{-}bpy)]$ (**15**)	2.113(2)	2.344(3)	115.1(1)º	–	[79a]
$[Cu(HF_2)(IPr)]$ (**18**)	1.872(4)	2.243(3)	108.9(7)º	–	[86]
$[Ir(HF_2)(cod)(IPr)]$ (**22**)	2.057(3); 2.062(2)	2.352(4); 2.387(4)	122.1(1)º; 132.4(1)º	2623; 1807	[97]
$[Rh(HF_2)(cod)(IPr)]$ (**23**)	2.089(3); 2.069(3)	2.331(5); 2.316(5)	129.3(2)º; 120.1(2)º	2530; 1890	[97]
$[Ir(HF_2)(cod)(I^iPr)]$ (**24**)	2.064(5); 2.082(4)	2.457(6); 2.587(6)	118.0(2)º; 116.3(2)º	2546; 1869	[97]
cis-$[Rh(HF_2)(6\text{-}^iPr)(PPh_3)_2]$ (**25**)	2.1217(13)	2.324(2)	127.44(8)º	2465; 2328; 1923	[98]
trans-$[Rh(HF_2)(6\text{-}Me)(PPh_3)_2]$ (**26**)	2.1460(12)	2.343(2)	122.96(6)º	2506; 1895	[99]
trans-$[Rh(HF_2)(6\text{-}Et)(PPh_3)_2]$ (**27b**)	2.1354(17)	2.314(3)	121.41(9)º	2422; 2334; 1883	[99]

IR bands of free HF: υ(HF) = 3960 cm^{-1}), and HF_2 in common bifluoride salts $\upsilon(HF_2)$ = 1284–1372 cm^{-1}.

Table 3. ^{1}H and ^{19}F NMR data of the FHF unit for selected neutral bifluoride complexes

Complex formula	T (ºC) (solvent)	δ H (M-F^1HF^2) (ppm)	J_H (Hz)	δ F^1 (proximal) (ppm)	J_{F1} (proximal) (Hz)	δ F^2 (distal) (ppm)	J_{F2} (distal) (Hz)	Reference
$[MoF(H)_2(HF_2)(PMe_3)_4)]$ (**4**)	RT (C_6D_6)	12.5 (d)	$J_{H\text{-}F2}$ = 410	−230 (br. s)	–	−182 (d)	$J_{F2\text{-}H}$ = 410	[35]
trans-$[RuH(HF_2)(dmpe)_2]$ (**5a**)	188 K (THF-d_8)	13.8 (d)	$J_{H\text{-}F2}$ = 274	−356.8 (br. d)	$J_{F1\text{-}F2}$ = 152	−173.1 (dd)	$J_{F2\text{-}H}$ = 274 $J_{F2\text{-}F1}$ = 152	[49]
trans-$[RuH(HF_2)(depe)_2]$ (**5b**)	193 K (THF-d_8)	13.3 (dd)	$J_{H\text{-}F1}$ = 36 $J_{H\text{-}F2}$ = 392	−352 (br. s)	–	−167 (dd)	$J_{F2\text{-}H}$ = 392 $J_{F2\text{-}F1}$ = 162	[60b]

trans-[RuH(HF_2)(dppe)$_2$] (**5c**)	193 K (THF-d_8)	12.6 (d)	J_{H-F2} = 306	−326 (br. s)	–	−168 (dd)	J_{F2-H} = 306 J_{F2-F1} = 125	[60b]
trans-[RuH(HF_2)(dppp)$_2$] (**5d**)	193 K (THF-d_8)	12.6 (d)	J_{H-F2} = 317	−355 (d)	J_{F1-F2} = 164	−162 (dd)	J_{F2-H} = 317 J_{F2-F1} = 164	[60b]
cis-[RuF(HF_2)(dmpe)$_2$] (**6a**)	298 K (C_6D_6)	14.2 (d)	J_{H-F2} = 328	−343 or -362 (m)	–	−174 (d)	J_{F2-H} = 328	[60a]
cis-[Ru(HF_2)$_2$(PMe_3)$_4$] (**6b**)	193 K (THF-d_8)	13.2 (d)	J_{H-F2} = 339	−291 (d)	J_{F1-F2} = 153	−160 (dd)	J_{F2-H} = 339 J_{F2-F1} = 153	[60b]
[Rh(HF_2)(PEt_3)$_3$] (**9**)	223 K (tol-d_8)	13.2 (dd)	J_{H-F1} = 42 J_{H-F2} = 382	−278.3 (br. d)	$J_{F1-P,trans}$ = 175	−176.4 (dd)	J_{F2-H} = 386 J_{F2-F1} = 116	[63]
[Rh(HF_2)(cod)(PPh_3)] (**11a**)	193 K (CD_2Cl_2)	12.2 (dd)	J_{H-F1} = 41 J_{H-F2} = 375	−258.3 (m)	–	−177.3 (dd)	J_{F2-H} = 373 J_{F2-F1} = 124	[64]
[Rh(HF_2)(cod)(P^iPr_3)] (**11b**)	193 K (CD_2Cl_2)	12.5 (br. dd)	J_{H-F1} = 32 J_{H-F2} = 366	−256.7 (m)	–	−176.3 (dd)	J_{F2-H} = 364 J_{F2-F1} = 134	[64]
[Rh(HF_2)(cod)(PCy_3)] (**11c**)	193 K (CD_2Cl_2)	12.5 (br. dd)	J_{H-F1} = 32 J_{H-F2} = 364	−258.3 (m)	–	−176.2 (dd)	J_{F2-H} = 360 J_{F2-F1} = 138	[64]
trans-[Ni(HF_2)(2-$C_4HF_2N_2$)(PEt_3)$_2$] (**12**)	223 K (tol-d_8)	11.4 (br. d)	J_{H-F2} = 427	−332.6 (m)	–	−180.4 (br. d)	J_{F2-H} = 392	[66]
trans-[NiF(2-C_5NF_4)(PEt_3)$_2$] (**13**)	190 K (tol-d_8)	11.58 (dd)	J_{H-F1} = 41 J_{H-F2} = 424	−339.1 (br. s)	–	−179.4 (dd)	J_{F2-H} = 422 J_{F2-F1} = 85	[67]
trans-[Pd(HF_2)(Ph)(PPh_3)$_2$] (**14a**)	213 K (CD_2Cl_2/tol-d_8)	12.5 (dd)	J_{H-F1} = 33 J_{H-F2} = 368	−254 (ddd)	J_{F1-H} = 33 J_{F1-F2} = 119 J_{F1-P} = 8	−174 (dd)	J_{F2-H} = 368 J_{F2-F1} = 119	[75,76]
trans-[Pd(HF_2)(Me)(PPh_3)$_2$] (**14b**)	293 K ($CDCl_3$)	12.4 (br. s)	–	–	–	–	–	[75]
[Pd(F)$_2$(HF_2)(Ar)(^{t}Bu-bpy)] (**15**)	203 K (CD_2Cl_2)	12.7 (dd)	J_{H-F1} = 31 J_{H-F2} = 370	−204.5 (m)	–	−177.6 (dd)	J_{F2-H} = 364 J_{F2-F1} = 116	[79a]
trans-[PtH(HF_2)(PCy_3)$_2$]	193 K (THF-d_8)	11.9 (dd)	J_{H-F1} = 48 J_{H-F2} = 412	−283.6 (d)	J_{F1-F2} = 112 J_{Pt-F1} = 572	−182.5 (dd)	J_{F2-H} = 400 J_{F2-F1} = 103	[82]
trans-[PtH(HF_2)(P^iPr_3)$_2$]	193 K (THF-d_8)	11.3 (dd)	J_{H-F1} = 43 J_{H-F2} = 393	−280 (d)	J_{F1-F2} = 116 J_{Pt-F1} = 588	−179 (dd)	J_{F2-H} = 400 J_{F2-F1} = 103	[82]

[Cu(HF_2)(IPr)] (**18**)	RT (CD_2Cl_2)	14.1 (br. s)	–	−220 (br. s)	–	−138 (br. s)	–	[86]
[Ir(HF_2)(cod)(IPr)] (**22**)	200 K (CD_2Cl_2)	11.7 (dd)	$J_{H\text{-}F1}$ = 40 $J_{H\text{-}F2}$ = 395	−238.9 (dd)	$J_{F1\text{-}H}$ = 40 $J_{F1\text{-}F2}$ = 120	−177.9 (dd)	$J_{F2\text{-}H}$ = 395 $J_{F2\text{-}F1}$ = 120	[97]
[Rh(HF_2)(cod)(IPr)] (**23**)	200 K (CD_2Cl_2)	12.9 (dd)	$J_{H\text{-}F1}$ = 50 $J_{H\text{-}F2}$ = 350	−253.6 (dd)	$J_{F1\text{-}H}$ = 50 $J_{F1\text{-}F2}$ = 150	−173.1 (dd)	$J_{F2\text{-}H}$ = 350 $J_{F2\text{-}F1}$ = 150	[97]
[Ir(HF_2)(cod)(I^{i}Pr)] (**24**)	198 K (CD_2Cl_2)	11.5 (dd)	$J_{H\text{-}F1}$ = 45 $J_{H\text{-}F2}$ = 403	−246.5 (dd)	$J_{F1\text{-}H}$ = 45 $J_{F1\text{-}F2}$ = 95	−184.3 (dd)	$J_{F2\text{-}H}$ = 403 $J_{F2\text{-}F1}$ = 99	[97]
cis-[Rh(HF_2)(6-^{i}Pr)(PPh_3)$_2$] (**25**)	204 K (THF-d_8)	12.64 (dd)	$J_{H\text{-}F1}$ = 42 $J_{H\text{-}F2}$ = 370	−272.6 (br. m)	–	−176.8 (dd)	$J_{F2\text{-}H}$ = 372 $J_{F2\text{-}F1}$ = 117	[98]
trans-[Rh(HF_2)(6-Me)(PPh_3)$_2$] (**26**)	190 K (THF-d_8)	12.6 (dd)	$J_{H\text{-}F1}$ = 42 $J_{H\text{-}F2}$ = 379	−312.0 (br. d)	$^1J_{F1\text{-}F2}$ = 125	−176.9 (dd)	$J_{F2\text{-}H}$ = 381 $J_{F2\text{-}F1}$ = 127	[99]

Acknowledgments

CSJC acknowledges the Royal Society for a University Research Fellowship and the EaStChem School of Chemistry for support. SPN acknowledges the EPSRC and is a Royal Society Wolfson Merit Award holder. AGH thanks the EPSRC (EP/K503162/1) and Syngenta for support.

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TOC:

A summary of the various preparation methods, characterization techniques and applications of transition metal bifluorides is presented in this review. The classification of the reported systems is also attempted in order to ensure a better understanding and to help guide future efforts towards fully exploiting their potential.