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On the Catalytic Hydrodefluorination of Fluoroaromatics Using Nickel Complexes: The True Role of the Phosphine

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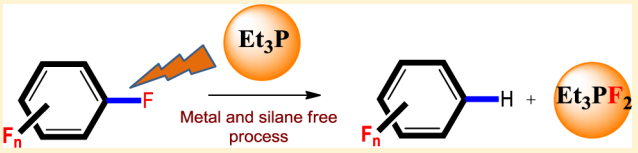
Supporting Information

ABSTRACT: Homogeneous catalytic hydrodefluorination (HDF) of fluoroaromatics under thermal conditions was achieved using nickel(0) compounds of the type [(dippe)Ni-(η^2-$C_6F_{6-n}H_n$)] where n = 0−2, as the catalytic precursors. These complexes were prepared *in situ* by reacting the compound [(dippe)Ni(μ-H)]$_2$ with the respective fluoroaromatic substrate. HDF seems to occur homogeneously, as tested by mercury drop experiments, producing the hydrodefluorinated products. However, despite previous findings by other groups, we found that these HDF reactions were actually the result of direct reaction of the alkylphosphine with the fluoroaromatic substrate. This metal- and silane-free system is the first reported example of a phosphine being able to hydrodefluorinate on its own.



INTRODUCTION

Organofluorine chemistry has grown enormously in significance and scope in the past three decades. Fluorine is unique in many ways for its ability to replace hydrogen in a variety of organic compounds without important distortion of the geometry. However, naturally occurring organofluorines are rare.[1] These fluoro compounds have a wide range of uses in industry.[2] Fluorine substituents increase the hydrophobicity of an organic substrate, which can increase the rate of transport of the drug to the active site and also enhance resistance to metabolic oxidation, which means less toxic byproducts and increased safety of a drug.[3]

The synthesis of polyfluoroaromatic molecules usually requires several steps and the use of harsh conditions (200−600 °C). Yields range from moderate to good (50−90%), and the reactions occur via electrophilic or nucleophilic fluorinations[4] conducted on activated enol-like functionalities, ethers, or allyl silanes.[5] An alternative approach for the synthesis of partially fluorinated products is the cleavage of C−F bonds of perfluorinated compounds mediated by transition metals,[6] involving an oxidative addition of the C−F bond, followed by fluorine elimination with the use of silanes or hydrogen (eq 1), in a reaction known as hydrodefluorination (HDF).[6b]

$$R_F\text{-}F \xrightarrow{L_nM} R_F\text{-}ML_{n-2}\text{-}F \xrightarrow[\text{“}-HF\text{”}]{H_2} R_F\text{-}H + L_nM \qquad (1)$$

Perutz reported in 1989 the coordination of fluoroaromatics to a rhodium center.[7] He found that [CpRh(PMe$_3$)(C$_2$H$_4$)] forms an isolable η^2-complex with C$_6$F$_6$. Additional examples of C−F bond oxidative addition with transition metal compounds include those using late transition metals, such as rhodium[8] and nickel,[9−11] and early transition metals, such as zirconium.[12]

Milstein reported the first catalytic version of that activation leading to HDF by transition metals in 1994,[13] using rhodium. Other examples of homogeneous catalytic HDF have appeared. In 2005, Holland[14] reported the reaction of perfluorinated aromatic compounds with silanes using 20 mol% of Fe(II) complexes as catalyst precursors. Another catalytic example using Ru complexes was reported by Whittlesey,[15] employing 1 mol% of a ruthenium catalyst using Et$_3$SiH as hydrogen source. A recent report shows catalytic HDF using [(NHC)-AuH][16] in the presence of DMAP and silanes. Recent examples of catalytic reactions of fluoroarenes with nickel compounds include the works reported by Cao[17] and Radius.[18]

In the case of heterofluoroaromatics, one of the first examples of oxidative addition of the C−F bond in pentafluoropyridine (PFP) was reported by Perutz,[6b] using Ni(COD)$_2$ in the presence of triethylphosphine or with [Ni(PEt$_3$)$_4$], resulting in the formation of *trans*-[Ni(PEt$_3$)$_2$(C$_5$F$_4$N)F]. Other stoichiometric reactions with transition metals and PFP have been found to occur at the 4-position for palladium or platinum,[6b] rhodium,[20] and gold,[21] and at the 2-position dominantly for nickel,[19] [Rh(SiPh$_3$)(PMe$_3$)$_3$].[22] Examples of catalytic HDF of PFP are relatively scarce, with relevant examples using rhodium,[20] gold,[21] palladium,[23] and copper.[24] Herein we report our findings on the search for a catalytic HDF system initially based on nickel compounds and the surprising results of the study where we found that PEt$_3$ was the actual HDF agent.

RESULTS AND DISCUSSION

Reaction of 1 with Hexafluorobenzene (C$_6$F$_6$). The reaction of a blood red solution of [(dippe)Ni(μ-H)]$_2$ (**1**) with C$_6$F$_6$ in THF results in an immediate color change to yellow-brown (eq 2). The molecular structure of **2** has been

$$\mathbf{1} + C_6F_6 \xrightarrow{-H_2} \mathbf{2} \qquad (2)$$

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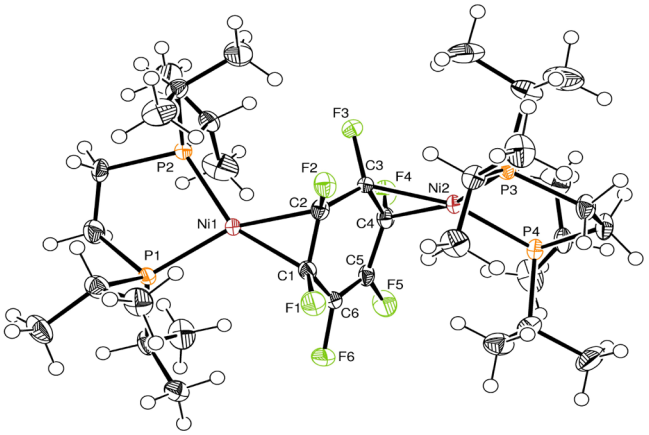

Figure 1. ORTEP drawing (50% probability) for complex **2**. Selected bond distances (Å): Ni1−P1 2.1648(8), Ni1−P2 2.1613(8), Ni1−C1 1.916(3), Ni1−C2 1.941(3), C2−C1 1.440(4), C1−C6 1.448(4), C2−C3 1.467(4), C6−C5 1.323(4). Selected bond angles (deg): P1−Ni1−P2 90.38(3), C2−Ni1−C1 43.84(12), C1−C2−C3 119.9(2), C3−C4−C5 117.8(2), C4−C5−C6 122.0(3).

determined by X-ray crystallography (130 K), and the corresponding ORTEP diagram is depicted in Figure 1.

The complex displays a C_2 axis of symmetry, which lies in the plane of the C_6F_6 ligand and passes through the midpoints of the bonds C2−C3 and C5−C6. In **2**, two [(dippe)Ni] moieties are antifacially coordinated to adjacent C=C bonds of a bridging C_6F_6 ligand. The Ni1−C1 and Ni2−C4 bond lengths are the same, 1.916(3) Å, and are slightly shorter than the Ni1−C2 and Ni2−C3 bond lengths, which are 1.941(3) and 1.940(3) Å, respectively. The arene ring shows significant elongation of the coordinated double bonds from typical aromatic values, for instance, C1−C2 and C3−C4 distances of 1.440(4) and 1.434(4) Å, respectively. The fluorine substituents show a considerable nonplanarity. The remaining C−C bond lengths of the C_6F_6 moiety are also significantly perturbed: the C5−C6 distance of 1.323(4) Å is shorter than expected for a C−C bond in C_6F_6 (1.394 Å),[25] whereas C2−C3 (1.467(4) Å), C4−C5 (1.453(4) Å), and C6−C1 (1.448(4) Å) are closer to single bonds. These distances are evidence of electron density donation/backbonding between the two [(dippe)Ni] fragments and the fluoroaromatic ring; therefore, the formally sp^2 carbons are more hybridized to sp^3-like. The Ni−C bond lengths of 1.928(3) Å (mean) are as expected for Ni(0)−η^2-fluoroarene complexes.[9,26]

The room-temperature $^{31}P\{^1H\}$ NMR spectrum of **2** features a resolved multiplet centered at 70.7 ppm ($^3J_{P-F}$ = 12 Hz) due to coupling to the fluorine atoms in the C_6F_6 moiety. The ^1H NMR spectrum exhibits three proton signals assigned to the dippe (δ 1.1, m, CH_3; δ 1.67, d, CH_2; δ 2.1, m, CH). The ^{19}F NMR spectrum shows a very broad signal at δ −172 due to the fluxionality of the C_6F_6 moiety, as reported for closely related nickel complexes.[26]

Upon warming of a THF solution in a sealed NMR tube to 80 °C for 4 h, the characteristic multiplet detected in the $^{31}P\{^1H\}$ and ^{19}F NMR spectra for complex **2** diminished in intensity, and several new signals were observed in the reaction mixture. Unfortunately, none of these signals can be unambiguously assigned to the expected oxidative addition product [(dippe)Ni(C_6F_5)F] (**3**) on the basis of $^2J_{P-P}$ in a Ni(II) complex.[27] However, when pentafluorobenzene was used under the very same reaction conditions, the C−F oxidative addition product, complex **5**, was isolated and fully characterized (*vide infra*).

Reaction of 1 with Pentafluorobenzene (C_6F_5H). To shed more light on the reactivity with fluoroaromatics, the reaction of complex **1** with C_6F_5H was investigated. Complex **4** was obtained in analogy to complex **2** (*vide supra*) and closely related nickel compounds bearing trialkyl monophosphines.[26]

The $^{31}P\{^1H\}$ NMR spectrum at room temperature for complex **4** displays a very broad signal centered at 71.8 ppm, indicative of a fluxional behavior, which corresponds to the product shown in Figure 2. The corresponding ^1H NMR

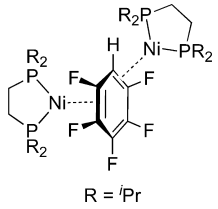

Figure 2. Complex **4**.

spectrum features an upfield-shifted broad multiplet at δ 3.0 for the aromatic proton, and the signals due to the alkyl substituents at δ 1.35 (m, CH_3), 1.92 (d, $-CH_2-$), and δ 2.3 (−CH−). The ^{19}F NMR spectrum shows five signals located at δ −132.1, −147.7, −153.2, −160.9, and −184.5, indicative of five different fluorine atoms and of a rather unsymmetrical coordination of the fluoro-aromatic moiety. Upon gentle warming of a sample of complex **4** to 80 °C for 4 h, compound **5** was obtained (Figure 3).

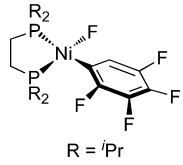

Figure 3. C−F oxidative addition product, complex **5**.

The room-temperature $^{31}P\{^1H\}$ NMR spectrum for **5** shows the signals expected for the structure depicted in Figure 3: two doublet of doublets located at δ 70.4 ($^2J_{P-F}$ = 30 Hz, $^2J_{P-P}$ = 10 Hz) assigned to the phosphorus *trans* to C, and the other at δ 65.6 ($^2J_{P-F}$ = 34 Hz, $^2J_{P-P}$ = 10 Hz) for the phosphorus *trans* to F. The ^{19}F NMR spectrum shows four multiplets located at δ −115.6, −141.2, −162.6, and −164.4 for the four nonequivalent fluorine atoms at the aromatic ring and the Ni−F resonance assigned at δ −345.4 as a multiplet with $^2J_{P-F}$ = 34 Hz. The selectivity of the [Ni(0)] fragment at the *ortho*-position in pentafluorobenzene is atypical, since nucleophilic substitution in C_6F_5H occurs at the *para*-position with respect to the H atom. In a few cases *meta*-substititution occurs.[1]

Single crystals suitable for an X-ray determination of **5** were obtained by slow evaporation of a THF/hexane solution. Figure 4 displays the corresponding ORTEP drawing. This structure allowed us to confirm the C−F activation of C_6F_5H at the *ortho*-position with respect to the original hydrogen atom. The values of the angles around the nickel atom are indicative of a distorted square-planar geometry, probably due to the chelating phosphine. The Ni(1)−C(1) bond distance in **5** is 0.099 Å longer that in the analogue, *trans*-$(PEt_3)_2NiF(C_6F_5H)$,

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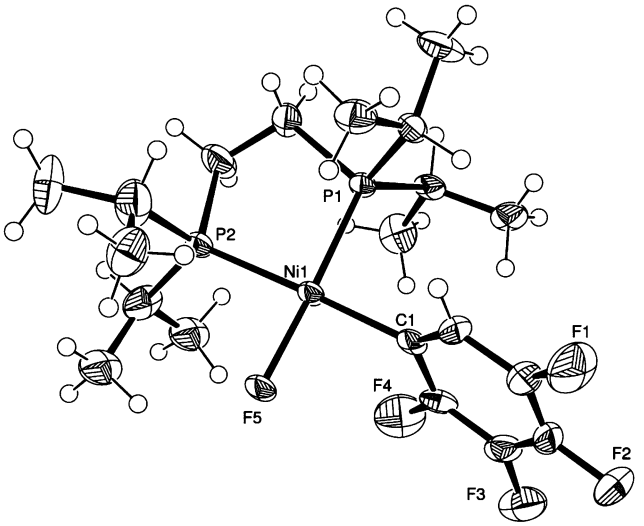

Figure 4. ORTEP drawing (50% probability) for complex **5**. Selected bond lengths (Å): Ni(1)−C(1) 1.957(8), Ni(1)−F(5) 1.850(4), Ni(1)−P(1) 2.139(2), Ni(1)−P(2) 2.191(2). Selected bond angles (deg): P(2)−Ni(1)−P(1) 88.14(7), P(1)−Ni(1)−C(1) 93.8(2), C(1)−Ni(1)−F(5) 88.7(3), F(5)−Ni(1)−P(2) 89.36(15), P(1)−Ni(1)−F(5) 177.49(17).

reported by Johnson and co-workers,[26] whereas the Ni(1)−F(5) bond distance is 0.066 Å shorter.

With the aim to apply the observed reactivity of the above-discussed nickel complexes into the catalytic HDF reactions, a variety of reaction conditions were assessed. Among them, the use of Et_3SiH was considered due to the characteristic of being a potential hydride source and taking advantage of the possible formation of a strong Si−F bond.[6d] When using a 1:1:6 ratio of Ni:C_6F_6:Et_3SiH at 120 °C for 3 d, the conversion toward HDF products was about 90%. Under these conditions, the selectivity was low, since a mixture of fluoroaromatic products was detected by GC-MS: C_6F_6 (6%), C_6F_5H (10%), $C_6F_4H_2$ (50%), and $C_6F_3H_3$ (34%). Using a load of 5 mol% of **1**, the fluoroaromatics were C_6F_6 (70%), C_6F_5H (22%), and $C_6F_4H_2$ (8%). Along with the low selectivity, the presence of black metallic nickel residues was also observed. Therefore, to suppress nickel metal formation due to decomposition and to improve yields and selectivity, we decided to use an extra amount of phosphine, considered initially as an ancillary ligand to avoid metal deposition. Relevant results are summarized in eq 3 and Table 1.

It is noteworthy that the alkylphosphines improved yields and selectivity. In the above results, the presence of minute amounts of Et_3SiF, detected by GC-MS, was constantly lower than expected. Therefore, we hypothesized that just the nickel−phosphine mixture could be the actual hydrodefluorinating system. Consequently, we performed experiments to test such a possibility. Key results are summarized in eq 4 and Table 2.

Again, good yields and selectivity were observed, but the source of hydrogen was still unclear. Therefore, the very same reaction from Table 2, entry 2, was done using deuterated dioxane as solvent to find out if the solvent was the hydrogen source of this reaction. The result was exactly the same as in entry 2; i.e., the HDF product obtained was not deuterated. Consequently, the hydrogen in the product is likely to arise only from the phosphine.

The use of phosphine as a sacrificial agent for the HDF of a variety of fluoroarenes in the presence of catalytic amounts of **1** was then assessed. In particular, PEt_3 was very effective for this purpose, as can be seen in the results included in Table 3.

The results in Table 3 indicate a high yield and selectivity toward HDF in the presence of a very basic phosphine such as PEt_3. In sharp contrast, the use of triphenylphosphine gave poor HDF results, <1%, and dippe gave again low yields, <50%. A mercury drop test using PEt_3 as in Table 2, entry 2, showed a high catalytic activity.

Other fluoroaromatic substrates with fewer fluorines in the aromatic ring, such as 1,2-, 1,3-, and 1,4-difluorobenzene, did not react in the presence or absence of nickel catalysts. These results are also in agreement with previous reports.[11b]

A careful analysis of the intermediates involved in the reactions in Table 3 was carried out. The $^{31}P\{^1H\}$ NMR spectrum indicated the presence of fluorophosphorous derivatives formed under the reaction conditions. We propose the possible formation of fluorophosphines of the type R_2PF (see Scheme 1).

Table 1. HDF Products of C_6F_6 Using Phosphines as Ancillary Ligands and Triethylsilane as the Hydrogen Source

$$2C_6F_6 + 12Et_3SiH + 6\ \text{phosphine} \xrightarrow{\mathbf{1}\ (5\%)} \text{HDF product} \quad (3)$$

entry	phosphine	HDF product (yield)[a]
1	triphenylphosphine	C_6F_6 (28%), C_6F_5H (62%), 1,2,4,5-$C_6F_4H_2$ (10%)
2	diisopropylphosphinoethane	C_6F_5H (2%), 1,2,4,5-$C_6F_4H_2$ (98%)
3	triethylphosphine	1,2,4,5-$C_6F_4H_2$ (100%)

[a]Determined by GC-MS. Reaction conditions: 5% **1**, dioxane, T = 120 °C, t = 3 d.

Table 2. HDF Products of C_6F_6 Using Phosphines as Ancillary Ligands

$$2C_6F_6 + 6\ \text{phosphine} \xrightarrow{\mathbf{1}\ (5\%)} \text{HDF products} \quad (4)$$

entry	phosphine	HDF products (yield)[a]
1	dippe	C_6F_5H (2%), 1,2,4,5-$C_6F_4H_2$ (98%)
2	PEt_3	1,2,4,5-$C_6F_4H_2$ (100%)

[a]Determined by GC-MS. Reaction conditions: 5% **1**, dioxane, T = 120 °C, t = 3 d.

Table 3. Catalytic HDF of Fluoroarenes by $[Ni(dippe)H]_2$ + PEt_3[a]

Entry	Substrate	Product	Yield	TON	TOF (h^{-1})
1	C_6F_6		100 %	40	0.55
2	C_6F_5N		100 %	40	0.55
3	C_6F_5H		98 %	39.2	0.54
4	1,2,3,4-tetrafluoro-benzene		94 %	37.6	0.52

[a]Reaction conditions: 5 mol% cat. **1**, dioxane, 6 equiv PEt_3, T = 120 °C, t = 72 h.

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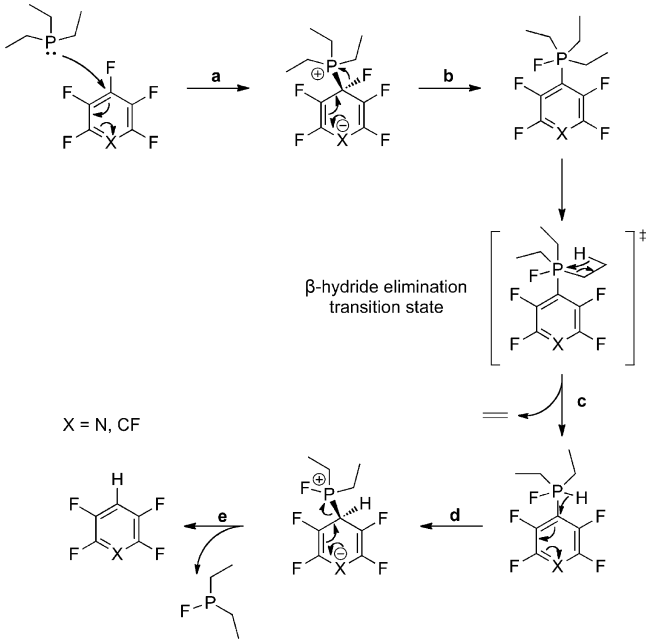
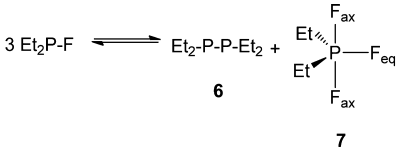
Scheme 1. Phosphine-Based Mechanistic Proposal for Hydrodefluorination



It is well known that such fluorophosphines are unstable toward their expected disproportionation reaction,[28] as shown in eq 5.



(5)

In the current case, compounds **6** and **7** were not directly detected, but some products of further reactivity or exchange were found (*vide infra*). The $^{31}P\{^{1}H\}$ NMR spectrum identified the formation of the difluorophosphorane **8** as the main component in the mixture of final products (Figure 5), displaying a

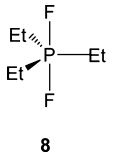


Figure 5. Phospho-fluorinated product, **8**.

signature signal at δ −11.6 (t, $^{1}J_{P-F}$ = 587 Hz). The ^{19}F NMR spectrum showed a doublet of septuplets at δ −40.0 (dsept, J_{P-F} = 588 Hz, $^{3}J_{F-H}$ = 10.5 Hz) due to the coupling of both axial fluorine atoms with the CH_2 of the Et moiety, each displaying a septuplet signal (see SI). These NMR data are in agreement with those reported for **8**.[29] Small amounts of a compound labeled as **9** can be seen, with the characteristic signals at δ −40.5 (d, $^{1}J_{P-F}$ = 620 Hz) in the ^{19}F NMR and at δ −16.3 (t, $^{1}J_{P-F}$ = 635 Hz) in the $^{31}P\{^{1}H\}$ NMR. These signals allow us to suggest the presence of a "Et_2-P-F_2" derivative that could not be fully characterized due to the low abundance.

Considering the presence of phospho-fluorinated products as the final fate of fluorine, control experiments in the absence of the nickel catalyst and silane revealed, to our surprise, very high

Table 4. HDF Products Using PEt_3 Only

fluoroarene + $3PEt_3$ → HDF product + **8** + **9** (6)

entry	fluoroarene	HDF product (yield)[a]
1	C_6F_6	1,2,4,5-$C_6F_4H_2$ (100%)
2	C_6F_5H	1,2,4,5-$C_6F_4H_2$ (100%)
3	C_5F_5N	2,3,5,6-C_5HF_4N (100%)
4	1,2,3,4-$C_6F_4H_2$	1,2,4-$C_6F_3H_3$ (100%)

[a]Determined by GC-MS and multinuclear NMR. Reaction conditions: dioxane, T = 120 °C, t = 3 d.

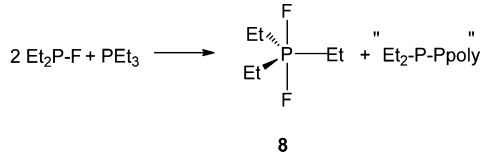
conversion to yield HDF of all substrates, as indicated in eq 6 and Table 4.

These results rule out the required participation of any nickel-based organometallic intermediates leading to HDF. Although there are several reports[30] in which the importance of the metal−phosphine complexes (metallophosphoranes) in C−F bond activation is highlighted, including a recent review in this field,[31] to the best of our knowledge there are no reactions reported where *the sole action of an alkylphosphine is able to selectively defluorinate a polyfluoroarene*. Closely related reactivity of organofluorophosphonium salts along with the use of a silane has been very recently reported by Stephan and co-workers for HDF of fluoroalkanes.[32a] Also related are Ozerov's findings of fluoroalkyl HDF with a silylium−carborane catalyst.[32b] Of note, compound **8** is the major organophosphorous product containing fluorine (>93%).

A follow-up to the reaction in Table 4, entry 1, using a sealed NMR tube monitoring by multinuclear NMR spectroscopy revealed that the reaction was actually complete in 3 h, with the immediate formation of **8** instead of Et_2PF as the HDF progressed. Again, only small amounts of **9** were observed during the course of the reaction. The relative amount of **9** barely changed after 3 h. Also for entry 1, the GC-MS trace allowed detection of a weak and broad peak consistent with the mass of a "Et_2-P-F_2" fragment (see SI). To shed additional light on this process, the reaction under the same conditions but using PMe_3 as the phosphine showed no progress after 3 h.

Considering the results in Table 4, and the evidence found in this study (*vide supra*), a tentative mechanistic proposal is depicted in Scheme 1.

The initial step in Scheme 1 is a nucleophilic attack by the phosphine (**a**), followed by F-migration (**b**). From there, a β-hydride elimination is proposed (**c**), considering the fact that the reaction does not depend on silane or on the participation of the solvent as a hydrogen source. Next, a hydride nucleophilic addition (**d**), followed by a final elimination of fluorophosphine Et_2PF, yields the hydrodefluorinated product (**e**). Such a fluorophosphine would be expected to decompose to products **8** and **9** via the well-known disproportion depicted above in eq 5, or alternatively following a closely related reaction between the fluorophosphine and PEt_3 depicted in eq 7.



(7)

This proposal is inspired by the known reactivity of chlorophosphines and alkylphosphines to yield **8** and a phosphorus polymer material.[33] Ethylene was not detected, probably due to evaporation from the reaction mixture at the high temperatures

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employed, or possibly polymerization. The lack of reactivity of PMe_3 supports the β-elimination proposal.

As presented earlier, many metal-mediated and catalytic HDF reactions have been studied, some of them postulated to be phosphine-assisted C−F bond activation at iridium[34] and platinum[35] along with a P−C bond cleavage and P−F bond formation, with retention of the oxidation state at the P atom and also with the formation of metallophosphoranes.[31] Here we found that HDF occurs by the sole action of the phosphine acting as fluorine acceptor and reducing agent, with oxidation of the P atom and with regioselectivity.

CONCLUSIONS

We demonstrated the formation of η^2-C═C complexes between fluoroaromatics and a Ni(0) fragment, along with the oxidative addition of the metal into the C−F bond of the fluoroarene. Also reported are the catalytic HDF reactions of polyfluoroarenes using a nickel catalyst and an added alkyl phosphine, to yield the hydrodefluorination product with high selectivity toward partially hydrodefluorinated products and excellent yields. We show for the first time that the same reactivity toward HDF was obtained without the use of a metal catalyst or a silane. Thus, the current results point out that many of the HDF reactions may not only be phosphine-mediated but indeed possibly metal- and silane-free.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all manipulations were performed under an argon atmosphere in an MBraun glovebox (<1 ppm H_2O and O_2) or using standard Schlenk techniques. Hexafluorobenzene, pentafluorobenzene, 1,2,3,4-tetrafluorobenzene, pentafluoropyridine, and 1,2-, 1,3-, and 1,4-difluorobenzene were purchased from Aldrich; all substances were reagent grade, stored over 3 Å molecular sieves, and manipulated in a drybox. All other solvents used were dried and distilled from sodium/benzophenone ketyl. Deuterated solvents for NMR experiments were purchased from Aldrich and stored over 3 Å molecular sieves in the glovebox. The nickel(I) complex (**1**)[36] was prepared from Super-Hydride and [(dippe)$NiCl_2$][37] suspended in hexane, similarly to the literature procedure.[38] All compounds were verified by the corresponding ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra. All catalytic experiments were loaded in a Schlenk flask with J-Young valves inside the glovebox. All of the HDF products were distilled from the flask by static vacuum on a vacuum line ($P < 10^{-3}$ mmHg) prior to their quantification and characterization. All NMR spectra of complexes and products were recorded at room temperature on a 300 MHz Varian Unity spectrometer. NMR determinations for air-sensitive samples were collected using sealed J-Young NMR tubes. The ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra of the hydrodefluorinated compounds were obtained from reaction solutions in $CDCl_3$ unless otherwise stated. ^1H NMR chemical shifts (δ, ppm) are reported relative to the residual proton resonance in the deuterated solvent. ^{19}F and $^{31}P\{H\}$ spectra are reported relative to external 10% trifluoroacetic acid and 85% H_3PO_4, respectively. GC-MS determinations were performed using an Agilent 5975C instrument equipped with a 30 m DB-5MS capillary (0.32 mm i.d.) column.

The following general procedures were used for synthetic and catalytic work.

*1. Stoichiometric Reaction of **1** with Fluoroaromatics.* To a solution of [(dippe)NiH]$_2$ (**1**) (0.0365 g, 0.056 mmol) in THF or dioxane (5 mL) was added the corresponding fluoroaromatic substrate (0.0210 g, 0.112 mmol in the case of C_6F_6; 0.0133 g, 0.112 mmol in the case of PEt_3). An immediate color change from deep purple to yellow-brownish and release of gas were observed. The flask was vented into the drybox and then heated to the desired temperature, typically in an oil bath at 120 °C. Using THF-d_8 or dioxane-d_8 as solvent, the amount of solution was reduced to 1 mL and then transferred into an NMR tube with a J-Young valve to permit multinuclear following by NMR spectroscopy. After up to 3 d, the reaction mixture was analyzed by both GC-MS and multinuclear NMR spectroscopy, cooling the reaction mixture to room temperature and then taking a sample from the original reaction mixture by separating the volatiles under a vacuum. The addition of hexane at −30 °C allowed crystallization of nickel-containing complexes **2** and **5**. Compound **2** can be crystallized shortly after reaction at room temperature and complex **5** after heating at 80 °C for 4 h. Complexes were further dried for 4 h under high vacuum.

*Complex **2**.* Yield 90%. Anal. Calcd for **2**, $C_{34}H_{64}F_6Ni_2P_4$: C, 49.31; H, 7.79; F, 13.76. Found: C, 49.1; H, 7.69; F, 13.5. ^1H NMR (22 °C, 300 MHz, THF-d_8): δ 1.1 (m, CH_3); 1.67 (d, CH_2); 2.1 (m, CH). ^{19}F NMR (22 °C, 282 MHz, THF-d_8): δ −172 (m, br). $^{31}P\{^1H\}$ NMR (22 °C, 121 MHz, THF-d_8): δ 70.7 ($^3J_{P-F}$ = 12 Hz). Crystals of **2** suitable for X-ray diffraction studies were obtained by cooling the THF-d_8 solution to −30 °C, layering with hexane, and isolating the crystals by decantation.

*Complex **4**.* ^1H NMR (22 °C, 300 MHz, THF-d_8): δ 1.35 (m, CH_3); 1.92 (d, $-CH_2-$); 2.3 (m, CH). ^{19}F NMR (22 °C, 282 MHz, THF-d_8): δ −132.1 (m); −147.7 (m); −153.2 (m); −160.9 (m); −184.5 (m). $^{31}P\{^1H\}$ (22 °C, 121 MHz, THF-d_8): δ 71.8 (m, br).

*Complex **5**.* Yield 88%. Anal. Calcd for **5**, $C_{20}H_{33}F_5NiP_2$: C, 49.11; H, 6.8; F, 19.42. Found: C, 48.9; H, 6.77; F, 19.2. ^1H NMR (22 °C, 300 MHz, THF-d_8): δ 1.33 (m, CH_3); 1.90 (d, $-CH_2-$); 2.31 (m, CH). ^{19}F NMR (22 °C, 282 MHz, THF-d_8): δ −115.6 (m); −141.2 (m); −162.6 (m); −164.4 (m); −345.4 (m, $^2J_{P-F}$ = 34 Hz). $^{31}P\{^1H\}$ NMR (22 °C, 121 MHz, THF-d_8): δ 70.4 (dd, $^2J_{P-P}$ = 10 Hz, $^2J_{P-F}$ = 30 Hz); 65.6 (dd, $^2J_{P-P}$ = 10 Hz, $^2J_{P-F}$ = 34 Hz).

*Signature Signals for Et_3PF_2 (**8**).* ^{19}F NMR (22 °C, 282 MHz, dioxane-d_8): δ −40.0 (dsept, J_{P-F} = 588 Hz, $^3J_{F-H}$ = 10.5 Hz). $^{31}P\{^1H\}$ NMR (22 °C, 121 MHz, dioxane-d_8): δ −11.6 (t, $^1J_{P-F}$ = 587 Hz). All data are in agreement with the literature values.[28]

*Signature Signals for Et_2F_2PH (**9**).* ^1H NMR (22 °C, 300 MHz, dioxane-d_8): δ 3.9 (m, P−H). ^{19}F NMR (22 °C, 282 MHz, dioxane-d_8): δ −40.5 (d, $^1J_{P-F}$ = 620 Hz). $^{31}P\{^1H\}$ NMR (22 °C, 121 MHz, dioxane-d_8): δ −16.3 (t, $^1J_{P-F}$ = 635 Hz).

2. HDF Catalytic Reactions. A procedure similar to that previously described was followed, but instead using 5 mol% of **1** (0.018 g, 0.002 mmol) in 1,4-dioxane with fluoroaromatic substrate (0.0210 g, 0.112 mmol in the case of C_6F_6; 0.0781 g, 0.672 mmol for Et_3SiH; and 0.0399 g, 0.336 mmol for PEt_3). The mixture was heated to 120 °C for 72 h. After this time, the reaction mixture was vacuum transferred for the separation of volatiles. The volatile fraction and the residue were analyzed by GC-MS and NMR.

3. HDF Reactions without Catalyst. A procedure similar to that previously described was followed, but using only the fluoroarene of choice and PEt_3 in a molar ratio of 1:3, respectively (for instance, 0.0210 g, 0.112 mmol of C_6F_6; 0.0399 g, 0.336 mmol of PEt_3).

X-ray Structure Determination. Crystals of **2** or **5** mounted on a glass fiber were studied with an Oxford Diffraction Gemini "A" diffractometer with a CCD area detector, using a sealed tube X-ray radiation source with $\lambda_{Mo\ K\alpha}$ = 0.71073 Å for **2** and $\lambda_{Cu\ K\alpha}$ = 1.54184 Å for **5**, with a monochromator of graphite at 130 K. Unit cell constants were determined with a set of 15/3 narrow frame/runs (1° in ω) scans. Data sets consisted of 207 and 1091 frames of intensity data collected with a frame width of 1° in ω for **2** and **5**, respectively, and a crystal-to-detector distance of 55.00 mm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated by using an orientation matrix determined from the narrow frame scans. CrysAlisPro and CrysAlis RED software packages[39a] were used for data collection and data integration. Analysis of the integrated data did not reveal any decay. Final cell constants were determined by a global refinement of 7225 (θ < 25.68°) and 1501 (θ < 68.10°) reflections for **2** and **5**, respectively. Collected data were corrected for absorbance by using analytical numeric absorption correction[39b] using a multifaceted crystal model based on expressions upon the Laue symmetry using equivalent reflections.

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Structure solution and refinement were carried out with the programs SHELXS97[39c] and SHELXL97;[39c] for molecular graphics, ORTEP-3 for Windows[39d] was used; and the software used to prepare material for publication was WinGX.[39e]

Full-matrix least-squares refinement was carried out by minimizing $(F_o^2 - F_c^2)^2$. All non-hydrogen atoms were refined anisotropically. H atoms attached to C atoms were placed in geometrically idealized positions and refined as riding on their parent atoms, with C—H = 0.95−1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for aromatic, methylene, methyne, and methyl groups.

■ ASSOCIATED CONTENT

Supporting Information

Figures with selected multinuclear NMR spectra, GC-MS, and crystallographic data for complex **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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