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Metal Heptafluoroisopropyl (M-hfip) Complexes for Use as hfip Transfer Agents

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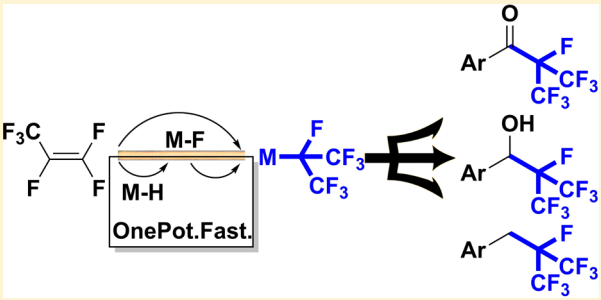
Supporting Information

ABSTRACT: New coinage-metal heptafluoroisopropyl (L_nM-hfip) complexes are synthesized from the metal fluoride and inexpensive hexafluoropropene (M = Ag, Cu; L = PPh_3, 2,2,6,6-tetramethylpiperidine (Htmp)). Reaction of the silver Htmp complex with a Ni dibromide complex led to efficient hfip transfer to afford L_2NiBr(hfip) (L = 2-ethylpyridine). Treatment of the Ni-hfip complex with $ZnPh_2$ gave the corresponding L_2NiPh(hfip) complexes, which were investigated for reductive elimination of $PhCF(CF_3)_2$. Although the desired reductive elimination proved unsuccessful, addition of carbon monoxide to L_2NiPh(hfip) effected an efficient heptafluoroisopropyl carbonylative cross-coupling. Further, while the silver complex does not undergo hfip transfer to organic electrophiles, the copper complex (phen)(PPh_3)Cu(hfip) (**3b**) effectively transfers the hfip unit to various substrates. We investigated the scope of **3b** with acid chlorides toward the synthesis of perfluoroisopropyl aryl ketones. Additionally, reaction conditions for hfip transfer to *p*-fluorobenzyl bromide and *p*-fluorobenzaldehyde were identified. As a bonus, **3b** was easily generated on a gram scale using commercially available copper hydride by taking advantage of a rapid hydrodefluorination to generate "Cu−F" in situ. Aspects of the observed reactivity are supported by DFT calculations.



INTRODUCTION

Fluorinated carbon fragments, i.e. fluoroalkyls and -aryls, have become quite common in many applications.[1,2] In the pharmaceutical industry,[3,4] for example, many household drugs now contain these functional groups,[5] which offer benefits in metabolic stability, solubility, lipophilicity, and bioavailability. Many of these fluoroalkyl-containing drugs have become "blockbusters", such as Celebrex, Prevacid, and Pantoprazole.

While many such fragments can be envisioned, only a few are currently readily accessible. For example, trifluoromethylation reactions have seen a period of rapid growth spurred by unique biological applications.[6] However, installation of other fluoroalkyl fragments such as CF_2H,[7] C_2F_5,[8] OCF_3,[9] and SCF_3[10] remains challenging. There has also been a huge investment in identifying new biologically active agents for use in both the agrochemical and pharmaceutical industries. For example, the heptafluoroisopropyl (hfip) group has recently been incorporated into insecticides (Figure 1),[11] prompting our current study of its synthesis, coordination chemistry, and transfer to organic electrophiles.

The success and application of fluoroalkylation routes generally hinges on the stability and ease of access of the critical reagent.

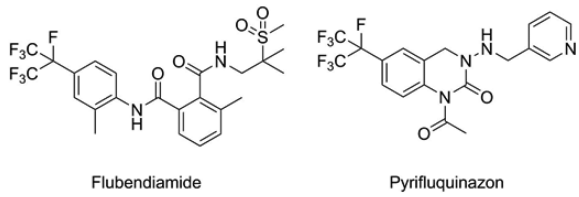


Figure 1. Biologically active compounds containing hfip group.

The Ruppert−Prakash reagent Me_3Si-CF_3, for example, has seen widespread adoption primarily because of its moderate cost and ready availability.[12] Recently, Grushin et al. successfully prepared a series of [Cu]CF_2CF_3 complexes generated from pentafluoroethane,[13] and Vicic et al. developed a zinc reagent of the type [Zn]CF_2H.[14] In both cases, the cost of preparation for these reagents remains low by using base metals and readily available hydrofluoroalkanes. The reactivity of these reagents depends heavily on the choice of ancillary ligand, with 1,10-phenanthroline (phen) giving rise to increased reactivity—such as the (phen)Cu(CF_3) Trifluoromethylator.[15] In this report, we find that changes in the coordination

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chemistry of copper leads to improved transfer of the hfip fragment to organic electrophiles.

To date, methodologies for the introduction of the hfip group to organic molecules remain scarce. One can generate the hfip nucleophile as the hfip anion $[CF(CF_3)_2]^-$ (Figure 2A)[16] or the metal complex [M]-hfip (Figure 2B).[17] In these

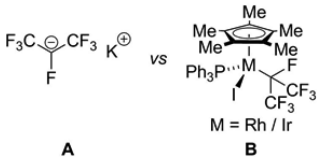
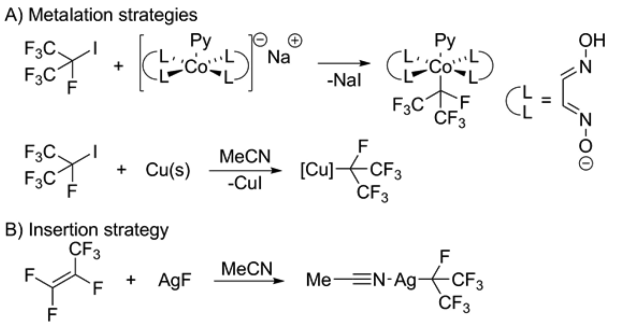


Figure 2. Heptafluoroisopropyl anion vs M-hfip complex.

procedures, two reagents provide a foundation to access the hfip moiety. The more obvious of the two is 2-iodoheptafluoropropane, which has been successfully metalated to yield hfip complexes (Scheme 1A)[18] Alternatively, one can generate

Scheme 1. (A) Metalation of Heptafluoro-2-iodopropane and (B) Addition of M−F to Hexafluoropropene



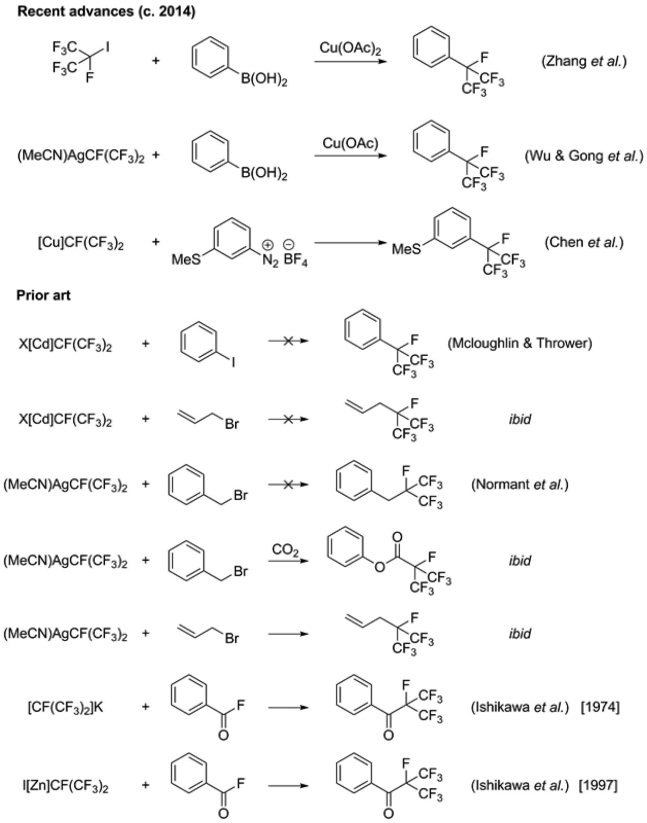
similar compounds from hexafluoropropene (HFP) and a source of fluoride (Scheme 1B).[19] This route benefits from the significantly less expensive starting material (23.7 (HFP) vs 192 $/mol (Ihfip)), and HFP can be generated selectively from waste polytetrafluoroethylene (PTFE).[20]

In reports that explore such reactivity, four reagents stand out: the hfip anion and hfip complexes of cadmium, silver, and copper (Scheme 2).[21] Evidently, each system has its own drawbacks, which could possibly be remediated with the development of new hfip organometalllic reagents. Herein, we report the synthesis and characterization of new Cu, Ni, and Ag hfip complexes. The reactivity of each compound is then tested with simple organic electrophiles to determine the nucleophilicity.

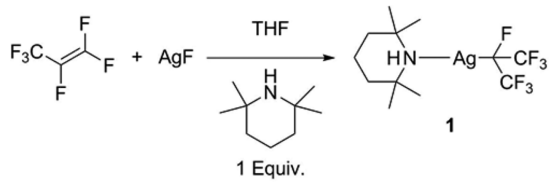
RESULTS AND DISCUSSION

Synthesis and Characterization of a Silver hfip Complex. Following a modified literature procedure,[19a] the new silver hfip complex **1** was prepared directly from HFP and silver fluoride in the presence of 2,2,6,6-tetramethylpiperidine (Htmp) (Scheme 3). As is typical for such reactions, only a single isomer is observed. The metal fluoride inserts HFP such that the less sterically hindered and the more $\delta+$ carbon (=CF_2) is oriented toward the fluoride. This choice of ligand was inspired by previous work with $AgCF_3$ complexes,[22] to target the neutral compound (vs $[Ag(CF_3)_2]^-$). The colorless powder **1** is slightly unstable at room temperature, becoming

Scheme 2. Reported Reactions of hfip Compounds



Scheme 3. Synthesis of Compound 1



progressively grayer over time. However, this did not preclude the collection of single-crystal X-ray diffraction data (Figure 3).

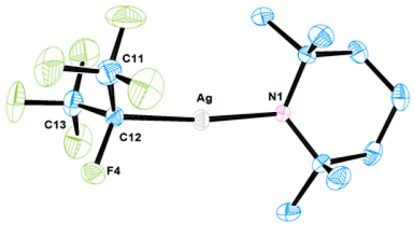


Figure 3. ORTEP representation of the molecular structure of **1**. Thermal ellipsoid probabilities are set to 35%, with hydrogen atoms omitted for clarity.

The molecular structure of complex **1** exhibits a linear coordination about Ag and features a hydrogen bond interaction (N−H···F) between the isopropyl fluoride (F4) and the tetramethylpiperidine amine (N1—H1′) from the neighboring complex in the crystal lattice (see Figure S40 in the Supporting Information). There is a slight distortion from linearity with the shortest C12−Ag−N1 angle being 173°.

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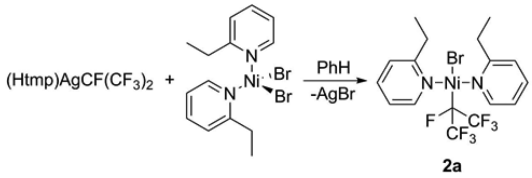
The ^{19}F NMR spectrum of **1** in C_6D_6 is consistent with the structure determined in the solid state. Whereas the trifluoromethyl group displays a chemical shift difference for the ^{106}Ag and ^{107}Ag isotopomers, the iPr fluoride does not and neither resonance displays Ag−F coupling. Consistent with previous reports, on dissolution in more polar and coordinating solvents an equilibrium between (Htmp)Ag[CF(CF_3)$_2$] and Ag$^+$[Ag{CF(CF_3)$_2$}$_2$]$^-$ is evident, with the neutral complex being favored.[17g]

Synthesis and Characterization of Nickel hfip Complexes. With the stable Ag complex **1** in hand, we proceeded to transmetalate the hfip fragment to other transition-metal halides.[23] Generally, the reaction with transition-metal halides led to decomposition of **1** by formation of HFP (*β*-fluoride elimination) or 2*H*-heptafluoropropane. Reaction with bis(2-ethylpyridine)nickel dibromide in benzene, however, yielded the singly transmetalated product **2a** (Scheme 4). Even when an excess of **1** was used, only **2a** was observed.

Scheme 4. Synthesis of Compound 2a



The nickel atom of complex **2a** adopts a square-planar geometry with the hfip and bromide trans to each other (Figure 4). While the C_α−F bond appears to be significantly longer[24]

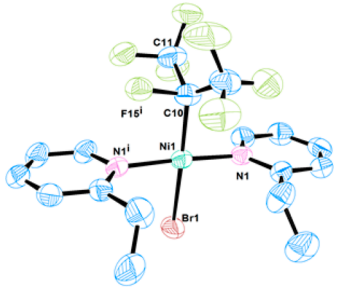


Figure 4. ORTEP representation of the disordered molecular structure of **2a** (ethyl groups can be syn, anti or anti, anti to hfip). Thermal ellipsoid probabilities are set to 35%, with hydrogen atoms omitted for clarity.

than that in **1** (1.59 Å (average) vs 1.420(2) Å in **1**), this is likely an artifact of the disorder in the crystal structure, as the calculated value is in line with other complexes (Table 1).

The ^{1}H NMR spectrum of **2a** has three broad signals centered at δ 4.5, 5.2, and 9.4, respectively. These are assigned to the CH_2Et and CHpy fragments which reside closest to the metal center. The dynamic process that contributes to these broad resonances is most evident in the variable-temperature ^{19}F NMR spectrum that exhibits the expected doublet and septet resonances only at elevated temperature (Figure S8). At room temperature the inequivalent CF_3 resonances are likely due to hindered rotation about the Ni−C and Ni−N bonds in the two rotamers observed in the solid-state structure.

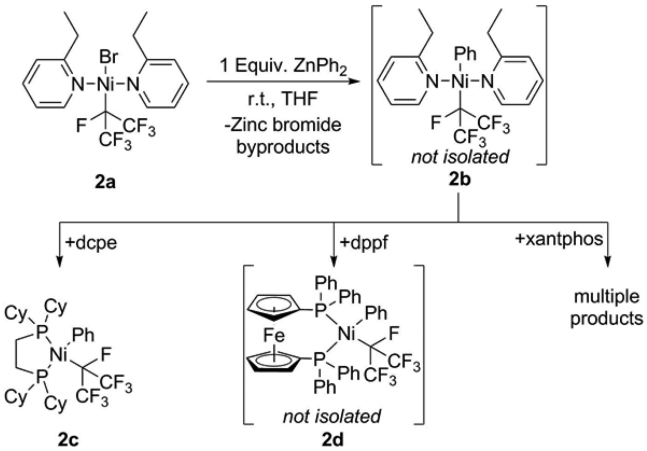
Table 1. Selected Bond Lengths[a]

	1	2a	2c	3a	3b
M−C	2.11/2.14	2.00/2.04	2.00	2.00/2.04	2.00/2.04
C_α−F	1.42/1.42	1.60[c]/1.42	1.44	1.43/1.43	1.44/1.43
C_β−F[b]	1.32/1.36	1.35/1.36	1.35	1.35/1.37	1.34/1.37

[a]All values are rounded and are given in Å: experimental/calculated. [b]Average for calculated values at the DFT/B3LYP level. [c]Accuracy likely affected by disorder.

As **2a** can be considered the oxidative addition product of Br-CF(CF_3)$_2$ to nickel(0), it may serve as a potential platform to study the cross-coupling synthesis of Ar-CF(CF_3)$_2$. To model such a reaction, we selected diphenylzinc as a potential coupling partner. Immediately upon addition of the zinc reagent to a solution of **2a** in THF, a reaction was observed to form complex **2b** (Scheme 5). This new complex (not isolated) was

Scheme 5. Synthesis of Phenyl Ni-hfip Complexes 2b−d



then treated in situ with bis(phosphines) to give stable products: 1,2-bis(dicyclohexylphosphino)ethane (dcpe; **2c**), 1,1′-bis(diphenylphosphino)ferrocene (dppf; **2d** (not isolated)), and xantphos (multiple products).

Complex **2c** was isolated as a bright yellow powder and crystallized from acetonitrile. The molecular structure of **2c** shows a distorted-square-planar Ni center with the hfip and the phenyl cis to each other (see Figure S1 in the Supporting Information). The C_α−F bond distance (1.437 Å) is now closer in length to that in complex **1**.

Synthesis and Characterization of Copper hfip Complexes. Reaction of **1** with copper chloride in benzene produces the solvated Cu-hfip complex disclosed previously[17c] and used extensively in arylboronic acid cross-coupling reactions[21a] and others.[18b,21] Looking to avoid the use of the costlier silver fluoride starting material (928 $/mol), we endeavored to synthesize the Cu complex from commercially available copper fluoride dihydrate (43 $/mol) and triphenylphosphine (45$/3 mol). The choice of copper fluorides is limited, since only a few have been reported and/or isolated,[25] with (PPh_3)$_3$CuF being successfully used as a source of nucleophilic fluoride. In one example, Szabó et al. demonstrated the substitution of allylic C−X bonds (X = Br, Cl, OTf) using said reagent to synthesize allylic C−F compounds.[26] Similarly, Grushin et al. employed this complex to easily generate $CuCF_3$ from Me_3SiCF_3.[27] In this regard, we expected the coinage-metal fluoride to yield a net addition of Cu−F across the HFP double bond, as seen with AgF.

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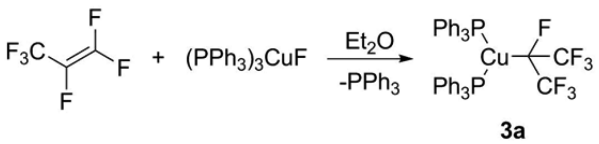
The copper(I) fluoride complex $CuF(PPh_3)_3$ was synthesized as previously reported,[24a] and treatment with HFP in Et_2O over a 24 h period afforded the hfip complex **3a** in high yield (80%) and excellent purity (>90%, Scheme 6). Solvents of higher polarity yielded impurities that are not trivially separated from **3a**. Moreover, the use of dichloromethane or *N,N*-dimethylformamide (DMF) yielded no product and only HFP oligomers. Like the previously reported pentafluoroethyl copper complex,[28] the molecular structure of **3a** features a hfip group and two PPh_3 ligands in a trigonal-planar array about the copper (Figure 5 (left)). As expected, the Cu−C bond (2.003(3) Å) is shorter than the Ag−C bond (2.114(2) Å) but is like those in the Cu−CF_2CF_3 (1.99 Å) and Cu−CF_3 (2.025(7) Å) analogues. On this note, the C_α−F bond distance gets progressively smaller with decreasing fluoroalkyl size (1.44 Å for **3a** vs 1.40 and 1.39 Å for CF_2CF_3 and CF_3, respectively).

Scheme 6. Synthesis of 3a from HFP and Copper(I) Fluoride



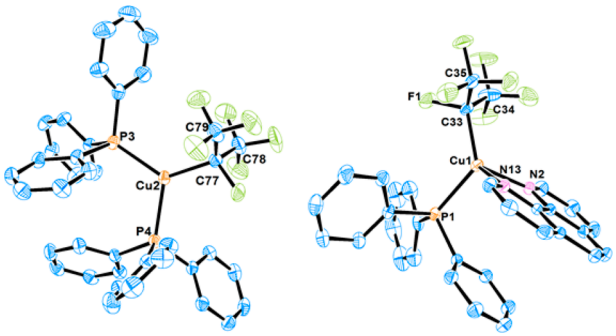
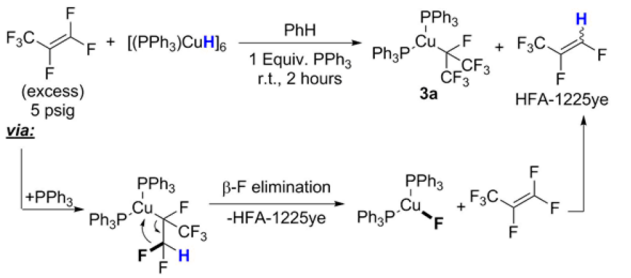


Figure 5. ORTEP representation of the molecular structures of (left) **3a** and (right) **3b**. Thermal ellipsoid probabilities are set to 35%, with hydrogen atoms omitted for clarity.

As the reaction to form **3a** was slow—likely related to the limited solubility of $[(PPh_3)_3CuF]$ in Et_2O—we sought an alternate Cu−X precursor that upon rapid insertion of HFP would undergo β-fluoride elimination to Cu−F followed by subsequent addition of HFP to yield **3a**. For example, Ogoshi et al. have taken advantage of β-fluoride elimination of a copper complex to generate fluorostyrenes.[29] To avoid side reactions, we selected X such that the produced fluoroalkene would be a gas at room temperature. We thus turned to commercially available $[(PPh_3)CuH]_6$ (Stryker's reagent). Although copper hydride has been used for hydrodefluorination of ArF compounds,[30] it has never been used with fluoroalkenes. When $[(PPh_3)CuH]_6$ with an additional 1 equiv of PPh_3 per Cu is exposed to HFP in benzene, it reacts in <2 h to give **3a** in excellent yield (81% based on $[(PPh_3)CuH]_6$, Scheme 7). Moreover, addition of phen to **3a** in Et_2O gave $[(phen)(PPh_3)Cu(hfip)]$ (**3b**) in high yield (>80% based on $(PPh_3)_2Cu(hfip)$) as a bright orange powder. This change in coordination number and ligand did not have a profound effect on the Cu−C or C_α−F bond lengths (Figure 5 (right) and Table 1).

Scheme 7. Synthesis of 3a from HFP and Stryker's Reagent



The ^{19}F NMR spectrum of **3a** in C_6D_6 shows an unusually broad resonance for C_α−F, indicating some fluxional behavior. This is supported by a broad signal in the ^{31}P NMR spectrum at −5 ppm for both PPh_3 ligands. While **3b** in C_6D_6 reveals a similar trend in the ^{31}P NMR spectrum (broad resonance at −5 ppm), the ^{19}F NMR spectrum now consists of sharp resonances with the typical $^3J_{FF}$ coupling constant (FC−CF_3) being quite apparent, although no J_{PF} value could be identified. The ^1H NMR spectrum also shows broadening of the signal assigned to phen-H lying closest to the metal center, resulting presumably from fast cleavage and re-formation of the Cu−PPh_3 bond.

Reactivity of M-hfip Complexes with Aroyl Chlorides. Having these four new M-hfip complexes in hand, we proceeded to test their reactivity with benzoyl chloride to determine which one may be a suitable platform for further nucleophilic studies. First, when **1** was mixed with benzoyl chloride in many solvents, no reaction was observed. This is in line with previously described reactivity for the analogous compound $(MeCN)Ag[CF(CF_3)_2]$.[17h] Second, when **2a** was mixed with benzoyl chloride, immediate formation of HCF$(CF_3)_2$ (Hhfip) was observed. In contrast, when **3a** or **3b** was mixed with benzoyl chloride in DMF, both produced fluorinated ketone **4a** in moderate (50%) and high (75%) yields, respectively. In the case of **3a** the reagent is unstable under the reaction conditions and produces an equivalent amount of benzoyl fluoride, arising presumably from β-fluoride elimination with concomitant formation of HFP. Optimizing the reaction of **3b** with benzoyl chloride, we found that DMF was required; all other solvents tested yielded no product and gave exclusively Hhfip. The reaction proceeds readily at room temperature over 24 h.

Existing methods for the synthesis of these compounds have been limited either by (a) generation of the $[CF(CF_3)_2]^-$ anion and accompanying HFP oligomers[16a] or (b) the use of acid fluorides, generated from acid chlorides.[17i,31] The reaction can be applied to a wide range of acid chlorides bearing various functional groups, including halide (**4e−g**), CN (**4i**), ether (**4k**), alkyl (**4c**), nitro (**4j,k**), naphthyl (**4l**), and thiophene (**4n**; Scheme 8). Some steric effects could be observed. For example, the ortho derivatives gave lower yields (**4d,k**). The extent of this effect is better measured using the 2,4,6-chloro-substituted benzoyl chloride that does not react with **3b**. In general, the electron-rich aroyl chlorides always gave lower yields, presumably due to reversibility under the reaction conditions. This is more evident in the case of 3,4,5-trimethoxybenzoyl chloride, for which the yield drops off as the reaction progresses. Similarly, this highlights the inherent difficulty in isolating these products, as the hfip group is readily substituted and therefore demands rigorously dry conditions. To

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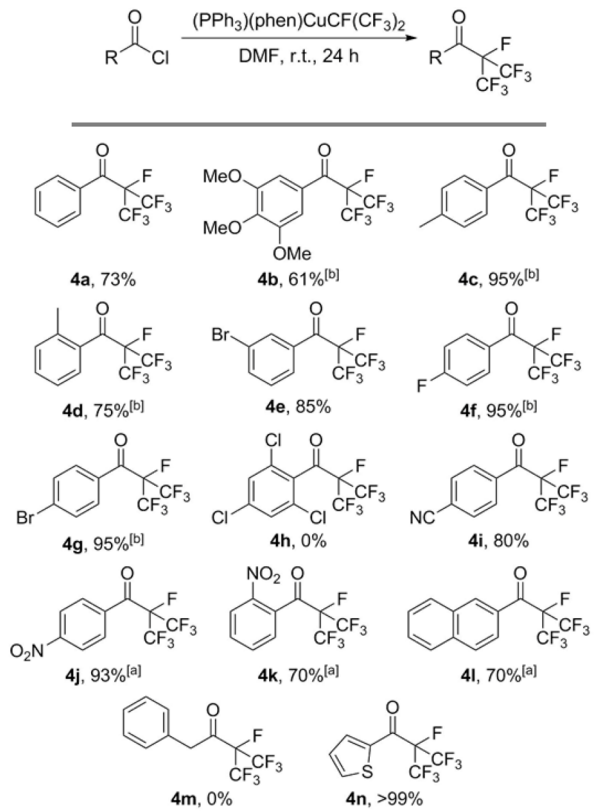
Scheme 8. Perfluoroisopropylation of Aroyl Chlorides[c]



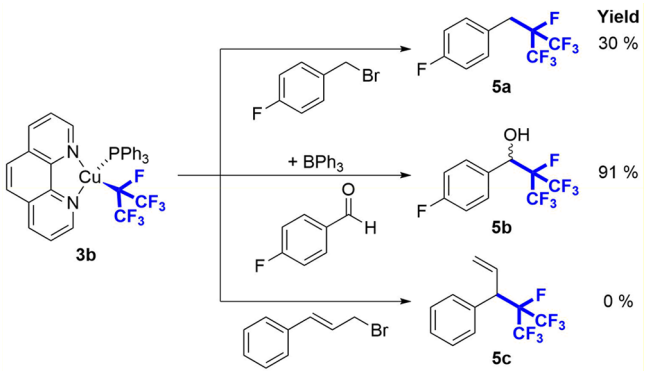
[a]1 equiv of **3b**. [b]4 h at room temperature. [c]Reaction conditions unless specified otherwise: 0.074 mmol of Cu, 0.049 mmol of acid chloride. and 0.027 mmol of internal standard in 0.5 mL of DMF at room temperature for 24 h. The reactions were performed in an NMR tube sealed with a plastic cap and wrapped with Parafilm without stirring. The yields were determined by ^{19}F NMR spectroscopy with hexafluorobenzene as an internal standard vs moles of electrophile. For details see the Supporting Information.

compound this issue, all of the products are volatile and could not be easily separated from DMF. However, they can be collected as the distillate with DMF.[32] Noticeably, phenyl acetyl chloride, the only alkyl acid chloride, does not react with **3b**.

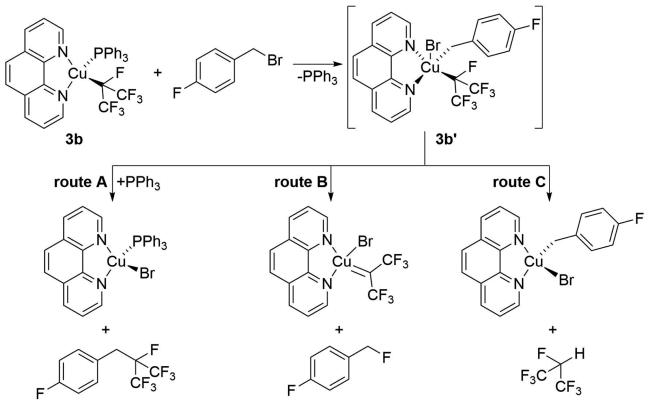
Reactivity of Cu-hfip Complexes with Other Electrophiles. Reactions of **3b** with several other electrophiles generally required ~1.5 equiv of **3b** due to competing formation of Hhfip.[33] Reaction of **3b** with 4-fluorobenzyl bromide (Scheme 9, top) gave an unusually low yield and produced several unidentifiable products on heating to 50 °C. To compound the issue, the product **5a** was unstable under regular workup conditions. In one attempt at isolation of **5a** by column chromatography, no product was collected. Although we expected the formation of benzyl fluoride to arise from β-fluoride transfer, we did not observe concomitant formation of HFP under the reaction conditions.

We suspect that the benzyl fluoride arises from α-fluoride transfer (Scheme 10, route B) from an intermediate copper(III) complex (**3b′**) and is in competition with product formation, corroborating the 30% yield. On the trend of alkyl halides, we found that those vicinal to a ketone do not react with **3a** (e.g., bromoacetophenone). We also found that bulkier benzhydryl halides do not substitute readily. Unfortunately, **5c** was not stable under the reaction conditions and slowly decomposed, precluding its isolation. Finally, aldehydes could be substituted

Scheme 9. Reactions of 3b with Other Electrophiles



Scheme 10. Reaction of 3b with a Benzyl Bromide and Suspected Decomposition Pathways of 3b′



by employing a weak Lewis acid as an additive. While **3b** does not react readily with 4-fluorobenzaldehyde, addition of a strong Lewis acid also does not produce the desired product. **3b** itself reacts with both trimethylsilyl trifluoromethanesulfonate (TMSOTf) and trifluoroborane etherate ($BF_3{\cdot}Et_2O$). However, addition of triphenylborane gave the desired product **5b** in 91% yield.

Reactivity of Ni(Ph)hfip (2b) toward Reductive Elimination. Upon heating complexes **2b–d** to 66 °C, (a) no reaction (**2c**), (b) decomposition to Hhfip (**2b**), or (c) a mixture of unknown products (**2d**) was observed. With the stable complex **2c** in hand, we attempted to effect the associatively induced reductive elimination by addition of excess triethyl phosphite, 2,6-dimethylphenyl isocyanide, or CO gas. Although addition of triethyl phosphite had no effect, the isocyanide reacted immediately to give a mixture of unidentified products. Addition of CO (3 atm) to **2c** (in either THF or benzene-d_6) at 50 °C instead produced the ketone in 90% yield (Scheme 11), with some Hhfip produced in a side reaction.

Scheme 11. Carbonylation and Reductive Elimination of the hfip Group

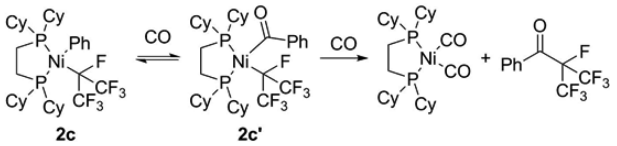


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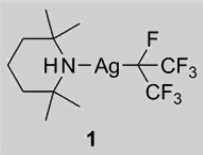
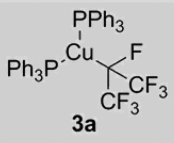
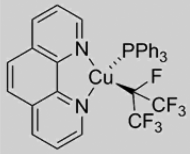
Table 2. Bond Dissociation Energies (BDE, ΔH_{0K}, and $\Delta G_{298\ K}$ at the B3LYP/DZVP2/aug-cc-pvdz-pp(M) Level in kcal/mol) and Charge Distribution of Some Reported Complexes

Complex	 1	 2a	 3a	 3b
Homolytic BDE ΔH_{0K} / ΔG_{298K} ΔG_{298K}(DMF)	71.1/57.3/62.9	46.4/28.4/22.2	80.7/64.1/66.6	55.1/40.0/44.1
Heterolytic BDE ΔH_{0K} / ΔG_{298K}/ ΔG_{298K}(DMF)	133.9/122.1/33.8	116.4/98.0/12.6[a]	90.3/74.3/1.8	86.4/72.6/32.4
Charge (NBO NPA)	M(0.555), C-$^{i}Pr^{F}$(-0.186)	M(0.716), C-$^{i}Pr^{F}$(-0.097)	M(0.598), C-$^{i}Pr^{F}$(-0.275)	M(0.748), C-$^{i}Pr^{F}$(-0.260)

[a]The Ni cation has a triplet ground state.

This suggests that catalytic perfluoroalkylcarbonylation[34] using nickel could be possible and will be explored further in due course.

Computational Chemistry. To provide insight into these reactivity trends, we carried out DFT calculations (at the B3LYP/DZVP2/aug-cc-pvdz-pp(M) level; Table 2). The calculated bond distances are in good agreement with experiment (Table 1). The calculated ^{31}P gas-phase NMR chemical shifts are within about 12 ppm of experiment, while those for ^{19}F differ by ∼20−30 ppm for $CF_3{}^{i}Pr^{F}$ and the $CF^{i}Pr^{F}$ (see the Supporting Information). This is typical of the usual errors in calculated chemical shifts for these nuclei.

There are two types of bond dissociation energies (BDEs) to consider for this system: homolytic with formation of a metal-centered radical and the perfluoroisopropyl radical and heterolytic with formation of a metal-centered cation and the perfluoroisopropyl anion. In the gas phase, homolytic cleavage always requires less energy than heterolytic cleavage. However, in solution, heterolytic cleavage can become favored due to solvation of the ions. In the gas phase, **1** and **3a** have significantly higher homolytic BDEs than do **2a** and **3b**, with **2a** having the lowest homolytic BDE. In DMF solution **3a** is predicted to have a heterolytic BDE of close to 0 kcal/mol and **2a** is predicted to have a heterolytic BDE of just above 10 kcal/mol. In contrast, **1** and **3b** have heterolytic BDEs of slightly greater than 30 kcal/mol in solution. The difference between the heterolytic BDEs in **3a** and **3b** arises from the bulky cation generated from **3b**, which is not as well solvated as is the smaller cation generated from **3a**. Furthermore, the perfluoroisopropyl anion can release fluoride to generate $CF_3(F)C{=}CF_2$. The fluoride affinity of perfluoropropene is $\Delta H_{298\ K}$ = 46.3 kcal/mol and $\Delta G_{298\ K}$ = 37.2 kcal/mol in the gas phase at the G3MP2 level[35] (see the Supporting Information). Inclusion of a solvent effect leads to the result that it is exothermic to release F^- from the $^{i}Pr^{F}$ anion by −6.3 kcal/mol.

The lack of reactivity observed for **1** is consistent with the calculated BDEs. The instability of **3a** is also consistent with the low energy for heterolytic cleavage and should be very sensitive to reaction conditions, especially as F^- can be generated from the perfluoroisopropyl anion. The BDEs for **2a** suggest that both heterolytic and homolytic cleavage could occur.

■ CONCLUSIONS

In summary, we have prepared a series of stable M-hfip complexes and investigated their reactivity. Isolation of the first stable Ni-hfip complexes demonstrates their potential for new cross-coupling reactions. The synthesis of **2a** was enabled by the underexploited salt metathesis reaction between Ag-R^F and transition-metal halides, whereby previous attempts had yielded ionic species such as $[Rh]^+[Ag(R^F)_2]^-$,[17f] the prior paradigm being that only copper complexes could be synthesized.[17b,21a] Further, this may enable access to metals in low oxidation states without the need for reduction. However, as demonstrated herein, a judicious choice of transition-metal starting material and ligand is necessary for success of these transfers.

Although the aforementioned reaction does yield the copper complex, we have discovered a new convenient synthesis of Cu-hfip complexes **3a**,**b**. An easily prepared, air-stable copper fluoride can be used to synthesize new Cu-hfip complexes, thus bypassing the need for silver. We have optimized these conditions to prevent side reactions, such as HFP oligomerization, which we found can occur in media other than Et_2O. Still, we wished to improve the reaction efficiency by decreasing the reaction time (likely limited by poor solubility of the Cu−F complex) and increasing the atom efficiency (Cu−F synthesis <50%). We have thus shown that a commercially available copper hydride can readily hydrodefluorinate HFP, generating Cu−F in situ which reacts rapidly with HFP to give the Cu-hfip complex.

On evaluating the reactivity of all new M-hfip complexes toward electrophiles, we showed that Cu complexes **3a**,**b** readily transfer the hfip fragment to benzoyl chloride. These findings have been supported by DFT calculations, which yielded parameters against which to compare for suspected reactivity/stability trends. It may serve as a preliminary screening mechanism to identify successful candidates to further expand the scope of hfip transfers.

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The trend in BDE explains quite readily the propensity for the formation of Hhfip or HFP over the course of the reaction. This is especially true in the case of **3b**, where without judicious choice of solvent (e.g., DMF) the desired reaction does not occur, although a balance must be struck between the M−C BDE (**3b** ≪ **3a**) and the desired reactivity. As a bonus **3b** also possesses a greater positive charge at Cu that could be beneficial for reactivity with less activated substrates.

Ongoing work is focused on (a) expanding the range of electrophiles that can undergo substitution with **3b** and (b) exploring conditions for *catalytic* cross-coupling for both **2c** and **3b** or analogues thereof. Preliminary results of the stoichiometric substitution reactions with **3b** are encouraging and indicate an enhanced reactivity of said reagent. Full details of these results will be published in due course.

■ EXPERIMENTAL SECTION

General Procedures. Experiments were conducted under nitrogen, using Schlenk techniques or an MBraun glovebox. All solvents were deoxygenated by purging with nitrogen. Hexanes, diethyl ether (Et_2O), 1,2-dimethoxyethane (DME), and tetrahydrofuran (THF) were dried on columns of activated alumina using a J. C. Meyer (formerly Glass Contour) solvent purification system. Benzene-d_6 (C_6D_6) was dried by stirring over activated alumina (ca. 10 wt %) overnight, followed by filtration. All solvents were stored over activated (heated at ca. 250 °C for >10 h under vacuum) 4 Å molecular sieves, and glassware was oven-dried at 120 °C for >2 h. The following chemicals were obtained commercially, as indicated: silver fluoride (AgF, Alfa, 99%), hexafluoropropene (HFP, Synquest, 99%), triphenylphosphine (PPh_3, Oakwood Chemical, 99%), copper(II) fluoride dihydrate ($CuF_2{\cdot}2H_2O$, Alfa), diphenylzinc ($ZnPh_2$, Strem Chemicals, 99%), all acid chlorides (Sigma-Aldrich, 99%), 4-fluorobenzyl bromide (Oakwood Chemicals, 99%), 4-fluorobenzaldehyde (Oakwood Chemicals, 99%), 3-bromo-1-phenyl-1-propene (cinnamyl bromide, Sigma-Aldrich, 97%), 2,2,6,6-tetramethylpiperidine (Htmp, Sigma-Aldrich, 99%), 1,10-phenanthroline, anhydrous (phen, Alfa, 99%), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos, Accela, 97%), 1,1′-bis(diphenylphosphino)ferrocene (dppf, Accela, 95%), 1,2-bis(dicyclohexylphosphino)ethane (dcpe, Strem, 98%), triethyl phosphite ($P(OEt)_3$, Sigma-Aldrich, 99%), and 2,6-dimethylphenyl isocyanide (XylCN, Sigma-Aldrich, 96%). ^{1}H, ^{19}F, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on a 300 MHz Bruker Avance instrument at room temperature (21−23 °C) unless stated otherwise. ^{1}H NMR spectra were referenced to residual proton peaks associated with the deuterated solvents (C_6D_6: 7.16 ppm). ^{19}F NMR spectra were referenced to internal standard hexafluorobenzene (C_6F_6, Oakwood, 99%), unless stated otherwise, set to −164.5 ppm. ^{13}C{^{1}H} NMR data were referenced to carbon peaks associated with the solvent (C_6D_6, 128.39 ppm; THF, 67.57 ppm). ^{31}P{^{1}H} NMR data were referenced to external H_3PO_4 (85% aqueous solution), set to 0.0 ppm. Electrospray ionization mass spectral data were collected using an Applied Biosystem API2000 triple quadrupole mass spectrometer. UV−vis spectra were recorded on a Cary 100 instrument, using sealable quartz cuvettes (1.0 cm path length). IR data were obtained on a Nicolet Nexus 6700 FT-IR spectrometer. For **3a**, the sample was prepared by allowing a benzene solution of **1** to evaporate on a NaCl plate under a stream of nitrogen. Elemental analyses were performed by Laboratoire d'analyze élémentaire, Université de Montréal (Montreal, Quebec, Canada). Note that the NMR spectra (^{1}H, ^{19}F, ^{19}F{^{1}H}, ^{31}P{^{1}H} and ^{13}C{^{1}H}) for the title compounds are displayed in the Supporting Information.

Synthesis of [(Htmp)Ag(hfip)] (1). AgF (500 mg, 3.94 mmol) was placed in a 100 mL ampule and mixed with 15 mL of THF. Colorless Htmp (612 mg, 4.34 mmol) was then added to the slurry. The reaction vessel was attached via a three-way valve to an HFP canister with a regulator and a Schlenk line. The solution was degassed using a regular freeze/pump/thaw method. The HFP was added to the degassed solution with the regulator set to 5 psi. The reaction mixture was stirred at 25 °C for ∼24 h and wrapped in tin foil. The solid became dark green after a few hours. As the reaction progressed, the solution became progressively clear with a slight silver mirror forming. The solution was filtered through a Celite pad (15 mL medium pore fritted funnel), and the remaining solvent was removed in vacuo to yield a colorless powder. A 10 mL portion of hexanes was added, and the solid was collected (30 mL medium pore fritted funnel), washed with hexanes (4 °C, 3 × 5 mL), and dried in vacuo to yield 1.44 g of **1** (3.55 mmol, 90% based on AgF). The isolated material was stored in a refrigerator under nitrogen in an amber container. ^{1}H NMR (300 MHz, C_6D_6): δ 1.17 (br, 2H, CH_2), 1.06 (m, J_{HH} = 6 Hz, 4H, CH_2), 0.76 (br, 12H, Me). ^{19}F NMR (282 MHz, C_6D_6): δ −68.45 (d, $^3J_{FF}$ = 13 Hz, 6F, CF_3), −68.50 (d, $^3J_{FF}$ = 13 Hz, 6F, CF_3), −211.03 (d "hept", $^3J_{FF}$ = 13 Hz, $^2J_{AgF}$ = 2 Hz, 1F, CF^iPr^F), −211.12 (d "hept", $^3J_{FF}$ = 13 Hz, $^2J_{AgF}$ = 2 Hz, 1F, CF^iPr^F). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 17.3 (Htmp), 32.0 (br, Htmp), 37.3 (Htmp), 54.0 (Htmp), 104.1 ("multiplet", CF^iPr^F), 127.1 (qdqd, $^1J_{CF}$ = 273 Hz, $^2J_{CF=}$ 24 Hz, $^3J_{CF}$ = $^2J_{AgC}$ = 5 Hz). IR: 3262(w), 2948(w, br), 1452(m, br), 1394(s), 1351(s), 1098(w), 932(s), 734(s), 692(s) cm^{-1}. ESI-MS: m/z (%) 562.15 (100), 563.16 (20), 564.15 (95), 566.15 (15) [M^+ − H + 2THF], 142.16 [L^+ − H]. See Figures S2−S4 for ^{1}H, ^{19}F, and ^{13}C{^{1}H} NMR spectra.

Synthesis of [(PyEt)$_2$NiBr(hfip)] (2a). The purple complex [$(PyEt)_2NiBr_2$][59] (1.000 g, 2.31 mmol) was placed in a 100 mL round-bottom flask and mixed with 30 mL of benzene. A 10 mL colorless solution of **1** in benzene (990 mg, 2.37 mmol) was then added to the slurry. The reaction mixture was stirred at 25 °C for 24 h. The solution became progressively pink as the reaction progressed. The deep pink solution with a light yellow precipitate (AgBr) was filtered through a Celite pad (15 mL medium-pore fritted funnel), and the remaining solvent was removed in vacuo to yield a light pink powder. Roughly 5 mL of hexanes was added, and the solid was collected (30 mL medium-pore fritted funnel), washed with hexanes (4 °C, 3 × 5 mL), and dried in vacuo to yield 1.05 g of **2a** (2.00 mmol, 87% based on [$(PyEt)_2NiBr_2$]). The isolated material was stored at room temperature under nitrogen. UV−vis (1.0 mM in THF): λ_{max} (ε) 495 nm (407 M^{-1} cm^{-1}). ^{1}H NMR (300 MHz, C_6D_6): δ 1.38 (t, $^3J_{HH}$ = 7 Hz, 6H, MeEt), 4.56 (br, 2H, CH_2Et), 5.19 (br, 2H, CH_2Et), 6.23 (td, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz, 2H, CHPy), 6.36 (d, $^3J_{HH}$ = 7 Hz, 2H, CHPy), 6.54 (td, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz, 2H, CHPy), 9.37 (br, 2H, CHPy). ^{19}F NMR (282 MHz, C_6D_6): δ −68.24 (br, $CF_3{}^iPr^F$), −68.68 (br, $CF_3{}^iPrF$), −70.11 (br, $CF_3{}^iPr^F$), −204.65 (br, CF^iPr^F). ^{1}H NMR (300 MHz, C_6D_6, 50 °C): δ 1.45 (td, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz, 6H, MeEt), 4.87 (br, 4H, CH_2Et), 6.34 (t "multiplet", $^3J_{HH}$ = 7 Hz, 2H, CHPy), 6.50 (d, $^3J_{HH}$ = 7 Hz, 2H, CHPy), 6.67 (t "multiplet", $^3J_{HH}$ = 7 Hz, 2H, CHPy), 9.49 (br, 2H, CHPy). ^{19}F NMR (282 MHz, C_6D_6, 50 °C): δ −68.56 (br, $CF_3{}^iPr^F$), −206.10 (br, CF^iPr^F). Anal. Calcd for $C_{17}H_{18}BrF_7N_2Ni$: C, 39.12, H, 3.48, N, 5.37. Found: C, 38.37, H, 3.71, N, 5.16. See Figures S5 and S6 for ^{1}H and ^{19}F NMR spectra. See Figures S7 and S8 for ^{1}H and ^{19}F NMR spectra at 50 °C.

In Situ Synthesis of [(PyEt)$_2$Ni(Ph)(hfip)] (2b). The pink complex [$(PyEt)_2NiBr(hfip)$] (20 mg, 0.04 mmol) was placed in a 5 mL round-bottom flask and mixed with 1 mL of THF. A 1 mL colorless solution of Ph_2Zn in THF (9 mg, 0.04 mmol) was then added to the solution, affording a yellow-brown solution after 10 min that was used as is. ^{19}F NMR (282 MHz, C_6D_6): δ −66.70 (br, $CF_3{}^iPr^F$ (**2b′**)), −67.39 ("quint", $^3J_{FF}$ = $^4J_{FF}$ = 9 Hz, $CF_3{}^iPr^F$ (**2b′′**), −68.00 (d, $^3J_{FF}$ = 10 Hz, $CF_3{}^iPr^F$ (**2b′′′**)), −68.01 (br, CF^iPr^F (**2b′**)), −69.14 ("quint", $^3J_{FF}$ = $^4J_{FF}$ = 9 Hz, $CF_3{}^iPr^F$ (**2b′′**)), −197.33 (br, CF^iPr^F (**2b′**)), −214.80 (sept, $^3J_{FF}$ = 9 Hz, CF^iPr^F (**2b′′**)), −215.26 (sept, $^3J_{FF}$ = 10 Hz, CF^iPr^F (**2b′′′**)). See Figure S9 for ^{19}F NMR spectra.

Synthesis of [(dcpe)Ni(Ph)(hfip)] (2c). To a 5 mL solution of complex **2b** in THF (100 mg, 0.19 mmol, vide supra) was added solid dcpe (89 mg, 0.21 mmol). On stirring at 25 °C over 1 h, the solution became progressively lighter yellow with concomitant formation of a black precipitate. The light yellow solution was filtered through a Celite pad (15 mL medium-pore fritted funnel), and the remaining solvent was removed in vacuo to yield a light yellow powder. Roughly 5 mL of acetonitrile was added and the solid was collected (15 mL

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medium-pore fritted funnel), washed with Et_2O (4 °C, 3 × 3 mL), and dried in vacuo to yield 105 mg of **2c** (0.14 mmol, 75% based on $(PyEt)_2NiBr_2$). UV−vis (1.5 mM in THF): λ_{max} (ε) 373 (882), 307 nm (2348 M^{-1} cm^{-1})). ^1H NMR (300 MHz, C_6D_6): δ 7.89 (m, 2H, Ar), 7.05 (m, 2H, Ar), 6.91 (m, 1H, Ar), 2.5−0.5 (overlap, 48H, Cy and CH_2Et). ^{19}F NMR (282 MHz, THF): δ −65.19 (dd, $^4J_{FP}$ = 5 Hz, $^3J_{FF}$ = 13 Hz, $CF_3{}^iPr^F$), −169.28 (dsept, $^4J_{FP}$ = 96 Hz, $^4J_{FF}$ = 13 Hz, CF^iPr^F). $^{13}C\{^1H\}$ NMR (75 MHz, THF): δ 153.1 (dd, $^2J_{PC}$ = 76 Hz, $^2J_{PC}$ = 43 Hz, CαAr), 137.9 (CAr), 124.9 (CAr), 121.1 (CAr), 36.2 ("multiplet", dcpe), 34.5 ("multiplet", dcpe), 29.9−24 (overlap(THF), dcpe), 20.0 ("multiplet", dcpe). $^{31}P\{^1H\}$ NMR (121 MHz, THF): δ 57.81 (dd, $^3J_{PF}$ = 96 Hz, $^2J_{PP}$ = 31 Hz, P-*trans*-hfip), 47.75 (dsept, $^2J_{PP}$ = 31 Hz, $^4J_{PF}$ = 6 Hz, P-*cis*-hfip). Compound **2c** proved to be quite hygroscopic and sensitive to air and moisture. Collection of elemental analysis data returned a value closest to $[(Cy_2PCH_2CH_2P(O)Cy_2)$-$Ni(Ph)(hfip)\cdot 2H_2O]$. Anal. Calcd for $C_{35}H_{57}F_7NiO_3P_2$: C, 53.93; H, 7.37. Found: C, 53.98; H, 7.28. See Figures S10−S13 for ^1H, ^{19}F, $^{13}C\{^1H\}$, and $^{31}P[^1H]$ NMR spectra.

In Situ Synthesis of [(dcpe)NiC(O)Ph(hfip)] (2c′). A J. Young NMR tube containing a 0.6 mL solution of complex **2c** in C_6D_6 or THF (20 mg, 0.028 mmol) was degassed, and CO (1 atm) was added. The tube was heated for 2 h at 50 °C to produce a mixture [6:7:1] of **2c**, **2c′** and **4a** respectively. ^{19}F NMR (282 MHz, C_6D_6): δ −66.24 ("quint", $^3J_{FF}$ = $^4J_{FF}$ = 9 Hz, $CF_3{}^iPr^F$), −67.22 ("quint", $^3J_{FF}$ = $^4J_{FF}$ = 9 Hz, $CF_3{}^iPr^F$), −167.619 (m, $^3J_{FF}$ = $^4J_{FF}$ = 9 Hz, $^3J_{FP}$ = 26 Hz, $^3J_{FP}$ = 120 Hz, CF^iPr^F). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 45.15 (m, $^3J_{FP}$ = 120 Hz), 39.48 (m, $^3J_{FP}$ = 26 Hz). *N.B.: for the reaction to go to completion (yield 90%) 3 atm of CO should be employed.* See Figures S21−S24 for ^{19}F and $^{31}P\{^1H\}$ NMR spectra of the reaction carried out at 1 atm (30% yield).

In Situ Synthesis of [(dppf)Ni(Ph)(hfip)] (2d). In a J. Young NMR tube containing a 0.6 mL solution of complex **2b** in THF (20 mg, 0.04 mmol) was placed solid dppf (21 mg, 0.04 mmol). The solution became deep orange and was used as is. ^{19}F NMR (282 MHz, C_6D_6): δ −65.16 (d, $^3J_{FF}$ = 9 Hz, $CF_3{}^iPr^F$ (2d)), −66.30 ("quint", $^3J_{FF}$ = $^4J_{FF}$ = 9 Hz, $CF_3{}^iPr^F$ (**2d′**)), −67.96 ("quint", $^3J_{FF}$ = $^4J_{FF}$ = 9 Hz, $CF_3{}^iPr^F$ (**2d′**)), −166.99 (br m, $^3J_{FF}$ = $^4J_{FF}$ = 9 Hz, $^3J_{FP}$ = 150 Hz, CF^iPr^F (**2d**)), −200.42 (sext, $^3J_{FP}$ = $^3J_{FF}$ = $^4J_{FF}$ = 9 Hz, CF^iPr^F (**2d′**)). See Figure S14 for ^{19}F NMR spectrum.

Synthesis of $[(PPh_3)_2Cu(hfip)]$ (3a). *Method A.* The colorless complex $[(PPh_3)_3CuF]$ (500 mg, 0.56 mmol) was placed in a 100 mL ampule and mixed with 30 mL of Et_2O. The reaction vessel was attached via a three-way valve to an HFP canister with a regulator and a Schlenk line. The solution was degassed using a regular freeze/pump/thaw method. The HFP was added to the degassed solution with the regulator set to 5 psi. The reaction mixture was stirred at 25 °C for ∼24 h. A colorless precipitate remained over the course of the reaction. The solvent was removed in vacuo, 10 mL of DME was added, and this solution was filtered through a Celite pad (15 mL medium-pore fritted funnel) to remove unreacted Cu−F. The volatiles were removed in vacuo, and roughly 10 mL of hexanes was added. The solid was collected (15 mL medium-pore fritted funnel), triturated with hexanes (3 × 10 mL), and dried in vacuo to yield 391 mg of **3a** (0.52 mmol, 90% based on $(PPh_3)_3CuF$). The isolated material was stored at room temperature under nitrogen.

Method B. The red complex $[(PPh_3)CuH]_6$ (5.23 g, 16 mmol based on monomeric unit) and PPh_3 (5.03 g, 19.2 mmol) were placed in a 1 L Schlenk round-bottom flask and mixed with 100 mL of benzene. The reaction vessel was attached via a three-way valve to an HFP canister with a regulator and a Schlenk line. The solution was degassed using a regular freeze/pump/thaw method. The HFP was added to the degassed solution with the regulator set to 5 psi and the reaction mixture stirred at 25 °C for ∼2 h. The solution became light yellow. The solvent was removed in vacuo, leaving a buff powder. The powder was dissolved in DME (100 mL) and stirred vigorously. The solution was then filtered (15 mL medium pore fritted funnel) and the solvent removed in vacuo. The solid was collected (30 mL medium-pore fritted funnel), triturated with cold Et_2O (−35 °C, 3 × 20 mL), and dried in vacuo to yield 9.81 g of **3a** (12.96 mmol, 81% based on $((PPh_3)CuH)_6)$. IR: 3053(m,br), 1480(m), 1434(s,sh), 1292(w), 1231(w), 1146(w), 1116(w), 1094(w), 741(s,sh), 639(s,sh) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 6.88 (m, 18H, Ar), 7.31 (m, 12H, Ar). ^{19}F NMR (282 MHz, C_6D_6): δ −68.93 (br, $CF_3{}^iPr^F$), −207.98 (br, CF^iPr^F). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ −4.66 (s, PPh_3). Anal. Calcd for $C_{39}H_{30}CuF_7P_2$: C, 61.87, H, 3.99. Found: C, 63.47, H, 4.12. See Figures S15−S17 for ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra.

Synthesis of $(PPh_3)_2$(phen)Cu(hfip) (3b). The colorless complex $[(PPh_3)_2Cu(hfip)]$ (500 mg, 0.66 mmol) was placed in a 20 mL scintillation vial and mixed with 10 mL of Et_2O. Phen (130 mg, 0.73 mmol) was then added slowly while the solution was vigorously stirred. The reaction mixture was stirred for 1 h as it changed from clear to deep orange with a significant amount of orange precipitate. Roughly 10 mL of hexanes was added, and the solid was collected (15 mL medium-pore fritted funnel). The solid was dissolved in 10 mL of DME, the solution was filtered through a Celite-padded frit (15 mL medium-pore fritted funnel), 50 mL of hexanes was added, and the solid was collected, washed with hexanes (3 × 10 mL), and dried in vacuo to yield 356 mg of **3b** (0.53 mmol, 80% based on **3a**). The isolated material was stored at room temperature under nitrogen. A second crop of product could be collected by crystallizing from the remaining solution at −35 °C. UV−vis (1.0 mM in benzene): λ_{max} (ε) 395 nm (1276 M^{-1} cm^{-1}). ^1H NMR (300 MHz, C_6D_6): δ 8.88 (br, 2H, phen), 7.49 (m, 6H, PPh_3), 7.28 (m, 2H, phen), 6.99 (s, 2H, phen), 6.90 (m, 9H, PPh_3), 6.72 (m, 2H, phen). ^{19}F NMR (282 MHz, C_6D_6): δ −67.39 (d, $^3J_{FF}$ = 10 Hz, $CF_3{}^iPr^F$), −209.05 (sept, $^3J_{FF}$ = 10 Hz, CF^iPr^F). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ −4.95 (br, PPh_3). Anal. Calcd for $C_{33}H_{23}CuF_7N_2P$: C, 58.71, H, 3.43, N, 4.15. Found: C, 58.18, H, 3.51, N, 4.15. See Figures S18−S20 for ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra.

Perfluoroisopropylation of Acid Chlorides: General Procedure. The copper complex **3b** (50 mg, 0.07 mmol) was loaded into an NMR tube and mixed with DMF. The benzoyl chloride (*A* mg, 0.05 mmol) was then added to the solution. The reaction was left to sit at room temperature for 24 h. The reaction mixture changed from deep orange-red to light orange with a significant amount of orange precipitate being formed. See Figures S25−S36 for ^{19}F NMR spectra.

*PhC(O)(hfip) (**4a**).* ^{19}F NMR (282 MHz, DMF): δ −73.95 (d, $^3J_{FF}$ = 7 Hz, $CF_3{}^iPrF$), −179.17 (m, $^3J_{FF}$ = 7 Hz, CF^iPr^F). GC-MS (retention time 3.91 min): expected, 274.1; found, 274.1.

*3,4,5-(OMe)$_3$-PhC(O)(hfip) (**4b**).* ^{19}F NMR (282 MHz, DMF): δ −73.93 (d, $^3J_{FF}$ = 7 Hz, $CF_3{}^iPr^F$), −177.79 (m, $^3J_{FF}$ = 7 Hz, CF^iPr^F). GC-MS (retention time 7.11 min): expected, 364.1 (100%); found, 364.1 (100%).

*p-Me-PhC(O)(hfip) (**4c**).* ^{19}F NMR (282 MHz, DMF): δ −74.50 (d, $^3J_{FF}$ = 7 Hz, $CF_3{}^iPr^F$), −179.19 (m, $^3J_{FF}$ = 7 Hz, CF^iPr^F). GC-MS (retention time 4.63 min): expected, 288.1; found, 288.1.

*o-Me-PhC(O)(hfip) (**4d**).* ^{19}F NMR (282 MHz, DMF): δ −74.19 (d, $^3J_{FF}$ = 7 Hz, $CF_3{}^iPr^F$), −177.46 (m, $^3J_{FF}$ = 7 Hz, CF^iPr^F). GC-MS: (rentention time: 4.34 min): expected, 288.1; found, 288.1.

*m-Br-Ph(CO)(hfip) (**4e**).* ^{19}F NMR (282 MHz, DMF): δ −74.50 (d, $^3J_{FF}$ = 7 Hz, $CF_3{}^iPr^F$), −179.85 (m, $^3J_{FF}$ = 7 Hz, CF^iPr^F). GC-MS (retention time 5.16 min): expected, 351.9 (100%), 353.9 (97.3%); found, 351.9 (100%), 353.9 (93%).

*p-F-PhC(O)(hfip) (**4f**).* ^{19}F NMR (282 MHz, DMF): δ −73.99 (d, $^3J_{FF}$ = 7 Hz, $CF_3{}^iPr^F$), −101.26 (m, F−Ar), −178.43 (m, $^3J_{FF}$ = 7 Hz, CF^iPr^F). GC-MS (retention time 3.75 min): expected, 292.0 (100%). Found: 291.9 (100%).

*p-Br-Ph(CO)(hfip) (**4g**).* ^{19}F NMR (282 MHz, DMF): δ −73.97 (d, $^3J_{FF}$ = 8 Hz, $CF_3{}^iPr^F$), −178.90 (d"multiplet", $^3J_{FF}$ = 8 Hz, CF^iPr^F). GC-MS (retention time 5.22 min): expected, 351.9 (100%), 353.9 (97.3%); found, 352.1 (100%), 354.0 (90%).

*p-CN-PhC(O)(hfip) (**4i**).* ^{19}F NMR (282 MHz, DMF): δ −73.9 (d, $^3J_{FF}$ = 7 Hz, $CF_3{}^iPr$), −179.45 (d"multiplet", $^3J_{FF}$ = 7 Hz, CF^iPr^F). GC-MS (retention time 5.30 min). expected, 299.0 (100%); found, 299.1 (100%).

*p-NO$_2$-PhC(O)(hfip) (**4j**).* ^{19}F NMR (282 MHz, DMF): δ −73.87 (d, $^3J_{FF}$ = 7 Hz, $CF_3{}^iPr^F$), −179.30 (m, $^3J_{FF}$ = 7 Hz, CF^iPr^F). GC-MS: N/A.

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*o-NO$_2$-PhC(O)(hfip) (**4k**).* ^{19}F NMR (282 MHz, DMF): δ −73.90 (d, $^3J_{FF}$ = 7 Hz, CF$_3$iPrF), −179.45 (m, $^3J_{FF}$ = 7 Hz, CF^{i}Pr^F). GC-MS: N/A.

*2-Naph(CO)iPrF (**4l**).* ^{19}F NMR (282 MHz, DMF): δ −74.21 (d, $^3J_{FF}$ = 7 Hz, CF$_3$^{i}Pr^F), −176.83 (m, $^3J_{FF}$ = 7 Hz, CF^{i}Pr^F). GC-MS (retention time 6.70 min): expected, 324.0 (100%); found, 324.1 (100%).

*2-Tp(CO)iPrF (**4n**).* ^{19}F NMR (282 MHz, DMF): δ −74.32 (d, $^3J_{FF}$ = 7 Hz, CF$_3$^{i}Pr^F), −179.83 (m, $^3J_{FF}$ = 7 Hz, CF^{i}Pr^F). GC-MS (retention time 4.20 min): expected, 280.1 (100%); found, 280.0 (100%).

*Synthesis of p-F-PhCH$_2$(hfip) (**5a**).* ^{19}F NMR (282 MHz, DMF): δ −75.86 (d, $^3J_{FF}$ = 7 Hz, CF$_3$^{i}Pr^F), −115.91 (m, F−Ar), −182.76 (t sept, $^3J_{FH}$ = 24 Hz, $^3J_{FF}$ = 7 Hz, CF^{i}Pr^F). GC-MS (retention time 3.82 min) expected, 278.0 (100%); found, 278.1 (100%).[36] See Figure S36 for ^{19}F NMR spectra.

*Synthesis of p-F-PhCH(OH)(hfip) (**5b**).* ^{19}F NMR (376.5 MHz, C$_6$D$_6$): −70.40 ("quint", $^3J_{FF}$ = $^4J_{FF}$ = 9 Hz, CF$_3$^{i}Pr^F), −73.23 ("quint", $^3J_{FF}$ = $^4J_{FF}$ = 9 Hz, CF$_3$^{i}Pr^F), −111.51 (m, F−Ar), −179.55 (d sept, $^3J_{FH}$ = 12 Hz, $^3J_{FF}$ = 9 Hz, CF^{i}Pr^F). GC-MS (retention time 5.01 min) expected, 294.0 (100%); found, 294.0 (100%).[37] See Figures S37 and S38 for ^{19}F NMR spectra.

Computational Methods. The geometries were optimized at the density functional theory (DFT)[38] level with the hybrid B3LYP[39,40] with the DFT-optimized DZVP2 basis set[41] for H, N, C, F, and P atoms and aug-cc-pVDZ-PP[42,43] basis sets for M = Ag, Ni, Cu using the Gaussian09 program system.[44] Vibrational frequencies were calculated to show that the structures were minima. The B3LYP/DZVP2/aug-cc-pVDZ-PP(M) geometries were used to predict the NMR chemical shifts for F (^{19}F NMR) and P (^{31}P NMR) in C$_6$H$_6$ using the ADF program system[45,46] with the BLYP[47] functional and the TZ2P basis set in ADF.[48] Scalar relativistic effects were included at the two-component zero-order regular approximation (ZORA) level for the NMR calculations.[49−51] The ^{19}F NMR and ^{31}P NMR chemical shifts are reported relative to their specific standards CFCl$_3$ and H$_3$PO$_4$ calculated at the same level.

Using the gas-phase geometries, the solvation free energies in DMF at 298 K were calculated using the self-consistent reaction field (SCRF) approach[52] with the COSMO parameters[53,54] as implemented in Gaussian 09[44] at the same B3LYP/DZVP2 level of theory using the COSMO radii. The Gibbs free energy in DMF solution, ΔG_{DMF}, was calculated from eq 1.

$$\Delta G_{DMF} = \Delta G_{gas} + \Delta G_{SOLV} \quad (1)$$

where ΔG_{gas} is the gas phase free energy and ΔG_{solv} is the solvation free energy in DMF. A dielectric constant of 37.22 corresponding to that of bulk DMF was used in the COSMO calculations.

The Natural Population Analysis based on the Natural Bond Orbitals (NBOs)[55,56] using NBO6[57,58] with wave functions are calculated at the B3LYP/DZVP2/aug-cc-pVDZ-PP(M) density functional theory level using Gaussian09.

The calculations were performed on a Xeon-based Dell Linux cluster at the University of Alabama, and a local AMD Opteron-based and Intel Xeon-based Linux cluster from Penguin Computing.

■ ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org." The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00837.

Additional crystallographic information, DFT studies, and ^{1}H, ^{19}F, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra. (PDF)
optimized Cartesian coordinates in Å (PDF)

Accession Codes

CCDC 1586727−1586731 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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