Oxidatively Induced Aryl-CF_3 Coupling at Diphosphine Nickel Complexes

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Supporting Information Placeholder

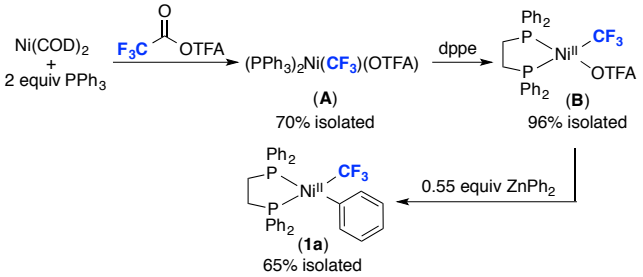
ABSTRACT: This communication describes the synthesis of a series of diphosphine $Ni^{II}(Ph)(CF_3)$ complexes and studies of their reactivity towards oxidatively induced Ph–CF_3 bond-forming reductive elimination. Treatment of these complexes with the one-electron outer-sphere oxidant ferrocenium hexafluorophosphate ($FcPF_6$) affords benzotrifluoride, but the yield varies dramatically as a function of diphosphine ligand. Diphosphines with bite angles of less than 92º afforded <10% yield of $PhCF_3$. In contrast, those with bite angles between 95º and 102º formed $PhCF_3$ in yields ranging from 62 to 77%.

Trifluoromethyl substituents have emerged as increasingly important moieties in pharmaceutical and agricultural chemistry.[1] As such, there has been substantial interest in the development of metal-mediated/catalyzed cross-coupling methods for the introduction of CF_3 groups onto (hetero)aromatic rings.[2] In many of these transformations, aryl–CF_3 bond-forming reductive elimination has been identified as a kinetic bottleneck. Stoichiometric organometallic studies are frequently used to identify metal/ligand combinations and reaction conditions that facilitate this challenging step of the catalytic cycle.[3-7] Despite significant efforts in this area, metal complexes that participate in high yielding aryl–CF_3 bond-forming processes remain relatively rare.[3-7]

Recent work from our group has explored aryl–CF_3 coupling at isolable high valent nickel centers. For instance, we have shown that the tris(pyrazolyl)borate (Tp) complexes $TpNi^{IV}(CF_3)_2(Ph)$[6] and $TpNi^{III}(CF_3)(Ph)$[7] undergo Ph–CF_3 bond-forming reductive elimination under mild conditions. Similarly, van der Vlugt and Klein have recently demonstrated oxidatively induced aryl–CF_3 coupling from a Ni^{II} pincer complex.[8] However, this promising reactivity has not yet been translated to Ni catalysis, largely due to limitations associated with the Tp/pincer ligand scaffolds. While these tridentate ligands are well suited for obtaining isolable high-valent Ni complexes, they limit the open coordination sites available for other steps of most catalytic cycles. Thus, a key objective is to translate these promising examples of high valent Ni-mediated aryl–CF_3 coupling to complexes bearing more catalytically relevant ligands.

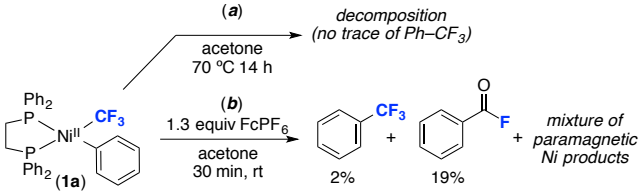
In this communication, we demonstrate that the treatment of Ni^{II} diphosphine (P~P) complexes of general structure $(P\sim P)Ni^{II}(CF_3)(aryl)$ with ferrocenium hexafluorophosphate ($FcPF_6$) leads to aryl–CF_3 coupling at room temperature. A competing unproductive decomposition pathway is identified and mitigated. Furthermore, ligand effects are systematically explored. These studies show that phosphines with bite angles between 95º and 102º afford the highest yields in this transformation.

We initially targeted (dppe)Ni(CF_3)(Ph) (**1a**, dppe = 1,2-bis(diphenylphosphinoethane) due to the widespread use of dppe as a ligand in nickel cross-coupling catalysis.[9] Complex **1a** was synthesized via the route outlined in Scheme 1. The CF_3 ligand was installed by oxidative addition of trifluoroacetic anhydride to *in situ*-generated $Ni^0(PPh_3)_2$. Carbonyl deinsertion afforded intermediate **A**,[10] which underwent ligand substitution with dppe to afford **B**. Finally, transmetalation between **B** and 0.55 equiv of $ZnPh_2$ afforded **1a** in 65% isolated yield.[11] Filtration of a THF solution of **1a** through a plug of basic alumina proved critical to remove Lewis acidic Zn^{II} by-products that can impact the reactivity of this complex. Following recrystallization from THF/pentane, compound **1a** was characterized by ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopy, HRMS, and single crystal X-ray diffraction (*vide infra*).



Scheme 1. Synthetic route to complex **1a**.

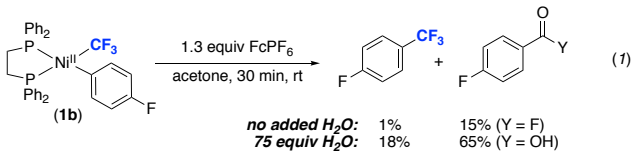
We first evaluated the reactivity of this Ni^{II} complex towards direct Ph–CF_3 coupling (Scheme 2a). Heating a solution of **1a** in acetone at 70 ºC for 14 h resulted in no detectable formation of benzotrifluoride. Instead, **1a** decomposed to generate a complex mixture of paramagnetic products. Importantly, similar observations have been made independently by Vicic[12] and Grushin[13] in studies of other $(P\sim P)Ni^{II}(aryl)(CF_3)$ complexes [P~P = 1,2-bis(diisopropylphosphino)ethane and 4,5-bis(diisopropylphosphino)-9,9-dimethyl xanthene, respectively].



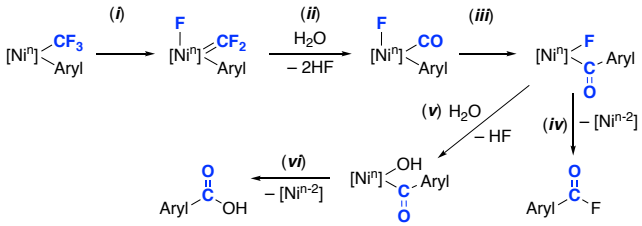
Scheme 2. (a) Thermolysis of Ni^{II} complex **1a** (no Ph–CF_3 coupling). (b) Oxidatively induced Ph–CF_3 coupling from **1a**.

Based on our work with the Ni^{III} model complex $TpNi^{III}(CF_3)(Ph)$, we hypothesized that the one-electron oxidation of **1a** would induce Ph–CF_3 coupling. To guide the selection of an appropriate oxidant, cyclic voltammetry (CV) of **1a** was conducted

in 0.1 M NBu_4PF_6 in MeCN at a scan rate of 100 mV/s. The CV of **1a** under these conditions shows an irreversible oxidation wave with an onset potential of ~ +0.1 V and a peak potential of +0.56 V vs. Fc/Fc^+ (Figure S10a). These results suggest that ferrocenium hexafluorophosphate ($FcPF_6$) should be a suitable oxidant in this system. Indeed, the treatment of **1a** with 1.3 equiv of $FcPF_6$ resulted in complete consumption of the Ni^{II} starting material within 30 min at room temperature.[14] Analysis of the crude reaction mixture by ^{19}F NMR spectroscopy revealed the formation of Ph–CF_3 (2% yield) and PhC(O)F (19% yield), along with a mixture of paramagnetic Ni by-products (Scheme 2b). Attempts to isolate/characterize Ni species from this transformation or to improve the yield of Ph–CF_3 by varying the solvent or temperature proved unsuccessful. Analogous results were obtained with the 4-fluorophenyl analogue **1b**, which reacted with $FcPF_6$ to afford 1% yield of *p*-$FC_6H_4CF_3$ and 15% yield of the corresponding acid fluoride (eq. 1).



Based on literature precedent with closely related (dppe)Pd^{II}(aryl)(CF_3) complexes,[3d,15] we hypothesize that PhCOF is formed via an initial α-fluoride elimination from **1a/b** (Scheme 3, step i). Subsequent reaction of the transient difluorocarbene intermediate with adventitious water would generate a Ni–carbonyl species (step ii), which can then undergo 1,1-migratory insertion (step iii) and reductive elimination to release the acid fluoride (step iv). If this mechanism were operating, the addition of excess H_2O should accelerate the hydrolysis reaction (step ii) and also promote carboxylic acid formation via steps v and vi in Scheme 3. To test this proposal, we added 75 equiv of H_2O to the reaction of **1b** with $FcPF_6$. Under these conditions, 4-fluorobenzoic acid was formed in 65% yield, consistent with the pathway outlined in Scheme 3.[16]

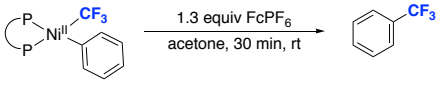


Scheme 3. Proposed pathway to acid fluoride and carboxylic acid products.

We hypothesized that the relative rates of undesired α-fluoride elimination versus the targeted aryl–CF_3 coupling could be modulated by changing the phosphine ligand. Previous studies of reductive elimination reactions from group 10 metal centers have shown that increasing the bite angle of the diphosphine is an effective strategy for accelerating $C(sp^2)$–X coupling.[17] As such, we next evaluated a series of (P~P)Ni^{II}(Ph)(CF_3) complexes, where P~P = diphosphine ligands with varied bite angles. The dppbz (**2,** 1,2-bis(diphenylphosphino)benzene, dppp (**3**, 1,3-bis(diphenylphosphino)propane, dppb (**4**, 1,4-bis(diphenylphosphino)butane), diop (**5**, 2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane), dppf (**6**, 1,1'-bis(diphenyl phosphino)ferrocene, and xantphos (**7**, 4,5-bis(diphenylphosphino)-9,9-dimethyl xanthene) complexes were all synthesized using the procedure outlined in Scheme 1. ^{31}P and ^{19}F NMR spectroscopic analyses of **2-7** show that all but **7** adopt a *cis* geometry in solution.[18]

We next examined the reactions of **2-7** with $FcPF_6$. The dppbz complex **2** did not undergo productive Ph–CF_3 coupling upon treatment with $FcPF_6$. In contrast, complexes with larger bite angle phosphines (**3-7**) all reacted with $FcPF_6$ to afford $PhCF_3$ in yields ranging from 3% (for **7**) to 77% (for **6**).[19,20,21] As summarized in Table 1, ligands with bite angles between 95-102° appear to be optimal for this reaction. In contrast, modest coupling yields are observed for diphosphines with smaller bite angles (between 86° and 92°). Finally, as expected, the *trans* configuration of the xantphos complex **7** results in a low yield of $PhCF_3$.

Table 1. Oxidatively induced Ph–CF_3 coupling as a function of phosphine ligand.[a]



compound	ligand	calculated bite angle [b]	yield Ph-CF_3[a]
2	dppbz	86.0°	<1%[c]
1a	dppe	87.7° (86.8°)	2%
3	dppp	91.9°	7%
4	dppb	95.3°	75%[d]
5	diop	102°	62%
6	dppf	100.6° (100.2°)	77%
7	xantphos	trans	3%

[a]Yields determined by ^{19}F NMR spectroscopy relative to 4,4'-difluorobiphenyl. [b]Bite angles determined by DFT (see Supporting Information, p. S31–S43). Experimental bite angles from X-ray crystal structures are shown in parentheses. [c]Reaction performed in 2:5 benzene:acetone due to the low solubility of **2** in acetone. [d]Due to the low stability of **4**, this complex was generated and then reacted with $FcPF_6$ *in situ*.

A final set of studies focused on a detailed comparison of complex **1a** (which affords <5% yield in the oxidatively induced $PhCF_3$ coupling) with complex **6** (which affords the highest yield of 77%). First, X-ray crystal structures of both **1a** and **6** were obtained, and the respective ORTEP diagrams are shown in Figure 1. These structures reflect the anticipated increase in phosphine bite angle upon moving from dppe (86.8°) to dppf (100.2°). This is accompanied by an increase in the acuteness of the C(1)-Ni-C(2) angle from 89.6° in **1a** to 83.2° in **6**. Literature studies have shown that this angle has a major impact on the rates of other reductive elimination reactions.[17] With the larger bite angle phosphine, both the Ni–CF_3 and Ni–P bond distances are significantly longer (by ~0.03 and ~0.05 Å, respectively), likely reflecting increased steric congestion at the Ni center with dppf relative to dppe.[22] In contrast, the Ni–Ph bond distance is identical in the two complexes (Ni–C(1) = 1.918 Å).

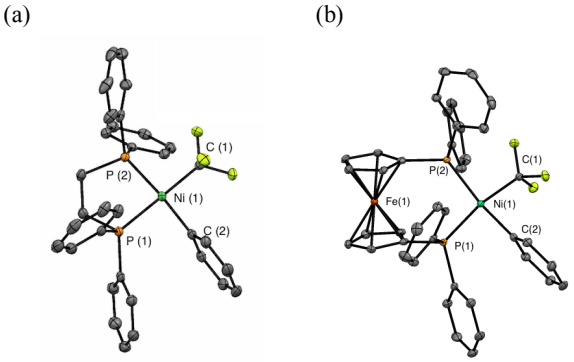


Figure 1. (a) ORTEP diagram of **1a**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent molecules omitted for clarity. Selected bond lengths C(1)–Ni 1.930(2), C(2)–Ni 1.918(2), P(1)–Ni 2.1633(6), P(2)–Ni 2.1963(6) and angles C(1)–Ni–C(2) 89.6. (b) ORTEP diagram of **6**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent molecules omitted for clarity. Selected bond lengths C(1)–Ni 1.963(3), C(2)–

Ni 1.918(3), P(1)–Ni 2.2192(7), P(2)–Ni 2.243(7) and angles C(1)–Ni–C(2) 83.2.

The electronic properties of **1-6** can also be compared. As shown in Table 2, the CO stretching frequencies of the zero-valent dicarbonyl complexes (P~P)Ni(CO)$_2$ show no clear trends with respect to the yield of $PhCF_3$ from the analogous (P~P)Ni(CF_3)(Ph) species.[23] For example, the dicarbonyl analogs of compounds **2**, **3**, and **4** have nearly identical CO stretching frequencies, but only **4** affords high yield of $PhCF_3$ upon treatment with $FcPF_6$. In addition, cyclic voltammetry (CV) was conducted with compounds **1** and **6** in 0.1 M NBu_4PF_6 in MeCN at a scan rate of 100 mV/s.[24] Both CVs show irreversible oxidation waves, with nearly identical onset potentials (at ~ +0.1 V) and similar peak potentials (+0.56 V for **1a** and +0.35 V for **6**). Furthermore, DFT calculations[25] on **6**$^+$, the product of single electron oxidation of **6**, show that the unpaired electron is localized on nickel. This suggests that the redox chemistry occurs at the Ni center rather than at Fe. Taken together, these data strongly suggest that the difference in $PhCF_3$ yield between these complexes results from steric rather than electronic differences between the different diphosphine ligands.

Table 2. Comparison of CO stretching frequencies of [(P~P)Ni(CO)$_2$ and yields of $PhCF_3$ coupling from [(P~P)Ni(CF_3)(Ph)].

compound	ligand	ν_{sym} , ν_{asym} (cm^{-1}) [23]	yield Ph-CF_3[c]
1	dppbz	2007, 1952[a]	<1%[c]
2	dppe	2004, 1945[a]	2%
3	dppp	2000, 1941[a]	7%
4	dppb	2002, 1944[a]	75%[d]
6	dppf	2001, 1939[b]	77%

[a] IR spectrum collected in benzene. [b] IR spectrum collected in CH_2Cl_2. [c] ^{19}F NMR yield from standard conditions.

In summary, this work shows that (P~P)Ni^{II}(CF_3)(Ph) complexes react with $FcPF_6$ to afford Ph–CF_3 coupling under mild conditions. α-Fluoride elimination from the Ni–CF_3 complex is a competing side reaction in these systems. The highest yields are obtained with P~P ligands that have bite angles close to 100º, such as dppf, diop, and dppb. The ligand effects elucidated herein could ultimately inform the development of Ni$^{I/III}$-catalyzed trifluoromethylation reactions.

ASSOCIATED CONTENT

Supporting Information. Experimental and spectral details for all new compounds and all reactions reported. 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 interests.

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(19) Trifluoromethyl Ni(III) complexes have been previously reported to undergo Ni-CF_3 homolysis at room temperature see: Zhang, C. P.; Wang, H.; Klein, A.; Biewer, C.; Stirnat, K.; Yamaguchi, Y.; Xu, L.; Gomez-Benitez, V.; Vicic, D. A five-coordinate nickel(II) fluoroalkyl complex as a precursor to a spectroscopically detectable Ni(III) species. *J. Am. Chem. Soc.* **2013**, 135, 8141–8144. However, radical scavenging experiments with TEMPO are inconsistent with the intermediacy of F_3C• in the present system. See Supporting Information for details.
(20) The analogous reaction of (dppf)Ni(CF_3)(4-FC_6H_4) (**6b**) with $FcPF_6$ afforded 1-CF_3-4-F-C_6H_4 in 72% yield, and no Ph–CF_3 was detected. Furthermore, the addition of 75 equiv of H_2O to this ttransformation had minimal impact on the yield of 1-CF_3-4-F-C_6H_4. Collectively, these results show (i) that the Ph groups of the phosphine ligands are not involved in this reaction and (ii) that carbene intermediates are unlikely. See Supporting Information for complete details.
(21) The remaining mass balance is currently unclear. Attempts to characterize the fate of the organic fragments were unsuccessful. Addition of excess LiCl to the crude reaction mixture following oxidation yielded a paramagnetic NMR spectrum consistent with (dppf)$NiCl_2$ as the primary nickel-containing product. See p. S30 for details.
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(24) Attempts to characterize **4** and **7** by CV were unsuccessful due to their instability under the CV conditions.
(25) Gaussian 09 was used at the M06 level for geometry optimization with acetone as solvent utilizing the SDD basis set on nickel/iron and the 6-31G(d) basis set for other atoms. See the Supporting Information for full details.

TOC Figure