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Influence of the Transmetalating Agent in Difficult Coupling Reactions: Control in the Selectivity of C−F Bond Activation by Ni(0) Complexes in the Presence of $AlMe_3$

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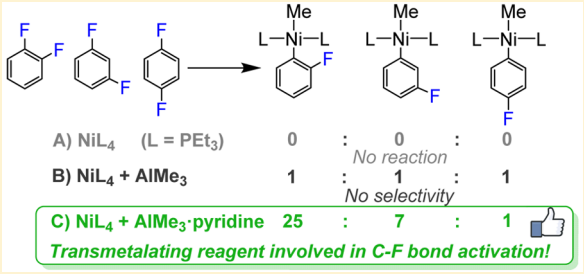
Supporting Information

ABSTRACT: Although $Ni(PEt_3)_4$ does not react with di- or trifluoroarenes at room temperature, upon the addition of aluminum hydrocarbons such as $AlMe_3$ an immediate reaction occurs, to give $AlMe_2F$ and Ni(II) complexes from C−F bond activation and transmetalation. The influence of additional Lewis basic compounds, such as pyridine, on selectivity in these systems provides insight into how selectivity in a cross-coupling reaction is controlled by the transmetalating agent and how the oxidative addition and transmetalation steps are not necessarily distinct.



INTRODUCTION

Fluorinated organics have unique properties which have led to their use in a wide variety of applications. Examples include pharmaceuticals,[1] Lewis acid catalysts,[2] and materials applications such as n-type semiconductors.[3] The low cost and availability of simple partially fluorinated arene precursors, such as the di-, tri-, and tetrafluorobenzenes, renders these as attractive starting materials to partially fluorinated organics. A combination of both C−H and C−F activation could provide a versatile synthetic pathway to convert these substrates to complex organics with a wide array of fluorination patterns; however, their use mandates the development of selectivity in these difficult bond activation reactions.[4]

The continued interest in the use of nickel in C−H and C−F catalytic functionalization stems from the availability and low cost of nickel relative to its heavier congeners, which are more commonly used in catalysis.[5] The ability of Ni to facilitate C−F bond oxidative addition was first described in a 1977 report which showed that $Ni(PEt_3)_4$ undergoes the oxidative addition of C_6F_6 to yield *trans*-$(Et_3P)_2NiF(C_6F_5)$.[6] In general, the ability of substrates to undergo C−F bond oxidative addition with $Ni(PEt_3)_4$ mirrors their propensity to react with nucleophiles.[6] Whereas C_6F_6 reacts slowly with $Ni(PEt_3)_4$ under ambient conditions, the more electrophilic nitrogen-containing substrate pentafluoropyridine reacts rapidly.[7] With less electrophilic substrates such as pentafluorobenzene, slightly more reactive sources of the $(Et_3P)_2Ni$ moiety such as $(Et_3P)_2Ni(\eta^2\text{-}C_{14}H_{10})$ are required for a clean conversion.[8] In contrast to these electrophilic substrates, the di- and trifluorobenzenes do not undergo C−F activation at any appreciable rate with sources of the $(Et_3P)_2Ni$ moiety. The activation of less activated arenes such as the tetra-, tri-, and difluorobenzenes has required the use of more electron rich donors, such as N-heterocyclic carbenes,[9] or electron-rich nitrogen donors.[10]

Cross-coupling of C−F bonds using Ni catalysts has seen considerable recent progress.[4d,11] Although cross-coupling involving fluorobenzene was demonstrated by Kumada as early as 1972,[12] yields and selectivity were poor. A 2001 report showed that N-heterocyclic carbene complexes of Ni act as catalysts for C−F functionalization of fluorobenzene and supported the hypothesis that a requirement for the activation of C−F bonds in weakly electrophilic substrates was the use of a highly electron rich metal center;[11g] however, since then numerous examples of Ni-catalyzed C−F bond cross-coupling reactions have emerged that feature only modestly electron donating ligands, with diphenylphosphines[13] and even triphenylphosphine[11a] utilized as the supporting ligands. These ligands are not featured in the stoichiometric oxidative addition chemistry of Ni with C−F bonds, raising questions as to the exact nature of the C−F bond cleavage step. The mechanism of C−F cleavage has been controversial even in stoichiometric oxidative addition transformations, with experimental evidence supporting traditional concerted and radical mechanisms for different substrates, whereas phosphine-assisted mechanisms have been proposed from a computational study.[7a,b]

The catalytic functionalization of di-, tri-, and tetrafluorobenzenes presents problems beyond that of the facile, but poorly understood, C−F cross-coupling of hexa- and pentafluorobenzenes. Most attempts at using di- and trifluorobenzenes as substrates yield a mixture of products from the unselective substitution of the multiple C−F bonds, thus yielding undesired di- and trisubstitution products.[9,11d,d,14] The di- and trisubstitution products have been attributed to π-bound intermediates after the C−C bond forming reduction

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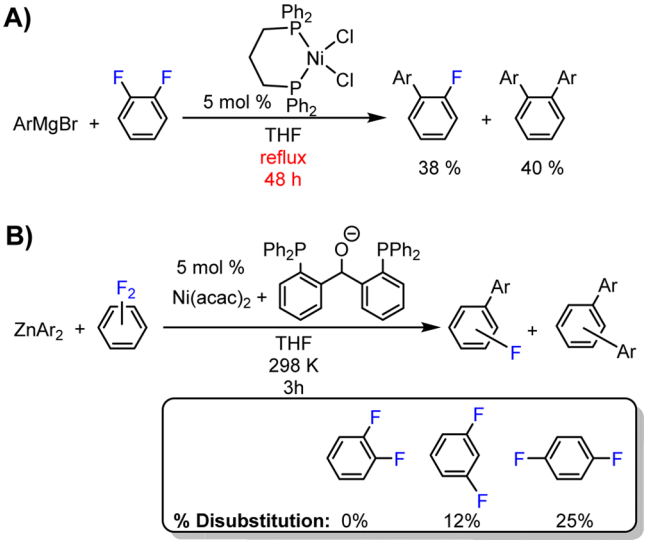
elimination step. These π-bound intermediates are capable of ring whizzing[8,15] and successive C−F bond activations and functionalizations of the substrate. An example of cross-coupling with 1,2-difluorobenzene is shown in Scheme 1; the reaction yields as much disubstituted product as monosubstituted product.[11b]

Scheme 1. (A) Example of C−F Bond Activation of 1,2-Difluorobenzene and (B) Mono- vs Disubstitution of the Difluorobenzenes Using a More Selective Catalytic System[13]



A solution to this problem is the introduction of directing groups, although this requires functionalized substrates and limits the range of fluorination patterns accessible.[4c,11a,c] Very recently ligand designs involving chelating phosphines and pendant alkoxide donors have emerged that are capable of monofunctionalization of substrates such as the di- and trifluorobenzenes, as shown in Scheme 1B.[13,14b] These systems have been suggested to work by the binding of the transmetalating agent to the oxygen donor. Despite this breakthrough, very little is known about the fundamental mechanistic issues involved in the design of successful catalytic systems for the functionalization of partially fluorinated aromatics. Even in the more selective system shown in Scheme 1B, varying amounts of disubstitution are observed, depending upon the substrate.

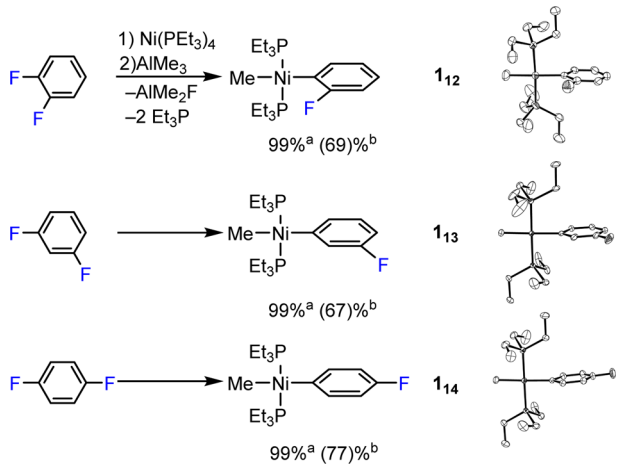
This paper describes a system that provides a significant acceleration of the C−F activation step by using a Lewis acidic Al-based transmetalating agent. This system provides fundamental mechanistic insight into the key issues that need to be addressed to advance the design of catalysts for the selective mono-functionalization of polyfluoroarenes.

RESULTS AND DISCUSSION

The attempted reaction of $Ni(PEt_3)_4$ with the di- and trifluorobenzenes at room temperature does not provide conversion to C−F bond activation products, unlike the reactions with highly electron deficient substrates such as hexafluorobenzene and pentafluoropyridine.[6,7,15a] The addition of the Lewis acids DIBAL, Ph_3B, Ph_2Zn, $SnCl_2$, and $FeCl_2$ failed to facilitate activation. This is in contrast to fluoroalkene substrates such as tetrafluoroethylene[5b] and hexafluoropropene,[4d] which have been reported to form nickel diphosphine adducts that undergo C−F activation after the addition of Lewis acids as weak as LiI.[16,17]

The addition of 1 equiv of $AlMe_3$ to solutions of $Ni(PEt_3)_4$ and 1,2-, 1,3-, or 1,4-difluorobenzene caused an immediate color change from purple to yellow. Analysis of each crude reaction mixture by ^1H, $^{31}P\{^1H\}$, ^{19}F, and $^{13}C\{^1H\}$ NMR confirmed instantaneous complete conversion of the reagents to the three isomers of *trans*-$(Et_3P)_2Ni(C_6FH_4)(Me)$ ($\mathbf{1}_{12,13,14}$), as shown in Scheme 2. The production of $AlMe_2F$ was confirmed from ^1H and ^{19}F NMR spectra.[18]

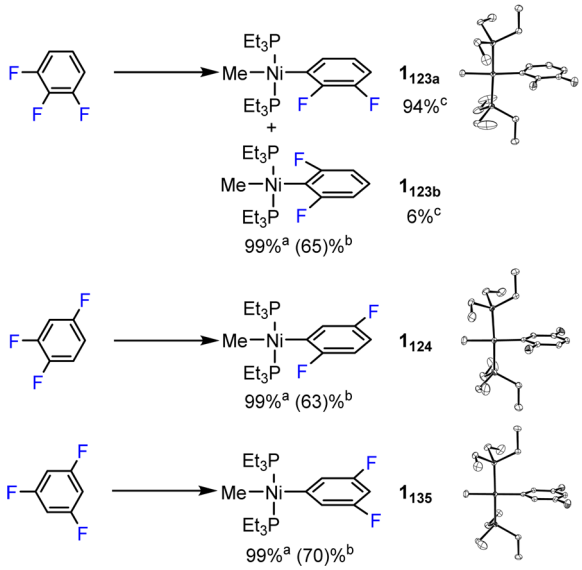
Scheme 2. Activation of the Difluorobenzenes by $Ni(PEt_3)_4$ in the Presence of $AlMe_3$



[a]Percent yield based on ^{19}F NMR spectra. [b]Isolated yield.

Similarly to the difluorobenzenes, the reaction of the trifluorobenzenes with $Ni(PEt_3)_4$ and $AlMe_3$ reacted to give isomers of *trans*-$(Et_3P)_2Ni(C_6F_2H_3)$ (Me) ($\mathbf{1}_{123a,123b,124,135}$), as shown in Scheme 3. The activation of 1,2,3-trifluorobenzene proceeded with good regioselectivity; the ^{19}F NMR spectra of

Scheme 3. Activation of the Trifluorobenzenes by $Ni(PEt_3)_4$ in the Presence of $AlMe_3$



[a]Percent yield based on ^{19}F NMR spectra. [b]Isolated yield. [c]Selectivity between 1-site and 2-site activation.

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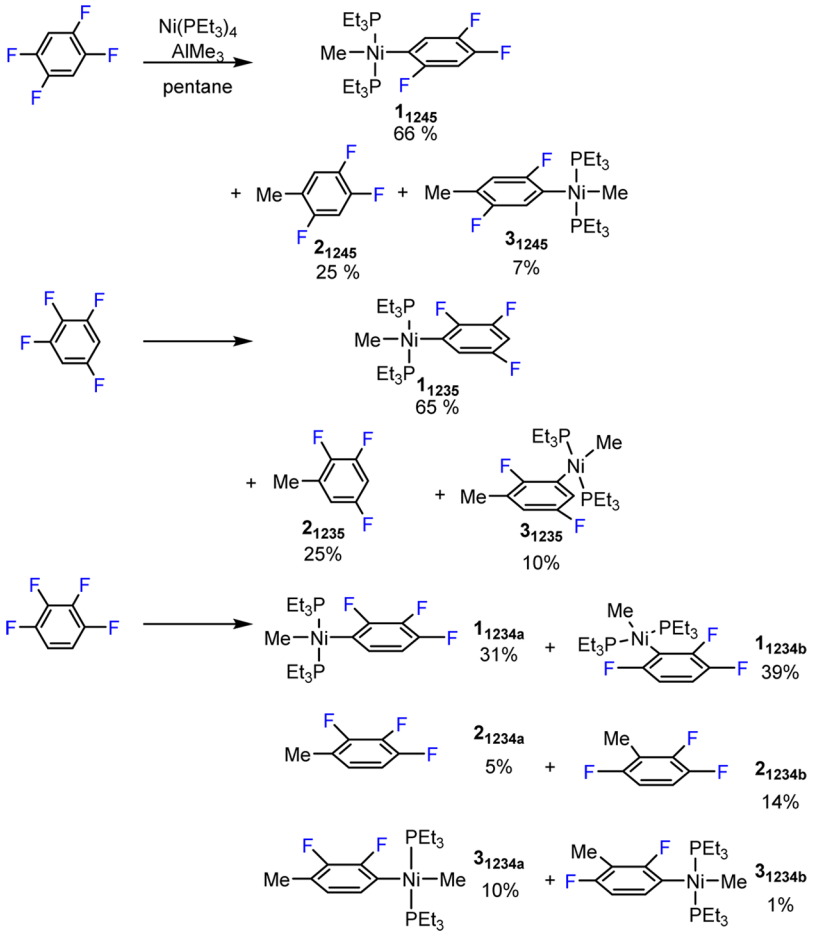
Scheme 4. Activation of the Tetrafluorobenzenes by $Ni(PEt_3)_4$ in the Presence of $AlMe_3$



the reaction mixtures showed a 94:6 mix of $\mathbf{1}_{123a}$ from activation at the 1-site and the isomer $\mathbf{1}_{123b}$ from activation at the 2-site, the latter of which could not be isolated. The assignment of $\mathbf{1}_{123b}$ is based on its NMR spectra, which features a ^{19}F shift similar to that observed in the C−F bond oxidative addition of 1,2,3-trifluorobenzene by a Ni carbene complex.[9] The carbene complex was reported to be slightly less selective, with an 85:15 conversion to C−F activation products at the 1- and 2-sites.[9] The activation of 1,2,4-tetrafluorobenzene with $Ni(PEt_3)_4$ and $AlMe_3$ occurred at the 2-site selectively to give $\mathbf{1}_{124}$, and 1,3,5-trifluorobenzene reacted to give $\mathbf{1}_{135}$, as shown in Scheme 3.

The difluorobenzene activation products $\mathbf{1}_{12,13,14}$ and trifluorobenzene activation products $\mathbf{1}_{123a,124,135}$ were isolated by crystallization from pentane after removal of the $AlMe_2F$ byproduct by filtration through silica. The modest isolated yields after recrystallization from pentane (63−77%) reflect the high solubility of these compounds, not the selectivity of the reactions; the NMR spectra of the crude reaction mixtures indicate quantitative conversion.

The activation of the more reactive tetrafluorobenzenes by $Ni(PEt_3)_4$ in the presence of $AlMe_3$ produced the compounds $\mathbf{1}_{1245,1235,1234a,1234b}$, but in modest NMR yields. The activation of 1,2,3,4-tetrafluorobenzene occurred with little selectivity, with activation at the 1-site vs 2-site producing $\mathbf{1}_{1234a}$ and $\mathbf{1}_{1234b}$ in a 46:54 ratio. Isolation of the tetrafluorobenzene activation products was complicated by the presence of significant impurities. These impurities were assigned by ^{19}F NMR spectroscopy to be the reductive elimination products $\mathbf{2}_{1245,1235,1234a,1234b}$, as well as the second C−F bond activation products $\mathbf{3}_{1245,1235,1234a,1234b}$, as shown in Scheme 4. The second activation products $\mathbf{3}_{1245,1235,1234a,1234b}$ were observed even in the presence of excess tetrafluorobenzene, suggesting that these products arise from reductive elimination from $\mathbf{1}_{1245,1235,1234a,1234b}$ rapid ring whizzing, and a second C−F bond activation. Reaction conditions that provide better yields of $\mathbf{1}_{1245,1235,1234a,1234b}$, without contamination by the second activation byproducts, are discussed later using alternate conditions.

Select ^{19}F, $^{31}P\{^1H\}$, ^1H, and ^{31}P NMR parameters for $\mathbf{1}_{12,13,14}$, $\mathbf{1}_{123a,123b,124,135}$, and $\mathbf{1}_{1245,1235,1234a,1234b}$ are provided in Table 1. The ^{19}F NMR shifts associated with the aryl substituents are similar to those of the structurally related C−F activation products.[5a] The ^1H NMR gives a triplet for the Ni−Me substituent in the range of δ −0.9 to −0.6, with a $^3J_{PH}$ coupling of about 9.0 Hz. Complexes $\mathbf{1}_{13}$, $\mathbf{1}_{14}$, and $\mathbf{2}_{135}$, which lack *o*-F substituents, feature $^{13}C\{^1H\}$ NMR shifts for the Ni−CH_3 group from δ −10.4 to −10.6, whereas the remaining complexes feature shifts from δ −9.8 to −9.9. The $^{31}P\{^1H\}$ NMR shifts for the species without *o*-F substituents are all near δ 18.8, whereas complexes with *o*-F substituents feature shifts from δ 19.6 to 20.2.

Single crystals suitable for characterization by X-ray crystallography were obtained for all the products except the minor regioisomer $\mathbf{1}_{123b}$ and the mixture of isomers $\mathbf{1}_{1234a,1234b}$. All featured nearly square planar geometries at the Ni center

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Table 1. Summary of NMR Data (ppm) for C−F Bond Activation Products $\mathbf{1}_{12,13,14,123a,123b,124,135,1234a,1234b,1245,1235}$

	^{19}F	^{31}P{^{1}H}	^{1}H Ni−CH_3	^{13}C{^{1}H} Ni−CH_3
$\mathbf{1}_{12}$	−88.4 (s)	19.7 (s)	−0.65 (t, $^3J_{PH}$ = 9.0 Hz)	−9.9 (t of d, $^2J_{PC}$ = 24.4 Hz, $^4J_{CF}$ = 3.7 Hz)
$\mathbf{1}_{13}$	−117.9 (m)	18.8 (d, $^5J_{PF}$ = 1.8 Hz)	−0.80 (t, $^3J_{PH}$ = 8.5 Hz)	−10.5 (t, $^2J_{PC}$ = 23.5 Hz)
$\mathbf{1}_{14}$	−126.5 (t, $^6J_{PF}$ = 2.8 Hz)	18.8 (d, $^6J_{PF}$ = 2.8 Hz)	−0.79 (t, $^3J_{PH}$ = 8.5 Hz)	−10.6 (t, $^2J_{PC}$ = 22.6 Hz)
$\mathbf{1}_{123a}$	−142.1 (d of t, $^3J_{FF}$ = 36.2 Hz, $^4J_{FP}$ 2.4 Hz), −115.9 (d, $^3J_{FF}$ = 36.2)	19.8(s)	−0.68 (t, $^3J_{PH}$ = 9.0 Hz)	−9.8 (t, $^2J_{PC}$ = 24.3 Hz)
$\mathbf{1}_{123b}$	−87.5 (s)	19.7 (s)	−0.56 (t, $^3J_{PH}$ = 9.5 Hz)	
$\mathbf{1}_{124}$	−97.1 (d, $^4J_{FF}$ = 21.6 Hz), −124.7 (d, $^4J_{FF}$ = 21.6 Hz)	19.6 (s)	−0.70 (t, $^3J_{PH}$ = 9.5 Hz)	−9.9 (t of d, $^2J_{PC}$ = 24.3 Hz, $^4J_{FC}$ = 3.6 Hz)
$\mathbf{1}_{135}$	−116.8 (s)	18.8 (s)	−0.85 (t, $^3J_{PH}$ = 9.0 Hz)	−10.4 (t, $^3J_{PC}$ = 23.8 Hz)
$\mathbf{1}_{1235}$	−120.9 (d of d of d, $^3J_{FF}$ = 35.8 Hz, $^4J_{FF}$ = 19.6 Hz, $^5J_{FH}$ = 6.2 Hz), −121.2 (overlapping d of t, $^4J_{FF}$ = 20.3 Hz, $^5J_{FF}$ = 7.7 Hz), −138.2 (d of d, $^3J_{FF}$ = 35.8 Hz, $^3J_{FH}$ = 10.4 Hz)	19.6 (d of d of d, $^4J_{PF}$ = 1.6 Hz, $^5J_{PF}$ = 1.6 Hz, $^6J_{PF}$ = 1.6 Hz)	−0.68 (t, $^3J_{HP}$ = 9.0 Hz)	−9.6 (t) $^3J_{CP}$ = 24.3 Hz
$\mathbf{1}_{1245}$	−93.2 (d, $^4J_{FF}$ = 18.1 Hz), −146.9 Hz (m), −148.7 Hz (m)	19.8 (s)	−0.69 (t, $^3J_{HP}$ = 9.0 Hz)	−10.0 (d of t, $^4J_{CF}$ = 3.0 Hz, $^3J_{CP}$ = 24.9 Hz)
$\mathbf{1}_{1234(a)}$	−113.0 (d, $^3J_{FF}$ = 35.7 Hz), −147.9 (overlapping d of d of d of d, $^3J_{FF}$ = 18.7 Hz, $^3J_{FH}$ = 6.9 Hz, $^4J_{FF}$ = 3.2 Hz, $^4J_{FH}$ = 3.2 Hz), −165.7 (d of d, $^3J_{FF}$ = 18.7 Hz, $^3J_{FF}$ = 35.7 Hz)	19.7 (s)	−0.69 (t, $^3J_{HP}$ = 9.0 Hz)	
$\mathbf{1}_{1234(b)}$	−93.1 (d, $^3J_{FF}$ = 18.7 Hz), −111.5 (d, $^3J_{FF}$ = 33.6 Hz), −146.3 (d of d, $^3J_{FF}$ = 18.7 Hz, $^3J_{FF}$ = 33.6 Hz)	20.1 (s)	−0.56 (t, $^3J_{HP}$ = 9.0 Hz)	

with trans-disposed phosphines. Crystallographic details are provided in Table 2 and in the Supporting Information.

Second Activation Products from Ring Whizzing. The mechanism by which $AlMe_3$ promotes C−F bond activation at room temperature is of interest both for fundamental reasons and for the development of new C−F coupling reactions under mild conditions. The addition of varying concentrations of $AlMe_3$ to 1,4-difluorobenzene in the absence of $Ni(PEt_3)_4$ yielded no notable change in the ^{19}F NMR spectrum, suggestive of a negligible Lewis acid/Lewis base interaction between the two reagents. Additionally, this mixture did not undergo reaction without the addition of $Ni(PEt_3)_4$. The addition of $AlMe_3$ to $Ni(PEt_3)_4$ in the absence of a fluorinated substrate led to rapid decomposition at room temperature, with the elimination of a black powder and free PEt_3. This mixture did not react with added 1,4-difluorobenzene. These experiments cannot rule out two different mechanistic paradigms: the first where $AlMe_3$ and $Ni(PEt_3)_4$ react to create an unstable metal complex capable of rapid C−F activation, and the second more traditional mechanism where an equilibrium π adduct[8,15a] of the type $(Et_3P)_2Ni(\eta^2\text{-}C_6H_4F_2)$ interacts with $AlMe_3$ to undergo oxidative addition and transmetalation, albeit perhaps in a single step rather than the more traditional two-step mechanism commonly proposed for these reaction steps.

Attempts to perform the reaction between 1,4-difluorobenzene and $AlMe_3$ in the presence of catalytic $Ni(PEt_3)_4$ provides some insight and supports π-bound complexes as intermediates in these C−F bond activations. For example, if the reaction mixture of 1,4-difluorobenzene with $Ni(PEt_3)_4$ and $AlMe_3$ that generates $\mathbf{1}_{14}$ is not immediately filtered through alumina to remove $AlMe_2F$ or any residual $AlMe_3$, the reaction continues to produce *trans*-$(Et_3P)_2Ni(4\text{-}MeC_6H_4)(Me)$ ($\mathbf{3}_{14}$). The reductive elimination from $\mathbf{1}_{14}$ most likely produces the π-bound intermediate $(Et_3P)_2Ni(\eta^2\text{-}C_6H_4F\text{-}4\text{-}Me)$ ($\mathbf{4}_{14}$), which then undergoes ring whizzing and a rapid second C−F activation prior to the dissociation of 4-fluorotoluene ($\mathbf{2}_{14}$). This is suggested by the fact that $\mathbf{3}_{14}$ accumulates prior to the observation of a significant amount of 4-fluorotoluene ($\mathbf{2}_{14}$) in solution, and $\mathbf{3}_{14}$ is produced even in the presence of an excess of 1,4-difluorobenzene. Attempts to isolate $\mathbf{3}_{14}$ have failed due to its conversion of *p*-xylene via reductive elimination at a rate comparable to the rate of its production; thus, its characterization is based on its ^{1}H and ^{31}P{^{1}H} NMR spectrum and the absence of a ^{19}F resonance for this species. Second activation compounds ($\mathbf{3}$) were observed for all the di-, tri-, and tetrafluorobenzene substrates studied (Scheme 5), and ^{1}H and ^{19}F NMR parameters for these species are as given in Tables 3 and 4.

Di- vs Trifluorobenzene Competition. The clean and rapid C−F activation of the di- and trifluorobenzenes in the presence of $AlMe_3$ and $Ni(PEt_3)_4$ allows for a variety of studies to be performed to gain a better understanding of what factors are important for catalytic monofunctionalization of polyfluorinated arenes. In general, the faster a polyfluorinated aromatic undergoes nucleophilic aromatic substitution, the more reactive it is to C−F bond oxidative addition; the order of reactivity is expected to be $C_6F_6 > C_6F_5H > C_6F_4H_2 > C_6F_3H_3 > C_6F_2H_4 > C_6FH_5$ with Ni(0) complexes.[5a] Thus, it might be expected that, in the catalytic functionalization of perfluorinated arenes, di- or trisubstitution products should arise only from ring whizzing, and not from competition between the substrate and monofunctionalized products after dissociation from the metal center. We tested this assumption under stoichiometric

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Table 2. Crystallographic Data for Compounds $1_{12,13,14,123a,124,135,1235,1245}$

	1_{12}	1_{13}	1_{14}	1_{123a}	1_{124}	1_{135}
formula	$C_{19}H_{37}FNiP_2$	$C_{19}H_{37}FNiP_2$	$C_{19}H_{37}FNiP_2$	$C_{19}H_{36}F_2NiP_2$	$C_{19}H_{36}F_2NiP_2$	$C_{19}H_{36}F_2NiP_2$
fw	405.13	405.13	405.14	423.13	423.13	423.13
cryst size (mm^3)	0.21 × 0.18 × 0.16	0.25 × 0.21 × 0.15	0.45 × 0.40 × 0.24	0.36 × 0.2 × 0.14	*0.38 × 0.35 × 0.15*	0.38 × 0.35 × 0.15
color	yellow	yellow	yellow	yellow	yellow	yellow
cryst syst	triclinic	triclinic	triclinic	orthorhombic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$Pna2_1$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.9294(5)	8.8535(4)	8.7209(4)	23.868(2)	9.0188(5)	12.4069(5)
b (Å)	9.0260(5)	9.1739(4)	9.1999(5)	8.7008(7)	9.0954(5)	13.6769(6)
c (Å)	15.6529(8)	14.9537(7)	14.9603(7)	10.7163(9)	15.6547(8)	14.8874(6)
α (deg)	104.318(2)	95.4440(10)	96.243(2)	90	105.4480(10)	107.1400(10)
β (deg)	95.468(2)	97.7340(10)	96.832(2)	90	95.214(2)	110.7570(10)
γ (deg)	112.444(2)	111.0600(10)	111.361(2)	90	112.3410(10)	90.2580(10)
V ($Å^3$)	1104.15(11)	1109.56(9)	1094.78(9)	2225.5(3)	1117.95(10)	2239.99(16)
Z	2	2	2	4	2	4
ρ_{calcd} (g cm^{-3})	1.219	1.213	1.229	1.263	1.257	1.255
μ (mm^{-1})	1.029	1.024	1.038	1.031	1.026	1.024
F(000)	436	436	436	904	452	904
θ range (deg)	2.95−30.00	3.04−38.49	2.97−35.00	3.02−30.00	2.92−34.998	2.93/33.26
θ comp (deg)	99.7	99.9	99.6	99.9	99.9	99.9
no. of rflns collected	26804	72918	59543	19024	52494	132123
R(int)	0.0745	0.0507	0.0315	0.0341	0.0392	0.0548
no. of data/restraints/params	6424/0/215	11686/0/225	9621/0/215	6421/1/225	9858/18/261	19701/0/447
GOF	1.058	1.044	1.118	1.027	1.025	1.043
R1, wR2 ($I > 2\sigma(I)$)[a]	0.0549/0.1250	0.0444/0.1067	0.0410/0.0760	0.0345/0.0730	0.0412/0.0837	0.0457/0.0816
R1, wR2 (all data)[a]	0.1149/0.1439	0.0591/0.1153	0.0615/0.0879	0.0511/0.0788	0.0724/0.0945	0.0873/0.0928
diff peak/hole (e $Å^{-3}$)	1.21/−0.39	0.95/−0.94	0.83/−0.68	0.61/−0.28	0.51/−0.34	0.42/−0.34

	1_{1235}	1_{1245}
formula	$C_{19}H_{35}F_3NiP_2$	$C_{19}H_{37}FNiP_2$
fw	441.12	405.13
cryst size (mm^3)	0.17 × 0.16 × 0.14	0.25 × 0.21 × 0.15
color	yellow	yellow
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.3705(13)	8.8535(4)
b (Å)	13.6600(13)	9.1739(4)
c (Å)	14.8513(14)	14.9537(7)
α (deg)	106.971(3)	95.4440(10)
β (deg)	110.937(3)	97.7340(10)
γ (deg)	90.913(3)	111.0600(10)
V ($Å^3$)	2221.4(4)	1109.56(9)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.319	1.213
μ (mm^{-1})	1.042	1.024
F(000)	936	436
θ range (deg)	2.93−29.99	3.04−38.49
θ comp (deg)	99.9	99.9
no. of rflns collected	105448	40493
R(int)	0.0995	0.0434
no. of data/restraints/params	12942/0/485	11686/0/225
GOF	1.04	1.044
R1, wR2 ($I > 2\sigma(I)$)[a]	0.0452/0.0784	0.0444/0.1067
R1, wR2 (all data)[a]	0.0795/0.0879	0.0591/0.1153
diff peak/hole (e $Å^{-3}$)	0.571/−0.439	0.95/−0.94

[a] $R1 = \sum||F_o| - |F_c||/[\sum|F_o|]$; $wR2 = \{[\sum w(F_o^2 - F_c)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

activation conditions by performing a competition reaction where a 5-fold excess of both 1,3-difluorobenzene and 1,3,5-trifluorobenzene were reacted with $Ni(PEt_3)_4$ and $AlMe_3$, as shown in Scheme 6. These substrates were chosen because they are the most similar among fluorobenzenes with different degrees of fluorination, lacking both *o*-F substituents and *p*-F substituents. Also, in a catalytic system, the monofunctionalization of 1,3,5-trifluorobenzene would generate a functionalized

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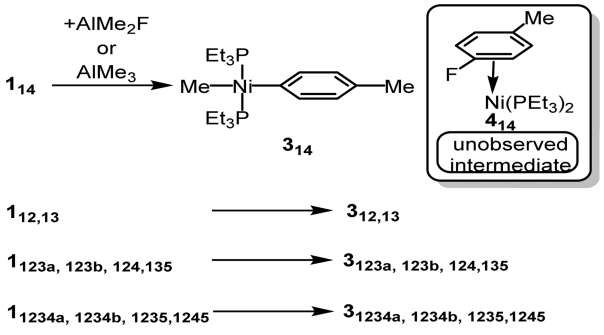
Scheme 5. Second Activation Products of the Di-, Tri-, and Tetrafluorobenzenes



1,3-difluoroarene that should have reactivity similar to that of 1,3-difluorobenzene; thus, this is a practical comparison.

The activation of 1,3,5-$C_6F_3H_3$ and 1,3-$C_6F_2H_4$ occurred with little selectivity and provided a 2.2:1 ratio of $\mathbf{1}_{135}$ and $\mathbf{1}_{13}$. This unexpected result suggests that, in catalytic C−F functionalization, rapid ring whizzing is not the only mechanism by which second activation products could be observed; rather, the direct competition between functionalization products and substrates is a potential problem.

Although the traditional approach to improving selectivity would involve ligand design, the strongly Lewis acidic transmetalating reagent is clearly involved directly in the C−F activation step and thus provides an additional means to tune reaction conditions. The effect oxygen and nitrogen donors have on selectivity was investigated, and the results are summarized in Table 6. The use of 1,4-dioxane, Et_2O, or THF as the reaction solvent all produced improvements in the selectivity of the reaction. THF provided the greatest selectivity, with 95% of the C−F activation products arising from the C−F activation of 1,3,5-$C_6F_3H_3$ vs 1,3-$C_6F_2H_4$. These reactions took 30−60 min to go to completion at room temperature, unlike the instantaneous reactions with $AlMe_3$ in the absence of an added donor. As a result, the reductive elimination products from the decomposition of thermally sensitive $\mathbf{1}_{14}$ and $\mathbf{1}_{135}$ are observed in significant amounts in solution. The second activation products from ring whizzing, $\mathbf{3}_{14}$ and $\mathbf{3}_{135}$, were not observed, due to the decreased rate of activation.

When used as a neat solvent, THF undergoes Lewis acid catalyzed polymerization, which limits its utility. As a stoichiometric additive, THF in C_6D_6 provided selectivity that was intermediate between the reactions performed in neat C_6D_6 and neat THF. Given that donors which formed strong adducts with $AlMe_3$ had better selectivity, a variety of nitrogen donors were also examined. Stoichiometric Et_3N provided nearly the same selectivity as stoichiometric THF. The best stoichiometric donor additives were found to be 1,4-diazabicyclo[2.2.2]octane (DABCO) and pyridine, the latter of which provided a 95% selectivity for 1,3,5-$C_6F_3H_3$ activation. A similar selectivity could be obtained by using isolated crystalline $AlMe_3$·(pyridine) in combination with $Ni(PEt_3)_4$ in hydrocarbon solvents.

Improved Monoactivation of the Tetrafluorobenzenes. Since the addition of pyridine to $AlMe_3$ showed improved selectivity, 1,2,3,5- 1,2,4,5-, and 1,2,3,4-tetrafluorobenzenes were all reacted with $Ni(PEt_3)_4$ and $AlMe_3$·(pyridine) complex to give the activation products $\mathbf{1}_{1245,1235,1234a,1234b}$, without the generation of impurities from reductive elimination or the second activation products $\mathbf{3}_{1245,1235,1234a,1234b}$ observed with $AlMe_3$. Unlike the nearly unselective $AlMe_3$ activation of 1,2,3,4-tetrafluorobenzene, the activation with $AlMe_3$·(pyridine) occurred with improved regioselectivity, as shown in Scheme 7. Similarly, improved regioselectivity was observed in the activation of 1,2,3-trifluorobenzene by $AlMe_3$·(pyridine), which occurred to give $\mathbf{1}_{123a}$ and $\mathbf{1}_{123b}$ in a 99:1 ratio, as shown in Scheme 8; with $AlMe_3$ as the transmetalating agent a 94:6 ratio was obtained.

Di-, Tri-, and Tetrafluorobenzene Competition Reactions. Improved selectivity with the $AlMe_3$·(pyridine) adduct was also observed in competition reactions between the difluorobenzenes. Reactions were carried out with a 5-fold excess of each of the three difluorobenzenes, and the results are summarized in Scheme 9. The reaction using $AlMe_3$ showed no selectivity among the difluorobenzenes, whereas when $AlMe_3$·(pyridine) was used, there was greater selectivity for 1,2-difluorobenzene activation.

Competition reactions with all of the di-, tri-, and tetrafluorobenzenes were also performed. The relative rates span 4 orders of magnitude and are summarized in Figure 1. These rates could be affected by many factors, including the thermodynamic stability of the $Ni(PEt_3)_2$ adducts of the arenes[15a] and their relative rate of formation, as well as the barrier to aluminum-aided C−F activation. There are a few predictions that can be made from these results. First, certain substrates should be easier to monofunctionalize than others, due to their reactivity relative to their functionalization products, assuming the substituent added does not influence activity. For example, 1,2-difluorobenzene should be easiest of the difluorobenzenes to monofunctionalize because it should be the most reactive relative to a monofluorinated product. Steric effects are likely to even further favor monosubstitution in the

Table 3. Summary of NMR Data for C−F Bond Activation Products $\mathbf{2}_{12,13,14,123a,123b,124,135,1234a,1234b,1245,1235}$

	^{19}F	^{1}H arene−CH_3
$\mathbf{2}_{12}$	−117.6 (m)	2.04 (s)
$\mathbf{2}_{13}$	−114.1 (m)	1.95 (s)
$\mathbf{2}_{14}$	−118.4 (m)	1.96 (s)
$\mathbf{2}_{123a}$	−139.8 (m), −143.3 (m)	2.0 (d, $^{4}J_{FH}$ = 2.2 Hz)
$\mathbf{2}_{123b}$	−112.8 (m)	2.08 (s)
$\mathbf{2}_{124}$	−120.2 (m), −124.0 (m)	1.94 (d, $^{4}J_{FH}$ = 1.8 Hz)
$\mathbf{2}_{135}$	−111.4 (t, $^{3}J_{FH}$ = 8.8 Hz)	1.88 (s)
$\mathbf{2}_{1235}$	−116.0 (m), −134.2 (m), −147.1 (m)	1.90 (d, $^{4}J_{FH}$ = 2.2 Hz)
$\mathbf{2}_{1245}$	−119.3 (m), −138.4 (m), −144.4 (m)	1.90 (s)
$\mathbf{2}_{1234(a)}$	−138.5 (m), −139.2 (m), −162.4 (m)	1.91 (s)
$\mathbf{2}_{1234(b)}$	−120.4 (m), −138.3 (m), −143.6 (m)	1.93 (s)

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Table 4. Summary of NMR Data for C−F Bond Activation Products $3_{12,13,14,123a,123b,124,135,1234a,1234b,1245,1235}$

	^{19}F	$^{31}P\{^1H\}$	^1H Ni−CH_3	^1H arene−CH_3
3_{12}	N/A	17.9 (s)	−0.78 (t) $^3J_{PH}$ = 8.8 Hz	2.69 (s)
3_{13}	N/A	18.0 (s)	overlapped by 1_{13} (−0.80)	2.20 (s)
3_{14}	N/A	18.8 (d) $^6J_{PF}$ = 2.8 Hz	−0.83 (t) $^3J_{PH}$ = 9.0 Hz	1.96 (s)
3_{123a}	−115.9 (s)	19.8 (s)	−0.72 (t) $^3J_{PH}$ = 8.8 Hz	2.0 (d) $^4J_{FH}$ = 2.2 Hz
3_{123b}	−87.5 (s)	20.2 (s)	−0.81 (t) $^3J_{PH}$ = 8.9 Hz	2.08 (s)
3_{124}	−122.9 (m)	18.1 (s)	−0.80 (overlapped t) $^3J_{PH}$ = 8.0 Hz	2.21 (s)
3_{135}	−119.0 (t, $^3J_{FH}$ = 9.3 Hz)	18.1 (s)	−0.80 (overlapped t) $^3J_{PH}$ = 9.1 Hz	1.96 (s)
3_{1235}	−99.4 (m), −134.2 (m)	18.7 (s)	−0.74 (t) $^3J_{PH}$ = 9.0 Hz	1.96 (d) $^4J_{FH}$ = 2.2 Hz
3_{1245}	−97.4 (m), −129.6 (m)	18.4 (s)	Overlapped by 1_{1245} (−0.69)	1.94 (s)
$3_{1234(a)}$	−138.5 (m), −139.2 (m)	20.3 (s)	−0.80 (t) $^3J_{PH}$ = 9.0 Hz	1.91 (s)
$3_{1234(b)}$	−120.4 (m), −138.3 (m)	20.5 (s)	−0.72 (t) $^3J_{PH}$ = 9.3 Hz	1.93 (s)

Scheme 6. Competition of 1,3-Difluorobenzene vs 1,3,5-Trifluorobenzene Activation by $Ni(PEt_3)_4$ in the Presence of $AlMe_3$ and Donor Solvents or Stoichiometric Additives

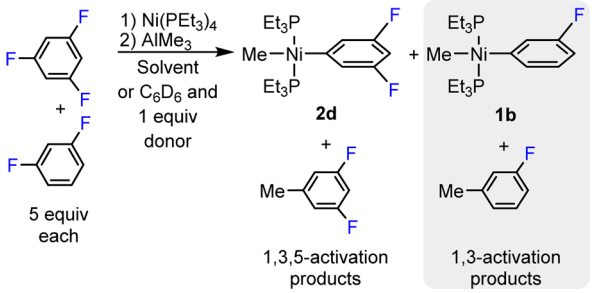


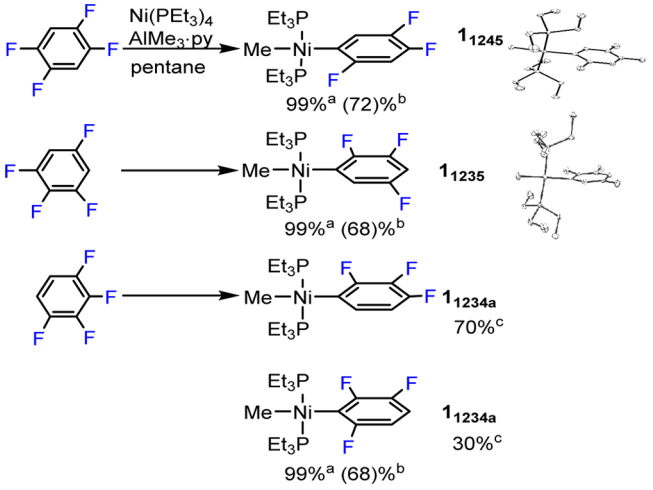
Table 6. Effects of Oxygen and Nitrogen Donors on the Competition Shown in Scheme 6

solvent	1,3,5-activation products[a,c,d]	1,3-activation products[b,c,d]
C_6D_6	69 (3)	31 (2)
1,4-dioxane (neat)	82 (4)	18 (4)
Et_2O (neat)	87 (35)	13 (8)
THF (neat)	95 (47)	5 (2)
donor[e]	1,3,5-activation products[a,c,d]	1,3-activation products[b,c,d]
THF (1 equiv)	85 (4)	15 (3)
Et_3N	84 (4)	16 (2)
1/2 DABCO	92 (6)	8 (1)
pyridine	95 (22)	5 (0)

[a]Percentage includes both the activation product 1_{135} and its reductive elimination product 3,5-difluorotoluene. [b]Percentage includes both the activation product 1_{13} and its reductive elimination product 3-fluorotoluene. [c]Percentages based upon ^{19}F NMR. [d]Percentage of reductive elimination product in parentheses. [e]1 equiv vs $AlMe_3$, in C_6D_6.

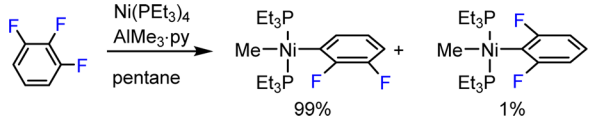
1,2-substituted product. The least reactive difluoroarene, 1,4-difluorobenzene, should be the hardest to monofunctionalize since it is the least reactive of the difluorinated arenes; thus, the monofunctionalized product can compete most effectively with this substrate. This result provides a rationale for the result shown in Scheme 1B,[13] where the disubstitution products in the catalytic functionalization of the 1,2-, 1,3-, and 1,4-difluorobenzenes accounted for 0, 12, and 25% of the product mixture, respectively. For the tri- and tetrafluorobenzenes the difficulty in achieving monofunctionalization should be related to not only the fluorination pattern of the starting material but also the product. For example, the monofunctionalization of 1,2,3,5-tetrafluorobenzene should be relatively facile, since it

Scheme 7. Tetrafluorobenzene Activation with $AlMe_3$·(pyridine)

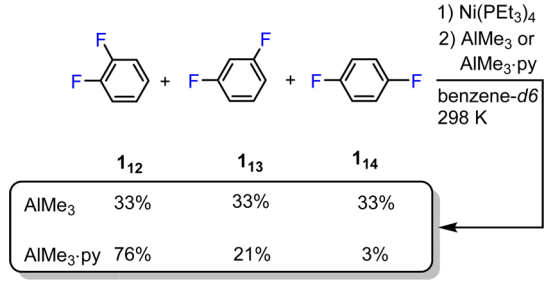


[a]Percent yield based on ^{19}F NMR spectra. [b]Isolated yield. [c]Selectivity between 1-site and 2-site activation.

Scheme 8. Improved Regioselectivity in 1,2,3-Trifluorobenzene Activation with $AlMe_3$·(pyridine)



Scheme 9. Difluorobenzene Competition using $AlMe_3$ and $AlMe_3$·(pyridine)



should be around 32 times more reactive than its mono-functionalization product, which would be 1,2,4-trifluoroarene; once again this ignores the electronic effect and steric effects of the added substituent. The selective monofunctionalization of 1,2,3,4-tetrafluorobenzene at the 1-site should be among the

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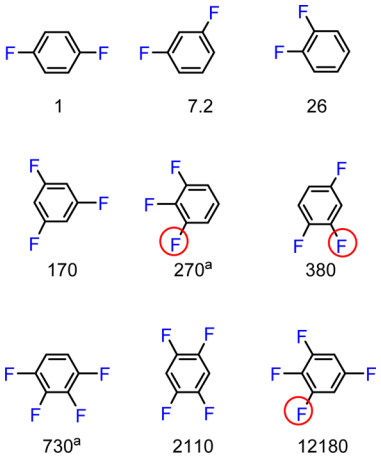

Figure 1. Rates of reaction with $Ni(PEt_3)_4$ and $AlMe_3$·(pyridine), relative to 1,4-difluorobenzene, with sites of selective activation circled in red. Based on ^{19}F NMR integrals of competition reaction between the two reactants and includes all reductive elimination products. a) for activation at both the 1- and 2-site.

hardest to accomplish. This substrate would be expected to react only ~3 times as fast as the 1,2,3-trifluoroarene product that such a monofunctionalization should afford, and the substituent added does not sterically protect the predicted site of functionalization of this trifluoroarene.

CONCLUSIONS

Although many nickel-based systems have been designed for C−F bond functionalization, little has been reported to date about the design principles necessary for monofunctionalization of the polysubstituted aromatics, despite some ligand design based success. Even the nature of the C−F activation steps remained unclear in these processes; many of the ligand designs that support catalysis use ligands that yield relatively electron poor Ni(0) moieties that have not been observed to give stoichiometric C−F bond activation. The ability of $AlMe_3$ to provide instant C−F bond activation of even the least reactive polyfluorinated aromatics using $Ni(PEt_3)_4$ implies that, in many catalytic cases, the C−F oxidative addition step and transmetalation step are intimately mixed. The nickel(II) fluoride intermediates commonly proposed in catalytic cycles for coupling reactions are unlikely to exist as such in these systems. The reduction in the activity of the Lewis acidic $AlMe_3$ by the addition of donor solvents had a strong impact on selectivity, providing an additional means to tune reactivity without necessitating novel ligand designs. Catalyst designs must also take into consideration the competition between functionalized products and the starting polyfluorinated aromatic.

The conclusions regarding the intimate involvement of transmetalating reagents in the activation of unreactive C−F bonds may be true for other difficult oxidative addition reactions such as C−O bonds, which have previously been shown to undergo catalytic functionalization using Lewis acids and Ni-based catalysts.[19] Further work is underway in our laboratory to explore the scope of this effect, as well as to better understand the influence of donor solvents on the selectivities observed in the activation of fluorinated aromatics.

EXPERIMENTAL SECTION

General Procedure. Unless otherwise stated, all reactions were performed under an inert nitrogen atmosphere using an Innovative Technology glovebox. Dry, oxygen-free solvents were used for all experiments. Anhydrous THF and pentane packed under argon were purchased from Alfa Aesar and dried with molecular sieves. Benzene-d_6 was freeze−pump−thawed three times and dried by passing through 5 g of Brockmann I activated aluminum oxide. All fluorinated aromatics, phosphines, and Lewis acids were purchased from Sigma-Aldrich and degassed prior to use. Literature procedures were used for the synthesis of $Ni(COD)_2$,[20] and $Ni(PEt_3)_4$.[21] ^1H, $^{31}P\{^1H\}$, ^{19}F, $^{19}F\{^1H\}$, and $^{13}C\{^1H\}$ NMR were recorded on a Bruker AMX spectrometer operating at 500 or 300 MHz with respect to the proton nuclei. All chemical shifts are reported in parts per million, and all coupling constants are reported in hertz. ^1H NMR spectra were referenced to residual protons (C_6D_5H, δ 7.15; THF, δ 3.62) with respect to tetramethylsilane at δ 0.00. $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4 at δ 0.0. ^{19}F and $^{19}F\{^1H\}$ NMR were referenced to external α,α,α-trifluorotoluene at δ −63.7. $^{13}C\{^1H\}$ NMR spectra were referenced to the solvent resonance (C_6D_6, δ 128.0). Elemental analyses were performed at the Centre for Catalysis and Materials Research, Windsor, Ontario, Canada.

Synthesis of $CH_3(PEt_3)_2Ni(2\text{-}FC_6H_4)$ (1_{12}). Crystalline $Ni(PEt_3)_4$ (1.0 g, 1.88 mmol), 1 mL of pentane, and 1,2-difluorobenzene (0.236 mg, 2.07 mmol) were placed in a 50 mL flask. A solution of $AlMe_3$ (149 mg, 2.07 mmol) in pentane (2.08 mL) was added dropwise at room temperature. This solution was then passed through 1 cm of dried 100 mesh silica to remove any excess $AlMe_3$ and aluminum byproducts. The solvent was removed under vacuum until the product began to crystallize. This solution was put into a−35 °C refrigerator overnight to finalize crystallization. The orange-yellow solid was isolated by filtration and dried under vacuum (total yield 0.528 g, 69.4%). Crystals suitable for characterization by X-ray crystallography were obtained directly from the recrystallized product. ^1H NMR (C_6D_6, 500 MHz, 298 K): δ −0.65 (t, $^3J_{PH}$ = 9.0 Hz, 3H, $NiCH_3$), 0.95 (coincident t of vt $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ + $^5J_{PH}$ = 15.5 Hz, and $^2J_{PP}$ > 50 Hz, 18H, $NiPCH_2CH_3$), 1.25 (m, 12H), 6.83 (m, 1H), 6.88 (m, 1H), 6.94 (m, 1H), 7.48 (m, 1H). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.46 MHz, 298 K): 19.7 (s, 2P). $^{19}F\{^1H\}$ NMR (C_6D_6, 470.55 MHz, 298 K): −89.4 (s, 1F). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.77 MHz, 298 K): −9.9 (t of d $^2J_{PC}$ = 24.4 Hz, $^4J_{FC}$ = 3.65 Hz, 1C), 8.4 (s, 6C), 14.7 (vt, $^1J_{PC}$ + $^3J_{PC}$ = 11.7 Hz, and $^2J_{PP}$ > 150 Hz, 6C, $NiPCH_2CH_3$), 112.5 (s, 1C), 122.6 (m, 1C), 122.9 (m, 1C), 139.5 (d of t $^2J_{FC}$ = 23.5 Hz $^4J_{PC}$ = 2.9 Hz, 1C), 153.6 (m, 1C), 168.3 (d of t $^3J_{PC}$ = 3.6 Hz, $^1J_{FC}$ = 221.7 Hz, 1C). Anal. Calcd for $CH_3(PEt_3)_2Ni(2\text{-}FC_6H_4)$: C, 56.33; H, 9.2. Found: C, 56.33; H, 9.57.

Synthesis of $CH_3(PEt_3)_2Ni(3\text{-}FC_6H_4)$ (1_{13}). Synthesis and crystallization were performed using the same procedure as for 1_{12}, but with 1,3-difluorobenzene in lieu of 1,2-difluorobenzene. The orange-yellow solid was isolated by filtration and dried under vacuum (total yield 0.508 g, 66.7%). Crystals suitable for characterization by X-ray crystallography were obtained directly from the recrystallized product. ^1H NMR (C_6D_6, 500 MHz, 298 K): δ −0.80 (t, $^3J_{PH}$ = 8.5 Hz, 3H, $NiCH_3$), 0.88 (coincident t of vt, $^3J_{HH}$ = 8.0 Hz, $^3J_{PH}$ + $^5J_{PH}$ = 14.5 Hz, $^2J_{PP}$ > 50 Hz, 18H, $NiPCH_2CH_3$), 1.19 (m, 12H,$NiPCH_2CH_3$), 6.60 (m, 1H, Ar−H), 6.94 (m, 1H, Ar−H), 7.27 (broad d $^3J_{FH}$ = 7.0 Hz, 1H, Ar−H), 7.36 (m, 1H, Ar−H). $^{31}P\{^1H\}$ NMR (C_6D_6, 202.46 MHz, 298 K): 18.8 (d, $^5J_{PF}$ = 1.82 Hz, 2P). $^{19}F\{^1H\}$ NMR (C_6D_6, 470.55 MHz, 298 K): −116.9 (s, 1F). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.77 MHz, 298 K): −10.5 (t, $^2J_{PC}$ = 23.5 Hz, 1C, $NiCH_3$), 8.4 (s, 6C, $NiPCH_2CH_3$), 14.5 (vt, $^1J_{PC}$ + $^3J_{PC}$ = 11.8 Hz, $^2J_{PP}$ > 150 Hz, 6C, $NiPCH_2CH_3$), 107.0 (d of t, $^2J_{FC}$ = 21.5 Hz, $^3J_{PC}$ = 2.1 Hz, 1C), 123.9 (d of t, $^2J_{FC}$ = 12.8 Hz, $^5J_{PC}$ = 2.6 Hz, 1C), 126.3 (m, 1C), 133.8 (m,1C), 162.2 (d of t $^1J_{FC}$ = 248.9 Hz, $^4J_{PC}$ = 2.8 Hz, 1C), 178.3 (t, $^2J_{PC}$ = 28.4 Hz, 1C). Anal. Calcd for $CH_3(PEt_3)_2Ni(3\text{-}FC_6H_4)$; C, 56.33; H, 9.2. Found: C, 55.95; H, 9.16.

Synthesis of $CH_3(PEt_3)_2Ni(4\text{-}FC_6H_4)$ (1_{14}). Synthesis and crystallization were performed using the same procedure as for 1_{12}, but with 1,4-difluorobenzene in lieu of 1,2-difluorobenzene. The

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orange-yellow solid was isolated by filtration and dried under vacuum (total yield 0.588 g, 77.3%). Crystals suitable for characterization by X-ray crystallography were obtained directly from the recrystallized product. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ −0.79 (t, $^3J_{PH}$ = 8.5 Hz, 3H, NiCH_3), 0.91 (coincident t of vt, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ + $^5J_{PH}$ = 15.0 Hz, $^2J_{PP}$ > 50 Hz, 18H, NiPCH$_2$CH_3), 1.19 (q of vt, $^3J_{HH}$ = 7.5 Hz, $^2J_{PH}$ + $^4J_{PH}$ = 6.5 Hz, $^2J_{PP}$ > 50 Hz, 12H, NiPCH_2CH$_3$), 6.90 (2nd order AA′BB′X, 2H, Ar-*H*), 7.32 (2nd order AA′BB′X m, 2H, Ar-*H*). ^{31}P{^{1}H} NMR (C_6D_6, 202.46 MHz, 298 K): 18.8 (d, $^6J_{PF}$ = 2.8 Hz). ^{19}F{^{1}H} NMR (C_6D_6, 470.55 MHz, 298 K): −126.5 (t, $^6J_{PF}$ = 2.8 Hz). ^{19}F NMR (C_6D_6, 470.55 MHz, 298 K): −126.5 (t of t of t, $^3J_{FH}$ = 10.0 Hz $^4J_{FH}$ = 7.0 Hz $^6J_{PF}$ = 2.8 Hz). ^{13}C{^{1}H} NMR (C_6D_6, 125.77 MHz, 298 K): −10.6 (t, $^2J_{PC}$ = 22.6 Hz, 1C, NiCH$_3$), 8.5 (s, 6C, NiPCH$_2$CH$_3$), 14.6 (vt, $^1J_{PC}$ + $^3J_{PC}$ = 11.9 Hz, $^2J_{PP}$ > 150 Hz, 6C, NiPCH$_2$CH$_3$), 113.0 (d of t $^2J_{FC}$ = 16.8 Hz, $^4J_{PC}$ = 2.0 Hz, 2C, Ar), 138.3 (d of t $^3J_{FC}$ = 3.8 Hz, $^3J_{PC}$ = 2.6 Hz, 2C, Ar), 160.6 (d of t, $^1J_{FC}$ = 237.2 Hz, $^5J_{PC}$ = 1.8 Hz, 1C, Ar), 164.5 (d of t, $^4J_{FC}$ = 3.6 Hz, $^2J_{PC}$ = 29.1 Hz, 1C, Ar). Anal. Calcd for CH$_3$(PEt$_3$)$_2$Ni(4-FC$_6$H$_4$): C, 56.33; H, 9.2. Found: C, 56.30; H, 9.40.

CH$_3$(PEt$_3$)$_2$Ni(C$_6$H$_4$CH$_3$) (3$_{14}$). Complex **3$_{14}$** was identified as a minor side product in the synthesis of **1$_{14}$** by ^{1}H and ^{31}P{^{1}H} NMR. Conversion to **3$_{14}$** increased if the reaction mixture was not worked up immediately to remove excess aluminum methyl species. Attempts to isolate **3$_{14}$** failed due to concomitant conversion to *p*-xylene. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ −0.75 (t overlapped by main product, $^3J_{PH}$ = 8.5 Hz, 3H, NiCH$_3$), δ 2.28 (s, 3H, CH_3), 6.99 (m, 2H, Ar-*H*), 7.46 (m, 2H, Ar-*H*). ^{31}P{^{1}H} NMR (C_6D_6, 202.46 MHz, 298 K): 18.7 (s, 2P).

Synthesis of CH$_3$(PEt$_3$)$_2$Ni(2,3-F$_2$C$_6$H$_3$) (1$_{123a}$). Crystalline Ni(PEt$_3$)$_4$ (1.0 g, 1.88 mmol), 1 mL of pentane, and 1,2,3-trifluorobenzene (273 mg, 2.07 mmol) were placed in a 50 mL flask. A solution of AlMe$_3$ (149 mg, 2.07 mmol) in pentane (2.08 mL) was added dropwise at room temperature. This solution was then passed through 1 cm of dried 100 mesh silica to remove any excess AlMe$_3$ and aluminum byproducts. The solvent was removed under vacuum until the product began to crystallize. This solution was put into a −35 °C refrigerator overnight to finalize crystallization. The orange-yellow solid was isolated by filtration and dried under vacuum (total yield 0.520 g, 65.4%). Crystals suitable for characterization by X-ray crystallography were obtained directly from the recrystallized product. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ −0.68 (t, $^3J_{PH}$ = 9.0 Hz, 3H, NiCH_3), 0.91 (coincident t of vt, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ + $^5J_{PH}$ = 15.0 Hz, $^2J_{PP}$ > 150 Hz, 18H, NiPCH$_2$CH_3), 1.21 (m, 12H, NiPCH_2CH$_3$), 6.67 (m, 1H), 6.75 (m, 1H), 7.12 (m, 1H). ^{31}P{^{1}H} NMR (C_6D_6, 202.46 MHz, 298 K): 19.8 (s, 2P). ^{19}F{^{1}H} NMR (C_6D_6, 470.55 MHz, 295 K): −142.1 (d, $^3J_{FF}$ = 36.2 Hz, 1F),−115.9 (d, $^3J_{FF}$ = 36.2 Hz, 1F). ^{19}F NMR (C_6D_6, 470.55 MHz, 294 K): −142.1 (d of d of t, $^3J_{FF}$ = 36.2 Hz, $^5J_{FP}$ = 2.3 Hz, $^3J_{FH}$ = 11.3 Hz, 1F). −115.9 (d of d, $^3J_{FF}$ = 36.2 Hz, $^4J_{FH}$ = 8.0 Hz, 1F). ^{13}C{^{1}H} NMR (C_6D_6, 125.77 MHz, 298 K): −9.8 (t of d, $^2J_{CP}$ = 24.1 Hz, $^3J_{CF}$ = 3.5 Hz, 1C), 8.4 (s, 6C), 14.6 (vt, $^1J_{CP}$+$^3J_{CP}$ = 12.7 Hz, $^2J_{PP}$ > 150 Hz, 6C), 109.8 (d, $^2J_{CF}$ = 13.0 Hz, 1C), 122.6 (d, $^3J_{CF}$ = 2.0 Hz, 1C), 133.4 (m, 1C), 150.3 (d of d of t, $^3J_{CP}$ = 2.5 Hz, $^2J_{CF}$ = 21.8 Hz, $^1J_{CF}$ = 251.2 Hz, 1C), 152.7 (m, 1C), 159.1 (m, 1C). Anal. Calcd for CH$_3$(PEt$_3$)$_2$Ni(2,3-F$_2$C$_6$H$_3$): C, 53.93; H, 8.58. Found: C, 53.97; H, 8.65

CH$_3$(PEt$_3$)$_2$Ni(2,6-F$_2$C$_6$H$_3$) (1$_{123b}$). Activation at the 2-site of 1,2,3-trifluorobenzene. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): −0.56 (t, $^3J_{HP}$ = 9.5 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 202.46 MHz, 298 K): 19.7 (s). ^{19}F{^{1}H} NMR (C_6D_6, 470.55 MHz, 298 K): −87.5 (s). ^{19}F NMR (C_6D_6, 470.55 MHz, 298 K): −87.5 (t, $^3J_{FH}$ = 6.1 Hz).

Synthesis of CH$_3$(PEt$_3$)$_2$Ni(2,5-F$_2$C$_6$H$_3$) (1$_{124}$). Synthesis and crystallization were performed using the same procedure as for **1$_{123a}$**, but with 1,2,4-trifluorobenzene in lieu of 1,2,3-trifluorobenzene. The orange-yellow solid was isolated by filtration and dried under vacuum (total yield 0.500 g, 62.89%). Crystals suitable for characterization by X-ray crystallography were obtained directly from the recrystallized product. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ −0.70 (t, $^3J_{HP}$ = 9.5 Hz, 3H), 0.90 (coincident t of vt $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ + $^5J_{HP}$ = 15.0 Hz, $^2J_{PP}$ > 50 Hz, 18H), 1.21 (m, 12H), 6.49 (m, 1H), 6.60 (m, 1H), 7.24 (d, $^3J_{HF}$ = 8.5 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 202.46 MHz, 298 K): 19.6 (s, 2P). ^{19}F{^{1}H} NMR (C_6D_6, 470.55 MHz, 298 K): −124.7 (d, $^4J_{FF}$ = 21.6 Hz, 1F), −97.1 (d, $^4J_{FF}$ = 21.6 Hz, 1F). ^{19}F NMR (C_6D_6, 470.55 MHz, 298 K): −124.7 (m, 1F), −97.1 (d, $^4J_{FF}$ = 21.6 Hz, 1F). ^{13}C{^{1}H} NMR (C_6D_6, 125.77 MHz, 298 K): −9.9 (t of d $^2J_{CP}$ = 24.3 Hz, $^4J_{CF}$ = 3.6 Hz, 1C), 8.3 (s, 1C), 14.6 (vt, $^1J_{CP}$ + $^3J_{CP}$ = 12.2 Hz, $^2J_{PP}$ > 150 Hz, 6C), 108.6 (d of d, $^3J_{CF}$ = 8.9 Hz, $^2J_{CF}$ = 24.5 Hz, 1C), 112.3 (m, 1C), 112.6 (d, $^2J_{CF}$ = 8.2 Hz, 1C), 124.2 (d of d of t, $^3J_{CF}$ = 17.2 Hz, $^2J_{CF}$ = 25.5 Hz, $^3J_{CP}$ = 2.8 Hz, 1C), 158.6 (m, 1C), 163.9 (d of t, $^1J_{CF}$ = 215.8 Hz, $^3J_{CP}$ = 3.8 Hz, 1C). Anal. Calcd for CH$_3$(PEt$_3$)$_2$Ni(2,5-F$_2$C$_6$H$_3$): C, 53.93; H, 8.58. Found: C, 54.05; H, 8.91

Synthesis of CH$_3$(PEt$_3$)$_2$Ni(3,5-F$_2$C$_6$H$_3$) (1$_{135}$). Synthesis and crystallization were performed using the same procedure as for **1$_{123a}$**, but with 1,3,5-trifluorobenzene in lieu of 1,2,3-trifluorobenzene. The orange-yellow solid was isolated by filtration and dried under vacuum (total yield 0.557 g, 70.06%). Crystals suitable for characterization by X-ray crystallography were obtained directly from the recrystallized product. ^{1}H NMR (C_6D_6, 500 MHz, 298 K): δ −0.85 (t, $^3J_{HP}$ = 9.0 Hz, 3H, NiCH_3), 0.84 (coincident t of vt, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ + $^5J_{HP}$ = 15.0 Hz, $^2J_{PP}$ > 50 Hz, 18H, NiPCH$_2$CH_3), 1.14 (m, 12H), 6.36 (2nd order m, 1H), 7.15 (m, 2H). ^{31}P{^{1}H} NMR (C_6D_6, 202.46 MHz, 298 K): 18.8 (s,2P). ^{19}F{^{1}H} NMR (C_6D_6, 470.55 MHz, 298 K): −116.8 (s, 2F). ^{19}F NMR (C_6D_6, 470.55 MHz, 298 K): −116.8 (m, 2F). ^{13}C NMR (C_6D_6, 125.77 MHz, 298 K) −10.4 (t, $^3J_{CP}$ = 23.8 Hz, 1C), 8.4 (s, 6C), 14.4 (vt, $^1J_{CP}$ + $^3J_{CP}$ = 12.2 Hz, and $^2J_{PP}$ > 150 Hz, 6C), 95.4 (t of t, $^2J_{CF}$ = 25.7 Hz, $^5J_{CP}$ = 2.0 Hz, 2C), 119.0 (m, 2C), 161.6 (d of d of t, $^3J_{CF}$ = 9.9 Hz, $^1J_{CF}$ = 252.3 Hz, $^4J_{CP}$ = 3.5 Hz, 1C), 182.5 (t, $^2J_{CF}$ = 28.3 Hz, 1C). Anal. Calcd for CH$_3$(PEt$_3$)$_2$Ni(3,5-F$_2$C$_6$H$_3$): C, 53.93; H, 8.58. Found: C, 54.02; H, 8.89.

Synthesis of CH$_3$(PEt$_3$)$_2$Ni(2,3,5-F$_3$C$_6$H$_2$) (1$_{1235}$). Crystalline Ni(PEt$_3$)$_4$ (1.0 g, 1.88 mmol), 1 mL of pentane, and 1,2,3,5-tetrafluorobenzene (310 mg, 2.07 mmol) were placed in a 50 mL flask (**A**). Crystalline AlMe$_3$·(pyridine) (312 mg, 2.07 mmol) and pentane (1.0 mL) were placed in a 10 mL flask (**B**). Solution **B** was added to solution **A** dropwise at room temperature with stirring. This solution was allowed to sit at room temperature under an inert atmosphere for 30 min. Next it was passed through 1 cm of dried 100 mesh silica to remove any excess AlMe$_3$·(pyridine) and aluminum byproducts. The solvent was removed under vacuum until the product began to crystallize. This solution was put into a −35 °C refrigerator overnight to finalize crystallization. The orange-yellow solid was isolated by filtration and dried under vacuum (total yield 0.597 g, 72.0%). Crystals suitable for characterization by X-ray crystallography were obtained directly from the recrystallized product. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ −0.69 (t, $^3J_{HP}$ = 9.0 Hz, 3H, NiCH_3), 0.85 (coincident t of vt, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ + $^5J_{HP}$ = 15.0 Hz, $^2J_{PP}$ > 50 Hz, 18H, NiPCH$_2$CH_3), 1.14 (m, 12H), 6.45 (2nd order m, 1H), 7.01 (m, 2H). ^{31}P{^{1}H} NMR (C_6D_6, 121.51 MHz, 298 K): 19.6 (overlapping d of d, $^5J_{PF}$ = 3.8 Hz, $^5J_{PF}$ = 3.8 Hz, 2P). ^{19}F NMR (C_6D_6, 282.40 MHz, 298 K): −120.9 (d of d of d, $^3J_{FF}$ = 35.8 Hz, $^4J_{FF}$ = 19.6 Hz, $^5J_{FH}$ = 6.2 Hz, 1F), −121.2 (overlapping d of t, $^4J_{FF}$ = 20.3 Hz, $^5J_{PF}$ = 7.7 Hz, 1F), −138.1 (d of d, $^3J_{FF}$ = 35.8 Hz,, $^3J_{FH}$ = 10.4 Hz, 1F) ^{13}C NMR (C_6D_6, 75.48 MHz, 298 K) −9.6 (t, $^3J_{CP}$ = 24.3 Hz, 1C), 8.2 (s, 6C), 14.4 (vt, $^1J_{CP}$ + $^3J_{CP}$ = 12.3 Hz, and $^2J_{PP}$ > 150 Hz, 6C), 97.8 (overlapping d of d, $^2J_{CF}$ = 25.7 Hz, $^5J_{CP}$ = 2.0 Hz, 1C), 117.7 (m, 1C), 149.0 (d of m, $^1J_{CF}$ = 235.7 Hz, 1C), 149.5 (d of m, $^1J_{CF}$ = 215.6 Hz, 1C), 155.9 (m, 1C), 159.2 (m, 1C). Anal. Calcd for CH$_3$(PEt$_3$)$_2$Ni(2,3,5-F$_3$C$_6$H$_2$): C, 51.73; H, 8.00. Found: C, 51.52; H, 8.06.

Synthesis of CH$_3$(PEt$_3$)$_2$Ni(2,4,5-F$_3$C$_6$H$_2$) (1$_{1245}$). Synthesis and crystallization were performed using the same procedure as for **1$_{1235}$**, but with 1,2,4,5-tetrafluorobenzene in lieu of 1,2,3,5-tetrafluorobenzene. The orange-yellow solid was isolated by filtration and dried under vacuum (total yield 0.563 g, 67.89%). Crystals suitable for characterization by X-ray crystallography were obtained directly from the recrystallized product. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ −0.71 (t, $^3J_{HP}$ = 9.0 Hz, 3H, NiCH_3), 0.87 (coincident t of vt, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ + $^5J_{HP}$ = 15.0 Hz, $^2J_{PP}$ > 50 Hz, 18H, NiPCH$_2$CH_3), 1.15 (m, 12H), 6.58 (2nd order m, 1H), 7.19 (m, 2H). ^{31}P{^{1}H} NMR (C_6D_6, 121.51 MHz, 298 K): 19.6 (coincident p (d of d of d), $^4J_{PF}$ =

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1.6 Hz, $^5J_{PF}$ = 1.6 Hz, $^6J_{PF}$ = 1.6 Hz, 2P). ^{19}F NMR (C_6D_6, 282.40 MHz, 298 K): −93.2 (d, $^4J_{FF}$ = 18.1 Hz, 1F), −146.9 (m, 1F), −148.7 (m, 1F) ^{13}C NMR (C_6D_6, 75.48 MHz, 298 K) −10.0 (d of t, $^4J_{CF}$ = 3.0 Hz, $^3J_{CP}$ = 24.9 Hz, 1C), 8.3 (s, 6C), 14.5 (vt, $^1J_{CP}$ + $^3J_{CP}$ = 12.2 Hz, and $^2J_{PP}$ > 150 Hz, 6C), 102.1 (d of d, $^3J_{CF}$ = 18.2 Hz, $^1J_{CF}$ = 39.6 Hz, 1C), 124.4 (d of d, $^3J_{CF}$ = 12.4 Hz, $^1J_{CF}$ = 27.7 Hz, 1C), 144.7 (m, 1C), 149.7 (d of m, $^1J_{CF}$ = 215.6 Hz, 1C), 159.8 (m, 1C), 162.8 (m, 1C). Anal. Calcd for $CH_3(PEt_3)_2Ni(2,3,5\text{-}F_3C_6H_2)$: C, 51.73; H, 8.00. Found: C, 51.79; H, 8.37.

Synthesis of $CH_3(PEt_3)_2Ni(2,3,4\text{-}F_3C_6H_2)$ ($\mathbf{1}_{1234a}$). Synthesis and crystallization were performed using the same procedure as for $\mathbf{1}_{1235}$, but with 1,2,3,4-tetrafluorobenzene in lieu of 1,2,3,5-tetrafluorobenzene. The orange-yellow solid was isolated by filtration and dried under vacuum (total yield 0.563 g, 67.89%). X-ray crystallography was not obtained due to the presence of the isomer $\mathbf{1}_{1234b}$. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ −0.69 (t, $^3J_{HP}$ = 9.0 Hz, 3H, NiCH_3), 0.87 (coincident t of vt, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ + $^5J_{HP}$ = 15.0 Hz, $^2J_{PP}$ > 50 Hz, 18H, NiPCH$_2$CH_3), 1.15 (m, 12H), 6.68 (2nd order m, 1H), 6.86 (m, 2H). ^{31}P{^{1}H} NMR (C_6D_6, 121.51 MHz, 298 K): 19.7 (s, 2P). ^{19}F NMR (C_6D_6, 282.40 MHz, 298 K): −113.0 (d, $^3J_{FF}$ = 21.4 Hz, 1F), −147.9 (d of m, $^3J_{FF}$ = 11.2 Hz, 1F), −165.7 (d of d, $^3J_{FF}$ = 11.2 Hz, $^3J_{FF}$ = 21.4 Hz, 1F) ^{13}C NMR (C_6D_6, 75.48 MHz, 298 K) −10.0 (t, $^3J_{CP}$ = 24.9 Hz, 1C), 8.3 (s, 6C), 14.5 (vt, $^1J_{CP}$ + $^3J_{CP}$ = 12.2 Hz, and $^2J_{PP}$ > 150 Hz, 6C), 102.1 (d of d, $^3J_{CF}$ = 18.2 Hz, $^1J_{CF}$ = 39.6 Hz, 1C), 124.4 (d of d, $^3J_{CF}$ = 12.4 Hz, $^1J_{CF}$ = 27.7 Hz, 1C), 144.7 (m, 1C), 149.7 (d of m, $^1J_{CF}$ = 215.6 Hz, 1C), 159.8 (m, 1C), 162.8 (m, 1C). Anal. Calcd for $CH_3(PEt_3)_2Ni(2,3,5\text{-}F_3C_6H_2)$: C, 51.73; H, 8.00. Found: C, 51.79; H, 8.37.

Synthesis of $CH_3(PEt_3)_2Ni(2,3,4\text{-}F_3C_6H_2)$ ($\mathbf{1}_{1234b}$). Synthesis and crystallization were performed using the same procedure as for $\mathbf{1}_{1235}$, but with 1,2,3,4-tetrafluorobenzene in lieu of 1,2,3,5-tetrafluorobenzene. The orange-yellow solid was isolated by filtration and dried under vacuum (total yield 0.563 g, 67.89%). X-ray crystallography was not carried out due to the presence of the isomer $\mathbf{1}_{1234a}$. ^{1}H NMR (C_6D_6, 300 MHz, 298 K): δ −0.56 (t, $^3J_{HP}$ = 9.0 Hz, 3H, NiCH_3), 0.94 (coincident t of vt, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ + $^5J_{HP}$ = 15.0 Hz, $^2J_{PP}$ > 50 Hz, 18H, NiPCH$_2$CH_3), 1.21 (m, 12H), 6.42 (2nd order m, 1H), 6.90 (m, 2H). ^{31}P{^{1}H} NMR (C_6D_6, 121.51 MHz, 298 K): 20.1 (s, 2P). ^{19}F NMR (C_6D_6, 282.40 MHz, 298 K): −93.1 (d, $^5J_{FF}$ = 11.2 Hz, 1F), −111.5 (d, $^3J_{FF}$ = 20.2 Hz, 1F), −146.3 (d of d, $^5J_{FF}$ = 11.2 Hz, $^3J_{FF}$ = 20.2 Hz, 1F). ^{13}C NMR (C_6D_6, 75.48 MHz, 298 K): −10.0 (t, $^3J_{CP}$ = 24.9 Hz, 1C), 8.3 (s, 6C), 14.5 (vt, $^1J_{CP}$ + $^3J_{CP}$ = 12.2 Hz, and $^2J_{PP}$ > 150 Hz, 6C), 102.1 (d of d, $^3J_{CF}$ = 18.2 Hz, $^1J_{CF}$ = 39.6 Hz, 1C), 124.4 (d of d, $^3J_{CF}$ = 12.4 Hz, $^1J_{CF}$ = 27.7 Hz, 1C), 144.7 (m, 1C), 149.7 (d of m, $^1J_{CF}$ = 215.6 Hz, 1C), 159.8 (m, 1C), 162.8 (m, 1C). Anal. Calcd for $CH_3(PEt_3)_2Ni(2,3,5\text{-}F_3C_6H_2)$: C, 51.73; H, 8.00. Found: C, 51.79; H, 8.37.

Activation Attempts with Different Lewis Acids. Crystalline $Ni(PEt_3)_4$ (0.079 g, 0.150 mmol), 0.60 mL of tetrahydrofuran, and 1,4-difluorobenzene (0.017 g, 0.150 mmol), were placed in a 2 dram vial. Solid BPh_3 (0.0363 g, 0.150 mmol) was slowly added to the solution at room temperature. The resultant ^{19}F{^{1}H} NMR shows a majority of starting materials, along with many unassigned peaks. None of the peaks present represented the desired product for these reactions. This procedure, with the same results, was done with the following compounds in place of BPh_3: $ZnEt_2$, $FeCl_3$, $FeCl_2$, DIBAL, $SnCl_2$, and $SnCl_3$.

Di- and Trifluorobenzene Competition. Crystalline $Ni(PEt_3)_4$ (0.050 g, 0.0941 mmol), 1,3-difluorobenzene (0.054 g, 0.471 mmol), 1,3,5-trifluorobenzene (0.062 g, 0.471 mmol), and 0.21 mL of C_6D_6 were placed in a 2 dram vial (**A**). Pure $AlMe_3$ (0.007 g, 0.0941 mmol) was added to 0.30 mL of C_6D_6 (**B**). Solution **B** was added dropwise to solution **A** with stirring. ^{1}H, ^{19}F, and ^{31}P NMR spectra were acquired immediately after the reaction mixture was prepared. ^{1}H, ^{19}F, and ^{31}P NMR shifts for $\mathbf{1}_{135}$ and $\mathbf{1}_{13}$ are the same as those reported above. ^{1}H, ^{19}F, and ^{31}P NMR shifts for $\mathbf{2}_{135}$ and $\mathbf{2}_{13}$ are reported in Table 3. Percentage of activation on the basis of ^{19}F NMR integrals: 66% $\mathbf{1}_{135}$, 3% $\mathbf{2}_{135}$, 29% $\mathbf{1}_{13}$, and 2% $\mathbf{2}_{13}$. The same reaction was carried out in the same manner but with substitution of C_6D_6 with 1,4-dioxane, THF, or Et_2O. Percentage of activation on the basis of ^{19}F NMR integrals: for 1,4-dioxane, 78% $\mathbf{1}_{135}$, 4% $\mathbf{2}_{135}$, 14% $\mathbf{1}_{13}$, and 4% $\mathbf{2}_{13}$; for THF, 48% $\mathbf{1}_{135}$, 47% $\mathbf{2}_{135}$, 3% $\mathbf{1}_{13}$,and 2% $\mathbf{2}_{13}$; for Et_2O, 52% $\mathbf{1}_{135}$, 35% $\mathbf{2}_{135}$, 5% $\mathbf{1}_{13}$, and 8% $\mathbf{2}_{13}$.

Crystalline $Ni(PEt_3)_4$ (0.050 g, 0.0941 mmol), 1,3-difluorobenzene (0.054 g, 0.471 mmol), 1,3,5-trifluorobenzene (0.062 g, 0.471 mmol), and 0.21 mL of C_6D_6 were placed in a 2 dram vial (**A**). Pure $AlMe_3$ (0.007 g, 0.0941 mmol) was added to 0.30 mL of C_6D_6. Next THF (0.007 g, 0.104 mmol) was added dropwise (**B**). Solution **B** was added dropwise to solution **A** with stirring. ^{1}H, ^{19}F, and ^{31}P NMR spectra were acquired immediately after reaction was prepared. ^{1}H, ^{19}F, and ^{31}P NMR shifts for $\mathbf{1}_{135}$ and $\mathbf{1}_{13}$ are the same as those reported above. ^{1}H, ^{19}F, and ^{31}P NMR shifts for $\mathbf{2}_{135}$ and $\mathbf{2}_{13}$ are reported in Table 3. Percentage of activation on the basis of ^{19}F NMR integrals: 81% $\mathbf{1}_{135}$, 4% $\mathbf{2}_{135}$, 12% $\mathbf{1}_{13}$, and 3% $\mathbf{2}_{13}$. The same reaction was carried out in the same manner but with substitution of THF with pyridine, trimethylamine, and 1,4-diazabicuclo[2,2,2]octane (DABCO). Percentage of activation on the basis of ^{19}F NMR integrals: for pyridine, 73% $\mathbf{1}_{135}$, 22% $\mathbf{2}_{135}$, 5% $\mathbf{1}_{13}$, and 0% $\mathbf{2}_{13}$; for trimethylamine, 80% $\mathbf{1}_{135}$, 4% $\mathbf{2}_{135}$, 14% $\mathbf{1}_{13}$, and 2% $\mathbf{2}_{13}$; for DABCO, 86% $\mathbf{1}_{135}$, 6% $\mathbf{2}_{135}$, 7% $\mathbf{1}_{13}$, and 1% $\mathbf{2}_{13}$.

Difluorobenzene Competition. Crystalline $Ni(PEt_3)_4$ (0.050 g, 0.0941 mmol), 1,2-difluorobenzene (0.054 g, 0.471 mmol), 1,3-difluorobenzene (0.054 g, 0.471 mmol), 1,4-difluorobenzene (0.054 g, 0.471 mmol), and 0.16 mL of C_6D_6 were placed in a 2 dram vial (**A**). Pure $AlMe_3$ (0.034 g, 0.471 mmol), was added to 0.3 mL of C_6D_6 (**B**). Solution **B** was added dropwise to solution **A** with stirring at room temperature. ^{1}H, ^{19}F, and ^{31}P NMR spectra were acquired immediately after the reaction mixture was prepared. Percentage of activation products: 33% $\mathbf{1}_{12}$, 33% $\mathbf{1}_{13}$, and 33% $\mathbf{1}_{14}$. The same reaction was carried out in the same manner but with substitution of $AlMe_3$ with crystalline $AlMe_3$·(pyridine). Percentage of activation on the basis of ^{19}F NMR integrals: for $AlMe_3$·(pyridine), 76% $\mathbf{1}_{12}$, 21% $\mathbf{1}_{13}$, and 3% $\mathbf{1}_{14}$.

Fluorinated Aromatic Competition Reactions. Crystalline $Ni(PEt_3)_4$ (1.35 g, 2.541 mmol) was dissolved in 8.1 mL of C_6D_6 in a 2 dram vial (**A**). Solution **B** was made 27 different times, as described in Table S1 in the Supporting Information. In general solution **B** consists of 0.471 mmol of two different fluorinated aromatics and 0.471 mmol of crystalline $AlMe_3$·(pyridine) dissolved in benzene topped up to 0.3 mL. A 0.3 mL portion of solution **A** was placed in a 2 dram vial. Solution **B** was added dropwise to solution **A** with stirring at room temperature. Reactions took anywhere from 1 to 30 min to go to completion. ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR spectra were obtained at first and up until completion of the reaction. ^{19}F NMR resonances were used to determine relative rates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00165.

Spectra for compounds $\mathbf{1}_{12,13,14,123a,123b,124,135,1234a,1234b,1245,1235}$ and $\mathbf{2}_{12,13,14,123a,123b,124,135,1234a,1234b,1245,1235}$ (PDF)

Crystallographic data for $\mathbf{1}_{12,13,14,123a,123b,124,135,\ 1245,1235}$ (CIF)

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Notes

The authors declare no competing financial interest.

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