Exploring Trifluoromethylation Reactions at Nickel: A Structural and Reactivity Study

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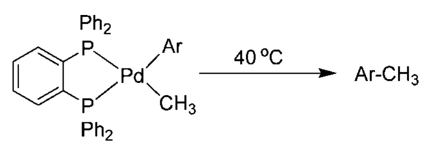
A variety of nickel(aryl)(CF_3) complexes supported by a chelating bisphosphine were successfully prepared in order to investigate the possibility of reductive elimination of Ar−CF_3. The first structural comparison of a Ni−CF_3 complex with a Ni−CH_3 complex is also presented. All of the new nickel(aryl)(CF_3) complexes were thermally stable and did not produce Ar−CF_3 under thermal conditions. Additives had very little effect on the reductive eliminations, although water was found to afford product in 22% yield.

Introduction

Introduction of a trifluoromethyl group into an organic molecule, or even the replacement of an existing functional group with a trifluoromethyl moiety, can alter the physical properties and biological activities of the parent compound in dramatic ways.[1,2] Trifluoromethylation is known to alter the shape and size of the reference substance, its acidity, its dipole moments and polarizability, its lipophilicity and transport behavior, and its chemical and metabolic stability.[1,2] For these reasons, CF_3-bearing aromatics and heteroaromatics are becoming increasingly attractive targets in the pharmaceutical fields. Chart 1 gives some selected CF_3-containing drugs which all show enhanced activities relative to their nonfluorinated analogues.[2]

Since there are no naturally occurring CF_3-containing molecules found in any abundance in nature, all molecules derived thereof have to be synthesized. Cross-coupling procedures would greatly facilitate the construction of molecules containing a trifluoromethyl group; however, they have been slow to develop. This gap in synthetic methodology parallels the fact that only recently have chemists been able to effect cross-coupling reactions using simple alkyl electrophiles and alkyl nucleophiles.[3–11] Metal-mediated fluoroalkyl cross-coupling poses additional challenges, because once a fluoroalkyl group is bound to a metal, unexpected modulations of reactivity are known to ensue. For instance, it has been reported that compound **1** readily loses Ar−CH_3 at 40 °C (eq 1), whereas the fluoroalkyl counterpart **2** did not reductively eliminate Ar−-CF_3 (eq 2), even under forcing conditions.[12] In fact, to our knowledge there is only one reported example of a well-defined reductive elimination of aryl−CF_3 from a palladium complex under reasonable reaction conditions, and catalysis with the same ligand was inneffective.[13]



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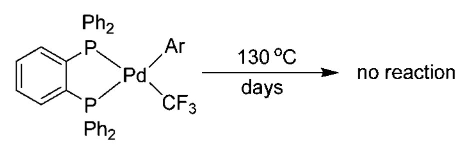

(2)

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The use of a nickel catalyst is an attractive alternative to palladium for fluoroalkyl cross-coupling, not only for cost reasons but also for the fact that nickel has demonstrated much more success in alkyl−alkyl cross-coupling reactions.[3,7,8,10,14–16] Moreover, having easily accessible multiple oxidation states in nickel raises the intriguing possibility of performing redox-triggered reactions such as oxidatively induced reductive eliminations (eq 3).[17,18] Such one-electron-redox chemistry would be inherently more difficult to perform with palladium. Importantly, these redox-triggered reactions are amenable to catalysis, as it is believed, for instance, that catalytic alkyl−alkyl

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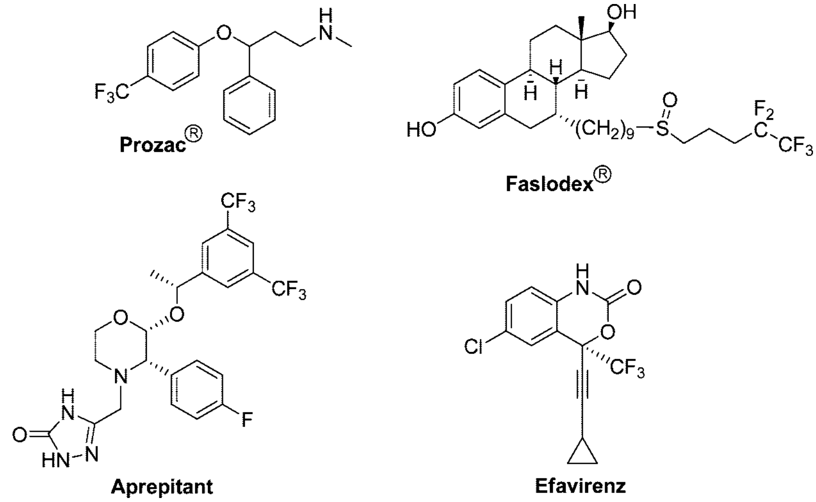
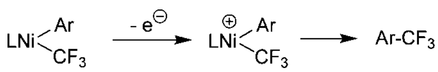
Chart 1. Selected Drugs Bearing a Trifluoromethyl Group



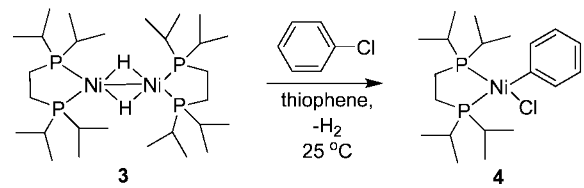
cross-coupling reactions involving terpyridine-based nickel catalysts operate by a stepwise redox shuttle out to Ni^{III}.[8] As there have been few reports of any $Ni-CF_3$ complexes in the literature,[19–26] the chemical foundations relevant to cross-coupling that functional group need to be established. Here we report our initial efforts to understand the many factors controlling trifluoromethylations with nickel.



(3)

Results and Discussion

We chose to investigate the dippe ligand system (dippe = 1,2-bis(diisopropylphosphino)ethane), as it is known that aryl halide complexes of nickel with this ligand can easily be made by the methods outlined in eqs 4 and 5.[27,28] The facile oxidative additions of aryl halides by the (dippe)Ni^0 fragment are desirable for any future catalytic cross-coupling processes involving the dippe ligand. Moreover, the resulting aryl halide complexes such as **4** and **5** are thermally stable, which permits the evaluation of a variety of transmetalation procedures to prepare new (dippe)Ni(aryl)(CF_3) complexes. Lastly, there is precedent that reductive elimination of toluene from Ni(aryl)(CH_3) complexes bearing chelating alkyl phosphines is facile, as Komiya and co-workers reported that (dmpe)Ni(aryl)(CH_3) complexes such as **6** readily decompose at room temperature to yield cross-coupled product (eq 6).[29]



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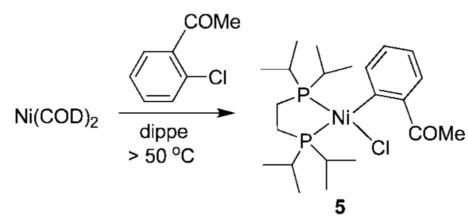

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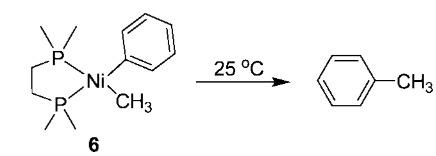

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Using the procedure for oxidative addition described by Carmona and co-workers (eq 7, Table 1), we were able to prepare the four new (dippe)Ni(aryl)(Br) complexes **7**−**10** in good isolated yields. Complexes **7**−**10** all show the signature pair of doublets in the ^{31}P NMR spectra (δ ~70−76) with a J_{P-P} value of approximately 20 Hz, characteristic of (dippe)Ni complexes in the +2 oxidation state.[30] Complexes **7**−**10** were also thermally stable, which then allowed us to try a number of techniques to replace the bromide with a trifluoromethyl group. We found the most reliable method to be the use of $F_3C-SiMe_3$ (Ruppert's reagent) in conjunction with cesium fluoride (eq 7, Table 1). Use of this protocol led to the synthesis of the four new (dippe)Ni(aryl)(CF_3) complexes **11**−**14**. The $Ni-CF_3$ resonances in the ^{19}F NMR spectra for **11**−**14** all appeared at δ ~−20 as doublets of doublets (J_{P-F} = 35, 15 Hz) stemming from the fluorine coupling to cis and trans phosphines on the metal complexes.

X-ray-quality crystals of the naphthalene complex **13** were grown, and the ORTEP diagram is provided in Figure 1. The geometry of the metal in **13** is square planar, with a $Ni-CF_3$ bond distance of 1.9312(14) Å. The only other crystallographi-

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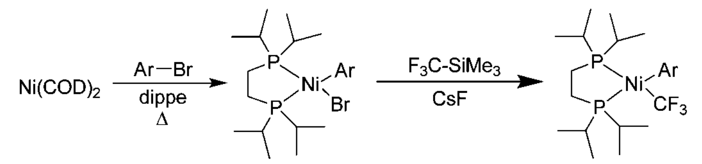
Table 1. Isolated Yields Obtained for the Oxidative Addition and Transmetalation Reactions Described in Eq 7



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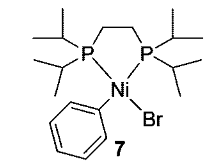
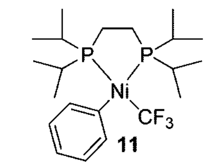
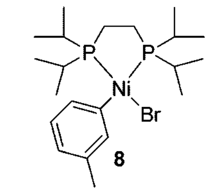
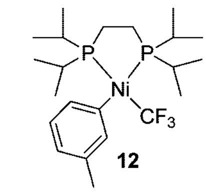
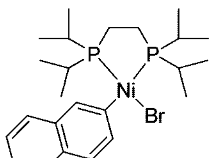
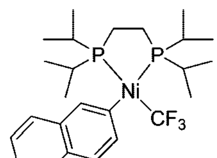
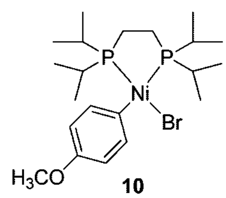
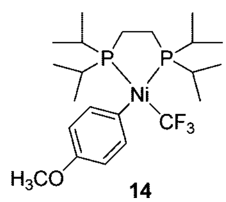
aryl halide product	*yield* (%)	*aryl CF₃ product*	*yield* (%)
 **7**	65	 **11**	57
 **8**	74	 **12**	54
 **9**	88	 **13**	70
 **10**	80	 **14**	68

cally characterized Ni−CF_3 complex reported previously was CpNi(CF_3)(PPh_3), which had a Ni−CF_3 distance of 1.946(29) Å.[31] The naphthalenyl ligand in **13** was modeled as disordered over two positions (53:47) for the X-ray structure determination, and with such a model the data could be refined to a final *R* value of 4.6% (see the Supporting Information).

During the course of preparing the (dippe)Ni(aryl)(CF_3) complexes as described in eq 7, we noticed that (dippe)Ni(CF_3)$_2$ (**15**) was formed as a common major side product, as confirmed by X-ray crystallography. Figure 2 (top) shows the ORTEP diagram of **15**, which again shows a square-planar geometry at nickel. The Ni−CF_3 bond length of 1.971(3) Å in complex **15** is considerably longer than that found for **13** (1.9312(14) Å), perhaps due to the increased sterics at the metal center for a compound containing two CF_3 groups. Since the formulation of complex **15** is strikingly similar to those of the known nonfluorinated analogues (dippe)Ni(CH_3)$_2$ (**16**)[32,33] and (dtbpe)NiMe$_2$ (**17**; dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane),[34] crystals of **16** were grown to compare the solid-state structures.

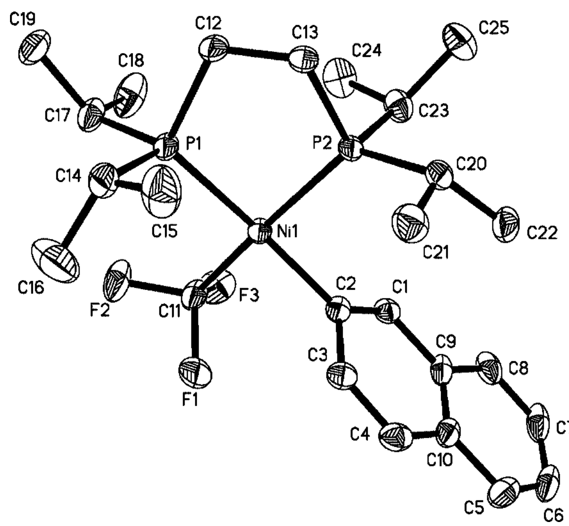


Figure 1. ORTEP diagram of **13**. Ellipsoids are shown at the 50% level. All hydrogens are omitted for clarity. Selected bond lengths (Å): Ni(1)−C(2) = 1.923(6), Ni(1)−C(11) = 1.9312(14), Ni(1)−P(2) = 2.1891(4), Ni(1)−P(1) = 2.2077(4). Selected bond angles (deg): C(2)−Ni(1)−C(11) = 86.4(2), C(2)−Ni(1)−P(2) = 90.1(2), C(11)−Ni(1)−P(2) = 167.73(5), C(2)−Ni(1)−P(1) = 167.63(11), C(11)−Ni(1)−P(1) = 97.86(4).

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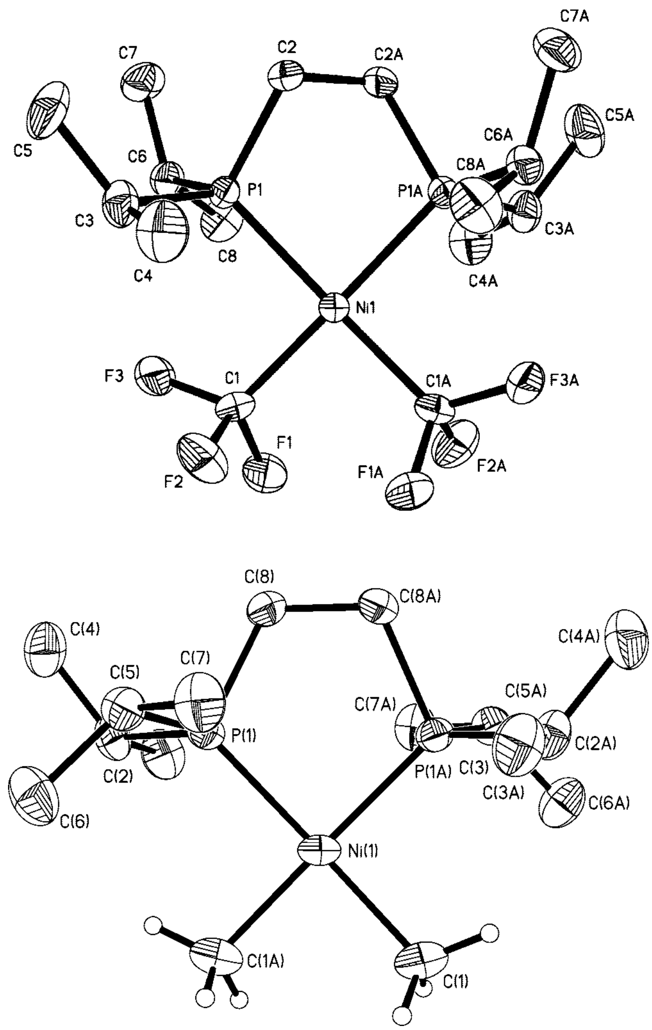
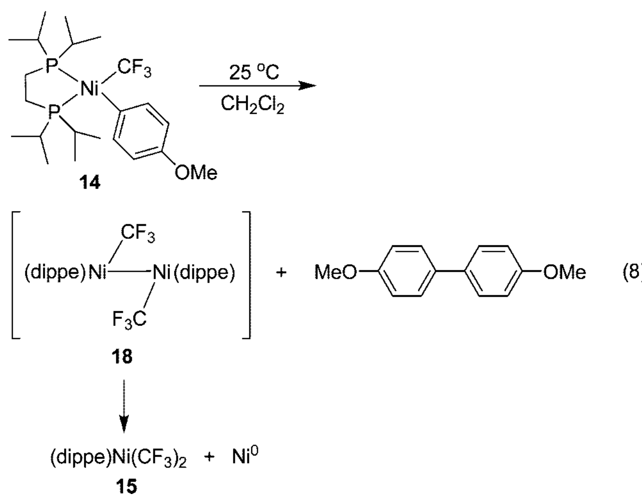


Figure 2. ORTEP diagrams of (dippe)Ni$(CF_3)_2$ (**15**, top) and (dippe)Ni$(CH_3)_2$ (**16**, bottom). Ellipsoids are shown at the 50% level. All hydrogens, except those on the methyls directly bound to nickel in **16**, are omitted for clarity. Selected bond lengths for **15** (Å): Ni(1)−C(1) = 1.971(3), Ni(1)−P(1) = 2.2050(9). Selected bond angles for **15** (deg): C(1)−Ni(1)−P(1) = 91.81(9), C(1A)−Ni(1)−C(1) = 90.28(17). Selected bond lengths for **16** (Å): Ni(1)−C(1) = 1.975(3), Ni(1)−P(1) = 2.1608(11). Selected bond angles for **16** (deg): C(1A)−Ni(1)−P(1) = 92.51(10), C(1)−Ni(1)−C(1A) = 86.85(18).

Crystals were obtained by cooling a pentane solution of **16**, and the ORTEP diagram is shown in Figure 2 (bottom). This study marks the first time a trifluoromethyl complex of nickel and its nonfluorinated analogue have been structurally characterized. The X-ray data show a number of interesting structural features. First, the Ni−CH_3 bond lengths in **16** and **17** (1.975(3) and 1.971(10) Å) and the Ni−CF_3 bond lengths in **15** (1.971(3) Å) are essentially the same. However, the Ni−P bond trans to the methyl in **16** is 2.1608(11) Å, while the Ni−P bond trans to the trifluoromethyl in **15** is much longer at 2.2050(9) Å. The fact that the methyl group should in theory exhibit a more pronounced trans influence than the trifluoromethyl group suggests a couple of possibilities for the anomalous bond lengths. First, the steric crowding introduced by the fluorines in **15** may push the phosphine ligand further away from the metal relative to the nonfluorinated analogue **16**. Since the Ni−P bond trans to the methyl is **17** is also elongated at 2.213(1) Å, the role of sterics in the bis-CF_3 complex is considered quite important. Indeed, the Me−Ni−Me bond angles in **16** and **17** (86.85(18) and 83.7(2)°, respectively) are much smaller than the CF_3−Ni−CF_3 bond angle in **15** (90.28(17)°). Alternatively, competitive electron donation from the nickel to a low-lying σ^* orbital of the trans Ni−CF_3 bond[35,36] may be a factor in the Ni−P elongation in **15**.

We found that none of the new (dippe)Ni(aryl)(CF_3) complexes yielded Ar−CF_3 upon heating. Solutions of (dippe)Ni(aryl)(CF_3) are stable in THF solvent for days at room temperature but eventually turn green and ultimately afford the biaryl and complex **15** (eq 8, for example). This reaction is accelerated in CH_2Cl_2 solvent, where substantial biphenyl production occurs only in hours. We tentatively attribute the common diamagnetic green intermediate (^{19}F NMR (CD_2Cl_2) δ −75.5 (dd, J = 41.6, 18.8 Hz)) to the formation of the dinuclear species **18**, containing a nickel−nickel bond. Related nickel(I) dimers are known,[37] and the presence of such an intermediate also nicely explains the formation of (dippe)Ni$(CF_3)_2$ as a major side product in the transmetalation procedure. In contrast to the reluctance of **11**−**14** to reductively eliminate Ar−CF_3, their nonfluorinated analogues were found to decompose within minutes at room temperature to afford Ar−CH_3 in near-quantitative yields.[38]



Because thermolysis of the (dippe)Ni(aryl)(CF_3) complexes did not yield any cross-coupled product, we explored the use of additives to facilitate reductive elimination reactions at **11** (Table 2). Two potent[39] oxidants based on Fe^{3+} and Ce^{4+} did not yield any of the desired trifluorotoluene, even when used in excess (Table 2, entries 1 and 2). Ar−H was detected as the major organic product in these oxidation reactions. Excess Ph−Br, which would be present in any catalytic trifluoromethylation process involving Ph−Br, did not lead to any products (Table 2, entry 3), even at elevated temperatures. Zinc reagents were found to initiate reductive elimination of Ar−CF_3, but only to a small degree (Table 2, entries 4 and 5). Surprisingly, the introduction of water had the most beneficial effect, producing the desired product in 22% yield (Table 2, entry 6). Unfortunately, water also had the undesired effect of hydrolysis, as PhCOF (^{19}F NMR δ +15.8) accounted for 69% of the other product. Similar reactivity had been observed by Grushin and

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(38) In a typical experiment, 1 equiv of MeLi was added to a cooled solution of (dippe)Ni(Ar)Br in THF at−30 °C. The solutions were then warmed to room temperature and stirred for 24 h before analysis.
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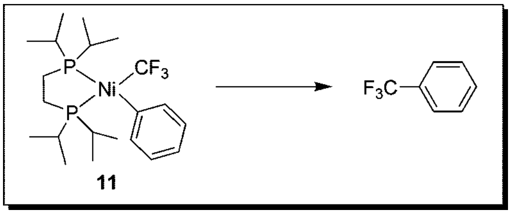
Table 2. Effect of Additives on the Thermolysis of 11



entry	additive (amt (equiv))	conditions	yield of $PhCF_3$ (%)[a]
1	$Fe(bpy)_3(PF_6)_3$ (1)	THF, 25 °C, 3 days	0
2	$(NH_4)_2Ce(NO_3)_6$ (5)	THF, 25 °C, 3 days	0
3	Ph−Br (95)	THF, 25 °C, 3 days	0
4	PhZnBr (25)	THF, 25 °C, 3 days	11
5	$ZnBr_2$ (5)	THF, 25 °C, 14 h	19
6	H_2O (100)	toluene, 80 °C, 5 h	22

[a] Yields determined by ^{19}F NMR relative to 2-fluoro-1,3-dimethylbenzene as an internal standard.

co-workers with a Pd−CF_3 complex.[40] A green solid had also precipitated in the reaction with water, which we attribute to $Ni(OH)_2$. Although attempts to further optimize the cross-coupling reactions in entries 4−6 were fruitless, the data do suggest that trifluoromethylations are indeed possible at nickel, even at room temperature. Ligands of other geometries and hapticities may better coax a reductive elimination of Ar−CF_3 at nickel, and these will be a focus of further study.

Experimental Section

General Considerations. All manipulations were performed using standard Schlenk and high-vacuum techniques[41] or in a nitrogen-filled drybox, unless otherwise noted. Solvents were distilled from Na/benzophenone or CaH_2. All reagents were used as received from commercial vendors, unless otherwise noted. Aluminum oxide (activated, neutral, Brockmann I, ∼150 mesh) was dried at 200 °C under vacuum for 2 days prior to use. Elemental analyses were performed by Desert Analytics. ^{1}H NMR spectra were recorded at ambient temperature (unless otherwise noted) on a Varian Oxford 300 MHz spectrometer and referenced to residual proton solvent peaks. ^{31}P spectra were recorded on the Varian Oxford spectrometer operating at 121 MHz and referenced to an 85% phosphoric acid external standard set to 0 ppm. ^{19}F spectra were recorded on the Varian Oxford spectrometer operating at 282 MHz and were referenced to $CFCl_3$ set to zero. A Rigaku SCXMini diffractometer (University of Hawaii) and a Bruker SMART APEX II CCD Platform diffractometer (University of Rochester) were used for X-ray structure determinations. Table 3 gives crystal data and structure refinement parameters for **13**, **15**, and **16**.

General Procedure To Prepare the (dippe)Ni(Ar)Br Complexes 7−10. A 100 mL round-bottom flask (RBF) was charged with $Ni(COD)_2$ (1.375 g, 5 mmol), dippe (1.52 mL, 5 mmol), and toluene (50 mL). The dark brown solution was stirred for 10 min at room temperature, and then 5 mmol of corresponding ArBr was added. The resulting solution was stirred at 50 °C for 3 days under a nitrogen atmosphere, at which time a yellow precipitate was observed. The resulting suspension was reduced in volume on a high-vacuum line, and the solids were filtered, washed with toluene and pentane, and dried under vacuum.

(dippe)Ni(Ph)Br (7). Yield: 65%. ^{1}H NMR (CD_2Cl_2): δ 7.85 (t, J = 6.3 Hz, 2H), 6.93 (t, J = 6.3, 2H), 6.75 (t, J = 6.3 Hz, 1H), 2.35 (m, 2H), 2.15 (m, 2H), 1.81−1.01 (m, 28H). ^{31}P NMR (CD_2Cl_2): δ 76.91 (d, J = 20.6 Hz), 71.23 (d, J = 20.6 Hz). Anal. Calcd (found) for $C_{20}H_{37}BrNiP_2$: C, 50.25 (50.54); H, 7.80 (7.95).

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Table 3. Crystal Data and Structure Refinement Parameters for 13, 15, and 16

	13	15	16
chem formula	$C_{25}H_{39}F_3NiP_2$	$C_{16}H_{32}F_6NiP_2$	$C_{16}H_{38}NiP_2$
formula wt	517.21	459.07	351.11
cryst dimens (mm)	0.36 × 0.16 × 0.12	0.30 × 0.20 × 0.10	0.24 × 0.13 × 0.13
color, habit	yellow, block	yellow, block	yellow, block
cryst syst	triclinic	monoclinic	monoclinic
wavelength (Å)	0.710 70	0.710 70	0.710 70
abs coeff (mm^{-1})	0.923	1.143	1.163
space group, Z	$P\bar{1}$, 2	$C2/c$, 4	$C2/c$, 4
a (Å)	8.5134(12)	14.267(4)	12.837(7)
b (Å)	11.8936(17)	8.586(2)	8.514(5)
c (Å)	13.4820(19)	17.109(4)	17.740(10)
α (deg)	105.110(2)	90	90
β (deg)	94.789(2)	99.819(4)	96.954(11)
γ (deg)	102.992(2)	90	90
V (Å^3)	1269.5(3)	2065.1(9)	1924.7(19)
ρ_{calcd} (Mg/m^3)	1.353	1.477	1.212
temp (K)	100	−100	−173
R indices ($I > 2\sigma(I)$)	0.0331, 0.0763	0.0491, 0.1258	0.0448, 0.0807
R indices (all data)	0.0457, 0.0821	0.0599, 0.1296	0.0704, 0.0875
goodness of fit	1.037	1.104	1.084
θ range (deg)	1.83−32.03	2.42−32.03	3−27.48
no. of data collected	22471	17421	6433
no. of unique data	8722	3580	2193
R_{int}	0.0242	0.0386	0.0510

(dippe)Ni(3-Me-Ph)Br (8). Yield: 74%. ^{1}H NMR (C_6D_6): δ 7.79 (d, J = 5.1 Hz, 1H), 7.71 (t, J = 6.3 Hz, 1H), 7.24 (t, J = 7.2, 1H), 6.91 (d, J = 7.2 Hz, 1H), 2.41 (s, 3H), 2.30 (m, 2H), 1.92 (m, 2H), 1.6−0.86 (m, 28 H). ^{31}P NMR ($CDCl_3$): δ 74.79 (d, J = 20.11 Hz), 69.75 (d, J = 20.11 Hz). Anal. Calcd (found) for $C_{21}H_{39}BrNiP_2$: C, 51.26 (51.10); H, 7.99 (8.07).

(dippe)Ni(naphthyl)Br (9). Yield: 83%. ^{1}H NMR (DMSO-d_6): δ 7.76 (m, 2H), 7.64 (t, J = 8.9 Hz, 2H), 7.45 (d, J = 8.4, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H), 2.27 (m, 2H), 1.90 (m, 2H), 1.6−1.13 (m, 28H). ^{31}P NMR (DMSO-d_6): δ 76.9 (m), 73.3 (d, J = 19.9 Hz). Anal. Calcd (found) for $C_{24}H_{39}BrNiP_2$: C, 54.58 (53.15); H, 7.44 (7.27).

(dippe)Ni(4-OMe-Ph)Br (10). Yield: 80%. ^{1}H NMR (CD_2Cl_2): δ 7.29 (t, J = 7.1 Hz, 2H), 6.64 (d, J = 7.5 Hz, 2H), 3.69 (s, 3H), 2.36 (m, 2H), 2.14 (m, 2H), 1.8−1.03 (m, 28H). ^{31}P NMR (CD_2Cl_2): δ 76.3 (d, J = 19.9 Hz), 70.6 (d, J = 20.1 Hz). Anal. Calcd (found) for $C_{21}H_{39}BrNiOP_2$: C, 49.64 (50.15); H, 7.74 (7.47).

General Procedure To Prepare the (dippe)Ni(Ar)(CF$_3$) Complexes 11−14. A 50 mL round-bottom flask (RBF) was charged with the corresponding (dippe)Ni(Ar)(Br) (**7**−**10**; 1 mmol), CsF (304 mg, 2 mmol), $CF_3Si(CH_3)_3$ (0.296 mL, 2 mmol), and THF (25 mL). The reaction mixture was stirred for 14 h at room temperature under a nitrogen atmosphere. The reactions were monitored by taking aliquots and measuring the ^{31}P NMR and ^{19}F spectra. When all starting material had been consumed, the reaction mixture was filtered through a 1 cm pad of alumina, and the filtrate was concentrated under high vacuum. The solids were washed with toluene and pentane and dried under vacuum.

(dippe)Ni(Ph)(CF$_3$) (11). Yield: 57%. ^{1}H NMR (THF-d_8): δ 7.47 (m, 2H), 7.2−6.9 (m, 3H), 2.30 (m, 1H), 2.08 (m, 2H), 1.83 (m, 2H), 1.06−0.96 (m, 27H). ^{31}P NMR (THF-d_8): δ 75.75 (m), 63.97 (dq, J = 35.6, 9.1 Hz). ^{19}F NMR (THF-d_8): δ −19.97 (dd, J = 34.6, 15.3). Anal. Calcd (found) for $C_{21}H_{37}F_3NiP_2$: C, 53.99 (54.50); H, 7.98 (7.69).

(dippe)Ni(3-Me-Ph)(CF$_3$) (12). Yield: 54%. ^{1}H NMR (CD_2Cl_2): δ 8.0 (d, J = 6.2 Hz, 1H), 7.85 (t, J = 6.3 Hz, 1H), 7.54 (t, J = 7.2, 1H), 7.02 (d, J = 7.2 Hz, 1H), 2.5 (s, 3H), 2.30 (m, 2H), 1.92 (m, 2H), 1.6−0.9 (m, 28 H). ^{31}P NMR (CD_2Cl_2): δ 75.53 (m), 63.97 (dq, J = 37, 10.9 Hz). ^{19}F NMR (CD_2Cl_2): δ −16.54 (dd, J = 37, 15.5 Hz). Anal. Calcd (found) for $C_{22}H_{39}F_3NiP_2$: C, 54.91 (54.62); H, 8.17 (7.90).

(dippe)Ni(naphthyl)(CF$_3$) (13). Yield: 70%. ^{1}H NMR (C_6D_6): δ 8.21−7.2 (m, 7H), 2.16 (m, 2H), 1.78 (m, 2H), 1.5−0.5 (m, 28H).

^{31}P NMR (C_6D_6): δ 77.14 (m), 65.82 (dq, J = 36.1, 10.1 Hz). ^{19}F NMR (C_6D_6): δ −19.6 (dd, J = 35.3, 15.5 Hz). Anal. Calcd (found) for $C_{25}H_{39}F_3NiP_2$: C, 58.05 (57.50); H, 7.60 (7.50).

(dippe)Ni(4-OMe-Ph)(CF$_3$) (14). Yield: 68%. ^{1}H NMR (THF-d_8): δ 7.29 (m, 2H), 6.66 (d, J = 7.6 Hz, 2H), 3.70 (s, 3H, OCH_3), 2.34 (m, 1H), 2.22 (m, 1H), 2.06 (m, 2H), 1.73−1.05 (m, 28H). ^{31}P NMR (THF-d_8): δ 75.9 (m), 64.3 (dq, J = 36, 9.5 Hz). ^{19}F NMR (THF-d_8): δ −19.7 (dd, J = 35.8, 15.9 Hz). Anal. Calcd (found) for $C_{22}H_{39}F_3NiOP_2$: C, 53.15 (52.80); H, 7.91 (7.75).

(dippe)Ni(CF$_3$)$_2$ (15). A 100 mL round-bottom flask was charged with (dippe)NiI$_2$ (575 mg, mmol), CsF (755 mg, 5 mmol), and $CF_3Si(CH_3)_3$ (0.735 mL, 5 mmol) in 50 mL of THF. An additional 5 mmol of CsF/$CF_3Si(CH_3)_3$ was added after 10 h. The reaction mixture was stirred at room temperature in a glovebox for 2 days and then was filtered through a pad of Celite. The filtrate was reduced in volume on a high-vacuum line, filtered, washed with a minimal amount of THF and then copious amounts of pentane, and dried. Yield: 26%. ^{1}H NMR (CD_2Cl_2): δ 2.27 (h, J = 7.2 Hz), 1.69 (d, J = 12.7 Hz, 4H), 1.43 (dd, J = 17.4, 7.3 Hz, 12H), 1.22 (dd, J = 12.1, 7.0 Hz, 12H). ^{31}P NMR (CD_2Cl_2): δ 75.1 (dd, J = 23.6, 30.5 Hz). ^{19}F NMR (CD_2Cl_2): δ −20.0 ((dd, J = 23.8, 30.8 Hz). Anal. Calcd (found) for $C_{16}H_{32}F_6NiP_2$: C, 41.86 (40.80); H, 7.03 (7.30).

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Supporting Information Available: CIF files giving crystal data for **13**, **15**, and **16** and figures giving NMR spectra of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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