ORGANOMETALLICS
Article

Organometallics **2010,** *29,* 6077–6091 6077
DOI: 10.1021/om1008499

Carbon−Hydrogen Bond Oxidative Addition of Partially Fluorinated Aromatics to a Ni(P^iPr_3)$_2$ Synthon: The Influence of Steric Bulk on the Thermodynamics and Kinetics of C−H Bond Activation

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Received September 1, 2010

The reaction of (P^iPr_3)$_2$NiCl$_2$ with the anthracene adduct (THF)$_3$Mg(η^2-$C_{14}H_{10}$) in THF provides the anthracene adduct (P^iPr_3)$_2$Ni(η^2-$C_{14}H_{10}$). In aromatic solvents (benzene, toluene, mesitylene) a thermal equilibrium exists between the bis(phosphine)nickel(0) anthracene adduct, (P^iPr_3)$_2$Ni(η^2-$C_{14}H_{10}$), and the monophosphine solvent adduct, (P^iPr_3)Ni(η^6-solvent). The reaction of (P^iPr_3)$_2$Ni(η^2-$C_{14}H_{10}$) with 1,2,4,5-$C_6F_4H_2$ affords the C−H activation product *trans*-(P^iPr_3)$_2$NiH(2,3,5,6-C_6F_4H). The thermodynamic C−F activation product is not obtained even after hours of heating at 100 °C. Similar reactions with 1,2,3,5-$C_6F_4H_2$ and pentafluorobenzene produce the desired C−H activation products, *trans*-(P^iPr_3)$_2$NiH-(2,3,4,6-C_6F_4H) and *trans*-(P^iPr_3)$_2$NiH(C_6F_5), respectively, in >95% yield. The reaction with 1,2,3,4-tetrafluorobenzene did not produce an observable C−H activation product. Unlike previously reported analogous C−H activation products with Ni(PEt_3)$_2$ synthons, the bulkier Ni(P^iPr_3)$_2$ moiety did not provide observable mononuclear or dinuclear η^2-fluoroarene adducts. Solutions of Ni(COD)$_2$ with 2 equiv of triisopropylphosphine and 1,2,4,5-$C_6F_4H_2$ reacted to give the 1,5-cyclooctadiene insertion and rearrangement product, (η^3-C_8H_{13})Ni(P^iPr_3)(2,3,5,6-C_6F_4H). The same reaction with 1,2,3,5- and 1,2,3,4-$C_6F_4H_2$ afforded analogous compounds, which demonstrates that C−H bond activation is kinetically accessible at room temperature with 1,2,3,4-tetrafluorobenzene despite the presence of a single *ortho*-fluorine substituent adjacent to the site of activation. The room-temperature reactions of the C−H activation products (P^iPr_3)$_2$NiH(Ar^F) (Ar^F = 2,3,5,6-C_6F_4H; C_6F_5) with 3-hexyne provided a mixture of the alkyne adduct (P^iPr_3)$_2$Ni(η^2-EtC≡CEt), with the liberation of Ar^FH, and the insertion product (P^iPr_3)$_2$Ni(CEt=CHEt)(Ar^F), even in the presence of excess fluorinated aromatic Ar^FH. The reaction of (P^iPr_3)$_2$Ni(η^2-EtC≡CEt) with 1,2,4,5-$C_6F_4H_2$ resulted in no reaction at room temperature, but heating at 50 °C provided the insertion product (P^iPr_3)$_2$Ni(CEt=CHEt)(Ar^F) as the initial product, followed by the product of reductive elimination, 1,2,4,5-C_6F_4H-CEt=CHEt. In contrast, the reaction of (PEt_3)$_2$Ni(η^2-EtC≡CEt) with 1,2,4,5-$C_6F_4H_2$ at 80 °C slowly produced (PEt_3)$_2$Ni(CEt=CHEt)(2,3,5,6-C_6F_4H), but very little 1,2,4,5-C_6F_4H-CEt=CHEt.

Introduction

Fluorinated organics have found extensive modern use in applications such as pharmaceuticals and agrochemicals.[1] Although fluorinating strategies based on both electrophilic and nucleophilic reagents have been devised for the preparation of these species,[2] an alternate synthetic approach starting from fluorinated precursors can also be envisaged.[3] For example, partially fluorinated arenes could be functionalized using transition metal catalysts capable of either C−H[4−6] or C−F[3,7−11]

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Published on Web 10/28/2010

bond activation. This could be a particularly efficient strategy for the synthesis of pharmaceuticals with polyfluorinated substituents.[12] Nickel complexes have been suggested as optimal catalysts for transformations that involve C−F activation not only because of the low cost of nickel but because of the reduced propensity of nickel complexes to undergo C−H bond activation[13−18] versus C−F bond activation[10,11,15−23] in partially fluorinated aromatics. In support of this suggested selectivity, DFT calculations have predicted that C−H bond oxidative addition of C_6H_6 to the $(H_2PCH_2CH_2PH_2)Ni$ fragment should be strongly thermodynamically disfavored.[18] Experimentally, the selective activation of C−F bonds in partially fluorinated benzenes by nickel complexes has been achieved only rarely, with the use of phosphine,[15,17] N-heterocyclic carbene,[23] and nitrogen donor ancillary ligands,[20] despite numerous examples that involve perfluorinated substrates.[7,9,11,19,20,22−25] The catalytic functionalization of aromatic C−F bonds via oxidative addition to Ni catalysts has been almost[7] entirely limited to substrates that do not contain reactive C−H bonds.[9,26]

In contrast to the predictions made using DFT calculations, the reactions of the anthracene complex $(PEt_3)_2Ni(\eta^2\text{-}C_{14}H_{10})$[27] with an excess of pentafluorobenzene produced the C−H activation product $(PEt_3)_2NiH(C_6F_5)$ as a kinetic product prior to C−F bond activation.[17] This species was in nearly thermoneutral equilibrium with mononuclear and dinuclear adducts, which prevented isolation. Similar C−H activation was observed in an analogous reaction with 1,2,4,5-tetrafluorobenzene.[15] In comparison to calculated predictions based on the oxidative addition of C_6H_6 to $(H_2PCH_2CH_2PH_2)Ni$,[18] the almost thermoneutral C−H activation of C_6F_5H from the mononuclear adduct, $(PEt_3)_2Ni(\eta^2\text{-}C_6F_5H)$, can be attributed partially to the stronger nickel−carbon bonds formed, due to the fluorine substituents,[28] as well as to the improved donor properties of phosphines bearing alkyl rather than H substituents.[29] However, an additional factor that could be used to provide further thermodynamic driving force for C−H bond oxidative additions is the steric bulk of the nonchelating ancillary ligand. Although complexes with the chelating ligand $H_2PCH_2CH_2PH_2$ can gain no energy from *cis*- to *trans*-isomerization upon oxidative addition, the energy for related nickel complexes bearing nonchelating donors has been calculated to be significant.[23] It can be hypothesized that increasingly sterically bulky nonchelating phosphines could thermodynamically favor the C−H bond activation of even weakly activated substrates.

During our investigation into this hypothesis, catalytic reactions have been reported where Ni complexes bearing bulky secondary alkyl phosphine donors mediate C−H bond functionalization via mechanisms that are proposed to involve C−H bond oxidative addition. This includes examples where partially fluorinated arenes undergo formal insertion of alkynes into sp^2 C−H bonds[5,30] and C−H bond stannylation reactions using $Bu_3SnCH{=}CH_2$,[4] which are shown in Figure 1. This nickel-mediated C−H bond functionalization methodology has also been extended to pyridines and related derivatives;[31,32] however, the proposed nickel hydride intermediates that arise from oxidative addition have not yet been isolated. Could the $Ni(PEt_3)_2$ moiety have entirely different reactivity than more sterically encumbered analogues, such as $PCyp_3$ (Cyp = cyclopentyl) or P^iPr_3? It is remarkable that these catalytic systems, which operate selectively at 80 °C, display no products that arise from C−F bond activation.

Herein, we report the synthesis of a new $(P^iPr_3)_2Ni$ synthon and study the effect of phosphine size on the ability to react with pentafluorobenzene and the tetrafluorobenzenes

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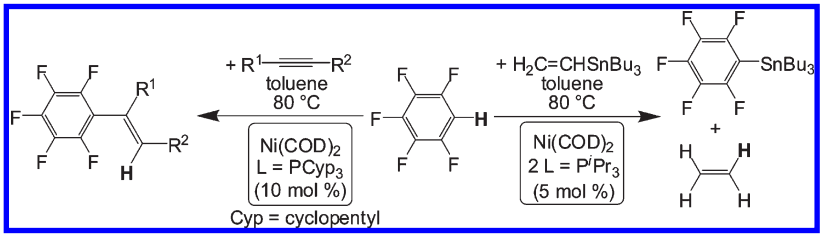
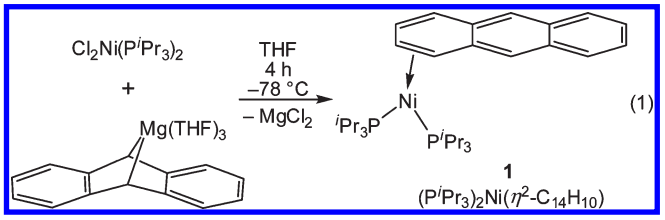


Figure 1. Two examples of the nickel-catalyzed C−H functionalization of a partially fluorinated aromatic, proposed to occur via C−H bond oxidative addition to nickel.

via C−H bond oxidative addition. Reactions that probe the utility of these $(P^iPr_3)_2Ni$ C−H bond activation products in catalytic C−H bond functionalization are also described.

Results and Discussion

It has been previously shown that that the anthracene and phenanthrene adducts $(PEt_3)_2Ni(\eta^2\text{-}C_{14}H_{10})$ serve as $(PEt_3)_2Ni$ synthons in reactions with the fluorinated benzenes.[15,17] A similar approach was taken to provide a $(P^iPr_3)_2Ni$ synthon using an anthracene adduct. The reaction of $(P^iPr_3)_2NiCl_2$ with an excess $(THF)_3Mg(\eta^2\text{-}C_{14}H_{10})$ in THF afforded the deep red, 16-electron complex **1**, as shown in eq 1. Complex **1** is very soluble in nonpolar organic solvents at room temperature, such as pentane and hexamethyldisiloxane. Multiple recrystallizations provided **1** in 71% yield.



Single crystals of **1** suitable for structural analysis by X-ray crystallography were obtained from slow evaporation of a pentane solution at −40 °C. An ORTEP depiction of the solid-state molecular structure is shown in Figure 2. X-ray crystallographic collection and refinement parameters are provided in Table 1. The $Ni(P^iPr_3)_2$ fragment is η^2-coordinated to the 1,2-position of anthracene. The geometry of the nickel metal center is approximately planar. There is a loss of planarity in the anthracene moiety due to back-bonding by nickel, as confirmed by a lengthened C(1)−C(2) distance of 1.427(4) Å, which is comparable to 1.422(4) Å in the analogous anthracene adducts $(PCy_3)_2Ni(\eta^2\text{-}C_{14}H_{10})$[33] and $(PEt_3)_2Ni(\eta^2\text{-}C_{14}H_{10})$.[27] The C(3)−C(4) bond length of 1.347(4) Å is indicative of a nearly localized double bond. The larger size of the P^iPr_3 donor compared to PEt_3 would be expected to result in a larger P−Ni−P angle in complex **1** compared to $(PEt_3)_2Ni(\eta^2\text{-}C_{14}H_{10})$, due to increased steric repulsion, but should be similar to that observed for $(PCy_3)_2Ni(\eta^2\text{-}C_{14}H_{10})$. This is confirmed in the observed angle of 119.07(3)°, which is significantly larger than the angles of 106.4(3)° and 108.9(1)° for the PEt_3 and $^nBu_3P$ analogues, respectively,[27] yet comparable to the PCy_3 analogue, whose angle is 118.3(1)°.[33]

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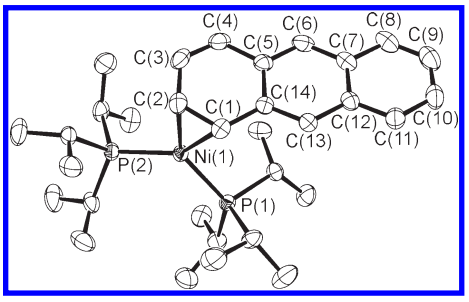


Figure 2. ORTEP depiction of the solid-state molecular structure of **1** as determined by X-ray crystallography. Hydrogen atoms are omitted for clarity. The 30% probability ellipsoids are shown. Selected bond lengths (Å): Ni(1)−P(1), 2.2197(8); Ni(1)−P(2), 2.2218(8); Ni(1)−C(1), 2.041(3); Ni(1)−C(2), 2.003(3); C(1)−C(2), 1.427(4); C(1)−C(14), 1.459(4); C(2)−C(3), 1.439(4); C(3)−C(4), 1.347(4); C(4)−C(5), 1.446(4); C(5)−C(14), 1.435(4). Selected bond angles (deg): P(1)−Ni(1)−P(2), 119.07(3); C(2)−C(1)−C(14), 119.7(3); C(1)−C(2)−C(3), 117.4(3); C(2)−C(3)−C(4), 123.0(3); C(3)−C(4)−C(5), 121.1(3); C(1)−C(5)−C(14), 119.1(3).

Complex **1** was characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. The variable-temperature ^1H and $^{31}P\{^1H\}$ NMR spectra in nonaromatic solvents, such as pentane and THF-d_8, are consistent with a fluxional complex. The 121.5 MHz $^{31}P\{^1H\}$ NMR experimental and modeled spectra of **1** in THF-d_8 between 233 and 298 K are shown in Figure 3. The 298 K $^{31}P\{^1H\}$ NMR spectrum displays a single broad resonance at δ 44.4. Below the coalescence temperature of 273 K, the peak resolves into two doublets, with a $^2J_{PP}$ value of 45 Hz. These variable-temperature NMR spectra can be modeled using the Arrhenius equation to estimate an 18.0 kcal·mol^{-1} activation energy for this process. At 298 K, the ^1H NMR spectrum displays only five resonances for the anthracene moiety in **1**, rather than 10 environments expected for a C_1 symmetric complex. The protons associated with C(1), C(2), C(3), and C(4) appear as broad singlets at δ 5.3 and 5.6 with peak widths at half-height of 35 Hz in the 300 MHz ^1H NMR spectrum, whereas the remaining protons of the anthracene moiety appear in the range δ 7.17−8.43. At 233 K, the resonances at δ 5.3 and 5.6 are resolved doublets with a $^3J_{HH}$ value of 8.5 Hz. At lower temperatures these peaks broaden, but decoalescence was not observed as low as 193 K. This suggests that unlike the 18.0 kcal·mol^{-1} barrier to ^{31}P exchange, the exchange of ^1H environments has a much lower barrier, though the lack of a slow-exchange spectrum prevents the estimation of the energy barrier. The ^1H environments could be exchanged by a haptotropic rearrangement between the 16-electron complex $(P^iPr_3)_2Ni(\eta^2\text{-}C_{14}H_{10})$ and the 18-electron complex $(P^iPr_3)_2Ni(\eta^4\text{-}C_{14}H_{10})$.

Table 1. Crystallographic Data for Compounds 1, 3, 4, 6, and 9

	1	3	4	6	9
empirical formula	$C_{32}H_{52}NiP_2$	$C_{24}H_{44}F_4NiP_2$	$C_{24}H_{43}F_4NiP_2$	$C_{23}H_{35}F_4NiP$	$C_{24}H_{52}NiP_2$
fw	557.39	529.24	528.23	477.19	461.31
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
a (Å)	16.302(3)	10.8870(9)	13.1370(6)	10.2723(12)	12.8640(15)
b (Å)	17.505(3)	13.4940(11)	11.9971(6	12.3685(14)	11.5975(13)
c (Å)	21.845(3)	20.7527(13)	17.7312(8)	18.484(2)	18.859(2)
α (deg)	90.0	90.0	90.0	90.0	90.0
β (deg)	90.0	113.002(3)	95.243(10)	98.796(10)	102.332(1)
γ (degrees)	90.0	90.0	90.0	90.0	90.0
V (Å^3)	6233.8(17)	2806.4(4)	2782.8(2)	2320.9(5)	2746.51(8)
space group	*Pbca*	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$
Z value	8	4	4	4	4
D_{calc} (g/cm^3)	1.188	1.253	1.261	1.366	1.116
μ(MoKα) (mm^{-1})	0.743	0.841	0.848	0.943	0.830
temperature (K)	173(2)	173(2)	213(2)	173(2)	173(2)
$2\theta_{max}$ (deg)	55.0	50.0	50.0	50.0	55.0
total no. of reflns	66 314	30 635	14 391	21 781	14 282
no. unique reflns; R_{int}	7129; 0.0903	6364; 0.0279	4891; 0.022	4087; 0.08	3095; 0.027
transmn factors	0.80−0.75	0.85−0.74	0.84−0.70	0.89−0.79	0.83−0.74
no. with $I \geq 2\sigma(I)$	5135	5407	4157	2951	2904
no. variables	336	315	393	280	130
reflns/params	15.3	17.2	10.6	10.5	22.3
R; wR_2 (all data)	0.081; 0.117	0.049; 0.0995	0.05; 0.111	0.0827; 0.1278	0.048; 0.104
GOF	1.068	1.066	1.029	1.038	1.202
residual density (e$^-$/Å^3)	0.700; −0.280	0.537; −0.260	0.499; −0.261	1.205; −0.364	0.631; −0.302

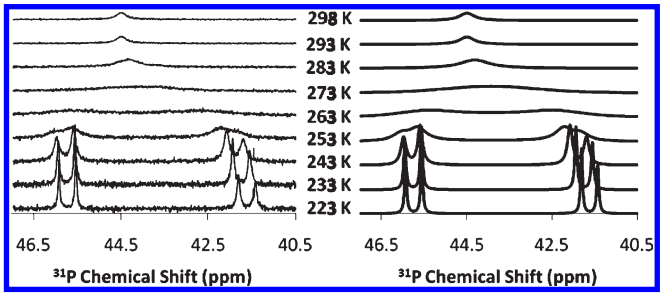
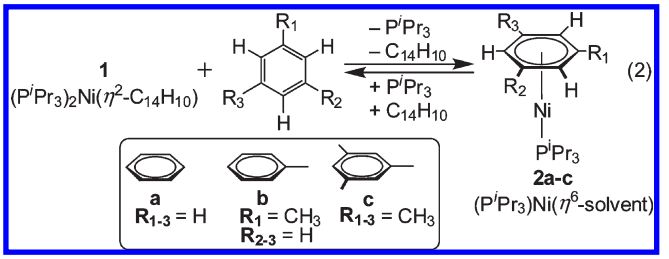


Figure 3. Experimental (left) and modeled (right) variable-temperature $^{31}P\{^1H\}$ NMR spectra for compound **1** obtained at 121.5 MHz in THF-d_8.

These processes have been examined in detail for systems bearing different phosphine donors.[34,35]

When compound **1** was dissolved in aromatic solvents, an additional peak appeared at δ 58 in the $^{31}P\{^1H\}$ NMR spectra at room temperature, along with one equivalent of triisopropylphosphine. Variable-temperature NMR spectroscopic studies were carried out using C_6D_6, toluene-d_8, and mesitylene as solvents and revealed a thermal equilibrium between **1** and the solvent adduct (P^iPr_3)Ni(η^6-solvent) complexes **2a**−**c**, as shown in eq 2. In all three solvents, the equilibrium strongly favored (P^iPr_3)Ni(η^6-solvent) at 333 K, and complex **1** was not present in significant amounts. When these samples were cooled back to room temperature from 333 K, the resonance associated with **1** reappeared. At 213 K, almost no complex **2** is observed. This temperature dependence of this equilibrium reaction is in accordance with the anticipated entropically favored formation of **2**, due to the three product species versus two reagents, and thus the enthalpically favored production of **1**. To further probe this equilibrium, compound **1** was dissolved in C_6D_6 with 50 equiv of triisopropylphosphine and heated to 333 K. Unlike in the absence of excess phosphine, a considerable amount of **1** was observed, as expected for an equilibrium reaction. The same experiment was performed in neat triisopropylphosphine with a stoichiometric amount of benzene, and the formation of **2a** was completely inhibited. The addition of anthracene was also shown to shift the equilibrium.



Complexes **2a**−**c** were further characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy at 333 K. The ^{13}C resonance of the methine carbon of the ^{i}Pr group was a doublet due to coupling to a single ^{31}P nucleus, further confirming the nature of this compound as a monophosphine complex; the bis(phosphine) complexes with chemically equivalent phosphine nuclei invariably exhibit virtual triplets for these carbons. In the ^1H NMR, the chemical shifts for the methyl substituents for the toluene and mesitylene adducts **2b** and **2c**, respectively, are almost unchanged relative to the unbound organic, whereas the aromatic protons were shifted significantly upfield: δ 5.9 for **2a**, δ 5.6−5.8 for **2b**, and δ 5.6 for **2c**. The $^{13}C\{^1H\}$ NMR spectra revealed significant upfield shifts for the coordinated aromatic carbons between δ 89.0 and 101.2. Comparison of the ^1H and $^{13}C\{^1H\}$ NMR spectra for **2a** observed from reaction of **1** with C_6H_6 species and the deuterated complex (P^iPr_3)Ni(η^6-C_6D_6), **2a-d_6**, further aided in the assignment of these spectra. For example, compound **2a** displays a singlet at δ 90.4, yet in the analogously deuterated compound, **2a-d_6**, there is a 1:1:1 triplet with a $^1J_{CD}$ value of 26 Hz, which is comparable to that observed for the solvent C_6D_6 at δ 128. Similar observations are made for **2b-d_8**, where the resonances corresponding to η^6-toluene−*C*D are 1:1:1 triplets found

(34) (a) Stanger, A. *Organometallics* **1991**, *10* (8), 2979. (b) Stanger, A.; Weismann, H. *J. Organomet. Chem.* **1996**, *515* (1−2), 183. (c) Li, T.; Garcia, J. J.; Brennessel, W. W.; Jones, W. D. *Organometallics* **2010**, *29* (11), 2430. (d) Atesin, T. A.; Li, T.; Lachaize, S.; Garcia, J. J.; Jones, W. D. *Organometallics* **2008**, *27* (15), 3811.

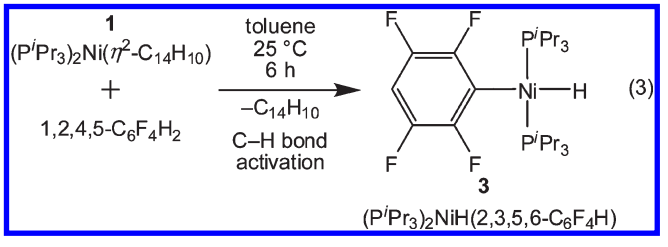
(35) Stanger, A.; Vollhardt, K. P. C. *Organometallics* **1992**, *11* (1), 317.

at δ 89.0, 89.5, and 91.9 with $^1J_{CD}$ values of 23.0, 20.1, and 23.0 Hz, respectively, whereas the *ipso*-carbon is a singlet at δ 101.8.

To probe the preference for an aromatic donor at 333 K, a competition experiment was conducted using a stoichiometric mixture of benzene, toluene, and mesitylene with compound **1** in hexamethyldisiloxane. The results indicated a slight preference for the more electron-donating mesitylene over benzene and toluene, resulting in a final mixture composition of **2a**−**c** of 26%, 19%, and 55%, respectively, as monitored by ^{1}H and ^{31}P NMR. This is in contrast to the electron-rich bis(phosphine)-nickel arene adducts, which preferentially bind to electron-poor arenes.[17,24] By monitoring the concentrations of individual species through integration over the temperature range 303 to 333 K, van't Hoff plots for equilibrium formation of **2a**−**c** were constructed, which provided estimated enthalpy changes for this reaction of 21.9, 21.1, and 26.4 kcal·mol^{-1}, respectively. The entropy changes were determined to be 58.7, 55.1, and 73.9 cal·mol^{-1}·K^{-1}. Although not displaying an obvious trend, these results suggest that the favored formation of **2c** versus **2a** or **2b** is the result of the more favorable ΔS of reaction, rather than a more favorable ΔH of reaction.

A few structurally related examples of LNi(η^6-arene) complexes, where L is a phosphine,[36] N-heterocyclic carbene,[37] or silylene[38] ligand, are known. The presence of an equivalent of ^{i}Pr$_3$P in the reactions that produced **2a**−**c** hampered the isolation of these products as solids. Attempts to scavenge the excess phosphine using Lewis acids such as BEt_3, $B(C_6F_5)_3$, or anhydrous $NiCl_2$ caused the decomposition of **2a**−**c**.

Synthesis and Characterization of a Stable C−H Bond Activation Product with 1,2,4,5-Tetrafluorobenzene. The reaction of the anthracene adduct ($P^iPr_3)_2Ni(\eta^2$-$C_{14}H_{10})$ (**1**) with a slight excess of 1,2,4,5-$C_6F_4H_2$ in toluene results in an immediate color change from red to orange. Analysis of the crude solution by NMR spectroscopy reveals that the C−H activated product, *trans*-($P^iPr_3)_2$NiH(2,3,5,6-C_6F_4H) (**3**), formed over the course of 6 h, as shown in eq 3. No C−F bond activation products or fluoroarene adducts of ($P^iPr_3)_2$Ni were observed. Complex **3** was easily isolated by removal of solvent under vacuum, extraction into pentane, removal of the insoluble anthracene byproduct by filtration, and crystallization at −40 °C. Divalent nickel hydride complexes that also contain Ni−C bonded aryl moieties are not common and are generally not accessible via C−H bond oxidative addition.[13]



Single crystals suitable for structural analysis of **3** by X-ray crystallography were directly obtained from this synthesis. An ORTEP depiction of the solid-state molecular structure is shown in Figure 4, and X-ray crystallographic collection and refinement parameters are included in Table 1. Complex **3**

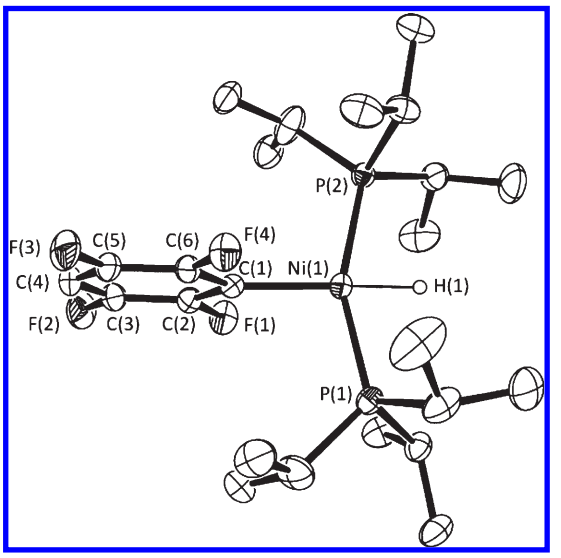


Figure 4. ORTEP depiction of the solid-state molecular structure of **3** as determined by X-ray crystallography. Hydrogen atoms, excluding the nickel hydride, are omitted for clarity. The methyl carbons associated with a 2-fold disorder on the isopropyl moiety are omitted for clarity. The 30% probability ellipsoids are shown. Selected bond lengths (Å): Ni(1)−H(1), 1.40(3); Ni(1)−P(1), 2.1661(6); Ni(1)−P(2), 2.1761(6); Ni(1)−C(1), 1.934(2); F(1)−C(2), 1.365(3); F(2)−C(3), 1.357(3); F(3)−C(5), 1.366(3); F(4)−C(6), 1.370(3). Selected bond angles (deg): P(1)−Ni(1)−P(2), 155.98(2); C(1)−Ni(1)−H(1), 177.6(11).

has *trans*-disposed triisopropylphosphine ligands and the anticipated pseudo-square-planar geometry around the nickel metal. The tetrafluorophenyl moiety is nearly orthogonal to the P−Ni−P plane. The acute P(1)−Ni(1)−P(2) angle of 155.98(2)° is attributed to the relief of steric crowding by the bulky triisopropylphosphine ligands; the phosphine donors bend away from the aromatic ring and toward the smaller hydride ligand. The electron density associated with the hydride was located in a difference map, and its position was refined isotropically. Although the location of hydrogen atoms in the electron density determined by X-ray crystallography can be erroneous, the crystallographic Ni(1)−H(1) bond distance of 1.40(3) Å is within the range expected.[22]

The solid-state molecular structure of complex **3** was confirmed through characterization by solution NMR spectroscopy and elemental analysis. The room-temperature ^{1}H NMR spectra in C_6D_6 revealed a distinctive hydride resonance at δ −16.25,[15,17,22,39] which was a triplet of triplets of triplets. The hydride was modeled using the WinDNMR[40] simulation program as coupling to two ^{31}P nuclei with a $^2J_{HP}$ value of 68.0 Hz, two *ortho*-fluorines with a $^4J_{HF}$ value of 8.7 Hz, and two *meta*-fluorines with a $^5J_{HF}$ of value 4.0 Hz. The experimental and modeled spectra are shown in Figure 5. The observed coupling constants are consistent with the previous spectroscopic characterization of the unisolable species ($PEt_3)_2$NiH(2,3,5,6-$C_6F_4H_2$)[15] and related nickel hydrides.[39]

The ^{31}P{^{1}H} NMR spectra reveal a singlet at δ 51.5, which is a broad doublet in the ^{31}P NMR due to coupling to the hydride. The ^{19}F{^{1}H} NMR spectra show two second-order

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(37) Lee, C. H.; Laitar, D. S.; Mueller, P.; Sadighi, J. P. *J. Am. Chem. Soc.* **2007**, *129* (45), 13802.
(38) Meltzer, A.; Praesang, C.; Milsmann, C.; Driess, M. *Angew. Chem., Int. Ed.* **2009**, *48* (17), 3170.
(39) Darensbourg, M. Y.; Ludwig, M.; Riordan, C. G. *Inorg. Chem.* **1989**, *28* (9), 1630.
(40) *WinDNMR, NMR Spectrum Calculations*; Hans J. Reich: Madison, WI, 2005.

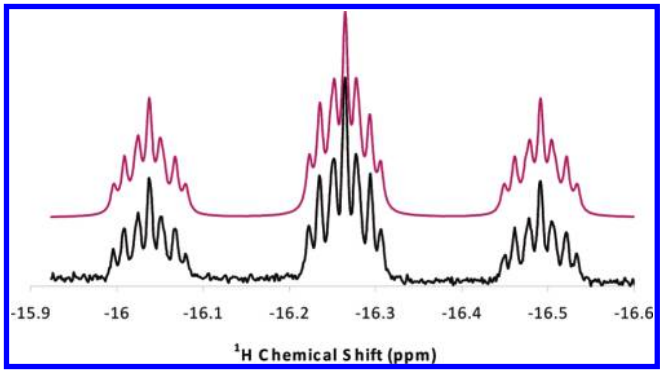


Figure 5. Experimental (bottom) and modeled (top) hydridic region ^{1}H NMR spectra for compound **3** obtained at 298 K in C_6D_6.

multiplets at δ −112.9 and −143.0. The $^{13}C\{^1H\}$ NMR spectra display a virtual triplet for the ^{i}Pr−CH resonance with a J_{CP} value of 10.8 Hz. To ensure that no exchange-broadened resonances for adducts were missed, low-temperature ^{1}H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra were collected, but showed no evidence of either mononuclear or dinuclear η^2-arene adducts,[17] which supports the hypothesis that the bulky phosphine donors do thermodynamically disfavor the *cis*-phosphine geometries adopted in these Ni(0) species. In the related C−H activation product $(PEt_3)_2NiH(C_6F_5)$, the η^2-arene complex is in equilibrium with the C−H activation product, with the latter disfavored by only 0.8 kcal·mol^{-1}.[17]

The crude reaction mixture from the synthesis of **3** was monitored by NMR spectroscopy for weeks at room temperature, and no conversion to C−F activation products was observed. Even upon heating to 100 °C for 3 h, toluene-d_8 solutions of complex **3** failed to convert to the anticipated thermodynamic C−F activation product[18] *trans*-$(P^iPr_3)_2NiF(2,4,5\text{-}C_6F_3H_2)$, as monitored by ^{1}H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectroscopy.[15] This could imply that the C−H activation product is so stabilized with respect to the adduct $(P^iPr_3)_2Ni(\eta^2\text{-}1,2,4,5\text{-}C_6F_4H_2)$ that the adduct is no longer kinetically accessible; this adduct is expected to be the common intermediate for both concerted C−H and C−F activation,[17,41] Alternatively, the C−F bond activation barrier could simply be much higher for the $(P^iPr_3)_2Ni$ moiety compared to the $(PEt_3)_2Ni$ moiety.

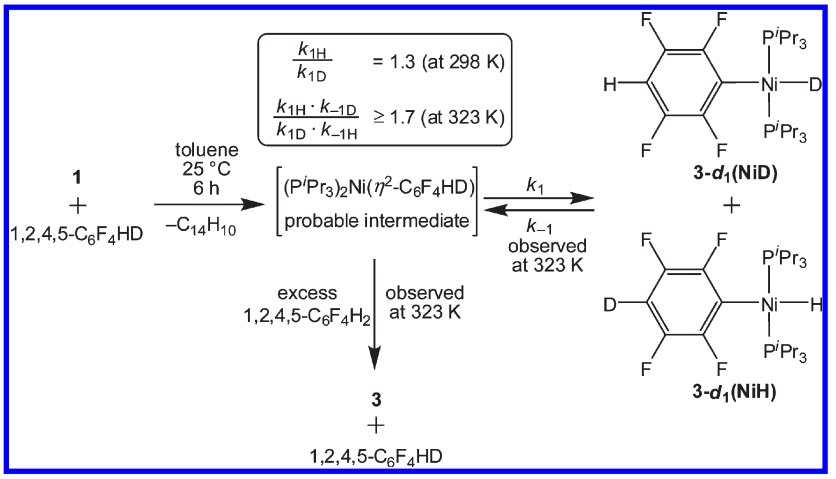
A series of experiments were performed to assess the reversibility of the C−H bond activation reaction that could form the transient adduct $(P^iPr_3)_2Ni(\eta^2\text{-}1,2,4,5\text{-}C_6F_4H_2)$. A deuterium labeling study performed by reacting **1** with the monodeuterated tetrafluorobenzene 1,2,4,5-C_6F_4HD resulted in a mixture of $(P^iPr_3)_2NiH(2,3,5,6\text{-}C_6F_4D)$, **3-$d_1$(NiH)**, and $(P^iPr_3)_2NiD(2,3,5,6\text{-}C_6F_4H)$, **3-$d_1$(NiD)**, as shown in Scheme 1. In the ^{19}F NMR spectrum, the *meta*-F nuclei of these species are separated by 0.3 ppm, which allows for their integration and a determination of a kinetic isotope effect (KIE) of 1.3 for the C−H bond activation step labeled with the rate constant k_1; the rate constant was only slightly larger for C−H bond activation, labeled k_{1H}, than the C−D bond, labeled k_{1D}. A similar intermolecular KIE has been observed in the catalytic functionalization of pyridine by a nickel complex, but was interpreted as suggesting that C−H bond breaking was not the rate-limiting step.[32] This KIE observed in the formation of **3-d_1** is a much smaller than the equilibrium isotope effect (EIE) of 2.1 observed in the activation of 1,2,4,5-C_6F_4HD by the $(PEt_3)_2Ni$ moiety at room temperature. The C−H/D activation reaction with the smaller PEt_3 ancillary ligand was reversible even at 233 K, and at this temperature the EIE increased to 3.4. The C−H bond reductive elimination from **3** must not occur at a significant rate at room temperature, or else a similar EIE would be observed. The relatively low KIE observed in the formation of **1** is suggestive of an early transition state for the oxidative addition step, where little C−H bond-breaking has occurred. An early transition state is also consistent with the stability of the C−H activation product compared to the unobserved η^2-arene intermediate. In an attempt to observe reversible oxidative addition and determine the EIE for the species **3-d_1(NiH)** and **3-d_1(NiD)**, a mixture of these complexes was heated to 50 °C. The ratio of **3-d_1(NiH)** to **3-d_1(NiD)** gradually increased to a maximum value of 1.7 after 0.5 h. This demonstrates the reversibility of the C−H oxidative addition reaction at 50 °C, and sets 1.7 as the minimum possible EIE. Unfortunately, it could not be confirmed that this was the true EIE for this reaction, due to scrambling reactions that generated **3** and **3-d_2**, $(P^iPr_3)_2NiD(2,3,5,6\text{-}C_6F_4D)$. The ^{19}F NMR resonances of the *meta*-F nuclei for **3** and **3-d_2** overlap with those of **3-d_1(NiD)** and **3-d_1(NiH)**, respectively, and results in a lower than actual isotope effect, as measured by peak integration. A value greater than 1.7 is consistent with the previously observed equilibrium isotope effect of 2.1 observed with PEt_3 as an ancillary ligand at room temperature; there is no obvious reason for these systems to exhibit significantly different EIEs. By using the KIE for the forward reaction, k_{1H}/k_{1D}, of 1.3 and an estimated EIE of 2.1 at 298 K, an inverse KIE for the reductive elimination step, k_{-1H}/k_{-1D}, of 0.6 can be estimated, consistent with the presence of a strong C−H bonding interaction in the transition state for oxidative addition/reductive elimination.[42] Heating a mixture of **3-d_1(NiD)** and **3-d_1(NiH)** to 50 °C with an excess of nondeuterated 1,2,4,5-tetrafluorobenzene resulted in their conversion to **3**, with the liberation of 1,2,4,5-C_6F_4HD, which demonstrates that intermolecular ring hopping of the $(P^iPr_3)_2Ni$ moiety from the proposed intermediate $(P^iPr_3)_2Ni(\eta^2\text{-}1,2,4,5\text{-}C_6F_4H_2)$ is facile, similar to polyfluorinated η^2-arene adducts of $(PEt_3)_2Ni$.[16,17,23,24] Similarly, heating a solution of **3** in the presence of 1,2,4,5-C_6F_4HD slowly produced **3-d_1(NiD)** and **3-d_1(NiH)**. IR spectroscopy of these complexes allowed for identification of a nickel hydride stretching frequency at 1903 cm^{-1}. The ratio of reduced masses for Ni−H versus Ni−D bonds can be used to estimate a stretching frequency for the latter of 1359 cm^{-1};[39] however, this region of the spectrum was obscured by intense peaks attributed to stretching modes for the other ligands.

Synthesis and Characterization of a C−H Bond Activation Product with 1,2,3,5-Tetrafluorobenzene. The reaction of the complex **1** with excess 1,2,3,5-$C_6F_4H_2$ in toluene was complete in 36 h. Analysis of the crude reaction mixture by $^{19}F\{^1H\}$ NMR spectroscopy reveals *trans*-$(P^iPr_3)_2NiH(2,3,4,6\text{-}C_6F_4H)$

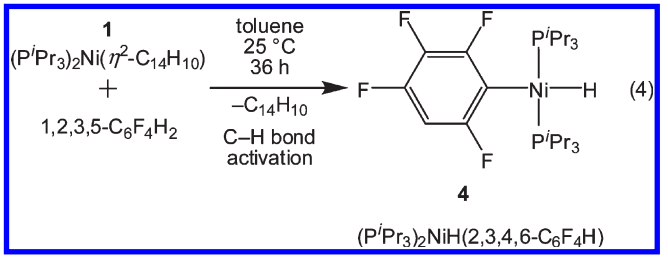
(41) Braun, T.; Cronin, L.; Higgitt, C. L.; McGrady, J. E.; Perutz, R. N.; Reinhold, M. *New J. Chem.* **2001**, *25* (1), 19.

(42) (a) Churchill, D. G.; Janak, K. E.; Wittenberg, J. S.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125* (5), 1403. (b) Jones, W. D. *Acc. Chem. Res.* **2003**, *36* (2), 140. (c) Parkin, G. *Acc. Chem. Res.* **2009**, *42* (2), 315.

Scheme 1



(**4**) as the major product, with less than 2% of other impurities, as shown in eq 4.



Single crystals of **4** suitable for structural analysis by X-ray crystallography were obtained by slow evaporation of a saturated hexamethyldisiloxane solution at −40 °C, and an ORTEP depiction of the solid-state molecular structure is shown in Figure 6. Data collection was performed at 213 K, because the yellow crystals shattered upon further cooling. There is disorder due to the two possible orientations of the fluorinated aryl ring; the molecules pack with little discrimination in the orientation of the 2,3,4,6-C_6F_4H moiety, presumably due to the similar sizes of fluorine and hydrogen. An associated disorder of one of the $^{i}Pr_3P$ ligands was also modeled. These factors limit the reliability of some of the bond lengths, but leave no doubt as to the connectivity of the molecule. Complex **4** has a similar structure to that of **3**, where the geometry around the nickel center is approximately square planar. The P(1)−Ni(1)−P(2) angle of 158.94(4)° is slightly larger than in **3**, and the Ni(1)−H(1) distance was found to be 1.54(4) Å.

Compound **4** was also characterized by multinuclear NMR spectroscopy. The room-temperature ^{1}H NMR spectrum confirms the solid-state molecular structure with a resonance for the hydridic proton at δ −16.38 with a resolved multiplet modeled as a triplet of doublets of doublets of doublets, as shown in Figure 7. The largest coupling is to the two phosphorus nuclei with a $^{2}J_{HP}$ value of 68.5 Hz, which was confirmed by ^{31}P NMR spectroscopy. Additional couplings to the two nonequivalent *ortho*-fluorines with $^{4}J_{HF}$ values of 8.9 and 8.7 Hz and coupling to a *meta*-fluorine with a $^{5}J_{HF}$ value of 3.5 Hz were also confirmed by modeling this multiplet, as shown at the top of Figure 7. The $^{19}F\{^{1}H\}$ NMR spectrum shows four resonances at δ −86.1, −105.8, −144.4, and −170.3, consistent with the observed connectivity. The $^{13}C\{^{1}H\}$ NMR spectrum displays a virtual triplet for the ^{i}Pr−CH resonance, similar to **3**, with a J_{CP} value of 10.3 Hz.

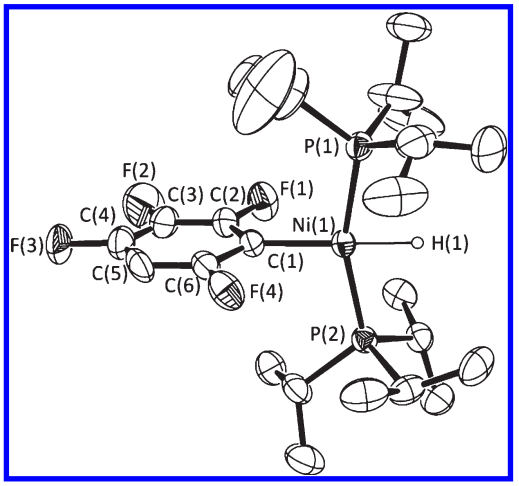


Figure 6. ORTEP depiction of the solid-state molecular structure of **4** as determined by X-ray crystallography. Hydrogen atoms, excluding the nickel hydride, and disorder are omitted for clarity. The 30% probability ellipsoids are shown. Selected bond lengths (Å): Ni(1)−H(1), 1.54(4); Ni(1)−P(1), 2.1719(12); Ni(1)−P(2), 2.1734(12); Ni(1)−C(1), 1.943(4); F(1)−C(2), 1.366(6); F(2)−C(3), 1.281(8); F(3)−C(4), 1.354(6); F(4)−C(6), 1.362(6). Selected bond angles (deg): P(1)−Ni(1)−P(2), 158.94(4); C(1)−Ni(1)−H(1), 172.9(16).

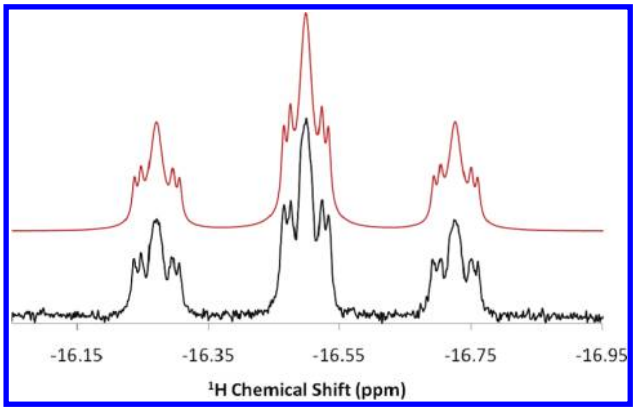


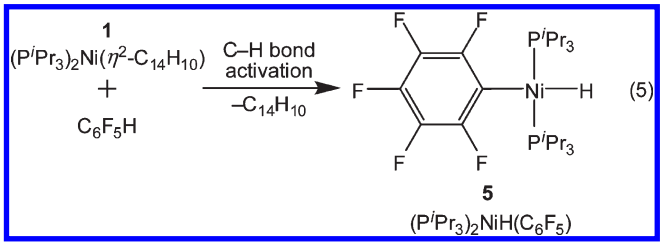
Figure 7. Experimental (bottom) and modeled (top) hydridic region ^{1}H NMR spectra for compound **4** obtained at 298 K in C_6D_6.

This C−H activated complex is modestly stable in solution at room temperature for weeks, gradually isomerizing to the

thermodynamically favored C−F activated product. Unlike compound **3**, heating a toluene solution of **4** to 50 °C results in conversion to the C−F activated compounds over the course of many days. The mechanism through which this occurs is currently under investigation, and the description of the C−F activation products is beyond the scope of this paper.

The substrate 1,2,3,4-tetrafluorobenzene, which has only a single fluorine substituent adjacent to either C−H bond, failed to produce the C−H activation product, $(P^iPr_3)_2NiH(2,3,4,5\text{-}C_6F_4H)$, either as an isolable product or as evidenced by NMR spectroscopy.

Synthesis and Characterization of a C−H Bond Activation Product of Pentafluorobenzene. As monitored by NMR spectroscopy, pentafluorobenzene reacts with a red-colored solution of **1** in C_6D_6 to provide the C−H activated complex *trans*-$(P^iPr_3)_2NiH(C_6F_5)$ (**5**) with less than 5% of other impurities, as shown in eq 5. Unlike complexes **3** and **4**, complex **5** could be isolated only as a viscous oil.



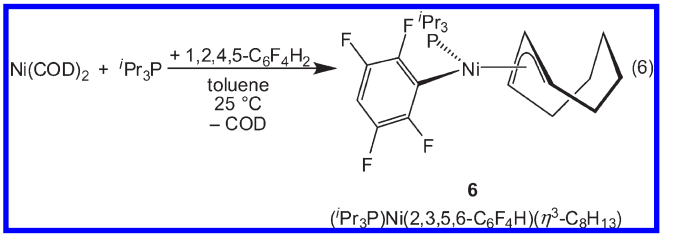
(5)

In the ^1H NMR, the hydride resonance is apparent from its upfield shift of δ −16.5 and is a triplet of triplets of triplets, analogous to complex **3**, with comparable coupling to two ^{31}P nuclei with a $^2J_{HP}$ value of 68.0 Hz, two *ortho*-fluorines with a $^4J_{HF}$ value of 9.9 Hz, and two *meta*-fluorines with a $^5J_{HF}$ value of 4.5 Hz. Further confirmation that this is indeed the C−H oxidative addition product was provided by the ^{31}P NMR spectrum, with a broad doublet at δ 51.2, indicating coupling to the nickel hydride with a $^2J_{PH}$ value of 68.0 Hz. The ^{19}F NMR spectrum displays three resonances at δ −110.7, −163.2, and −164.6 for the *ortho*-, *para*-, and *meta*-fluorines. The *para*-fluorine exhibits a triplet of triplets with coupling to two pairs of equivalent *meta*- and *ortho*-fluorines, whereas the ^{19}F resonances corresponding to the *ortho*- and *meta*-fluorines are both second-order multiplets. A variable-temperature NMR study did not reveal any evidence of η^2-arene adducts in equilibrium with hydride **5**, and an EPR spectroscopic study did not reveal paramagnetic impurities. Over the course of weeks at room temperature, complex **5** converts to C−F activation products, the description of which are beyond the scope of this paper.

It is of interest to ascertain if complexes **2a** and **2b** play a role in these C−H bond activation reactions when performed in benzene or toluene. To further investigate the mechanism of this reaction, complex **1** was reacted with pentafluorobenzene in the presence of a large excess of triisopropylphosphine in toluene. By comparison with an analogous reaction in the absence of added triisopropylphosphine, it was determined that excess triisopropylphosphine did not slow the rate of C−H bond activation. This suggests that complex **2b**, $(P^iPr_3)Ni(\eta^6\text{-}C_7H_8)$, is not necessary for C−H bond activation.

Unexpected Insertion Products via Reactions of $Ni(COD)_2$ with Fluorinated Aromatics. The nickel-catalyzed examples of polyfluoroarene C−H bond functionalization reported to date have both utilized combinations of secondary alkyl phosphines with $Ni(COD)_2$ as catalyst precursors.[4,5] In an attempt to synthesize C−H activation products directly in a similar manner to those reported catalytically, and without the need for the highly reactive species **1**, we employed $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) with triisopropylphosphine in an attempt to make a $(P^iPr_3)_2Ni$ synthon *in situ*. This would be advantageous, as complex **1** is only moderately stable at 50 °C, yet the catalysts prepared from $Ni(COD)_2$ and phosphines can withstand temperatures up to 80 °C for extended periods of time without decomposition.[4,5]

A solution of $1,2,4,5\text{-}C_6F_4H_2$ was added to a mixture of $Ni(COD)_2$ and 2 equiv of triisopropylphosphine in C_6D_6. Initial analysis of the crude solution via $^{19}F\{^1H\}$ NMR spectroscopy revealed not only the desired C−H activated complex **3** as a minor product (33% of the sample) but another species with four fluorine environments, which was later identified as the allylic cyclooctene adduct $(\eta^3\text{-}C_8H_{13})Ni(P^iPr_3)(2,3,5,6\text{-}C_6F_4H)$, **6**, as shown in eq 6. After two days, resonances associated with **6** continued to grow in intensity from the initial quantity of 67% to 85% of the sample, which indicates that the insertion of 1,5-cyclooctadiene is slower than C−H bond activation.



(6)

Single crystals suitable for structural analysis of **6** by X-ray crystallography were obtained from slow evaporation of a cold pentane solution, and an ORTEP depiction of the solid-state molecular structure is shown in Figure 8. X-ray crystallographic collection and refinement parameters are included in Table 1. The nickel metal resides in a pseudo-square-planar coordination sphere, with the allylic donor occupying two coordination sites. The allylic moiety features C(7)−C(8) and C(8)−C(9) distances of 1.394(6) and 1.410(6) Å, respectively. The eight-membered ring adopts a boat conformation directed away from the triisopropylphosphine ligand. Related allylic complexes of Ni not arising from C−H bond activation are known.[43]

Compound **6** has been further characterized by elemental analysis and ^1H, ^{31}P, ^{19}F, and $^{13}C\{^1H\}$ NMR spectroscopy. The $^{19}F\{^1H\}$ NMR spectrum reveals fluorine resonances at δ −114.7, −115.2, −142.8, and −143.0. The presence of four ^{19}F environments indicates that rotation around both the Ni−C bond of the $2,3,5,6\text{-}C_6F_4H$ moiety and about the Ni-allyl moiety must be slow on the NMR time scale. The ^1H NMR spectra is also consistent with a C_1 symmetric compound. A series of overlapping doublets between δ 0.85 and 0.97 correspond to the diastereotopic protons on C(10) and C(14), while a complicated multiplet between δ 1.15 and 1.4 accounts for the remaining diastereotopic protons on C(11), C(12), and C(13). Three multiplets at δ 3.78, 4.02, and 4.85 belong to the allylic protons on C(7), C(8), and C(9).

(43) (a) Henc, B.; Jolly, P. W.; Salz, R.; Stobbe, S.; Wilke, G.; Benn, R.; Mynott, R.; Seevogel, K.; Goddard, R.; Krueger, C. *J. Organomet. Chem.* **1980**, *191* (2), 449. (b) Henc, B.; Jolly, P. W.; Salz, R.; Wilke, G.; Benn, R.; Hoffmann, E. G.; Mynott, R.; Schroth, G.; Seevogel, K.; et al. *J. Organomet. Chem.* **1980**, *191* (2), 425.

The proposed mechanism for the synthesis of **6** is a classic chain-walking mechanism whereby oxidative addition C−H activation of the fluoroarene to the nickel phosphine moiety is followed by the insertion of 1,5-cyclooctadiene, as shown in Scheme 2. A β-elimination and dissociation of 1,4-cyclooctadiene followed by $^{i}Pr_3P$ coordination could regenerate the C−H activation product **3**; however, this process would be expected to lead to at least a partial isomerization of the extra equivalent of 1,5-cyclooctadiene present in solution to 1,4-cyclooctadiene, which was not observed by ^{1}H NMR spectroscopic analysis of the reaction mixture. This suggests that the β-elimination is rapidly followed by reinsertion, without dissociation of 1,4-cyclooctadiene. An additional insertion and β-elimination provides a 1,3-cyclooctadiene complex, which then inserts again into the Ni−H bond to provide the η^3-C_8H_{13} moiety observed in compound **6**.

Analogous reactions were performed with 1,2,3,5- and 1,2,3,4-tetrafluorobenzene, as shown in eqs 7 and 8, respectively. Immediate analysis of the crude mixture by NMR spectroscopy for the reaction of $Ni(COD)_2$ with 1,2,3,4-$C_6F_4H_2$ revealed COD insertion products **8a**,**b**.

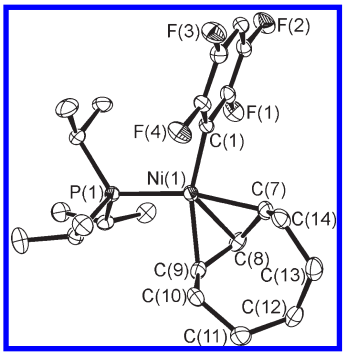
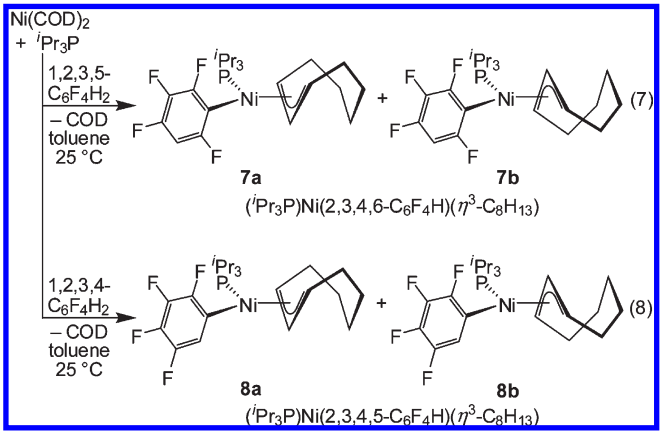


Figure 8. ORTEP depiction of the solid-state molecular structure of **6** as determined by X-ray crystallography. Hydrogen atoms are omitted for clarity. The 30% probability ellipsoids are shown. Selected bond lengths (Å): Ni(1)−P(1), 2.2033(12); Ni(1)−C(1), 1.921(4); Ni(1)−C(7), 2.066(4); Ni(1)−C(8), 1.967(4); Ni(1)−C(9), 2.101(5); C(7)−C(8), 1.394(6); C(8)−C(9), 1.410(6); C(9)−C(10), 1.508(6); C(7)−C(14), 1.503(6). Selected bond angles (deg): P(1)−Ni(1)−C(1), 105.59(12); C(7)−C(8)−C(9), 122.3(4); C(7)−Ni(1)−C(8), 40.37(18); C(7)−Ni(1)−C(9), 72.23(18); C(1)−Ni(1)−C(9), 159.19(18); C(7)−Ni(1)−P(1), 165.74(14).

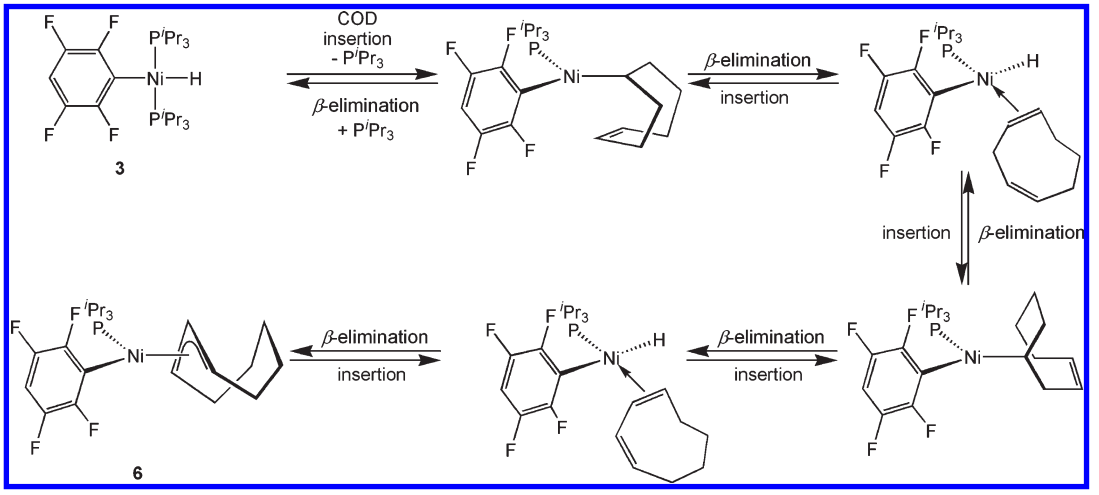
These result from trapping the kinetically accessible hydride species from the C−H activation of 1,2,3,4-$C_6F_4H_2$ that we had previously been unable to observe, because its formation from **1** is thermodynamically unfavorable. These compounds have been characterized by ^{1}H, ^{31}P, and ^{19}F NMR spectroscopy.



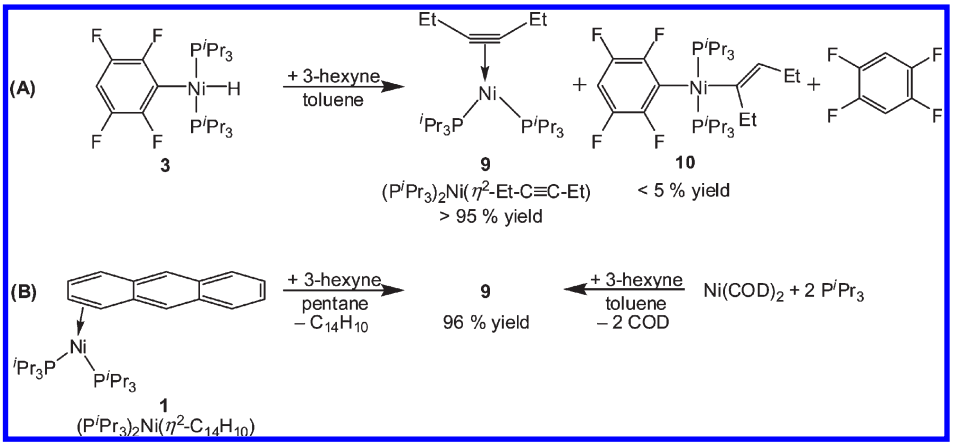
The $^{31}P\{^1H\}$ NMR spectra of both product mixtures showed two separate, yet similar resonances for this monophosphine species, with both pairs in equal quantities by integration. Similarly, the $^{19}F\{^1H\}$ NMR spectra contained two sets of resonances for four fluorine environments. This is attributed to hindered rotation around the Ni−aryl bond, resulting in the diastereomers **7a**,**b** and **8a**,**b** for 1,2,3,5- and 1,2,3,4-tetrafluorobenzene, respectively. These reactions also contained less than 5% C−F activation impurities.

Catalytic Transformations via Alkyne Insertion. Although complex **1** does not react with 1,2,3,4-$C_6F_4H_2$ to generate a thermodynamically favorable C−H activation product, the isolation of **8a**,**b**, which arises from the trapping of a kinetically accessible hydride, suggests that nickel catalysts should be able to facilitate the catalytic functionalization of C−H bonds that undergo thermodynamically disfavored oxidative addition, provided the barrier to C−H activation is not too high. Trapping these transient hydrides via reactions with other small molecules, such as alkynes[5] and Bu_3Sn-CH=CH_2,[4] should result in viable catalytic cycles. The isolable hydrides **3**, **4**, and **5** provide a chance to examine their potential reactivity.

Scheme 2



Scheme 3



Surprisingly, the reaction of compound **3** with stoichiometric amounts of 3-hexyne failed to yield more than 3% of the desired insertion product, (P^{i}Pr$_3$)$_2$Ni(CEt=CHEt)-(2,3,5,6-C$_6$F$_4$H) (**10**). Immediate analysis of the crude reaction mixture by ^{31}P{^{1}H} NMR spectroscopy at room temperature revealed a singlet at δ 55 as the major product, identified as the π-coordinated 3-hexyne adduct (P^{i}Pr$_3$)$_2$Ni(η^2-EtC≡CEt) (**9**), as shown in Scheme 3A. The only significant byproduct was identified as a trace amount of the desired insertion product **10** at δ 36 in the ^{31}P{^{1}H} NMR spectrum. This reaction remains unchanged at room temperature for weeks, even in the presence of 1,2,4,5-tetrafluorobenzene.

Compound **9** is synthesized quantitatively through the reaction of **1** with 3-hexyne in pentane, as shown in Scheme 3B. Alternatively, compound **9** can be conveniently prepared through the reaction of Ni(COD)$_2$, 2 equiv of triisopropylphosphine, and 3-hexyne in pentane. Compound **9** has been fully characterized by ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopy. Orange-colored single crystals suitable for structural analysis of **9** by X-ray crystallography were obtained from slow evaporation of a cold pentane solution, and an ORTEP depiction of the solid-state molecular structure is shown in Figure 9. X-ray crystallographic collection and refinement parameters are included in Table 1. Compound **9** has crystallographic symmetry, where the nickel metal resides on a C_2 axis, in a pseudoplanar geometry with a P(1)−Ni(1)−P(1)′ angle of 115.19(4)°. The 3-hexyne moiety is η^2-coordinated to the metal center. A longer C(3)−C(3)′ bond length of 1.275(6) Å than the expected carbon−carbon triple bond for an alkyne of 1.20 Å is a result of back-bonding from the Ni(P^{i}Pr$_3$)$_2$ fragment and is in agreement with comparative values in the literature between 1.272 and 1.305 Å, where the longer bond length is attributed to systems with a chelating phosphine backbone.[44]

Although the formation of compound **9** from **3** would suggest that C−H bond activation of 1,2,4,5-tetrafluorobenzene by **9** is thermodynamically unfavorable, this product

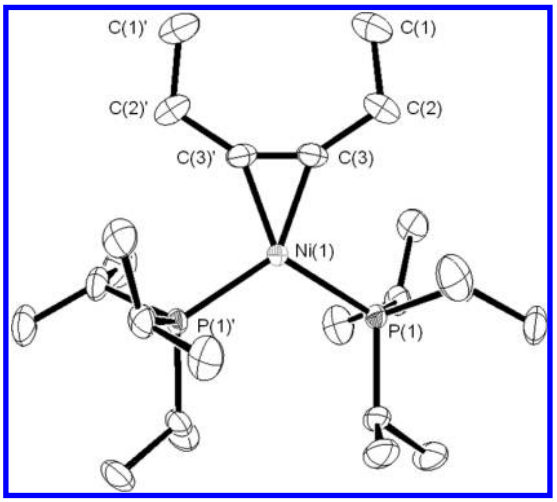
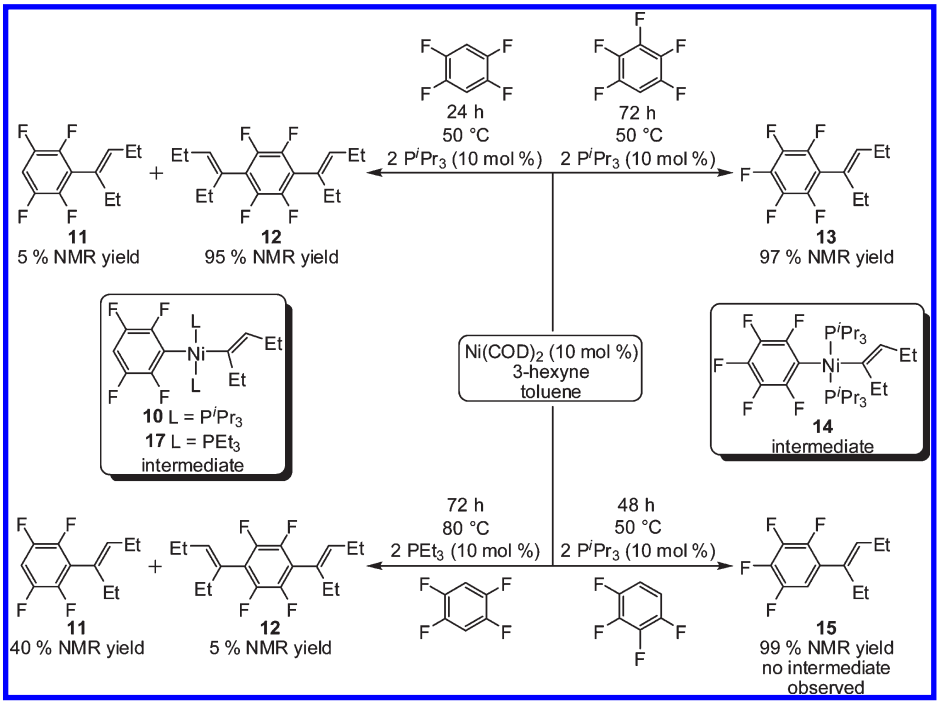


Figure 9. ORTEP depiction of the solid-state molecular structure of **9** as determined by X-ray crystallography. Hydrogen atoms are omitted for clarity. The 30% probability ellipsoids are shown. Selected bond lengths (Å): Ni(1)−P(1), 2.1864(7); Ni(1)−C(3), 1.904(3); C(3)−C(3)′, 1.275(6). Selected bond angles (deg): P(1)−Ni(1)−P(1)′, 115.19(4); C(3)−Ni(3)−C(3)′, 39.14(18); C(3)−Ni-(1)−P(1), 103.38(9); C(3)′−Ni(1)−P(1), 141.12(9); C(3)′−C(3)−C(2), 146.27(18); Ni(1)−C(3)−C(2), 143.1(2); C(1)−C(2)−C(3), 116.3(3).

appears to be kinetically accessible; heating a toluene solution of **9** and 1,2,4,5-tetrafluorobenzene to 50 °C affords dissociation of the coordinated alkyne, allowing for the reaction to proceed in the presence of a fluoroarene. The room-temperature reaction of compound **1** (10 mol %) or a mixture of Ni(COD)$_2$ (10 mol %) and triisopropylphosphine (10 mol %) with 1,2,4,5-C$_6$F$_4$H$_2$ and 3-hexyne results in the immediate formation of compound **9** with trace amounts of the insertion product, compound **10**, as shown in Scheme 4. Upon heating to 50 °C, the reaction mixture converts primarily to compound **10**, which has been characterized by ^{1}H, ^{31}P, and ^{19}F NMR spectroscopy, in addition to trace amounts of the reductively eliminated monofunctionalized compound 1,2,4,5-C$_6$F$_4$H-CEt=CHEt (**11**). The ^{31}P{^{1}H} NMR spectrum of **10** reveals a singlet at δ 39.4, which is ~20 ppm upfield from compounds **3** and **9**, while the ^{1}H NMR spectrum has a broad triplet at δ 5.61 attributed to the alkene hydrogen on the inserted alkyne fragment. The ^{19}F NMR spectrum displays four fluorine environments at δ

(44) (a) Bach, M. A.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2005**, *24* (13), 3047. (b) Bartik, T.; Happ, B.; Iglewsky, M.; Bandmann, H.; Boese, R.; Heimbach, P.; Hoffmann, T.; Wenschuh, E. *Organometallics* **1992**, *11* (3), 1235. (c) Bennett, M. A.; Johnson, J. A.; Willis, A. C. *Organometallics* **1996**, *15* (1), 68. (d) Mindiola, D. J.; Waterman, R.; Jenkins, D. M.; Hillhouse, G. L. *Inorg. Chim. Acta* **2003**, *345*, 299. (e) Rosenthal, U.; Pulst, S.; Arndt, P.; Baumann, W.; Tillack, A.; Kempe, R. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50* (3), 377. (f) Waterman, R.; Hillhouse, G. L. *Organometallics* **2003**, *22* (25), 5182.

Scheme 4



−110.3, −114.7, −142.1, and −142.5 that are not in exchange due to hindered rotation about the Ni−C bond of the 2,3,5,6-C_6F_4H moiety. After 24 h at 50 °C, the reaction mixture consists mainly of the doubly activated product 1,2,4,5-$C_6F_4H(CEt{=}CHEt)_2$ (**12**), which appears as a singlet at −143.5 in the $^{19}F\{^1H\}$ NMR spectra, with trace amounts of the monofunctionalized product 1,2,4,5-C_6F_4H-CEt=CHEt (**11**), which displays two fluorine resonances at −140.5 and −143.4, and unreacted 1,2,4,5-$C_6F_4H_2$. The relative ratio of products **11** and **12** in the ^{19}F NMR is 5:95. This suggests that the C−H bond functionalization of **11** is slightly faster than that of 1,2,4,5-tetrafluorobenzene. The initial formation of primarily **11** rather than **12** in this reaction rules out the possibility that this preference for **12** is the result of **10** undergoing reductive elimination without loss of **11** via some adduct of $(P^iPr_3)_2Ni$, followed by rapid intramolecular oxidative addition of the remaining C−H bond activation.

The stoichiometric reaction of the pentafluorobenzene C−H activation product **5** with 3-hexyne differs than the analogous reaction between **3** and 3-hexyne, because it instead produces essentially equal amounts of compound **9** and the insertion product $(P^iPr_3)_2Ni(CEt{=}CHEt)(C_6F_5)$ (**14**) upon mixing. Compound **14** was characterized by ^1H, ^{31}P, and ^{19}F NMR spectroscopy. The ^{31}P NMR spectrum reveals a singlet at δ 38.3, comparable to the ^{31}P chemical shift for compound **10**, and the ^1H NMR spectrum has a triplet at δ 5.25 characteristic of the hydrogen on the inserted alkyne fragment. The ^{19}F NMR spectrum contains five fluorine environments at δ −107.9, −112.5, −162.2, −163.4, and −164.0. Heating this mixture to 50 °C drives the reaction to complete reductive elimination of the functionalized product C_6F_5−CEt=CHEt, **13**, as shown in Scheme 4. The catalytic alkenylation of 1,2,3,4-$C_6F_4H_2$ and 3-hexyne with $Ni(COD)_2$ (10 mol %) and triisopropylphosphine (10 mol %) is practically quantitative in producing 1,2,3,4-C_6F_4H-CEt=CHEt (**15**), as shown in Scheme 4. However, the intermediate insertion product was not observed by NMR spectroscopy, which reveals that reductive elimination is more rapid for this substrate with a single fluorine adjacent to the site of functionalization; this can be attributed to the weaker Ni−C bond to the aryl group in this species. Unlike 1,2,3,5- and 1,2,4,5-tetrafluorobenzene, the substrate 1,2,3,4-tetrafluorobenzene failed to produce an observable C−H bond activation complex, $(P^iPr_3)_2NiH(2,3,4,5\text{-}C_6F_4H)$, as it is thermodynamically unfavorable. Despite this, the transient hydride can be trapped using an alkyne, showing that this C−H activation product is kinetically accessible. Compound **15** was characterized by ^1H and ^{19}F NMR spectroscopy, where there are four fluorine environments at δ −141.1, −142.4, −156.7, and −159.2.

Surprisingly, the alkyne adduct of the less bulky adduct $(PEt_3)_2Ni(\eta^2\text{-}EtC{\equiv}CEt)$ (**16**), synthesized analogously to compound **9**, displayed similar reactivity.[45] Heating a solution of compound **16** (10 mol %) with 1,2,4,5-tetrafluorobenzene at 80 °C causes alkyne dissociation followed by insertion into the C−H activation product, $(PEt_3)_2NiH(2,3,5,6\text{-}C_6F_4H)$, which produced observable amounts of $(PEt_3)_2Ni(CEt{=}CHEt)$-$(2,3,5,6\text{-}C_6F_4H)$ (**17**). Compound **17** was characterized by ^{31}P and ^{19}F NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum revealed a singlet at δ 13.3, which is slightly upfield from the ^{31}P resonance observed for **16** at δ 26.8. The ^{19}F NMR spectrum displays four fluorine environments at δ −113.4, −117.4, −142.0, and −142.3, which are not in exchange due to hindered rotation about the Ni−C bonds, analogous to compound **10**. Heating this mixture for 3 days at 80 °C eventually produced the monoinsertion product **11** in a modest 40% yield, which amounts to only four catalytic turnovers; unsurprisingly, considering the low conversion, very little of the doubly functionalized product **12** was observed, as shown in Scheme 4. The reductive elimination of the functionalized product appears to be a slow step in the catalytic cycle for alkenylation for both the P^iPr_3 and PEt_3 ancillary ligands, as judged by the persistence of the resonances associated with **10** and **17**, respectively. The alkyne adducts **9** and **16** also appear in these spectra as resting

(45) Begum, R. A.; Sharp, P. R. *Organometallics* **2005**, *24* (11), 2670.

states, and thus it can be concluded that C−H bond oxidative addition steps with **10** and **17** are also slow. It should be noted that with PEt_3 as the ancillary ligand catalysis did not occur at a significant rate at 50 °C, but heating the reaction mixture at 80 °C for prolonged periods of time resulted in significant decomposition and the precipitation of nickel, which results in dramatically decreased yields as the catalyst decomposes. It appears that the main downfall of the PEt_3 ancillary ligand in these reactions is not its propensity to undergo side reactions, such as C−F bond activation, but rather the higher temperatures required for both the oxidative addition and reductive elimination steps that occur during catalytic alkenylation, and the inability of PEt_3 to sufficiently kinetically stabilize Ni(0) with respect to the free metal under these conditions.

Conclusions

This work provides the first examples of the isolation and complete characterization of products from the oxidative addition of aromatic C−H bonds to nickel. This was achieved by using the sterically encumbered P^iPr_3 ancillary ligand to destabilize Ni(0) complexes with *cis*-disposed phosphine donors relative to their oxidative addition products, which have *trans*-disposed donors. The anthracene adduct $(P^iPr_3)_2Ni(\eta^2\text{-}C_{14}H_{10})$ proved to be an effective $(P^iPr_3)_2Ni$ synthon and reacts with, 1,2,4,5-tetrafluorobenene, 1,2,3,5-tetrafluorobenzene, and pentafluorobenzene via C−H bond activation, with no evidence for mononuclear or dinuclear Ni(0) adducts. The C−H activation product of 1,2,4,5-$C_6F_4H_2$ displayed remarkable thermal stability and did not undergo C−F bond activation even with heating to 100 °C. Deuterium labeling studies suggest that the reaction is not rapidly reversible at room temperature. The C−H activation products arising from 1,2,3,5-$C_6F_4H_2$ and pentafluorobenzene were also isolated, but were less thermally stable. The substrate 1,2,3,4-tetrafluorobenzene did not produce $(P^iPr_3)_2NiH(2,3,4,5\text{-}C_6F_4H)$ as an isolable product. However, trapping the transient hydride from oxidative addition of 1,2,3,4-$C_6F_4H_2$ to $(P^iPr_3)_2Ni$ with alkyne shows that this C−H activation product is kinetically accessible, despite only a single *ortho*-fluorine adjacent to the activated bond. The alkyne adduct $(P^iPr_3)_2Ni(\eta^2\text{-EtC}{\equiv}\text{CEt})$ proved to be a useful precursor in the alkenylations of C_6F_5H and 1,2,3,4- and 1,2,4,5-$C_6F_4H_2$ into new organofluorines. Somewhat surprisingly, similar catalytic reactivity was observed using the phosphine PEt_3 as the ancillary ligand. The alkyne adduct $(PEt_3)_2Ni(\eta^2\text{-EtC}{\equiv}\text{CEt})$ was also effective in catalytic alkenylation at relatively high temperatures; this $(PEt_3)_2Ni$ moiety is known to provide thermodynamic C−F bond activation products under ambient conditions,[15,16] thus highlighting the possibility of using kinetic C−H activation products in catalysis.

Experimental Section

General Procedures. Unless otherwise stated, all manipulations were performed under an inert atmosphere of nitrogen using either standard Schlenk techniques or an MBraun glovebox. Dry, oxygen-free solvents were employed throughout. Anhydrous pentane, toluene, and THF were purchased from Aldrich, sparged with dinitrogen, and passed through activated alumina under a positive pressure of nitrogen gas; toluene and hexanes were further deoxygenated using a Grubbs-type column system.[46] Benzene-d_6 was dried by heating at reflux with Na/K alloy in a sealed vessel under partial pressure, then trap-to-trap distilled and freeze−pump−thaw degassed three times. Toluene-d_8 was purified in an analogous manner by heating at reflux over Na. THF-d_8 was purified in an analogous manner by heating at reflux over K. ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra were recorded on a Bruker AMX spectrometer operating at 300 or 500 MHz with respect to proton nuclei. All chemical shifts are recorded in parts per million, and all coupling constants are reported in hertz. ^1H NMR spectra were referenced to residual protons (C_6D_5H, δ 7.16; C_7D_7H, δ 2.09; C_4D_7HO, δ 1.73) with respect to tetramethylsilane at δ 0.00. $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4 at δ 0.00. $^{13}C\{^1H\}$ NMR spectra were referenced relative to solvent resonances (C_6D_6, δ 128.0; C_7D_8, δ 20.4; C_4D_8O, δ 25.37). $^{19}F\{^1H\}$ NMR spectra were referenced to an external sample of 80% CCl_3F in $CDCl_3$ at δ 0.0. Elemental analyses were performed by the Center for Catalysis and Materials Research, Windsor, Ontario. The compounds benzene-d_6, toluene-d_8, and THF-d_8 were purchased from Cambridge Isotope Laboratory. The compounds anthracene, pentafluorobenzene, 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetrafluorobenzene, and 3-hexyne were purchased from Aldrich and used as received. The compound triisopropylphosphine was purchased from Strem and used as received. The anthracene adduct $(THF)_3Mg(\eta^2\text{-}C_{14}H_{10})$,[35] *trans*-$[Cl_2Ni(P^iPr_3)_2]$,[47] the anthracene adduct $(PEt_3)_2Ni(\eta^2\text{-}C_{14}H_{10})$, 1,2,4,5-$C_6F_4HD$,[15] and $Ni(COD)_2$[48] were prepared by literature methods.

Synthesis of the Anthracene Adduct $(P^iPr_3)_2Ni(\eta^2\text{-}C_{14}H_{10})$, 1. To a mixture of *trans*-$[Cl_2Ni(P^iPr_3)_2]$ (15 g, 33 mmol) and $(THF)_3Mg(\eta^2\text{-}C_{14}H_{10})$ (15.36 g, 37 mmol) was added slowly 200 mL of THF at −78 °C, and the solution was stirred for 1 h. The purple solution was slowly warmed to 0 °C over 3 h, and the color changed to brown. The mixture was stirred for an additional 2 h at 0 °C, followed by removal of the solvent. The resulting solid was extracted into 200 mL of pentane, and $MgCl_2$ was filtered off. The filtrate was placed in the freezer, and over the course of 30 min colorless crystals of the paramagnetic compound $ClNi(P^iPr_3)_2$ precipitated from solution and were isolated by filtration (2.7 g, 14.5% yield). The filtrate was concentrated by 75% and placed in the freezer. X-ray quality red crystals of the desired compound **1** precipitated from the solution overnight and were filtered and dried under vacuum (8.96 g, 48.2% yield). Concentration of the mother liquor yielded a second crop containing a low melting solid; isolation of this solid was achieved through recrystallization from hexamethyldisiloxane in the freezer (4.22 g, 23% yield). Both solids were confirmed by NMR spectroscopy to be **1** (71% total yield). Compound **1** is very soluble in hydrocarbon solvents; however, when dissolved in aromatic solvents such as benzene, toluene, and mesitylene, it provides equilibrium amounts of $(P^iPr_3)Ni(\eta^6\text{-solvent})$, **2a**−**c**, respectively. ^1H NMR (THF-d_8, 298 K, 300.13 MHz): δ 1.18 (br, 36H, ^{i}Pr−CH_3); 2.04 (br, 6H, ^{i}Pr−C*H*); 5.32 and 5.55 (br, 2H, Ni−C*H*, $W_{1/2}$ = 35.0 Hz); 7.17, 7.41, 7.60, 7.98, and 8.43 (br, 8H, anthracene−*H*). $^{31}P\{^1H\}$ NMR (THF-d_8, 298 K, 121.5 MHz): δ 44.4 (br, $W_{1/2}$ = 18.0 Hz). $^{31}P\{^1H\}$ NMR (THF-d_8, 233 K, 121.5 MHz): δ 40.5 and 44.3(d, $^2J_{PP}$ = 45 Hz). $^{13}C\{^1H\}$ NMR (THF-d_8, 298 K, 75.5 MHz): δ 21.1 (s, ^{i}Pr−CH_3); 22.5 (d, ^{i}Pr−C*H*, $^1J_{CP}$ = 18 Hz); 122.7, 123.8, 126.0, 126.9, 127.2, and 128.9 (s, anthracene−C*H*); 132.8 and 138.1 (br, anthracene−*ipso*-C*H*). Anal. Calcd for $C_{32}H_{52}NiP_2$ (MW 557.40): C, 68.95; H, 9.40. Found: C, 69.02; H, 9.78.

$(P^iPr_3)Ni(\eta^6\text{-}C_6H_6)$, 2a. ^1H NMR (C_6H_6, 333 K, 300.13 MHz): δ 1.04 and 1.08 (d, 18H, ^{i}Pr−CH_3, $^3J_{HH}$ = 6.9 Hz); 1.72 (br, 3H, ^{i}Pr−C*H*); 5.87 (s, 6H, η^6-C_6H_6)). $^{31}P\{^1H\}$ NMR (C_6H_6, 333 K, 121.5 MHz): δ 59.4 (s). $^{13}C\{^1H\}$ NMR (C_6H_6, 333

(46) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15* (5), 1518.

(47) This compound was prepared analogously to the synthesis of $Cl_2Ni(PEt_3)_2$ reported in: Stanger, A.; Vollhardt, K. P. C. *Organometallics* **1992**, *11*, 317–320.

(48) Krysan, D. J.; Mackenzie, P. B. *J. Org. Chem.* **1990**, *55* (13), 4229.

K, 75.5 MHz): δ 21.0 (s, ^{i}Pr−CH_3); 24.8 (d, ^{i}Pr−CH, $^{1}J_{CP}$ = 18 Hz); 90.4 (s, η^6-C_6H_6).

($P^{i}Pr_3$)Ni(η^6-C_6D_6), 2a-d_6. ^{1}H NMR (C_6D_6, 333 K, 300.13 MHz): δ 1.04 and 1.08 (d, 18H, ^{i}Pr−CH_3, $^{3}J_{HH}$ = 6.9 Hz); 1.72 (br, 3H, ^{i}Pr−CH). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 333 K, 121.5 MHz): δ 59.4 (s). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 333 K, 75.5 MHz): δ 21.0 (s, ^{i}Pr−CH_3); 24.8 (d, ^{i}Pr−CH, $^{1}J_{CP}$ = 18 Hz); 90.4 (1:1:1 t, η^6-C_6D_6, $^{1}J_{CD}$ = 26 Hz).

($P^{i}Pr_3$)Ni(η^6-C_7H_8), 2b. ^{1}H NMR (C_7H_8, 333 K, 300.13 MHz): δ 1.03 and 1.07 (d, 18H, ^{i}Pr−CH_3, $^{3}J_{HH}$ = 6.7 Hz); 1.69 (br, 3H, ^{i}Pr−CH); 2.07 (s, 3H, η^6-toluene−CH_3); 5.6−5.8 (overlapping m, 5H, η^6-toluene−H). $^{31}P\{^{1}H\}$ NMR (C_7H_8, 333 K, 121.5 MHz): δ 60.9 (s). $^{13}C\{^{1}H\}$ NMR (C_7H_8, 333 K, 75.5 MHz): δ 20.8 (s, η^6-toluene−CH_3); 20.9 (s, ^{i}Pr−CH_3); 22.0 (d, ^{i}Pr−CH, $^{1}J_{CP}$ = 19.4 Hz); 89.0, 89.5, and 91.9 (s, η^6-toluene−CH); 101.8 (s, η^6-toluene−CCH_3).

($P^{i}Pr_3$)Ni(η^6-C_7D_8), 2b-d_8. ^{1}H NMR (C_7D_8, 333 K, 300.13 MHz): δ 1.03 and 1.07 (d, 18H, ^{i}Pr−CH_3, $^{3}J_{HH}$ = 6.7 Hz); 1.69 (br, 3H, ^{i}Pr−CH). $^{31}P\{^{1}H\}$ NMR (C_7D_8, 333 K, 121.5 MHz): δ 60.9 (s). $^{13}C\{^{1}H\}$ NMR (C_7D_8, 333 K, 75.5 MHz): δ 20.8 (m, η^6-toluene-CD_3); 20.9 (s, ^{i}Pr−CH_3); 22.0 (d, ^{i}Pr−CH, $^{1}J_{CP}$ = 19.4 Hz); 89.0, 89.5, and 91.9 (1:1:1 t, η^6-toluene−CD, $^{1}J_{CD}$ = 23.0, 20.1, and 23.0 Hz); 101.8 (s, η^6-toluene−CCD_3).

($P^{i}Pr_3$)Ni(η^6-mesitylene), 2c. ^{1}H NMR (mesitylene, 333 K, 300.13 MHz): δ 1.00 and 1.04 (d, 18H, ^{i}Pr−CH_3, $^{3}J_{HH}$ = 6.6 Hz); 1.66 (br, 3H, ^{i}Pr−CH), 2.03 (s, 9H, mesitylene−CH_3); 5.59 (s, 3H, mesitylene−CH). $^{31}P\{^{1}H\}$ NMR (mesitylene, 333 K, 121.5 MHz): δ 61.3 (s). $^{13}C\{^{1}H\}$ NMR (mesitylene, 333 K, 75.5 MHz): δ 21.1 (s, ^{i}Pr−CH_3); 22.0 (s, mesitylene−CH_3); 25.4 (d, ^{i}Pr−CH, $^{1}J_{CP}$ = 17.8 Hz); 95.0 (s, mesitylene−CH); 101.2 (s, mesitylene−CCH_3).

Reaction of 1 with 50 equiv of Triisopropylphosphine. Compound **1** (50 mg, 0.09 mmol) and triisopropylphosphine (719 mg, 4.5 mmol, 50 equiv) were dissolved in benzene. The solution was heated to 333 K in a J. Young tube. The formation of **2a** was partially inhibited (20% compound **1** remained).

Reaction of 1 in Neat Triisopropylphosphine with Benzene. Compound **1** (50 mg, 0.09 mmol) and benzene (8 mg, 0.09 mmol) were dissolved in triisopropylphosphine. The solution was heated to 333 K in a J. Young tube. The formation of **2a** was completely inhibited.

Competition Reaction to Determine Preference for Aromatic in ($P^{i}Pr_3$)Ni(η^6-solvent) Complexes. Compound **1** (30 mg, 0.054 mmol) and a mixture of benzene (4.5 mg, 0.054 mmol), toluene (5.4 mg, 0.054 mmol), and mesitylene (6.5 mg, 0.054 mmol) were dissolved in 0.75 mL of hexamethyldisiloxane in a J. Young tube. The reaction mixture was heated to 333 K. Final reaction composition: **2a**, 26%; **2b**, 19%; **2c**, 55%.

Synthesis of ($P^{i}Pr_3$)$_2$NiH(2,3,5,6-C_6F_4H), 3. Complex **1** (500 mg, 0.89 mmol) and 1,2,4,5-tetrafluorobenzene (150 mg, 0.99 mmol) were stirred for 6 h in toluene. The solvent was removed *in vacuo*, and the resultant solid extracted with pentane. The precipitated anthracene was filtered, and the yellow filtrate placed in the freezer. Yellow-colored X-ray quality crystals of the desired compound precipitated from solution and were filtered off and dried *in vacuo* (312 mg, 66% isolated yield). Concentration of the mother liquor failed to yield a suitable second crop. ^{1}H NMR (C_6D_6, 298 K, 300.13 MHz): δ −16.25 (ttt, 1H, Ni−H, $^{2}J_{HP}$ = 68.0 Hz, $^{4}J_{HF}$ = 8.7 Hz, $^{5}J_{HF}$ = 4.0 Hz); 1.01 and 1.05 (d, 36H, ^{i}Pr−CH_3, $^{3}J_{HH}$ = 6.4 Hz); 1.76 (m, 6H, ^{i}Pr−CH), 6.65 (tt, 1H, 4-Ar−H, $^{3}J_{HF}$ = 8.9 Hz, $^{4}J_{HF}$ = 7.4 Hz). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 298 K, 121.5 MHz): δ 51.5 (s). ^{31}P NMR (C_6D_6, 298 K, 121.5 MHz): δ 51.5 (br d, $^{2}J_{PH}$ = 68.0 Hz). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 75.5 MHz): δ 19.7 (s, ^{i}Pr−CH_3); 26.0 (AMM′ virtual t, ^{i}Pr−CH, J_{CP} = 10.8 Hz); 99.7 (t, 4-Ar−C, $^{2}J_{CF}$ = 24.0 Hz); 145.5 (ddm, 3,5-Ar−C, $^{1}J_{CF}$ = 249.4 Hz, $^{2}J_{CF}$ = 26.3 Hz); 146.6 (dtm, 1-Ar−C, $^{2}J_{CF}$ = 134.5 Hz, $^{3}J_{CF}$ = 13.4 Hz); 148.2 (ddm, 2,6-Ar−C, $^{1}J_{CF}$ = 214.3 Hz, $^{2}J_{CF}$ = 26.8 Hz). $^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −112.9 (AA′MM′ second-order m, 2F, 2,6-Ar−F); −143.0 (AA′MM′ second-order m, 2F, 3,5-Ar−F). IR: ν_{NiH} = 1902.94 cm^{-1} (br). Anal. Calcd for $C_{24}H_{44}F_4NiP_2$ (MW 529.24): C, 54.47; H, 8.38. Found: C, 54.45; H, 8.71.

Reaction of 1 with 1,2,4,5-C_6F_4HD. Complex **1** (50 mg, 0.09 mmol) and 1,2,4,5-C_6F_4HD (14 mg, 0.09 mmol) were dissolved in C_6D_6 and immediately analyzed by $^{19}F\{^{1}H\}$ NMR spectroscopy. The initial reaction mixture consisted primarily of the starting materials, but also contained the C−H bond activation products, **3-d_1(NiH)** and **3-d_1(NiD)**. Through integration of the *meta*-fluorine peaks that are separated by 0.3 ppm, a kinetic isotope effect (KIE) of 1.3 was obtained for C−H bond activation. This sample mixture was then heated to 50 °C to demonstrate the reversibility of the C−H oxidative addition reaction, achieving a maximum value of 1.7 for the equilibrium isotope effect (EIE). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 298 K, 121.5 MHz): δ 51.5 (s, **3-d_1(NiH)**); 51.8 (1:1:1 t, **3-d_1(NiD)**, $^{2}J_{PD}$ = 10.1 Hz). $^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −112.9 (overlapping AA′MM′ second-order m, **3-d_1(NiH)** and **3-d_1(NiD)**, *ortho-F*); −143.0 (AA′MM′ second-order m, **3-d_1(NiD)**, *meta-F*); −143.3 (AA′MM′ second-order m, **3-d_1(NiH)**, *meta-F*).

Reaction of 3-d_1(NiH) and 3-d_1(NiD) with 1,2,4,5-$C_6F_4H_2$. A mixture of **3-d_1(NiH)** and **3-d_1(NiD)** was heated to 50 °C for 1 h with an excess of nondeuterated 1,2,4,5-tetrafluorobenzene, which resulted in their conversion to **3** with the liberation of 1,2,4,5-C_6F_4HD.

Synthesis of ($P^{i}Pr_3$)$_2$NiH(2,3,4,6-C_6F_4H), 4. Complex **1** (500 mg, 0.89 mmol) and 1,2,3,5-tetrafluorobenzene (150 mg, 0.99 mmol) were stirred for 36 h in toluene. The solvent was removed *in vacuo*, and the resultant solid extracted with hexamethyldisiloxane. The precipitated anthracene was filtered, and the dark yellow filtrate placed in the freezer. Yellow-colored X-ray quality crystals of the desired compound precipitated from solution and were filtered off and dried *in vacuo* (340 mg, 72% isolated). Concentration of the mother liquor failed to yield a suitable second crop. ^{1}H NMR (C_6D_6, 298 K, 300.13 MHz): δ −16.38 (tddd, 1H, Ni−H, $^{2}J_{HP}$ = 68.5 Hz, $^{4}J_{HF}$ = 8.8 Hz, $^{4}J_{HF}$ = 8.7 Hz, $^{5}J_{HF}$ = 3.5 Hz); 1.01 and 1.07 (d, 36H, ^{i}Pr−CH_3, $^{3}J_{HH}$ = 6.7 Hz); 1.76 (m, 6H, ^{i}Pr−CH); 6.51 (m, 1H, 5-Ar−H). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 298 K, 121.5 MHz): δ 51.6 (s). ^{31}P NMR (C_6D_6, 298 K, 121.5 MHz): δ 51.6 (br d, $^{2}J_{PH}$ = 68.5 Hz). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 75.5 MHz): δ 19.7 (s, ^{i}Pr−CH_3); 26.0 (AMM′ virtual t, ^{i}Pr−CH, J_{CP} = 10.3 Hz); 98.6 (dd, 5-Ar−C, $^{2}J_{CF}$ = 40.4 Hz, $^{2}J_{CP}$ = 19.0 Hz); 134.0 (tm, *ipso*-Ar−C, $^{2}J_{CF}$ = 75.4 Hz); 137.2 (dm, 6-Ar−C, $^{1}J_{CF}$ = 237.9 Hz); 147.8 (dm, 2-Ar−C, $^{1}J_{CF}$ = 237.9 Hz); 153.5 (dd, 4-Ar−C, $^{1}J_{CF}$ = 225.3 Hz; $^{2}J_{CF}$ = 37.2 Hz); 160.4 (ddd, 3-Ar−C, $^{1}J_{CF}$ = 225.3 Hz; $^{4}J_{CF}$ = 31.0 Hz, $^{2}J_{CF}$ = 10.4 Hz). $^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −86.1 (d, 1F, 2-Ar−F, $^{3}J_{FF}$ = 13.7 Hz); −105.8 (d, 1F, 6-Ar−F, $^{5}J_{FF}$ = 34.4 Hz); −144.4 (d, 1F, 4-Ar−F, $^{3}J_{FF}$ = 19.7 Hz); −170.3 (ddd, 1F, 3-Ar−F, $^{5}J_{FF}$ = 34.4 Hz, $^{3}J_{FF}$ = 19.7 Hz, $^{3}J_{FF}$ = 13.7 Hz). IR: ν_{NiH} = 1892.13 cm^{-1} (br). Anal. Calcd for $C_{24}H_{44}F_4NiP_2$ (MW 529.24): C, 54.47; H, 8.38. Found: C, 53.98; H, 8.76.

Synthesis of ($P^{i}Pr_3$)$_2$NiH(C_6F_5), 5. Compound **1** (500 mg, 0.897 mmol) and excess pentafluorobenzene (200 mg, 1.2 mmol) were stirred in toluene for 2 h. The solvent was removed *in vacuo*, and the resultant oil extracted in pentane. The precipitated anthracene was filtered, and the dark yellow filtrate placed in the freezer. A brown-colored viscous oil was confirmed to be compound **5** by NMR spectroscopy (94% yield by NMR) and found to contain <5% C−F activation impurities. ^{1}H NMR (C_6D_6, 298 K, 300.13 MHz): δ −16.5 (ttt, 1H, Ni−H, $^{2}J_{HP}$ = 68.0 Hz, $^{4}J_{HF}$ = 9.9 Hz, $^{5}J_{HF}$ = 4.5 Hz); 0.96 and 1.01 (d, 36H, ^{i}Pr−CH_3, $^{3}J_{HH}$ = 7.1 Hz); 1.70 (m, 6H, ^{i}Pr−CH). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 298 K, 121.5 MHz): δ 51.2 (s). ^{31}P NMR (C_6D_6, 298 K, 121.5 MHz): δ 51.2 (br d, $^{2}J_{PH}$ = 68.0 Hz). $^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 75.5 MHz): δ 19.7 (s, ^{i}Pr−CH_3); 26.0 (AMM′ virtual t, ^{i}Pr−CH, J_{CP} = 11.8 Hz); 100.3 (tm, *ipso*-Ar−C, $^{2}J_{CF}$ = 22.9 Hz); 136.3 (ddm, 2,6-Ar−C, $^{1}J_{CF}$ = 230.8 Hz, $^{2}J_{CF}$ = 14.7 Hz); 136.3 (dddd, 3,5-Ar−C, $^{1}J_{CF}$ = 226.31 Hz, $^{2}J_{CF}$ = 29.5 Hz, $^{2}J_{CF}$ = 9.8 Hz); 147.0 (ddm, 4-Ar−C,

$^1J_{CF}$ = 218.4 Hz, $^2J_{CF}$ = 29.5 Hz). $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −110.7 (AA′MM′N second-order m, 2F, 2,6-Ar−*F*); −163.2 (tt, 1F, 4-Ar−*F*, $^3J_{FF}$ = 19.6 Hz, $^4J_{FF}$ = 2.5 Hz); −164.6 (AA′MM′N second-order m, 2F, 3,5-Ar−*F*).

Reaction of 1, C_6F_5H, and 50 equiv of Triisopropylphosphine. A toluene solution of **1** (20 mg, 0.036 mmol), C_6F_5H (6 mg, 0.036 mmol), and triisopropylphosphine (287 mg, 1.79 mmol) was monitored by $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectroscopy. The rate of formation of **5** was unchanged compared to the analogous reaction in the absence of added triisopropylphosphine.

Synthesis of (η^3-C_8H_{13})Ni(P^iPr_3)(2,3,5,6-C_6F_4H), 6. A mixture of $Ni(COD)_2$ (18.3 mg, 0.07 mmol), triisopropylphosphine (21.4 mg, 0.14 mmol, 2 equiv), and 1,2,4,5-$C_6F_4H_2$ (10 mg, 0.07 mmol) was dissolved in toluene and reacted overnight. The crude mixture was placed in the freezer, whereupon yellow-colored X-ray quality crystals precipitated from solution. ^1H NMR (C_6D_6, 298 K, 300.13 MHz): δ 0.85, 0.9, 0.92, and 0.97 (d, allylic cyclooctene−C*H*$_2$, $^3J_{HH}$ = 6.0 Hz); 1.02 and 1.07 (d, 36H, ^{i}Pr−C*H*$_3$, $^3J_{HH}$ = 7.1 Hz); 1.15−1.4 (m, allylic cyclooctene−C*H*$_2$); 1.69 (m, 6H, ^{i}Pr−C*H*); 3.78 (overlapped m, allylic−C*H*); 4.02 (qdd, allylic−C*H*, $^3J_{HH}$ = 9.0 Hz, $^3J_{HP}$ = 4.0 Hz, $^3J_{HF}$ = 1.3 Hz); 4.85 (apparent t, allylic−C*H*, $^3J_{HH}$ = 8.5 Hz); 6.54 (overlapped tt, 1H, 4-Ar−*H*, $^3J_{HF}$ = 8.9 Hz, $^4J_{HF}$ = 7.4 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 121.5 MHz): δ 46.9 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 75.5 MHz): δ 19.2 and 19.8 (s, ^{i}Pr−*C*H$_3$); 23.2 (s), 27.6 (br), 28.4 (s), 30.4 (br), and 31.6 (s) (allylic cyclooctene−*C*H$_2$) 26.0 (d, ^{i}Pr−*C*H, $^1J_{CP}$ = 18.5 Hz); 68.9 (br), 75.9 (d, $^2J_{CP}$ = 20.6 Hz), and 108.3 (br) (allylic−*C*H); 100.2 (tm, 4-Ar−*C*, $^2J_{CF}$ = 23.8 Hz); 140.1 (m, 1-Ar−*C*); 145.1 (ddm, 2,6-Ar−*C*, $^1J_{CF}$ = 228.7 Hz, $^2J_{CF}$ = 25.4 Hz); 148.1 (ddm, 3,5-Ar−*C*, $^1J_{CF}$ = 224.5 Hz, $^2J_{CF}$ = 25.4 Hz). $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −114.7 (ddd, Ar−*F*, $^5J_{FF}$ = 33.8 Hz, $^3J_{FF}$ = 16.5 Hz, $^4J_{FF}$ = 3.5 Hz); −115.2 (ddt, Ar−*F*, $^5J_{FF}$ = 33.8 Hz, $^3J_{FF}$ = 16.5 Hz, $^4J_{FF}$ = 3.5 Hz); −142.9 (dd, Ar−*F*, $^5J_{FF}$ = 29.0 Hz, $^3J_{FF}$ = 16.7 Hz); −143.0 (dd, Ar−*F*, $^5J_{FF}$ = 29.0 Hz, $^3J_{FF}$ = 16.7 Hz). Anal. Calcd for $C_{23}H_{35}F_4NiP$ (MW 477.18): C, 57.89; H, 7.39. Found: C, 58.34; H, 7.47.

Synthesis of (η^3-C_8H_{13})Ni(P^iPr_3)(2,3,4,6-C_6F_4H), 7. A mixture of $Ni(COD)_2$ (300 mg, 1.09 mmol), triisopropylphosphine (349.6 mg, 2.18 mmol, 2 equiv), and 1,2,3,5-$C_6F_4H_2$ (163.7 mg, 1.09 mmol) was dissolved in 10 mL of toluene and stirred overnight. The crude reaction mixture was analyzed by NMR spectroscopy and contains two diastereomers, **7a** and **7b**, which could not be separated in addition to C−F activation impurities (< 5%). ^1H NMR (C_6D_6, 298 K, 300.13 MHz): δ 0.87, 0.91, 0.93, and 0.98 (overlapping d, allylic cyclooctene−C*H*$_2$, $^3J_{HH}$ = 7.2 Hz); 1.05 (br m, 18H, ^{i}Pr−C*H*$_3$, $^3J_{HH}$ = 7.1 Hz); 1.15−1.4 (m, allylic cyclooctene−C*H*$_2$); 1.75 (overlapped m, 3H, ^{i}Pr−C*H*); 3.75 (overlapped m, allylic−C*H*); 4.05 (overlapped pentet of doublets, allylic−C*H*, $^3J_{HH}$ = 9.0 Hz, $^3J_{HP}$ = 3.6 Hz); 4.86 (overlapped dd, allylic−C*H*, $^3J_{HF}$ = 10.7 Hz, $^3J_{HF}$ = 8.4 Hz); 6.47 and 6.53 (overlapped ddddd, 5-Ar−*H*, $^5J_{HF}$ = 19.4 Hz, $^3J_{HF}$ = 10.3 Hz, $^3J_{HF}$ = 10.3 Hz, $^4J_{HF}$ = 4.8 Hz, $^5J_{HP}$ = 2.4 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 121.5 MHz): δ 45.3 and 45.6 (m). $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −88.2 (dd, 6-Ar−*F*, $^4J_{FF}$ = 13 Hz, $^4J_{FF}$ = 3.2 Hz); −88.6 (dt, 6-Ar−*F*, $^4J_{FF}$ = 13 Hz, $^4J_{FF}$ = 4.0 Hz); −107.3 (dt, 2-Ar−*F*, $^5J_{FF}$ = 33.0 Hz, $^4J_{FF}$ = 3.0 Hz); −108.1 (dm, 2-Ar−*F*, $^5J_{FF}$ = 33.0 Hz, $^4J_{FF}$ = 3.0 Hz); −143.8 (dt, 4-Ar−*F*, $^3J_{FF}$ = 16.0 Hz, $^4J_{FF}$ = 2.0 Hz); −143.9 (dt, 4-Ar−*F*, $^3J_{FF}$ = 16.0 Hz, $^4J_{FF}$ = 2.0 Hz); −169.8 (ddd, 3-Ar−*F*, $^5J_{FF}$ = 20.0 Hz, $^3J_{FF}$ = 12.9 Hz, $^3J_{FF}$ = 12.9 Hz); −169.9 (ddd, 3-Ar−*F*, $^5J_{FF}$ = 20.0 Hz, $^3J_{FF}$ = 12.9 Hz, $^3J_{FF}$ = 12.9 Hz).

Synthesis of (η^3-C_8H_{13})Ni(P^iPr_3)(2,3,4,5-C_6F_4H), 8. A mixture of $Ni(COD)_2$ (500 mg, 1.82 mmol), triisopropylphosphine (582.6 mg, 3.64 mmol, 2 equiv), and 1,2,3,4-$C_6F_4H_2$ (272.8 mg, 1.82 mmol) was dissolved in 10 mL of toluene and stirred for 48 h. The crude reaction mixture was analyzed by NMR spectroscopy and contains two diastereomers, **8a** and **8b**, which could not be separated in addition to C−F activation impurities (< 5%). ^1H NMR (C_6D_6, 298 K, 300.13 MHz): δ 0.79, 0.80, 0.82, 0.83, 0.85, 0.89, and 0.93 (overlapping d, allylic cyclooctene−C*H*$_2$, $^3J_{HH}$ = 7.5 Hz); 1.28 and 1.39 (m, 18H, ^{i}Pr−C*H*$_3$); 1.83 (overlapped m, 3H, allylic cyclooctene−C*H*$_2$ and ^{i}Pr−C*H*); 3.66 (overlapped m, allylic−C*H*); 3.85 (overlapped quartet of doublets, allylic−C*H*, $^3J_{HH}$ = 9.0 Hz, $^3J_{HP}$ = 4.0 Hz); 4.71 and 4.85 (apparent t, allylic−C*H*, $^3J_{HF}$ = 10.7 Hz, $^3J_{HF}$ = 8.4 Hz); 5.38 (br qt); 6.74 (tm). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 121.5 MHz): δ 44.2 and 46.5 (m). $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −113.4 (ddd, 2-Ar−*F*, $^5J_{FF}$ = 36.0 Hz, $^3J_{FF}$ = 15.7 Hz); −113.8 (ddd, 2-Ar−*F*, $^5J_{FF}$ = 36.0 Hz, $^3J_{FF}$ = 15.7 Hz, $^4J_{FP}$ = 3.8 Hz); −144.1 (dd, 5-Ar−*F*, $^3J_{FF}$ = 20.0 Hz, $^3J_{FF}$ = 15.7 Hz); −144.3 (dd, 5-Ar−*F*, $^3J_{FF}$ = 20.0 Hz, $^3J_{FF}$ = 16.0 Hz); −161.2 (ddd, 3-Ar−*F*, $^3J_{FF}$ = 20.0 Hz, $^3J_{FF}$ = 15.0 Hz, $^4J_{FF}$ = 2.0 Hz); −161.4 (ddd, 3-Ar−*F*, $^3J_{FF}$ = 20.0 Hz, $^3J_{FF}$ = 15.0 Hz, $^4J_{FF}$ = 2.0 Hz); −167.0 (ddd, 4-Ar−*F*, $^3J_{FF}$ = 20.0 Hz, $^3J_{FF}$ = 20.0 Hz, $^4J_{FF}$ = 2.0 Hz); −167.2 (ddd, 4-Ar−*F*, $^3J_{FF}$ = 20.0 Hz, $^3J_{FF}$ = 20.0 Hz, $^4J_{FF}$ = 2.0 Hz).

Synthesis of the 3-Hexyne Adduct (P^iPr_3)$_2$Ni(η^2-EtC≡CEt), 9. Compound **1** (250 mg, 0.449 mmol) and 3-hexyne (37 mg, 0.449 mmol) were stirred in 5 mL of pentane for 30 min. The precipitated anthracene was filtered, and the resultant solution placed in the freezer. Orange-colored X-ray quality crystals precipitated from the solution and were filtered and dried *in vacuo* (200 mg, 96.7% yield). ^1H NMR (C_6D_6, 298 K, 300.13 MHz): δ 1.22 and 1.26 (d, 36H, ^{i}Pr−C*H*$_3$, $^3J_{HH}$ = 7.3 Hz); 1.42 (t, 6H, hexyne−C*H*$_3$, $^3J_{HH}$ = 7.3 Hz); 2.07 (m, 6H, ^{i}Pr−C*H*); 2.88 (qd, 4H, hexyne−C*H*$_2$, $^3J_{HH}$ = 7.3 Hz, $^4J_{HP}$ = 2.5 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 121.5 MHz): δ 54.8 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 75.5 MHz): δ 16.2 (s, hexyne−*C*H$_3$); 20.4 (s, ^{i}Pr−*C*H$_3$); 23.1 (AMM′ virtual t, hexyne−*C*H, $^3J_{CP}$ = 7.0 Hz); 26.6 (AMM′ virtual t, ^{i}Pr−*C*H, J_{CP} = 7.5 Hz); 81.1 (br, hexyne−*C*). Anal. Calcd for $C_{24}H_{52}NiP_2$ (MW 461.31): C, 62.49; H, 11.36. Found: C, 62.31; H, 11.59.

Alternate Synthesis of 9. $Ni(COD)_2$ (200 mg, 0.727 mmol) and 3-hexyne (60 mg, 0.727 mmol) were stirred in 5 mL of pentane for 30 min. The orange-colored solution was placed in the freezer. Orange-colored crystals precipitated from the solution and were filtered and dried *in vacuo* (319 mg, 95.2% yield).

Reaction of 3 with 3-Hexyne. Compound **3** (25 mg, 0.05 mmol) and 3-hexyne (4 mg, 0.05 mmol) were dissolved in C_6D_6, and the orange-colored solution was immediately analyzed by NMR spectroscopy. The crude NMR spectra revealed the major product to be compound **9** (> 95%) with trace impurities attributed to a mixture of compound **3** and the alkyne insertion product, (P^iPr_3)$_2$Ni(CEt=CHEt)(2,3,5,6-C_6F_4H) (**10**).

Characterization of (P^iPr_3)$_2$Ni(CEt=CHEt)(2,3,5,6-C_6F_4H), 10. ^1H NMR (C_6D_6, 298 K, 300.13 MHz): δ 0.87 and 1.39 (t, 6H, Et-C*H*$_3$, $^3J_{HH}$ = 7.8 Hz); 2.15 (dq, 2H, Et-C*H*$_2$, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.3 Hz); 2.45 (m, 2H, Et-C*H*$_2$, $^3J_{HH}$ = 7.8 Hz); 5.61 (br, H, C*H*); 6.30 (tt, 1H, 4-Ar−*H*, $^3J_{HF}$ = 9.2, $^4J_{HF}$ = 6.2 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 121.5 MHz): δ 39.4 (s). $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −110.3 (ddd, 1F, 2-Ar−*F*, $^3J_{FF}$ = 36.3 Hz, $^5J_{FF}$ = 16.9 Hz, $^4J_{FF}$ = 4.9 Hz); −114.7 (ddd, 1F, 6-Ar−*F*, $^3J_{FF}$ = 34.7 Hz, $^5J_{FF}$ = 17.2 Hz, $^4J_{FF}$ = 4.9 Hz); −142.1 (dd, 1F, 3-Ar−*F*, $^3J_{FF}$ = 34.0 Hz, $^5J_{FF}$ = 16.7 Hz), −142.5 (dd, 1F, 3-Ar−*F*, $^3J_{FF}$ = 36.3 Hz, $^5J_{FF}$ = 16.9 Hz).

Synthesis of (*E*)-1,2,4,5-Tetrafluoro-3-(hex-3-en-3-yl)benzene, 11. A solution of 1,2,4,5-$C_6F_4H_2$ (55 mg, 0.36 mmol) and 3-hexyne (30 mg, 0.36 mmol) was added to a mixture of $Ni(COD)_2$ (10 mg, 0.036 mmol) and triisopropylphosphine (11.6 mg, 0.73 mmol, 2 equiv) in C_6D_6. The reaction mixture was heated to 50 °C for 24 h. The products were determined by NMR spectroscopic analysis to be a mixture of compound **11** (3% yield by NMR) and the doubly activated product 1,2,4,5-tetrafluoro-3,6-di((*E*-hexen-3-yl)benzene (**12**) (95% yield by NMR spectroscopy). ^1H NMR (C_6D_6, 298 K, 300.13 MHz): δ 0.79 and 0.85 (t, 6H, Et−C*H*$_3$, $^3J_{HH}$ = 7.8 Hz); 1.81 (dq, 2H, Et−C*H*$_2$, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.3 Hz); 2.08 (q, 2H, Et−C*H*$_2$, $^3J_{HH}$ = 7.8 Hz); 5.30 (t, H, C*H*, $^3J_{HH}$ = 7.3 Hz); 6.51 (tt, 1H, 4-Ar−*H*,

$^3J_{HF}$ = 9.2, $^4J_{HF}$ = 6.2 Hz). $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −140.5 (AA′MM′ second-order m, 2F, 2,6-Ar−*F*); −143.4 (AA′MM′ second-order m, 2F, 3,5-Ar−*F*).

1,2,4,5-Tetrafluoro-3,6-di((*E*-hexen-3-yl)benzene, 12. ^1H NMR (C_6D_6, 298 K, 300.13 MHz): δ 0.85 and 1.10 (t, 6H, Et−CH_3, $^3J_{HH}$ = 7.8 Hz); 1.91 (dq, 2H, Et−CH_2, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.3 Hz); 2.32 (q, 2H, Et−CH_2, $^3J_{HH}$ = 7.8 Hz); 5.41 (t, H, C*H*, $^3J_{HH}$ = 7.3 Hz). $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −143.5 (s, 4F, 2,3,5,6-Ar−*F*).

Synthesis of (*E*)-1,2,3,4,5-Pentafluoro-6-(hex-3-en-3-yl)benzene, 13. A C_6D_6 solution of compound **1** (25 mg, 0.045 mmol), C_6F_5H (76 mg, 0.45 mmol), and 3-hexyne (37 mg, 0.45 mmol) was immediately analyzed by NMR spectroscopy to be a mixture **9** and the 3-hexyne insertion product **14**. The mixture was heated to 50 °C for 3 days, yielding the monoinsertion product **13** (97% yield by NMR). ^1H NMR (C_6D_6, 298 K, 300.13 MHz): δ 0.84 and 0.93 (t, 6H, Et−CH_3, $^3J_{HH}$ = 7.1 Hz); 1.91 (dq, 2H, Et−CH_2, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.4 Hz); 2.13 (q, 2H, Et−CH_2, $^3J_{HH}$ = 7.4 Hz); 5.25 (t, H, C*H*, $^3J_{HH}$ = 7.7 Hz). $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −142.7 (AA′MM′X second-order m, 2F, 2,6-Ar−*F*); −157.5 (t, 2F, 4-Ar−*F*, $^3J_{FF}$ = 21.0 Hz,); −163.1 (AA′MM′X second-order m, 2F, 3,5-Ar−*F*).

Characterization of (P^iPr_3)$_2$Ni(CEt=CHEt)(C_6F_5), 14. ^1H NMR (C_6D_6, 298 K, 300.13 MHz): δ 0.75 and 1.41 (t, 6H, Et−CH_3, $^3J_{HH}$ = 7.4 Hz); 2.27 (dq, 2H, Et−CH_2, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.4 Hz); 2.49 (m, 2H, Et−CH_2, $^3J_{HH}$ = 7.4 Hz); 5.25 (t, H, C*H*, $^3J_{HH}$ = 7.7 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 121.5 MHz): δ 38.3 (s). $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −107.9 (dddd, 1F, 2-Ar−*F*, $^3J_{FF}$ = 38.6 Hz, $^5J_{FF}$ = 12.0 Hz, $^4J_{FF}$ = 8.6 Hz, $^4J_{FF}$ = 3.0 Hz); −112.5 (dddd, 1F, 6-Ar−*F*, $^3J_{FF}$ = 36.7 Hz, $^5J_{FF}$ = 12.0 Hz, $^4J_{FF}$ = 8.6 Hz, $^4J_{FF}$ = 3.0 Hz); −162.2 (tm, 1F, 4-Ar−*F*, $^3J_{FF}$ = 20.0 Hz), −163.4 (dddd, 1F, 3-Ar−*F*, $^3J_{FF}$ = 37.5 Hz, $^5J_{FF}$ = 20.7 Hz, $^4J_{FF}$ = 12.2 Hz, $^4J_{FF}$ = 4.8 Hz); −164.0 (dddd, 1F, 5-Ar−*F*, $^3J_{FF}$ = 37.5 Hz, $^5J_{FF}$ = 20.7 Hz, $^4J_{FF}$ = 12.2 Hz, $^4J_{FF}$ = 4.8 Hz).

Synthesis of (*E*)-1,2,3,4-Tetrafluoro-5-(hex-3-en-3-yl)benzene, 15. A solution of 1,2,3,4-$C_6F_4H_2$ (55 mg, 0.36 mmol) and 3-hexyne (30 mg, 0.36 mmol) was added to a mixture of Ni(COD)$_2$ (10 mg, 0.036 mmol) and triisopropylphosphine (11.6 mg, 0.73 mmol, 2 equiv) in C_6D_6. The reaction mixture was heated to 50 °C for 48 h (99% yield by NMR). ^1H NMR (C_6D_6, 298 K, 300.13 MHz): δ 0.74 and 0.86 (t, 6H, Et−CH_3, $^3J_{HH}$ = 7.7 Hz); 1.92 (dq, 2H, Et−CH_2, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.0 Hz); 2.17 (q, 2H, Et−CH_2, $^3J_{HH}$ = 7.7 Hz); 5.23 (t, H, C*H*, $^3J_{HH}$ = 7.0 Hz); 6.37 (dddd, 1H, 6-Ar−*H*, $^3J_{HF}$ = 13.6, $^5J_{HF}$ = 8.6 Hz, $^4J_{HF}$ = 2.6 Hz, $^4J_{HF}$ = 2.6 Hz). $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −141.1 (ddd, 1F, 2-Ar−*F*, $^3J_{FF}$ = 21.3 Hz, $^5J_{FF}$ = 12.5 Hz, $^4J_{FF}$ = 1.9 Hz); −142.4 (ddd, 1F, 5-Ar−*F*, $^3J_{FF}$ = 21.0 Hz, $^5J_{FF}$ = 12.3 Hz, $^4J_{FF}$ = 2.4 Hz); −156.7 (ddd, 1F, 3-Ar−*F*, $^3J_{FF}$ = 21.3 Hz, $^3J_{FF}$ = 19.7 Hz, $^4J_{FF}$ = 1.9 Hz); −159.2 (ddd, 1F, 4-Ar−*F*, $^3J_{FF}$ = 21.3 Hz, $^3J_{FF}$ = 19.7 Hz, $^4J_{FF}$ = 1.9 Hz).

Synthesis of the 3-Hexyne Adduct (PEt_3)$_2$Ni(η^2-EtC≡CEt), 16. The anthracene adduct (PEt_3)$_2$Ni(η^2-$C_{14}H_{10}$) (28.6 mg, 0.061 mmol) and 3-hexyne (5 mg, 0.061 mmol) were dissolved in pentane, whereupon the solution turned orange. The precipitated anthracene was filtered, and the resultant solution was used in subsequent reactions (quantitative by NMR). ^1H NMR (C_6D_6, 298 K, 300.13 MHz): δ 0.99 (t, 18H, Et−CH_3, $^3J_{HH}$ = 7.2 Hz); 1.44 (q, 12H, Et−CH_2, $^3J_{HH}$ = 7.2 Hz); 1.47 (m, 6H, hexyne−CH_3); 2.92 (qd, 4H, hexyne−CH_2, $^3J_{HH}$ = 7.3 Hz, $^4J_{HP}$ = 2.5 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 121.5 MHz): δ 26.8 (s).

Reaction of 16 with 1,2,4,5-$C_6F_4H_2$. 1,2,4,5-Tetrafluorobenzene was added to a solution of **16** (10 mol %) in C_6D_6. The orange-colored solution was heated for 3 days at 80 °C and then analyzed by NMR spectroscopy. The crude NMR spectra revealed a mixture of compound **16**, compound **11** (40% yield by NMR), and compound **12** (5% yield by NMR). The only other significant impurity was attributed to the alkyne insertion product before reductive elimination, **17**.

Characterization of (PEt_3)$_2$Ni(CEt=CHEt)(2,3,5,6-C_6F_4H), 17. $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K, 121.5 MHz): δ 13.3 (s). $^{19}F\{^1H\}$ NMR (C_6D_6, 298 K, 282.4 MHz): δ −113.4 (ddd, 1F, 2-Ar−*F*, $^3J_{FF}$ = 36.7 Hz, $^5J_{FF}$ = 17.3 Hz, $^4J_{FF}$ = 4.3 Hz); −117.4 (ddd, 1F, 6-Ar−*F*, $^3J_{FF}$ = 36 Hz, $^5J_{FF}$ = 17.3 Hz, $^4J_{FF}$ = 4.3 Hz); −142.0 (dd, 1F, 3-Ar−*F*, $^3J_{FF}$ = 35.0 Hz, $^5J_{FF}$ = 17.2 Hz), −142.3 (dd, 1F, 3-Ar−*F*, $^3J_{FF}$ = 36.0 Hz, $^5J_{FF}$ = 17.2 Hz).

X-ray Crystallography. The X-ray structures were obtained at low temperatures, with the crystals covered in Paratone and placed rapidly into the cold N_2 stream of the Kryo-Flex low-temperature device. The data were collected using the SMART[49] software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). A hemisphere of data was collected using a counting time of 10−30 s per frame. Details of crystal data, data collection, and structure refinement are listed in Table 1. Data reductions were performed using the SAINT[50] software, and the data were corrected for absorption using SADABS.[51] The structures were solved by direct methods using SIR97[52] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELX-97[53] and the WinGX[54] software package, and thermal ellipsoid plots were produced using ORTEP32.[55]

Acknowledgment is made to the Natural Sciences and Engineering Research Council (NSERC) of Canada for a discovery grant for S.A.J. and a postgraduate scholarship for J.A.H., and to the donors of the American Chemical Society Petroleum Research Fund for partial support of this research.

Supporting Information Available: Full details of crystallographic information in CIF format for compounds **1**, **3**, **4**, **6**, and **9** in addition to select experimental NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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