ORGANOMETALLICS

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Synthesis of Fluoroalkyl Palladium and Nickel Complexes via Decarbonylation of Acylmetal Species

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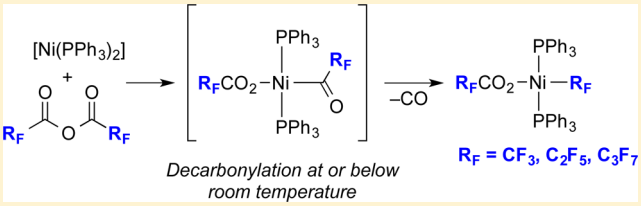
Supporting Information

ABSTRACT: The synthesis and characterization of a series of fluoroalkyl palladium(II) and nickel(II) complexes via decarbonylation of the corresponding acylmetal species is reported. At palladium(II), labile supporting ligands such as tri-*o*-tolylphosphine are required to achieve decarbonylation within 30 min at 85 °C. In contrast, decarbonylation at $(PPh_3)_2Ni(C(O)R_F)(OCOR_F)$ (R_F = fluoroalkyl) complexes proceeds rapidly at or below room temperature.



INTRODUCTION

Efficient and functional group tolerant trifluoromethylation methods would provide valuable approaches for fine-tuning the pharmacokinetics, metabolic stability, and bioavailability of biologically active molecules. Transition-metal catalysis is an attractive and widely studied approach for the late-stage fluoroalkylation of complex organic molecules.[1,2] However, most of the fluoroalkyl (R_F) sources employed in transition-metal-catalyzed fluoroalkyl cross-coupling reactions (e.g., R_FI, R_FSiMe_3, R_FSiEt_3, R_FH, Togni reagent, Umemoto reagent) are expensive, toxic, and/or volatile. In contrast, fluoroalkyl carboxylic acid derivatives are relatively inexpensive, safe, and easy-to-handle alternatives. Despite these advantages, current decarboxylative fluoroalkylation reactions with, for example, trifluoroacetate salts remain impractical due to the requirements for superstoichiometric quantities of transition-metal reagents and forcing conditions (often ≥150 °C).[1,3,4] We recently proposed an alternative approach involving metal-catalyzed decarbonylative fluoroalkylation with fluorinated anhydrides or fluorinated esters as R_F donors.[5] Our proposed catalytic cycle for fluoroalkylation with these reagents has four steps: (1) oxidative addition of the anhydride or ester to L_nPd^0 to generate $L_nPd^{II}(C(O)R_F)(OR)$, (2) CO deinsertion from $L_nPd^{II}(C(O)R_F)(OR)$ leading to $L_nPd^{II}(R_F)(OR)$, (3) aryl group transfer to Pd^{II} via transmetalation or C–H activation, and (4) aryl–R_F bond-forming reductive elimination[2g,6] to release the fluoroalkylated product and return L_nPd^0 to the catalytic cycle. We previously demonstrated the feasibility of each elementary step of this proposed cycle at Pd model complexes supported by the RuPhos ligand.[2g,7] This investigation revealed that CO deinsertion at Pd^{II} is a particularly challenging transformation. For example, to achieve full conversion, the complex $(RuPhos)Pd(C(O)CF_3)(OC(O)CF_3)$ had to be heated for 1.5 h in refluxing benzene.

The challenges associated with the CO deinsertion step are a major hindrance to the development of the envisioned catalytic fluoroalkylation reaction for several reasons. First, background reactions between transmetalating reagents (e.g., aryl zincs, aryl stannanes, or aryl boron reagents) and electrophilic fluorinated anhydrides and esters occur at elevated temperatures. Second, slow CO deinsertion relative to transmetalation can lead to acetylation of the aryl group instead of the targeted fluoroalkylation reaction. For example, a high-yielding $Pd^{0/II}$-catalyzed trifluoroacetylation of arylboronic acids with phenyl-trifluoroacetate has been reported and presumably proceeds via this pathway.[8]

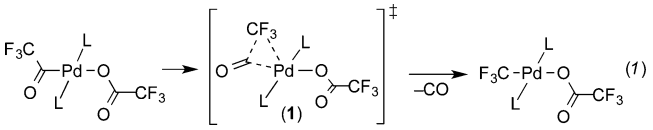
In the current paper, we describe two approaches for accelerating this critical CO deinsertion step. The first involves the synthesis of Pd^{II} perfluoroacyl complexes containing labile supporting ligands, with the hypothesis that such ligands should facilitate the generation of coordinatively unsaturated Pd intermediates necessary for rapid CO deinsertion.[9,10] In addition, we explore CO deinsertion from analogous fluoroacyl Ni^{II} complexes.[11] This second approach is predicated on literature reports suggesting that decarbonylation is often more facile at first-row metal centers in comparison to their second- and third-row analogues.[12−16] We demonstrate herein the feasibility of CO deinsertion at a variety of M^{II}–$C(O)R_F$ complexes (M = Ni, Pd). Furthermore, we show that changing the supporting ligand and/or the metal center can have a dramatic impact on the rates of these reactions.

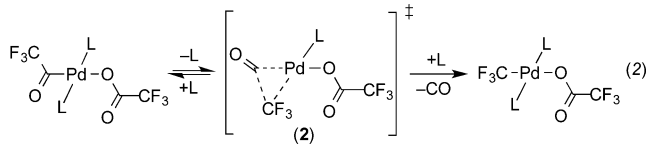
RESULTS AND DISCUSSION

Accelerating CO Deinsertion via Modification of the Supporting Ligands at Pd^{II}–$C(O)R_F$ Complexes. CO insertion/deinsertion is generally accepted to proceed via a three-center transition state (eqs 1 and 2).[17] In principle, CO insertion/deinsertion via a pentacoordinate Pd^{II} transition state such as **1** is feasible, but it is expected to be a high-energy pathway (eq 1).[18] CO insertion/deinsertion via a tetracoordinate Pd transition state such as **2** is, in general, a much more

Received: May 19, 2014

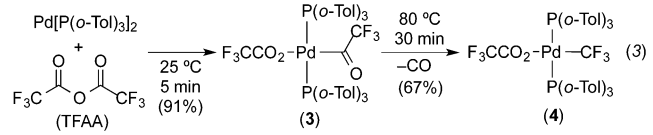
   dx.doi.org/10.1021/om500535x | *Organometallics* XXXX, XXX, XXX–XXX





facile process for Pd^{II} complexes (eq 2).[18] However, the pathway depicted in eq 2 requires pre-equilibrium dissociation of a spectator ligand (L), which could potentially become the limiting step of the overall transformation.

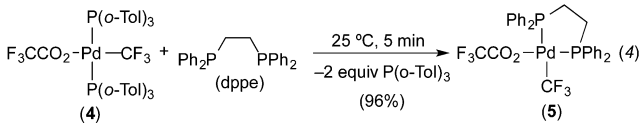
We envisioned that the use of a labile monodentate supporting ligand (L) should lead to a high equilibrium concentration of a coordinatively unsaturated tricoordinate Pd^{II} intermediate and thus accelerate the rate of decarbonylation via the pathway shown in eq 2. On the basis of this reasoning, our initial investigations focused on complexes bearing the sterically bulky ligand P(*o*-Tol)$_3$. The treatment of Pd[P(*o*-Tol)$_3$]$_2$ with trifluoroacetic anhydride in THF at room temperature afforded the Pd^{II} oxidative addition product **3** in 91% isolated yield (eq



3). Isolated samples of **3** were analytically pure; however, the ^{19}F and ^{31}P NMR spectra of this complex appear broad at room temperature, likely due to reversible dissociation of the phosphine ligand and/or conformational dynamics of bulky ligands around the sterically congested Pd center.

Decarbonylation at complex **3** was next investigated. Consistent with our hypothesis, this transformation proceeded to form Pd^{II} trifluoromethyl complex **4** quantitatively within just 30 min in refluxing benzene (eq 3). For comparison, the corresponding Ruphos complex (RuPhos)Pd(C(O)CF$_3$)(OC(O)CF$_3$) underwent significantly slower decarbonylation (i.e., the reaction took 1.5 h to reach completion under analogous conditions).[5] Analytically pure samples of **4** were isolated in 67% yield by recrystallization from diisopropyl ether. The room-temperature ^{19}F and ^{31}P NMR spectra of **4** show broad resonances. A VT-NMR study of complex **4** revealed that both ligand dissociation and conformational dynamics contribute to the broadness of NMR spectra at room temperature. At −50 °C, several previously broad resonances in the ^{19}F NMR spectrum resolved into sharp triplets, while other broad resonances resolved into doublets. We assign the triplets in the ^{19}F NMR spectrum to conformational isomers of the bis-phosphine complex **4**, while the doublets are assigned to the corresponding monophosphine species. The ligand dissociation is also supported by the fact that a signal for free P(*o*-Tol)$_3$ is observed in the $^{31}P\{^1H\}$ NMR spectrum of **4** at both 25 and −50 °C.[19]

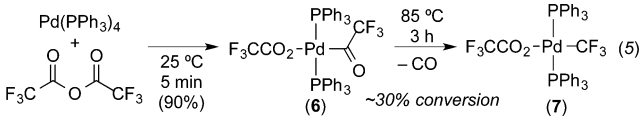
To facilitate complete NMR characterization, complex **4** was treated with 1,2-bis(diphenylphosphino)ethane (dppe) (eq 4). Ligand exchange proceeded within 5 min at room temperature to afford complex **5** in 96% yield as an analytically pure



crystalline solid that was fully characterized using 1D and 2D NMR spectroscopic techniques. The ^{19}F NMR spectrum of **5** exhibits two characteristic resonances in a 1:1 integral ratio, a doublet of doublets at −27 ppm ($^3J_{F-P}$ = 66 and 26 Hz) and a singlet at −75 ppm. In addition, the ^{31}P NMR spectrum of **5** shows an apparent quintet at 57 ppm ($^2J_{P-P} \approx {}^3J_{P-F} \approx 26$ Hz) and a quartet of doublets at 44 ppm ($^3J_{P-F}$ = 66 Hz and $^2J_{P-P}$ = 27 Hz) in a 1:1 integral ratio. The observed multiplicities and coupling constants are characteristic of square-planar *cis*-bis(phosphine) Pd−CF$_3$ adducts.[20]

As discussed above, we hypothesize that phosphine dissociation is required for CO deinsertion to occur efficiently at these Pd^{II} complexes. Consistent with this proposal, the addition of 3 equiv of exogeneous P(*o*-Tol)$_3$ greatly inhibited decarbonylation at **3**. For example, after benzene solutions of **3** were refluxed for 3 h in the presence of 3 equiv of P(*o*-Tol)$_3$, the starting material (**3**) could be recovered in 63% yield.

In addition, complex **6**, which contains smaller PPh_3 ligands, undergoes decarbonylation at a much slower rate than **3** (eq 5).



For instance, heating **6** to 85 °C for 3 h resulted in only ∼30% conversion to the decarbonylated product **7**, as detected by NMR analysis of the crude reaction mixture.[21] The slower rate of decarbonylation from **6** versus **3** is proposed to be due to the smaller size of PPh_3 versus P(*o*-Tol)$_3$, which renders the former ligand significantly less labile.

We next examined the scope of perfluoroalkyl (R_F) groups that can participate in decarbonylation at palladium(II) P(*o*-Tol)$_3$ complexes. A series of $Pd^{II}(R_F)(OC(O)R_F)$ complexes were prepared via a one-pot procedure involving (1) reaction of $Pd^0[P(o\text{-Tol})_3]_2$ with the corresponding carboxylic anhydride at room temperature for 20 min, (2) removal of solvent and dissolution of the crude $[P(o\text{-Tol})_3]_2Pd(C(O)R_F)(OC(O)R_F)$ in benzene, and (3) heating the resulting benzene solution to reflux for 30 min. Finally, to facilitate purification and characterization, the in situ generated $[P(o\text{-Tol})_3]_2Pd(R_F)(OC(O)R_F)$ complexes were reacted with dppe to form the more stable bidentate phosphine adducts (Table 1).[22] This procedure worked well to provide the perfluoroethyl and perfluoropropyl derivatives **8** and **9** in 87% and 50% isolated yields, respectively. In addition, the difluoromethyl complex **11** was prepared via a slight modification of the standard procedure. In this case, substitution of the carboxylate ligand of (dppe)Pd(CF$_2$H)(OC(O)CF$_2$H) (**10**) for chloride (via reaction of **10** with NaCl) was necessary to obtain a stable product. In contrast, cyclic fluorinated anhydrides provided poor results. Product **13** was obtained in only 16% isolated yield; furthermore, attempts to prepare **12** under our standard conditions yielded no detectable product.

Accelerating CO Deinsertion via Substitution of Pd^{II} for Ni^{II}. We next turned our attention to decarbonylation reactions at analogous Ni^{II} fluoroacyl complexes. As detailed in the Introduction, literature reports led us to hypothesize that

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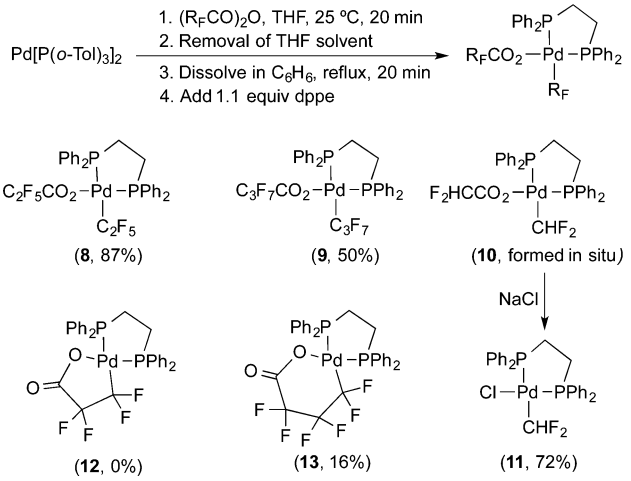
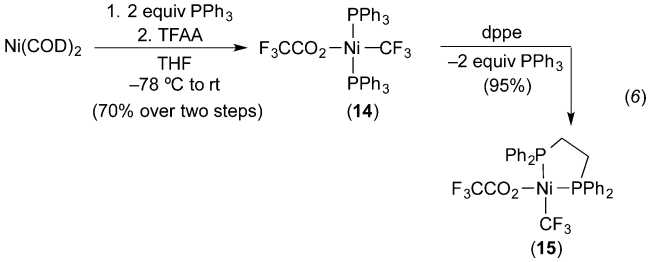
Table 1. Perfluoroalkyl Palladium(II) Complexes Prepared via Decarbonylation from $[P(o\text{-Tol})_3]_2Pd(C(O)R_F)(OC(O)R_F)$



these transformations should be faster at a first-row transition-metal center.[12−16] Our initial experiments focused on PPh_3 as a simple and readily available supporting ligand for Ni. This ligand also enabled straightforward comparison to the analogous PPh_3 palladium complex **6**. The treatment of $Ni(COD)_2$ with 2 equiv of PPh_3 followed by 1.5 equiv of trifluoroacetic anhydride (TFAA) produced the decarbonylation product **14** directly in 70% isolated yield (eq 6).

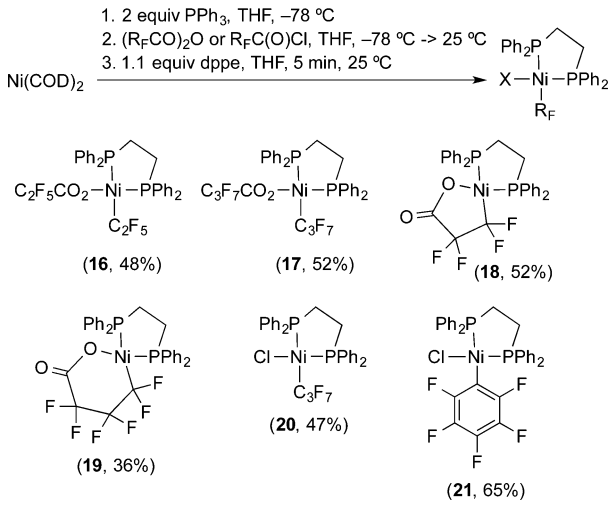


Importantly, the initial reaction temperature was −78 °C, and the reaction mixture was warmed to 25 °C over 20 min. While the exact temperature at which decarbonylation occurs has proven difficult to pinpoint, these results clearly show that decarbonylation at Ni^{II} proceeds rapidly at or below room temperature. This represents a striking contrast to (and improvement over) the corresponding palladium system, complex **6**. We hypothesize that this reaction is facile because tetracoordinate Ni^{II} centers can easily expand their coordination number to 5.[23] As such, decarbonylation should be able to proceed without dissociation of a phosphine ligand. Consistent with this proposal, exogenous phosphine does not appear to inhibit decarbonylation in this system.

Complex **14** was characterized via NMR and IR spectroscopy as well as by elemental analysis. The ^{19}F NMR spectrum of **14** exhibits two characteristic resonances at −20 and −75 ppm in a 1:1 integral ratio, while the ^{31}P NMR spectrum contains a single resonance at 40 ppm. Peaks in both the ^{19}F and ^{31}P NMR spectra of **14** are broad, and $^3J_{F-P}$ coupling is not resolved in the temperature range from −55 to +25 °C. This suggests that complex **14** is fluxional. The treatment of **14** with 1.05 equiv of 1,2-bis(diphenylphosphino)ethane (dppe) resulted in rapid ligand exchange to afford **15** in 95% yield within 1 min at room temperature (eq 6).[24] Complex **15** was characterized via 1D and 2D NMR spectroscopy. The observation of $^3J_{F-P}$ coupling in both the ^{19}F and ^{31}P NMR spectra of **15** strongly supports the proposed structure. Specifically, the ^{19}F NMR spectrum of **15** contains a doublet of doublets at −29 ppm ($^3J_{F-P}$ = 43 and 10 Hz) and a singlet at −75 ppm in a 1:1 integral ratio. In addition, the ^{31}P NMR spectrum of **15** shows an apparent quintet at 45 ppm ($^2J_{P-P} \approx {}^3J_{P-F} \approx 45$ Hz) as well as a doublet of quartets at 56 ppm ($^2J_{P-P}$ = 46 Hz and $^3J_{P-F}$ = 10 Hz) in a 1:1 integral ratio.

We next investigated decarbonylation of other fluoroacyl ligands at nickel(II) triphenylphosphine complexes. A convenient one-pot procedure was developed involving (1) treatment of $Ni(COD)_2$ with 2 equiv of PPh_3, (2) addition of the corresponding anhydride or acyl chloride, and (3) trapping with dppe to facilitate purification and characterization of the Ni^{II} perfluoroalkyl products.[25] This approach proved successful for the preparation of a series of Ni^{II} perfluoroalkyl adducts (Table 2). For example, when higher analogues of

Table 2. Perfluoroalkyl Nickel(II) Complexes Prepared via Decarbonylation from in Situ Generated $(PPh_3)_2Ni(C(O)R_F)(X)$



TFAA were used, the corresponding products **16** and **17** were isolated in 48% and 52% yields, respectively. Cyclic carboxylic anhydrides afforded **18** and **19** in 52% and 36% isolated yields. Notably, the Pd^{II} analogue of **18** was not accessible via the decarbonylation procedure above. Finally, the use of acid chlorides in place of anhydrides afforded the corresponding Ni^{II} perfluoroalkyl chloride complexes **20** and **21** in 47% and 65% isolated yields. Importantly, for all of the complexes **16**−**21**, the moderate isolated yields are not due to the formation of side products; instead, they are the result of material losses during isolation and purification.

Reactivity of Fluoroalkyl Nickel and Palladium Complexes with Transmetalating Reagents. The next step of our proposed catalytic cycle for arene trifluoromethylation involves transmetalation from an aryl organometallic reagent.[5] As such, we have also conducted preliminary investigations to assess the viability of this transformation at representative Pd^{II} and Ni^{II} perfluoroalkyl species. We first probed the reaction of Pd^{II} trifluoromethyl complex **4** and Ni^{II} trifluoromethyl complex **14** with phenyllithium, phenylmagnesium bromide, and diphenylzinc. As shown in eq 7, all of these

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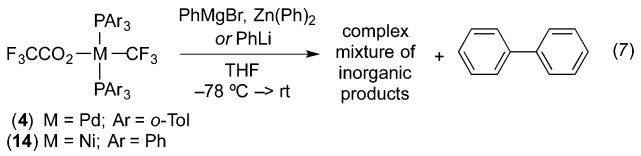
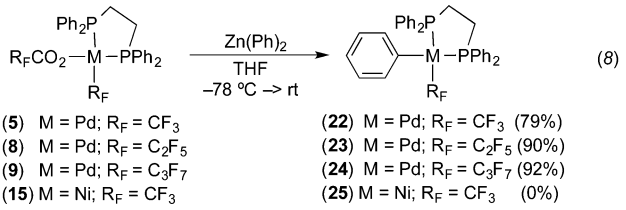


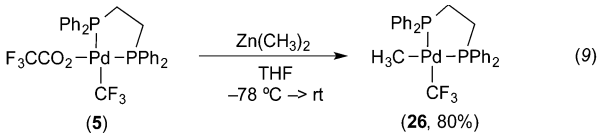
transformations afforded an inseparable mixture of inorganic products, along with large amounts of biphenyl. It has been reported previously that complexes of the general structure $(P)_2M(CF_3)(aryl)$ (M = Pd, Ni, $(P)_2$ = bidentate phosphine) decompose with concomitant release of the corresponding biaryl.[6,26] Thus, it is possible that the desired aryl nickel and palladium species are generated in our transformation but then undergo rapid decomposition.

We hypothesized that the bidentate dppe ligand would stabilize the desired transmetalation products by limiting disproportionative decomposition to form biphenyl. Indeed, the treatment of dppe complexes **5**, **8**, and **9** with diphenylzinc afforded the targeted $(dppe)Pd^{II}(R_F)(Ph)$ products **22**–**24** in high isolated yields (eq 8). Complexes **22**–**24** are stable under



ambient conditions, and their structures were confirmed by NMR spectroscopy and elemental analysis. Preliminary studies suggest that these Pd^{II} complexes are unreactive toward aryl–R_F bond-forming reductive elimination, as would be expected on the basis of Grushin's prior studies of complex **22**.[27] Notably, the reaction of Ni^{II} dppe complex **15** with diphenylzinc under analogous conditions afforded an inseparable mixture of inorganic products.

We also found that dimethylzinc is an appropriate transmetalating reagent for Pd^{II} complex **5**.[28] Treatment of **5** with $Zn(CH_3)_2$ in anhydrous THF resulted in the formation of air-stable complex **26** in 80% isolated yield (eq 9).



CONCLUSIONS

This report describes the synthesis and characterization of a series of fluoroalkyl palladium and nickel complexes via decarbonylation of the corresponding acylmetal species. At Pd^{II}, the decarbonylation reaction is accelerated by the presence of the sterically large ligand P(*o*-Tol)$_3$. For example, complete decarbonylative decomposition of $[P(o\text{-Tol})_3]_2Pd(C(O)CF_3)(OCOCF_3)$ was achieved within 30 min in refluxing benzene. The rate of this reaction is much faster than that at Pd^{II} complexes containing the smaller PPh_3 ligand or the hemilabile bidentate RuPhos ligand. The accessibility of three-coordinate Pd^{II} intermediates via ligand dissociation is proposed to be crucial for these transformations. In contrast, analogous Ni^{II} complexes of the general structure $(PPh_3)_2Ni(C(O)R_F)(OCOR_F)$ decarbonylate under much milder conditions, typically at or below room temperature. This is likely because decarbonylation at nickel can proceed without ligand dissociation via a pentacoordinate transition state. These studies implicate Ni-based systems as highly attractive targets for achieving catalytic decarbonylative trifluoromethylation reactions.[26] As such, current efforts in our group are focused on strategies to achieve both transmetalation and aryl–CF_3 bond-forming reductive elimination at Ni centers.

EXPERIMENTAL SECTION

General Procedures. All syntheses were conducted under nitrogen unless otherwise stated. All reagents were purchased from commercial sources and used as received. $Pd[P(o\text{-Tol})_3]_2$ was prepared via a literature procedure.[29] Tetrahydrofuran, dichloromethane, and diethyl ether were purified using a solvent purification system consisting of a copper catalyst, activated alumina, and molecular sieves. ^{1}H, ^{19}F, and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. Elemental analyses were performed by Atlantic Microlab, Inc.

Preparation of $(P(o\text{-Tol})_3)_2Pd(C(O)CF_3)(OC(O)CF_3)$ (3). A Schlenk flask was charged with a stirbar and $Pd[P(o\text{-Tol})_3]_2$ (4.00 g, 6.92 mmol). The flask was sealed, placed under vacuum, and then refilled with nitrogen. The flask was evacuated and refilled with nitrogen three more times. Dry THF (100 mL) was added via cannula. Trifluoroacetic anhydride (TFAA; 1.13 mL, 8 mmol) was then added dropwise over a period of 10 min. The resulting solution was stirred at room temperature for 20 min and then filtered through a pad of Celite. The volatiles were removed under reduced pressure. The residue was suspended in diethyl ether (100 mL), and the product slowly crystallized over a period of 4 h at room temperature. The crystals were collected, washed with several portions of diethyl ether, and then dried under vacuum. The product was obtained as a white solid (5.08 g, 91% yield). Both ^{1}H NMR spectroscopic analysis and elemental analysis show the presence of 1 equiv of cocrystallized diethyl ether that could not be removed even after prolonged drying under vacuum. The cocrystallized diethyl ether was taken into account when the reaction yield was calculated. The ^{1}H, ^{19}F, and ^{31}P NMR spectra of **3** show very broad resonances. Additionally, the ^{31}P NMR spectrum of **3** contains a singlet at −29.6 ppm, corresponding to free P(*o*-Tol)$_3$. ^{1}H NMR ($CDCl_3$ at 23 °C): δ 10.0–6.0 (br s, 24H), 4.0–1.0 (br s, 18H), 3.48 (q, J = 7.1 Hz, 4H, diethyl ether), 1.21 (t, J = 7.1 Hz, 6H, diethyl ether). ^{19}F NMR ($CDCl_3$ at 23 °C): δ −73.2 (br, 3F), −74.8 (br, 3F). ^{31}P{^{1}H} NMR ($CDCl_3$ at 23 °C): δ 20.5–6.7 (brs). IR (ATR, cm^{-1}): 3058 (w), 2973 (m), 1700 (s), 1677 (s), 1590 (m), 1566 (m), 1444 (s), 1405 (s), 1381 (m), 1279 (m), 1231 (m), 1191 (s). Anal. Calcd for $PdC_{46}H_{42}F_6O_3P_2{\cdot}C_2H_5OC_2H_5$: C, 60.10; H, 5.24; F, 11.41. Found: C, 60.03; H, 5.32; F, 11.69.

Preparation of $(P(o\text{-Tol})_3)_2Pd(CF_3)(OC(O)CF_3)$ (4). $(P(o\text{-Tol})_3)_2Pd(COCF_3)(OCOCF_3)$ (**3**; 2.50 g, 2.70 mmol) was dissolved in benzene (150 mL), and the resulting solution was heated at reflux for 1 h. The reaction mixture was then filtered through a pad of Celite, and the volatiles were removed under reduced pressure. The residue was then dissolved in diisopropyl ether (150 mL). This solution was allowed to stand for 4 h, during which time the product crystallized. The crystals were collected, washed with several portions of diisopropyl ether, and dried under vacuum to afford **4** as a yellow solid (1.82 g, 67% yield). Both ^{1}H NMR spectroscopic analysis and elemental analysis show the presence of 1 equiv of cocrystallized diisopropyl ether that could not be removed even after prolonged drying under vacuum. The cocrystallized diisopropyl ether was taken into account when the reaction yield was calculated. The ^{1}H, ^{19}F, and ^{31}P NMR spectra of **4** show very broad resonances. Additionally, the ^{31}P NMR spectrum of **4** contains a singlet at −29.6 ppm, corresponding to free P(*o*-Tol)$_3$. NMR spectra for **4** are provided in the Supporting Information. IR (ATR, cm^{-1}): 3059 (w), 2968 (m), 2870 (w), 1698 (s), 1591 (m), 1566 (m), 1445 (s), 1405 (m), 1380 (m), 1281 (m), 1190 (s). FAB MS (m/z): $[M - CF_3COO]^+$ calcd for

dx.doi.org/10.1021/om500535x | Organometallics XXXX, XXX, XXX–XXX

$C_{43}H_{42}F_3P_2Pd$ 783.2, found 783.5. Anal. Calcd for $PdC_{45}H_{42}F_6O_2P_2 \cdot C_3H_7OC_3H_7$: C, 61.29; H, 5.65; F, 11.41. Found: C, 61.04; H, 5.34; F, 11.50.

Preparation of (dppe)Pd(CF_3)(OC(O)CF_3) (5). $(P(o\text{-}Tol)_3)_2Pd(CF_3)(OCOCF_3)\cdot C_3H_7OC_3H_7$ (**4**; 250 mg, 0.25 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe; 115 mg, 0.29 mmol) were dissolved in dichloromethane (7 mL). The reaction mixture was stirred at room temperature for 5 min, and it was then filtered through a pad of Celite. Diisopropyl ether was slowly added to the solution until the product started to crystallize. The mixture was cooled to 5 °C for 4 h, to promote crystallization. The crystalline product was then collected, washed with several portions of diisopropyl ether, and dried under reduced pressure to afford **5** as a white solid (154 mg, 90% yield). Samples for elemental analysis were recrystallized an additional three times from dichloromethane/diisopropyl ether. ^{1}H NMR (CD_2Cl_2 at 25 °C): δ 7.87−7.80 (m, 4H), 7.77−7.71 (m, 4H), 7.66−7.61 (m, m, 2H) 7.60−7.49 (m, 10H), 2.51−2.42 (m, 2H), 2.28−2.18 (m, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 25 °C): δ 160.73 (q, $^2J_{C-F}$ = 36.1 Hz), 136.15 (qdd, $^1J_{C-F}$ = 381.47 Hz, $^2J_{C-P}$ = 215.9 and 8.9 Hz), 133.50 (d, $^3J_{C-P}$ = 11.6 Hz), 133.08 (d, $^3J_{C-P}$ = 11.6 Hz), 132.39 (d, $^4J_{C-P}$ = 2.7 Hz), 131.89 (d, $^4J_{C-P}$ = 2.7 Hz), 129.36−129.16 (two overlapping d), 127.92 (d, $^1J_{C-P}$ = 40.9 Hz), 127.24 (d, $^1J_{C-P}$ = 55.2 Hz), 116.22 (qd, $^1J_{C-F}$ = 290.9 Hz, $^4J_{C-P}$ = 7.5 Hz), 30.61 (dd, $^1J_{C-P}$ = 36.8 Hz, $^2J_{C-P}$ = 18.4 Hz), 23.66 (dd, $^1J_{C-P}$ = 30.0 Hz, $^2J_{C-P}$ = 8.2 Hz). ^{19}F NMR (CD_2Cl_2 at 25 °C): δ −26.6 (dd, $^3J_{F-P}$ = 66 and 27 Hz, 3F), −74.6 (s, 3F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2 at 25 °C): δ 56.6 (apparent quin, $^2J_{P-P}$ = $^3J_{P-F}$ = 26 Hz, 1P), 44.0 (qd, $^3J_{P-F}$ = 66 Hz, $^2J_{P-P}$ = 28 Hz, 1P). ^{19}F/^{13}C HSQC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −74.6/116.3 (peak corresponding to the Pd-CF_3 group was not observed in ^{19}F/^{13}C HSQC. However, the Pd-CF_3 group was observed in ^{19}F/^{13}C HMBC as a ^1J artifact). ^{19}F/^{13}C HMBC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −26.6/136.3 (^1J correlation), −74.6/116.4 (^1J correlation), −74.6/160.8. IR (ATR, cm^{-1}): 3068 (w), 2976 (w), 1682 (s), 1486 (m), 1436 (s), 1418 (m), 1314 (m), 1182 (s), 1136 (s), 1082 (s). HRMS electrospray (m/z): $[M - OCOCF_3]^+$ calcd for $C_{27}H_{24}F_3P_2Pd$ 573.0335, found 573.0348; $[M - CO_2CF_3 + CH_3CN]^+$ calcd for $C_{29}H_{27}F_3NP_2Pd$ 614.0600, found 614.0610. Anal. Calcd for $PdC_{29}H_{24}F_6O_2P_2$: C, 50.71; H, 3.52; F, 16.60. Found: C, 50.46; H, 3.59; F, 16.37.

Preparation of (PPh_3)$_2$Pd(C(O)CF_3)(OC(O)CF_3) (6). A Schlenk flask was charged with a stirbar and $(PPh_3)_4Pd$ (8.00 g, 6.92 mmol). The flask was sealed, placed under vacuum, and then refilled with nitrogen. The flask was evacuated and refilled with nitrogen three more times. Dry THF (250 mL) was added via cannula. Trifluoroacetic anhydride (TFAA; 3.40 mL, 24.0 mmol) was then added dropwise over a period of 10 min. The resulting solution was stirred at room temperature for 20 min, and then the volatiles were removed under reduced pressure. The resulting white crystalline residue was suspended in EtOAc (100 mL), collected via filtration, washed with several portions of EtOAc, and dried under vacuum to afford the product as a white solid (5.23 g, 90% yield). ^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.64−7.58 (m, 12H), 7.49−7.44 (m, 6H), 7.44−7.38 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$ at 25 °C): δ 219.54 (q, $^2J_{C-F}$ = 38.2 Hz), 159.69 (q, $^2J_{C-F}$ = 36.2 Hz), 134.39 (t, $^2J_{C-P}$ = 6.9 Hz), 131.0 (two overlapping t), 128.55 (t, $^3J_{C-P}$ = 4.9 Hz), 128.54 (t, $^1J_{C-P}$ = 23.5 Hz), 115.51 (q, $^1J_{C-F}$ = 291.5 Hz), 111.65 (qt, $^1J_{C-F}$ = 301.3 Hz, $^3J_{C-P}$ = 16.6 Hz). ^{19}F NMR ($CDCl_3$ at 25 °C): δ −75.0 (s, 3F), −75.5 (s, 3F). $^{31}P\{^1H\}$ NMR ($CDCl_3$ at 25 °C): δ 17.5 (s). ^{19}F/^{13}C HSQC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −75.1/111.8, −75.6/115.7. ^{19}F/^{13}C HMBC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −75.0/219.5, −75.6/111.8 (^1J correlation), −75.5/159.7, −75.5/115.5 (^1J correlation). IR (ATR, cm^{-1}): 3059 (w), 1752 (w), 1684 (s), 1665 (s), 1481 (s), 1436 (s), 1422 (s), 1229 (s), 1177 (s), 1136 (s), 1095 (s). FAB MS (m/z): $[M - CF_3COO]^+$ calcd for $C_{38}H_{30}F_3OP_2Pd$, 727.1; found 727.5; $[(PPh_3)_2PdCF_3]^+$ calcd for $C_{37}H_{30}F_3P_2Pd$, 699.1, found, 699.5. Anal. Calcd for $PdC_{40}H_{30}F_6O_3P_2$: C, 57.12; H, 3.60; F, 13.55, found C, 57.09; H, 3.70; F, 13.66.

General Procedure 1. Preparation of dppe-Supported Perfluoroalkyl Palladium Complexes. A Schlenk flask was charged with a stirbar and $Pd[P(o\text{-}Tol)_3]_2$ (2.00 g, 3.46 mmol). The flask was sealed, placed under vacuum, and then refilled with nitrogen. The flask was evacuated and refilled with nitrogen three more times. Dry THF (100 mL) was added via cannula. The corresponding anhydride (5.0 mmol) was then added dropwise over a period of 5 min. The resulting solution was stirred at room temperature for 20 min and was then filtered through a pad of Celite. The volatiles were removed under reduced pressure, and the resulting residue was taken up in benzene (150 mL) and heated at reflux for ∼30 min, during which time the color changed from yellow to deep red and then back to yellow. The benzene solution was cooled to room temperature, and dppe (1.35 g, 3.4 mmol) was added. The reaction mixture was filtered through a pad of Celite, and benzene was removed under reduced pressure. The residue was dissolved in diisopropyl ether (100 mL), and the product slowly crystallized over ∼4 h. The crystals were collected, washed with several portions of diisopropyl ether, and dried under vacuum. Samples for elemental analysis were generally recrystallized three additional times from dichloromethane/diisopropyl ether.

Preparation of (dppe)Pd(C_2F_5)(OC(O)C_2F_5) (8). Complex **8** was obtained via general procedure 1 (white solid, 1.92 g, 87% yield). ^{1}H NMR (CD_2Cl_2 at 25 °C): δ 7.85−7.79 (m, 4H), 7.74−7.69 (m, 4H), 7.66−7.61 (m, 2H), 7.60−7.50 (m, 10H), 2.43−2.34 (m, 2H), 2.24−2.14 (m, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 25 °C; resonances of fluoroalkyl groups are assigned from the ^{19}F/^{13}C HSQC spectrum): δ 160.85 (t, $^2J_{C-F}$ = 25.2 Hz), 133.62 (d, $^3J_{C-P}$ = 11.6 Hz), 133.28 (d, $^3J_{C-P}$ = 11.6 Hz), 132.31 (d, $^4J_{C-P}$ = 2.7 Hz), 131.88 (d, $^4J_{C-P}$ = 2.7 Hz), 129.68 (m, Pd-CF_2), 129.24−129.07 (two overlapping d), 127.67 (d, $^1J_{C-P}$ = 42.2 Hz), 127.27 (d, $^1J_{C-P}$ = 54.5 Hz), 121.15 (m, CF_3), 118.50 (qt, $^1J_{C-F}$ = 286.1 Hz, $^2J_{C-F}$ = 35.4 Hz, CF_3) 106.56 (m, CO-CF_2−), 30.48 (dd, $^1J_{C-P}$ = 36.1 Hz, $^2J_{C-P}$ = 17.7 Hz), 24.28 (dd, $^1J_{C-P}$ = 29.3 Hz, $^2J_{C-P}$ = 8.9 Hz). ^{19}F NMR (CD_2Cl_2 at 25 °C): δ −81.5 (s, 3F), −83.5 (s, 3F), −96.6 (dd, $^3J_{F-P}$ = 40 and 32 Hz, 2F), −119.6 (s, 2F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2 at 25 °C): δ 55.9 (td, $^3J_{P-F}$ = 32 Hz, $^2J_{P-P}$ = 27 Hz, 1P), 44.1 (tdq, $^3J_{P-F}$ = 39 Hz, $^2J_{P-P}$ = 26 Hz, $^4J_{P-F}$ = 3 Hz, 1P). ^{19}F/^{13}C HSQC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −81.6/121.2, −83.6/118.5, −96.7/129.7, −119.7/106.6. ^{19}F/^{13}C HMBC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −81.6/121.2 (^1J correlation), −81.6/129.7, −83.6/106.6, −83.6/118.5 (^1J correlation), −96.7/121.2, −119.7/118.5, −119.7/160.9. IR (ATR, cm^{-1}): 3066 (w), 1693 (s), 1485 (w), 1437 (s), 1386 (m), 1319 (s), 1300 (s), 1226 (m), 1150 (s), 1104 (s). HRMS electrospray (m/z): $[M - OCOC_2F_5]^+$ calcd for $C_{28}H_{24}F_5P_2Pd$ 623.0303, found 623.0312; $[M - CO_2C_2F_5 + CH_3CN]^+$ calcd for $C_{30}H_{27}F_5NP_2Pd$ 664.0568, found 664.0575. Anal. Calcd for $PdC_{31}H_{24}F_{10}O_2P_2$: C, 47.32; H, 3.07; F, 24.14. Found: C, 47.08; H, 3.02; F, 24.05.

Preparation of (dppe)Pd(C_3F_7)(OC(O)C_3F_7) (9). Complex **9** was obtained via general procedure 1 (white solid, 1.12 g, 50% yield). ^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.82−7.76 (m, 4H), 7.73−7.68 (m, 4H), 7.60−7.46 (m, 12H), 2.38−2.26 (m, 2H), 2.19−2.08 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$ at 25 °C; resonances of fluoroalkyl groups are assigned from the ^{19}F/^{13}C HSQC spectrum): δ 161.15 (t, $^3J_{C-F}$ = 25.9 Hz), 133.66 (d, $^3J_{C-P}$ = 12.3 Hz), 132.59 (m, Pd-CF_2−), 133.27 (d, $^3J_{C-P}$ = 11.6 Hz), 132.25 (d, $^4J_{C-P}$ = 2.7 Hz), 131.88 (d, $^4J_{C-P}$ = 2.7 Hz), 129.26 (d, $^2J_{C-P}$ = 10.2 Hz), 129.14 (d, $^2J_{C-P}$ = 11.6 Hz), 127.70−127.27 (two overlapping d), 118.51 (m, $-CF_3$), 117.85 (m, $-CF_3$), 110.87 (m, $-CF_2$-), 108.47 (m, $-CF_2$-), 108.41 (m, $-CF_2$-), 30.20 (dd, $^1J_{C-P}$ = 36.1 Hz, $^2J_{C-P}$ = 17.7 Hz), 24.17 (dd, $^1J_{C-P}$ = 29.3 Hz, $^2J_{C-P}$ = 8.9 Hz). ^{19}F NMR ($CDCl_3$ at 25 °C): δ −80.3 (t, $^3J_{F-F}$ = 8 Hz, 3F), −80.8 (t, $^3J_{F-F}$ = 8 Hz, 3F), −93.3 (m, 2F), −116.5 (q, $^3J_{F-F}$ = 10 Hz, 2F), −120.4 (s, 2F), −127.0 (s, 2F). $^{31}P\{^1H\}$ NMR ($CDCl_3$ at 25 °C): δ 55.9 (apparent q, $^2J_{P-P}$ = $^3J_{P-F}$ = 28 Hz, 1P), 44.1 (td, $^3J_{P-F}$ = 40 Hz, $^2J_{P-P}$ = 28 Hz, 1P). ^{19}F/^{13}C HSQC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −80.4/118.5, −80.9/117.9, −93.4/132.6, −116.6/108.5, −120.5/110.9, −127.1/108.4. ^{19}F/^{13}C HMBC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −80.4/110.9, −80.9/108.5, −116.6/108.5, −116.6/161.5, −120.5/110.9 (^1J correlation), −120.5/118.5, −127.1/108.5, −127.1/117.9. IR (ATR, cm^{-1}): 3065 (w), 1494 (s), 1486 (m), 1438 (s), 1384 (m), 1331 (s), 1210 (s), 1175 (s). HRMS electrospray (m/z): $[M - OCOC_3F_7]^+$ calcd for $C_{29}H_{24}F_7P_2Pd$ 673.0271, found 673.0278; [M −

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$CO_2C_3F_7$ + $CH_3CN]^+$ calcd for $C_{31}H_{27}F_7NP_2Pd$ 714.0536, found 714.0540. Anal. Calcd for $PdC_{33}H_{24}F_{14}O_2P_2$: C, 44.69; H, 2.73; F, 29.99. Found: C, 44.76; H, 2.74; F, 29.91.

Preparation of (dppe)Pd(CHF_2)(Cl) (11). A Schlenk flask was charged with a stirbar and $Pd[P(o\text{-Tol})_3]_2$ (2.00 g, 3.46 mmol). The flask was sealed, placed under vacuum, and then refilled with nitrogen. The flask was evacuated and refilled with nitrogen three more times. Dry THF (100 mL) was added via cannula. Difluoroacetic anhydride (4.0 mmol, 0.89 mL) was then added dropwise over a period of 5 min. The resulting solution was stirred at room temperature for 20 min and then filtered through a pad of Celite. The volatiles were removed under reduced pressure, and the residue was taken up in benzene (150 mL) and heated to reflux for 30 min, until the color of the solution changed from yellow to deep red and then back to yellow. The reaction mixture was cooled to room temperature, and then dppe (1.35 g, 3.4 mmol) was added. The reaction mixture was filtered through a pad of Celite, and the resulting benzene solution (containing the difluoromethylcarboxylate intermediate **10**) was stirred intensively with an aqueous solution of brine for 3 h. The benzene layer was separated from the brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was dissolved in methyl *tert*-butyl ether (150 mL), from which the product slowly crystallized. The product was collected, washed with several portions of MTBE, and dried under vacuum to afford the product as a white solid (1.19 g, 72% yield). Samples for elemental analysis were recrystallized several additional times from dichloromethane/MTBE. ^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.90−7.79 (m, 4H), 7.75−7.65 (m, 4H), 7.55−7.35 (m, 12H), 6.85 (tdd, $^2J_{(H-F)}$ = 49.3 Hz, $^3J_{(H-P)}$ = 20.7 and 2.9 Hz, 1H), 2.51−2.33 (m, 2H), 2.22−2.06 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$ at 25 °C): δ 133.94 (tdd, $^1J_{C-F}$ = 304.5, $^2J_{C-P}$ = 177.1 and 19.1 Hz), 133.56 (d, $^3J_{C-P}$ = 12.3 Hz), 133.26 (d, $^3J_{C-P}$ = 11.6 Hz), 131.74 (d, $^4J_{C-P}$ = 2.1 Hz), 131.06 (d, $^4J_{C-P}$ = 2.1 Hz), 130.28 (d, $^1J_{C-P}$ = 34.1 Hz), 129.07 (d, $^2J_{C-P}$ = 10.2 Hz), 128.98 (d, $^2J_{C-P}$ = 10.9 Hz), 128.46 (d, $^1J_{C-P}$ = 50.4 Hz), 30.57 (dd, $^1J_{C-P}$ = 34.1 Hz, $^2J_{C-P}$ = 20.4 Hz), 23.65 (dd, $^1J_{C-P}$ = 26.6 Hz, $^2J_{C-P}$ = 10.2 Hz). ^{19}F NMR ($CDCl_3$ at 23 °C): δ −89.0 (apparent q, $^2J_{(F-H)}$ = $^3J_{(F-P)}$ = 48 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$ at 25 °C): δ 53.7 (td, $^3J_{P-F}$ = 49 Hz, $^2J_{P-P}$ = 35 Hz), 31.7 (td, $^3J_{P-F}$ = 53 Hz, $^2J_{P-P}$ = 35 Hz). $^{19}F/^{13}C$ HSQC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −89.1/133.8. IR (ATR, cm^{-1}): 3053 (w), 2898 (w), 1572 (w), 1482 (m), 1434 (s), 1408 (s), 1310 (m), 1277 (m), 1242 (m), 1186 (m), 1102 (s), 1010 (s), 996 (s). HRMS electrospray (m/z): $[M - Cl]^+$ calcd for $C_{27}H_{25}F_2P_2Pd$: 555.0429, found 555.0436. $[M - Cl + CH_3CN]^+$ calcd for $C_{29}H_{28}F_2NP_2Pd$ 596.0694, found 596.0693; $[M - CHF_2]^+$ calcd for $C_{26}H_{24}ClP_2Pd$ 539.0071, found 539.0074. Anal. Calcd for $PdC_{27}H_{25}ClF_2P_2$: C, 54.84; H, 4.26; Cl, 6.00; F, 6.43. Found: C, 54.95; H, 4.32; Cl, 5.94; F, 6.28.

Preparation of (dppe)Pd($CF_2CF_2CF_2COO$) (13). Complex **13** was obtained via general procedure 1 (white solid, 310 mg, 16% yield). Methyl *tert*-butyl ether (MTBE) was used for crystallization instead of diisopropyl ether. In order to remove cocrystallized solvent, the sample for elemental analysis was dried under vacuum at 90 °C for 8 h. ^{1}H NMR (CD_2Cl_2 at 25 °C): δ 7.81−7.73 (m, 8H), 7.65−7.61 (m, 2H), 7.59−7.50 (m, 10H), 2.66−2.56 (m, 2H), 2.26−2.17 (m, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 25 °C; resonances of fluoroalkyl partially assigned from the $^{19}F/^{13}C$ HSQC spectrum): δ 164.01 (t, $^2J_{C-F}$ = 25.2 Hz), 133.60 (d, $^3J_{C-P}$ = 11.6 Hz), 132.76 (d, $^3J_{C-P}$ = 11.6 Hz), 132.56 (d, $^4J_{C-P}$ = 2.7 Hz), 131.92 (d, $^4J_{C-P}$ = 2.1 Hz), 129.48 (d, $^2J_{C-P}$ = 10.2 Hz), 129.25 (d, $^2J_{C-P}$ = 11.6 Hz), 128.30 (d, $^1J_{C-P}$ = 39.5 Hz), 128.15 (m, $-CF_2-$Pd), 126.39 (d, $^1J_{C-P}$ = 55.9 Hz), 113.08 (broad t, $^1J_{C-F}$ = 265.7 Hz), 108.81 (tt, $^1J_{C-F}$ = 260.9 Hz, $^2J_{C-F}$ = 30.5 Hz), 31.09 (dd, $^1J_{C-P}$ = 36.8 Hz, $^2J_{C-P}$ = 18.4 Hz), 21.83 (dd, $^1J_{C-P}$ = 30.7 Hz, $^2J_{C-P}$ = 8.2 Hz). ^{19}F NMR (CD_2Cl_2 at 25 °C): δ −96.0 (m, 2F), −118.9 (m, 2F), −128.7 (br, 2F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2 at 25 °C): δ 57.5 (td, $^3J_{P-F}$ = 41 Hz, $^2J_{P-P}$ = 32 Hz, 1P), 37.3 (m, 1P). $^{19}F/^{13}C$ HSQC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −96.0/128.2, −118.9/108.8, −128.7/113.1. $^{19}F/^{13}C$ HMBC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −96.0/113.1, −96.0/128.2 (^1J correlation), −118.9/108.8 (^1J correlation), −118.9/113.1, −118.9/164.0, −128.7/108.8, −128.7/113.1 (^1J correlation), −128.7/128.2. IR (ATR, cm^{-1}): 3058 (w), 2919 (w), 1680 (s), 1483 (m), 1436 (s), 1374 (m), 1276 (m), 1222 (m), 1161 (s), 1104 (s), 1056 (s), 992 (s). HRMS electrospray (m/z): $[M + H]^+$ calcd for $C_{30}H_{25}F_6O_2P_2Pd$ 699.0263, found 699.0262.

Preparation of $(PPh_3)_2$Ni(CF_3)(OC(O)CF_3) (14). In a nitrogen-filled glovebox, a Schlenk flask was charged with a stirbar, triphenylphosphine (4.20 g, 16 mmol), and $Ni(COD)_2$ (2.00 g, 7.27 mmol). The flask was sealed with a septum and then removed from the glovebox. Dry THF (150 mL) was added via cannula, and the resulting dark red mixture was stirred at 25 °C for 15 min. The solution was then cooled to −78 °C, and trifluoroacetic anhydride (TFAA) (1.70 mL, 12 mmol) was added dropwise. The solution was slowly warmed to room temperature over ∼20 min, and volatiles were then removed under reduced pressure via the side arm of the reaction flask. Diethyl ether (200 mL) was added to the residue, and the product precipitated in the form of yellow crystals. The product was collected, washed with several portions of diethyl ether, and dried under vacuum to afford **14** as a yellow crystalline powder (4.04 g, 70% yield). ^{1}H NMR ($CDCl_3$ at 23 °C): δ 7.90−7.78 (m, 12H), 7.52−7.37 (m, 18H). $^{13}C\{H\}$ NMR ($CDCl_3$ at 23 °C): δ 160.11 (q, $^2J_{C-F}$ = 37.5 Hz), 134.39 (br s), 130.49 (br s), 130.07 (br s), 128.40 (br s), 123.28 (br q, $^1J_{C-F}$ = 361.7 Hz), 113.88 (q, $^1J_{C-F}$ = 290.9 Hz). ^{19}F NMR ($CDCl_3$ at 23 °C): δ −75.5 (s, 3F), −8.8 (br s, 3F). $^{31}P\{^1H\}$ NMR ($CDCl_3$ at 23 °C): δ 22.6 (br s). $^{19}F/^{13}C$ HSQC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −9.0/123.3, −75.7/114.0. IR (ATR, cm^{-1}): 3058 (w), 1675 (s), 1482 (s), 1434 (s), 1415 (s), 1190 (s). Anal. Calcd for $NiC_{39}H_{30}F_6O_2P_2$: C, 61.21; H, 3.95; F, 14.90. Found: C, 61.12; H, 3.95; F, 14.81.

Preparation of (dppe)Ni(CF_3)(OC(O)CF_3) (15). A 20 mL vial was charged with $(PPh_3)_2$Ni(CF_3)($OOCCF_3$) (**14**; 153 mg, 0.20 mmol), 1,2-bis(diphenylphosphino)ethane (dppe; 105 mg, 0.26 mmol), and dry dichloromethane (10 mL). The resulting solution was stirred at 25 °C for 5 min, and then the reaction mixture was filtered through a pad of Celite. The volatiles were removed under reduced pressure, and the residue was dissolved in diisopropyl ether. The product slowly separated in the form of yellow crystals. The product was collected, washed with several portions of diisopropyl ether, and dried under reduced pressure to afford **15** as a yellow solid (123 mg, 96% yield). Samples for elemental analysis were recrystallized three additional times from dichloromethane/diisopropyl ether. ^{1}H NMR (CD_2Cl_2 at 23 °C): δ 8.07−8.00 (m, 4H), 7.82−7.75 (m, 4H), 7.67−7.51 (m, 12H), 2.31−2.19 (m, 4H), 2.12−2.00 (m, 4H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 23 °C): δ 160.73 (q, $^2J_{C-F}$ = 36.1 Hz), 133.48 (d, $^3J_{C-P}$ = 10.9 Hz), 133.42 (qdd, $^1J_{C-F}$ = 234.3 Hz, $^2J_{C-P}$ = 137.6 Hz, $^2J_{C-P}$ = 39.5 Hz multiplet partially overlaps with other nearby peaks), 133.07 (d, $^3J_{C-P}$ = 11.6 Hz), 132.05 (d, $^4J_{C-P}$ = 2.7 Hz), 131.82 (d, $^4J_{C-P}$ = 2.0 Hz), 129.24 (d, $^2J_{C-P}$ = 10.2 Hz), 129.14 (d, $^2J_{C-P}$ = 10.9 Hz), 127.84 (d, $^1J_{C-P}$ = 50.4 Hz), 127.00 (d, $^1J_{C-P}$ = 40.9 Hz), 114.94 (q, $^1J_{C-F}$ = 290.2 Hz), 29.40 (dd, $^1J_{C-P}$ = 33.4 Hz, $^2J_{C-P}$ = 17.0 Hz), 22.28 (dd, $^1J_{C-P}$ = 30.0 Hz, $^2J_{C-P}$ = 7.9 Hz). ^{19}F NMR (CD_2Cl_2 at 23 °C): δ −29.0 (dd, $^3J_{F-P}$ = 43 and 10 Hz, 3F), −75.1 (s, 3F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2 at 23 °C): δ 56.5 (dq, $^2J_{P-P}$ = 46 Hz, $^3J_{P-F}$ = 11 Hz, 1P), 45.8 (apparent quintet, $^2J_{P-P}$ = $^3J_{P-F}$ = 45 Hz, 1P). $^{19}F/^{13}C$ HSQC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −29.2/133.5, −75.2/115.0. $^{19}F/^{13}C$ HMBC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −75.1/160.7. IR (ATR, cm^{-1}): 3054 (w), 1685 (s), 1573 (w), 1485 (m), 1436 (s), 1421 (s), 1313 (m), 1183 (s). Anal. Calcd for $NiC_{29}H_{24}F_6O_2P_2$: C, 54.50; H, 3.78; F, 17.84. Found: C, 54.53; H, 3.69; F, 17.97.

General Procedure 2. Synthesis of dppe-Supported Perfluoroalkyl Nickel Complexes. In a nitrogen-filled glovebox, a Schlenk flask was charged with triphenylphosphine (1.00 g, 3.81 mmol) and $Ni(COD)_2$ (500 mg, 1.82 mmol). The flask was sealed with a septum and then removed from the glovebox. Dry THF (50 mL) was added via cannula, and the resulting dark red mixture was stirred at 25 °C for 15 min. The solution was then cooled to −78 °C, and the corresponding carboxylic anhydride or carboxylic chloride (3 mmol) was added dropwise. The solution was slowly warmed to room temperature over a period of 1 h, and then dppe (876 mg, 2.20 mmol) was added. The resulting solution was stirred at room temperature for 5 min and then filtered through a pad of Celite. The volatiles were removed under reduced pressure, and the resulting residue was

dx.doi.org/10.1021/om500535x | *Organometallics* XXXX, XXX, XXX−XXX

suspended in diisopropyl ether (50 mL). The product separated in the form of yellow crystalls. The product was collected, washed with several portions of diisopropyl ether, and dried under reduced pressure. Samples for elemental analysis were recrystallized three additional times from dichloromethane/diisopropyl ether.

Preparation of (dppe)Ni(C_2F_5)(OC(O)C_2F_5) (16). Product **16** was prepared according to general procedure 2 (yellow solid, 640 mg, 48% yield). ^{1}H NMR (CD_2Cl_2 at 23 °C): δ 8.06−8.00 (m, 4H), 7.82−7.76 (m, 4H), 7.66−7.59 (m, 4H), 7.59−7.50 (m, 8H), 2.21−2.12 (m, 4H), 2.10−2.00 (m, 4H). ^{13}C{^{1}H} NMR (CD_2Cl_2 at 25 °C): δ 160.89 (t, $^2J_{C-F}$ = 26.0 Hz), 133.60 (d, $^3J_{C-P}$ = 10.2 Hz), 133.20 (d, $^3J_{C-P}$ = 10.9 Hz), 131.97 (d, $^4J_{C-P}$ = 2.7 Hz), 131.85 (d, $^4J_{C-P}$ = 2.0 Hz), 129.19 (d, $^2J_{C-P}$ = 10.2 Hz), 129.03 (d, $^2J_{C-P}$ = 10.9 Hz), 128.47 (m, Ni−CF_2−CF_3 resonance not observed in ^{13}C spectrum but shift extracted from ^{19}F/^{13}C HSQC and HMBC experiments), 127.62 (d, $^1J_{C-P}$ = 50.4 Hz), 126.67 (d, $^1J_{C-P}$ = 40.9 Hz), 120.63 (qtd, $^1J_{C-F}$ = 285.4 Hz, $^2J_{C-F}$ = 32.0 Hz, $^3J_{C-P}$ = 8.2 Hz, Ni−CF_2−CF_3), 118.26 (qt, $^1J_{C-F}$ = 286.1 Hz, $^2J_{C-F}$ = 35.4 Hz, CO−CF_2−CF_3), 105.49 (tq, $^1J_{C-F}$ = 263.0 Hz, $^2J_{C-F}$ = 38.1 Hz, CO−CF_2−CF_3), 28.98 (dd, $^1J_{C-P}$ = 35.4 Hz, $^2J_{C-P}$ = 16.4 Hz), 22.30 (dd, $^1J_{C-P}$ = 30.0 Hz, $^2J_{C-P}$ = 8.9 Hz). ^{19}F NMR (CD_2Cl_2 at 23 °C): δ −80.3 (s, 3F, Ni−CF_2−CF_3), −83.6 (br s, 3F, CO−CF_2−CF_3), −102.1 (br t, $^3J_{F-P}$ = 25 Hz, 2F, Ni−CF_2−CF_3), −119.8 (br s, 2F, CO−CF_2−CF_3). ^{31}P{^{1}H} NMR (CD_2Cl_2 at 23 °C): δ 54.9 (dt, $^2J_{P-P}$ = 49 Hz, $^3J_{P-F}$ = 26 Hz), 45.3 (dt, $^2J_{P-P}$ = 49 Hz, $^3J_{P-F}$ = 28 Hz). ^{19}F/^{13}C HSQC NMR (CD_2Cl_2 at 25 °C): δ_F/ δ_C −80.4/120.7, −83.7/118.5, −102.3/128.5, −119.9/105.6. ^{19}F/^{13}C HMBC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −80.3/128.4, −80.3/120.8 (^1J correlation), −83.6/105.4, −83.6/118.3 (^1J correlation), −102.1/120.7, −119.8/105.4 (^1J correlation), −119.8/118.3, −119.8/161.0. IR (ATR, cm^{-1}): 1696 (s), 1485 (w), 1439 (s), 1393 (m), 1319 (s), 1296 (s), 1225 (m), 1154 (s). Anal. Calcd for $NiC_{31}H_{24}F_{10}O_2P_2$: C, 50.37; H, 3.27; F, 25.70. Found: C, 50.23; H, 3.32; F, 25.76.

Preparation of (dppe)Ni(C_3F_7)($OCOC_3F_7$) (17). Product **17** was prepared according to general procedure 2 (yellow solid, 790 mg, 52% yield). ^{1}H NMR ($CDCl_3$ at 23 °C): δ 8.06−7.97 (m, 4H), 7.80−7.74 (m, 4H), 7.60−7.43 (m, 12H), 2.17−2.07 (m, 2H), 2.06−1.96 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$ at 23 °C; resonances of fluoroalkyl groups are assigned from the ^{19}F/^{13}C HSQC spectrum): δ 161.06 (br), 133.65 (d, $^3J_{C-P}$ = 10.9 Hz), 133.18 (d, $^3J_{C-P}$ = 10.9 Hz), 131.87, 131.83, 131.09 (m, Ni-CF_2−), 129.25 (d, $^2J_{C-P}$ = 10.2 Hz), 129.05 (d, $^2J_{C-P}$ = 10.9 Hz), 127.73 (d, $^1J_{C-P}$ = 50.4 Hz), 126.56 (d, $^1J_{C-P}$ = 40.2 Hz), 118.17 (m, −CF_3), 117.81 (m, −CF_3), 110.98 (m, −CF_2−), 108.21 (m, −CF_2−), 107.38 (m, −CF_2−), 28.95 (dd, $^1J_{C-P}$ = 34.1 Hz, $^2J_{C-P}$ = 16.4 Hz), 22.32 (dd, $^1J_{C-P}$ = 29.3 Hz, $^2J_{C-P}$ = 8.9 Hz). ^{19}F NMR ($CDCl_3$ at 23 °C): δ −80.5 (s, 3F), −80.8 (s, 3F), −98.4 (br, 2F), −116.9 (br, 2F), −118.3 (s, 2F), −127.1 (s, 2F). ^{31}P{^{1}H} NMR ($CDCl_3$ at 25 °C): δ 54.2 (dt, $^2J_{P-P}$ = 44 Hz, $^3J_{P-F}$ = 25 Hz, 1P), 44.3 (dt, $^2J_{P-P}$ = 44 Hz, $^3J_{P-F}$ = 29 Hz, 1P). ^{19}F/^{13}C HSQC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −80.6/118.2, −80.9/117.8, −98.5/131.1, −117.0/107.4, −118.4/111.0, −127.2/108.2. ^{19}F/^{13}C HMBC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −80.5/111.0, −80.8/108.2, −118.3/111.2 (^1J correlation), −118.3/118.1, −127.1/107.6, −127.1/118.0. IR (ATR, cm^{-1}): 1698 (s), 1486 (w), 1437 (m), 1385 (w), 1330 (s), 1210 (s), 1174 (s), 1119 (s), 1078 (s). Anal. Calcd for $NiC_{33}H_{24}F_{14}O_2P_2$: C, 47.23; H, 2.88; F, 31.70. Found: C, 47.37; H, 2.92; F, 31.70.

Preparation of (dppe)Ni($CF_2CF_2CO_2$) (18). Product **18** was prepared according to general procedure 2 (yellow solid, 572 mg, 52% yield). ^{1}H NMR (CD_2Cl_2 at 25 °C): δ 8.87−7.78 (m, 8H), 7.63−7.48 (m, 12H), 2.44−2.34 (m, 2H), 2.21−2.10 (m, 2H). ^{13}C{^{1}H} NMR (CD_2Cl_2 at 25 °C; resonances of fluoroalkyl group partially assigned from the ^{19}F/^{13}C HSQC spectrum): δ 168.98 (t, $^2J_{C-F}$ = 25.9 Hz), 133.24 (d, $^3J_{C-P}$ = 10.9 Hz), 132.73 (d, $^3J_{C-P}$ = 11.6 Hz), 132.03 (d, $^4J_{C-P}$ = 2.7 Hz), 131.66 (d, $^4J_{C-P}$ = 2.1 Hz), 129.59 (m, Ni−CF_2−), 129.41 (d, $^2J_{C-P}$ = 10.2 Hz), 129.16 (d, $^2J_{C-P}$ = 10.9 Hz), 128.46 (d, $^1J_{C-P}$ = 38.2 Hz), 126.97 (d, $^1J_{C-P}$ = 41.8 Hz), 110.83 (tt, $^1J_{C-F}$ = 267.0 Hz, $^2J_{C-F}$ = 21.8 Hz), 29.91 (dd, $^1J_{C-P}$ = 34.8 Hz, $^2J_{C-P}$ = 17.7 Hz), 21.93 (dd, $^1J_{C-P}$ = 30.7 Hz, $^2J_{C-P}$ = 8.9 Hz). ^{19}F NMR (CD_2Cl_2 at 25 °C): δ −110.3 (m, 2F), −120.0 (br, 2F). ^{31}P{^{1}H} NMR (CD_2Cl_2 at 25 °C): δ 59.1 (dt, $^2J_{P-P}$ = 29 Hz, $^3J_{P-F}$ = 20 Hz, 1P), 38.5 (app quartet, $^2J_{P-P}$ = $^3J_{P-F}$ = 30 Hz, 1P). ^{19}F/^{13}C HSQC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −110.3/129.6, −120.0/110.8. ^{19}F/^{13}C HMBC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −110.3/110.8, −110.3/129.6 (^1J correlation), −110.3/169.0−120.0/110.8 (^1J correlation), −120.0/129.6, −120.0/169.0. IR (ATR, cm^{-1}): 3054 (w), 2956 (w), 1698 (s), 1619 (w), 1587 (w), 1483 (m), 1436 (m), 1351 (m), 1245 (s), 1137 (m), 1098 (s), 1038 (s). Anal. Calcd for $NiC_{29}H_{24}F_4O_2P_2$: C, 57.94; H, 4.02; F, 12.64. Found: C, 57.64; H, 4.02; F, 12.66.

Preparation of (dppe)Ni($CF_2CF_2CF_2COO$) (19). Product **19** was prepared according to general procedure 2 (yellow solid, 422 mg, 36% yield). ^{1}H NMR (CD_2Cl_2 at 25 °C): δ 7.96−7.90 (m, 4H), 7.86−7.80 (m, 4H), 7.66−7.61 (m, 2H), 7.61−7.57 (m, 2H), 7.57−7.51 (m, 8H), 2.46−2.36 (m, 2H), 2.06−1.96 (m, 2H). ^{13}C{^{1}H} NMR (CD_2Cl_2 at 25 °C; resonances of fluoroalkyl partially assigned from the ^{19}F/^{13}C HSQC spectrum): δ 163.72 (t, $^2J_{C-F}$ = 22.5 Hz), 133.47 (d, $^3J_{C-P}$ = 10.9 Hz), 132.88 (d, $^3J_{C-P}$ = 10.2 Hz), 132.21 (d, $^4J_{C-P}$ = 2.0 Hz), 131.75 (d, $^4J_{C-P}$ = 2.7 Hz), 129.35 (d, $^2J_{C-P}$ = 10.2 Hz), 129.17 (d, $^2J_{C-P}$ = 10.9 Hz), 127.97 (d, $^1J_{C-P}$ = 38.8 Hz), 126.87 (d, $^1J_{C-P}$ = 51.1 Hz), 126.75 (m, −CF_2−Ni), 111.65 (br triplet, $^1J_{C-F}$ = 261.6 Hz), 107.79 (tt, $^1J_{C-F}$ = 260.2 Hz, $^2J_{C-F}$ = 28.6 Hz), 30.42 (dd, $^1J_{C-P}$ = 36.1 Hz, $^2J_{C-P}$ = 17.7 Hz), 21.23 (dd, $^1J_{C-P}$ = 30.7 Hz, $^2J_{C-P}$ = 8.2 Hz). ^{19}F NMR (CD_2Cl_2 at 25 °C): δ −100.8 (t, $^2J_{F-P}$ = 32 Hz, 2F), −120.4 (m, 2F), −130.0 (br, 2F). ^{31}P{^{1}H} NMR (CD_2Cl_2 at 25 °C): δ 58.3 (dt, $^2J_{P-P}$ = 44 Hz, $^3J_{P-F}$ = 33 Hz, 1P), 38.2 (m, 1P). ^{19}F/^{13}C HSQC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −100.8/126.8, −120.4/107.8, −130.0/111.7. ^{19}F/^{13}C HMBC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −100.8/111.7, −120.4/107.8 (^1J correlation), −120.4/111.7, −120.4/163.8, −130.0/111.7 (^1J correlation), −130.0/126.8. IR (ATR, cm^{-1}): 3064 (w), 2956 (w), 2918 (w), 1687 (s), 1482 (m), 1434 (m), 1379 (m), 1288 (m), 1221 (m), 1164 (s), 1102 (s), 1052 (s). Anal. Calcd for $NiC_{30}H_{24}F_6O_2P_2$: C, 55.34; H, 3.72; F, 17.51. Found: C, 55.19; H, 3.70; F, 17.25.

Preparation of (dppe)Ni(C_3F_7)(Cl) (20). Product **20** was prepared according to general procedure 2 (yellow solid, 570 mg, 47% yield). This compound slowly decomposes in solution. The analytical sample contained an unidentified decomposition product of general formula (dppe)NiX_2 (~15% based on ^{31}P NMR spectroscopy analysis). All attempts to further purify the title complex resulted in extensive decomposition. ^{1}H NMR ($CDCl_3$ at 23 °C): δ 7.91−7.80 (m, 8H), 7.28−7.40 (m, 12H), 2.20−2.08 (m, 2H), 1.99−1.88 (m, 2H). ^{13}C{H} NMR ($CDCl_3$ at 23 °C): δ 133.72 (d, $^3J_{C-P}$ = 10.2 Hz), 133.81 (low intensity m that overlaps with nearby peaks; resonance observed in ^{19}F/^{13}C HSQC spectrum), 133.51 (d, $^3J_{C-P}$ = 10.9 Hz), 131.71, 131.29, 128.92−128.61 (four overlapping d), 118.42 (qt, $^1J_{C-F}$ = 286.8 Hz, $^2J_{C-F}$ = 40.87 Hz), 111.62 (tq, $^1J_{C-F}$ = 256.8 Hz, $^2J_{C-F}$ = 32.8 Hz), 29.66 (dd, $^1J_{C-P}$ = 34.7 Hz, $^2J_{C-P}$ = 18.4 Hz), 24.63 (dd, $^1J_{C-P}$ = 27.2 Hz, $^2J_{C-P}$ = 9.9 Hz). ^{19}F NMR ($CDCl_3$ at 23 °C): δ −80.4 (t, $^3J_{F-F}$ = 10 Hz, 3F), −89.9 (m, 2F), −115.3 (br s, 2F). ^{31}P{^{1}H} NMR ($CDCl_3$ at 25 °C): δ 60.4 (dt, $^2J_{P-P}$ = 49 Hz, $^3J_{P-F}$ = 35 Hz, 1P), 44.4 (dt, $^2J_{P-P}$ = 49 Hz, $^3J_{P-F}$ = 28 Hz, 1P). ^{19}F/^{13}C HSQC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −80.5/118.4, −90.0/133.8, −115.4/111.6. ^{19}F/^{13}C HMBC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −80.4/111.7, −80.4/118.6 (^1J correlation). IR (ATR, cm^{-1}): 3055 (w), 1485 (m), 1438 (s), 1326 (s), 1211 (s), 1188 (s). Anal. Calcd for $NiC_{29}H_{24}ClF_7P_2$: C, 52.65; H, 3.66; Cl, 5.36; F, 20.10. Found: C, 53.02; H, 3.81; Cl, 5.46; F, 18.16.

Preparation of (dppe)Ni(C_6F_5)(Cl) (21). Product **21** was prepared according to general procedure 2 (yellow solid, 775 mg, 65% yield). ^{1}H NMR (CD_2Cl_2 at 23 °C): δ 7.97 (m, 4H), 7.68 (m, 4H), 7.60 (m, 2H), 7.57−7.52 (m, 6H), 7.41 (m, 4H), 2.44−2.32 (m, 2H), 2.11−1.98 (m, 2H). ^{13}C{^{1}H} NMR (CD_2Cl_2 at 23 °C): δ 145.89 (app dd, $^1J_{C-F}$ = 226.8 Hz, $^3J_{C-P}$ = 27.3 Hz), 138.19 (app d, $^1J_{C-F}$ = 240 Hz), 137.16 (app d, $^1J_{C-F}$ = 252 Hz), 133.62 (d, $^3J_{C-P}$ = 10.2 Hz), 132.95 (d, $^3J_{C-P}$ = 10.2 Hz), 131.81 (d, $^4J_{C-P}$ = 2.7 Hz), 131.81 (d, $^4J_{C-P}$ = 2.0 Hz), 129.15 (d, $^1J_{C-P}$ = 43.6 Hz), 128.90 (d, $^2J_{C-P}$ = 10.2 Hz) 128.67 (d, $^2J_{C-P}$ = 10.9 Hz), 128.63 (d, $^1J_{C-P}$ = 41.8 Hz), 123.37 (m), 27.80 (dd, $^1J_{C-P}$ = 31.3 Hz, $^2J_{C-P}$ = 18.4 Hz), 22.94 (dd, $^1J_{C-P}$ = 28.6 Hz, $^2J_{C-P}$ = 12.3 Hz). ^{19}F NMR (CD_2Cl_2 at 23 °C): δ −118.6 (m, 2F), −161.7 (app t, $^3J_{F-F}$ = 20 Hz, 1F), −163.6 (m, 2F). ^{31}P{^{1}H}

dx.doi.org/10.1021/om500535x | Organometallics XXXX, XXX, XXX−XXX

NMR (CD_2Cl_2 at 23 °C): δ 61.6 (d, $^2J_{P-P}$ = 60 Hz), 48.0 (br d, $^2J_{P-P}$ = 52 Hz). $^{19}F/^{13}C$ HSQC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −118.6/145.9, −162.7/137.0, −164.4/135.8. $^{19}F/^{13}C$ HMBC NMR (CD_2Cl_2 at 25 °C): δ_F/δ_C −118.6/123.4, −118.6/135.8, −118.6/137.0, −162.6/135.8, −162.6/137.0 (^1J correlation), −162.6/145.9, −164.4/123.4, −164.4/135.8 (^1J correlation), −164.4/137.0, −164.4/145.9. IR (ATR): cm^{-1} 3076 (w), 1495 (s), 1448 (s), 1435 (s), 1343 (m), 1102 (s).

General Procedure 3. Preparation of Complexes with General Structure (dppe)Pd(R_F)(Ph). In a glovebox, a Schlenk flask was charged with a stirbar, diphenylzinc (120 mg, 0.55 mmol), and the corresponding (dppe)Pd(R_F)($OOCR_F$) complex (0.36 mmol). The flask was sealed and removed from the glovebox. Dry THF (20 mL) was added via cannula. The resulting solution was stirred at room temperature for 20 min, and then water (0.2 mL) was introduced via the septum. The reaction mixture was stirred at room temperature for an additional 20 min until $Zn(OH)_2$ had completely precipitated. The THF solution was dried over anhydrous Na_2SO_4, and the volatiles were removed under reduced pressure. The residue was crystallized from diethyl ether. The product was collected, washed with several portions of diethyl ether, and dried under vacuum. Samples for elemental analysis were recrystallized three additional times from mixture of dichloromethane and diisopropyl ether.

Preparation of (dppe)Pd(CF_3)(Ph) (22). Product **22** was prepared according to general procedure 3 (white solid, 188 mg, 79% yield. ^1H NMR ($CDCl_3$ at 25 °C): δ 7.80−7.74 (m, 4H), 7.52−7.44 (m, 4H), 7.43−7.38 (m, 2H), 7.33−7.26 (m, 10H), 7.20 (t, J = 6.9 Hz, 2H), 6.81 (app t, J = 6.9 Hz, 2H), 6.77 (t, J = 6.9 Hz, 1H), 2.34−2.16 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$ at 25 °C): δ 158.85 (app d of quintets, $^2J_{C-P}$ = 112.4 Hz, $^3J_{C-F}$ = $^2J_{C-P}$ = 8.9 Hz), 143.63 (qdd, $^1J_{C-F}$ = 373.3 Hz, $^2J_{C-P}$ = 195.5 and 13.6 Hz), 136.70, 133.35−133.19 (two overlapping d), 131.43 (d, $^1J_{C-P}$ = 34.1 Hz), 130.83 (d, $^4J_{C-P}$ = 2.1 Hz), 130.76 (d, $^4J_{C-P}$ = 2.1 Hz), 130.19 (d, $^1J_{C-P}$ = 41.5 Hz), 128.95 (d, $^2J_{C-P}$ = 9.5 Hz), 128.66 (d, $^2J_{C-P}$ = 10.2 Hz), 126.64 (d, $^3J_{C-P}$ = 7.5 Hz, Pd−C−*CH*), 122.34, 27.48 (dd, $^1J_{C-P}$ = 25.9 Hz, $^2J_{C-P}$ = 18.4 Hz), 26.40 (dd, $^1J_{C-P}$ = 25.2 Hz, $^2J_{C-P}$ = 15.0 Hz). ^{19}F NMR ($CDCl_3$ at 25 °C): δ −17.5 (dd, $^3J_{F-P}$ = 51 and 12 Hz, 3F). $^{31}P\{^1H\}$ NMR ($CDCl_3$ at 25 °C): δ 40.1 (qd, $^3J_{P-F}$ = 50 Hz, $^2J_{P-P}$ = 17 Hz), 38.3 (app quintet, $^3J_{P-F}$ = $^2J_{P-P}$ = 18 Hz). $^{19}F/^{13}C$ HSQC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −17.6/143.7. $^{19}F/^{13}C$ HMBC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −17.5/143.7 (^1J correlation), −17.5/158.8. IR (ATR, cm^{-1}): 3052 (w), 1565 (m), 1470 (m), 1434 (s), 1308 (w), 1239 (m), 1103 (m), 1080 (s), 950 (s). HRMS electrospray (m/z): $[M - Ph]^+$ calcd for $C_{27}H_{24}F_3P_2Pd$ 573.0335, found 573.0343; $[M - F]^+$ calcd for $C_{33}H_{29}F_2P_2Pd$ 631.0742, found 631.0747.

Preparation of (dppe)Pd(C_2F_5)(Ph) (23). Product **23** was obtained according to general procedure 3 (white solid, 725 mg, 90% yield). ^1H NMR ($CDCl_3$ at 25 °C): δ 7.77−7.72 (m, 4H), 7.52−7.45 (m, 4H), 7.41 (t, J = 7.2 Hz, 2H), 7.33−7.24 (m, 10H), 7.15 (t, J = 7.0 Hz, 2H), 6.75 (app t, J = 7.3 Hz, 2H), 6.72 (t, J = 6.8 Hz, 1H), 2.24−2.14 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$ at 25 °C): δ 158.22 (app d, $^2J_{C-P}$ = 107.7 Hz), 136.93, 136.11 (m, Pd-CF_2−), 133.35 (d, $^3J_{C-P}$ = 12.3 Hz), 133.21 (d, $^3J_{C-P}$ = 11.6 Hz), 131.55 (d, $^1J_{C-P}$ = 33.4 Hz), 130.77 (d, $^4J_{C-P}$ = 2.0 Hz), 130.73 (d, $^4J_{C-P}$ = 2.1 Hz), 130.24 (d, $^1J_{C-P}$ = 42.2 Hz), 128.85 (d, $^2J_{C-P}$ = 10.2 Hz), 128.66 (d, $^2J_{C-P}$ = 10.2 Hz), 126.50 (d, $^3J_{C-P}$ = 7.5 Hz, Pd−C−*CH*), 122.72 (qtd, $^1J_{C-F}$ = 284.8 Hz, $^2J_{C-F}$ = 30.0 Hz, $^3J_{C-P}$ = 9.5 Hz, -CF_3), 122.02, 27.01 (dd, $^1J_{C-P}$ = 25.9 Hz, $^2J_{C-P}$ = 18.4 Hz), 26.60 (dd, $^1J_{C-P}$ = 25.9 Hz, $^2J_{C-P}$ = 15.0 Hz). ^{19}F NMR ($CDCl_3$ at 25 °C): δ −80.1 (s, 3F), −89.6 (dd, $^3J_{F-P}$ = 42 and 32 Hz, 2F). $^{31}P\{^1H\}$ NMR ($CDCl_3$ at 25 °C): δ 39.6 (tdq, $^3J_{P-F}$ = 32 Hz, $^2J_{P-P}$ = 17 Hz, $^4J_{P-F}$ = 3 Hz, 1P), 38.9 (td, $^3J_{P-F}$ = 41 Hz, $^2J_{P-P}$ = 17 Hz, 1P). $^{19}F/^{13}C$ HSQC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −80.1/122.7, −89.6/136.1. $^{19}F/^{13}C$ HMBC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −80.1/122.7 (^1J correlation), −80.1/136.1, −89.6/122.7. IR (ATR, cm^{-1}): 3055 (w), 1564 (m), 1472 (m), 1434 (s), 1292 (s), 1191 (s), 1145 (s), 1099 (m). HRMS electrospray (m/z): $[M - Ph]^+$ calcd for $C_{28}H_{24}F_5P_2Pd$ 623.0303, found 623.0314; $[M - Ph + CH_3CN]^+$ calcd for $C_{30}H_{27}F_5NP_2Pd$ 664.0568, found 664.0577. Anal. Calcd for $PdC_{34}H_{29}F_5P_2$: C, 58.26; H, 4.17; F, 13.55. Found: C, 58.22; H, 4.15; F, 13.46.

Preparation of (dppe)Pd(C_3F_7)(Ph) (24). Product **24** was prepared according to general procedure 3 (white solid, 485 mg, 92% yield). ^1H NMR ($CDCl_3$ at 25 °C): δ 7.77−7.72 (m, 4H), 7.52−7.45 (m, 4H), 7.42 (t, J = 7.5 Hz, 2H), 7.33−7.25 (m, 10H), 7.17 (t, J = 7.0 Hz, 2H), 6.75 (app t, J = 7.3 Hz, 2H), 6.72 (t, J = 6.9 Hz, 1H), 2.24−2.14 (m, 4H). $^{13}C\{^1H\}$ NMR ($CDCl_3$ at 25 °C): δ 157.87 (app dd, $^2J_{C-P}$ = 117.1 and 12.3 Hz), 139.31 (m, Pd-CF_2−), 136.98, 133.38 (d, $^3J_{C-P}$ = 12.3 Hz), 133.17 (d, $^3J_{C-P}$ = 10.9 Hz), 131.57 (d, $^1J_{C-P}$ = 32.7 Hz), 130.74 (two overlapping signals), 130.3 (d, $^1J_{C-P}$ = 42.9 Hz), 128.81 (d, $^2J_{C-P}$ = 9.5 Hz), 128.67 (d, $^2J_{C-P}$ = 7.5 Hz), 126.50 (d, $^3J_{C-P}$ = 7.5 Hz, Pd−C−*CH*), 121.99, 119.21 (qt, $^1J_{C-F}$ = 289.5 Hz, $^2J_{C-F}$ = 34.7 Hz, −CF_3), 112.04 (tq, $^1J_{C-F}$ = 252.0 Hz, $^2J_{C-F}$ = 30.7 Hz, −CF_2CF_3), 26.97 (dd, $^1J_{C-P}$ = 24.5 Hz, $^2J_{C-P}$ = 18.4 Hz), 26.42 (dd, $^1J_{C-P}$ = 25.2 Hz, $^2J_{C-P}$ = 15.7 Hz). ^{19}F NMR ($CDCl_3$ at 23 °C): δ −79.7 (t, $^3J_{F-F}$ = 13 Hz, 3F), −87.6 (m, 2F), −118.3 (s, 2F). $^{31}P\{^1H\}$ NMR ($CDCl_3$ at 25 °C): δ 39.5−38.9 (two overlapping m). $^{19}F/^{13}C$ HSQC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −79.7/119.2, −87.6/139.3, −118.3/112.0. $^{19}F/^{13}C$ HMBC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −79.7/112.0, −79.7/119.2 (^1J correlation), −87.6/112.0, −118.3/112.0 (^1J correlation), −118.3/119.2. IR (ATR, cm^{-1}): 3061 (w), 1566 (m), 1473 (m), 1436 (s), 1325 (s), 1213 (s), 1180 (s), 1142 (s), 1099 (m). HRMS electrospray (m/z): $[M - Ph]^+$ calcd for $C_{29}H_{24}F_7P_2Pd$ 673.0271, found 673.0283; $[M - Ph + CH_3CN]^+$ calcd for $C_{31}H_{27}F_7NP_2Pd$ 714.0536, found 714.0542. Anal. Calcd for $PdC_{35}H_{29}F_7P_2$: C, 55.98; H, 3.89; F, 17.71. Found: C, 55.86; H, 3.89; F, 17.90.

Preparation of (dppe)Pd(CF_3)(CH_3) (26). A Schlenk flask was charged with a stirbar and (dppe)Pd(CF_3)($OOCCF_3$) (300 mg, 0.44 mmol). The flask was sealed, placed under vacuum, and then refilled with nitrogen. The flask was evacuated and refilled with nitrogen three more times. Dry THF (15 mL) was added via cannula followed by dimethylzinc (1 mL of 1.2 M solution in THF). The resulting solution was stirred at room temperature for 20 min, and then water (0.2 mL) was introduced via the septum. The reaction mixture was stirred at room temperature for an additional 20 min until $Zn(OH)_2$ had completely precipitated. The THF solution was dried over anhydrous Na_2SO_4, and the volatiles were removed under reduced pressure. The residue was recrystallized from diethyl ether. The product was collected, washed with several portions of diethyl ether, and dried under vacuum. The product was obtained as a white crystalline solid (207 mg, 80% yield). Samples for elemental analysis were recrystallized several additional times from dichloromethane/diisopropyl ether. ^1H NMR ($CDCl_3$ at 25 °C): δ 7.71−7.65 (m, 4H), 7.62−7.57 (m, 4H), 7.49−7.38 (m, 12H), 2.34−2.24 (m, 2H), 2.21−2.12 (m, 2H), 0.59 (app t, $^3J_{H-P}$ = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$ at 25 °C): δ 146.60 (qdd, $^1J_{C-F}$ = 374.7 Hz, $^2J_{C-P}$ = 201.0 and 15.6 Hz), 133.35 (d, $^3J_{C-P}$ = 11.6 Hz), 133.18 (d, $^3J_{C-P}$ = 12.9 Hz), 132.03 (d, $^1J_{C-P}$ = 31.3 Hz), 130.95 (d, $^4J_{C-P}$ = 2.1 Hz), 130.56 (d, $^4J_{C-P}$ = 1.4 Hz), 130.29 (d, $^1J_{C-P}$ = 40.2 Hz), 128.95 (d, $^2J_{C-P}$ = 9.5 Hz), 128.79 (d, $^2J_{C-P}$ = 9.5 Hz), 28.44 (dd, $^1J_{C-P}$ = 27.2 Hz, $^2J_{C-P}$ = 19.8 Hz), 27.38 (dd, $^1J_{C-P}$ = 25.2 Hz, $^2J_{C-P}$ = 15.7 Hz), 0.25 (ddq, $^2J_{C-P}$ = 89.2 and 8.9 Hz, $^3J_{C-F}$ = 6.8 Hz). ^{19}F NMR ($CDCl_3$ at 25 °C): δ −19.3 (dd, $^3J_{F-P}$ = 53 and 18 Hz, 3F). $^{31}P\{^1H\}$ NMR ($CDCl_3$ at 25 °C): δ 47.4 (qd, $^3J_{P-F}$ = 52 Hz, $^2J_{P-P}$ = 16 Hz), 47.4 (app quintet, $^3J_{P-F}$ = $^2J_{P-P}$ = 17 Hz). $^{19}F/^{13}C$ HSQC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −19.4/146.8. $^{19}F/^{13}C$ HMBC NMR ($CDCl_3$ at 25 °C): δ_F/δ_C −19.3/0.3, −19.3/146.6 (^1J correlation). IR (ATR, cm^{-1}): 3053 (w), 2955 (w), 2888(w), 1587 (w), 1573 (w), 1483 (m), 1435 (s), 1411 (m), 1309 (m), 1186 (m), 1158 (m), 1102 (m), 1074 (s). HRMS electrospray (m/z): $[M - CH_3]^+$ calcd for $C_{27}H_{24}F_3P_2Pd$ 573.0335, found 573.0342; $[M - CH_3 + CH_3CN]^+$ calcd for $C_{29}H_{27}F_3NP_2Pd$ 614.0600, found 614.0603. Anal. Calcd for $PdC_{28}H_{27}F_3P_2$: C, 57.11; H, 4.62; F, 9.68. Found: C, 56.04; H, 4.57; F, 9.81

dx.doi.org/10.1021/om500535x | Organometallics XXXX, XXX, XXX−XXX

■ ASSOCIATED CONTENT

Supporting Information

Figures giving spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the NSF (CHE-1111563) for support of this research. AM is a Howard Hughes Medical Institute International Student Research Fellow.

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