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Catalytic Cycle for Palladium-Catalyzed Decarbonylative Trifluoromethylation using Trifluoroacetic Esters as the CF_3 Source

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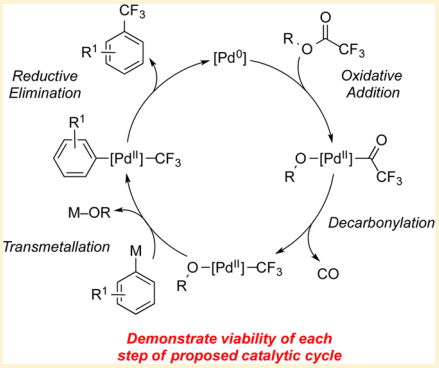
Supporting Information

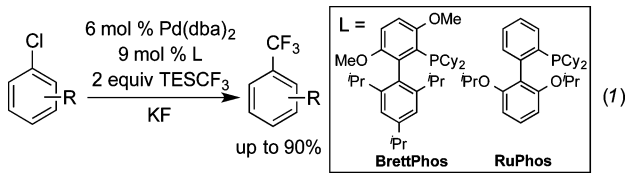
ABSTRACT: This paper demonstrates a catalytic cycle for Pd-catalyzed decarbonylative trifluoromethylation using trifluoroacetic esters as CF_3 sources. The proposed cycle consists of four elementary steps: (1) oxidative addition of a trifluoroacetic ester to Pd^0, (2) CO deinsertion from the resulting trifluoroacyl Pd^{II} complex, (3) transmetalation of a zinc aryl to Pd^{II}, and (4) aryl–CF_3 bond-forming reductive elimination. The use of RuPhos as the supporting ligand enables each of these steps to proceed under mild conditions (<100 °C). These studies set the stage for the development of catalytic arene trifluoromethylation and perfluoroalkylation reactions using inexpensive trifluoroacetic acid derived CF_3 sources.



INTRODUCTION

Trifluoromethyl and other fluoroalkyl groups are prevalent in a variety of biologically active molecules. They are commonly used to modulate the bioavailability, binding affinity, and metabolic stability of pharmaceuticals and agrochemicals.[1] However, wider application of fluoroalkylated compounds (particularly fluoroalkylated aromatics and heteroaromatics) is inhibited by limitations in the synthetic methods available for preparing these molecules. Over the past decade, significant effort has been directed toward the development of more ecologically sustainable, inexpensive, and broadly applicable methods for the late-stage perfluoroalkylation of arenes and heteroarenes.[2] Copper-catalyzed and/or -mediated cross-coupling reactions have received the most attention.[2,3] These reactions generally proceed with high levels of chemo- and regioselectivity; furthermore, they can involve diverse perfluoroalkylating reagents and aryl precursors. However, the Cu-mediated/catalyzed reactions are commonly limited by the requirement for superstoichiometric quantities of metal, expensive trifluoromethylating reagents, and/or forcing reaction conditions.[2,3]

In contrast, low-valent Pd and Ni complexes (i.e. $Pd^{0/II}$ and $Ni^{0/II}$) have generally proven ineffective as catalysts for arene trifluoromethylation.[4,5] Studies of well-defined Ni and Pd complexes have shown that, due to the unique electronic properties of the CF_3 ligand,[6] aryl–CF_3 bond-forming reductive elimination from nickel(II)[7,8] and palladium(II)[9,10] centers is an extremely challenging process.[11] As such, only a single example of $Pd^{0/II}$-catalyzed trifluoromethylation of aryl halides has been reported.[12] As shown in eq 1, this system utilizes a biarylmonophosphine ligand (BrettPhos[13] or RuPhos[14]) in conjunction with $TESCF_3$ as the trifluoromethyl source. While this transformation represents an exciting breakthrough for the field, its practical utility is constrained by the high cost and limited availability of $TESCF_3$ and perfluoroalkyl derivatives thereof.



(1)

We targeted more practical $Pd^{0/II}$-catalyzed trifluoromethylation reactions using trifluoroacetic ester or anhydride derivatives (CF_3CO_2R) as readily available and inexpensive alternatives to $TESCF_3$. We hypothesized that these reagents could participate in decarbonylative cross-coupling with organometallic reagents to form trifluoromethylated products via the catalytic cycle shown in Scheme 1.[15−20] This cycle would involve (i) oxidative addition of the anhydride/ester at Pd^0 to generate a Pd^{II} trifluoroacyl complex, (ii) decarbonylation to release CO and form a Pd^{II}–CF_3 adduct, (iii) transmetalation with a M–aryl species to yield a Pd^{II}(aryl)-(CF_3) intermediate, and (iv) aryl–CF_3 bond-forming reductive elimination to release the trifluoromethylated product. To our knowledge, this decarbonylative approach to arene trifluoromethylation has not been pursued previously at any metal center.

The proposed step i (oxidative addition of CF_3CO_2R to Pd^0)[21] as well as step iii (transmetalation at Pd^{II})[22−24] both have significant precedent in the literature. However, there are currently only two reported examples of aryl–CF_3 bond-

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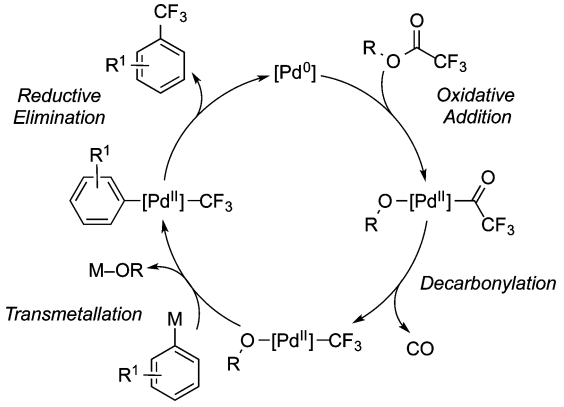
Scheme 1. Proposed Catalytic Cycle for Decarbonylative Trifluoromethylation



forming reductive elimination from Pd^{II} centers (step iv).[12,25] Furthermore, decarbonylation at trifluoroacylpalladium complexes (step iii) is currently unprecedented.[26] Several other second- and third-row transition-metal trifluoroacyl complexes are known to undergo decarbonylation; however, these transformations often require high temperatures and long reaction times.[27−30] For instance, decarbonylation at the Pt^{II} complex $CF_3COPt(Cl)(PPh_3)_2$ requires heating under vacuum at 210 °C for 4 h.[31] Thus, we anticipated that CO deinsertion could present a major bottleneck for the envisioned trifluoromethylation reaction.

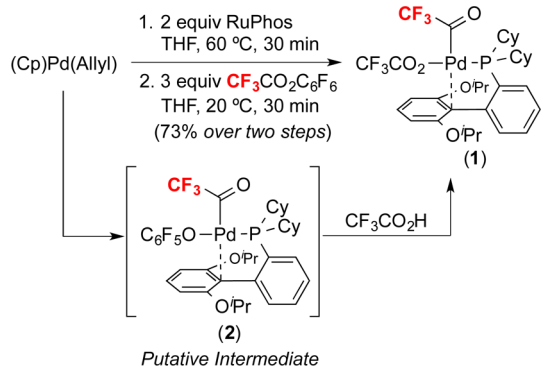
In order to identify appropriate supporting ligands, reagents, and reaction conditions for the proposed decarbonylative trifluoromethylation sequence, we sought to assess the feasibility of each elementary step in the proposed catalytic cycle in Scheme 1. We demonstrate herein that all of the elementary steps are feasible under relatively mild reaction conditions (<100 °C) using RuPhos-ligated Pd complexes.

RESULTS AND DISCUSSION

Selection of Ligand. The proposed decarbonylative trifluoromethylation requires a supporting ligand that will enable both challenging steps of the catalytic cycle: CO deinsertion and aryl−CF_3 bond-forming reductive elimination. CO insertion/deinsertion reactions generally proceed via three-center transition states.[32] As such, CO deinsertion from a coordinatively unsaturated three-coordinate Pd^{II} species is expected to be significantly more facile than that from a square-planar tetracoordinate Pd^{II} center.[33] On the basis of this analysis, we hypothesized that a sterically bulky monophosphine ligand such as RuPhos[14] would be well suited for promoting this elementary step. Previous work has shown that RuPhos (and close analogues thereof) can act as a bidentate ligand, with the aromatic ring of the biaryl functionality serving as a second binding site.[34] In this binding mode, the aromatic ring serves as a hemilabile ligand, such that coordinatively unsaturated tricoordinate Pd^{II} species are readily accessible. As such, bulky biarylmonophosphines such as RuPhos are predicted to enable CO deinsertion at Pd^{II} under mild reaction conditions. In addition, Buchwald has demonstrated that RuPhos promotes aryl−CF_3 bond-forming reductive elimination from Pd^{II}(aryl)(CF_3) complexes.[12]

Step i: Oxidative Addition of Trifluoroacetyl Esters to Pd^0. A RuPhos-ligated Pd^0 species was generated by treatment of (Cp)Pd(allyl) with 2 equiv of RuPhos at 60 °C for 30 min (Scheme 2).[35] This Pd^0 intermediate was then reacted in situ with pentafluorophenyl trifluoroacetate.[36,37] Monitoring this

Scheme 2. Oxidative Addition of $CF_3CO_2C_6F_5$ to (RuPhos)Pd^0 To Form 1

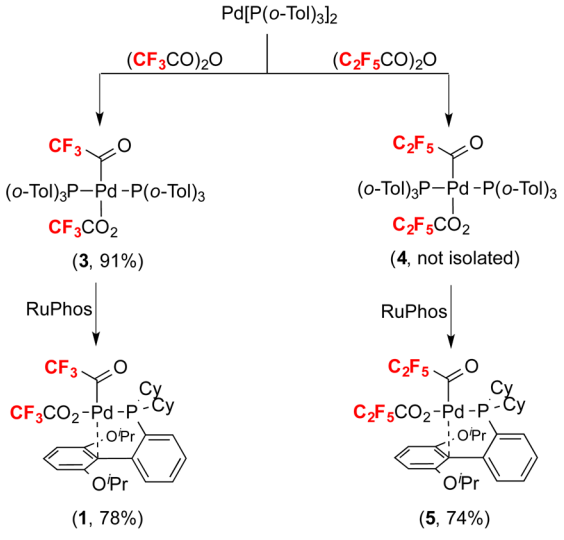


reaction by 1D ^{19}F-NMR and 2D $^{19}F/^{13}C$ HMBC NMR spectroscopy showed the formation of oxidative addition product **2** within 30 min at 20 °C. Upon workup, **2** underwent ligand exchange with trifluoroacetate in solution (presumably generated via hydrolysis of the ester) to yield product **1** in 73% isolated yield over two steps.

Product **1** was characterized via 1D and 2D ^{13}C, ^{31}P, and ^{19}F NMR spectroscopy as well as HRMS. The presence of both trifluoroacyl and trifluoroacetate ligands is apparent from the ^{13}C NMR spectrum of **1**. The ^{13}C signal for the C═O of the trifluoroacyl ligand appears as a quartet of doublets ($^2J_{CF}$ = 38.2 Hz and $^3J_{CP}$ = 7.5 Hz) at 207.5 ppm. In contrast, the C═O of the trifluoroacetate appears significantly upfield (160.7 ppm) and does not show coupling to phosphorus (quartet, $^2J_{CF}$ = 34.7 Hz). The ^{13}C NMR spectrum of **1** implicates bidentate coordination of RuPhos through phosphorus and one aromatic carbon. The bound carbon atom appears as a doublet ($^2J_{CP}$ = 4.1 Hz) at 106 ppm. Importantly, similar bidentate binding of biarylmonophosphines has been documented previously.[34,38]

To further confirm the structure of **1**, we independently synthesized this complex via an alternative route. As shown in Scheme 3, the treatment of Pd[P(*o*-Tol)$_3$]$_2$ with trifluoroacetic

Scheme 3. Alternate Synthesis of 1



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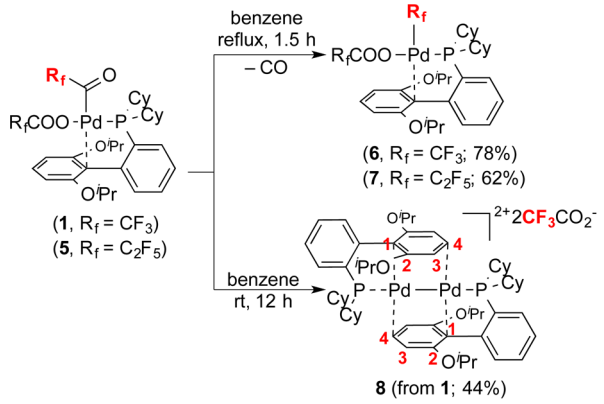
anhydride (TFAA) afforded oxidative addition product **3** in 91% isolated yield. The P(*o*-Tol)$_3$ ligands of **3** were then displaced by 1.1 equiv of RuPhos to afford **1** in 78% yield. The approach shown in Scheme 3 was also used to prepare the corresponding perfluoroethyl complex **5** starting from Pd[P(*o*-Tol)$_3$]$_2$ and pentafluoropropionic anhydride.

Step ii: CO Deinsertion. We next investigated the key CO deinsertion reaction at perfluoroacyl complexes **1** and **5**. Gratifyingly, heating benzene solutions of **1** and **5** at reflux for 1.5 h resulted in clean decarbonylation to yield the corresponding perfluoroalkyl complexes **6** and **7** (Scheme 4).

Scheme 4. Decarbonylation at 1 and 5

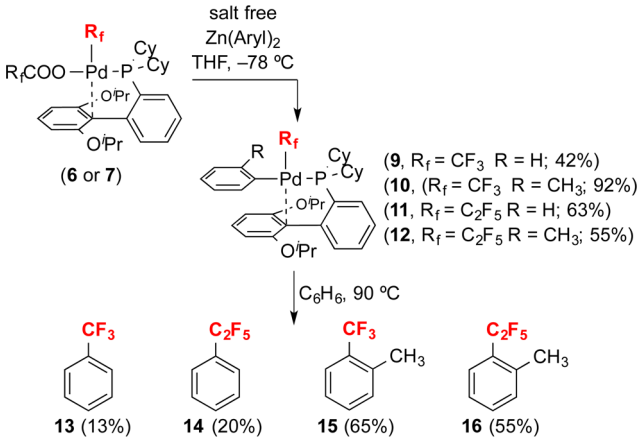


These decarbonylation reactions proceeded in quantitative yield as determined by ^{19}F and ^{31}P NMR spectroscopy, and the pure products were isolated via recrystallization in 78% and 62% yields, respectively.

Interestingly, when benzene solutions of **1** were allowed to stand at room temperature (rather than reflux), completely different reactivity was observed. Under these conditions, **1** slowly decomposed to form the dicationic palladium(I) dimer **8**, which was isolated in 44% yield after 12 h at room temperature. The structure of **8** was determined on the basis of NMR and HRMS analysis (see the Supporting Information for full spectra and a detailed discussion of assignments).[39] Complex **8** has C_{2h} symmetry; therefore, both phosphine ligands are chemically equivalent, leading to just one set of signals in the ^{13}C and ^{1}H NMR spectra. However, virtual coupling is observed in the ^{13}C NMR spectrum, and this is a diagnostic feature of symmetric *trans*-diphosphine complexes.[40] In addition, in the ^{13}C NMR spectrum, the signals for C1–C4 are shifted to 94.1, 151.4, 86.7, and 80.5 ppm, respectively. These chemical shifts present strong evidence that aromaticity in the π-coordinated benzene ring is partially disrupted upon binding to the dicationic Pd–Pd unit. Moreover, a molecular ion isotope pattern between 571 and 575 Da with 0.5 Da spacing in the HRMS of **8** is indicative of a species with the molecular formula $[(\text{RuPhos})_2\text{Pd}_2]^{2+}$.[41] While the exact mechanism for the formation of **8** is unclear, it likely involves conproportionation between (RuPhos)Pd^0 and a (RuPhos)Pd^{2+} species.[42] A number of related dinuclear Pd^{I}–Pd^{I} complexes stabilized by π coordination to arenes have been reported in the literature.[43]

Step iii: Transmetalation. We next investigated transmetalation reactions of the (RuPhos)Pd^{II}(perfluoroalkyl) products **6** and **7**. Diarylzincs were found to be particularly effective transmetalating reagents for this system (Scheme 5).

Scheme 5. Transmetalation and Reductive Elimination



Specifically, the reaction of **6** and **7** with salt-free diphenylzinc and di-*o*-tolylzinc afforded complexes **9**–**12** in 42–92% isolated yields.[44] ^{19}F and ^{31}P NMR analyses of the crude reaction mixtures of **9**–**12** showed no side products; thus, the variation in isolated yield merely reflects loss of product during the isolation process. The structures of complexes **9**–**12** were determined using 1D ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectroscopy as well as by 2D ^{19}F/^{13}C and ^{1}H/^{13}C NMR correlation experiments. The stereochemistry of **9**–**12** was assigned on the basis of ^{1}H/^{1}H ROESY NMR spectra (see the Supporting Information for full details).

Step iv: Reductive Elimination. Complexes **9**–**12** are stable in both $CDCl_3$ and benzene solution at room temperature for at least 10 h. However, heating benzene solutions of **9**–**12** at 90 °C for 12 h resulted in aryl–CF_3 bond-forming reductive elimination to yield **13**–**16** (Scheme 5). The yields of **13**–**16** were determined using ^{19}F NMR spectroscopy with 1,4-bis(trifluoromethyl)benzene as an internal standard. In all cases, complete consumption of the starting complexes **9**–**13** was observed. Compounds **13** and **14** were obtained in only 13% and 20% yields, respectively. In contrast, the 2-tolylpalladium complexes **10** and **12** afforded reductive elimination products **15** and **16** in significantly higher yields (65% and 55%, respectively). These results are consistent with Buchwald's prior report of the trifluoromethylation of aryl chlorides with $TESCF_3$.[12] In this system, RuPhos provided modest yields with simple aryl chlorides; however, a dramatic enhancement in yield was observed with sterically hindered aryl chloride electrophiles. Interestingly, in our system the conversion rates for all of the complexes **9**–**12** are approximately the same. This suggests that additional steric bulk on the σ-aryl ligand does not significantly increase the rate of reductive elimination but more likely limits unproductive decomposition pathways.

CONCLUSIONS

This paper describes a detailed study designed to assess the feasibility of Pd-catalyzed decarbonylative trifluoromethylation reactions using trifluoroacetate esters as inexpensive and readily available trifluoromethylating reagents. Each step of the proposed catalytic cycle has been interrogated using RuPhos as a supporting ligand. It was found that pentafluorophenyl trifluoroacetate undergoes oxidative addition to (RuPhos)$_n$Pd^0 under mild conditions. The resulting product (RuPhos)Pd(COCF$_3$)(CO$_2$CF$_3$) eliminates CO in refluxing benzene (80

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°C) to afford (RuPhos)Pd(CF_3)(CO_2CF_3). Next, transmetalation with diarylzinc reagents yields (RuPhos)Pd(CF_3)(aryl). Finally, heating of (RuPhos)Pd(CF_3)(aryl) complexes to 90 °C for 12 h affords aryl−CF_3 reductive elimination products. These exciting results demonstrate the potential feasibility of using perfluoroalkyl esters as CF_3 sources in cross-coupling reactions. The current challenge is to integrate these elementary steps into a complete catalytic cycle for arene fluoroalkylation. Key to this goal is identifying perfluoroalkyl esters and transmetalating reagents that are compatible with one another. In addition, the relative rates of CO deinsertion, transmetalation, and reductive elimination must be controlled, such that the desired aryl-R_F bond formation outcompetes undesired aryl−C(O)R_F coupling.[21a] For instance, currently, the CO deinsertion reaction and aryl−CF_3 reductive elimination reactions require significantly higher temperatures than the other two steps of the porposed cycle. Efforts to address these challenges are currently underway in our laboratory and will be reported in due course.

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*-Tol)$_3$]$_2$ was obtained according to the literature procedure.[45] Tetrahydrofuran, dichloromethane, and diethyl ether were purified using an Innovative Technologies (IT) solvent purification system consisting of a copper catalyst, activated alumina, and molecular sieves. NMR spectra were obtained on a Varian VNMRS 700, Varian VNMRS 500, Varian Inova, or Varian MR400 spectrometer. ^{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. Mass spectral data was obtained on a Micromass magnetic sector mass spectrometer with an electrospray ionization mode. FT-IR spectra were obtained on a Perkin-Elmer "Spectrum BX" instrument with ATR accessory (ZnSe ATR crystal). Elemental analyses were performed by Atlantic Microlab, Inc.

Preparation of (P(*o*-Tol)$_3$)$_2$Pd($COCF_3$)($OCOCF_3$) (3). A Schlenk flask was charged with a stirbar and Pd[P(*o*-Tol)$_3$]$_2$ (4.00 g; 6.92 mmol). The flask was sealed, evacuated under reduced pressure, 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). Product slowly separated over a period of 4 h in a form of yellowish crystals. This precipitate was filtered and washed with several portions of diethyl ether. After drying under vacuum, 5.08 g (91%) of a yellowish solid was obtained. ^{1}H NMR and elemental analysis showed that the crystallized compound contains exactly 1 equiv of diethyl ether that could not be removed even after prolonged drying under vacuum. The cocrystallized ether was taken into account when the reaction yield was calculated. ^{1}H, ^{19}F, and ^{31}P NMR spectra of **3** contain only very broad resonances. We explain this on the basis of reversible dissociation of the P(*o*-Tol)$_3$ ligand and dynamic equilibrium between several species in the solution. This is supported by the fact that the ^{31}P NMR spectrum of **3** contains a singlet at −29.6 ppm that corresponds to a free P(*o*-Tol)$_3$ ligand. ^{1}H NMR ($CDCl_3$ at 23 °C; δ): 10.0−6.0 (br, 24H), 4.0−1.0 (br, 18 H), 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 (br). 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 (RuPhos)Pd($COCF_3$)($OCOCF_3$) (1). *Method 1: Oxidative Addition of $CF_3COOC_6F_5$ to in Situ Generated (RuPhos)$_n$Pd^0.* CpPd(allyl) (200 mg; 0.94 mmol) and RuPhos (933 mg; 2.00 mmol) were combined in a Schlenk flask. The Schlenk flask was flushed with nitrogen for 15 min, and then degassed THF (20 mL) was added via cannula. The resulting red solution was heated to 60 °C for 30 min. The solution was cooled to −78 °C, and $CF_3COOC_6F_5$ (840 mg; 3.00 mmol) was added dropwise over a period of 5 min. The reaction mixture was slowly warmed to room temperature. After it was stirred at room temperature for 1 h, the reaction mixture was concentrated under reduced pressure at room temperature. The resulting residue was dissolved in 100 mL of diisopropyl ether, and this solution was filtered through Celite. Hexanes (60 mL) were added to the diisopropyl ether solution, and the resulting mixture was allowed to stand at −20 °C for 8 h. During this period, the product precipitated in the form of yellowish crystals. The product was collected by filtration and washed with two 5 mL portions of cold diisopropyl ether. After drying under vacuum, 541 mg (73%) of a yellowish crystalline solid was obtained.

Method 2: Ligand Exchange Reaction of P(o-Tol)$_3$)$_2$Pd($COCF_3$)($OCOCF_3$) (3) with RuPhos. Under a nitrogen atmosphere, a solution of (P(*o*-Tol)$_3$)$_2$Pd($COCF_3$)($OCOCF_3$)·Et_2O (**3**; 1.00 g, 1.00 mmol) and RuPhos (513 mg; 1.1 mmol) in THF (20 mL) was stirred at 0 °C for 10 min. The resulting solution was then concentrated under reduced pressure at 0 °C. Diethyl ether (10 mL) was added to the residue, and the resulting suspension was stirred at 0 °C for 15 min. The product was separated by filtration and then washed with two 5 mL portions of cold diethyl ether. After drying under vacuum, 615 mg (78%) of a yellowish crystalline solid was obtained. ^{1}H NMR (acetone-d_6 at 25 °C): δ 7.87 (apparent t, J = 7.7 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.53−7.48 (multiple peaks, 2H), 6.85 (dd, J = 7.9 and 3.2 Hz, 1H), 6.59 (d, J = 8.6 Hz, 2H), 4.64 (septet, J = 6.1 Hz, 2H), 2.40 (m, 2H), 2.24 (m, 2H), 1.90 (m, 2H), 1.83 (m, 4H), 1.73 (m, 2H), 1.57 (m, 2H), 1.44 (m, 2H), 1.40 (d, J = 6.1 Hz, 6H), 1.36 (m, 2H), 1.16 (m, 2H), 1.04 (m, 2H), 1.02 (d, J = 6.1 Hz, 6H). ^{13}C{^{1}H} NMR (acetone-d_6 at 25 °C; δ): 207.53 (qd, $^2J_{C-F}$ = 38.2 Hz, $^3J_{C-P}$ = 7.5 Hz), 161.99, 160.65 (q, $^2J_{C-F}$ = 34.7 Hz), 145.61 (d, J = 17.7 Hz), 138.25, 133.92 (d, J = 45.0 Hz), 132.76−132.40 (three overlapping signals as revealed by ^{1}H/^{13}C HMBC), 127.82 (d, J = 6.1 Hz), 117.37 (qd, $^1J_{C-F}$ = 292.2 Hz, $^4J_{C-P}$ = 7.5 Hz), 109.99 (qd, $^1J_{C-F}$ = 300.4 Hz, $^3J_{C-P}$ = 17.0 Hz), 106.12 (d, $^2J_{C-P}$ = 4.1 Hz), 106.05, 71.83, 33.31 (d, J = 29.3 Hz), 29.56 (d, J = 2.1 Hz), 29.05 (d, J = 1.3 Hz), 27.27 (d, J = 14.3 Hz), 27.09 (d, J = 11.6 Hz), 26.76, 22.08, 21.92. ^{19}F NMR (acetone-d_6 at 25 °C; δ): −74.32 (s, 3F), −75.03 (s, 3F). ^{31}P{^{1}H} NMR (acetone-d_6 at 25 °C; δ): 45.45 (s). ^{19}F/^{13}C HSQC NMR (acetone-d_6 at 25 °C; δ_F/δ_C): −74.32/109.99, −75.03/117.37. ^{19}F/^{13}C HMBC NMR (acetone-d_6 at 25 °C; δ_F/δ_C): −74.32/207.53, −75.03/117.37 (^1J correlation), −75.03/160.65. IR (ATR; cm^{-1}): 2978 (w), 2937 (m), 2853 (m), 1747 (m), 1702 (s), 1686 (s), 1588 (m), 1450 (m), 1410 (m), 1377 (w), 1256 (s), 1224 (s), 1190 (s), 1178 (s), 1128 (s), 1108 (s). HRMS electrospray (m/z): [M − $OOCCF_3$]$^+$ calcd for $C_{32}H_{43}F_3O_3PPd$ 669.1931, found 669.1947; [M − $OCOCF_3$ − CO]$^+$ calcd for $C_{31}H_{43}F_3O_2PPd$ 641.1982, found 641.2001.

Preparation of (RuPhos)Pd(COC_2F_5)($OCOC_2F_5$) (5). A Schlenk flask was charged with a stirbar and Pd[P(*o*-Tol)$_3$]$_2$ (1.90 g; 2.66 mmol). The flask was sealed, evacuated under reduced pressure, and then refilled with nitrogen. The flask was evacuated and refilled with nitrogen three more times. Dry THF (100 mL) was added via cannula. Perfluoropropionic anhydride (0.66 mL, 3.0 mmol) was then added dropwise over a period of 5 min. This solution was stirred for 20 min at room temperature and then filtered through a pad of Celite, and the volatiles were removed under reduced pressure. The resulting residue was dissolved in benzene (35 mL), and RuPhos (700 mg; 1.5 mmol) was added in one portion. The resulting homogeneous solution was stirred at room temperature for 20 min, and then the volatiles were removed under reduced pressure. The residue was dissolved in dibutyl ether (30 mL). The product slowly precipitated in the form of yellowish crystals. The product was collected by filtration and washed with several portions of dibutyl ether and then with hexanes. After drying under vacuum, 989 mg (74% yield based on RuPhos) of

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product was obtained. ^{1}H NMR ($CDCl_3$ at 25 °C; δ): 7.59 (apparent t, J = 7.5 Hz, 1H), 7.49 (t, J = 8.4 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.3 Hz, 1H), 6.76 (dd, J = 7.5 and 2.2 Hz, 1H), 6.48 (d, J = 8.5 Hz, 2H), 4.54 (septet, J = 6.0 Hz, 2H), 2.22−2.15 (multiple peaks, 4H), 1.85−1.76 (multiple peaks, 6H), 1.72−1.66 (br, 2H), 1.62−1.53 (br, 2H), 1.40−1.31 (br, 2H), 1.36 (d, J = 6.0 Hz, 6H), 1.25 (m, 2H), 1.22−1.12 (multiple peaks, 4H), 1.00 (d, J = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$ at 25 °C; δ): 207.98 (td, $^2J_{C-F}$ = 40.2 Hz, $^3J_{C-P}$ = 7.0 Hz), 161.37 (t, $^2J_{C-F}$ = 25.9 Hz), 161.04, 144.68 (d, J = 17.0 Hz), 137.38, 133.07 (d, J = 43.6 Hz), 131.78 (d, J = 11.6 Hz), 131.47 (d, J = 1.7 Hz), 130.94, 126.71 (d, J = 6.1 Hz), 121.44−114.17 (two overlapping multiplets, 2 × CF_2), 106.64 (m, CF_3), 105.98, 105.29, 101.53 (tqd, $^1J_{C-F}$ = 269.8 Hz, $^2J_{C-F}$ = 36.1 Hz, $^3J_{C-P}$ = 14.3 Hz), 71.19, 34.28 (d, J = 29.3 Hz), 28.26 (two overlapping signals), 26.75 (two overlapping d), 25.85, 21.74, 21.67. ^{19}F NMR ($CDCl_3$ at 25 °C; δ): −80.18 (s, 3F), −82.40 (s, 3F), −-112.23 (s, 2F), −118.44 (broad s, 2F). ^{31}P{^{1}H} NMR ($CDCl_3$ at 25 °C; δ): 42.25 (s). ^{19}F/^{13}C HSQC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −80.18/117.33, −82.40/118.70, −112.23/101.53, −118.44/106.64. ^{19}F/^{13}C HMBC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −80.18/101.53, −80.18/117.33 (^1J correlation), −112.23/101.53 (^1J correlation), −112.23/117.33, −112.23/207.98. IR (ATR): cm^{-1} 2978 (w), 2987 (w), 2937 (m), 2855 (w), 1716 (s), 1684 (s), 1588 (m), 1569 (m), 1451 (s), 1384 (m), 1327 (s), 1256 (s), 1202 (s), 1162 (s), 1110 (s), 1069 (s). HRMS electrospray (m/z): [M − $OCOC_2F_5$]$^+$ calcd for $C_{33}H_{43}F_5O_3PPd$ 719.1899, found 719.1916; [M − $OCOC_2F_5$ − CO]$^+$ calcd for $C_{32}H_{43}F_5O_2PPd$ 691.1950, found 691.1969.

Preparation of (RuPhos)Pd(CF_3)($OCOCF_3$) (6). (RuPhos)Pd($COCF_3$)($OCOCF_3$) (**1**) (300 mg; 0.38 mmol) was refluxed in benzene (25 mL) for 1.5 h. ^{19}F and ^{31}P NMR analysis of the crude reaction mixture showed complete conversion to product **6**. The benzene solution was filtered through a pad of Celite, and the volatiles were removed under reduced pressure. The residue was dissolved in diisopropyl ether (5 mL). The product slowly crystallized over a period of 12 h. Yellowish crystals were collected by filtration, washed with a small amount of diisopropyl ether, and dried under vacuum. A 227 mg amount (78%) of product was obtained. ^{1}H NMR ($CDCl_3$ at 25 °C; δ): 7.63 (apparent triplet, J = 7.3 Hz, 1H), 7.54 (t, J = 8.5 Hz), 7.43 (t, J = 7.3 Hz), 7.38 (t, J = 7.3 Hz), 6.68 (broad d, J = 6.2 Hz), 6.50 (d, J = 8.5 Hz), 4.60 (septet, J = 6.2 Hz), 2.26 (m, 2H), 2.16 (br, 2H), 1.90 (br, 2H), 1.80 (multiple peaks, 4H), 1.68 (br, 2H), 1.58 (m, 2H), 1.41−1.11 (multiple peaks, 8H), 1.30 (d, J = 5.8 Hz, 6H), 0.99 (d, J = 6.2 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$ at 25 °C; δ): 163.49, 161.25 (q, J = 34.1 Hz), 144.85 (d, J = 16.3 Hz), 138.82, 134.17 (d, J = 44.3 Hz), 131.75 (d, J = 12.3 Hz), 131.54 (d, J = 1.5 Hz), 131.40, 126.58 (d, J = 6.1 Hz), 118.59 (qd, $^1J_{C-F}$ = 379.4 Hz, $^3J_{C-P}$ = 15.0 Hz), 116.39 (q, $^1J_{C-F}$ = 290.9 Hz), 105.73, 102.92, 71.60, 35.93 (d, J = 27.9 Hz), 29.28, 29.01, 27.00 (two overlapping d), 25.93, 21.96, 21.30. ^{19}F NMR ($CDCl_3$ at 25 °C; δ): −10.38 (d, J = 29.8 Hz, 3F), −74.90 (s, 3F). ^{31}P{^{1}H} NMR ($CDCl_3$ at 25 °C; δ): 51.35 (q, J = 29.7 Hz). ^{19}F/^{13}C HSQC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −10.38/118.59, −74.90/116.39. ^{19}F/^{13}C HMBC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −74.90/161.33. IR (ATR; cm^{-1}): 2978 (w), 2931 (m), 2856 (m), 1698 (s), 1589 (m), 1445 (s), 1405 (m), 1378 (m), 1258 (s), 1193 (s), 1173 (s), 1130 (s), 1108 (s), 1068 (s). HRMS electrospray (m/z): [M − $OCOCF_3$]$^+$ calcd for $C_{31}H_{43}F_3O_2PPd$ 641.1982, found 641.1994.

Preparation of (RuPhos)Pd(C_2F_5)($OCOC_2F_5$) (7). (RuPhos)Pd(COC_2F_5)($OCOC_2F_5$) (**5**; 220 mg; 0.25 mmol) was refluxed in benzene (50 mL) for 1.5 h. ^{19}F and ^{31}P NMR analysis of the crude reaction mixture showed complete conversion to product **7**. This benzene solution was filtered through a pad of Celite, and the volatiles were removed under reduced pressure. The residue was dissolved in diethyl ether (5 mL). The product slowly crystallized over a period of several hours. Yellowish crystals were collected by filtration, washed with a small amount of ether, and dried under vacuum to afford 133 mg (62%) of product **7**. ^{1}H NMR ($CDCl_3$ at 25 °C; δ): 7.63 (apparent t, J = 7.3 Hz, 1H), 7.54 (t, J = 7.5 Hz), 7.42 (t, J = 7.7 Hz), 7.37 (t, J = 7.7 Hz), 6.69 (broad d, J = 7.3 Hz), 6.46 (d, J = 8.5 Hz), 4.55 (septet, J = 6.2 Hz), 2.29 (m, 2H), 2.22 (br, 2H), 1.91 (br, 2H), 1.81 (br, 4H), 1.69 (br, 2H), 1.61 (m, 2H), 1.38−1.22 (multiple peaks, 6H), 1.34 (d, J = 5.8 Hz, 6H), 1.18 (m, 2H), 1.00 (d, J = 6.2 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$ at 25 °C; δ): 163.45, 161.63 (t, J = 22.5 Hz), 144.78 (d, J = 16.4 Hz), 139.14, 133.86 (d, J = 44.3 Hz), 131.90 (d, J = 11.6 Hz), 131.41 (d, J = 1.4 Hz), 131.30, 126.54 (d, J = 6.1 Hz), 121.53−115.68 (three overlapping multiplets CF_2, CF_3 and CF_3), 106.69 (tqd, $^1J_{C-F}$ = 263.0 Hz, $^2J_{C-F}$ = 37.5 Hz, $^3J_{C-P}$ = 6.8 Hz), 105.61, 103.01, 71.60, 36.14 (d, J = 26.6 Hz), 29.32, 28.92 (d, J = 3.4 Hz), 27.22−26.96 (two overlapping d), 25.96, 21.73, 21.48. ^{19}F NMR ($CDCl_3$ at 25 °C; δ): −76.10 (d, J = 34.8 Hz, 2F), −78.98 (s, 2F), −82.58 (s, 3F), −119.10 (s, 3F). ^{31}P{^{1}H} NMR ($CDCl_3$ at 25 °C; δ): 49.11 (t, J = 33.9 Hz). ^{19}F/^{13}C HSQC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −76.10/118.35, −78.98/118.46, −82.58/118.75, −119.10/106.64. ^{19}F/^{13}C HMBC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −76.10/118.35 (^1J correlation), −76.10/118.46, −78.98/118.35, −78.98/118.46 (^1J correlation), −82.58/106.64, −82.58/118.75 (^1J correlation), −119.10/106.64 (^1J correlation), −119.10/118.75, −119.10/161.61. IR (ATR; cm^{-1}): 2987 (w), 2938 (m), 2922 (m), 2859 (m), 1692 (s), 1588 (s), 1570 (m), 1447 (s), 1386 (s), 1333 (s), 1287 (m), 1255 (s), 1206 (s), 1161 (s), 1108 (s), 1061 (s), 1026 (s). HRMS electrospray (m/z): [M − $OCOC_2F_5$]$^+$ calcd for $C_{32}H_{43}F_5O_2PPd$ 691.1950, found 691.1962.

Preparation of [(RuPhos)$_2$Pd$_2$](CF_3COO)$_2$ (8). A solution of (RuPhos)Pd($COCF_3$)($OCOCF_3$) (**1**; 200 mg; 0.26 mmol) in benzene (7 mL) was allowed to stand for 24 h at room temperature. During this time the solution changed from yellow to deep red, and bright red crystals slowly crystallized from solution. The benzene supernatant was removed by decanting, and two 2 mL portions of benzene were used to wash the crystals. After drying under vacuum, 78 mg (44%) of a bright orange powder was obtained. ^{1}H NMR (acetone-d_6 at 25 °C; δ): 8.61 (m, 1H), 8.12 (m, 1H), 7.80 (t, J = 7.3 Hz, 1H), 7.75 (t, J = 7.7 Hz, 1H), 7.41 (d, J = 7.7 Hz, 1H), 5.60 (d, J = 7.0 Hz, 2H), 4.39 (septet, J = 6.1 Hz), 3.26 (m, 2H), 2.19−2.09 (multiple peaks, 4H), 1.83 (m, 4H), 1.74 (m, 2H), 1.59 (m, 2H), 1.51 (m, 2H), 1.46−1.35 (multiple peaks, 4H), 1.23 (m, 2H), 0.95 (d, J = 6.1 Hz, 6H), 0.81 (d, J = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR (acetone-d_6 at 25 °C; δ): 159.03 (q, J = 36.7 Hz), 151.39, 144.54 (virtual t, J = 27.2 Hz), 138.27 (virtual t, J = 42.2 Hz), 133.31, 132.90, 131.41 (virtual t, J_{C-P} = 16.4 Hz), 129.37 (virtual t, J_{C-P} = 6.2 Hz), 116.42 (q, J = 290.9 Hz), 94.08, 86.69, 80.45, 73.30, 36.18 (virtual t, J = 20.6 Hz), 29.83, 29.32, 26.17−26.00 (two overlapping t), 25.74, 20.58, 19.95. ^{19}F NMR (acetone-d_6 at 25 °C; δ): −76.38 (s). ^{31}P{^{1}H} NMR (acetone-d_6 at 25 °C; δ): 61.46 (s). ^{19}F/^{13}C HSQC NMR (acetone-d_6 at 25 °C; δ_F/δ_C): −76.38/116.45. ^{19}F/^{13}C HMBC NMR (acetone-d_6 at 25 °C; δ_F/δ_C): −76.38/116.45 (^1J correlation), −76.38/159.03. HRMS electrospray (m/z): [M − $OCOCF_3$]$^+$ calcd for $C_{62}H_{86}F_3O_6P_2Pd$ 1257.3905, found 1257.3921, [M − 2$OCOCF_3$]$^{2+}$ calcd for $C_{30}H_{43}O_2PPd$ 572.2030, found 572.2049.

Preparation of (RuPhos)Pd(CF_3)(Ph) (9). A Schlenk flask was charged with a stirbar, diphenylzinc (200 mg; 0.91 mmol), and (RuPhos)Pd(CF_3)($OCOCF_3$) (**6**; 450 mg; 0.60 mmol). The flask was sealed, evacuated under reduced pressure, and then refilled with nitrogen. The flask was evacuated and refilled with nitrogen three more times. 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. The reaction mixture was stirred at room temperature for an additional 20 min. Then the THF solution was dried over anhydrous Na_2SO_4 and filtered. The volatiles were removed under reduced pressure. The resulting residue was dissolved in diisopropyl ether, and the product was allowed to crystallize from solution over a period of several hours. Colorless crystals were collected by filtration, washed with a small amount of diisopropyl ether, and dried under vacuum. A 180 mg amount (42%) of **9** was obtained. ^{1}H NMR ($CDCl_3$ at 25 °C; δ): 7.53 (apparent t, J = 6.9 Hz, 1H), 7.42−7.32 (multiple peaks, 3H), 7.23 (d, J = 7.4 Hz, 2H), 7.18 (broad d, J = 4.7 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 6.88 (t, J = 7.4 Hz, 2H), 6.82 (t, J = 7.1 Hz, 1H), 4.52 (septet, J = 6.0 Hz, 2H), 1.88−1.78 (br, 2H), 1.76−1.44 (multiple peaks, 12H), 1.32−1.02 (multiple peaks, 8H), 1.28 (d, J = 6.0 Hz, 6H), 0.99 (d, J = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$ at 25 °C; δ): 154.11, 145.09 (br), 141.31 (d, J = 13.6 Hz), 140.84 (m, CF_3), 136.54 (d, J = 2.0 Hz), 134.73 (d, J = 6.8 Hz),

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130.73, 129.81, 128.60, 127.20 (d, J = 21.8 Hz), 126.56 (d, J = 4.1 Hz), 126.09, 123.34, 122.57, 110.93, 74.09, 31.82 (d, J = 19.8 Hz), 28.20, 27.28 (d, J = 13.0 Hz), 26.87 (d, J = 9.5 Hz), 26.67, 25.99, 22.30, 21.18. ^{19}F NMR ($CDCl_3$ at 25 °C; δ): −27.80 (d, J = 44.8 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$ at 25 °C; δ): 14.77 (q, J = 45.8 Hz). ^{19}F/^{13}C HSQC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −27.80/140.84. ^{19}F/^{13}C HMBC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −27.80/140.84 (^1J correlation), −27.80/145.09. IR (ATR; cm^{-1}): 3051 (w), 2968 (w), 2928 (s), 2850 (m), 1598 (m), 1579 (w), 1566 (m), 1450 (s), 1374 (m), 1331 (w), 1270 (s), 1224 (m), 1088 (s), 1046 (s). HRMS electrospray (m/z): [M − F]$^+$ calcd for $C_{37}H_{48}F_2O_2PPd$ 699.2389, found 699.2383.

Preparation of Zn(o-$C_6H_4CH_3$)$_2$. 2-Iodotoluene (6.00 g; 27.5 mmol) and dry diethyl ether (120 mL) were introduced into a flame-dried 250 mL Schlenk flask. This ether solution was cooled to −78 °C, and a 2.5 M solution of nBuLi in hexanes (11.5 mL; 28 mmol) was added dropwise. The resulting suspension was stirred at −78 °C for 30 min. Then a 1.9 M $ZnCl_2$ solution in 2-methyltetrahydrofuran (7.2 mL; 13.7 mmol) was added slowly over a period of 10 min at −78 °C. The reaction mixture was warmed to room temperature and stirred at room temperature for 30 min. The volatiles were removed under vacuum via the side arm of the Schlenk flask, and the residue was washed with several portions of dry pentane. Dry toluene (25 mL) was added to the residue, and the resulting suspension was cannula-transferred to a septum-sealed centrifuge tube. The LiCl precipitate was separated by centrifugation, and the remaining clear toluene solution of Zn(o-$C_6H_4CH_3$)$_2$ was used directly in the step below. It was assumed that concentration of the Zn(o-$C_6H_4CH_3$)$_2$ reagent in toluene is 0.5 M.

Preparation of (RuPhos)Pd(CF_3)(o-$C_6H_4CH_3$) (10). A Schlenk flask was charged with a stirbar and (RuPhos)Pd(CF_3)($OCOCF_3$) (**6**; 400 mg; 0.50 mmol). The flask was sealed, evacuated under reduced pressure, and then refilled with nitrogen. The flask was evacuated and refilled with nitrogen three more times. Dry THF (20 mL) was added via cannula. The resulting solution was cooled to −78 °C, and then the Zn(o-$C_6H_4CH_3$)$_2$ solution in toluene (1.2 mL; approximately 0.6 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 20 min, and then water (0.2 mL) was introduced. The reaction mixture was stirred at room temperature for an additional 20 min, and then the THF solution was dried over anhydrous Na_2SO_4 and filtered. The volatiles were removed under reduced pressure. The resulting residue was dissolved in acetone (1.5 mL), from which the product slowly crystallized over a period of several hours. The crystals were collected by filtration, washed with a small amount of acetone, and dried under vacuum. A 230 mg amount (63%) of colorless crystals was obtained. Analytical data for **10**: rotation about Pd-(o-Tol) bond is hindered on the NMR time scale at 25 °C. Therefore, several signals in the ^{1}H and ^{13}C NMR spectra are broadened at 25 °C. VT ^{1}H NMR experiments revealed that at −40 °C rotation about Pd-(o-Tol) is slow on the ^{1}H NMR time scale (the RuPhos fragment loses the plane of symmetry in the ^{1}H NMR spectrum). ^{1}H NMR ($CDCl_3$ at 25 °C; δ): 7.50 (apparent t, J = 6.6 Hz, 1H), 7.39−7.33 (multiple peaks, 3H), 7.17 (d, J = 7.5 Hz, 1H), 7.14 (br, 1H), 7.00 (br, 2H), 6.81 (dd, J = 8.3, 1.0 Hz, 1H), 6.77 (t, J = 7.0 Hz, 1H), 6.71 (t, J = 7.7 Hz, 1H), 4.59−4.50 (two overlapping septets, 2H), 2.47 (s, 3H), 1.99−0.63 (overlapping broad resonances, 22H), 1.31 (d, J = 6.0 Hz, 3H), 1.27 (broad d, J = 5.5 Hz, 3H), 1.01 (broad d, J = 4.6 Hz, 3H), 0.97 (d, J = 6.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$ at 25 °C; δ): 154.40, 154.33, 146.47 (br), 141.65 (d, J = 12.9 Hz), 141.35, 140.35 (m, CF_3), 135.84, 134.58 (br), 130.91 (br), 129.93 (br), 128.61 (br), 127.88 (br d, J = 19.1 Hz), 127.42, 126.48 (d, J = 4.1 Hz), 123.14 (br), 122.92 (br), 122.58, 110.83, 110.72, 73.98 (br), 73.74 (br), 32.55 (two overlapping broad resonances, Cy signals), 28.61−25.59 (overlapping broad resonances, Cy signals), 27.47, 27.40, 26.19, 22.34, 22.27, 21.24 (two overlapping broad resonances). ^{19}F NMR ($CDCl_3$ at 25 °C; δ): −27.74 (d, J = 46.0 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$ at 25 °C; δ): 13.79 (q, J = 45.8 Hz). ^{19}F/^{13}C HSQC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −27.74/140.19. ^{19}F/^{13}C HMBC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −27.74/140.19 (^1J correlation), −27.74/146.47. IR (ATR; cm^{-1}): 3064 (w), 2918 (s), 2850 (m), 2361 (w), 2338 (w), 2162 (w), 1599 (m), 1578 (m), 1453 (s), 1384 (m), 1373 (m), 1269 (m), 1225 (m), 1105 (m), 1084 (s), 1040 (s), 978 (s). HRMS electrospray (m/z): [M − F]$^+$ calcd for $C_{38}H_{50}F_2O_2PPd$ 713.2551, found 713.2538.

Preparation of (RuPhos)Pd(C_2F_5)(Ph) (11). A Schlenk flask was charged with a stirbar, diphenylzinc (180 mg; 0.82 mmol), and (RuPhos)Pd(C_2F_5)($OCOC_2F_5$) (**7**; 500 mg; 0.58 mmol). The flask was sealed, evacuated under reduced pressure, and then refilled with nitrogen. The flask was evacuated and refilled with nitrogen three more times. 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. The reaction mixture was stirred at room temperature for an additional 20 min, and then the THF solution was dried over anhydrous Na_2SO_4 and filtered. The volatiles were removed under reduced pressure. The resulting residue was dissolved in diethyl ether, and the product slowly crystallized over the period of several hours. Colorless crystals were collected by filtration, washed with a small amount of diethyl ether, and dried under vacuum. A 413 mg amount (92%) of **11** was obtained. ^{1}H NMR ($CDCl_3$ at 25 °C; δ): 7.52 (apparent t, J = 6.7 Hz, 1H), 7.41−7.36 (multiple peaks, 2H), 7.34 (t, J = 7.1 Hz, 1H), 7.18 (ddd, J = 7.5, 3.2, 1.2 Hz, 2H), 7.11 (d, J = 7.5 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 6.81 (t, J = 6.7 Hz, 2H), 6.78 (t, J = 7.2 Hz, 1H), 4.50 (septet, J = 6.1 Hz, 2H), 1.81−1.73 (br, 2H), 1.73−1.67 (br, 2H), 1.63−1.56 (multiple peaks, 6H, Cy protons), 1.50−1.40 (br, 2H), 1.34−1.27 (br, 2H), 1.25 (d, J = 6.1 Hz, 6H), 1.18−1.09 (multiple peaks, 4H), 1.08−1.00 (multiple peaks, 4H), 0.98 (d, J = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$ at 25 °C; δ): 153.98, 143.41 (broad), 141.34 (d, J = 14.3 Hz), 136.63 (d, J = 2.7 Hz), 134.69 (d, J = 7.5 Hz), 133.08 (m, CF_2), 130.80, 129.40, 128.55, 127.37 (d, J = 21.8 Hz), 126.49 (d, J = 4.8 Hz), 125.94, 123.69, 122.40, 122.26 (qtd, $^1J_{C-F}$ = 286.1 Hz, $^2J_{C-F}$ = 31.3 Hz, $^3J_{C-P}$ = 8.2 Hz), 111.10, 74.05, 32.02 (d, J = 19.1 Hz), 28.15, 27.30 (d, J = 12.3 Hz), 27.10 (d, J = 4.1 Hz), 26.92 (d, J = 9.5 Hz), 26.01, 22.28, 21.19. ^{19}F NMR ($CDCl_3$ at 25 °C; δ): −79.83 (s, 3F), −102.50 (broad doublet, J = 23.2 Hz, 2F). ^{31}P{^{1}H} NMR ($CDCl_3$ at 25 °C; δ): 13.57 (broad triplet, J = 28.6 Hz). ^{19}F/^{13}C HSQC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −79.83/122.26, −102.50/133.08. ^{19}F/^{13}C HMBC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −79.83/122.26 (^1J correlation), −79.83/133.08. IR (ATR; cm^{-1}): 3057 (w), 2974 (w), 2929 (m), 2848 (w), 1596 (m), 1564 (m), 1452 (s), 1384 (m), 1292 (m), 1267 (m), 1231 (w), 1187 (m), 1138 (m), 1101 (m), 1039 (s). HRMS electrospray (m/z): [M − F]$^+$ calcd for $C_{38}H_{48}F_4O_2PPd$ 749.2363, found 749.2345; [M − Ph]$^+$ calcd for $C_{32}H_{43}F_5O_2PPd$ 691.1956, found 691.1938.

Preparation of (RuPhos)Pd(C_2F_5)(o-$C_6H_4CH_3$) (12). A Schlenk flask was charged with a stirbar and (RuPhos)Pd(C_2F_5)($OCOC_2F_5$) (**7**; 400 mg; 0.50 mmol). The flask was sealed, evacuated under reduced pressure, and then refilled with nitrogen. The flask was evacuated and refilled with nitrogen three more times. Dry THF (20 mL) was added via cannula. The resulting solution was cooled to −78 °C, and then a Zn(o-$C_6H_4CH_3$)$_2$ solution in toluene (1.2 mL; approximately 0.6 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 20 min, and then water (0.2 mL) was introduced. The reaction mixture was stirred at room temperature for an additional 20 min, and then the THF solution was dried over anhydrous Na_2SO_4 and filtered. The volatiles were removed under reduced pressure. The resulting residue was dissolved in methanol (1.5 mL), and the product slowly crystallized over a period of several hours. The crystals were collected by filtration, washed with a small amount of methanol, and dried under vacuum. A 214 mg amount (55%) of **12** was obtained. Analytical data for **12**: ^{1}H, ^{19}F, and ^{13}C NMR spectra show that rotation about the Pd−(o-Tol) bond is slow on the NMR time scale at 25 °C. According to ^{1}H and ^{13}C NMR spectra, the RuPhos fragment does not possess a plane of symmetry. Moreover, according to the ^{19}F NMR spectrum, the fluorine atoms of the CF_2 group are diastereotopic. ^{1}H NMR ($CDCl_3$ at 25 °C; δ): 7.52 (apparent t, J = 6.5 Hz, 1H), 7.40−7.34 (multiple peaks, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.19 (m, 2H), 7.12 (m, 1H), 6.85 (d, J = 8.3 Hz, 1H), 6.70 (m, 2H), 6.65 (m, 1H), 4.56−4.48 (two overlapping septets, 2H), 2.23 (m, 1H), 2.12 (s, 3H), 1.93−0.83 (many overlapping multiplets, 19H), 1.21 (two overlapping d, 6H), 1.12 (d, J = 6.0 Hz, 3H), 0.78 (d, J = 6.0 Hz, 3H), 0.63 (m, 1H), 0.46 (m, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$

at 25 °C; δ): 155.45, 153.24, 144.63 (br), 141.31 (d, J = 15.0 Hz), 140.98, 136.94, 134.73 (d, J = 8.2 Hz), 133.23 (m, CF_2), 131.06, 129.63, 128.58 (d, J = 2.0 Hz), 127.76 (br d, J = 22.9 Hz), 127.54, 126.38 (d, J = 4.1 Hz), 123.56 (broad multiplet), 122.74, 122.50, 122.45 (m, CF_3), 112.35, 109.54, 76.73, 71.03, 34.32 (d, J = 19.1 Hz), 32.07 (d, J = 18.4 Hz), 29.83, 29.80, 27.62 (d, J = 12.3 Hz), 27.13 (d, J = 10.3 Hz), 26.97 (d, J = 2.3 Hz), 26.92 (d, J = 8.8 Hz), 26.71 (d, J = 12.9 Hz), 26.41, 26.35 (d, J = 3.4 Hz), 25.98, 25.87, 22.45, 21.95, 21.64, 20.91. ^{19}F NMR (CD_2Cl_2 at 25 °C; δ): −79.87 (s, 3F), −101.19 (dd, $^2J_{F-F}$ = 31.5 Hz, $^3J_{F-P}$ = 275.3 Hz, 1F), −102.44 (dd, $^2J_{F-F}$ = 275.3 Hz, $^3J_{(F-P)}$ = 23.2 Hz, 1F). $^{31}P\{^1H\}$ NMR (CD_2Cl_2 at 25 °C; δ): 11.31 (broad multiplet). $^{19}F/^{13}C$ HSQC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −79.87/122.45. $^{19}F/^{13}C$ HMBC NMR ($CDCl_3$ at 25 °C; δ_F/δ_C): −79.87/122.45 (^1J correlation), −79.83/133.23. IR (ATR; cm^{-1}): 3048 (w), 2976 (w), 2927 (m), 2850 (m), 1596 (m), 1577 (m), 1449 (s), 1384 (m), 1373 (m), 1292 (m), 1266 (m), 1228 (m), 1185 (s), 1148 (s), 1101 (s), 1037 (s). HRMS electrospray (m/z): $[M - F]^+$ calcd for $C_{39}H_{50}F_4O_2PPd$ 763.2519, found 763.2507; $[M - C_6H_4CH_3]^+$ calcd for $C_{32}H_{43}F_5O_2PPd$ 691.1956, found 691.1929.

Reductive Elimination Studies: Representative Procedure. A J. Young NMR tube was charged with (RuPhos)Pd(CF_3)(*o*-$C_6H_4CH_3$) (**10**; 25 mg; 0.034 mmol), C_6D_6 (0.5 mL) and 1,4-bis(trifluoromethyl)benzene (approximately 2 mg; 0.01 mmol). The NMR tube was degassed through three freeze−pump−thaw cycles. A ^{19}F NMR spectrum was acquired to quantify the initial ratio of of **10** and the 1,4-bis(trifluoromethyl)benzene internal standard. The NMR tube was then heated in the oil bath for 12 h (oil bath kept at 90 °C). ^{19}F NMR spectroscopy was used to determine the yield of α,α,α-trifluoroxylene, on the basis of the initially determined relative amount of 1,4-bis(trifluoromethyl)benzene internal standard. The formation of reductive elimination product was confirmed also by GC-MS.

■ ASSOCIATED CONTENT

Supporting Information

Figures and tables giving experimental details and spectroscopic data for 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.

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