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New bis(fluoro-ponytailed) bipyridine ligands for Pd-catalyzed Heck reactions under fluorous biphasic catalysis condition

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Abstract—Three highly fluorinated bipyridine derivatives (4,4′-bis($R_fCH_2OCH_2$)-2,2′-bpy) {R_f=$HCF_2(CF_2)_7$ (**1a**), n-C_8F_{17} (**1b**), n-$C_{10}F_{21}$ (**1c**)} have been synthesized using 4,4′-bis($BrCH_2$)-2,2′-bpy and the corresponding fluorinated alkoxides. The fluorine contents of ligands **1a–c** are 58.3, 59.8, and 62.3%, respectively. Despite its high fluorine content, the ligand **1a** with a –CF_2H polar terminal group is more soluble in organic solvents. The ligand **1b** is a white solid and is still moderately soluble in CH_2Cl_2. The ligand **1c** has a high fluorophilicity, the partition ratio being 42:1 for the n-C_8F_{18}/CH_2Cl_2 system. The reaction of ligands **1a–c** with [$PdCl_2(CH_3CN)_2$] results in the novel Pd complexes [$PdCl_2$(4,4′-bis-($R_fCH_2OCH_2$)-2,2′-bpy)] where R_f=$HCF_2(CF_2)_7$ (**2a**), n-C_8F_{17} (**2b**), n-$C_{10}F_{21}$ (**2c**), respectively. The Pd complex **2b** is a pale yellow solid, and has been tested unsatisfactorily for FBC. Insoluble in organic solvents, the Pd complex **2c** dissolves only in fluorinated solvents, for instance FC77, which is mainly n-C_8F_{18}. The novel Pd complex **2c** has been tested as a catalyst in Heck reactions under a fluorous biphasic catalysis condition. It was found that the Pd complex **2c**, after an easy separation, keeps its catalytic activity (>90% yield), even after seven runs. The TGA studies indicate that the Pd complexes **2a–c** are stable up to 330 °C.

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1. Introduction

The concept of fluorous biphasic catalysis (FBC) was first introduced by Horváth and Rabai in 1994.[1] In the past decade, this field has evolved rapidly.[2] FBC has already been applied to a variety of common organic reactions, e.g., hydroboration of alkenes,[3] hydroformylation of alkenes,[1,4] epoxidation of alkenes,[5,6] Wacker oxidation of alkenes,[7] palladium allylic alkylation,[8] and oxidation of alcohols,[9] aldehydes, thioethers, and alkanes.[10,11]

The Heck reaction has been regarded as one of the most important tools to create C–C bonds.[12] However, Heck reactions remain a tough challenge for chemists in designing recyclable systems because the catalytic cycle is unstable, responsive to various factors, and the reaction needs at least three reagents[13]—electrophile, unsaturated olefin, and base. Sinou et al.[14] reported the use of perfluorinated phosphines for Pd-catalyzed Heck reactions in which the Pd catalyst was generated in situ, and its catalytic ability dropped to 70% upon reusage in the third run. Curran et al. and Gladysz and Rocaboy[15–17] used the soluble fluorous palladacycle complexes in Heck reactions, with palladacycle complexes being proposed as the catalyst precursor. We have prepared novel Pd complexes with bis(fluoro-ponytailed) bipyridines as ligands, replacing fluorinated phosphines, for use in the Heck reaction.[18] The new, fluorinated bipyridine derivatives are prepared from fluorinated alkanols.[19]

2. Results and discussion

2.1. Preparation of ligands 1a–c

Reported in this paper are our results on the successful application of fluorinated bipyridine Pd[6b] complexes to catalyze the Heck reaction under FBC,[20,21] the yield, selectivity, and recyclability all being satisfactory. 4,4′-Bis(fluoro-ponytailed)-2,2′-bpy ligands were prepared by making use of fluorinated alkanols.[6b] As shown in Scheme 1, the fluorinated alkoxides R_fCH_2ONa {R_f=$HCF_2(CF_2)_7$ (**a**), n-C_8F_{17} (**b**), n-$C_{10}F_{21}$ (**c**)} were obtained by stirring 30% CH_3ONa/CH_3OH with the corresponding fluorinated alkanols. The nucleophilic attack of a slight excess of R_fCH_2ONa on 4,4′-bis-($BrCH_2$)-2,2′-bpy[22–24] gave rise to the synthesis of a series of 4,4′-bis(fluoro-ponytailed)-2,2′-bpy ligands **1a–c**. The reactions were clean with quantitative yields of crude products, which could be easily purified as white solids by sublimation.

Keywords: Fluorinated bipyridine; Fluorophilicity; Heck reaction; Fluorous biphasic catalysis; TGA.

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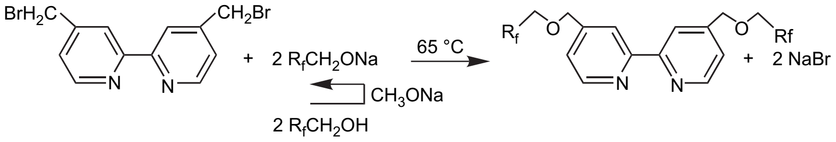


[R_f: $HCF_2(CF_2)_7$ (**1a**), *n*-C_8F_{17} (**1b**), *n*-$C_{10}F_{21}$ (**1c**)]

Scheme 1.

With a high fluorine content,[25,26] the ligands **1a**–**c** have been measured for their solubility in organic solvents as well as the fluorous solvent FC77, which is mainly *n*-C_8F_{18}, to give distribution ratios shown in Table 1. Although **1a** has a high fluorine content, the presence of polar-CF_2H group makes it more soluble in FC77 than **1b** and **1c**. The ligand **1a** is more soluble in organic solvents than in FC77. On the other hand, the partition ratio of ligand **1c**, with the highest fluorine content among the ligands,[25–27] has been recorded to be 1:42 and ~0.1:100 in the CH_2Cl_2/FC77 and DMF/FC77 systems, respectively. It was preliminarily judged that the Pd complex made from ligand **1c** would be the choice among ligands **1a**–**c** in the study of recyclable Heck reactions.

Table 1. Distribution ratios of ligands **1a**–**c** in different solvent systems

Ligand	CH_2Cl_2/FC77	DMF/FC77
(**1a**) (F%: 58.3)	100:0	100:0
(**1b**) (F%: 59.8)	1.07:1	1:4.5
(**1c**) (F%: 62.3)	1:42	<0.1:100

2.2. Preparation and catalytic activity of Pd complexes 2a–c

Three new Pd complexes, [$PdCl_2$(4,4′-bis($R_fCH_2OCH_2$)-2,2′-bpy)] where R_f=$HCF_2(CF_2)_7$ (**2a**), *n*-C_8F_{17} (**2b**), *n*-$C_{10}F_{21}$ (**2c**), were easily prepared from [$PdCl_2(CH_3CN)_2$] and the corresponding ligands **1a**, **1b**, and **1c**, respectively, as shown in Eq. 1. The bipyridine Pd complexes **2a**–**c** have a cis conformation, different from the bidentate pyridine Pd complexes carrying the trans conformation reported by Kawano et al.[28] The reaction of equal amounts of [$PdCl_2(CH_3CN)_2$] and ligands proceeded smoothly, stirring overnight in air at room temperature, followed by removal of the solvents to yield the air and moisture stable Pd complexes. The Pd complex **2a** was not soluble in FC77. The Pd complex **2b** was slightly soluble in FC77. The Pd complex **2b** had been used in the Heck reaction under DMF/FC77 biphasic condition. But we obtained a very low yield during the second run, which can be attributed to the greater solubility of **2b** in DMF. In contrast to **2a** and **2b**, the Pd complex **2c** showed a very high reactivity and selectivity during Heck reaction under FBC process.

The Pd-catalyzed reaction of iodobenzene (**3a**) with methyl acrylate (**4**) was selected to demonstrate the feasibility of recycling use with Pd complex **2c** as the catalyst under DMF/FC77 biphasic system at 140 °C for 6 h in each run, as shown in Eq. 2. At the end of each run, the fluorous layer containing Pd complex **2c** was recycled to proceed to the next. The products were quantified with GC analysis by comparison to standards. The results are shown in Table 2. The Heck reaction under FBC exhibited a good recyclability, the yield being better than 88% after the seventh run. The Heck reaction here also exhibited a 100% selectivity favoring the trans product.

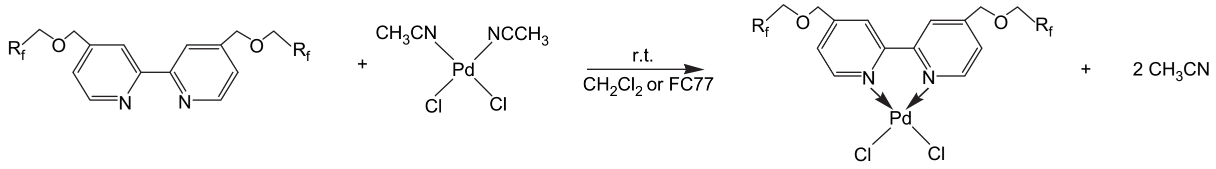
As Pd complex **2c** could be prepared easily by stirring the ligand **1c** and [$PdCl_2(CH_3CN)_2$] at room temperature, the Heck reaction was also carried out with the Pd catalyst generated in situ. Thus, the ligand **1c** and [$PdCl_2(CH_3CN)_2$] were charged into FC77 at a 1:1 molar ratio and the fluorous phase was refluxed for 2 h before addition of DMF containing substrates and base. At the end of the first run, the fluorous layer was recovered and used for the second run. Similar recovery procedure was undertaken during the later runs. The yields of eight consecutive runs are summarized in Table 3. The results were very similar to those in Table 2. The Pd catalyst was effectively recovered and reused for seven times before an observable drop in yields took place.

Table 2. Recycling results of Heck reaction catalyzed by Pd complex **2c** under DMF/FC77 biphasic system

Cycle no.	Yield[a] (%)	TON	Cycle no.	Yield[a] (%)	TON
1	96.8	193.6	5	92.0	184.0
2	98.5	197.0	6	98.5	197.0
3	95.3	190.6	7	88.0	176.0
4	100.0	200.0	8	77.0	154.0

Note: reaction conditions: 140 °C; 6 h; DMF (3 mL); FC77 (3 mL); iodobenzene (102 mg, 0.5 mmol), methyl acrylate (64.5 mg, 0.75 mmol), NEt_3 (50.6 mg, 0.5 mmol), 0.5 mol % Pd complex **2c** (3.64 mg); the two layers separated using a separatory funnel at 0 °C after each run. The fluorous layer containing Pd complex **2c** was washed with 2 mL DMF (or CH_2Cl_2) before proceeding to the next run.

[a] Based on GC yield.



(1)

[R_f = $HCF_2(CF_2)_7$ (**1a**), *n*-C_8F_{17} (**1b**), *n*-$C_{10}F_{21}$ (**1c**)]

[R_f = $HCF_2(CF_2)_7$ (**2a**), *n*-C_8F_{17} (**2b**), *n*-$C_{10}F_{21}$ (**2c**)]

Table 3. Recycling results of Pd catalyst, generated in situ, in the Heck reaction under DMF/FC77 biphasic system

Cycle no.	Yield[a] (%)	TON	Cycle no.	Yield[a] (%)	TON
1	99	198	5	98	196
2	94	188	6	99	198
3	96	192	7	100	200
4	98	196	8	72	144

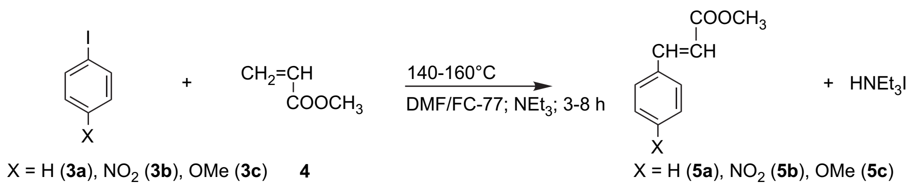
Note: reaction conditions: 140 °C; 6 h; DMF (3 mL); FC77 (3 mL); iodobenzene (102 mg, 0.5 mmol), methyl acrylate (64.5 mg, 0.75 mmol), NEt_3 (50.6 mg, 0.5 mmol), 0.5 mol % Pd catalyst {$[PdCl_2(CH_3CN)_2]$ (0.7 mg), ligand **1c** (3.2 mg), initial in situ generation, 2 h}; the two layers separated using a separatory funnel at 0 °C after each run. The fluorous layer containing Pd catalyst was washed with 2 mL DMF (or CH_2Cl_2) before proceeding to the next run.

[a] Based on GC yield.

The data in Tables 2 and 3 suggest that the Pd complex **2c** is an effective and fluorous-phase soluble catalyst for the Heck reaction under the DMF/FC77 biphasic system. The Pd complex **2c** is not only easily recyclable itself, but also easily generated in situ from the component ligand **1c** and the Pd metal ion precursor.

2.3. Substituted iodobenzene as substrate

In order to see how applicable this Pd-catalyzed Heck reaction is, two substituted iodobenzenes, *p*-IC_6H_4X [X=NO_2 (**3b**), OMe (**3c**)], were used as substrates for reactions under FBC as shown in Eq. 2.



(2)

The reaction of **3b** with **4** was successfully carried out under FBC. The results are listed in Table 4. The strong electron-withdrawing NO_2 group at the *para* position expedites the reaction to a great extent. The first four runs could be completed in just 3 h at 140 °C. For cycle nos. 5–8, the normal time of 6 h was required for the reactions to complete. Overall, the recyclability was excellent with yields being 100% for eight consecutive runs.

When *p*-IC_6H_4OMe (**3c**) was used as the substrate in Heck reactions with Pd complex **2c** as the catalyst, the electron-releasing OMe group was expected to slow down the reactions. As shown in Table 5, the recyclability of Heck reaction was also successful, although a longer time and a higher temperature were required. The yields dropped to <90% at the second run with 6 h at 140 °C. By increasing the temperature (to 160 °C) and/or time (to 8 h), the reusage of Pd complex **2c** was still good, average yields being ca. 90% for eight consecutive runs.

Table 4. Recycling results of Pd complex **2c** as the catalyst in the Heck reaction under FBC system using 4-nitro-iodobenzene as substrate

Cycle no.	Temp (°C)	Time (h)	Yield (%)	TON	TOF
1	140	3	100	200	66.7
2	140	3	100	200	66.7
3	140	3	100	200	66.7
4	140	3	100	200	66.7
5	140	6	100	200	33.3
6	140	6	100	200	33.3
7	140	6	100	200	33.3
8	140	6	100	200	33.3

Table 5. Recycling results of Pd complex **2c** as the catalyst in the Heck reaction under FBC system using 4-methoxy-iodobenzene as substrate

Cycle no.	Temp (°C)	Time (h)	Yield (%)	TON	TOF
1	140	5	100.0	200.0	40.0
2	140	6	87.2	174.4	29.1
3	160	6	82.3	164.6	27.4
4	160	6	83.8	167.6	27.9
5	160	8	92.0	184.0	23.0
6	160	8	94.0	188.0	23.5
7	160	8	93.6	187.2	23.4
8	160	8	86.0	172.0	21.5

2.4. Thermal studies

The thermal studies (see Supplementary data) showed that the ligands **1a–c** were all stable up to 260 °C. Surprisingly the associated Pd complexes **2a–c** were even more stable, with decomposition temperatures being >330 °C. The Pd complexes of this type are not only air and moisture stable, but also thermally robust. As a consequence, the Heck reaction catalyzed by the novel Pd complex **2c** should be feasible at even higher temperature.

3. Conclusion

In summary, we have completed the synthesis of a new series of 4,4′-bis(fluoro-ponytailed)-2,2′-bpy ligands, with intrinsically high fluorine contents. From these ligands we have also prepared the corresponding Pd complexes, among which Pd complex **2c** has been successfully used, with good recyclability, in the Heck reaction under FBC. The Pd complex **2c**, either directly used or generated in situ, can be employed to catalyze effectively the Heck reaction and reused with good yields for eight consecutive runs. A range of electron-withdrawing and electron-releasing substrates, e.g., *p*-IC_6H_4X [X=H (**3a**), NO_2 (**3b**), OMe (**3c**)], were tested in Heck reactions catalyzed by Pd complex **2c**. Judged from the results in Tables 2, 4, and 5, the Pd complex **2c** is one of the best catalysts for use in Heck reaction under FBC.

4. Experimental

4.1. General procedures

Gas chromatographic/mass spectrometric data were obtained using an Agilent 6890 Series gas chromatograph with a series 5973 mass selective detector. The reaction was monitored with an HP 6890 GC using a 30 m×0.250 mm HP-1 capillary column with a 0.25 µm stationary phase film thickness. Temperature program was a 2 min hold at 50 °C and then taken to 260 °C at 10 °C/min and held for 12 min at 260 °C. The flow rate was 1 mL/min and splitless. Infrared spectra were obtained on a Perkin Elmer RX I FT-IR Spectrometer. NMR spectra were recorded on Bruker AM 500 and Joel AM 200 spectrometers using 5 mm sample tubes. CD_3OD, CD_2Cl_2, CD_3Cl, and deuterated Me_2SO were the references for both ^1H and ^{13}C NMR spectra and Freon® 11 ($CFCl_3$) was the reference for ^{19}F NMR spectra. Thermogravimetric analyses (TGA) were performed on a TA Instruments TGA51.

4.2. Starting materials

Chemicals, reagents, and solvents employed were commercially available and used as received. $HCF_2(CF_2)_7CH_2OH$ was obtained from Daikin Taiwan. $C_8F_{17}CH_2OH$ and $C_{10}F_{21}CH_2OH$ were purchased from Aldrich and SynQuest.

4.3. Preparation of 4,4′-bis($R_fCH_2OCH_2$)-2,2′-bpy 1a–c where R_f=$HCF_2(CF_2)_7$ (a), *n*-C_8F_{17} (b), *n*-$C_{10}F_{21}$ (c)

General procedure: 30% CH_3ONa/CH_3OH (1.1 g) and R_fCH_2OH (6.0 mmol) were charged into a round-bottomed flask, then continuously stirred under N_2 atmosphere at 65 °C for 4 h before CH_3OH was vacuum removed to drive the reaction to the fluorinated alkoxide side. The resultant fluorinated alkoxide (6.0 mmol) was then dissolved in 20 mL of dry CH_3CN (or HFE 7100), and 4,4′-bis($BrCH_2$)-2,2′-bpy (5.8 mmol) was added. The mixture was refluxed for 4 h, and the completion of the reaction was checked by sampling the reaction mixtures and analyzing the aliquots with GC/MS. The product was purified by vacuum sublimation to obtain white solids. The vacuum level was 0.1 Torr, and the sublimation temperature was 50 °C above its mp.

4.3.1. Compound 1a. Yield (sublimed) 85%; ^1H NMR (500 MHz, $CDCl_3$) δ 8.69 (2H, d, $^3J_{HH}$=4.5 Hz, H_6), 8.33 (2H, s, H_3), 7.36 (2H, d, $^3J_{HH}$=4.5 Hz, H_5), 6.03 (1H, tt, $^2J_{HF}$=51.9 Hz, $^3J_{HF}$=5.5 Hz, CF_2H), 4.78 (4H, s, bpy–CH_2), 4.04 (4H, t, $^3J_{HF}$=13.7 Hz, CF_2CH_2); ^{19}F NMR (470.5 MHz, $CDCl_3$) δ −119 (s, 2F, CH_2CF_2), −121 (s, 6F), −123 (s, 4F), −129 (s, 2F, HCF_2CF_2–), −137 (d, 2F, $^2J_{HF}$=52 Hz, HCF_2–); ^{13}C NMR (113 MHz, $CDCl_3$) δ 72.4 (bpy–CH_2), 67.1 (CH_2CF_2), 118.9, 122.5, 147.9, 149.9, 155.7 (bpy), 105.0–116.3 $(CF_2)_8$; GC/MS (*m*/*z*; EI): 614 (M^+−$OCH_2C_8F_{16}$), 198 ($C_5H_3NCH_2C_5H_3NCH_2O^+$), 183 ($C_5H_3NCH_2C_5H_3NCH_3^+$), 91 ($C_5H_3NCH_2^+$); FTIR ($cm^{-1}$): 1595.6, 1558.3 ($\nu$bpy, m), 1208.3, 1140.3 (νCF_2, vs); mp: 86–88 °C.

4.3.2. Compound 1b. Yield (sublimed) 80%; ^1H NMR (500 MHz, $CDCl_3$) δ 8.67 (2H, d, $^3J_{HH}$=4.9 Hz, H_6), 8.40 (2H, s, H_3), 7.34 (2H, d, $^3J_{HH}$=4.9 Hz, H_5), 4.77 (4H, s, bpy–CH_2), 4.04 (4H, t, $^3J_{HF}$=13.5 Hz, CF_2CH_2); ^{19}F NMR (470.5 MHz, $CDCl_3$) δ −80.8 (3F), −119.3 (2F), −121.9 (6F), −122.7 (2F), −123.2 (2F), −126.1 (2F); ^{13}C NMR (113 MHz, $CDCl_3$) δ 73.0 (bpy–CH_2), 67.7 (CH_2CF_2), 119.2, 121.9, 146.9, 149.6, 156.1 (bpy), 108.0–119.0 (C_8F_{17}); GC/MS (*m*/*z*; EI): 632 (M^+−$OCHC_8F_{17}$), 198 ($C_5H_3NCH_2C_5H_3NCH_2O^+$), 183 ($C_5H_3NCH_2C_5H_3NCH_3^+$), 91 ($C_5H_3NCH_2^+$); FTIR ($cm^{-1}$): 1602.0, 1559.8, 1465.0 (νbpy, m), 1203.7, 1144.7 (νCF_2, vs); mp: 113–115 °C.

4.3.3. Compound 1c. NMR data were collected in $CDCl_3$ at 60 °C to increase the solubility. Yield (sublimed) 65%; ^1H NMR (500 MHz, $CDCl_3$) δ 8.69 (2H, d, $^3J_{HH}$=5.1 Hz, H_6), 8.40 (2H, s, H_3), 7.38 (2H, d, $^3J_{HH}$=4.2 Hz, H_5), 4.80 (4H, s, bpy–CH_2), 4.06 (4H, t, $^3J_{HF}$=13.3 Hz, CF_2CH_2); ^{19}F NMR (470.5 MHz, $CDCl_3$) δ −80.7 (3F), −119.3 (2F), −121.7 (6F), −121.8 (4F), −122.6 (2F), −123.1 (2F), −126.0 (2F); ^{13}C NMR (113 MHz, $CDCl_3$) δ 73.1 (bpy–CH_2), 68.1 (CH_2CF_2), 119.8, 122.2, 144.7, 149.4, 154.1 (bpy), 105.5–116.2 ($C_{10}F_{21}$); GC/MS (*m*/*z*; EI): 732 (M^+−$OCHC_{10}F_{21}$), 198 ($C_5H_3NCH_2C_5H_3NCH_2O^+$), 183 ($C_5H_3NCH_2C_5H_3NCH_3^+$), 91 ($C_5H_3NCH_2^+$); FTIR ($cm^{-1}$): 1602.4, 1561.7 ($\nu$bpy, m), 1215.0, 1150.5 (νCF_2, vs); mp: 140–142 °C.

4.4. Preparation of Pd complexes 2a–c where R_f=$HCF_2(CF_2)_7$ (a), *n*-C_8F_{17} (b), *n*-$C_{10}F_{21}$ (c)

Equimolar $[PdCl_2(CH_3CN)_2]$ (134.9 mg, 0.52 mmol) and respective ligands **1a–c** (0.52 mmol) in different reactions were charged into a round-bottomed flask, and CH_2Cl_2 (3 mL) added as solvent. The color of the solution changed from red to yellow after mixing for several minutes. The solution was further stirred at room temperature for 24 h before the solvents and volatiles were removed under vacuum. The resulting yellow solids were collected as spectroscopically pure products.

4.4.1. Compound 2a. Yield 96%; ^1H NMR (500 MHz, Me_2SO-*d*) δ 9.08 (2H, d, $^3J_{HH}$=5.8 Hz, H_6), 8.34 (2H, s, H_3), 7.73 (2H, dd, $^3J_{HH}$=5.8 Hz, H_5), 7.19 (2H, tt, $^2J_{HF}$=50.3 Hz, $^3J_{HF}$=5.3 Hz, CF_2H), 4.96 (4H, s, bpy–CH_2), 4.41 (4H, t, $^3J_{HF}$=14.6 Hz, CF_2CH_2); ^{19}F NMR (470.5 MHz, Me_2SO-*d*) δ −119.1 (s, 2F, CH_2CF_2), −121.9 (s, 6F), −122.9 (s, 4F), −128.7 (s, 2F, HCF_2CF_2), −138.5 (d, 2F, $^2J_{HF}$=52 Hz, HCF_2); ^{13}C NMR (113 MHz, Me_2SO-*d*) δ 71.0 (bpy–CH_2), 66.8 (CH_2CF_2), 120.5, 124.2, 149.3, 151.6, 155.6 (bpy), 105.0–116.4 $(CF_2)_8$; FTIR (cm^{-1}): 1654.0, 1559.9 (νbpy, m), 1209.9, 1146.9 (νCF_2, vs); HRMS (FAB): (M^+; *m*/*z*=) $C_{30}N_2H_{16}F_{32}O_2Pd^{35}Cl_2$ calcd 1219.9113, found 1219.9169; $C_{30}N_2H_{16}F_{32}O_2Pd^{35}Cl^{37}Cl$ calcd 1221.9041, found 1221.9041; $C_{30}N_2H_{16}F_{32}O_2Pd^{37}Cl_2$ calcd 1223.9054, found 1223.9009.

4.4.2. Compound 2b. NMR data were collected in DMF-*d* at 90 °C because of solubility. Yield 96%; ^1H NMR (500 MHz, DMF-*d*) δ 9.29 (2H, d, $^3J_{HH}$=5.9 Hz, H_6), 8.48 (2H, s, H_3), 7.82 (2H, d, $^3J_{HH}$=5.9 Hz, H_5), 5.08 (4H, s, bpy–CH_2), 4.47 (4H, t, $^3J_{HF}$=14.3 Hz, C_8F_{17}–CH_2); ^{19}F NMR (470.5 MHz, DMF-*d*) δ −80.9 (3F), −119.1 (2F), −121.3 (6F), −122.1 (2F), −122.7 (2F), −125.5 (2F); ^{13}C NMR (113 MHz, DMF-*d*) δ 72.4 (bpy–CH_2), 68.3 (CH_2CF_2), 121.7, 125.3, 15.6, 153.1, 157.2 (bpy), 105.0–120.0 (C_8F_{17}); FTIR (cm^{-1}): 1622.9, 1558.8, 1436.9 (νbpy, m), 1203.7, 1148.4 (νCF_2, vs); HRMS (FAB): (M$^+$; *m/z*=) $C_{30}N_2H_{14}F_{34}O_2Pd^{35}Cl_2$ calcd 1255.8924, found 1255.8920; $C_{30}N_2H_{14}F_{34}O_2Pd^{35}Cl^{37}Cl$ calcd 1257.8928, found 1257.8954; $C_{30}N_2H_{14}F_{34}O_2Pd^{37}Cl_2$ calcd 1259.8899, found 1259.8844.

4.4.3. Compound 2c. NMR data were collected in DMF-*d* at 90 °C because of solubility. Yield 96%; ^{1}H NMR (500 MHz, DMF-*d*) δ 9.29 (2H, d, $^3J_{HH}$=5.8 Hz, H_6), 8.47 (2H, s, H_3), 7.81 (2H, d, $^3J_{HH}$=5.8 Hz, H_5), 5.08 (4H, s, bpy–C*H*$_2$), 4.47 (4H, t, $^3J_{HF}$=14.6 Hz, $C_{10}F_{21}$–C*H*$_2$); ^{19}F NMR (470.5 MHz, DMF-*d*) δ −80.9 (3F), −121.0 (4F), −121.31 (6F), −122.1 (2F), −122.7 (2F), −125.5 (2F); ^{13}C NMR (113 MHz, DMF-*d*) δ 74.2 (bpy–CH_2), 68.2 (CH_2CF_2), 120.3, 124.5, 140.9, 151.8, 157.3 (bpy), 105.0–116.0 ($C_{10}F_{21}$); FTIR (cm^{-1}): 1622.9, 1558.3 (νbpy, m), 1208.3, 1150.5 (νCF_2, vs); HRMS (FAB): (M$^+$; *m/z*=) $C_{34}N_2H_{14}F_{42}O_2Pd^{35}Cl_2$ calcd 1455.8869, found 1455.8842; $C_{34}N_2H_{14}F_{42}O_2Pd^{35}Cl^{37}Cl$ calcd 1457.8767, found 1457.8741; $C_{34}N_2H_{14}F_{42}O_2Pd^{37}Cl_2$ calcd 1459.8737, found 1459.8734.

4.5. Recycling studies of the Heck reaction with Pd complex 2c as catalyst

4.5.1. Heck reaction with C_6H_5I as the substrate. Under the fluorous biphasic system, the vessel was charged with DMF (3 mL), FC77 (3 mL), C_6H_5I (102 mg, 0.50 mmol), $H_2C{=}CHCO_2Me$ (64.5 mg, 0.75 mmol), NEt_3 (50.6 mg, 0.50 mmol), and the 0.5 mol % Pd complex {**2c** (3.64 mg) or components $[PdCl_2(CH_3CN)_2]$ (0.7 mg), ligand **1c** (3.2 mg)}. The reaction mixture was refluxed at 140 °C for 6 h before the reaction was stopped and the two layers separated using a separatory funnel at 0 °C. The FC77 fraction was retained for recycling experiments.

4.5.2. Heck reaction with *p*-$IC_6H_4NO_2$ as the substrate. In a typical run, the reaction vessel was charged with *p*-$IC_6H_4NO_2$ (123.5 mg, 0.50 mmol), $H_2C{=}CHCO_2Me$ (64.5 mg, 0.75 mmol), NEt_3 (50.6 mg, 0.50 mmol), and the Pd complex **2c** (0.5 mol %, 3.64 mg) or the recovered Pd catalyst after each run. Then the reaction mixture was set to reflux in DMF/FC77 (2 mL each), at 140 °C for 3–6 h before the reaction was stopped and the two layers separated using a separatory funnel at 0 °C. The FC77 fraction was retained for recycling experiments.

4.5.3. Heck reaction with *p*-IC_6H_4OMe as the substrate. In a typical run, the reaction vessel was charged with *p*-IC_6H_4OMe (117 mg, 0.50 mmol), $H_2C{=}CHCO_2Me$ (64.5 mg, 0.75 mmol), NEt_3 (50.6 mg, 0.50 mmol), and the Pd complex **2c** (0.5 mol %, 3.64 mg) or the recovered Pd catalyst after each run. Then the reaction mixture was set to reflux in DMF/FC77 (2 mL each), at 140–160 °C for a period of 5–8 h before the reaction was stopped and the two layers separated using a separatory funnel at 0 °C. The FC77 fraction was then used for recycling experiments.

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Supplementary data

TGA data for the three ligands **1a–c** and the three Pd complexes **2a–c**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.12.053.

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