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Homogeneous catalysis in supercritical carbon dioxide with rhodium catalysts tethering fluoroacrylate polymer ligands

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Abstract—Rhodium(I) complexes for homogeneous catalysis in supercritical carbon dioxide, $scCO_2$, have been prepared from the reaction of phosphine containing fluoroacrylate polymeric ligands with $[Rh(\mu\text{-}Cl)(COD)]_2$. The fluoroacrylate polymer used was prepared via a free radical initiator polymerization reaction from 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate monomer and *N*-acryloxysuccinimide, NASI. Diphenylphosphinopropylamine, DPPA, was attached to the copolymer as it replaces the NASI group, thus providing the copolymer a phosphine ligand for coordination. ^{31}P NMR and UV–Vis spectra were used to confirm the coordination of phosphine in the polymer to Rh(I). The synthesized catalysts possess excellent solubility in $scCO_2$. Hydrogenation of 1-octene in $scCO_2$ resulted in conversion (70%) to *n*-octane within 12 h (reaction conditions 70°C, 172 bar, 1:4000 catalyst/substrate mole ratio). © 2002 Elsevier Science Ltd. All rights reserved.

Catalysis by metal complexes in homogeneous solutions has undergone important developments in nontraditional reaction media such as water,[1] fluorous solvents,[2] ionic liquids[3] and supercritical CO_2.[4] The difficulty of the catalyst separation and recovery is a major problem in homogenous catalysis for chemical transformations. Attachment of certain functional groups to organic and inorganic polymers has been attempted as a strategy to facilitate catalyst separation from the reaction mixture. Various polymers have been chemically modified to serve as support for homogeneous catalysts. In many cases, these polymers contain phosphine ligands such as diarylphosphine-terminated poly(ethyleneoxide)[5] and diarylphosphine-terminated polyethylene;[6] phosphine-containing derivatives of various addition polymers, such as polystyrene,[7] poly(*N*-alkylacrylamides),[8,9] poly(4-pentanoic acid)[10] and poly(maleic anhydride)-*c*-poly(methylvinyl ether).[11]

Recently, there has been a considerable interest in performing homogeneously catalyzed reactions in fluorous solvents and especially in $scCO_2$.[12] Compared to conventional organic solvents, CO_2 has many advantages, including its non-toxicity, non-flammability and ease of separation of the products and/or catalysts from the reaction mixture. In addition, in the supercritical state, the physicochemical properties of the solvent can be tuned by changing its density, hence resulting in activity and selectivity control with temperature and pressure.[13] However, the metal-containing catalyst must be soluble in the supercritical fluid. Although the solubilities of many species in $scCO_2$ can be increased significantly by using organic and inorganic compounds (so called modifiers), this normally is not a desired approach in organic synthesis since these compounds can lead to the formation of undesired by-products. Although salts are generally insoluble in $scCO_2$, a careful choice of the counter ion can greatly increase the solubility of charged complexes. Anions such as trifluoromethyl sulfonate tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, (BARF),[14,15] and cations, such as fluorotetraalkylammonium and morpholinium[16] have been shown to increase solubility. For example, several of us have recently described the synthesis and crystal structure of [(COD)Rh(Et-DuPHOS)]BARF (COD=cyclooctadiene; Et-DuPHOS=1,2-bis((2*R*,5*R*)-2,5-diethylphospholane)benzene).[17a] This catalyst has shown reasonable solubility in $scCO_2$ and has been used in regioselective homogeneous hydroformylation of styrene.[17b,c] Another approach to increase the solubility of catalysts in supercritical fluids, that was initially developed for fluorous biphasic systems[18,19] entails attaching long perfluoroalkyl groups to phosphine ligands. Phosphine ligands with $-CF_3$ (sometimes $-C_6F_5$) groups were attached to catalyst in order to increase solubility in $scCO_2$.[20]

Keywords: homogeneous catalysis; supercritical carbon dioxide; rhodium(I) complex; hydrogenation; 1-octene.

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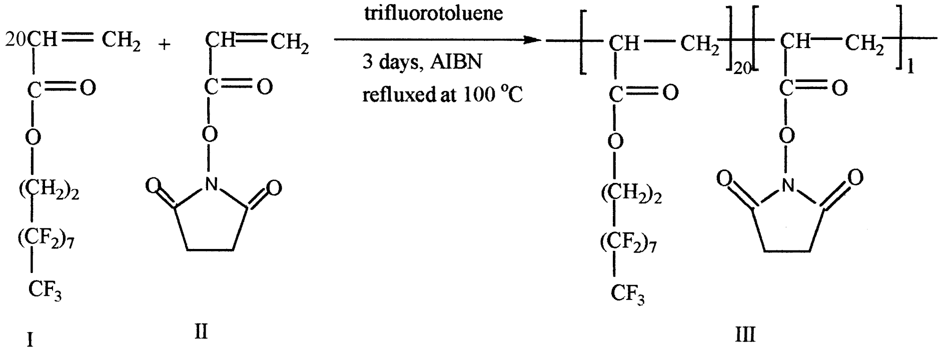
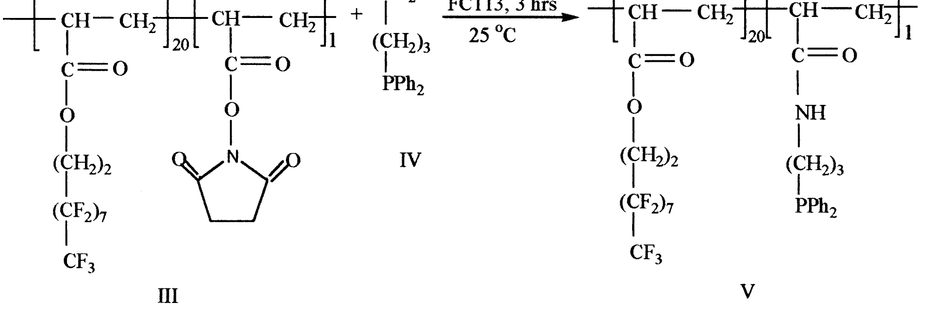


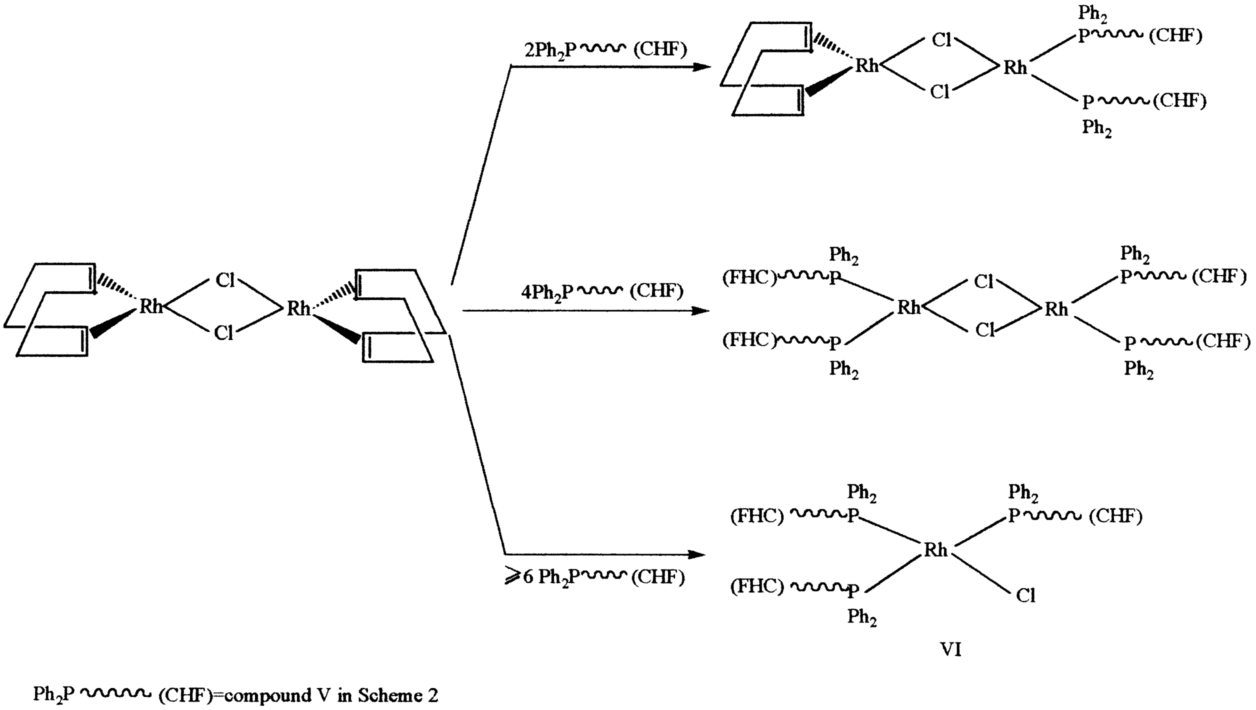
Scheme 1.

Horvath and Rabai designed and synthesized a phosphine ligand in which three perfluoroalkyl 'pony tails' afford solubility in $scCO_2$.[21] Fluorinated catalysts are obtained by ligand modification by attaching fluorinated substituents or tails such as $(CH_2)_x(CF_2)_yCF_3$ to the ancillary ligand's backbone.[22] Examples of these fluorinated metal complexes include $HRh(CO)(P[CH_2CH_2-(CF_2)_5CF_3]_3)_3$,[23,24] $ClRh(P[CH_2CH_2-(CF_2)_5CF_3]_3)_3$,[18] $ClM(CO)(P[CH_2CH_2-(CF_2)_5CF_3])_2$ (M=Ir, Rh),[23,24] fluorinated porphyrin complexes,[25,26] fluorinated cyclopentadienyl[27] and other complexes.[28] The intervening methylene groups serve as insulating spacers to isolate the strong electron-withdrawing effect of fluoroalkyl chain groups from the ligating phosphorus group.[12] Beckman and co-workers proposed that the solubility enhancement resulted from special interaction of electron rich fluorine in C–F bonds with relatively electron poor CO_2 molecules.[29] A recent paper by DeSimone and workers described the effect of solvent density on the NMR spectra of fluorinated and non-fluorinated hydrocarbons dissolved in $scCO_2$.[30] Leitner's group has used $-C_8H_4F_{13}$ substituted phosphine and phosphite ligands with the catalyst precursor [(COD)Rh(hfacac)] (hfacac= hexafluoroacetylacetonate) in 1-octene hydroformylation.[31,20a] The first example of homogeneous hydrogenation in $scCO_2$ was the hydrogenation of cyclopropene by $MnH(CO)_5$ via a radical mechanism.[32] Burk and Tumas studied the asymmetric hydrogenation of several α-enamides using cationic Rh complexes containing the Et-DuPHOS ligand.[33] The complex Rh(hfacac)-$(R_2PCH_2PR_2)$ (where $R=C_6H_4$-*m*-$(CH_2)_2(CF_2)_5CF_3$) was shown as an active catalyst for the hydrogenation of isoprene.[34] Noyori et al. found that $Ru(OCOCH_3)_2(H_8$-BINAP) is active as a catalyst in $scCO_2$ for the hydrogenation of α,β-unsaturated carboxylic acids such as tiglic acid.[35] Although the aforementioned studies have made significant advancements in the solubility problem of organometallic catalysts in $scCO_2$, the recovery of catalyst from the reaction mixture remains a largely unresolved issue. Our approach in addressing the problem of catalyst recovery is to prepare catalysts attached to a polymer support that is soluble in $scCO_2$. Only two classes of polymeric materials are known to be soluble in $scCO_2$ at readily accessible conditions ($T<100$°C; $P<500$ bar): amorphous, low-melting point silicones and highly fluorinated polymers.[36]

A large amount of work has been generated to demonstrate the solubility of hydrocarbon polymers containing fluorinated octyl acrylates in $scCO_2$.[37] It is argued that the copolymer solubility depends on the number of fluorinated side groups and the molecular weight of the hydrocarbon chain. Fluorinated groups play a significant role in polymer solubility and the polarity of the polymer also plays a role in fixing solubility levels. Krukonis and co-workers have shown that CO_2 at or near room temperature and at pressures below 600 bar dissolves many poly(dimethyl)- and poly(phenylmethyl)silicones, perfluoroalkyl polyethers, chloro and bromotrifluoroethylene polymers.[38,39] Beckman and co-workers have reported the solubility of poly(perfluoropropyleneoxide) and also polydimethylsiloxenes in $scCO_2$.[40,41] However, to the best of our knowledge, there has been no report on fluoropolymer based catalyst soluble in $scCO_2$. Bergbreiter and co-workers have synthesized a variety of copolymers for fluorous-phase soluble polymeric support by using different fluoroacrylate monomers and NASI.[42] They have shown that Rh(I) and Pd(0) catalysts with phosphines based on these copolymers can be used in biphasic hydrogenation reactions. In this work, we



Scheme 2.



Scheme 3.

describe high-yield monophasic synthesis of Wilkinson catalyst analogues in which a phosphine-bearing fluoroalkyl polymer is coordinated to Rh(I). The catalysts have high solubility in $scCO_2$ and have shown reasonable catalytic activity in the homogeneous hydrogenation reaction of 1-octene in $scCO_2$.

1. Result and discussion

The general method of synthesis is given in Schemes 1–3. Details of synthetic procedures, analytical and spectroscopic analyses are in Section 2.

In the polymer, the fluoroacrylate group increases the solubility in $scCO_2$ and the NASI group is the reactive group to be subsequently exchanged with DPPA to be chelated to rhodium. The copolymer was synthesized by varying the molar ratio of the flouroacrylate, I, to the NASI group, II. Reactions with I/II ratios of 7:1; 15:1 and 20:1 were synthesized and the resulting copolymers were all found soluble in $scCO_2$. Scheme 1 shows the reaction with a I/II ratio of 20:1, which yielded the highest solubility of the resulting polymers and catalysts.

The ^1H NMR spectrum of product V (Scheme 2) showed the loss of the NASI methylene peak at δ 2.8 and the formation of two new peaks between δ 7.2 and 7.8 with a 4:1 ratio, characteristic of the aromatic protons of DPPA. This ratio of NMR peaks also confirms that the 20:1 mixing ratio of I/II

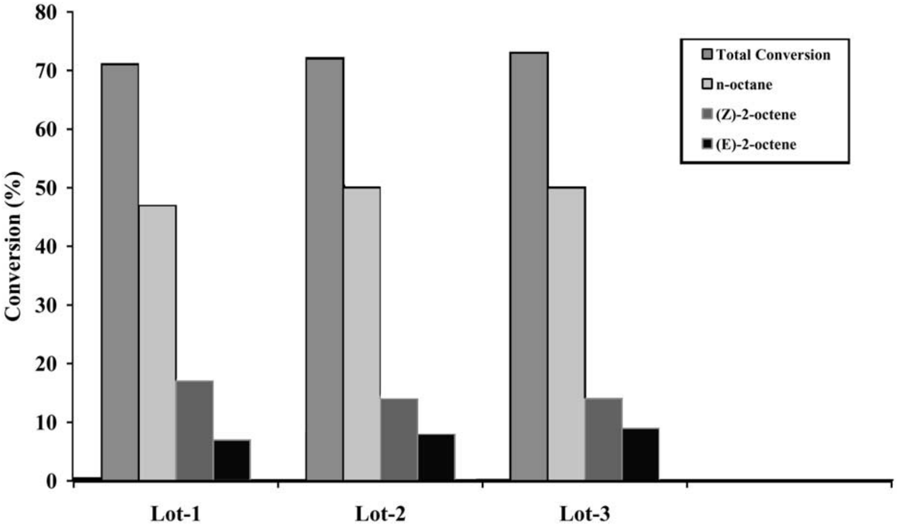


Figure 1. Hydrogenation reactions of 1-octene in $scCO_2$ with polymer catalyst VI. Reaction conditions: 70°C, 6.2 bar H_2, 172 bar total pressure, total reaction time of 12 h, H_2/1-octene molar ratio of 3:1, and Rh/1-octene molar ratio of 1:4000.

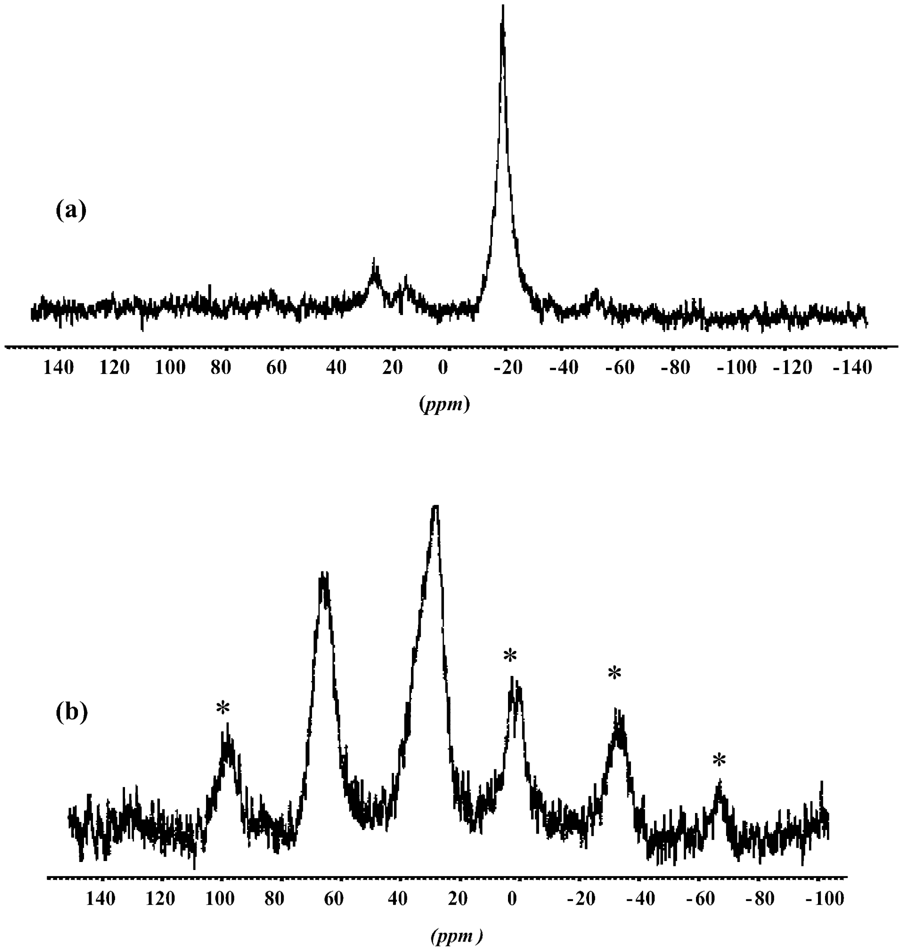


Figure 2. ^{31}P NMR spectra of (a) the phosphine-bearing polymer V and (b) the catalyst VI. The structures of the two compounds are shown in Schemes 2 and 3, respectively. The asterisks in the spectrum of VI denote spinning side bands, the position of which changed at a different spinning speed while the strong bands at about 30 and 67 ppm did not change position.

was maintained in the product III. A broad peak due to the $-OCH_2-$ of the fluroacrylate appeared at δ 4.5. The reaction of III with DPPA, IV, was followed by ^{31}P NMR spectra, which showed a peak at δ -16, characteristic of the product V (Scheme 2) and a small peak at δ 29, characteristic of phosphine oxide impurities.[42] The amount of phosphine oxide varied but typically was $<10\%$, as determined by integration of ^{31}P NMR signals.

Rhodium complexes were prepared as shown in Scheme 3, by the reaction of the phosphine-containing polymer ligand with the catalyst precursor $[Rh(\mu\text{-}Cl)(COD)]_2$. The rhodium–phosphine coordination was indicated by analysis of solid-^{31}P NMR and solution UV–Vis spectroscopy (in addition to the color change accompanying the reaction). Fig. 2 shows a representative example of solid-state ^{31}P NMR spectra for one of the polymer-bound rhodium catalysts we isolated. The solid-state spectrum for the starting polymer is also shown in Fig. 2 for comparison. The spectrum for the catalyst showed the disappearance of the ^{31}P NMR peak for the free phosphine peak that was observed at δ -16 in the starting polymer and the formation of broad singlets centered at about δ 30 and δ 67 (weaker singlets also appeared near δ 2). The exact peak positions varied within a few ppm of these numbers when the syntheses were repeated. The positions of these resonances are typical for metal-coordinated phosphine ligands.[43,44] The appearance of two ^{31}P NMR peaks although spinning side bands also are observed and their breadth are indicative of more than one coordinated phosphine environment in the catalyst. We are also aware that some phosphine oxide contamination may be present and contribute to the NMR signals observed. The stoichiometry of the reaction certainly plays a role in determining the resulting catalyst, as shown in Scheme 3. When the molar ratio of $V/[Rh(\mu\text{-}Cl)(COD)]_2$ is 6:1 or higher, a Wilkinson catalyst analogue with three phosphines per rhodium atom may form. However, the coordinating phosphine may come from the same or different polymer chain. In order to reduce the possibility of cross linking of polymer chains, we have synthesized some catalysts with $V/[Rh(\mu\text{-}Cl)(COD)]_2$ ratios higher than 6:1. The catalysis results presented below are for the catalyst prepared with a 6:1 stoichiometric ratio of $V/[Rh(\mu\text{-}Cl)(COD)]_2$. Based on the elemental analysis results (vide infra), the conclusion was reached that the third structure, denoted 'VI' in Scheme 3, is the most reasonable arrangement of phosphine ligands around the rhodium. The appearance of two ^{31}P NMR signals in approximetaly a 2:1 intensity ratio is also consistent with this structure.

Spectrophotometric analysis was performed with electronic spectroscopy. Solutions of the $[Rh(\mu\text{-}Cl)(COD)]_2$ precursor were titrated with aliquots of V (FC113 solutions, 1,1,2-trichlorotrifluoroethane) and the titration was followed by UV–Vis absorption spectroscopy. The absorption spectra indicate the release of the COD ligand from the precursor and the formation of Rh–P adducts, as evidenced by new peaks at ca. 285 and 330 nm, which increase in intensity as a function of concentration of V and are not observed in FC113 solutions of the Rh precursor (λ_{max} ca. 350 nm) or the polymer ($\lambda_{max}<250$ nm) alone.

The solubility of the rhodium catalysts described above in $scCO_2$ were measured qualitatively. A stainless steel 8-mL reactor equipped with sapphire windows was used in both solubility and hydrogenation reaction studies. The windows allow the reactor interior to be visually monitored and enabled us to determine the phase of the reaction mixture. The cell was placed on a stir-plate, agitated by a magnetic stir bar and temperature was controlled with heating tape. In a typical experiment, a 5–10 mg catalyst sample was introduced through an opening on the top of the cell, a thermocouple was then connected and the cell was finally flushed then charged with CO_2. The catalyst completely dissolved and the mixture formed a single clear phase when the pressure and temperature reached super critical values. The qualitative solubility is 1.97×10^{-3} g cat./g CO_2.

1.1. Hydrogenation of 1-octene in $scCO_2$

Hydrogen gas is completely miscible with supercritical fluids such as $scCO_2$. Catalytic hydrogenation reactions in $scCO_2$ were performed in an 8-mL stainless steel reactor. Control hydrogenation experiments without the catalyst added were carried out with an identical amount of the substrate and under identical conditions. In a typical $scCO_2$ hydrogenation reaction experiment, the reactor was first charged with CO_2 to remove air inside the reactor. Then 1-octene (0.08 mL) and 5 mg of catalyst VI (Rh/1-octene molar ratio is 1:4000) were introduced to the reactor. Hydrogen gas was introduced (6.2 bar), then the reactor was heated to 60°C, and CO_2 was charged to 172 bar. The final temperature was adjusted to 70°C. The reaction was run for 12 h with continuous stirring. The system was cooled and depressurized slowly into a vial that contained hexanes. The samples were analyzed by gas chromatography. About 70% total conversion was obtained (Fig. 1). Although *n*-octane was the major product, we observed some isomerization mostly to 2-octene. Reasonable reproducibility was obtained (Fig. 1) among catalyst samples taken from three different batches, with duplicate hydrogenation experiments run for each batch.

2. Experimental

2.1. General

All syntheses were performed under an inert purified N_2 atmosphere using standard Schlenk techniques. All solvents were dried and distilled using standard procedures. Reagents were obtained from commercial sources and used without further purification. $[Rh(\mu\text{-}Cl)(COD)]_2$ was prepared following literature methods.[45] ^1H and ^{31}P NMR spectra were recorded on a Varian XL200E.

2.1.1. Synthesis of fluoroacrylate polymer III. 1*H*,1*H*,2*H*,2*H*-Heptadecafluorodecyl acrylate monomer (zonyl TAN) (I) was obtained from DuPont. A 11.0 g (21.2 mmol) sample of this monomer and 156 mg (1.063 mmol) of NASI were dissolved in 60 mL of trifluorotoluene. The Schlenk flask used was evacuated and flushed with N_2 three times and then fitted with a reflux condenser. Azobisisobutyronitrile, $(CH_3)_2C(CN)N{=}NC(CN)(CH_3)_2$, (AIBN), (1% of the total molar weight, 37.0 mg, 0.23 mmol) was added after heating to 95°C. The reaction was allowed to proceed for 48 h at 100°C under N_2 and was then cooled down to room temperature. The volume of the solution was reduced to 30 mL by vacuum and the copolymer (III) was precipitated by adding the solution into 80 mL of freshly distilled MeOH. The copolymer was isolated by filtration and dried under vacuum 5 h (7.70 g, 70% yield). The copolymer contains a fluoroacrylate/NASI ratio of 20:1, as calculated by integrating relevant peaks in the ^1H NMR spectra. ^1H NMR (300 MHz, FC113 with an external chloroform-*d* lock) δ 1.5–2.0 (br m, 1H); 2.5 (br m 4H); 2.9 (br s 4H); 4.4 (br s 2H). IR (KBr cm^{-1}) 3000 aliphatic C–H stretching, 1730–1800 C=O; 1200–1150 C–F. Elemental analysis: calc. for $C_{267}H_{147}O_{44}F_{340}N_1$: C, 30.43; H, 1.39; O, 6.69: F, 61.35; N, 0.13; Found: C, 29.88; H, 1.10; O, 6.19; F, 62.24; N, 0.13.

2.1.2. Synthesis of diphenylphosphinopropylamine-ligated fluoroacrylate polymer V. Copolymer III (2.2 g, 0.212 mmol) was dissolved in 35 mL of freshly distilled FC113. Molecular sieves were added to the solution, which was kept in the refrigerator overnight and then filtered through oven dried $MgSO_4$ to absorb any remaining water. Diphenylphosphinopropylamine, $NH_2(CH_2)_3PPh_2$ (DPPA) (237 mg, 1.058 mmol) was dissolved in 5 mL of CH_2Cl_2 and transferred via a syringe to the reaction vessel. 0.5 mL of triethylamine was then added to consume any unreacted NASI groups. The white compound was formed immediately and the solution was stirred for 3 h at room temperature in order to ensure the completeness of the reaction. The solvent was reduced to 5 mL under vacuum. The white product was completely precipitated into 50 mL of freshly-distilled MeOH and the product was isolated by filtration and dried for 6 h under vacuum. The product V was transferred into a N_2 flushed Schlenk tube and kept under N_2 until use. ^1H NMR (300 MHz, FC113 with an external chloroform-*d* lock) δ 1.5–2.0 (br m, 1H); 2.5 (br m 4H); 4.4 (br s 2H); 7.2–7.8 (br s 10H). ^{31}P NMR (121 MHz, solid) δ −16; 28 (<%15 intensity of −16 peak). Elemental analysis: calc. for $C_{248}H_{160}O_{41}F_{340}N_1P_1$: C, 31.31; H, 1.50; O, 6.16; N, 0.13; P, 0.29. Found: C, 30.97; H, 1.32; O, 6.00; N, 0.18; P, 0.20.

2.1.3. Synthesis of neutral rhodium complexes of the diphenylphosphinopropylamine-ligated flouroacrylate polymer VI. A 50 mL Schlenk flask was charged with 150 mg (0.0145 mmol) of copolymer V, 0.889 mg (1.8×10^{-3} mmol) of $[Rh(\mu\text{-}Cl)(COD)]_2$ and 20 mL of FC113. This mixture corresponds to a 1:6 molar ratio of $[Rh(\mu\text{-}Cl)(COD)]_2$/polymer. After stirring for 3 h under N_2 atmosphere, the solvent was removed under vacuum and the residue was taken up in 70 mL of MeOH, filtered and then washed with CH_2Cl_2 to remove any unreacted rhodium dimer. 112.5 mg of the product VI were obtained after vacuum drying (75% yield). ^{31}P NMR (121 MHz, external chloroform-*d* lock) δ −16.5; 29.6 and 66.9 broad peak. Elemental analysis: calc. for $C_{834}H_{480}O_{123}F_{1020}N_3P_3Cl_1Rh_1$: C, 31.17; H, 1.49; O, 6.13; N, 0.13; P, 0.29; Rh, 0.32. Found: C, 30.83; H, 1.35; O, 5.90; N, 0.20; P, 0.20; Rh, 0.24.

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