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The first fluorous biphase hydrogenation catalyst incorporating a perfluoropolyalkylether: [RhCl(PPh$_2$(C$_6$H$_4$C(O)OCH$_2$CF(CF$_3$)(OCF$_2$CF(CF$_3$))$_n$F))$_3$] with n = 4–9

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ABSTRACT

The phosphine oxide (4-diphenylphosphinyl) poly(hexafluoropropylene oxide) methylene benzoate [(C$_6$H$_5$)$_2$P(O)(C$_6$H$_4$C(O)OCH$_2$CF(CF$_3$)(OCF$_2$CF(CF$_3$))$_n$F] (with n = 4–9) **1**, was prepared by the reaction of [4-diphenylphosphinyl] benzoyl chloride with poly(hexafluoropropylene oxide) (pHFPO) methylene alcohol and triethylamine. Subsequent reduction of **1** with HSiCl$_3$ produced the phosphine **2**, (4-diphenylphosphino) pHFPO methylene benzoate, [(C$_6$H$_5$)$_2$P(C$_6$H$_4$C(O)OCH$_2$CF(CF$_3$)(OCF$_2$CF(CF$_3$))$_n$F]. The phosphine ligand **2** was incorporated into tris(4-diphenylphosphino) pHFPO methylene benzoate rhodium chloride **4**. Partition coefficients in perfluoromethylcyclohexane (PFMCH):toluene were determined using ^{19}F NMR spectroscopy for both **2** and **4** as 98:2 and 81:19, respectively. Compound **4** was also shown to function as a fluorous biphase catalyst, catalyzing the hydrogenation of 2-cyclohexen-1-one in biphasic (1:1 toluene:PFMCH; 1:3:3 toluene:hexanes:Krytox® K6 [F(CF(CF$_3$)CF$_2$O)$_5$CF$_2$CF$_3$]) and monophasic (1:3:3 toluene:hexanes:PFMCH) solvent systems with average turnover frequencies of 30.7, 17.1 and 20.6 h^{-1}, respectively. Rh leaching studies were undertaken to confirm the recycling ability of the catalyst **4** and the average percentage loss of Rh per cycle in the three solvent systems (1:1 toluene:PFMCH; 1:3:3 toluene:hexanes:Krytox® K6 [F(CF(CF$_3$)CF$_2$O)$_5$CF$_2$CF$_3$]; 1:3:3 toluene:hexanes:PFMCH) was determined to be 0.35%, 0.17% and 0.30%, respectively.

1. Introduction

Perfluoropolyalkylethers (PFPAEs) are polymeric or oligomeric compounds that consist of repeat units such as –[CF$_2$CF$_2$CF$_2$O]$_x$–, –[CF$_2$CF$_2$O]$_x$–, –[CF$_2$O]$_x$–or, as in this paper, –[OCF$_2$CF(CF$_3$)]$_x$– and are commercially available and recognized by such trade names as Demnum® (Daikin, Japan), Fomblin® (Solvay Solexis) and Krytox® (DuPont, USA) [1]. Examples of industrial applications of these fluids include use as hard disk lubricants, high temperature greases, vacuum pump fluids, hydraulic oils, aerospace jet engine oils, satellite instrumentation bearing greases, antilock braking system fluids, spark plug and boot lubricants, stone coatings, cosmetic additives and ski wax substitutes [2–5]. Furthermore the PFPAE employed herein, polyhexafluoropropylene oxide (pHFPO) with the repeat unit –[OCF$_2$CF(CF$_3$)]$_x$, has been used to extract porphyrins, heterocyclic bases and metal complexes into fluorous solvents through non-covalent interactions [6–8]. In this paper, consideration will be given to pHFPO and the extension of its applications to include utilization in a fluorous triarylphosphine suitable for Fluorous Biphase Catalysis (FBC).

While homogeneous catalysis offers many advantages over heterogeneous catalysis, such as selectivity and efficiency, the problem of separation and recycling of the catalyst remains a significant one. The potential of FBC as a solution to this problem was first proposed by Vogt in 1991 [9] and Horváth and Rábai in 1994 [10] and has advanced further since then, finding such applications as hydroboration [11], hydrosilylation [12,13], hydroformylation [10,14,15] and hydrogenation [16–19]. Furthermore, FBC has become an area of considerable interest within green chemistry [20–23] due to its focus on the recycling of catalysts. While the work described herein employs fluorous solvents in FBC, it may be noted that another green chemistry approach that has been investigated elsewhere is to utilize perfluoro-tagged catalysts in non-fluorous solvents such as methanol [24] and super-critical CO$_2$ [25].

FBC requires that the catalyst be preferentially soluble in the fluorous phase of a biphasic system, which then becomes monophasic at elevated temperatures (Fig. 1). Subsequent cooling returns the system to a biphasic state for facile separation.

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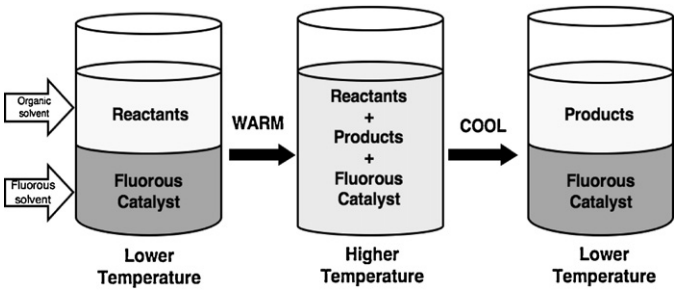


Fig. 1. The thermomorphic solubility of a FBC system.

In order to obtain the desired solubility properties of the catalyst, both trialkyl- and triaryl-phosphine ligands have been adapted to include perfluoroalkyl segments or fluorous 'ponytails'. However, the electron-withdrawing nature of the fluorous ponytails can also have the effect of lessening the coordinating ability of the phosphine ligand and can therefore require the presence of an 'insulator' or 'spacer' such as alkyl, silyl or $-(OCH_2)_n-$ groups.

Fig. 2 provides a sampling of various representative fluorinated phosphine ligands that have been prepared [16,18,24,26–36].

While considerable efforts have been made investigating the utility of various spacers, little consideration has been given to alternate fluorous ponytails, other than perfluoroalkyl chains. Such $-(CF_2)_x-$ chains (x = 3–10 typically) or telomers as they are also known, are typically derived from poly(tetrafluoroethylene) (pTFE). However a problem arises with such ponytails that when the chains are short they tend to be too soluble in the organic phase, while longer chains can display an undesired crystallinity [37], which lowers the absolute solubility in both phases. One attempt to deal with the problem of crystallinity has been to use Teflon® tape as means of catalyst recovery [38].

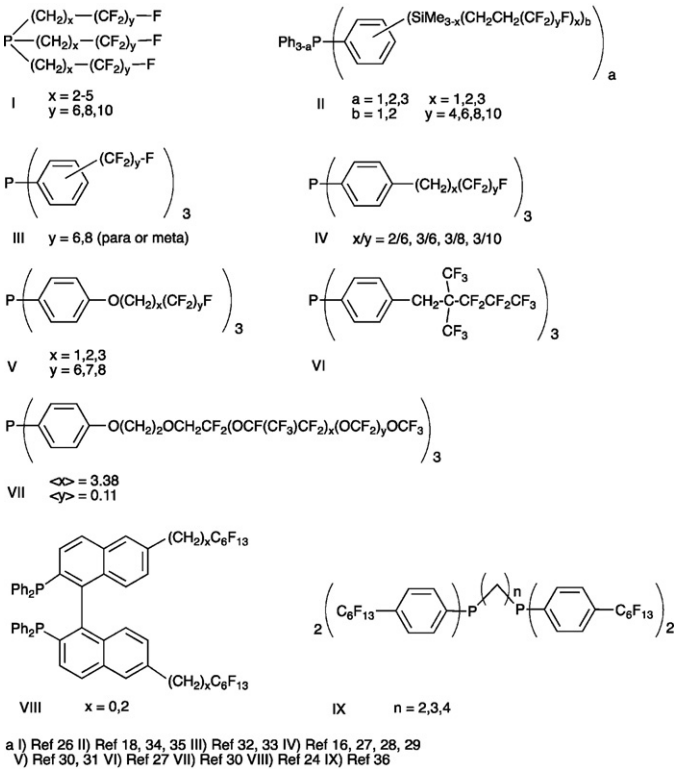


Fig. 2. Sampling of previously synthesized fluorous phosphine ligands. (I) Ref. [26], (II) Refs. [18,34,35], (III) Refs. [32,33], (IV) Refs. [16,27–29], (V) Refs. [30,31], (VI) Ref. [27], (VII) Ref. [30], (VIII) Ref. [24], (IX) Ref. [36].

An alternate strategy would be to employ a different fluorous moiety in the ponytail. Due to the potential effect on properties such as solubility, there has been interest expressed previously in the incorporation of heteroatoms such as oxygen into the ponytails, as in the case of a perfluoropolyalkylether (PFPAE) [39]. More specifically, the work reported herein was motivated by the thought that more flexible ponytails might lead to more favorable partition coefficients and that perhaps the desired flexibility might be obtained by employing PFPAE ponytails rather than perfluorotelomers. The addition of ether linkages disrupts the ability of the polymer to crystallize and allows for the polymer to remain liquid over longer chain lengths and broad temperature ranges. Specifically, pHFPO may be highly suited to this application due to its stability towards oxidation and thermal degradation; it is stable with low volatility and low temperature dependence of viscosity from −100 to 400 °C [40]. While PFPAEs have been incorporated into (non-phosphine) catalysts [41] and have been appended to (non-catalytic) phosphines [30,42,43], never have PFPAEs been incorporated into phosphines which were then employed for catalysis. As such this is the first report of incorporation of a PFPAE into a phosphine ligand to be employed in a catalyst.

Herein we report:

a) the synthesis and characterization of a triarylphosphine ligand that incorporates the perfluoropolyalkylether pHFPO with a $-C(O)OCH_2-$ spacer;
b) the preparation of a Wilkinson's catalyst derivative using this ligand;
c) partition coefficients for the ligand and the hydrogenation catalyst, along with Rh leaching studies;
d) its catalytic activity in the hydrogenation of 2-cyclohexen-1-one and the efficient recycling of the catalyst using fluorous biphase conditions.

The solvent systems used in the partition coefficient studies as well as the specific reaction conditions employed in the catalytic studies are similar to previous studies [16]; this was done in order to establish clear comparisons between perfluoroalkyl and perfluoropolyalkylether 'ponytails' regarding their potential utility in FBC.

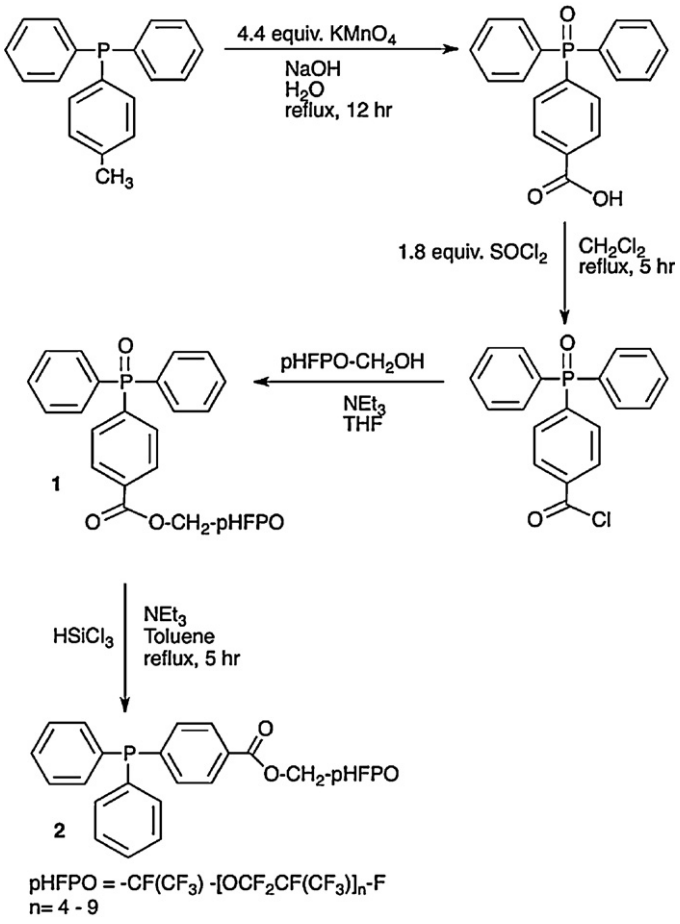
2. Results and discussion

2.1. Ligand synthesis

The synthetic route to the ligand (4-diphenylphosphino) pHFPO methylene benzoate **2** is shown in Scheme 1.

Starting from commercially available diphenyl [(4-methyl)-phenyl] phosphine, the carboxylic acid phosphine oxide (diphenyl [(4-carboxy)phenyl] phosphine oxide) is obtained by oxidation with $KMnO_4$, in the presence of NaOH [44]. In addition to the formation of the carboxylic acid in preparation for esterification, it was also necessary to oxidize the phosphorus centre due to its nucleophilicity. The compound was obtained in 85–97% yield and characterized by ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR, as well as FT-IR. IR bands at ~2700 cm^{-1} (O–H str.), 1706 cm^{-1} (C=O str.) and 1088 cm^{-1} (C–O str.), along with the deshielded ^{13}C nucleus at 166.8 ppm in the ^{13}C NMR confirmed the presence of the carboxylic acid, while the shift in the $^{31}P\{^1H\}$ NMR signal to 26.04 ppm (DMSO-d_6) confirmed that the phosphine had also been oxidized.

Subsequently, the carboxylic acid was converted to the acid chloride, 4-diphenylphosphinyl benzoyl chloride using $SOCl_2$ [45]. The FT-IR of the product no longer exhibited a band at ~2700 due to the –OH stretch, while bands were observed at 1774



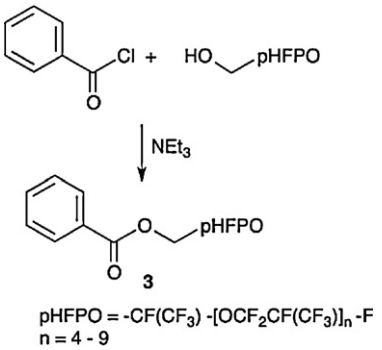
Scheme 1. Synthetic route to (4-diphenylphosphino) pHFPO methylene benzoate **2**.

and 1739 cm^{-1} corresponding to the C=O stretch of the acid chloride.

It was hoped that the acid chloride could then be readily converted to the ester by reaction with pHFPO-CH_2OH, but the feasibility of this reaction was first tested using a non-phosphine benzyl analogue. Benzoyl chloride was found to react with pHFPO-CH_2OH to give the ester, pHFPO methylene benzoate **3** (Scheme 2). No band corresponding to an O–H stretch appeared in the IR, but a C=O stretch at 1745 cm^{-1} was still present. In addition, a characteristic $^2J_{C-F}$ coupling of 33 Hz was observed in the ^{13}C NMR due to the methylene carbon, now appearing as a doublet at 58.39 ppm.

Given the success of the model reaction, pHFPO-CH_2OH (having an average molecular weight of 1150 g/mol with a homologue distribution of n = 4–9 based on GC/MS and ^{19}F NMR analysis) was then reacted with the acid chloride, 4-diphenylphosphinyl benzoyl chloride. This resulted in the ester, (4-diphenylphosphinyl) pHFPO methylene benzoate **1**. As in the case of the model reaction, the IR spectrum was lacking in a band due to an O–H stretch, while the C=O stretch appeared at 1745 cm^{-1}. Again in the ^{13}C NMR spectrum, the methylene carbon signal appeared as a doublet at 59.59 ppm with a $^2J_{C-F}$ coupling of 31.4 Hz. There was only one signal in the $^{31}P\{^1H\}$ NMR spectrum, a singlet at 25.89 ppm (in $CDCl_3$), consistent with a triarylphosphine oxide. Also MALDI-TOF-MS corroborated the lithium salts of $(C_6H_5)_2P(C_6H_4C(O)OCH_2CF(CF_3)(OCF_2CF(CF_3))_nF$ with n = 4–9 having peaks at 1124.9, 1290.9, 1456.8, 1622.8, 1788.8, 1954.8 g/mol.

The phosphine oxide **1** was then reduced to the desired ligand, (4-diphenylphosphino) pHFPO methylene benzoate **2**, a pale yellow viscous liquid, using $HSiCl_3$ and NEt_3 in toluene. The



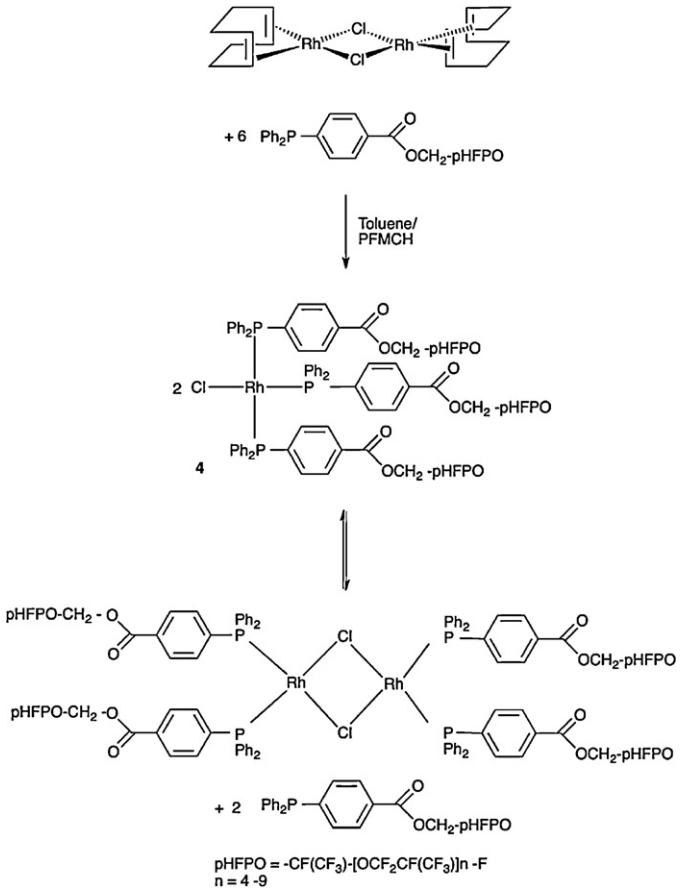
Scheme 2. Reaction to form the pHFPO ester analogue, **3**.

reduction was confirmed by the $^{31}P\{^1H\}$ in which the signal moved upfield to −3.75 ppm (in $CDCl_3$).

2.2. Synthesis of the Rh(I) hydrogenation catalyst

The synthesis of the Wilkinson's-type catalyst followed the biphasic method whereby a solution of **2** in perfluoromethylcyclohexane (PFMCH) was stirred for one day under N_2 with a toluene solution of $[RhCl(COD)]_2$ (Scheme 3).

Characterization of the resulting complex **4**, $[RhCl(PPh_2(C_6H_4R_F))_3]$ (where $R_F = C(O)OCH_2CF(CF_3)(OCF_2CF(CF_3))_nF$ with n = 4–9), a red oil, was accomplished primarily through $^{31}P\{^1H\}$ NMR. An AB_2X pattern consisting of a doublet of doublets at 31.7 ppm ($^1J_{PRh}$ = 143.1 Hz, $^2J_{PP}$ = 36.4 Hz, 2P) and a doublet of



Scheme 3. Synthesis of the fluorous Rh(I) hydrogenation catalyst **4** and the dimerization of **4**.

triplets at 47.66 ppm ($^1J_{PRh}$ = 187.8 Hz, $^2J_{PP}$ = 35.2 Hz, 1P) was observed. However a doublet appearing at 51.51 ppm (d, $^1J_{PRh}$ = 189.98 Hz) was suggestive of an equilibrium between **4** and a chloro-bridged dimer as shown in Scheme 3, as has been observed previously [16]. The signal due to the dimer appears in the room temperature $^{31}P\{^1H\}$ NMR spectrum in a ratio of approximately 1:12 with the monomer, but when the system is cooled to 273 K, the dimer signal is no longer present.

An excess of ligand **2** was used in this reaction, with any unreacted ligand being oxidized to the ligand oxide, **1**. It is not possible to remove this excess ligand oxide from the resulting product mixture, however it does not interfere with the catalysis.

2.3. Partition coefficients

Partition coefficients, indicating the relative affinity of the catalyst for the fluorous solvent, are obviously useful predictors in the effectiveness of a fluorous biphase catalytic system. It has been argued that a complex must have a fluorine content of >60% in order to display a preference for the fluorinated solvent [46]. However the results of Hope and co-workers [47] would suggest that the percentage of fluorous content is not as critical as the extent to which the fluorous portion of the compound is able to surround the organic core, an ability that presumably would be enhanced by using more flexible perfluoropolyalkylether 'ponytails' as in this study.

Partition coefficients were obtained by ^{19}F NMR spectroscopy at 25 °C in PFMCH/toluene; this solvent system and temperature were employed elsewhere [48] and was therefore chosen here for purposes of comparison. The results are shown in Table 1.

The ligand **2** displays a high ratio of 98:2 (P = 49) as it partitions between the fluorous and organic solvents respectively. This result compares favorably with those reported previously for ligands with perfluoroalkyl 'ponytails' R_f ($R_f = C_nF_{2n+1}$, n = 6, 8, 10) in the same solvent system (PFMCH/toluene), whether trialkyl phosphines $[R_f(CH_2)_x]_3P$ (x = 2–5), (with values ranging from 98.8:1.2 to >99.7:<0.3) [26,49] triarylphosphines with alkyl spacers $[R_f(CH_2)_xC_6H_4]_nPPh_{3-n}$ (x = 2, 3; n = 6,8,10) (with values ranging from 19.5:80.5 to 66.6:33.4) [16,25,27] or triarylphosphines with silyl spacers $[Ph_{3-n}P(C_6H_4\text{-}p\text{-}SiMe_{3-x}(CH_2CH_2R_f)_x)_n]$ (x = 1, 2, 3; n = 4, 6, 8, 10) (with values ranging from 21:79 to 89:<11) [18,34,35]. Deelman reports higher P values for triarylphosphines with silyl spacers (n = 4, 6, 8, 10) where the aryl ring substitutions are in the meta position or 3,5-disubstitution (with values of up to >238) [34].

Comparing the partition coefficients in these systems, it is noteworthy that ligand **2** does compare favorably with the triarylphosphines having perfluoroalkyl 'ponytails' with either alkyl or silyl spacers. This is true despite ligand **2** having a lower fluorous content compared with these other ligands, and only one fluorous "ponytail" per phosphine rather than more than one, such as ligands I–VII and IX in Fig. 2. For instance in the results cited above where Deelman [34] reports P values higher than those reported herein, it should be noted that those phosphine ligands possess 6, 9, 12 or 18 flourous ponytails per phosphine in contrast to the one ponytail per phosphine in the ligand reported here. While fluorous phosphine ligand 2 does not display the highest partition coefficient yet observed, nevertheless when allowing for the relatively low fluorous content of 2, these results indicate that phosphine ligands with perfluoropolyalkylether 'ponytails' do indeed have significant potential for improving partition coefficients in FBC presumably due to their flexible nature.

The partition coefficient for catalyst **4** was 81:19. To observe a decrease in the partition coefficient as the ligand coordinates to a metal centre, is not entirely unexpected since the fluorous content of the complex is less than that of the free ligand. Previous studies [47] have similarly suggested that in some cases the partitioning into the fluorous phase decreases upon complexation of the ligand to form the catalyst.

Of course it is important to note that the ultimate goal is not merely high partition coefficients, but the ability of the catalyst to be recycled and (as discussed below) catalyst **4** did in fact demonstrate good recycling ability. As for the apparent discrepancy between the lower partition coefficient values of the complex and its good recycling ability, one should note that the partition coefficients are determined using toluene and PFMCH but when the recycling of the catalyst takes place, the product molecule is also present in the organic phase; this may also alter the affinity of the catalyst for the organic phase. As a result, it was thought that rhodium leaching studies would be superior to partition coefficient determinations, as a method of determining the recycling ability of the catalyst. These studies are discussed later in the paper.

2.4. Catalytic hydrogenation and catalyst recycling

Once again for purposes of the comparison of perfluoropolyalkylether 'ponytails' with those featuring perfluoroalkyls, the hydrogenation reaction that was chosen to test the catalytic ability of **4** was the same as that employed in previous studies employing perfluoroalkyl moieties [16].

The hydrogenations were done using three solvent systems: 1:1 toluene:PFMCH and 1:3:3 toluene:hexanes:Krytox® K6 $[F(CF(CF_3)CF_2O)_5CF_2CF_3]$ that remain biphasic even at high temperatures and a solvent system (1:3:3 solution of toluene:hexanes:PFMCH) that becomes monophasic at 36.5 °C (as illustrated in Fig. 3). The results are shown in Table 2, including cycle by cycle TOF and average TOF values.

It may be noteworthy that in the biphasic 1:1 toluene:PFMCH system, the $t_{99\%}$ value for the first cycle is 22.22 h while the value drops significantly in subsequent cycles 2–6. It may be that this is indicative of an inductive period in which the actual catalyst is formed from the catalyst precursor.

In this study, catalyst **4** displayed turnover frequencies ($TOF_{99\%}$; product/catalyst mole ratio per hour calculated at 99% completion)

Table 1
Partition coefficients for the ligand **2** and the hydrogenation catalyst **4**.

Solute	Solvent system	Method	Percent partitioning fluorous:organic (P)
$[4\text{-Poly(HFPO)}_nCH_2OC(O)C_6H_4P(C_6H_5)_2]_3RhCl$ n = 4–9			
(Fluorine in catalyst = 52%)	$CF_3C_6F_{11}$:	^{19}F-NMR 25 °C	81:19 (±3)
Average MW ≈ 4452 g/mol	$CH_3C_6H_5$		(4.26)
$4\text{-Poly(HFPO)}_nCH_2OC(O)C_6H_4P(C_6H_5)_2$ n = 4–9			
(Fluorine in ligand = 54%)	$CF_3C_6F_{11}$:	^{19}F-NMR 25 °C	98:2 (±1)
Average MW ≈ 1438 g/mol	$CH_3C_6H_5$		(49)
$4\text{-Poly(HFPO)}_nCH_2OC(O)C_6H_4P(O)(C_6H_5)_2$ n = 4–9			
(Fluorine in ligand oxide = 53%)	$CF_3C_6F_{11}$:	^{19}F-NMR 25 °C	96:4 (±3)
Average MW ≈ 1454 g/mol	$CH_3C_6H_5$		(24)

Note: Percent partitioning was done in triplicate.

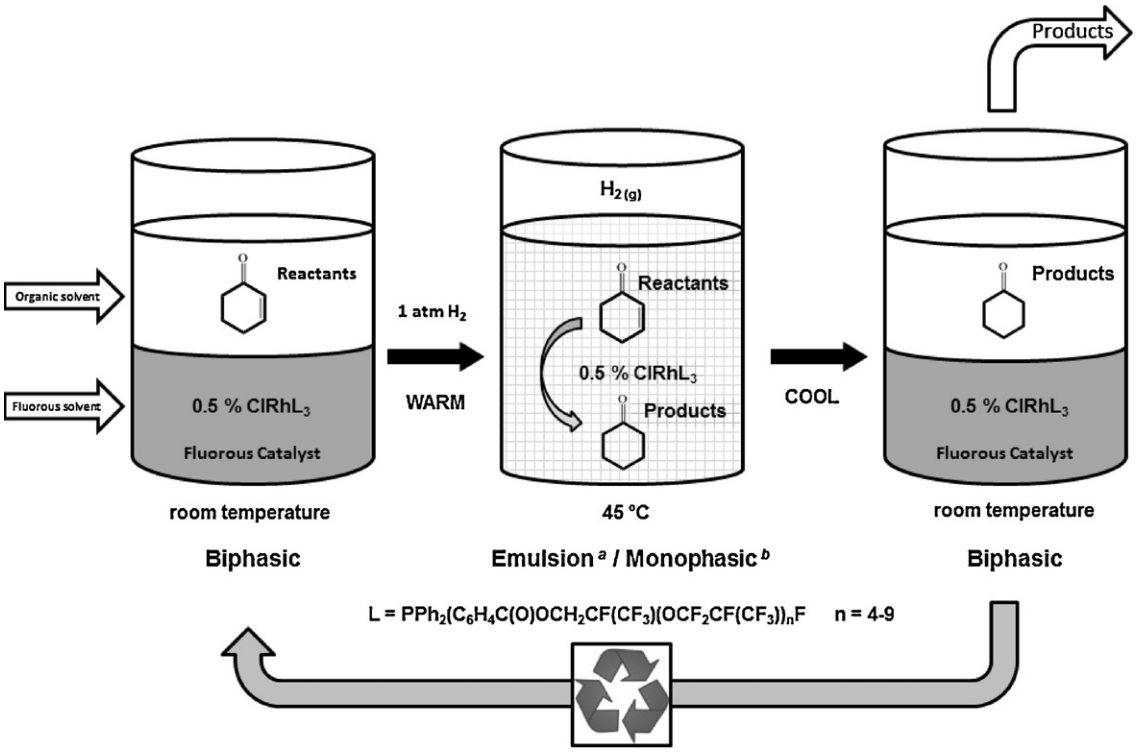


Fig. 3. Catalytic hydrogenation of cyclohexenone under biphasic (emulsion) and monophasic conditions. (a) Reaction 1 utilizes 1:1 toluene:PFMCH as the solvent system, Reaction 2 utilizes 1:3:3 toluene:hexanes:
Krytox® K6 [$F(CF(CF_3)CF_2O)_5CF_2CF_3$] as the solvent system. (b) 1:3:3 solution of toluene:hexanes:PFMCH.

Table 2
Hydrogenation data summary for monophasic and biphasic conditions.

Complex	Conditions	Cycle	$TOF_{99\%}$ (h^{-1})	$t_{99\%}$ (h)	AVG. TOF (± std. dev.)
Tris (4-diphenylphosphino pHFPO methylene benzoate) rhodium chloride	Biphasic	1	8.15	22.22	30.7 ± 6.8
	1:1 toluene: PFMCH	2	34.53	5.30	
		3	25.23	7.18	
		4	40.17	4.51	
		5	30.48	5.94	
		6	23.45	7.73	
Tris (4-diphenylphosphino pHFPO methylene benzoate) rhodium chloride	Biphasic	1	17.82	10.17	17.1 ± 2.0
	1:3:3 toluene:hexanes:	2	18.61	9.73	
	Krytox® K6 [$F(CF(CF_3)CF_2O)_5CF_2CF_3$]	3	14.80	12.24	
Tris (4-diphenylphosphino pHFPO methylene benzoate) rhodium chloride	Monophasic	1	21.83	8.30	20.6 ± 0.7
	1:3:3 toluene:hexanes:PFMCH	2	19.42	9.33	

of 30.7 h^{-1} in toluene:PFMCH, 17.1 h^{-1} in toluene:hexanes:Krytox®K6 and 20.6 h^{-1} in the monophasic toluene:PFMCH:hexanes system. Interestingly, the TOF values were superior in the biphasic toluene:PFMCH system compared to the monophasic toluene:PFMCH:hexanes system; Gladysz and co-workers [16] similarly reported higher TOF values in the biphasic system compared with a monophasic one. Nevertheless compound **4** does act as a true Fluorous Biphase Catalyst (Fig. 3) in toluene:PFMCH:hexanes and thereby demonstrates "proof of concept" and the successful application of PFPAEs in phosphine ligands for FBC catalysts.

The $TOF_{99\%}$ values for catalyst **4** reported in this study at 45 °C and 1 atm (30.7 h^{-1} in toluene:PFMCH; 17.1 h^{-1} in toluene:hexanes:Krytox®K6; 20.6 h^{-1} in the monophasic toluene:PFMCH:hexanes system) are comparable to both fluorous and non-fluorous Wilkinson's catalysts for the hydrogenation of cyclohexen-1-one. That is, when comparing to fluorous catalysts employing perfluoropolyalkyl 'ponytails' the $TOF_{99\%}$ values reported herein in biphasic conditions are less than those reported by Gladysz and co-workers [16] (47.5 h^{-1} in biphasic conditions at 45 °C and 1 atm H_2). However the values in this study obtained in monophasic conditions are in fact higher than those reported elsewhere for catalysts employing perfluoropolyalkyl analogues (8.25 h^{-1} in monophasic conditions at 45 °C and 1 atm H_2) [16]. When comparing to non-fluorous catalysts, the TOF value reported by Bezuidenhoudt and co-workers was somewhat higher (78 h^{-1}). However in that case, a higher temperature (80 °C) and pressure (10 bar) was employed [50].

As important as the TOF values, is the recycling ability of the catalyst since that is the critical feature of FBC. The system reported herein shows potential with respect to the recycling of the catalyst. Whether in biphasic or monophasic conditions, the catalyst was recycled and run through multiple hydrogenation cycles while exhibiting no significant trend of diminishing catalytic ability. This would seem to suggest that leaching of the catalyst into the organic phase is not significant here. For example, the highest TOF values were obtained in the final (third) cycle of the biphasic toluene:Krytox®K6:hexanes, and in the fourth cycle of the biphasic toluene:PFMCH system. When considering the standard deviations

Table 3
Determination of Rh leaching into the organic phase.

Conditions	Cycle	Rh in organic phase (μg)	% Rh loss	Avg. % Rh loss per cycle (± std. dev.)
Biphasic 1:1 toluene:PFMCH	1–8[a]	11.96	2.8	0.35
Biphasic	1	1.164	0.27	0.17 (± 0.09)
1:3:3 toluene:hexanes:Krytox® K6 [$F(CF(CF_3)CF_2O)_5CF_2CF_3$]	2	0.522	0.12	
	3	0.52	0.12	
Monophasic	1	2.102	0.49	0.30 (±0.26)
1:3:3 toluene:hexanes:PFMCH	2	0.5185	0.12	

[a] The organic phases from cycles 1–8 were combined in the 1:1 toluene:PFMCH biphasic system.

for the average TOF values, it should be noted that this study involves a homologue distribution (which varies from batch to batch due to the industrial manufacturing process). This may lead to consistency issues such as microdroplet size (in the case of the biphase systems). Nevertheless very little apparent diminishing of catalytic ability was observed with repeated recycling.

To further confirm the recycling ability of the catalyst, leaching studies were undertaken. After each catalytic cycle, the organic phase was removed and the solvent evaporated. The residue was then analyzed for rhodium by ICP-AAS. The results are shown in Table 3.

These results confirm that very little catalyst is lost into the organic phase with each catalytic cycle; the average percentage loss of Rh per cycle ranges from 0.17% to 0.35% in the three systems employed. Indeed the loss of Rh is significantly lower than that predicted by the partition coefficients, likely due to the fact that the conditions for partition coefficient determinations do not exactly match those of the catalytic cycles. The extent of Rh leaching found here using PFPAE ponytails (0.17–0.35% per cycle) is also comparable to that reported by Deelman and co-workers using perfluoroalkyl 'ponytails' (0.1–0.3%) [18,19].

3. Conclusions

For the first time, perfluoropolyalkylether moieties have been employed in a triarylphosphine ligand for Fluorous Biphase Catalysis. The partition coefficient values compare favorably to analogous ligands employing perfluoroalkyl 'ponytails', likely due to the flexibility of the perfluoropolyalkylethers. The resulting Wilkinson-type Rh(I) complex is thus not only able to catalyze the hydrogenation of 2-cyclohexen-1-one, but it also displays ability to be recycled. Rhodium leaching studies further support the strong ability of this catalyst to be recycled. While the partition coefficient and turnover frequency results reported herein, may not represent significant improvements on the state of the art, nevertheless they do suggest potential for such improvements with the introduction of a new class of Fluorous Biphase catalysts, those employing perfluoropolyalkylether 'ponytails'. It is hoped that other triarylphosphine ligands with other PFPEs, with more than one 'ponytail' per phosphine and having varying perfluoropolyalkyl ether lengths, fluorous content, insulator groups, and points of attachment will allow for the fine-tuning of these catalysts.

4. Experimental

4.1. General

All non-aqueous reactions were carried out under an atmosphere of nitrogen using oven- or flame-dried glassware, unless otherwise noted. All catalytic reactions were degassed prior to admitting hydrogen and were verified to be fully reproducible through several repetitions. Solvents were dried using standard methods, and oxygen was removed via freeze-pump-thawing. Hydrogen gas (Praxair, 5.0) was used as received. The identity of molecular compounds was checked by their solution-state NMR spectra, IR spectra where appropriate as well as mass spectrometry. Bruker AVANCE III 400 MHz, Bruker AVANCE III 500 MHz as well as Bruker AVANCE II 600 MHz "QNP 600" running TopSpin 2.1 were employed as required for obtaining solution-state NMR. For gas chromatography/mass spectrometry (GC/MS) analyses of the hydrogenation products an Agilent Technologies 6890N GC was coupled with an Agilent Technologies 7638B series injector and Agilent Technologies 5975B inert mass spectrometer detector (MSD) was employed with electron impact (EI) as the mode of ionization. All starting materials were commercially available, if not described below. Matrix assisted laser desorption ionization-time-of-flight mass spectrometry (MALDI-TOF-MS) experiments were determined with a Bruker Ultraflex with a positive ionization method. For sample preparation, samples were 1/50 diluted in perfluorokerosene. 1 μL of LiCl/MeOH (10 mg/mL) was deposited on the target first and dried, then 0.5 μL of sample solution was spotted on top of the LiCl layer and dried, and finally 0.5 μL of α-cyano-4-hydroxycinnamic acid (CCA) matrix was applied on top and dried. IR (attenuated total reflectance, ATR) spectra were recorded with a Thermo Nicolet 380 FT-IR instrument using ZnSe or Germanium crystals. All IR (KBr DRIFT) spectra were recorded with a Mattson Galaxy Series FT-IR 3000. The ICP-AAS analyses for the Rh leaching studies were performed by Canadian Microanalytical Services, Ltd.

4.2. Preparation of diphenyl [4-carboxyphenyl] phosphine oxide

In a typical synthesis $KMnO_4$ (22.161 g, 140 mmol) was added in 4 portions to a solution of diphenyl [(4-methyl)phenyl] phosphine (Aldrich, 96%) (10.083 g, 32 mmol), water (130 mL) and NaOH (2.220 g, 56 mmol). The mixture was allowed to reflux for 12 h, after which point the hot brown suspension was filtered. The residual MnO_2 was washed with hot water. The filtrate was acidified with 50% H_2SO_4 precipitating out the crude white product that was collected and dissolved in 10% NaOH and extracted with Et_2O to remove residual starting material. The aqueous phase was again treated with 50% H_2SO_4 re-precipitating the desired white product. The product was collected via filtration and dried in a vacuum oven at 75 °C yielding the product as a white powder (9.980 g, 31 mmol, 97%). Alternatively: p-tolyldiphenylphosphine (Aldrich, 96%) (2.142 g, 7.75 mmol), pyridine (15 mL) and H_2O (50 mL) were added to a 250 mL three neck round-bottom flask equipped with magnetic stir bar, condenser and N_2 blanket and heated to approximately 70 °C. $KMnO_4$ (6.224 g, 39.4 mmol) were added in 5 small portions at 30 min intervals. Following the last addition, solution temperature was raised to 90 °C and allowed to stir for 20 h (reflux). The hot suspension was filtered, and the residual MnO_2 washed with hot water. The filtrate was cooled to room temperature and acidified in an ice bath using concentrated HCl to precipitate the crude product. ^{1}H NMR indicated incomplete oxidation and so was reoxidized in water (60 mL), KOH (0.484 g,

8.62 mmol) and $KMnO_4$ (1.630 g, 10.3 mmol) and allowed to reflux overnight. The suspension was filtered while hot and the resulting filtrate was cooled on an ice bath and acidified using concentrated HCl precipitating out the crude product. The white solid was filtered using Whatman #40 filter paper and washed with cold deionized water affording the product (2.018 g, 6.26 mmol, 80%) as white crystals. ^{1}H NMR (600 MHz, DMSO-d_6, 25 °C): δ = 8.11 (dd, ^{3}J = 8.5 Hz, ^{4}J = 2.3 Hz, 2H), 7.78 (dd, $^3J_{HP}$ = 11.4 $^3J_{HH}$ = 8.5 Hz, 2H), 7.71–7.65 (m, 6H) 7.55 (td, ^{3}J = 8.3 Hz, ^{4}J = 3.0, 4H); ^{13}C NMR (151 MHz, DMSO-d_6, 25 °C): δ = 166.61 (s, C=O), 137.32 (d, $^1J_{CP(ipso)}$ = 99.7 Hz), 133.86 (d, $^4J_{CP(para)}$ = 2.7 Hz), 132.22 (d, $^4J_{CP(para)}$ = 2.4 Hz), 132.03 (d, $^1J_{CP(ipso)}$ = 103.2 Hz), 131.79 (d, $^2J_{CP(ortho)}$ = 10.0 Hz), 131.48 (d, $^2J_{CP(ortho)}$ = 9.8 Hz), 129.36 (d, $^3J_{CP(meta)}$ = 11.9 Hz), 128.83 (d, $^3J_{CP(meta)}$ = 11.8 Hz); ^{31}P{^{1}H} NMR (242.88 MHz, DMSO-d_6, 25 °C): δ 26.04 (s, P=O); FT-IR (KBr DRIFT): ν = 3060 (aromatic C–H stretch); 2885, 2764, 2597, 2475 (COOH split OH stretch); 1706 (C=O stretch); 1255 (P=O), 1156, 1109, 695 (st, mono-sub. arom. C–H out-of-plane bend) cm^{-1}.

4.3. Preparation of [4-diphenylphosphinyl] benzoyl chloride

The synthesis was accomplished according to the method of El-Deek et al. [45]. To a stirred solution of DCM (30 mL) and diphenyl [4-carboxyphenyl] phosphine oxide (0.642 g, 1.99 mmol), $SOCl_2$ (0.416 g, 3.50 mmol) was added via syringe and refluxed for 5 h. Following 3 h of reflux, the solution changed from a turbid white suspension to a clear colorless solution. The solution was allowed to cool to room temperature and evaporated under nitrogen and finally the volatiles pumped off under reduced pressure affording the product as an off-white solid (0.671 g, 1.97 mmol, 99%). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) δ = 7.52 (td, J = 7.8, 2.7 Hz, 4H), 7.61 (t, J = 7.5 Hz, 2H), 7.68 (dd, J = 12.2, 7.5 Hz, 4H) 7.87 (dd, $^3J_{HP}$ = 11.3 Hz, $^3J_{HH}$ = 8.4 Hz, 2H), 8.23–8.19 (d, 2H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ = 167.93 (s, C = O), 139.96 (d, $^1J_{CP(ipso)}$ = 99.1 Hz), 136.07 (d, $^4J_{CP(para)}$ = 2.8 Hz), 132.68 (d, $^4J_{CP(para)}$ = 8.3 Hz), 132.38 (d, $^1J_{CP(ipso)}$ = 102.2 Hz), 132.20 (d, $^2J_{CP(ortho)}$ = 10.3 Hz), 132.08 (d, $^2J_{CP(ortho)}$ = 10.1 Hz), 130.96 (d, $^3J_{CP(meta)}$ = 12.0 Hz), 128.89 (d, $^3J_{CP(meta)}$ = 12.5 Hz); ^{31}P{^{1}H} NMR (242.88 MHz, $CDCl_3$, 25 °C): δ = 29.954 (s, P=O); IR(KBr Drift): ν = 3055, 1774 (C=O), 1739 (C=O), 2846, 1593, 1437 (st), 1393 (P-Phenyl), 1202 (st), 1116 (st), 721 (st), 695 (st, mono-sub. arom. C–H out-of-plane bend), 539 cm^{-1}.

4.4. Preparation of (4-diphenylphosphinyl) pHFPO methylene benzoate (1)

To a stirred solution of pHFPO methylene alcohol (4.00 g, 3.48 mmol) and triethylamine (1.795 g, 17.4 mmol), [4-diphenylphosphinyl] benzoyl chloride (3.814 g, 11.2 mmol) and dry THF (8 mL) were added yielding a peach colored solution. The solution was allowed to stir for 12 h at room temperature and was then diluted with 20 mL of Freon I E-fluid [$F(CF(CF_3)CF_2O)CFHCF_3$]. The resulting peach-coloured opaque mixture was extracted with several portions of 70/30 solution of CH_3CN/H_2O until no more color was apparent in the organic phase. The resulting peach colored fluorous phase was collected, dried over $MgSO_4$ and the solvent was removed under reduced pressure affording **1** as a very viscous colorless liquid (72%). MALDI-TOF-MS $[M + 166n + Li]^+$ = 1124.9 (n = 4), 1290.9 (n = 5), 1456.8 (n = 6), 1622.8 (n = 7), 1788.8 (n = 8), 1954.8 (n = 9). ^{31}P{^{1}H} NMR (242.92 MHz, $CDCl_3$, 25 °C): δ = 25.89 (s, P=O); IR (ATR): ν = 1745 (C=O), 1312, 1228, 1114, 981, 806, 749, 710 cm^{-1} ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): 4.91 (dq, $^3J_{H-F}$ = 24.1 Hz, $^4J_{H-F}$ = 14.0 Hz, 2H, –O**CH$_2$**CF(CF_3)–), 7.5 (m, 4H), 7.59 (t, ^{3}J = 6.5 Hz, 2H), 7.68 (m, 4H), 7.82 (t, ^{3}J = 10.1 Hz, 2H) 8.12 (d, ^{3}J = 8.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C) δ = 163.85 (s, C=O), 139.08 (d, $^1J_{CP(ipso)}$ = 100.0 Hz), 132.40 (m, not clearly resolvable, overlapping ortho and para signals), 132.03 (d, $^2J_{CP(ortho)}$ = 10.1 Hz), 132.02 (d. br. $^4J_{CP(para)}$ = 2.9 Hz), 131.48 (d, $^1J_{CP(ipso)}$ = 103.8 Hz), 129.66 (d, $^3J_{CP(meta)}$ = 12.0 Hz), 128.72 (d, $^3J_{CP(meta)}$ = 12.2 Hz), 117.35 (qd, $^1J_{CF}$ = 288.3, $^2J_{CF}$ = 31.0, –OCF_2CF(**CF_3**)–), 115.75 (td, $^1J_{CF}$ = 287.8, $^2J_{CF}$ = 31.9, –O**CF_2**$CF(CF_3)$–), 106.88 (dq,$^1J_{CF}$ = 251.6 Hz, $^2J_{CF}$ = 35.6 Hz, –CH_2CF(**CF_3**)O–) 102.37 (ds, $^1J_{CF}$ = 272.8 Hz, $^2J_{CF}$ = 38.0 Hz, –**CF**(CF_3)O–), 60.27 (d, $^2J_{CF}$ = 31.2 Hz, –**CH_2**$CF(CF_3)$O–); ^{19}F NMR (376.41 MHz, $CDCl_3$, 25 °C): δ = −146.22 (–OCF_2**CF**(CF_3)–), −135.18 (–CH_2**CF**(CF_3)–), −134.73, −131.04 (–OCF_2**CF_2**CF_3), −84.26, −84.12, −82.81 (–**CF_2**–), −81.44(–**CF_3**); IR (ATR) ν = 3049 (arom. C–H), 1747 (C=O), 1308 (C–F), 1232, 1198, 1118, 985, 806, 730, 696 (st, mono-sub. arom. C–H out-of-plane bend) cm^{-1}.

4.5. Preparation of (4-diphenylphosphino) pHFPO methylene benzoate (2)

To a stirred solution of toluene (35 mL) and $HSiCl_3$ (0.557 g; 0.415 mL; 4.11 mmol) under N_2, (4-diphenylphosphinyl) pHFPO methylene benzoate (1.196 g; 0.0822 mmol) was added. Triethylamine (0.633 mL; 0.459 g; 4.54 mmol) was added via syringe and the solution was heated to reflux for 5 h. Following the reflux period, the excess $HSiCl_3$ as well as approximately half of the toluene was removed under reduced pressure. Saturated $NaHCO_3$ (3 mL) was added and the mixture was allowed to stir for 5 min, and filtered through diatomaceous earth (Celite). The RBF and residual SiO_2 were washed with several portions of toluene (∼10 mL) and Freon I E-fluid [$F(CF(CF_3)CF_2O)CFHCF_3$] fluorinated solvent. The fluorous phase was collected and dried over $MgSO_4$ and the solvents were removed in vacuo. The reduced product **2** was collected as a pale yellow viscous liquid (80–84% based on average molecular weight). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 4.89 (dq, $^3J_{H-F}$ = 26.3, $^4J_{H-F}$ = 13.4, 2H, –O**CH_2**$CF(CF_3)$–), 7.38 (m), 7.51 (m), 7.61 (m), 7.70 (m), 7.84 (m), 7.98 (m), 8.14 (m); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.50 (s, C=O), 146.09 (d, J = 15.6 Hz, unassigned), 135.95 (d, $^1J_{CP(ipso)}$ = 10.6 Hz), 134.07 (d, $^2J_{CP(ortho)}$ = 20.2 Hz), 133.29 (d, $^2J_{CP(ortho)}$ = 18.6 Hz), 132.40 (s, $CP_{(para)}$), 132.09 (d, $^1J_{CP(ipso)}$ = 10.0 Hz), 129.70 (d, $^3J_{CP(meta)}$ = 6.1 Hz), 129.55 (s, unassigned), 128.77 (d, $^3J_{CP(meta)}$ = 7.1 Hz), 127.86 (s, $CP_{(para)}$), 116.90 (qd, $^1J_{CF}$ = 289.5, $^2J_{CF}$ = 31.9, –OCF_2CF(**CF_3**)–) 115.42 (td, $^1J_{CF}$ = 289.04, $^2J_{CF}$ = 33.9, –O**CF_2**$CF(CF_3)$–), 107.69 (m, –CF_2**CF_2**CF_3), 106.00, 102.14 (ds, $^1J_{CF}$ = 271.6 Hz, $^2J_{CF}$ = 37.40, –**CF**(CF_3)–), 59.59 (d, $^2J_{CF}$ = 31.4 Hz); ^{31}P{^{1}H} NMR (242.92 MHz, $CDCl_3$, 25 °C): δ = −3.75 (s, P:), 28.82 (s, P=O impurity); ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$, 25 °C): δ = −146.3 (–OCF_2**CF**(CF_3)–), −134.89 (–CH_2**CF**(CF_3)–), −131.25 –OCF_2 **CF_2**CF_3), −84.38, −84.25, −82.98 (–**CF_2**–), −81.60 (–**CF_3**); IR (ATR): ν = 3060 (ar. C–H); 1741 (C=O), 1304, 1224, 1117 (pHFPO C–F), 983, 803, 749, 696 (monosub. arom. C–H out-of-plane oop. bend) cm^{-1}.

4.6. Preparation of pHFPO methylene benzoate (3)

To a stirred solution of pHFPO methylene alcohol (1.982 g, 1.72 mmol) and triethylamine (0.347 g, 3.43 mmol), benzoyl chloride (0.472 g, 3.46 mmol) was added resulting in a thick white paste. The mixture was extracted with several portions of 50/50 solution of H_2O/CH_3CN affording **3** as a viscous colorless liquid. ^{1}H NMR (60 MHz, NEAT, 25 °C): δ = 4.2 (br. d, 2H, $^3J_{H-F}$ not clearly resolved, –C(O)O–**CH_2**$CF(CF_3)$–)–, 6.74–7.36 (m, 5H, ArH); ^{13}C NMR (15.089 MHz, NEAT, 25 °C): δ = 58.39 (d, $^2J_{C-F}$ = 33 Hz.), {87.88, 90.07, 92.46, 95.41, 97.96, 100.47, 102.61, 106.98, 109.04, 110.74, 113.05, 115.48, 117.22} (F[$CF(CF_3)CF_2O$]–), 126.56, 128.30, 129.60, 132.83, 136.59, 145.21, 147.32, 163.82 (C=O) ppm; ^{19}F NMR (56.45 MHz, NEAT, 25 °C): δ = −146.21 (–OCF_2**CF**(CF_3)–), –135.14

(–CH_2**CF**(CF_3)–), −131.49 (–OCF_2**CF_2**CF_3), −84.29, −83.53 (–**CF_2**–), −81.77 (–**CF_3**); IR (ATR): ν = 1745 (C=O), 1312, 1228, 1114, 981, 806, 749, 710 cm^{-1}; GC/MS (EI 70 eV): m/z = 235 ($C_6H_5C(O)OCH_2CF(CF_3)^+$), 169 ($CF_3CF_2CF_2^+$), 135 ($C_6H_5C(O)O^+$), 105 ($C_6H_5CO^+$), 77 ($C_6H_5^+$), 69 ($CF_3^+$).

4.7. Preparation of tris (4-diphenylphosphino) pHFPO methylene benzoate rhodium chloride (4)

The synthesis was accomplished according to the procedure of Gladysz et al. [16]. Degassed (4-diphenylphosphino) pHFPO methylene benzoate (1.102 g, 0.766 mmol) was dissolved in degassed PFMCH (10 mL) in a 50 mL 3-neck RBF in a glovebox (Solution 1). Solution 2, a degassed solution of cyclooctadiene rhodium chloride dimer [Rh(COD)(μ-Cl)]$_2$ (0.0629 g, 0.091 mmol) in toluene (7.5 mL) was added to solution 1 in the glovebox and allowed to stir for 1 day. Following the stirring period, the upper organic layer was decanted. The lower fluorinated phase was washed once with 2 mL of dry degassed toluene and the volatiles from the fluorinated layer were removed in vacuo affording **4** as a red oil (52% yield by $^{31}P\{^1H\}$ NMR). $^{31}P\{^1H\}$ NMR (202.43 MHz, $CDCl_3$, 25 °C): δ = 31.7 (dd; $^1J_{PRh}$ = 143.1 Hz, $^2J_{PP}$ = 36.4 Hz, 2P), 47.66 (dt, $^1J_{PRh}$ = 187.8 Hz, $^2J_{PP}$ = 35.2 Hz, 1P), 51.51 (d, $^1J_{PRh}$ = 190.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 60.13 (d, $^2J_{C-F}$ = 30.1 Hz); 128.3; 128.6; 128.8; 129.6; 129.7; 132.0; 132.1; 132.3; 132.4; 132.44; 163.9 (C=O); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.82 (dq, $^3J_{HF}$ = 25.3 Hz, $^4J_{HF}$ = 13.3 Hz, 2H), 7.39–7.44 ppm (m, 4H) 7.49–7.62 ppm (m, 6H), 7.71–7.76 (m, 2H), 8.01–8.04 (m, 2H); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, 25 °C): δ = −145.09 (m, –OCF_2**CF**(CF_3)–), −133.9 (m), −133.5 (m), −129.8 (m, –OCF_2**CF_2**CF_3), −83.01, −82.87 (–**CF_2**–), −81.53, −80.70, −80.19 (–**CF_3**); IR(ATR): ν = 1744 (C=O stretch); 1307, 1234, 1197, 1115 (pHFPO C–F stretches), 976 (st), 743, 696 (monosub. arom. C–H out-of-plane bend) cm^{-1}.

4.8. Partition coefficients

The following is representative of the partition coefficient protocol. In a glovebox, a 5 mL vial was charged with 2 mL of a PFMCH solution containing 0.038 g of tris(4-diphenylphosphino) pHFPO methylene benzoate. To the vial, 2 mL of dry degassed toluene were added. The vial was sealed with a compression cap fitting, wrapped with Parafilm, vigorously shaken for 20 minutes and placed in a constant temperature bath at 25 °C for 48 hours and allowed to equilibrate. Following the 48 h equilibration period, a 0.50 mL aliquot was removed from each phase (organic and fluorous) and transferred to separate Wilmad external coaxial NMR tubes. A coaxial stem insert containing a 10% (v/v) α,α,α-trifluorotoluene in toluene solution was inserted as the external standard. The samples were analyzed by ^{19}F NMR (integration of the signal at −62.39 ppm corresponding to the external standard α,α,α-trifluorotoluene against the multiplet at −146.3 ppm for ligand **3** and at −145.09 ppm for catalyst **4**, corresponding to the (–OCF_2**CF**(CF_3)–) of the pHFPO fluorous tail). The procedure was repeated in triplicate, giving an average partition coefficient.

4.9. Rh leaching studies

At the conclusion of each catalytic cycle, the organic phase was removed and the solvent was allowed to evaporate. The rhodium content was then determined by ICP-AAS. In the case of the 1:3:3 toluene:hexanes:Krytox®K6 [$F(CF(CF_3)CF_2O)_5CF_2CF_3$] biphasic system and the PFMCH:hexanes:toluene monophasic system, the organic phase was analyzed after each cycle. In the case of the PFMCH:toluene biphasic system, the organic phases for all eight cycles were combined and analyzed for the rhodium content.

4.10. Catalytic hydrogenation

4.10.1. Biphasic conditions (1:1 toluene:PFMCH)

These conditions were selected to allow for comparisons with Soós and Gladysz' catalysts described earlier. The following is representative and is illustrated in Fig. 3 (Reaction 1). In an inert atmosphere glovebox, a glass 3-necked 6 mL reactor with J-young valves equipped with a small magnetic stir bar and hydrogenation balloon was charged with 2 mL of a degassed PFMCH solution containing tris-pHFPO-modified triarylphosphine rhodium chloride (0.019 g, 4.20E−03 mmol, 0.5 mol%). To this solution, 2 mL of dry, degassed toluene was added as well as 74 μL of degassed 2-cyclohexen-1-one. The reactor was sealed and removed from the glovebox and the contents degassed via freeze-pump-thaw method. The system was backfilled with hydrogen and set in a 45 °C constant temperature water bath. The biphasic system was vigorously stirred and the reaction's progress was analyzed via GC/MS (3.0 h, 50% conversion to cyclohexanone; 6.1 h, 99% conversion). Upon completion of the reaction, the contents of the reactor were degassed and returned to the glovebox. The organic phase was removed via pipette and the vial recharged with a fresh aliquot of substrate (74 μL) and toluene (2 mL). This was repeated through 6 cycles for a total of 1096 turnovers. A seventh cycle was run, raising the temperature in an attempt to render the system monophasic, however the catalytic activity dropped. An eighth cycle was then employed to test if the heating had caused the catalyst to degrade. These last two cycles were not included in the TOF determinations.

4.10.2. Biphasic conditions (1:3:3 toluene:hexanes:Krytox®K6 [$F(CF(CF_3)CF_2O)_5CF_2CF_3$])

The following is representative and is illustrated in Fig. 3 (Reaction 2). In an inert atmosphere glovebox, a glass 3-necked 6 mL reactor with J-young valves equipped with a small magnetic stir bar and hydrogenation balloon was charged with 2 mL of a degassed PFMCH solution containing tris-pHFPO-modified triarylphosphine rhodium chloride (0.01936 g, 4.20E−03 mmol, 0.5 mol%). The PFMCH was removed in vacuo and 2 mL of Krytox®K6 [$F(CF(CF_3)CF_2O)_5CF_2CF_3$] was added to the reaction flask. To this solution, 2 mL of dry, degassed hexanes was added, 0.7 mL of dry, degassed toluene, as well as 74 μL of degassed 2-cyclohexen-1-one. The reactor was sealed and removed from the glovebox and the contents degassed via freeze–pump-thaw method. The system was backfilled with hydrogen and set in a 45 °C constant temperature water bath. The biphasic system was vigorously stirred and the reaction's progress was analyzed via GC/MS (4.1 h, 50% conversion to cyclohexanone; 10.7 h, 99% conversion). Upon completion of the reaction, the contents of the reactor were degassed and returned to the glovebox. The organic phase was removed via pipette and the vial recharged with a fresh aliquot of substrate (74 μL) and toluene (2 mL). This was repeated through 3 cycles for a total of 548 turnovers with no apparent catalyst loss.

4.10.3. Monophasic conditions

The monophasic conditions were achieved using a solvent system comprising a 1:3:3 solution of toluene:hexanes:PFMCH as illustrated in Fig. 3. In an inert atmosphere glovebox, a glass 3-necked 6 mL reactor with J-young valves equipped with a small magnetic stir bar and hydrogenation balloon was charged with 2.14 mL of a PFMCH solution containing tris-pHFPO-modified triarylphosphine rhodium chloride (0.019 g, 4.20E−03 mmol, 0.5 mol%), this was a bright orange solution. To this solution, 2.14 mL of dry, degassed hexanes, 0.7 mL of dry, degassed toluene as well as 74 μL of degassed 2-cyclohexen-1-one were added. The reactor was sealed and removed from the glovebox and the contents degassed via freeze–pump-thaw method. The system was

backfilled with hydrogen and set in a 45 °C constant temperature water bath. The monophasic system was vigorously stirred and the reaction's progress was analyzed via GC/MS (3.5 h, 50% conversion to cyclohexanone; 8.8 h, 99% conversion). Upon completion of the reaction, the contents of the reactor were degassed and returned to the glovebox. The organic phase was removed via pipette and the vial recharged with a fresh aliquot of substrate (74 μL) and toluene (2 mL). This was repeated through 2 cycles for a total of 366 turnovers with no apparent catalyst loss.

4.10.4. Calculation of turnover frequencies

For each cycle, a 2nd order polynomial fit of the data was used to calculate the time taken to reach 99% completion. The $TOF_{99\%}$ value was then calculated from that time. The R^2 correlation for the 2nd order polynomial fit was 0.986 or greater in all cases. The average TOF value reported is the average $TOF_{99\%}$, averaged over all cycles (with the exception of the 1:1 toluene:PFMCH biphasic system where the first cycle was not included in the average calculation, as it clearly represented an induction period).

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