Synthesis, Reactivity, and Metal Complexes of Fluorous Triarylphosphines of the Formula $P(p\text{-}C_6H_4(CH_2)_3(CF_2)_{n-1}CF_3)_3$ (n = 6, 8, 10)

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Reactions of p-$BrC_6H_4CH{=}O$ with Wittig reagents derived from $[Ph_3PCH_2CH_2R_{fn}]^+I^-$ (R_{fn} = $(CF_2)_{n-1}CF_3$; n = 6 (**6a**), 8 (**6b**), 10 (**6c**)) give p-$BrC_6H_4CH{=}CHCH_2R_{fn}$ (86−93%), which are treated with H_2 and Wilkinson's catalyst to yield p-$BrC_6H_4(CH_2)_3R_{fn}$ (91−94%). Reactions with n-BuLi and PCl_3 (0.33 equiv) give, after workup, mixtures of the title compounds (**9a**−**c**) and the corresponding phosphine oxides (**10a**−**c**). Treatment with H_2O_2 gives pure **10** (**a**/**b**/**c** 88/57/24%), which are reduced with Cl_3SiH/Et_3N to **9** (**a**/**b**/**c** 69/82/43%). Fluorous phase affinities increase with perfluoroalkyl chain length, as quantified by $CF_3C_6F_{11}$/toluene partition coefficients (**9a**, 19.5:80.5; **9b**, 66.6:33.4). Reaction of **9b**, $[Ir(COD)(\mu\text{-}Cl)]_2$, and CO gives *trans*-$Ir(CO)(Cl)[P(p\text{-}C_6H_4(CH_2)_3R_{f8})_3]_2$ (76%). The IR ν_{CO} value is only slightly greater than that of Vaska's complex (1958 vs 1952 cm^{-1}), indicating nearly negligible inductive effects of the perfluoroalkyl groups. Reaction of **9b** and $[Rh(COD)(\mu\text{-}Cl)]_2$ yields $Rh[P(p\text{-}C_6H_4(CH_2)_3R_{f8})_3]_3(Cl)$ (82−93%), which gives small equilibrium amounts of $[Rh[P(p\text{-}C_6H_4(CH_2)_3R_{f8})_3]_2(\mu\text{-}Cl)]_2$ and **9b** in solution, and catalyzes the hydrogenation of alkenes under both biphasic ($CF_3C_6F_{11}$/toluene) and monophasic ($CF_3C_6H_5$) conditions.

Introduction

The development of catalysts that have high affinities for "fluorous" phases has proceeded rapidly since Horváth and Rábai described the concept and successful application of "fluorous biphase catalysis" in 1994.[1,2] This technique makes use of (1) the temperature-dependent miscibility of organic solvents with perfluorocarbons, perfluoroethers, or perfluoroamines,[3] and (2) "pony tails" of the formula $(CH_2)_m(CF_2)_{n-1}CF_3$ (abbreviated $(CH_2)_mR_{fn}$), which when added to catalysts in sufficient numbers provide exceptional degrees of fluorous phase immobilization. Reactions can be conducted in mixtures of organic and fluorous solvents under monophasic conditions at higher temperatures, and the products (which normally have much greater affinities for the organic solvent) separated from the fluorous catalyst under biphasic conditions at lower temperatures. The recovered catalyst solution is then directly reused.

Most of the fluorous metal catalysts developed to date feature fluorous phosphines.[1,4−7] This has in turn

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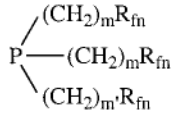
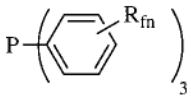
Chart 1. Previously Reported Fluorous Phosphines ($R_{fn} = (CF_2)_n{-}_1CF_3$)



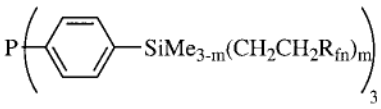
1

m = m' = 2; n = 6,8,10[8a]
m = m' = 3-5; n = 8[8b]
m/m' = 2/3, 3/2, 3/4, 4/3; n = 8[8b]



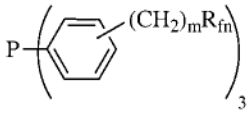
2

para: n = 6[4,6a,9a,b], 8[6h,9b]
meta: n = 6[4], 8[6h]



3

m = 1; n = 6,8[6f]
m = 2, 3; n = 6,8[12a]



4

para: m/n = 2/6[6j,7f,14a], 2/8[6h,6k]
(*this work*: 3/6, 3/8, 3/10)
meta: m/n = 2/6[7a]

required syntheses of new phosphines and the development of methodologies that are practical on larger scales. Earlier we reported convenient multigram syntheses of symmetrically and unsymmetrically substituted fluorous trialkylphosphines of the formula $P((CH_2)_mR_{fn})_2((CH_2)_{m'}R_{fn})$ (**1**; Chart 1).[8] To help insulate the phosphorus from the electron-withdrawing perfluoroalkyl group, two to five methylene groups were employed ($2 < m/m' \leq 5$). However, many catalysts function best with tri*aryl*phosphine ligands. In this paper, we report our initial studies with fluorous triarylphosphines that contain one pony tail per ring.

Several other groups have already made significant contributions to this subject, and we wish to place our work in the context of these earlier reports at the outset. One direction has been the synthesis of fluorous triarylphosphines of the formula $P(C_6H_4R_{fn})_3$ (**2**; Chart 1),[4,6a,h,9,10] in which no insulating methylene segment separates a *p*- or *m*-perfluoroalkyl group from the aryl ring. Such phosphines will be much less basic than triphenylphosphine and are often unsuitable as direct replacements. However, they should be good replacements for tris(*p*-/*m*-(trifluoromethyl)phenyl)phosphines $P(C_6H_4CF_3)_3$[11]—which are also components of many metal catalysts.[7d,e] An advantage of this approach is that fluorous iodides IR_{fn} undergo efficient copper-mediated coupling with aryl halides, rendering ArR_{fn} species easily accessible. Halogenated derivatives are readily metalated to aryl nucleophiles, which react with PCl_3 to give **2** in good yields.

Another direction has been fluorous triarylphosphines of the formula $P(C_6H_4X(R_{fn})_2)_3$, where X is an insulating segment. One possibility for X would be a silyl−methylene grouping, as exemplified by **3** (Chart 1). Elegant studies of such ligands, which contain as many as nine pony tails, have been reported by van Koten and Deelman.[6f,g,12] Other heteroatoms have also been employed.[13] Another possibility would be a simple methylene segment—i.e., ligands of the formula $P(C_6H_4(CH_2)_mR_{fn})_3$ (**4**).[14] These can be expected to closely mimic triphenylphosphine and constitute the focus of this paper. Data on other fluorous aromatic compounds[3,15] suggest that **4** should not have very high fluorous phase affinities, at least in comparison to aliphatic systems **1**. However, in preliminary efforts we have found analogues with two pony tails per phenyl ring, $P(C_6H_3((CH_2)_mR_{fn})_2)_3$ (**5**), to be much more synthetically challenging.[16] Hence, we sought to fully optimize procedures with the simpler system **4**.

A related research direction has been the synthesis of moderately fluorinated phosphines to enhance catalyst solubility in supercritical CO_2.[7] Some of this work has utilized the types of ligands described above. Bidentate phosphines belonging to all of the preceding categories have also been reported.[7g,9a,12b,17,18] Phosphorus donor ligands with $O(CH_2)_2R_{f6}$ substituents have also been synthesized.[6c] However, fluorous trialkyl or triaryl phosphites have to date only received scant attention.[7b,9a,19]

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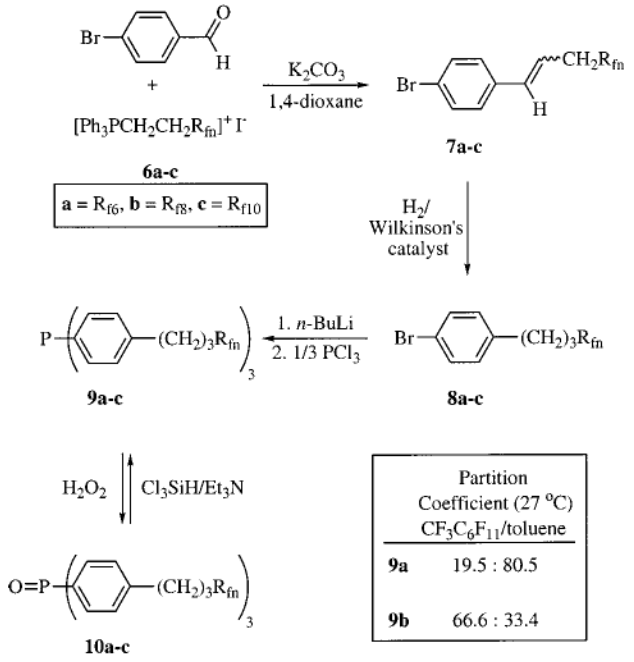
Scheme 1. Syntheses of Fluorous Triarylphosphines and Phosphine Oxides



Results

1. Syntheses of Phosphines. We recently reported facile syntheses of the fluorous phosphonium salts $[Ph_3PCH_2CH_2R_{fn}]^+I^-$ (n = 6 (**6a**), 8 (**6b**), 10 (**6c**)), and high-yield Wittig reactions with benzaldehyde, phthalaldehydes, and related compounds.[15] The resulting alkenes were easily hydrogenated to the corresponding fluorous arenes. As shown in Scheme 1, a similar sequence was used to prepare brominated fluorous arenes. Phosphonium salts **6a**−**c**, *p*-bromobenzaldehyde, and K_2CO_3 were heated in 1,4-dioxane. Workups gave the fluorous bromostyrenes p-$BrC_6H_4CH{=}CHCH_2R_{fn}$ (**7a**−**c**) in 86−93% yields as mixtures of *Z*/*E* isomers. These and all new compounds below were characterized by NMR and microanalysis, as described in the Experimental Section. The $^3J_{HH}$ values associated with the CH=CH ^{1}H NMR signals showed that *Z* isomers dominated ((92−91):(8−9)), consistent with literature precedent for unstabilized ylides.

Hydrogenations of **7a**−**c** were attempted. To our surprise, considerable carbon−bromine hydrogenolysis occurred under most conditions—including PtO_2 and all other heterogeneous catalysts assayed. Ethanol solutions of Wilkinson's catalyst were eventually utilized (Scheme 1). However, it was necessary to limit the temperature and pressure to 40 °C and 75 psig to prevent overreduction. Workups gave the fluorous bromoarenes p-$BrC_6H_4(CH_2)_3R_{fn}$ (**8a**−**c**) in 91−94% yields. The compounds with R_{f10} pony tails, **7c** and **8c**, were much less soluble than **7a**,**b** and **8a**,**b** in both nonfluorous and fluorous solvents, a trend noted for other R_{f6}/R_{f8}/R_{f10} homologues earlier.[8a,15] The hydrogenation of **7c** was best conducted in mixtures of ethanol and $C_6H_5CF_3$. The latter solvent is able to solubilize appreciable concentrations of both nonfluorous and fluorous compounds.[20]

Next, lithium/bromine exchange reactions of **8a**−**c** were attempted. Preliminary experiments were conducted with 2 equiv of *t*-BuLi. The *t*-BuBr generated in this common procedure is often annihilated by the second equivalent of *t*-BuLi.[21] However, subsequent additions of PCl_3 appeared to give some *tert*-butyl-substituted phosphines. Hence, analogous sequences were conducted with 1 equiv of *n*-BuLi. Workups gave the target phosphines $P(p\text{-}C_6H_4(CH_2)_3R_{fn})_3$ (**9a**−**c**), together with some of the corresponding phosphine oxides $O{=}P(p\text{-}C_6H_4(CH_2)_3R_{fn})_3$ (**10a**−**c**) and a fluorohydrocarbon byproduct. To simplify purification, aqueous H_2O_2 was added to oxidize **9a**−**c** to **10a**−**c**. Filtrations through silica gel gave phosphine oxides **10a**−**c** in 88%, 57%, and 24% yields, respectively, as analytically pure waxy solids.

Phosphine oxides have been reduced to phosphines with Cl_3SiH/Et_3N (1:1).[22] As shown in Scheme 1, analogous reactions in $CF_3C_6H_5$ gave phosphines **9a**−**c** in 69%, 82%, and 43% yields, respectively, as analytically pure white solids. The syntheses of **9b** and **10b** were routinely conducted on 1−2 g scales and should be easily amenable to further scale-up. The ^{31}P NMR signals of **9a**−**c** (δ −7.1 to −7.4) and **10a**−**c** (δ 29.4−29.9) were very close to those of $P(p\text{-}C_6H_4CH_3)_3$ and $O{=}P(p\text{-}C_6H_4CH_3)_3$ (δ −7.26, 29.88; all data for $CDCl_3$),[23] respectively, consistent with similar electronic properties. The R_{f8} phosphine **9b** was very soluble in $CF_3C_6F_{11}$ and $CF_3C_6H_5$, as well as organic solvents such as toluene and $CHCl_3$.The R_{f10} compounds **9c** and **10c** were again much less soluble than the others. Quantitative data on *relative* solubilities were sought. Thus, $CF_3C_6F_{11}$/toluene partition coefficients were determined by GLC as reported previously[3,8b,15] and are summarized in Scheme 1.

2. Reactions of Fluorous Phosphines. We sought to probe the electronic properties of **9a**−**c**. Many fluorous phosphine analogues of Vaska's complex have been previously prepared,[8b,c,24] and the IR ν_{CO} values mirror the donor/acceptor properties of the iridium fragment. As depicted in Scheme 2, reaction of $[Ir(COD)(\mu\text{-}Cl)]_2$, **9b**, and carbon monoxide gave the expected canary yellow bis(phosphine) complex *trans*-$Ir(CO)(Cl)[P(p\text{-}C_6H_4(CH_2)_3R_{f8})_3]_2$ (**11b**) in 76% yield after workup. The IR spectrum showed a ν_{CO} value very similar to that of Vaska's complex (1958 cm^{-1} vs a range of 1950 cm^{-1} [25] to 1952 cm^{-1},[24] Nujol). The $^{31}P\{^1H\}$ NMR signals were also very similar (δ 22.9 vs 23.5,[26] $CDCl_3$). Hence, the fluorocarbon chain is well-insulated from the metal. However, the direction of the IR shift is consistent with a small residual electron withdrawing effect, in accord with Gaussian 94 calculations on the two-methylene spacer ligand $P(p\text{-}C_6H_4(CH_2)_2R_{f6})_3$[7l] and analogous to that seen with five-methylene spacers in aliphatic fluorous phosphines **1**.[8b]

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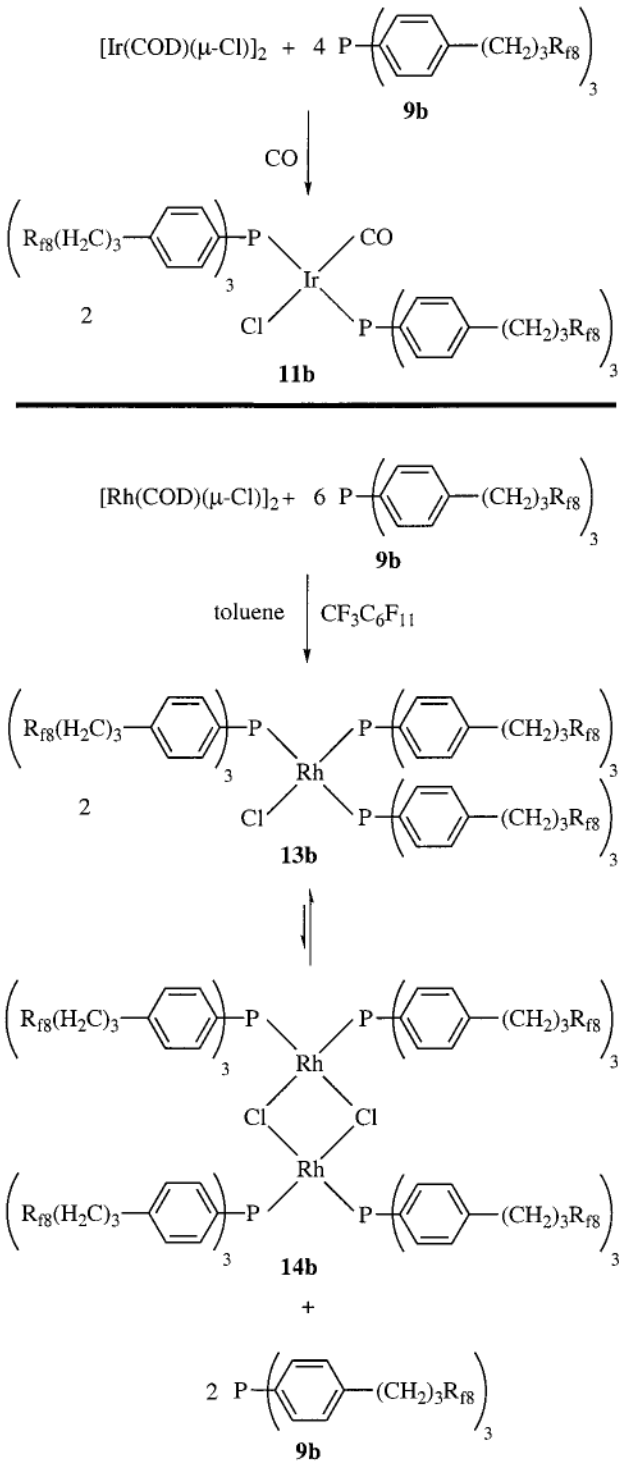
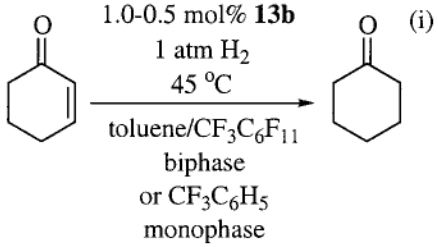
Scheme 2. Syntheses of Fluorous Triarylphosphine Complexes



We sought to apply the preceding phosphines in catalysis. Reactions of the rhodium complex [Rh(COD)-(μ-Cl)]$_2$ and aliphatic fluorous phosphines **1** (m/n = 2/6,8; ≥3 equiv/Rh) give analogues of Wilkinson's catalyst, Rh-[P((CH$_2$)$_2$R$_{fn}$)$_3$](Cl) (**12a**,**b**), in high yields.[5b] Accordingly, [Rh(COD)(μ-Cl)]$_2$ and **9b** were similarly reacted in toluene/$CF_3C_6F_{11}$ under biphasic conditions, as shown in Scheme 2. Workup of the fluorous phase gave a red solid (82−93%) with a microanalysis that fit the target complex Rh[P(*p*-C$_6$H$_4$(CH$_2$)$_3$R$_{f8}$)$_3$]$_3$(Cl) (**13b**). This material was quite soluble in fluorous solvents such as $CF_3C_6F_{11}$ (ca. 0.010 g/mL, ambient temperature) or $CF_3C_6H_5$ but virtually insoluble in nonfluorous solvents. Although a partition coefficient was not measured (atomic absorption analyses would be required), it is clearly much higher than that of the constituent phosphine **9b**.

As observed for Wilkinson's catalyst[27] and related compounds,[6g] ^{31}P NMR spectra showed one signal for the trans phosphines of **13b** and a less intense signal for the remaining phosphine (rhodium-coupled dd and dt). A representative trace is depicted in Figure 1. All spectra also showed three other species, the relative ratios of which were condition-dependent (concentration, temperature). On the basis of equilibria documented for Wilkinson's catalyst and analogues,[6g,27] two could be confidently assigned as the dirhodium bridging chloride [Rh[P(*p*-C$_6$H$_4$(CH$_2$)$_3$R$_{f8}$)$_3$]$_2$(μ-Cl)]$_2$ (**14b**) and **9b**. The remaining signal was reproducibly obtained in two separate laboratories. It is not due to the phosphine oxide **10b** (ca. δ 29 under these conditions), and remains under investigation. A $CF_3C_6F_{11}$ solution was repeatedly extracted with toluene. This removed essentially all **9b**, shifting the equilibrium nearly completely to **14b** and leaving the unassigned (and apparently very fluorous) substance.

A $CF_3C_6F_{11}$ solution of **13b** was combined with a toluene solution of 2-cyclohexen-1-one (1:95 mol ratio). As shown in eq i, the biphasic mixture was placed under



1 atm of H_2 and heated to 45 °C. These conditions were chosen to facilitate comparisons to hydrogenations with **12a** described earlier. Catalyst **12a** exhibited induction periods and after several recycles decomposed to rhodium metal. When eq i was monitored by GLC, induction periods were also noted (ca. 0.5 h). However, hydrogenations were complete in 2 h as opposed to 8 h with **12a**. In contrast, 1-dodecene was not as efficiently hydrogenated, mainly due to the slower conversion of internal alkenes generated during the reaction. More quantitative rate comparisons were not attempted, since **13b** and **12a** must have different partition coefficients, with a higher concentration of **13b** likely in the nonfluorous phase. Similar hydrogenations were conducted under monophasic conditions in $CF_3C_6H_5$ (e.g., 1:198 **13b**/2-cyclohexen-1-one). These also showed induction periods and were somewhat slower than under biphasic conditions.

Discussion

Our syntheses of fluorous phosphines **9a**−**c** (Scheme 1) can be contrasted with those of other systems of the type P(C$_6$H$_4$(CH$_2$)$_m$R$_{fn}$)$_3$ (**4**) in the literature. First, consider the length of the methylene spacer or m value.

(27) (a) Eaton, D. R.; Suart, S. R. *J. Am. Chem. Soc.* **1968**, *90*, 4170−4172. (b) Jardine, F. H. *Prog. Inorg. Chem.* **1981**, *28*, 63−202.

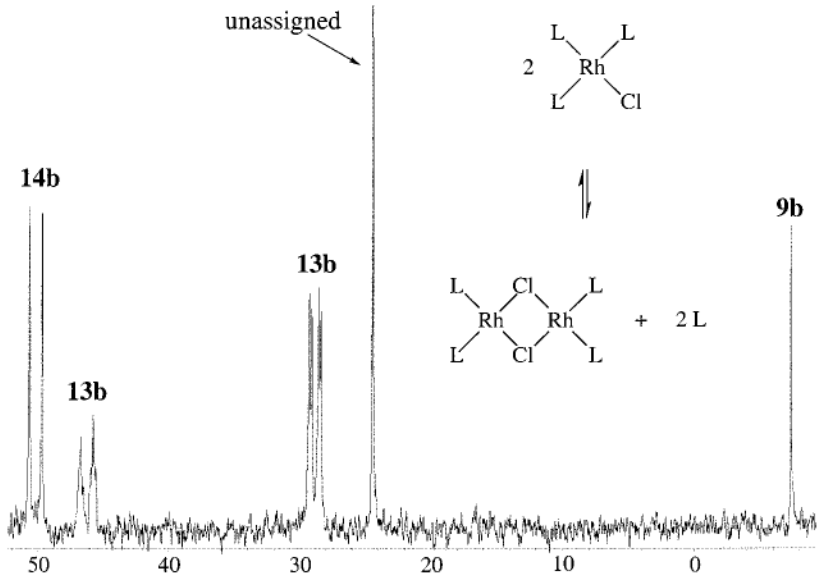


Figure 1. Representative ^{31}P NMR spectrum of **13b** (0.0029 M in 2:1 v/v C_6H_6/C_6F_6).

The phosphonium salts **6a**−**c** are easily prepared from commercial fluorous iodides $ICH_2CH_2R_{fn}$,[15] and the subsequent Wittig/hydrogenation sequence affords three methylene groups. All previous approaches give spacers with two methylene groups.[6h,j,7a,f,14] As we have emphasized earlier,[3] the spacer length represents a tuning element. Hence, there is no preset "ideal length", and strategies that can be generalized to families of fluorous compounds are advantageous. In this regard, we note that fluorous iodides with longer methylene segments are readily available,[8a,b] and our methodology is undoubtedly extendable to targets with higher *m* values.

Syntheses of systems **4** with two methylene groups can be divided into two categories. The first utilizes aryl halide building blocks. Some early work featured copper-catalyzed couplings of the Grignard reagents *p*- and *m*-BrC_6H_4MgBr with fluorous iodides $ICH_2CH_2R_{f6}$.[7a,14b] The resulting aryl bromides were isolated in 45−46% yields and ≥90% purities. Reactions with *n*-BuLi and PCl_3 gave the para-[7f] and meta-substituted[7a] phosphines $P(C_6H_4(CH_2)_2R_{f6})_3$ in 67% yields. This route has also been used to prepare $P(p\text{-}C_6H_4(CH_2)_2R_{f8})_3$, which is the direct lower methylene homologue of **9b** (first step, 46%; second step, 61%).[6h] A 94% yield for the second step has recently been reported (>95% purity; 70% after recrystallization).[6k] An improved synthesis of $P(p\text{-}C_6H_4(CH_2)_2R_{f6})_3$ has also been reported.[6j] This features a palladium-catalyzed coupling of *p*-BrC_6H_4I and the fluorous zinc reagent $IZnCH_2CH_2R_{f6}$ (56% on 30 g scales), followed by reaction of the aryl bromide with *t*-BuLi and PCl_3 (78%). This paper also included a system similar to **4** (branched R_{fn}) with a single methylene spacer. In accord with our experience, small amounts of phosphine oxide byproducts were often noted.

The second category utilizes phosphorus-containing building blocks. The triarylphosphine oxide $O{=}P(p\text{-}C_6H_4Br)_3$ undergoes high-yield 3-fold Heck reactions with a variety of alkenes.[14a] Subsequent reduction of the product derived from $H_2C{=}CHR_{f6}$ affords $P(p\text{-}C_6H_4(CH_2)_2R_{f6})_3$ (80% overall). The phosphine $P(p\text{-}C_6H_4Br)_3$ can be triply lithiated, although this has so far only been utilized to prepare systems of the type **3**.[12a] Such routes avoid the metalation of a fluorous aryl halide and an ensuing condensation with PCl_3. While such sequences work well for many aryl halides, fluorous aryl halides that contain methylene spacers appear to be problematic. Nearly all research groups have noted that lithiations must be conducted under carefully controlled conditions to obtain optimum yields. A system with a much shorter perfluoroalkyl segment than **9b**, $P(p\text{-}C_6H_4(CH_2)_3R_{f4})_3$, could only be prepared in 14% yield.[7g]

We have extensively tested and reproduced the lithiation/PCl_3 sequence in Scheme 1. The lower yield of phosphine oxide **10c** is likely connected to the lower solubilities of the R_{f10} compounds. This has the potential to complicate aryllithium generation and reactivity. Otherwise, the procedures in Scheme 1 are very simple. None of the workups require chromatography, outside of simple silica gel filtrations. Fluorous alkenes **7a**−**c** are less polar than the principal byproducts, whereas the phosphine oxides **10a**−**c** are more polar. This represents one of the advantages of the H_2O_2 oxidation, which might be viewed as a debit from the standpoint of synthetic efficiency. Another advantage is that **10a**−**c** can be stored indefinitely under ambient laboratory conditions, in contrast to phosphines **9a**−**c**.

The partition coefficients of **9a**,**b** in Scheme 1 show the expected increase in fluorous phase affinities with increasing perfluoroalkyl chain length. However, neither compound would be significantly retained in a fluorous solvent under extraction conditions. Indeed, we could exploit this to shift the equilibrium in Figure 1. The phosphine $P(p\text{-}C_6H_4(CH_2)_2R_{f6})_3$, which has one less methylene group than **9a**, gives a 75:25 distribution in FC-72/toluene (conditions comparable to but not identical with ours).[6j] Hence, these do not quailfy as "immobilized" ligands. Nonetheless, **9b**,**c** would certainly be readily extractable into fluorous solvents, although the low absolute solubility of the latter should be kept in mind. Deelman and Van Koten have carefully characterized the relative and absolute solubilities of the silylated fluorous phosphines **3** (Chart 1), some of which are highly immobilized, and find comparable trends.[12a] They also observe, like us, that the corresponding tris(phosphine)rhodium chloride complexes exhibit greater

fluorous phase affinities than the phosphines and have speculated on the origin of the effect.[6g]

Our preliminary data show that the rhodium complex **13b** is at least as good an alkene hydrogenation catalyst precursor as the related aliphatic complex **12a**, which was the first analogue of Wilkinson's catalyst to be studied under fluorous biphase conditions.[5a] However, we seek more highly immobilized systems that would not be as susceptible to phosphine leaching prior to undertaking quantitative recycling and reactivity studies. Others have also studied hydrogenations catalyzed by various rhodium/fluorous phosphine combinations.[6d–g] Complexes derived from **3** have been particularly well-characterized and exhibit a number of impressive performance characteristics, including turnover frequencies that exceed those of Wilkinson's catalyst.[6g]

In summary, this paper has described our first-generation synthetic approach to fluorous triarylphosphines. The various derivatives prepared, physical measurements, and catalyst screening results provide valuable benchmark data for guiding future work. The inductive effect of a *p*-perfluoroalkyl group is nearly completely screened by three methylene groups. Extensions to more "highly fluorous" phosphines with additional pony tails, as well as new applications of aliphatic homologues, will be reported in due course.[28]

Experimental Section

General Considerations. All reactions were conducted under rigorously anaerobic conditions. Reagent and solvent sources and purifications, instrumentation, and partition coefficient measurements were identical with those given in two previous papers.[8b,15] The following chemicals were new to this study and used as received unless noted: *p*-BrC_6H_4CHO (Acros), *n*-BuLi (Aldrich, 2.5 or 1.6 M in hexanes, standardized),[29] *t*-BuLi (Aldrich, 1.5 M in pentane, standardized),[29] PCl_3 (Aldrich, freshly distilled), H_2O_2 (Aldrich, 30% aqueous), Cl_3SiH (Aldrich), and Et_3N (Aldrich).

***p*-$BrC_6H_4CH{=}CHCH_2R_{f8}$ (7b).** A flask was charged with $[Ph_3PCH_2CH_2R_{f8}]^+I^-$ (**6b**;[15] 4.337 g, 5.18 mmol), *p*-BrC_6H_4CHO (0.765 g, 4.13 mmol), K_2CO_3 (1.493 g, 10.8 mmol), and 1,4-dioxane (55 mL). The mixture was vigorously stirred, H_2O (1.0 mL) was added, and the flask was placed in a 90 °C oil bath. After 12 h, the bath was removed and H_2O (5.0 mL) was added. The mixture was cooled with stirring. Volatiles were removed by oil pump vacuum, and CH_2Cl_2 (100 mL) and H_2O (20 mL) were added. The aqueous layer was separated and washed with CH_2Cl_2 (2 × 50 mL). The combined CH_2Cl_2 layers were washed with H_2O (2 × 20 mL) and dried ($MgSO_4$). The solvent was removed and the residue taken up in a minimum of CH_2Cl_2/hexanes (1:1 v/v). This was added to a silica gel/hexane plug (2 × 3 cm), which was rinsed with CH_2Cl_2/hexane (1:4 v/v, 200 mL; aspirator assisted). The solvent was removed from the filtrate by rotary evaporation and oil pump vacuum to give **7b** as a white solid (2.179 g, 3.54 mmol, 86%; 92:8 *Z*/*E*), mp 42.3–43.3 °C (capillary). Anal. Calcd for $C_{17}H_8F_{17}Br$: C, 33.19; H, 1.31. Found: C, 33.40; H, 1.34. NMR (δ, $CDCl_3$): ^{1}H (*Z*/*E*) 3.02 (tdd (*Z* + *E*), $^3J_{HF}$ = 18.0 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.5 Hz, CH_2CF_2), 5.76/6.11 (dt, $^3J_{HH}$ = 7.5/6.9 Hz, $^3J_{HH}$ = 11.4/15.9 Hz, =C*H*CH_2), 6.73/6.54 (d, $^3J_{HH}$ = 11.7/15.9 Hz, ArC*H*=), 7.07/7.23 (m, 2H), 7.48/7.44 (m, 2H); ^{19}F −81.1 (t, $^3J_{FF}$ = 9.3 Hz, 3F), −113.3 (m, 2F), −122.2 (m, 6F), −123.2 (m, 2F), −123.4 (m, 2F), −126.5 (m, 2F).

***p*-$BrC_6H_4CH{=}CHCH_2R_{f6}$ (7a).** Compounds **6a** (10.01 g, 13.6 mmol),[15] *p*-BrC_6H_4CHO (2.09 g, 11.3 mmol), and K_2CO_3 (3.91 g, 28.3 mmol) were combined in a procedure analogous to that for **7b**. An identical workup gave **7a** as a clear oil (5.314 g, 10.3 mmol, 91%; 92:8 *Z*/*E*). Anal. Calcd for $C_{15}H_8F_{13}Br$: C, 34.97; H, 1.56. Found: C, 35.13; H, 1.62. NMR (δ, $CDCl_3$): ^{1}H (*Z*/*E*) 3.03 (tdd (*Z* + *E*), $^3J_{HF}$ = 18.0 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz, CH_2CF_2), 5.76/6.11 (dt, $^3J_{HH}$ = 7.5/7.2 Hz, $^3J_{HH}$ = 11.4/15.9 Hz, =C*H*CH_2), 6.73/6.54 (d, $^3J_{HH}$ = 11.7/15.6 Hz, ArC*H*=), 7.07/7.23 (m, 2H), 7.48/7.44 (m, 2H); ^{19}F −81.0 (t, $^3J_{FF}$ = 9.3 Hz, 3F), −113.3 (m, 2F), −122.2 (m, 2F), −123.1 (m, 2F), −123.4 (m, 2F), −126.4 (m, 2F).

***p*-$BrC_6H_4CH{=}CHCH_2R_{f10}$ (7c).** Compounds **6c** (8.001 g, 8.54 mmol),[15] *p*-BrC_6H_4CHO (1.318 g, 7.12 mmol), and K_2CO_3 (2.459 g, 17.79 mmol) were combined in a procedure analogous to that for **7b**. An identical workup gave **7c** as a white solid (4.745 g, 6.63 mmol, 93%; 91:9 *Z*/*E*), mp 63.1–64.6 °C (capillary). Anal. Calcd for $C_{19}H_8F_{21}Br$: C, 31.91; H, 1.13. Found: C, 32.24; H, 1.04. NMR (δ, $CDCl_3$): ^{1}H (*Z*/*E*) 3.02 (tdd (*Z* + *E*), $^3J_{HF}$ = 18.3 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.5 Hz, CH_2CF_2), 5.76/6.11 (dt, $^3J_{HH}$ = 7.2/7.8 Hz, $^3J_{HH}$ = 12.0/15.9 Hz, = C*H*CH_2), 6.73/6.54 (d, $^3J_{HH}$ = 12.0/16.2 Hz, ArC*H*=), 7.07/7.21 (m, 2H), 7.48/7.43 (m, 2H); ^{19}F −81.3 (t, $^3J_{FF}$ = 9.3 Hz, 3F), −113.5 (m, 2F), −122.3 (m, 10F), −123.3 (m, 2F), −123.6 (m, 2F), −126.7 (m, 2F).

***p*-$BrC_6H_4(CH_2)_3R_{f8}$ (8b).** A Fisher-Porter bottle was charged with **7b** (2.007 g, 3.26 mmol), $Rh(PPh_3)_3(Cl)$ (0.126 g, 0.136 mmol), and ethanol (30 mL), purged with H_2, pressurized with H_2 (75 psi gauge reading), and placed in a 42 °C oil bath. The mixture was stirred (7.5 h) and then cooled. The solvent was removed by rotary evaporation. The residue was taken up in a minimum amount of hexane. This was added to a silica gel/hexane plug (2 × 3 cm), which was rinsed with hexane (200 mL). Solvent was removed from the filtrate by rotary evaporation and oil pump vacuum to give **8b** as a white solid (1.827 g, 2.96 mmol, 91%), mp 34.7–35.7 °C (capillary). Anal. Calcd for $C_{17}H_{10}F_{17}Br$: C, 33.08; H, 1.64. Found: C, 33.26; H, 1.57. NMR (δ, $CDCl_3$): ^{1}H 1.91 (m, C$H_2$$CH_2CF_2$), 2.10 (m, CH_2CF_2), 2.64 (t, $^3J_{HH}$ = 7.5 Hz, ArCH_2), 7.03 (m, 2H), 7.40 (m, 2H); ^{13}C{^{1}H} (partial) 21.9 (t, $^3J_{CF}$ = 3 Hz, *C*$H_2CH_2CF_2$), 30.4 (t, $^2J_{CF}$ = 23 Hz, *C*H_2CF_2), 34.6 (s, Ar*C*H_2), 120.3 (s), 130.3 (s, 2C), 131.9 (s, 2C), 139.7 (s); ^{19}F −81.3 (t, $^3J_{FF}$ = 9.0 Hz, 3F), −114.7 (m, 2F), −122.5 (m, 6F), −123.3 (m, 2F),-124.0 (m, 2F), −126.6 (m, 2F).

***p*-$BrC_6H_4(CH_2)_3R_{f6}$ (8a).** Compounds **7a** (2.287 g, 4.44 mmol), $Rh(PPh_3)_3(Cl)$ (0.143 g, 0.155 mmol), ethanol (30 mL), and H_2 were combined in a procedure analogous to that for **8b**. An identical workup gave **8a** as a clear oil (2.175 g, 4.20 mmol, 94%). Anal. Calcd for $C_{15}H_{10}F_{13}Br$: C, 34.84; H, 1.95. Found: C, 35.08; H, 2.10. NMR (δ, $CDCl_3$): ^{1}H 1.90 (m, CH_2-CH_2CF_2), 2.07 (m, CH_2CF_2), 2.64 (t, $^3J_{HH}$ = 7.2 Hz, ArCH_2), 7.04 (m, 2H), 7.40 (m, 2H); ^{13}C{^{1}H} (partial) 21.9 (t, $^3J_{CF}$ = 3.5 Hz, *C*$H_2CH_2CF_2$), 30.4 (t, $^2J_{CF}$ = 22 Hz, *C*H_2CF_2), 34.6 (s, Ar*C*H_2), 120.3 (s), 130.3 (s, 2C), 131.9 (s, 2C), 139.7 (s); ^{19}F −81.3 (t, $^3J_{FF}$ = 9.0 Hz, 3F), −114.8 (m, 2F), −122.5 (m, 2F), −123.5 (m, 2F), −124.0 (m, 2F), −126.7 (m, 2F).

***p*-$BrC_6H_4(CH_2)_3R_{f10}$ (8c).** Compounds **7c** (3.001 g, 4.20 mmol), $Rh(PPh_3)_3(Cl)$ (0.135 g, 0.146 mmol), ethanol (30 mL), $CF_3C_6H_5$ (10 mL), and H_2 were combined in a procedure analogous to that for **8b**. An identical workup gave **8c** as a white solid (2.776 g, 3.87 mmol, 92%), mp 68.2–69.7 °C (capillary). Anal. Calcd for $C_{19}H_{10}F_{21}Br$: C, 31.82; H, 1.41. Found: C, 32.05; H, 1.37. NMR (δ, $CDCl_3$): ^{1}H 1.91 (m, CH_2-CH_2CF_2), 2.05 (m, CH_2CF_2), 2.64 (t, $^3J_{HH}$ = 7.5 Hz, ArCH_2), 7.04 (m, 2H), 7.40 (m, 2H); ^{13}C{^{1}H} (partial) 21.9 (t, $^3J_{CF}$ = 3 Hz, *C*$H_2CH_2CF_2$), 30.4 (t, $^2J_{CF}$ = 22.5 Hz, *C*H_2CF_2), 34.6 (s, Ar*C*H_2), 120.3 (s), 130.3 (s, 2C), 131.9 (s, 2C), 139.7 (s); ^{19}F −81.3 (t, $^3J_{FF}$ = 9.3 Hz, 3F), −114.7 (m, 2F), −122.3 (m, 10F), −123.2 (m, 2F), −124.0 (m, 2F), −126.7 (m, 2F).

O=P(*p*-$C_6H_4(CH_2)_3R_{f8}$)$_3$ (10b). A three-necked flask was charged with **8b** (2.776 g, 4.50 mmol) and THF (75 mL), fitted

(28) Soós, T.; Gladysz, J. A. Manuscript in preparation.
(29) Duhamel, L.; Plaquevent, J.-C. *J. Org. Chem.* **1979**, *44*, 3404–3405.

with a thermometer, and cooled to −78 °C. Then *n*-BuLi (2.88 mL, 1.56 M in hexane, 4.50 mmol) was added dropwise with stirring over 10 min (green solution). After an additional 15 min, PCl_3 (0.130 mL, 1.50 mmol) was added dropwise with stirring (yellow solution). The mixture was warmed to room temperature over 5 h. Volatiles were removed by oil-pump vacuum. The residue was dissolved in degassed $CF_3C_6H_5$ (40 mL), and the solution was washed with degassed aqueous NH_4Cl (2 × 10 mL) and dried ($MgSO_4$). The sample was concentrated and applied to a silica gel/$CF_3C_6H_5$ plug (2 × 2 cm). The plug was rinsed with hexanes (25 mL) and $CF_3C_6H_5$ (50 mL). The combined filtrate was treated with H_2O_2 (5 mL, 30% aqueous) with stirring. After 15 min, the solution was washed with H_2O (2 × 10 mL) and dried ($MgSO_4$). The sample was concentrated and applied to a silica gel/$CF_3C_6H_5$ plug (2 × 2 cm). The plug was rinsed with hexanes (25 mL) and $CF_3C_6H_5$ (25 mL). These filtrates were discarded. The plug was flushed with acetone (100 mL) and methanol (200 mL). Solvent was removed from the filtrates by rotary evaporation and oil pump vacuum to give **10b** as a waxy white solid (1.417 g, 0.854 mmol, 57%), mp 135.0−137.0 °C (capillary). Anal. Calcd for $C_{51}H_{30}F_{51}OP$: C, 36.93; H, 1.82. Found: C, 37.11; H, 1.80. NMR (δ, $CDCl_3$): ^{1}H 1.96 (m, 3CH_2CH$_2$CF$_2$), 2.10 (m, 3CH$_2$CF$_2$), 2.74 (t, $^3J_{HH}$ = 7.5 Hz, 3ArCH$_2$), 7.26 (dd, J_{HH} = 8.1 Hz, J_{HP} = 2.5 Hz, 6H), 7.55 (dd, J_{HH} = 8.1 Hz, J_{HP} = 11.7 Hz, 6H); ^{13}C{^{1}H} (partial)[30] 21.8 (br s, *C*H$_2$CH$_2$CF$_2$), 30.5 (t, $^2J_{CF}$ = 22.2 Hz, *C*H$_2$CF$_2$), 35.2 (s, Ar*C*H$_2$), 128.7 (d, $^3J_{CP}$ = 12.6 Hz, *m*-Ph), 130.8 (d, $^1J_{CP}$ = 106.2 Hz, *i*-Ph), 132.6 (d, $^2J_{CP}$ = 10.0 Hz, *o*-Ph), 145.2 (d, $^4J_{CP}$ = 2.5 Hz, *p*-Ph); ^{31}P{^{1}H} 29.4 (s); ^{19}F −80.9 (t, $^3J_{FF}$ = 9.0 Hz, 9F), −114.3 (m, 6F), −122.1 (m, 18F), −122.9 (m, 6F), −123.6 (m, 6F), −126.3 (m, 6F).

O=P(*p*-C$_6$H$_4$(CH$_2$)$_3$R$_{f6}$)$_3$ (10a). Compounds **8a** (3.169 g, 6.13 mmol), THF (70 mL), and *n*-BuLi (2.44 mL, 2.5 M in hexanes, 6.10 mmol) were combined in a procedure analogous to that for **10b**. After 45 min, PCl_3 (0.161 mL, 1.85 mmol) was added dropwise with stirring. The mixture was slowly warmed to room temperature over 5 h. Volatiles were removed by oil pump vacuum (^{31}P NMR: >90:10 **9a**:**10a**). The residue was dissolved in $CF_3C_6H_5$ (15 mL) and washed with H_2O (2 × 15 mL). Then H_2O_2 (0.75 mL, 30% aqueous) was added with stirring. After 15 min, volatiles were removed by oil pump vacuum. The residue was dissolved in a minimum of $CF_3C_6H_5$ and the solution applied to a silica gel/$CF_3C_6H_5$ plug (2 × 2.5 cm). The plug was rinsed with hexanes (40 mL) and $CF_3C_6H_5$ (30 mL). These filtrates were discarded. The plug was rinsed with acetone (280 mL). Solvent was removed from the filtrates by rotary evaporation and oil pump vacuum to give **10a** as a waxy yellow solid (2.228 g, 1.64 mmol, 88%), mp 110.2−111.2 °C (capillary). Anal. Calcd for $C_{45}H_{30}F_{39}OP$: C, 39.78; H, 2.22. Found: C, 39.96; H, 2.30. NMR (δ, $CDCl_3$): ^{1}H 1.96 (m, 3CH_2CH$_2$CF$_2$), 2.10 (m, 3CH$_2$CF$_2$), 2.74 (t, $^3J_{HH}$ = 7.5 Hz, 3ArCH$_2$), 7.26 (dd, J_{HH} = 8.1 Hz, J_{HP} = 2.5 Hz, 6H), 7.58 (dd, J_{HH} = 8.1 Hz, J_{HP} = 11.7 Hz, 6H); ^{13}C{^{1}H} (partial)[30] 21.8 (br s, *C*H$_2$CH$_2$CF$_2$), 30.5 (t, $^2J_{CF}$ = 21.3 Hz, *C*H$_2$CF$_2$), 35.2 (s, Ar*C*H$_2$), 128.8 (d, $^3J_{CP}$ = 13.0 Hz, *m*-Ph), 130.8 (d, $^1J_{CP}$ = 105.5 Hz, *i*-Ph), 132.6 (d, $^2J_{CP}$ = 10.6 Hz, *o*-Ph), 145.2 (d, $^4J_{CP}$ = 3.1 Hz, *p*-Ph); ^{31}P{^{1}H} 29.4 (s); ^{19}F −81.3 (t, $^3J_{FF}$ = 9.3 Hz, 9F), −114.7 (m, 6F), −122.5 (m, 6F), −123.5 (m, 6F), −124.0 (m, 6F), −126.7 (m, 6F).

O=P(*p*-C$_6$H$_4$(CH$_2$)$_3$R$_{f10}$)$_3$ (10c). Compounds **8c** (2.151 g, 3.00 mmol), THF (120 mL), and *n*-BuLi (1.88 mL, 1.6 M in hexane, 3.00 mmol) were combined in a procedure analogous to that for **10b**. After 25 min, PCl_3 (0.088 mL, 0.137 g, 1.0 mmol) was added dropwise with stirring. The mixture was slowly warmed to room temperature over 10 h. An identical workup gave **10c** as a waxy white solid (0.475 g, 0.243 mmol, 24%), mp 158.9−159.9 °C (capillary). Anal. Calcd for $C_{57}H_{30}F_{63}OP$: C, 34.95; H, 1.54. Found: C, 35.08; H, 1.71. NMR (δ, $CDCl_3$): ^{1}H 1.96 (m, 3CH_2CH$_2$CF$_2$), 2.06 (m, 3CH$_2$CF$_2$), 2.75 (t, $^3J_{HH}$ = 7 Hz, 3ArCH$_2$), 7.26 (dd, J_{HH} = 8.0 Hz, J_{HP} = 2.2 Hz, 6H), 7.58 (dd, J_{HH} = 8.0 Hz, J_{HP} = 12.0 Hz, 6H); ^{13}C{^{1}H} (partial)[30] 21.6 (s, *C*H$_2$CH$_2$CF$_2$), 30.2 (t,$^2J_{CF}$ = 22.8 Hz, *C*H$_2$CF$_2$), 35.0 (s, Ar*C*H$_2$), 128.6 (d, $^3J_{CP}$ = 12.0 Hz, *m*-Ph), 132.4 (d, $^2J_{CP}$ = 9.0 Hz, *o*-Ph); ^{31}P{^{1}H} 29.9 (s).

P(*p*-C$_6$H$_4$(CH$_2$)$_3$R$_{f8}$)$_3$ (9b). A flask was charged with **10b** (1.658 g, 1.000 mmol), Cl_3SiH (1.01 mL, 10.0 mmol), Et_3N (1.39 mL, 10.0 mmol), and $CF_3C_6H_5$ (40 mL). The mixture was stirred for 15 min (^{31}P NMR: complete reaction). Degassed aqueous NH_4Cl (15 mL) was added. The organic layer was separated, and the aqueous phase was extracted with degassed $CF_3C_6H_5$ (2 × 10 mL). The combined organic layers were dried ($MgSO_4$). Solvent was removed by rotary evaporation, and $CF_3C_6H_5$ (10 mL) was added. The sample was filtered through silica gel/$CF_3C_6H_5$ (1 × 2 cm; vacuum assisted). Solvent was removed from the filtrate by oil pump vacuum to give **9b** as a white solid (1.350 g, 0.822 mmol, 82%), mp 120.0−121.0 °C (capillary). Anal. Calcd for $C_{51}H_{30}F_{51}P$: C, 37.29; H, 1.84. Found: C, 37.28; H, 1.96. MS (EI, *m*/*z*): 1642 (M$^+$, 100), 1623 (M$^+$ − F, 17), 1105 (M$^+$ − C$_6$H$_4$(CH$_2$)$_3$R$_{f8}$, 7.5). NMR (δ, $CDCl_3$): ^{1}H 1.93 (m, 3CH_2CH$_2$CF$_2$), 2.08 (m, 3CH$_2$CF$_2$), 2.68 (t, $^3J_{HH}$ = 7.5 Hz, 3ArCH$_2$), 7.13 (m, 6H), 7.20 (m, 6H); ^{13}C{^{1}H} (partial)[30] 21.9 (t, $^3J_{CF}$ = 3 Hz, *C*H$_2$CH$_2$CF$_2$), 30.5 (t, $^2J_{CF}$ = 21.3 Hz, *C*H$_2$CF$_2$), 35.0 (s, Ar*C*H$_2$), 128.8 (d, $^3J_{CP}$ = 6.7 Hz, *m*-Ph), 134.1 (d, $^2J_{CP}$ = 19.1 Hz, *o*-Ph), 135.3 (d, $^1J_{CP}$ = 10.7 Hz, *i*-Ph), 141.5 (s, *p*-Ph); ^{31}P{^{1}H} −7.4 (s); ^{19}F −81.3 (t, $^3J_{FF}$ = 9.0 Hz, 9F), −114.7 (m, 6F), −122.5 (m, 18F), −123.3 (m, 6F), −124.0 (m, 6F), −126.7 (m, 6F).

P(*p*-C$_6$H$_4$(CH$_2$)$_3$R$_{f6}$)$_3$ (9a). Compounds **10a** (0.900 g, 0.662 mmol), Cl_3SiH (0.67 mL, 6.60 mmol), Et_3N (0.92 mL, 6.60 mmol), and $CF_3C_6H_5$ (20 mL) were combined in a procedure analogous to that for **9b**, and volatiles were removed by oil pump vacuum. Then $CF_3C_6F_{11}$ (10 mL) and CH_2Cl_2 (15 mL) were added. The mixture was shaken. The $CF_3C_6F_{11}$ layer was separated, and the volatiles were removed. The residue was dissolved in $CF_3C_6H_5$ (10 mL). The solution was filtered through a silica gel/$CF_3C_6H_5$ plug (1 × 2 cm; vacuum assisted). Solvent was removed from the filtrate by oil pump vacuum to give **9a** as a white solid (0.620 g, 0.461 mmol, 69%), mp 91.5−92.7 °C (capillary). Anal. Calcd for $C_{45}H_{30}F_{39}P$: C, 40.25; H, 2.25. Found: C, 40.41; H, 2.37. NMR (δ, $CDCl_3$): ^{1}H 1.93 (m, 3CH_2CH$_2$CF$_2$), 2.08 (m, 3CH$_2$CF$_2$), 2.70 (t, $^3J_{HH}$ = 7.5 Hz, 3ArCH$_2$), 7.16 (m, 6H), 7.21 (m, 6H); ^{13}C{^{1}H} (partial)[30] 21.9 (t, $^3J_{CF}$ = 3 Hz, *C*H$_2$CH$_2$CF$_2$), 30.6 (t, $^2J_{CF}$ = 21.3 Hz, *C*H$_2$CF$_2$), 35.0 (s, Ar*C*H$_2$), 128.8 (d, $^3J_{CP}$ = 7.0 Hz, *m*-Ph), 134.1 (d, $^2J_{CP}$ = 19.5 Hz, *o*-Ph), 135.3 (d, $^1J_{CP}$ = 10.7 Hz, *i*-Ph), 141.6 (s, *p*-Ph); ^{31}P{^{1}H} −7.3 (s); ^{19}F −81.4 (t, $^3J_{FF}$ = 9.0 Hz, 9F), −114.7 (m, 6F), −122.5 (m, 6F), −123.5 (m, 6F), −124.1 (m, 6F), −126.8 (m, 6F).

P(*p*-C$_6$H$_4$(CH$_2$)$_3$R$_{f10}$)$_3$ (9c). A flask was charged with **10c** (0.490 g, 0.250 mmol), Cl_3SiH (0.25 mL, 2.5 mmol), Et_3N (0.35 mL, 2.5 mmol), and $CF_3C_6H_5$ (20 mL) and fitted with a condenser. The mixture was refluxed (2 h) and cooled. A workup identical with that for **9b** gave **9c** as a white solid (0.210 g, 0.108 mmol, 43%), mp 139.7−140.5 °C (capillary). Anal. Calcd for $C_{57}H_{30}F_{63}P$: C, 35.24; H, 1.56. Found: C, 35.34; H, 1.39. NMR (δ, 2:1 v/v $CF_3C_6F_{11}/C_6D_{12}$): ^{1}H 2.04 (m, 3CH_2CH$_2$CF$_2$), 2.15 (m, 3CH$_2$CF$_2$), 2.78 (m, 3ArCH$_2$), 7.18 (m, 6H), 7.34 (m, 6H); ^{31}P{^{1}H} −7.1 (s).

***trans*-Ir(CO)(Cl)[P(*p*-C$_6$H$_4$(CH$_2$)$_3$R$_{f8}$)$_3$]$_2$ (11b).** A Schlenk flask was charged with [Ir(COD)(μ-Cl)]$_2$ (0.0261 g, 0.0388 mmol), **9b** (0.255 g, 0.155 mmol), and $CF_3C_6H_5$ (10 mL). The sample was stirred, and CO (1 atm) was added. After 2 h, volatiles were removed by oil pump vacuum, and ether was added. The resulting slurry was filtered, and the yellow powder was dried by oil pump vacuum to give **11b** (0.210 g, 0.0593 mmol, 76%): mp 146.0−146.7 °C (capillary). Anal. Calcd for $C_{103}H_{60}ClF_{102}IrOP_2$: C, 34.93; H, 1.70. Found: C, 35.08; H, 1.87. IR (cm^{-1}, Nujol): ν_{CO} 1958 s. NMR (δ, $CDCl_3$): ^{1}H 1.95

(30) Aryl resonances of **9a**,**b** and **10a**−**c** were assigned on the basis of chemical shifts and J_{CP} values: Kalinowski, H.-O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; Wiley: New York, 1988; pp 588−589. The *i*/*o*/*m*/*p* positions are defined with respect to phosphorus.

(m, 6CH_2CH$_2$CF$_2$), 2.04 (m, 6CH$_2$CF$_2$), 2.71 (t, $^3J_{HH}$ = 7.2 Hz, 6ArCH$_2$), 7.19 (m, 12H), 7.62 (m, 12H); ^{31}P{^{1}H} 22.9 (s); ^{19}F −81.4 (t, $^3J_{FF}$ = 9.0 Hz, 18F), −114.7 (m, 12F), −122.5 (m, 36F), −123.3 (m, 12F), −123.9 (m, 12F), −126.8 (m, 12F).

Rh[P(*p*-C$_6$H$_4$(CH$_2$)$_3$R$_{f8}$)$_3$]$_3$(Cl) (13b). A round-bottom flask was charged with solutions of **9b** (0.164 g, 0.100 mmol) in $CF_3C_6F_{11}$ (20 mL) and [Rh(COD)(μ-Cl)]$_2$ (0.0082 g, 0.016 mmol) in toluene (20 mL). The biphasic system was stirred. After 1 day, the upper layer was decanted, and volatiles were removed from the lower layer by oil pump vacuum (10^{-6} Torr, 1 day). This gave **13b** as a red wax (0.140 g, 0.0276 mmol, 82%). Anal. Calcd for $C_{153}H_{90}ClF_{153}P_3Rh$: C, 36.27; H, 1.79. Found: C, 36.43; H, 2.06. A similar procedure in which the residue was washed with toluene (3 mL) gave **13b** in 93% yield. Anal. Found: C, 36.12; H, 1.68. An equilibrium with **14b** and **9b** is apparent in solution (see Scheme 2 and text). NMR (δ): ^{1}H ($CDCl_3$) 1.55−1.95 (m, 36H), 2.15 (m, 18H), 6.7−6.9 (m, 18H), 7.6−7.9 (m, 18H); ^{31}P (2:1 v/v C_6H_6/C_6F_6; Figure 1) 28.8 (dd, $^1J_{PRh}$ = 142.5 Hz, $^2J_{PP}$ = 35.6 Hz, 2P), 46.2 (dt, $^1J_{PRh}$ = 188.2 Hz, $^2J_{PP}$ = 35.6 Hz, 1P) and other species at 50.1 (d, $^1J_{PRh}$ = 202.4 Hz, **14b**), −7.4 (s, **9b**), and 24.4 (s, unassigned); ^{31}P ($C_6H_5CF_3$, partial) 29.0 (dd, $^1J_{PRh}$ = 143.4 Hz, $^2J_{PP}$ = 36.5 Hz, 2P), 46.3 (dt, $^1J_{PRh}$ = 191.5 Hz, $^2J_{PP}$ = 36.5 Hz, 1P).

Catalytic Hydrogenations. The following are representative. **A**. A Schlenk tube was charged with a solution of **13b** in $CF_3C_6F_{11}$ (0.500 mL, 0.0026 M, 0.00130 mmol, 1.05 mol %), $CF_3C_6F_{11}$ (0.5 mL), toluene (1.0 mL), and 2-cyclohexen-1-one (0.012 mL, 0.124 mmol, 95 equiv/Rh), flushed with H_2 (5 min), fitted with an H_2-filled balloon, and immersed in a 45 °C bath. The biphasic sample was vigorously stirred and analyzed by GLC (1 h, 15% conversion to cyclohexanone; 2 h, >99% conversion). Cyclohexanone from closely related reactions has been isolated and characterized.[5a]

B. A Schlenk tube was similarly charged with $CF_3C_6H_5$ (5 mL), **13b** (0.0158 g, 0.0312 mmol, 0.5 mol %, giving a 0.0062 M solution), dodecane GLC standard, and 2-cyclohexen-1-one (0.060 mL, 0.629 mmol, 198 equiv/Rh) and treated with H_2 as in procedure A (2 h, <1% conversion; 4 h, 10% conversion; 24 h, >99% conversion).

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