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Synthesis and properties of fluorous arenes and triaryl phosphorus compounds with branched fluoroalkyl moieties ("split pony tails")

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Abstract

Most compounds designed for immobilization in fluorous media feature linear pony tails of the formula $(CH_2)_m(CF_2)_{n-1}CF_3$ $[(CH_2)_mR_{fn}]$. This paper presents a first-generation approach to compounds with branched or "split" pony tails of the formula $(CH_2)_lCH[(CH_2)_mR_{fn}]_2$. Allyl tri(*n*-butyl)tin is reacted twice with perfluorooctyl iodide ($R_{f8}I$; first, photochemical, 78–81%; second, thermal with radical initiator, 71%; 13–18 g scales) to give the secondary alkyl iodide $ICH(CH_2R_{f8})_2$ (**3**). A subsequent $Ni(Cl)_2(PPh_3)_2$-catalyzed reaction with allyl tri(*n*-butyl)tin yields the branched alkene $H_2C{=}CHCH_2CH(CH_2R_{f8})_2$ (74%). A palladium-catalyzed Heck coupling with $O{=}P(p\text{-}C_6H_4Br)_3$ gives the fluorous phosphine oxide $O{=}P(p\text{-}C_6H_4CH{=}CHCH_2CH(CH_2R_{f8})_2)_3$ (84%), and Pd/C-catalyzed hydrogenation affords $O{=}P(p\text{-}C_6H_4(CH_2)_3\text{-}CH(CH_2R_{f8})_2)_3$ (>99%). Reduction with $SiHCl_3$ gives $P(p\text{-}C_6H_4(CH_2)_3CH(CH_2R_{f8})_2)_3$, which is protected as the air-stable borane adduct $H_3B{\cdot}P(p\text{-}C_6H_4(CH_2)_3CH(CH_2R_{f8})_2)_3$ (**9**, 64%). The $CF_3C_6F_{11}$/toluene partition coefficient of **9** is much higher than that of the analog with *p*-$(CH_2)_3R_{f8}$ groups (96.6:3.4 versus 37.3:62.7). The iodide **3** is unreactive towards PAr_3 at 175–250 °C. However, a CuBr-catalyzed reaction with C_6H_5MgBr gives $C_6H_5CH(CH_2R_{f8})_2$, which also exhibits a high partition coefficient (97.9:2.1).

Keywords: Fluorous; Tin; Radical substitution; Radical addition; Heck reaction; Phosphine-boranes

1. Introduction

Over the last decade, many new catalysts with high affinities for fluorous solvents have been synthesized [1–4]. This has been prompted by the rapid growth, following the initial report of Horváth and Rábai [1] of "fluorous biphase catalysis". As most often practiced, this protocol exploits the markedly temperature-dependent miscibilities of organic and fluorous solvents [5]. Most combinations give two phases at room temperature, as illustrated in Scheme 1. However, with moderate heating, one phase is obtained. Reactions can be catalyzed under monophasic conditions at the high temperature limit, and the products and catalyst are separated under biphasic conditions at the low temperature limit. Most fluorous solvents in current use are saturated perfluorocarbons.

High catalyst affinities for fluorous phases can be achieved by attaching "pony tails" of the formula $(CH_2)_m(CF_2)_{n-1}CF_3$, abbreviated $(CH_2)_mR_{fn}$ so that n represents the number of fluorinated carbons. The $(CH_2)_m$ segment can be viewed as a "tuning element", the length of which modulates the electron-withdrawing effect of the perfluoroalkyl groups on the reaction center [6]. Not surprisingly, a variety of transition-metal-containing fluorous catalysts has been prepared, [4] and many of these have been based upon fluorous phosphines. There are also many reactions catalyzed by phosphines alone [7], and the applicability of fluorous phosphines to such processes has been demonstrated [8]. Fluorous phosphines have further been used to prepare Wittig reagents that give easily recycled phosphine oxides [9].

Triaryl phosphines offer unique properties, and several fluorous versions have been developed. The first examples involved simple *para*-R_{f6} substituents [10–12].[1] These phosphines were much less basic than non-fluorous analogs due to the lack of $(CH_2)_m$ segments, and displayed only modest fluorous phase affinities. Aryl-containing compounds are difficult to render highly fluorophilic, and studies have shown that at least two R_{f8} pony tails per ring are necessary [13]. Both issues were nicely addressed by van Koten, Deelman, and co-workers [14,15], who used *para*-silicon substituents as anchors for one, two, or three pony tails of

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[1] For R_{f8} analogs, see [10] and [11].

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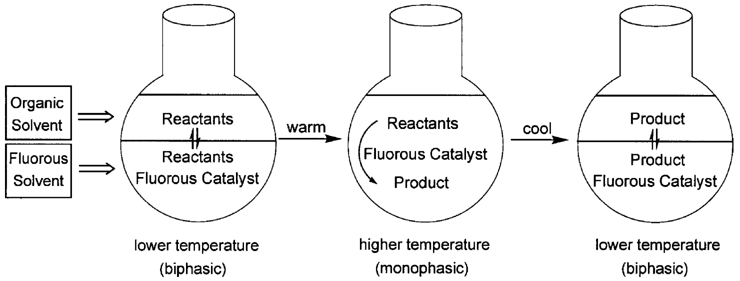

Scheme 1. A common protocol for fluorous biphase catalysis and catalyst recycling.

the formula $(CH_2)_2R_{fn}$ ($n = 6, 8, 10$) [16]. Others have described systems with alkoxide aryl substituents $O(CH_2)_mR_{fn}$ ($m/n = 1/7, 3/8$) [17].

Although the silicon-substituted fluorous triaryl phosphines have proved to have wide utility in catalysis [15], there has remained a demand for well "insulated", highly fluorophilic, non-heteroatom-based systems. Several groups have synthesized phosphines with one $(CH_2)_2R_{fn}$ or $(CH_2)_3R_{fn}$ substituent per aryl ring [12,18–22]. However, in every case analogous routes to more fluorophilic systems with two such substitutents have been problematic. This includes our own efforts with reactions of PCl_3 and magnesium or lithium derivatives of the fluorous aryl iodides $IC_6H_3((CH_2)_3R_{f8})_2$ [13c,23]. Therefore, we sought to develop routes to arenes and triaryl phosphines with *branched* pony tails of the general formula $(CH_2)_lCH[(CH_2)_mR_{fn}]_2$. Such substituents offer "two pony tails for the price of one", and we refer to them as "split pony tails". In this paper, we describe our successful first-generation route to such compounds. There are scattered reports of other types of fluorous molecules with branched pony tails [24], and these are summarized in Section 3.

2. Results

2.1. Syntheses of triaryl phosphorus compounds

The synthesis of fluorous triaryl phosphines can be approached by phosphorus–carbon bond disconnection, or carbon–carbon bond disconnection. Most of the above examples have been prepared by reactions of PCl_3 with aryl magnesium or lithium compounds. However, in an important development, Xiao and co-workers established the viability of three-fold Heck reactions of the phosphine oxide $O{=}P(p\text{-}C_6H_4Br)_3$ (**1**) and a variety of terminal alkenes, including cases with perfluoroalkyl substituents [20]. In view of our mixed experience with the PCl_3 strategy, we set out to test the efficacy of the Xiao protocol for the introduction of split pony tails. Accordingly, **1** was prepared from *p*-dibromobenzene in a one-flask lithiation–PCl_3 addition–oxidation sequence in 38% yield following previously established methods [25,26].[2]

A terminal alkene with a substituent of the formula $(CH_2)_lCH[(CH_2)_mR_{fn}]_2$ was sought. We established earlier that the photolysis of commercially available perfluorooctyl iodide ($R_{f8}I$) and allyl tri(*n*-butyl)tin gives the alkene $R_{f8}CH_2CH{=}CH_2$ (**2**), as shown in Scheme 2 [27]. This free radical chain substitution can be conducted on 13–15 g scales and reliably gives 78–81% yields [27,28]. A subsequent thermal reaction of **2** and additional $R_{f8}I$ was conducted in the presence of the free radical initiator VAZO (1,1′-azobis(cyclohexanecarbonitrile)). The addition product, secondary iodide $ICH(CH_2R_{f8})_2$ (**3**), was obtained in 71% yield after recrystallization (Scheme 2).[3] Compound **3** could easily be prepared on 13–18 g scales, and like many alkyl iodides, solutions were moderately light sensitive.

As illustrated in Scheme 2, **3** was then refluxed with allyl tri(*n*-butyl)tin in the presence of a Ni(II) catalyst. This Stille-like but possibly radical cross-coupling [30] gave the target alkene $H_2C{=}CHCH_2CH(CH_2R_{f8})_2$ (**4**) in 74% yield on multigram scales. Compounds **3** and **4** were characterized by NMR (^1H, ^{13}C), mass spectrometry, and microanalysis, as summarized in Section 4. All features were routine, and fully supported the assigned structures. Compound **2** exhibited good solubility in both fluorous and non-fluorous solvents. Compounds **3** and **4** showed lower solubilities in non-fluorous solvents (e.g. moderate in $CDCl_3$), but dissolved to appreciable extents in acetone, ether, and THF. When hot hexane solutions of **3** were cooled, gels were reproducibly obtained. The flasks could be inverted without loss of material. More polar solvents also gave gels, although seemingly with less entrained solvent.

As shown in Scheme 3, the phosphine oxide **1** and alkene **4** (3.3 equivalents) were reacted under Heck conditions similar to those reported by Xiao and co-workers [20]. The Herrmann–Beller dimeric palladacycle catalyst **5** (Scheme 4) was employed (1.8 mol% or 3.6:100 Pd/**1**). A mixed DMF–$CF_3C_6H_5$ solvent system was used to ensure that all reactants were at least partially dissolved. Workup gave the unsaturated fluorous phosphine oxide $O{=}P(p\text{-}C_6H_4CH{=}CHCH_2CH(CH_2R_{f8})_2)_3$ (**6**) in 84% yield. In accord with Xiao's precedent, only the all-*trans* C=C isomer was detected. A subsequent reaction with hydrogen (1 atm, 3 d) in the presence of 10% Pd/C afforded the saturated phosphine oxide $O{=}P(p\text{-}C_6H_4(CH_2)_3CH(CH_2R_{f8})_2)_3$ (**7**) in

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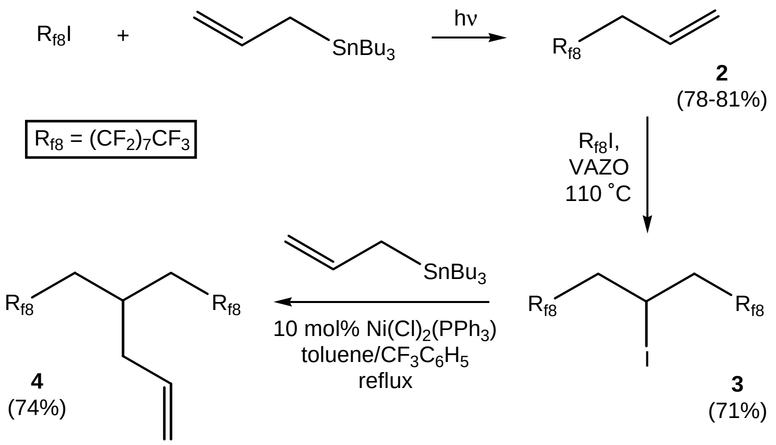
[2] Since full details have not been reported for these steps, we give our procedure in Section 4. No effort was made to optimize the yield of **1**.

[3] We thank L.J. Alvey for a preliminary experiment.



Scheme 2. Syntheses of building blocks with split pony tails.

>99% yield. Wilkinson's catalyst effected only partial conversion under comparable conditions.

The phosphine oxide **7** was reduced using an excess of a standard reagent, $HSiCl_3$. Best results were obtained with a two-stage addition (room temperature and 110 °C). Although the resulting fluorous triaryl phosphine $P(p\text{-}C_6H_4(CH_2)_3CH(CH_2R_{f8})_2)_3$ (**8**) should not, by analogy to related systems [22], be highly air sensitive,[4] it was nonetheless protected in situ as the borane adduct $H_3B{\cdot}P(p\text{-}C_6H_4(CH_2)_3CH(CH_2R_{f8})_2)_3$ (**9**). Such borane derivatives are usually more convenient to handle, and can often be converted to metal complexes without prior deprotection [31]. A chromatographic workup gave **9** as a yellow wax in 64% yield. All new phosphorus-containing compounds were characterized by ^1H, ^{13}C, and ^{31}P NMR. Although **9** gave an acceptable microanalysis, **6** and **7** did not. Compound **9** was very slightly soluble in hexane. Both **9** and **7** were essentially insoluble in other organic solvents, and only moderately soluble in fluorous solvents.

2.2. *Other experiments*

In the course of the preceding investigations, other reactions that might provide convenient routes to compounds with split pony tails were examined. Since the secondary iodide **3** is easily prepared in quantity, various functionalizations were attempted. For example, PPh_3 and the fluorous primary alkyl iodides $R_{fn}(CH_2)_2I$ react to give phosphonium salts that can be applied in Wittig reactions [13a]. However, these displacements require more forcing conditions (DMF, 105–110 °C) than with non-fluorous iodides. Interestingly, PPh_3 and **3** were recovered unchanged after 50 h at 175 °C without solvent in a sealed tube (Scheme 5). The more nucleophilic phosphine $P(p\text{-tol})_3$ (72 h, 250 °C) as well as $P(OEt)_3$ (22–60 h, 160 °C) gave similar results, and further experiments and observations are detailed elsewhere [28].

Additional carbon–carbon bond forming reactions of **3** were investigated. Our attention was drawn to copper-catalyzed cross-couplings of Grignard reagents that had been applied to fluorous secondary alkyl iodides [32]. As shown in Scheme 5, **3** and C_6H_5MgBr reacted in the presence of CuBr (6 mol%) in THF to give the fluorous arene $C_6H_5CH(CH_2R_{f8})_2$ (**10**) in high yield. However, purification proved challenging. In our hands, the removal of residual **3** and the byproduct $R_{f8}(CH_2)_3R_{f8}$ could not be achieved by recrystallization or conventional column chromatography. However, chromatography on fluorous reverse phase silica gel [33] provided pure **10** in 63% yield. The solubility properties of **10** were similar to those of **4**.

An analogous sequence was attempted with the Grignard reagent $p\text{-}BrC_6H_4MgBr$, which was generated from $p\text{-}BrC_6H_4Br$ according to literature procedures [34]. Although the corresponding product $p\text{-}BrC_6H_4CH(CH_2R_{f8})_2$ (**11**) formed, conversions were lower than with **10** (ca. 80% by ^1H NMR). Upon scale-up, conversions decreased. Despite intensive efforts, analytically pure **11** could not be isolated.[5] Attempts to effect bromine–lithium or bromine–magnesium exchange with crude **11**, and subsequent reactions with PCl_3 are described elsewhere [28]. A variety of other carbon–carbon bond-forming cross-coupling reactions were also investigated, many of which are similarly described elsewhere [28]. Of these, a Heck reaction of phenyl iodide and the alkene **4** was the most promising.

The $CF_3C_6F_{11}$/toluene partition coefficients of the borane–phosphine adduct **9** and arene **10** were measured by ^{19}F NMR and GC as described in Section 4. The results from two independent runs (**9**, 96.4:3.6 and 96.9:3.1; **10**, 98.0:2.0

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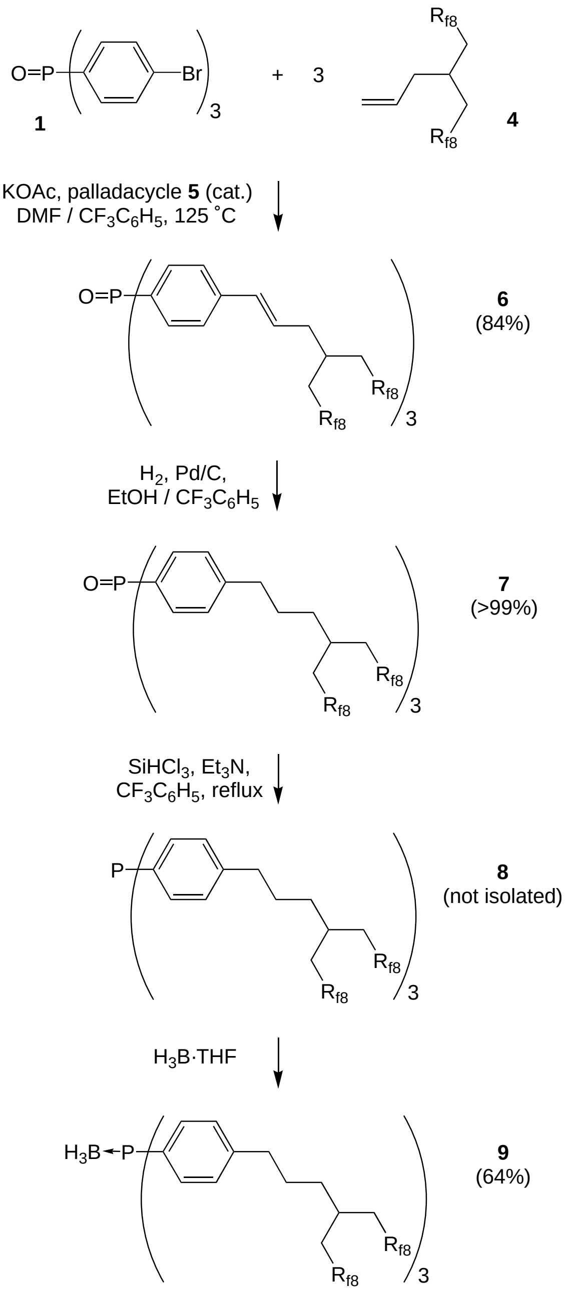
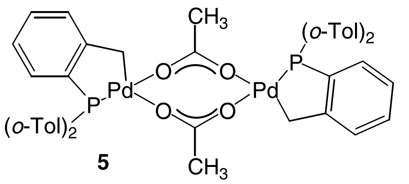
[4] Any air or other sensitivity of fluorous phosphines should be viewed in the context of their molecular weights. That of **8** (3021.7) is more than 10 times that of PPh_3 (262.3). Therefore, per unit mass of dissolved triaryl phosphine, a much higher fraction of the former can be decomposed by a given concentration of a reactive impurity in the solvent.

[5] The maximum purity after fluorous reverse phase chromatography was 95%, as assayed by ^1H NMR (δ, $CF_3C_6F_5/CDCl_3$, 1:4 (v/v)): 7.46 (d, $J_{HH} = 8.3$ Hz, 2H of C_6H_4), 7.17 (d, $J_{HH} = 8.3$ Hz, 2H of C_6H_4), 3.60 (quint, $J_{HH} = 6.8$ Hz, $C_6H_4C\underline{H}$), 2.52 (m, $2CH_2$).



Scheme 3. Syntheses of triaryl phosphorus compounds with split pony tails.

and 97.7:2.3) were averaged. These values are listed in Fig. 1, together with those for selected reference molecules. In order to provide a good comparison for **9**, the previously characterized fluorous triaryl phosphine $P(p\text{-}C_6H_4(CH_2)_3R_{f8})_3$ (**12**) was treated with H_3B under similar conditions to give the adduct $H_3B{\cdot}P(p\text{-}C_6H_4(CH_2)_3R_{f8})_3$ (**13**). Fluorous arenes of the formula $C_6H_4((CH_2)_3R_{f8})_2$ (**14**) provide comparisons for **10**. The trends are analyzed in Section 3.



Scheme 4. Structure of palladacycle **5**.

3. Discussion

3.1. Merits of syntheses

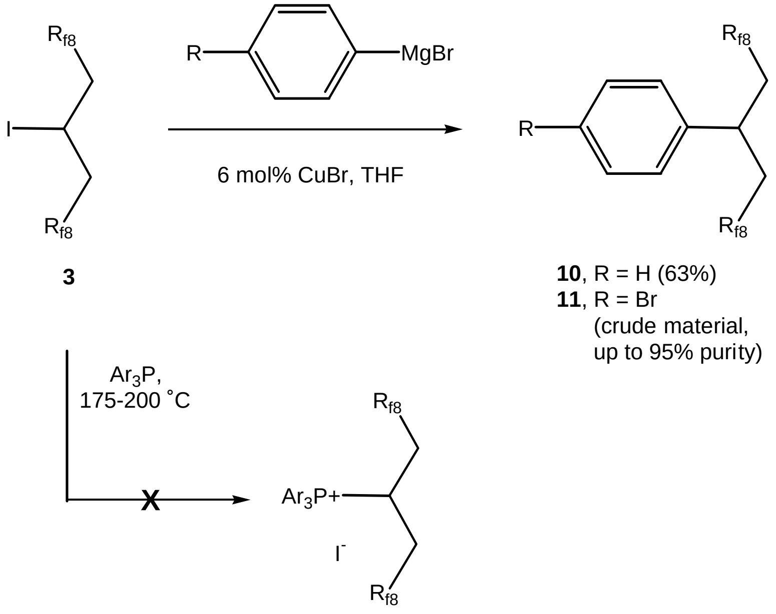
As shown in Schemes 2 and 3, the synthesis of the protected fluorous triaryl phosphine **9** entails seven steps from commercially available materials. The overall yield from $R_{f8}I$ (Scheme 2) is 22%. Apart from the free phosphine **8**, all compounds are stable in air for extended periods. Only the reduction of the phosphine oxide **7** has not yet been tested on a multigram scale, and there would seem to be little chance for complications. There is a conspicuous reliance on radical-based carbon–carbon bond forming reactions in Scheme 2. The Heck reaction in Scheme 3, which completes the carbon skeleton, nicely illustrates the versatility of the methodology developed by Xiao and co-workers [20].

To our knowledge, **8** represents the only fluorous triaryl phosphine with more than one R_{fn} segment of appreciable length per ring, outside of the silicon-containing systems of van Koten and co-workers [14,15]. Three of their compounds that are closely related to **8** are depicted in Fig. 2 (**15a–c**). Different synthetic approaches to **15a–c** were also investigated [14a]. One involving a three-fold lithiation of the phosphine $P(p\text{-}C_6H_4Br)_3$, followed by addition of the appropriate silyl halide, was distinctly superior to routes based upon PCl_3 and aryl magnesium or lithium compounds. Thus, there appears to be a general problem associated with either the generation or reactivity of high-fluorous-content aryl magnesium and lithium species, the exact nature of which can at present only be speculated about [28].

For this reason, we chose not to investigate the halogenation of the fluorous arene **10** (Scheme 5). Although this otherwise attractive building block might have provided pure **11** or the corresponding iodide, these are not in our view promising precursors to triaryl phosphorus compounds. We note in passing that several fluorous triaryl phosphites with more than one pony tail per ring have been reported, but some of these syntheses are not very efficient [35,36].

3.2. Other fluorous compounds with branched pony tails

The triaryl phosphines **15b** and **c** can be viewed as having doubly- and triply-branched pony tails, respectively. These involve a silicon “stem” or branch point. Similar diphosphines or fluorous dppe ($Ar_2PCH_2CH_2PAr_2$) derivatives have been synthesized [14b]. Curran and co-workers has reported the fluorous triaryl phosphine **16** (Fig. 2), which features a triple branch point *within* the six-carbon perfluoroalkyl segment [19]. Such moieties are conveniently constructed via the addition of CsF to the alkene $(CF_3)_2C{=}CFCF_2CF_3$.



Scheme 5. Other reactions of **3**.

This generates a tertiary perfluoroalkyl cesium compound that reacts with benzyl halides.

Curran et al. has also described a convenient synthesis of the fluorous benzylic bromide **17** (Fig. 2), and applied it as a protecting group for carbohydrates [16]. Suitable disaccharides derivatives with three such moieties showed no tendency to partition into organic phases. Vincent has synthesized the fluorous carboxylic acid **18** via a malonate ester synthesis, and the corresponding dicopper tetracarboxylate **19** [24a,b]. The former can be used to extract transition metal ions into fluorous solvents, and the latter pyridines.

The tertiary alcohols **20a** and **b**, which feature carbon branch points, have been prepared in 70–72% yields by additions of the Grignard reagents $R_{fn}(CH_2)_2MgI$ to ethyl acetate [24d]. These have been used as protecting groups for carboxylic acids, and many partition coefficients of the resulting esters have been measured. The tertiary alcohol **21** has been prepared in 40% yield by the addition of $R_{f6}(CH_2)_2MgI$ to dimethyl carbonate, and elaborated into the triply-branched benzylic bromide **22** (Fig. 2) [24c]. This, as well as the silicon analog **17**, have been used to prepare chiral fluorous β-amino alcohols, one of which exhibited a high partition coefficient (97:3, FC-72/toluene).

3.3. Physical properties

One obvious question is the degree to which branching within pony tails affects solubilities. In some cases, molecules

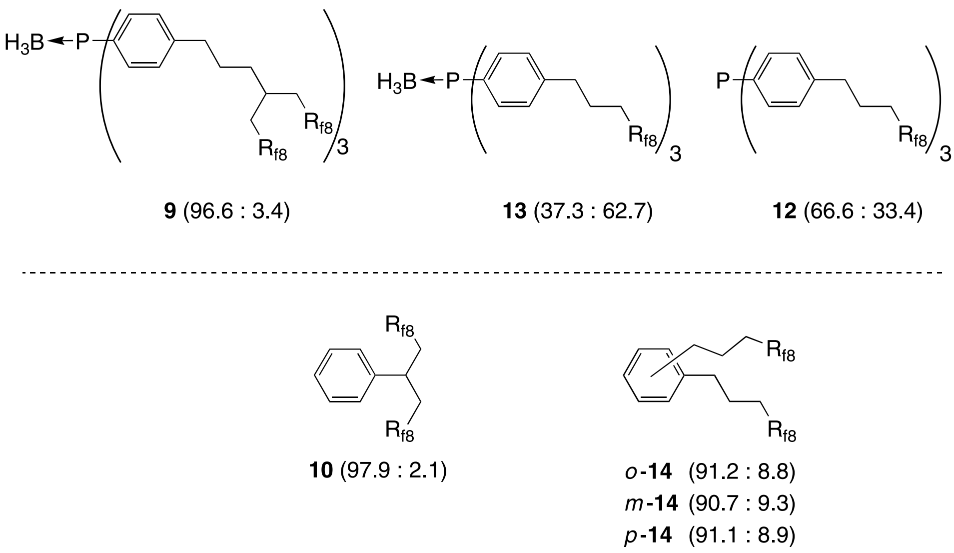


Fig. 1. Summary of partition coefficients ($CF_3C_6F_{11}$/toluene, 25 °C).

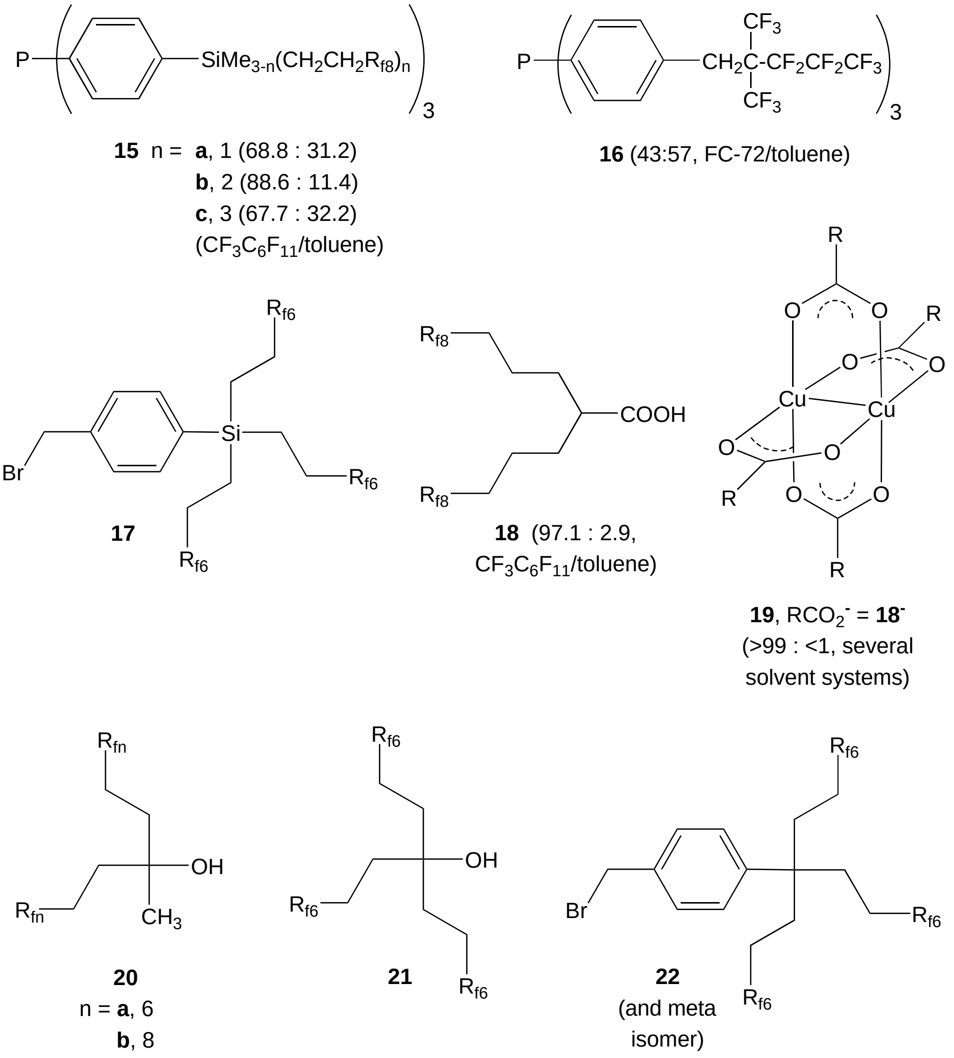


Fig. 2. Some other fluorous compounds with branched pony tails, with partition coefficients were available.

with a high fluorous content are poorly soluble in nearly all solvents at room temperature [8]. For some applications, this is advantageous. It would not be surprising if branching were to enhance solubilities. However, among the species given above, there are not yet enough data or suitable model compounds for comparisons.

With regard to fluorophilicities, the most obvious question is whether a doubly branched pony tail has the same affect as two linear pony tails of the same aggregate formula. As shown in Fig. 1, the arene **10** exhibits a somewhat higher $CF_3C_6F_{11}$/toluene partition coefficient than the two-pony-tailed arenes **14** (97.9:2.1 versus ca. 91:9). However, the latter contain three extra methylene groups. When the usual affect of such a perturbation is considered—for example, with fluorous pyridines [13b]—the values become approximately equal. Unfortunately, no constitutionally isomeric compounds are yet available for comparison.

Another question is how the fluorophilicity of a molecule with a branched pony tail compares to one with one linear pony tail that has half the number of atoms. For example, the aryl groups in the borane adducts **9** and **13** (Fig. 1) feature pony tails of the formulae $(C_6H_{11})(R_{f8})_2$ and $(C_3H_6)R_{f8}$, respectively. Not surprisingly, the former exhibits a much higher partition coefficient (96.6:3.4 versus 37.6:62.7). Since **13** has a much lower partition coefficient than the corresponding phosphine **12** (66.6:33.4), the partition coefficient of the unprotected phosphine **8** can be estimated as $\geq$99:$\leq$1. Thus, **8** constitutes the first highly fluorophilic triaryl phosphine that lacks a skeletal heteroatom.

When available, partition coefficients for the compounds with branched pony tails in Fig. 2 are given. The phosphines **15** exhibit an anomalous trend [14a]. The partition coefficient for **15c**, which has three pony tails per aryl ring, is *lower* than that of **15b**, which has only two. This represents, to our knowledge, the only case where an increase in the number of pony tails results in a decrease in fluorophilicity. The corresponding fluorous dppe ($Ar_2PCH_2CH_2PAr_2$) systems show the expected monotonic increase (28.6:71.4, 92.3:7.7, >98:<2) [14b].

3.4. Conclusion

The highly fluorophilic triaryl phosphine **8**, which features a branched or "split" pony tail on each ring, has been synthesized and fully characterized as its protected borane adduct **9**. The convenient seven-step procedure features air stable intermediates that can be prepared on large scales. Several of these intermediates hold promise as building blocks for additional types of compounds with branched pony tails. Other fluorous compounds with branched pony tails are becoming available (Fig. 2), and this architectural motif is certain to see increasing use in fluorous chemistry.

4. Experimental

4.1. General

Reactions were conducted under inert atmospheres in solvents that were distilled as follows: toluene, ethyl ether, THF, and Et_3N, from Na and benzophenone; CH_2Cl_2 and DMF, from CaH_2; $CF_3C_6H_5$ and $CF_3C_6F_{11}$, from P_2O_5. Workups were conducted under aerobic conditions with distilled reagent grade solvents. Perfluorooctyl iodide ($R_{f8}I$; Lancaster, 97%), allyl tri(*n*-butyl)tin (Lancaster, 97%), 1,1′-azobis(cyclohexanecarbonitrile) (VAZO; Fluka, ≥97%), palladacycle **5** (Strem, ≥98%), *p*-BrC_6H_4Br (Lancaster, 97%), $Ni(Cl)_2(PPh_3)_2$ (ABCR, 99%), KF (Acros, 99%), $MgSO_4$ (Riedel-de Haën, extra pure), CH_3CO_2K (reagent grade), Mg turnings (reagent grade), H_2O_2 (30% in H_2O, reagent grade), 10% Pd/C (Acros), $SiHCl_3$ (Aldrich, ≥99%), CuBr (Aldrich, 98%), $H_3B{\cdot}THF$ (Acros, 1.0 M in THF), and $H_3B{\cdot}SMe_2$ (Acros, 2.0 M in THF) were used as received. Solutions of *n*-BuLi (Acros, 1.6 M in hexane) [37] and C_6H_5MgBr (Fluka, 0.8 M in THF) were standardized. Most instrumental procedures were described earlier [8b]. DSC measurements were recorded using a Mettler-Toledo DSC-821 instrument [38].

4.2. $O{=}P(p\text{-}C_6H_4Br)_3$ (**1**)

A Schlenk flask, equipped with a thermometer and a septum, was charged with *p*-BrC_6H_4Br (11.796 g, 50.000 mmol) and THF (50 ml) [25]. The mixture was cooled to −80 °C (acetone and CO_2). A solution of *n*-BuLi (33.1 mL, 1.51 M in hexane, 50.0 mmol) was slowly added, keeping the inner temperature below −75 °C. A white suspension formed. A solution of PCl_3 (1.44 ml, 2.27 g, 16.5 mmol) in THF (25 ml) was added dropwise over 2 h. The suspension turned to a grape color and was allowed to warm to room temperature overnight. Then, H_2O_2 (6% in H_2O, 50 ml; prepared from a 30% solution) was added. The mixture was stirred for 30 min, and the phases were allowed to separate. The aqueous phase was extracted with ethyl ether (3 × 50 ml). The organic phases were combined, washed with water (3 × 30 ml) and dried ($MgSO_4$). The volatiles were removed by rotary evaporation and oil pump vacuum to yield a white solid (7.830 g). The crude product was dissolved in a mixture of acetone (41 ml), chloroform (17 ml), and ethyl ether (35 ml). Then hexane (40 ml) was added, and the sample was stored in the refrigerator. After 14 h, the white precipitate was collected by filtration. The filtrate was concentrated to ca. 100 ml, and a second crop was similarly precipitated. The combined crops were dried under oil pump vacuum to give **1** as a white powder (3.231 g, 6.274 mmol, 38%), mp 178.3 °C (DSC; lit 179–180 °C) [25].

NMR (δ, $CDCl_3$): ^1H 7.65 (m, 6H of 3 C_6H_4), 7.52 (m, 6H of 3 C_6H_4); $^{13}C\{^1H\}$[6] 133.3 (d, $J_{CP} = 10.6$ Hz), 132.0 (d, $J_{CP} = 12.8$ Hz), 130.6 (d, $J_{CP} = 106.0$ Hz, *i*-C_6H_4), 127.7 (d, $J_{CP} = 3.2$ Hz, *p*-C_6H_4); $^{31}P\{^1H\}$ 27.8 (s). MS (positive FAB, 3-NBA, *m/z*): 1030 ($[2M]^+$, 15%), 515 (M^+, 100%), 359 ($[M–C_6H_4Br]^+$, 18%). Calculated for $C_{18}H_{12}Br_3PO$: C, 41.98; H, 2.35. Found: C, 42.05; H, 2.47.

4.3. $ICH(CH_2R_{f8})_2$ (**3**)

A Fisher–Porter bottle was charged with $R_{f8}CH_2CH{=}CH_2$ (**2**; [27] 12.000 g, 26.077 mmol), $R_{f8}I$ (14.237 g, 26.077 mmol), and VAZO (0.510 g, 2.09 mmol), briefly evacuated and refilled with nitrogen (3×), and pressurized with nitrogen (3.8 bar). The mixture was stirred at 110 °C for 4 h and allowed to cool. The bottle was vented and the off-white solid dissolved in refluxing hexane (ca. 75 ml). The solution was cooled to 0 °C and gelled. The gel was suction filtered and dried by oil pump vacuum to give **3** as soft, white flakes (18.604 g, 18.491 mmol, 71%), mp 55.7 °C (DSC) [29]. In some cases, purification required a second gel precipitation from acetone. Although solid **3** is light-stable, solutions show decomposition after several hours.

NMR (δ, $CF_3C_6F_5/CDCl_3$, 1:4 (v/v)): ^1H 4.63 (quint, $J_{HH} = 6.6$ Hz, CHI), 3.01 (m, 2 CH_2); $^{13}C\{^1H\}$ (partial) 36.6 (t, $J_{CF} = 23.0$ Hz, CH_2), −1.2 (s, ICH). MS (positive FAB, 3-NBA, *m/z*): 1005 (M^+, 20%), 987 ($[M–F]^+$, 18%), 879 ($[M–I]^+$, 25%), 573 ($[C_8F_{17}CH_2CHI]^+$, 10%). Calculated for $C_{19}H_5F_{34}I$: C, 22.68; H, 0.50. Found: C, 22.99; H, 0.37.

4.4. $H_2C{=}CHCH_2CH(CH_2R_{f8})_2$ (**4**)

A Schlenk flask, equipped with a septum and a condenser, was charged with **3** (5.025 g, 5.000 mmol), allyl tri(*n*-butyl)tin (4.65 ml, 4.96 g, 15.0 mmol), $Ni(Cl)_2(PPh_3)_2$ (0.327 g, 0.500 mmol), toluene (15 ml), and $CF_3C_6H_5$ (5 ml). The mixture was kept at 120 °C for 24 h. The initially deep red solution decolorized and a gray solid precipitated. Then KF (2.905 g, 50.00 mmol) was added. The mixture was stirred at room temperature for 24 h. The dark gray solid was removed by filtration and washed with $CF_3C_6H_5$ (50 ml).

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[6] The *ipso*, *ortho*, *meta*, and *para* carbons are designated with reference to the phosphorus atom.

The combined organic phases were washed with water (2 × 15 ml) and dried ($MgSO_4$). The volatiles were removed by rotary evaporation and oil pump vacuum. The oil or greasy crude product was washed (with shaking) with acetonitrile (2 × 20 ml) and methanol (2 × 20 ml). If needed, the mixtures can be cooled to freeze the lower fluorous product and facilitate solvent decantation. Drying by oil pump vacuum gave **4** as a white grease (3.395 g, 3.690 mmol, 74%), which was pure enough for further use. Kugelrohr distillation (110 °C, 7×10^{-6} bar) gave **4** as an analytically pure white wax.

NMR (δ, $CF_3C_6F_5/CDCl_3$, 1:4 (v/v)): ^1H 5.74 (m, =CH), 5.17–5.12 (m, $H_2C=$), 2.53 (m, CH), 2.34 (m, $=CHC\underline{H}_2$), 2.22 (m, $2CH_2R_{f8}$); $^{13}C\{^1H\}$ (partial)[7] 133.8 (s, =CH), 119.2 (s, $H_2C=$), 39.1 (s, $=CH\underline{C}H_2$), 33.9 (t, $J_{CF} = 21.1$ Hz, $\underline{C}H_2R_{f8}$), 25.3 (s, CH). MS (positive FAB, 3-NBA, *m/z*): 919 (M^+, 65%), 487 ($[M–CH_2C_8F_{17}]^+$, 100%). Calculated for $C_{22}H_{10}F_{34}$: C, 28.71; H, 1.10. Found: C, 28.73; H, 1.18.

4.5. $O{=}P(p\text{-}C_6H_4CH{=}CHCH_2CH(CH_2R_{f8})_2)_3$ (**6**)

A Schlenk flask, equipped with a condenser, was charged with **4** (1.104 g, 1.200 mmol), **1** (0.170 g, 0.330 mmol), palladacycle **5** (0.0056 g, 0.0060 mmol), CH_3CO_2K (0.1081 g, 1.320 mmol), $CF_3C_6H_5$ (3 ml), and DMF (6 ml). The mixture was kept at 125 °C for 24 h. It turned dark brown, and was allowed to cool. The volatiles were removed by oil pump vacuum. The solid was extracted with $CF_3C_6H_5$ (50 ml). The yellow solution was washed with water (2 × 10 ml) and dried ($MgSO_4$). The solvent was removed by rotary evaporation. The dark brown gum or oil (1.009 g) was dissolved in a minimum of $CF_3C_6H_5$. Hexane was added, and **6** precipitated as a solid or oil, which was isolated by decantation and washed with hexane (0.839 g, 0.277 mmol, 84%). A second crop of **6** could often be obtained by storing the filtrate in the refrigerator.

NMR (δ, $CF_3C_6F_5/CDCl_3$, 4:1 (v/v)): ^1H 7.59 (m, 6H of $3C_6H_4$), 7.43 (m, 6H of $3C_6H_4$), 6.51 (d, $J_{HH} = 15.9$ Hz, $3C_6H_4C\underline{H}$), 6.23 (m, $3{=}C\underline{H}CH_2$), 2.63 (m, 3CH), 2.52 (m, $3{=}CH\underline{C}H_2$), 2.25 (m, $6CH_2R_{f8}$); $^{13}C\{^1H\}$ (partial) (see footnotes 6 and 7)[8] 133.9 (s, $C_6H_4\underline{C}H{=}$), 132.8 (d, $J_{CP} = 10.6$ Hz, *o*-C_6H_4), 128.2 (s, $=\underline{C}HCH_2$), 126.4 (d, $J_{CP} = 12.2$ Hz, *m*-C_6H_4), 38.4 (s, $=CH\underline{C}H_2$), 34.3 (t, $J_{CF} = 20.6$ Hz, $\underline{C}H_2R_{f8}$), 26.1 (s, $\underline{C}HCH_2R_{f8}$); $^{31}P\{^1H\}$ 28.5 (s).

4.6. $O{=}P(p\text{-}C_6H_4(CH_2)_3CH(CH_2R_{f8})_2)_3$ (**7**)

A Schlenk flask was charged with **6** (0.100 g, 0.0330 mmol), Pd/C (10%, 0.013 g), $CF_3C_6H_5$ (12 ml), and ethanol (10 ml), purged with hydrogen, and fitted with a balloon filled with hydrogen. The suspension was vigorously stirred for 3 days. The solid was allowed to settle, and the supernatant removed using a filter syringe. The residue was analogously extracted with $CF_3C_6H_5$ (2 × 20 ml). The organic phases were combined and the volatiles removed by rotary evaporation and oil pump vacuum to give **7** as a yellow gum (0.100 g, 0.0330 mmol, >99%).

NMR (δ, $CF_3C_6F_5/CDCl_3$, 4:1 (v/v)): ^1H 7.59 (m, 6H of $3C_6H_4$), 7.28 (m, 6H of $3C_6H_4$), 2.82 (t, $J_{HH} = 7.0$ Hz, $3C_6H_4C\underline{H_2}$), 2.56 (m, 3CH), 2.29 (m, $6CH_2R_{f8}$), 1.81 (m, $3CH_2C\underline{H_2}CH_2$), 1.77 (m, $3CH_2CH_2C\underline{H_2}$); $^{13}C\{^1H\}$ (partial) (see footnotes 6–8) 132.6 (d, $J_{CP} = 10.0$ Hz, *o*-C_6H_4), 128.7 (d, $J_{CP} = 12.7$ Hz, *m*-C_6H_4), 35.9 (s, $C_6H_4\underline{C}H_2$), 34.6 (overlapping m and s, $\underline{C}H_2R_{f8}$, $\underline{C}H_2CH$), 27.8 (s, $CH_2\underline{C}H_2CH_2$), 25.9 (s, $\underline{C}HCH_2R_{f8}$); $^{31}P\{^1H\}$ 30.0 (s). Calculated for $C_{84}H_{45}F_{102}PO$: C, 33.20; H, 1.49. Found: C, 34.12; H, 1.76.

4.7. $H_3B{\cdot}P(p\text{-}C_6H_4(CH_2)_3CH(CH_2R_{f8})_2)_3$ (**9**)

A Schlenk flask, equipped with a septum and a condenser, was charged with **7** (0.149 g, 0.0491 mmol), Et_3N (0.070 ml, 0.50 mmol), and $CF_3C_6H_5$ (5 ml). Then $SiHCl_3$ (0.0510 ml, 0.0677 g, 0.500 mmol) was added via syringe over 20 min with stirring. After an additional hour, the mixture was kept at 110 °C for 4 h. A second portion of $SiHCl_3$ (0.0510 ml, 0.0677 g, 0.500 mmol) was added. After an additional 15 h at 110 °C, the mixture was cooled to ambient temperature, and the excess $SiHCl_3$ was carefully removed (partial oil pump vacuum, leaving solvent). Then $H_3B{\cdot}THF$ (0.100 ml, 1.0 M in THF, 0.100 mmol) was slowly added by syringe to the crude phosphine **8**. The mixture was stirred for 18 h, and water (10 ml) and $CF_3C_6H_5$ (50 ml) were added. The aqueous phase was extracted with $CF_3C_6H_5$ (2 × 20 ml). The combined organic phases were dried ($MgSO_4$). The cloudy filtrate was concentrated to ca. 10 ml and centrifuged at 4000 rpm for 10 min. The clear supernatant was decanted from the beige residue, which was discarded. Silica gel (2 g) was added to the supernatant. The mixture was dried in vacuo and loaded on top of a silica gel column (10 cm). The column was extracted with ethyl acetate/hexane (1:10 (v/v)). The solvent was removed from the extract by rotary evaporation. The residue was dissolved in $CF_3C_6F_{11}$ (10 ml). The solution was washed with toluene (2 × 5 ml), and the solvent was removed by oil pump vacuum to give **9** as a yellow wax (0.0958 g, 0.0316 mmol, 64%).

NMR (δ, $CF_3C_6F_5/CDCl_3$, 4:1 (v/v)): ^1H 7.54 (m, 6H of $3C_6H_4$), 7.37 (m, 6H of $3C_6H_4$), 2.81 (t, $J_{HH} = 7.0$ Hz, $3C_6H_4C\underline{H_2}$), 2.60 (m, 3CH), 2.33 (m, $6CH_2R_{f8}$), 1.82 (2 m, $3CH_2C\underline{H_2}C\underline{H_2}$); $^{13}C\{^1H\}$ (partial) (see footnotes 6–8) 133.7 (d, $J_{CP} = 10.3$ Hz, *o*-C_6H_4), 129.0 (d, $J_{CP} = 14.8$ Hz, *m*-C_6H_4), 35.9 (s, $C_6H_4\underline{C}H_2$), 34.6 (overlapping m and s, $\underline{C}H_2R_{f8}$, $\underline{C}H_2CH$), 28.0 (s, $CH_2\underline{C}H_2CH_2$), 26.0 (s, $\underline{C}HCH_2R_{f8}$); $^{31}P\{^1H\}$ 20.8 (br s). Calculated for $C_{84}H_{48}BF_{102}P$: C, 33.22; H, 1.59. Found: C, 33.71; H, 1.52.

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[7] In order to reduce the number of interfering peaks, the $CF_3C_6F_5$ was replaced by C_6F_6 for ^{13}C NMR spectra. The non-aromatic carbon signals were assigned by ^1H–^{13}C correlation (HETCOR) experiments. The aromatic carbon signals of **6**, **7**, and **9** were assigned by analogy to those of related fluorous phosphine oxides [22].

[8] The signals for the *ipso* and *para* carbon atoms were not detected.

4.8. $H_3B{\cdot}P(p\text{-}C_6H_4(CH_2)_3R_{f8})_3$ (**13**)

A solution of $P(p\text{-}C_6H_4(CH_2)_3R_{f8})_3$ (**12**; 0.0420 g, 0.0256 mmol) [22] in $CF_3C_6H_5$ (1.5 ml) was treated with $H_3B{\cdot}SMe_2$ (2.0 M in THF; 0.0200 ml, 0.0400 mmol). After 48 h, the volatiles were removed by oil pump vacuum. The white powder was taken up in a mixture of toluene and $CF_3C_6F_{11}$ (16 ml, 50:50 (v/v)). The solvent was removed from the fluorous phase by rotary evaporation and oil pump vacuum to give **13** as a white solid (0.0141 g, 0.00851 mmol, 33%), mp 137.0 (DSC).

NMR (δ, $CDCl_3$): ^1H 7.49 (m, 6H of $3C_6H_4$), 7.24 (m, 6H of $3C_6H_4$), 2.73 (t, $J_{HH} = 7.7$ Hz, $3C_6H_4C\underline{H}_2$), 2.07 (m, $C\underline{H}_2R_{f8}$), 1.94 (m, $CH_2\underline{C}H_2CH_2$); $^{13}C\{^1H\}$ (partial) (see footnote 6) 144.2 (s, $p\text{-}C_6H_4$), 133.4 (d, $J_{CP} = 9.3$ Hz, $o\text{-}C_6H_4$), 128.8 (d, $J_{CP} = 10.4$ Hz, $m\text{-}C_6H_4$), 127.1 (d, $J_{CP} = 58.9$ Hz, $i\text{-}C_6H_4$), 34.9 (s, $C_6H_4\underline{C}H_2$), 30.3 (t, $J_{CP} = 22.3$ Hz, $\underline{C}H_2R_{f8}$), 21.6 (s, $CH_2\underline{C}H_2CH_2$); $^{31}P\{^1H\}$ 19.5 (br s). Calculated for $C_{51}H_{33}BF_{51}P$: C, 36.98; H, 2.01. Found: C, 36.06, H, 1.95.

4.9. $C_6H_5CH(CH_2R_{f8})_2$ (**10**)

A Schlenk flask, equipped with a septum and a condenser, was charged with **3** (0.503 g, 0.500 mmol), CuBr (0.0040 g, 0.028 mmol), and THF (6 ml). The suspension was briefly refluxed, and a portion of a C_6H_5MgBr solution (ca. 0.1 ml of 0.625 ml, 0.80 M in THF, 0.500 mmol total) was added via syringe with vigorous stirring. The resulting yellow color discharged after a few seconds. The remaining C_6H_5MgBr was added within 5–10 min, and the sample was briefly refluxed. The orange suspension was stirred at ambient temperature for 20 h, quenched with saturated aqueous NH_4Cl, and extracted with ethyl ether (3 × 50 ml). The combined organic phases were dried ($MgSO_4$). The solvent was removed by rotary evaporation. The yellowish-white solid was dissolved in a minimum of ethyl ether and loaded on a fluorous reverse phase silica gel column (1.5 cm × 25 cm) [33]. The column was successively eluted with 150 ml portions of acetonitrile and THF–acetonitrile mixtures (1:1.6, 1:1.5, 1:1.4, and 1:1.3 (v/v)), and finally hexane (250–300 ml). The solvent was removed from the second and third fractions by rotary evaporation and oil pump vacuum to give **10** as a clear oil (0.251 g). The fourth fraction yielded impure **10** (0.074 g), which could be purified by a second analogous column (total yield: 0.302 g, 0.316 mmol, 63%). A portion was dissolved in ethyl ether (5 ml). The solvent was allowed to slowly evaporate, and white needles of **10** formed. However, the single crystals diffracted poorly.

NMR (δ, $CF_3C_6F_5/CDCl_3$, 1:4 (v/v)): $^1H = 7.21{-}7.36$ (m, C_6H_5), 3.60 (quint, $J_{HH} = 6.8$ Hz, $C_6H_5C\underline{H}$), 2.52 (m, 2 CH_2); $^{13}C\{^1H\}$ (partial) 142.0, 129.1, 127.6, 126.9 (4 s, C_6H_5), 37.0 (t, $J_{CF} = 20.8$ Hz, CH_2), 31.8 (s, $C_6H_5\underline{C}H$). GC: 99.3 area% purity. Calculated for $C_{25}H_{10}F_{34}$: C, 31.40; H, 1.05. Found: C, 31.26; H, 1.52.

4.10. Partition coefficients

(A) A 5 ml flask was charged with **9** (0.0368 g, 0.0121 mmol) and $CF_3C_6F_{11}$ (2.00 ml). After complete dissolution of **9**, toluene (2.00 ml) was added and the mixture was vigorously shaken (20 min). The flask was kept at 25 °C for 48 h. Then aliquots (each 0.500 ml) were taken from both phases. The $CF_3C_6F_{11}$ aliquot was evaporated to dryness. A solution of the internal standard C_6F_6 (0.0738 g, 0.397 mmol) in $CF_3C_6H_5$ (12.7016 g) was prepared. Portions of this standard solution were added gravimetrically to the above aliquots ($CF_3C_6F_{11}$: 0.6413 g solution, 0.0199 mmol C_6F_6; toluene: 0.0596 g solution, 0.00185 mmol C_6F_6). Then C_6D_6 was added (0.05 ml each) and the samples were analyzed by ^{19}F NMR (integration of CF_3 signal against C_6F_6). The procedure was repeated, giving an average partition coefficient of 96.6:3.4 (0.00840 g of **9** in 0.500 ml of $CF_3C_6F_{11}$; 0.000292 g of **9** in 0.500 ml of toluene). A 2.00/0.500 scale factor gives a total mass recovery of 0.0348 g (95%). (B) A 5 ml flask was charged with **10** (0.0307 g, 0.0321 mmol) and $CF_3C_6F_{11}$ (2.00 ml). After complete dissolution of **10**, toluene (2.00 ml) was added and the mixture was vigorously shaken (20 min). The flask was kept at 25 °C for 48 h. Then aliquots (each 0.500 ml) were taken from both phases. A solution of the internal standard *n*-undecane (0.0508 g, 0.325 mmol) in $CF_3C_6H_5$ (24.155 g) was prepared. Portions of this standard solution were added gravimetrically to the above aliquots ($CF_3C_6F_{11}$: 0.5906 g solution, 0.00798 mmol *n*-undecane; toluene: 0.5944 g solution, 0.00793 mmol *n*-undecane). The samples were analyzed by GC (two injections each). The procedure was repeated, giving an average partition coefficient of 97.9:2.1.

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References

[1] I.T. Horváth, J. Rábai, Science 266 (1994) 72.

[2] J.A. Gladysz, D.P. Curran, Tetrahedron 58 (2002) 3823 (and following articles in this special issue entitled “Fluorous Chemistry”).

[3] (a) I.T. Horváth, Acc. Chem. Res. 31 (1998) 641;
(b) E. de Wolf, G. van Koten, B.-J. Deelman, Chem. Soc. Rev. 28 (1999) 37;
(c) M. Cavazzini, F. Montanari, G. Pozzi, S. Quici, J. Fluorine Chem. 94 (1999) 183;
(d) E.G. Hope, A.M. Stuart, J. Fluorine Chem. 100 (1999) 75;
(e) J. Yoshida, K. Itami, Chem. Rev. 102 (2002) 3693;
(f) A.P. Dobbs, M.R. Kimberly, J. Fluorine Chem. 118 (2002) 3.

[4] R.C. da Costa, J.A. Gladysz, in: M. Beller, C. Bolm, (Eds.), Transition Metals for Organic Synthesis, Wiley–VCH, Weinheim, 2004, in press.

[5] L.P. Barthel-Rosa, J.A. Gladysz, Coord. Chem. Rev. 190–192 (1999) 587 (survey of practical considerations and underlying physical principles).
[6] H. Jiao, S. Le Stang, T. Soós, R. Meier, P. Rademacher, K. Kowski, L. Jafarpour, J.-B. Hamard, S.P. Nolan, J.A. Gladysz, J. Am. Chem. Soc. 124 (2002) 1516.
[7] (a) G. Buono, O. Chiodi, M. Wills, Syn. Lett. 377 (1999);
(b) X. Lu, C. Zhang, Z. Xu, Acc. Chem. Res. 34 (2001) 535;
(c) E. Vedejs, O. Daugulis, J.A. MacKay, E. Rozners, Syn. Lett. 1499 (2001);
(d) D. Basavaiah, Chem. Rev. 103 (2003) 811.
[8] (a) M. Wende, R. Meier, J.A. Gladysz, J. Am. Chem. Soc. 123 (2001) 11490;
(b) M. Wende, J.A. Gladysz, J. Am. Chem. Soc. 125 (2003) 5861.
[9] A. Galante, P. Lhoste, D. Sinou, Tetrahedron Lett. 42 (2001) 5425.
[10] (a) B. Betzemeier, P. Knochel, Angew. Chem. 109 (1997) 2736;
B. Betzemeier, P. Knochel, Angew. Chem., Int. Ed. Engl. 36 (1997) 2623;
(b) P. Bhattacharyya, D. Gudmunsen, E.G. Hope, R.D.W. Kemmitt, D.R. Paige, A.M. Stuart, J. Chem. Soc., Perkin Trans. 1 24 (1997) 3609.
[11] W. Chen, J. Xiao, Tetrahedron Lett. 41 (2000) 3697.
[12] S. Schneider, W. Bannwarth, Angew. Chem., Int. Ed. 39 (2000) 4142;
S. Schneider, W. Bannwarth, Angew. Chem. 112 (2000) 4293.
[13] (a) C. Rocaboy, D. Rutherford, B.L. Bennett, J.A. Gladysz, J. Phys. Org. Chem. 13 (2000) 596;
(b) C. Rocaboy, F. Hampel, J.A. Gladysz, J. Org. Chem. 67 (2002) 6863;
(c) C. Rocaboy, J.A. Gladysz, Chem. Eur. J. 9 (2003) 88.
[14] (a) B. Richter, E. de Wolf, G. van Koten, B.-J. Deelman, J. Org. Chem. 65 (2000) 3885;
(b) E. de Wolf, B. Richter, B.-J. Deelman, G. van Koten, J. Org. Chem. 65 (2000) 5424.
[15] (a) B. Richter, A.L. Spek, G. van Koten, B.-J. Deelman, J. Am. Chem. Soc. 122 (2000) 3945–3951;
(b) E. de Wolf, E.A. Speets, B.-J. Deelman, G. van Koten, Organometallics 20 (2001) 3686.
[16] D.P. Curran, R. Ferritto, Y. Hua, Tetrahedron Lett. 39 (1998) 4937 (for the first report of a fluorous arene with a $Si((CH_2)_2R_{fn})_3$ moiety).
[17] (a) D. Sinou, G. Pozzi, E.G. Hope, A.M. Stuart, Tetrahedron Lett. 40 (1999) 849;
(b) D. Sinou, D. Maillard, G. Pozzi, Eur. J. Org. Chem. (2002) 269.
[18] (a) S. Kainz, D. Koch, W. Baumann, W. Leitner, Angew. Chem. 109 (1997) 1699;
S. Kainz, D. Koch, W. Baumann, W. Leitner, Angew. Chem., Int. Ed. Engl. 36 (1997) 1628;
(b) S. Kainz, D. Koch, W. Baumann, W. Leitner, Angew. Chem., Int. Ed. 36 (1998) 1628;
S. Kainz, D. Koch, W. Baumann, W. Leitner, Angew. Chem. 109 (1997) 1699;
(c) S. Kainz, A. Brinkmann, W. Leitner, A. Pfaltz, J. Am. Chem. Soc. 121 (1999) 6421.
[19] Q. Zhang, Z. Luo, D.P. Curran, J. Org. Chem. 65 (2000) 8866.
[20] (a) W. Chen, L. Xu, J. Xiao, Org. Lett. 2 (2000) 2675;
(b) W. Chen, L. Xu, Y. Hu, A.M. Banet Osuna, J. Xiao, Tetrahedron 58 (2002) 3889.
[21] S. Darses, M. Pucheault, J.-P. Genet, Eur. J. Org. Chem. 1121 (2001).
[22] T. Soós, B.L. Bennett, D. Rutherford, L.P. Barthel-Rosa, J.A. Gladysz, Organometallics 20 (2001) 3079.
[23] D. Rutherford, B.L. Bennett, L.P. Barthel-Rosa, T. Soós, unpublished results.
[24] (a) J. Loiseau, E. Fouquet, R.H. Fish, J.-M. Vincent, J.-B. Verlhac, J. Fluorine Chem. 108 (2001) 195;
(b) M. El Bakkari, N. McClenaghan, J.-M. Vincent, J. Am. Chem. Soc. 124 (2002) 12942;
(c) Y. Nakamura, S. Takeuchi, K. Okumura, Y. Ohgo, Tetrahedron 57 (2001) 5565;
(d) J. Pardo, A. Cobas, E. Guitián, L. Castedo, Org. Lett. 3 (2001) 3711.
[25] R. Benassi, M.L. Schenetti, F. Taddei, P. Vivareli, P.J. Dembech, J. Chem. Soc., Perkin Trans. 2 (1974) 1338.
[26] V. Ravindar, H. Hemling, H. Schumann, J. Blum, Synth. Commun. 22 (1992) 841.
[27] L.J. Alvey, D. Rutherford, J.J.J. Juliette, J.A. Gladysz, J. Org. Chem. 63 (1998) 6302.
[28] M. Wende, Doctoral Dissertation, Friedrich-Alexander-Universität Erlangen-Nürnberg, 2003.
[29] G. Gambaretto, L. Conte, G. Fornasieri, C. Zarantonello, D. Tonei, A. Sassi, R. Bertani, J. Fluorine Chem. 121 (2003) 57 (this paper describes an independent, slightly longer synthesis of **3** that appeared when this manuscript was being reviewed).
[30] R. Shimizu, T. Fuchikami, Tetrahedron Lett. 37 (1996) 8405.
[31] (a) N. Brodie, S. Jugé, Inorg. Chem. 37 (1998) 2438;
(b) C. Darcel, E.B. Kaloun, R. Merdès, D. Moulin, N. Riegel, S. Thorimbert, J.P. Genêt, S. Jugé, J. Organomet. Chem. 624 (2001) 333;
(c) M. Ingleson, N.J. Patmore, G.D. Ruggiero, C.G. Frost, M.F. Mahon, M.C. Willis, A.S. Weller, Organometallics 20 (2001) 4434.
[32] R. Shimizu, E. Yoneda, T. Fuchikami, Tetrahedron Lett. 37 (1996) 5557.
[33] (a) D.P. Curran, Z. Luo, J. Am. Chem. Soc. 121 (1999) 9069;
(b) D.P. Curran, Syn. Lett. 9 (2001) 1488.
[34] S. Kainz, Z. Luo, D.P. Curran, W. Leitner, Synthesis 1425 (1998).
[35] (a) T. Mathivet, E. Monflier, Y. Castanet, A. Mortreux, J.-L. Couturier, Tetrahedron Lett. 40 (1999) 3885;
(b) T. Mathivet, E. Monflier, Y. Castanet, A. Mortreux, J.-L. Couturier, Tetrahedron 58 (2002) 3877.
[36] S. Le Stang, R. Meier, C. Rocaboy, J.A. Gladysz, J. Fluorine Chem. 119 (2003) 141.
[37] A.F. Burchat, J.M. Chong, N. Nielsen, J. Organomet. Chem. 542 (1997) 281.
[38] H.K. Cammenga, M. Epple, Angew. Chem. 107 (1995) 1284;
H.K. Cammenga, M. Epple, Angew. Chem., Int. Ed. Engl. 34 (1995) 1171.