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# Synthesis, structure, and reactivity of fluorous phosphorus/carbon/phosphorus pincer ligands and metal complexes†

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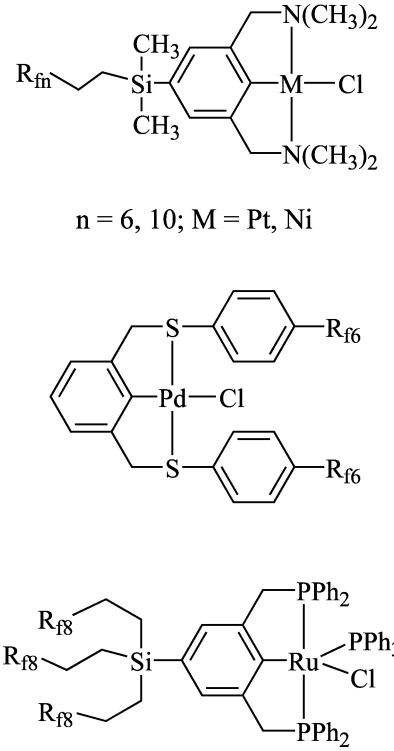
Reactions of the diphosphine 1,3-$C_6H_4(CH_2PH_2)_2$ and fluorous alkenes $H_2C{=}CHR_{fn}$ ($R_{fn} = (CF_2)_{n-1}CF_3$; $n = 6, 8$) at 75 °C in the presence of AIBN give the title ligands 1,3-$C_6H_4(CH_2P(CH_2CH_2R_{fn})_2)_2$ (**3**-$R_{fn}$) and byproducts 1,3-$C_6H_4(CH_3)(CH_2P(CH_2CH_2R_{fn})_2)$ (**4**-$R_{fn}$) in 1 : 3 to 1 : 5 ratios. Workups give **3**-$R_{fn}$ in 4–17% yields. Similar results are obtained photochemically. Reaction of 1,3-$C_6H_4(CH_2Br)_2$ and $HP(CH_2CH_2R_{f8})_2$ (**5**) at 80 °C (neat, 1 : 2 mol ratio) gives instead of simple substitution the metacyclophane $[1,3\text{-}C_6H_4(CH_2\overline{P(CH_2CH_2R_{f8})_2}\underline{CH_2\text{-}1,3\text{-}C_6H_4CH_2}\overline{P(CH_2CH_2R_{f8})_2}\underline{CH_2}]^{2+}2Br^-$, which upon treatment with $LiAlH_4$ yields **3**-$R_{f8}$ (20%), **4**-$R_{f8}$, and other products. Efforts to better access **3**-$R_{f8}$, either by altering stoichiometry or using various combinations of the phosphine borane $(H_3B)PH(CH_2CH_2R_{f8})_2$ and base, are unsuccessful. Reactions of **3**-$R_{fn}$ with $Pd(O_2CCF_3)_2$ and $[IrCl(COE)_2]_2$ (COE = cyclooctene) give the palladium and iridium pincer complexes (2,6,1-$C_6H_3(CH_2\overline{P(CH_2CH_2R_{fn})_2})_2)Pd(O_2CCF_3)$ (**10**-$R_{fn}$; 80–90%) and (2,6,1-$C_6H_3(CH_2\overline{P(CH_2CH_2R_{f8})_2})_2)Ir(Cl)(H)$ (**11**-$R_{f8}$; 29%), which exhibit $CF_3C_6F_{11}$/toluene partition coefficients of >96 : <4. The crystal structure of **10**-$R_{f8}$ shows $CH_2CH_2R_{f8}$ groups with all-*anti* conformations that extend in parallel above and below the palladium square plane to create fluorous lattice domains. NMR monitoring shows a precursor to **11**-$R_{f8}$ that is believed to be a COE adduct.

## Introduction

There has been dramatic growth in the use of pincer ligands for transition metal catalysts over the last decade.[1] This has in turn prompted a variety of approaches to recoverable pincer ligands and complexes.[2–10] These include immobilization on scaffolds such as large self-assembled hyperbranched spheres,[2] hyperbranched polyglycerol,[3] and fullerenes,[4] or supports such as silica,[5] PEG,[6] carbosilane dendrimers,[7] polyisobutylene,[8] and clays.[9] Some efforts have involved fluorous derivatives, examples of which are provided in Scheme 1.[10] Fluorous compounds are recoverable by a variety of techniques, as thoroughly summarized in recent reviews.[11] In the last few months, some mechanistic caveats that bear upon the recyclability of certain polymer-bound palladium sulfur/carbon/sulfur (SCS) pincer catalyst systems have appeared.[12]

We recently reported fluorous phosphapalladacycles and sulfapalladacycles that were excellent catalyst precursors for Heck and Suzuki couplings of aryl halides.[13] However, these merely served as steady-state sources of catalytically active palladium nanoparticles under the conditions investigated. The remaining fluorous palladacycles could be efficiently recycled, but each cycle exhibited an induction period and activity eventually ceased. We thought that tridentate fluorous phosphorus/carbon/phosphorus (PCP) pincer ligands might give more stable palladium complexes better disposed towards molecular catalysis. Our attention was also drawn to iridium PCP pincer complexes, which are catalysts for another important class of reactions, alkane dehydrogenations.[14]

Accordingly, we set out to prepare fluorous PCP pincer ligands of the general formula **I**, and develop their coordination chemistry. Although compounds with aromatic rings are more challenging to render highly fluorophilic,[15] it was thought that the four ponytails would provide very biased partition coefficients. In this paper, we report (1) three independent routes to such ligands, (2) their facile metalation to give palladium and iridium derivatives, and (3) a crystal structure of one of the palladium derivatives. Some preliminary catalysis data are also discussed. Companion efforts involving fluorous SCS pincer ligands have also been initiated, and will be described separately.[16]




**Scheme 1** Representative fluorous pincer complexes ($R_{fn} = (CF_2)_{n-1}CF_3$).

† Electronic supplementary information (ESI) available: Additional experiments and details relevant to Scheme 3. See http://www.rsc.org/suppdata/dt/b5/b502309b/

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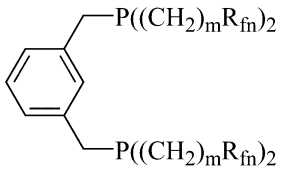



**I**

($R_{fn} = (CF_2)_{n-1}CF_3$)

## Results

### 1. Fluorous pincer ligands *via* radical additions

In previous work, we have described many free radical chain additions of $R_{3-n}PH_n$ species to fluorous terminal alkenes $H_2C{=}CHR_{fn}$.[17] Thus, our attention was drawn to the diprimary diphosphine 1,3-$C_6H_4(CH_2PH_2)_2$ (**1**), which is available from α,α′-dibromo-*m*-xylene or 1,3-$C_6H_4(CH_2Br)_2$ (**2**) *via* an Arbuzov/reduction sequence.[18] As shown in Scheme 2, **1** and $H_2C{=}CHR_{f8}$ were reacted neat at 75 °C in the presence of the radical initiator AIBN. The process was monitored by $^{31}$P NMR, which showed a sequence of intermediates as the phosphorus–hydrogen bonds reacted, and a signal appropriate for the target molecule 1,3-$C_6H_4(CH_2P(CH_2CH_2R_{f8})_2)_2$ (**3**-$R_{f8}$). Another species (**4**-$R_{f8}$) also formed, which was always the major product when addition was complete. The **3**-$R_{f8}$/**4**-$R_{f8}$ ratios ranged from 1 : 3 to 1 : 5. In some cases, small amounts of $P(CH_2CH_2R_{f8})_3$[17a] were noted. No other byproducts were detected.

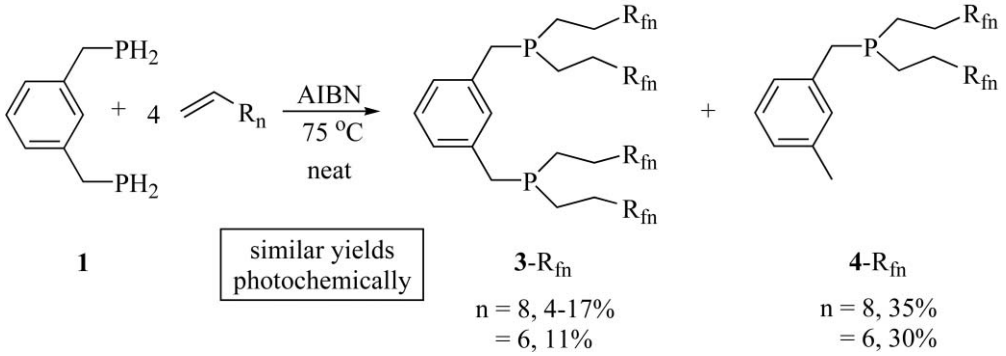
In a few runs, **3**-$R_{f8}$ was isolated in 15–17% yields. However, in most cases only 4–5% yields were obtained, despite the high and quite clean NMR conversions to **3**-$R_{f8}$ and **4**-$R_{f8}$.[19] Compounds **3**-$R_{f8}$ and **4**-$R_{f8}$ were air-sensitive white solids that were characterized by NMR ($^1$H, $^{13}$C, $^{31}$P) and microanalysis, as summarized in the Experimental section. The NMR properties of **3**-$R_{f8}$ were very similar to those of other PCP pincer ligands.[20] Those of **4**-$R_{f8}$, coupled with a mass spectrum, showed it to be the monophosphine 1,3-$C_6H_4(CH_3)(CH_2P(CH_2CH_2R_{f8})_2)$, allowing a yield of 35% to be calculated. Thus, **4**-$R_{f8}$ is derived from the cleavage of a benzylic carbon–phosphorus bond. As summarized in Table 1, **3**-$R_{f8}$ and **4**-$R_{f8}$ were soluble in both fluorous and non-fluorous solvents, with the exception of hexane.

Many experiments were conducted in efforts to increase the **3**-$R_{f8}$/**4**-$R_{f8}$ ratio. These included higher loadings of AIBN, other temperatures (70–100 °C), alternative initiators (VAZO, 80–100 °C), and solvents such as THF or $CF_3C_6H_5$ ((trifluoromethyl)benzene). However, none were successful. Photochemical reactions of **1** and $H_2C{=}CHR_{f8}$, either at room temperature or 0 °C, gave similar yields of **3**-$R_{f8}$ and **4**-$R_{f8}$. Thermal and photochemical reactions of **1** and $H_2C{=}CHR_{f6}$, which has a shorter ponytail, gave comparable yields of the lower homologs **3**-$R_{f6}$ and **4**-$R_{f6}$. Thus, the formation of **4**-$R_{fn}$ under free radical chain conditions is general, but its exact origin remains mechanistically obscure. Hence, other approaches to **3**-$R_{fn}$ were investigated.

### 2. Fluorous pincer ligands *via* nucleophilic substitution

Other groups have shown that the benzyl bromide **2** and/or substituted derivatives can be condensed with secondary phosphines to give, after deprotonation, pincer ligands 1,3-$C_6H_4(CH_2PR_2)_2$ in high yields.[20] Thus, reactions of **2** and the fluorous secondary phosphine $HP(CH_2CH_2R_{f8})_2$ (**5**-$R_{f8}$)[21] were investigated. No products formed under homogeneous conditions in refluxing acetone, toluene, and THF, or under heterogeneous conditions in DMF at 100 °C, even at high concentrations. This is consistent with the diminished nucleophilicites often found for fluorous nucleophiles, especially when only two methylene groups separate the perfluoroalkyl segments and the reactive site.[22]

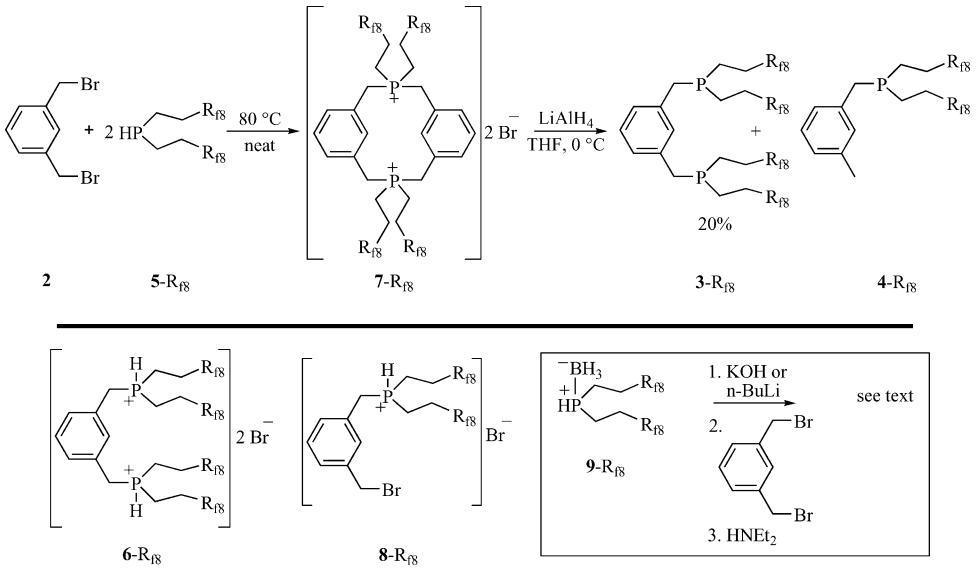
Thus, as shown in Scheme 3, **2** (mp 75–77 °C) and **5**-$R_{f8}$ (mp 80 °C) were intimately mixed in a 1 : 2 mol ratio, and heated to 80 °C in the absence of solvent. The sample melted and resolidified, and was cooled. The product could not be dissolved in any common solvent, including THF, $CF_3C_6F_{11}$ (perfluoro(methylcyclohexane)) and $CF_3C_6H_5$. A FAB mass spectrum did not show any peak consistent with the dication of the desired primary product, the bis(phosphonium salt) **6**-$R_{f8}$ (Scheme 3; *e.g.* *m*/*z* 978.0 or 1956.0 for $z = 2$ or 1; 1955.0, dication − $H^+$).[23] However, a strong peak appropriate for the dication of the metacyclophane **7**-$R_{f8}$ (Scheme 3) was apparent (*m*/*z* 1029.0 and 1029.5, $z = 2$, 100 : 67; calc. 100 : 63), as well




**Scheme 2** Synthesis of fluorous pincer ligands **3**-$R_{fn}$ *via* free radical chain additions.

**Table 1** Solubility profiles of selected compounds at room temperature

| | $C_6F_{11}CF_3$ | $C_6H_5CF_3$ | Hexane | Diethyl ether | THF | $CH_2Cl_2$ | Acetone |
|---|---|---|---|---|---|---|---|
| **3**-$R_{f8}$ | High | High | None | Low | High | Med | Med |
| **4**-$R_{f8}$ | High | High | Low | Med | High | Med | Med |
| **3**-$R_{f6}$ | High | High | Low | Low | High | Med | High |
| **4**-$R_{f6}$ | High | High | Low | Med | High | Med | High |
| **9**-$R_{f8}$ | High | High | None | Low | Med | Low | Low |
| **10**-$R_{f8}$ | Med | High | None | Low | Med | Med | Med |
| **10**-$R_{f6}$ | High | High | None | Low | Med | Med | Med |
| **11**-$R_{f8}$ | High | High | Low | Med | Med | Med | Med |




**Scheme 3** Synthesis of fluorous pincer ligand **3**-$R_{f8}$ *via* nucleophilic substitutions.

as a slightly more intense peak for a related monocation (*m*/*z* 2057.6).

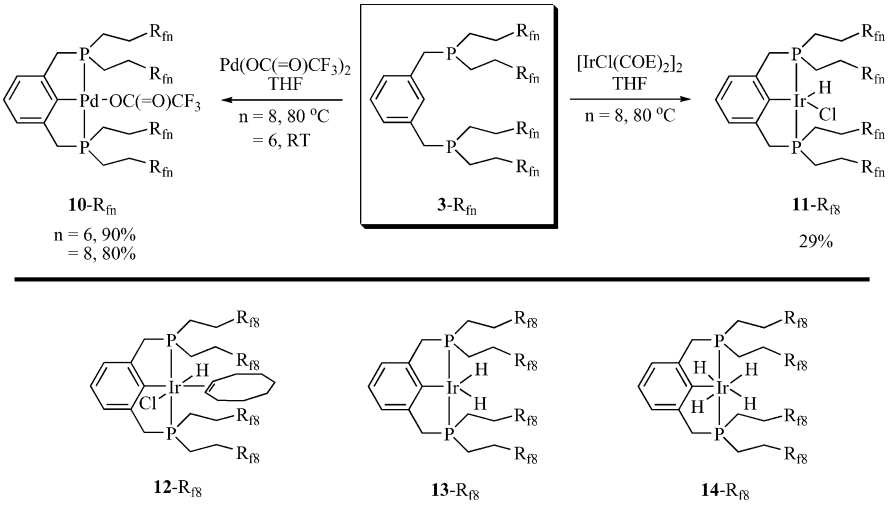
We sought to salvage the inauspicious start in Scheme 3. The carbon–phosphorus bonds of phosphonium salts can often be cleaved reductively. One common protocol involves $LiAlH_4$.[24] The benzylic linkages in **7**-$R_{f8}$ should be more reactive, and two products—the target pincer ligand **3**-$R_{f8}$ and the monophosphine byproduct **4**-$R_{f8}$—would be possible. Thus, the residue was treated with a slight excess of $LiAlH_4$. Column chromatography gave **3**-$R_{f8}$ in 20% overall yield from **2**. The $^{31}P$ NMR spectrum of the crude reaction mixture showed a number of byproducts, with **3**-$R_{f8}$ representing 45% of the integral trace. These included **4**-$R_{f8}$, the secondary phosphine **5**-$R_{f8}$, and the primary phosphine $H_2PCH_2CH_2R_{f8}$,[21a] all of which eluted faster than **3**-$R_{f8}$ from the column.

A variety of other conditions were investigated in hope of increasing the yield of **3**-$R_{f8}$. The first-formed species in Scheme 3 must be the monophosphonium salt **8**-$R_{f8}$. A higher concentration of **5**-$R_{f8}$ should increase the rate of displacement of the remaining benzylic bromide to give **6**-$R_{f8}$. However, reactions using 1 : 4 mol ratios of **2** and **5**-$R_{f8}$ gave nearly identical results.[25] In order to generate the metacyclophane **7**-$R_{f8}$, the deprotonation of **8**-$R_{f8}$ (or **6**-$R_{f8}$) is required. Hence, these results suggest that proton transfer from **8**-$R_{f8}$ to **5**-$R_{f8}$ is intrinsically faster than the displacement of bromide. Reactions were also conducted with 10 : 1 mol ratios of **2** and **5**-$R_{f8}$, with the idea that it might be possible to isolate **8**-$R_{f8}$. Excess **2** was removed, and base was added. However, no $^{31}P$ NMR signal was observed in the region expected for the monophosphine 1,3-$C_6H_4(CH_2Br)(CH_2P(CH_2CH_2R_{f8})_2)$ (−18 to −22 ppm).

The proton transfer equilibria and polyalkylations that plague Scheme 3 should be eliminated with phosphorus nucleophiles that lack hydrogen substituents, *and* can be alkylated only once. The most obvious candidate would be an anion derived from the fluorous secondary phosphine borane $(H_3B)PH(CH_2CH_2R_{f8})_2$ (**9**-$R_{f8}$).[21b,26,27] Following an established procedure,[26a] **9**-$R_{f8}$, KOH, and **2** were combined in ethanol. After several days, workup and removal of the borane protecting group with $HNEt_2$ gave mainly **5**-$R_{f8}$, and only traces of the target pincer ligand **3**-$R_{f8}$. Similar sequences involving *t*-BuOK or *n*-BuLi (−78 °C) and THF were also unsuccessful, and additional details are provided in the ESI.†

## 3. Metal derivatives of fluorous pincer ligands

Despite the modest yields of the fluorous pincer ligands **3**-$R_{fn}$ in Schemes 2 and 3, the masses isolated are commonly greater than the masses of the educts **1** or **2**. Thus, some coordination chemistry could be developed. As shown in Scheme 4, the trifluoroacetate complex $Pd(O_2CCF_3)_2$ and **3**-$R_{f6}$ or **3**-$R_{f8}$ were combined in THF. In accord with much precedent,[1] workup gave the air-stable palladium pincer complexes




**Scheme 4** Metal complexes of fluorous pincer ligands **3**-$R_{fn}$.

(2,6,1-$C_6H_3(CH_2\overline{P(CH_2CH_2R_{fn})_2})_2$)Pd($O_2CCF_3$) (**10**-$R_{fn}$) in 80–90% yields. These were characterized by microanalysis, NMR ($^1$H, $^{13}$C, $^{31}$P), and mass spectrometry, as described in the Experimental section. The $^{31}$P NMR chemical shifts were *ca.* 60 ppm downfield of the free ligands. One aryl $^{13}$C NMR signal was a triplet, and was assigned to the palladium-bound carbon. The P*C*H$_2$ signals gave apparent triplets due to virtual coupling.[28]

As summarized in Table 1, **10**-$R_{f6}$ and **10**-$R_{f8}$ were soluble in most fluorous and non-fluorous solvents at room temperature. Although hexane was an exception, solubilities in hot hexane were appreciable. When such solutions of **10**-$R_{f8}$ were slowly cooled, single crystals were obtained. X-Ray data were collected as described in the Experimental section. Refinement gave the molecular structure depicted in Fig. 1. One fluorine atom (F46A) showed disorder that could not be resolved. Key bond lengths and angles are given in Table 2. They are generally close to those found in other neutral palladium PCP pincer complexes.[26b,29]

The ponytails exhibit *anti* C–C–C–C conformations, with the torsion angles of the *anti* F–C–C–F segments averaging 176.1°.[30] One ponytail on each phosphorus atom extends above the palladium square plane, and the other below. Both run parallel to the ponytails on the *trans* phosphorus atom, which

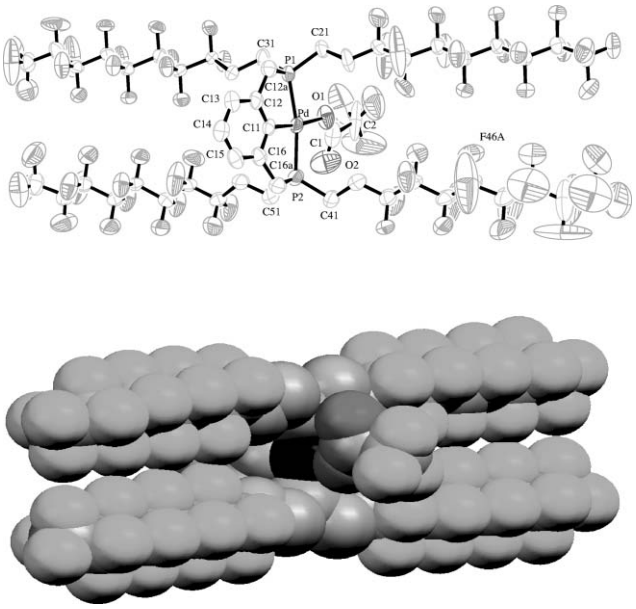



**Fig. 1** Molecular structure of the fluorous palladium pincer complex **10**-$R_{f8}$.

**Table 2** Selected bond lengths [Å], bond angles [°], and intermolecular contacts [Å] for **10**

| | | | |
|---|---|---|---|
| Pd(1)–C(11) | 2.008(11) | P(2)–C(51) | 1.832(13) |
| Pd(1)–O(1) | 2.126(9) | C(11)–C(12) | 1.393(16) |
| Pd(1)–P(1) | 2.275(3) | C(11)–C(16) | 1.417(15) |
| Pd(1)–P(2) | 2.298(3) | C(12A)–C(12) | 1.508(16) |
| P(1)–C(12a) | 1.817(12) | C(12)–C(13) | 1.394(15) |
| P(1)–C(21) | 1.834(11) | C(13)–C(14) | 1.382(17) |
| P(1)–C(31) | 1.830(10) | C(14)–C(15) | 1.382(18) |
| P(2)–C(16a) | 1.825(13) | C(15)–C(16) | 1.370(16) |
| P(2)–C(41) | 1.829(12) | C(16)–C(16A) | 1.522(17) |
| | | | |
| C(11)–Pd(1)–O(1) | 173.2(4) | Pd(1)–P(1)–C(12a) | 103.5(4) |
| C(11)–Pd(1)–P(1) | 83.6(3) | Pd(1)–P(2)–C(41) | 119.6(4) |
| O(1)–Pd(1)–P(1) | 89.9(3) | Pd(1)–P(2)–C(51) | 116.4(4) |
| C(11)–Pd(1)–P(2) | 84.0(3) | Pd(1)–P(2)–C(16a) | 102.7(4) |
| O(1)–Pd(1)–P(2) | 102.7(3) | C(21)–P(1)–C(31) | 104.2(5) |
| P(1)–Pd(1)–P(2) | 166.98(12) | C(21)–P(1)–C(12a) | 109.2(6) |
| O(1)–C(1)–O(2) | 132.1(18) | C(31)–P(1)–C(12a) | 105.7(5) |
| O(1)–C(1)–C(2) | 111(2) | C(41)–P(2)–C(51) | 105.5(6) |
| Pd(1)–P(1)–C(21) | 116.8(4) | C(41)–P(2)–C(16a) | 107.2(6) |
| Pd(1)–P(1)–C(31) | 116.8(4) | C(51)–P(2)–C(16a) | 104.0(6) |
| | | | |
| F(24b)–F(44a) | 2.987 | F(38b)–F(58a) | 2.827 |
| F(26b)–F(46a) | 2.743 | F(33a)–F(58b) | 2.932 |
| F(28b)–F(48a) | 2.716 | F(35a)–F(56b) | 2.981 |
| F(34b)–F(54a) | 2.715 | F(37a)–F(54b) | 2.932 |
| F(36b)–F(56a) | 2.744 | | |

are nearly in van-der-Waals contact (Fig. 1, bottom). As can be seen in Fig. 2, the crystal lattice is divided into fluorous and non-fluorous domains, with the ponytails of neighboring molecules in comparable van-der-Waals contact. Other square planar metal complexes with fluorous phosphines crystallize similarly.[31] The van-der-Waals radius of fluorine is 1.40 Å,[32] and some of the shorter fluorine–fluorine distances are included in Table 2.

The iridium bis(cyclooctene) complex [IrCl(COE)$_2$]$_2$[33] has often been used to prepare pincer complexes.[20d,34] Thus, **3**-$R_{f8}$ and [IrCl(COE)$_2$]$_2$ were reacted in THF at 80 °C. As shown in Scheme 4, workup gave the expected iridium(III) complex (2,6,1-$C_6H_3(CH_2\overline{P(CH_2CH_2R_{f8})_2})_2$)Ir(Cl)(H) (**11**-$R_{f8}$) in 29% yield. Complex **11**-$R_{f8}$ was characterized analogously to **10**-$R_{f8}$, and its solubility characteristics and many NMR properties were similar. However, due to the trigonal pyramidal geometry and unsymmetrical equatorial substitution pattern, the ponytails on each phosphorus become diastereotopic, and separate $^{13}$C signals were observed. The hydride ligand gave a characteristic upfield $^1$H NMR signal (−25.3 ppm) that was coupled to both phosphorus atoms.

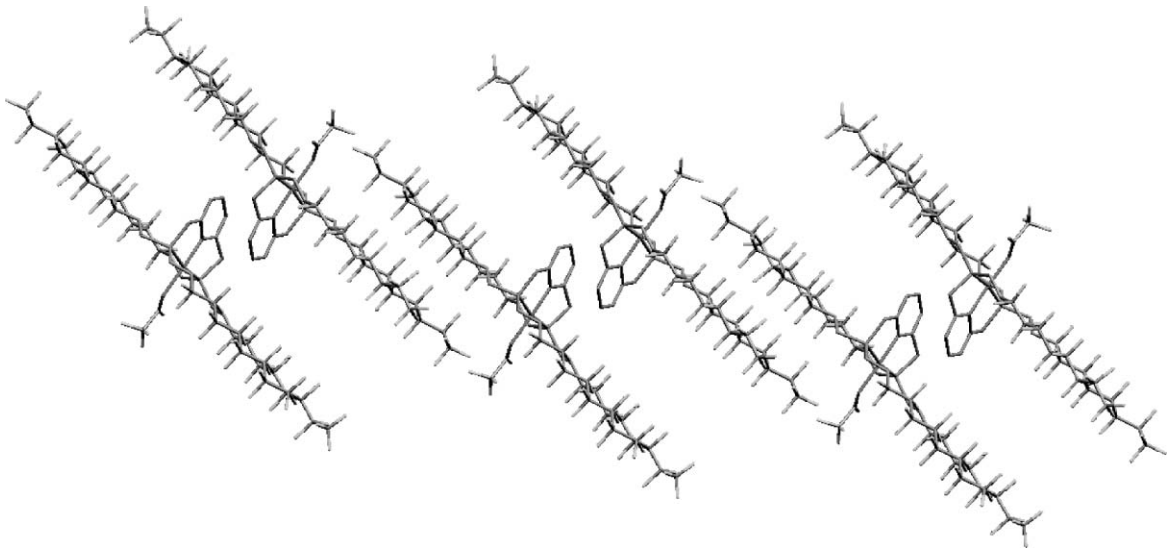


**Fig. 2** Packing diagram for **10**-$R_{f8}$.

The reaction of **3**-$R_{f8}$ and $[IrCl(COE)_2]_2$ was monitored by NMR in $[D_8]$THF. As shown in Fig. 3, the $^1H$ signals of **3**-$R_{f8}$ disappeared over the course of a few hours. *Two* triplets for iridium hydride ligands appeared. The more intense triplet (−24.2 ppm) was due to an intermediate and gradually disappeared as the other, arising from **11**-$R_{f8}$, intensified. This species was also evident in the $^{31}P$ NMR spectrum, and was tentatively assigned as the octahedral cyclooctene complex **12**-$R_{f8}$ (Scheme 4). A closely related dihydride complex has been previously characterized by NMR.[34a] Hence, the rate determining step in the formation of **11**-$R_{f8}$ is not carbon–hydrogen bond activation, but rather a simple dissociation of an alkene ligand. Although Fig. 3 gives the impression of a clean reaction, some insoluble brown material formed concurrently. Thus, the modest isolated yield of **11**-$R_{f8}$ is not due solely to workup losses.

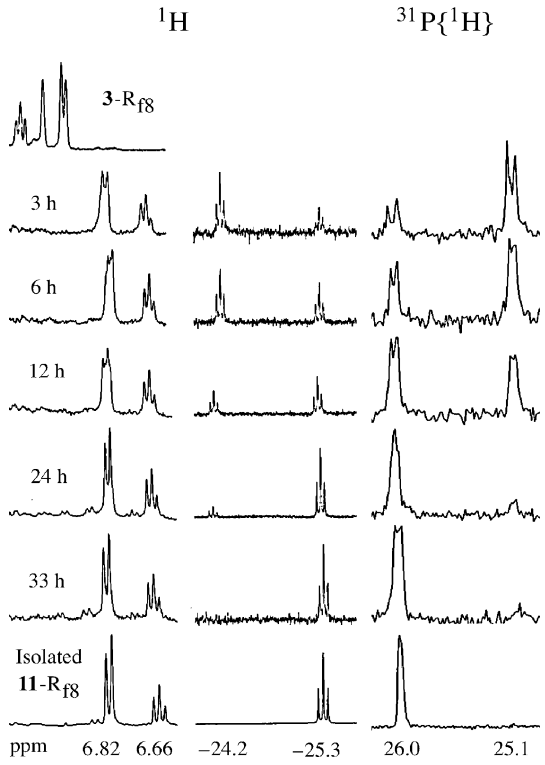



**Fig. 3** NMR monitoring of the reaction of **3**-$R_{f8}$ and $[IrCl(COE)_2]_2$ ($[D_8]$THF, 80 °C) to give the transient **12**-$R_{f8}$ and iridium fluorous pincer complex **11**-$R_{f8}$.

Finally, the $CF_3C_6F_{11}$/toluene partition coefficients of **10**-$R_{f8}$ and **11**-$R_{f8}$ were measured by HPLC and $^{19}F$ NMR, as described in the Experimental section. Quite high fluorophilicities were observed (96.4 : 3.6, 98.0 : 2.0), which are further analyzed below.

## Discussion

This study has shown that the fluorous PCP pincer ligands **3**-$R_{fn}$ can be synthesized in only a few steps (Schemes 2, 3), and are readily metalated (Scheme 4). However, all routes to **3**-$R_{fn}$ feature one step where the isolated yield is low. Although spectroscopic yields are somewhat higher, in no case do they approach those of the non-fluorous counterparts. The latter are usually accessed *via* reactions of phosphorus nucleophiles with the dibromide **2**. Syntheses of "heavy" fluorous analogs often present additional challenges, and the diminished nucleophilicities of our fluorous phosphines and related anions are likely responsible for at least some of the difficulties in Scheme 3. Perhaps analogs with longer insulating methylene segments would give cleaner chemistry.

Surprisingly, the major product under either thermal or photochemical conditions in Scheme 2 is the *mono*phosphine **4**-$R_{fn}$. This indicates that there are intrinsic problems associated with free radical chain additions of the diprimary diphosphine **1**, at least with respect to fluorous terminal alkenes. In other exploratory experiments, **1** was treated with excesses of the fluorous alkyl iodides $ICH_2CH_2R_{fn}$ ($n$ = 6, 8) at 70 °C in DMF.[35] However, these are weaker alkylating agents,[22] and no reactions occurred. Importantly, there are only a limited number of possible retrosynthetic pathways to **3**-$R_{fn}$, and the most obvious candidates have been thoroughly examined in this study. Hence, in order to realize convenient, high-yield syntheses, new reaction technologies will likely be required.

Nonetheless, when fluorous ponytails are grafted onto **1** or **2**, their masses greatly increase. The quantities of **3**-$R_{fn}$ thus available allowed both palladium and iridium complexes to be prepared (Scheme 4), the former in particularly good yield. Several palladium PCP pincer complexes are effective catalyst precursors for Heck alkenylations of aryl halides.[36] Thus, some exploratory reactions were conducted with **10**-$R_{f8}$, using $(i\text{-Pr})_2$NEt as the base. Material that had been isolated by extraction was quite active catalytically. However, material that had been purified by column chromatography was nearly inactive. This underscores the importance of removing trace impurities, a task that in the case of fluorous catalysts is usually facilitated by their phase properties.

Furthermore, the mechanisms of Heck reactions promoted by immobilized palladium SCS pincer complexes have recently been studied in detail.[12] Many careful experiments establish that these complexes merely serve as precursors for pincer-free palladium(0) species that are likely non-molecular, and which constitute the active catalysts. Our own preliminary data with fluorous palladium SCS pincer complexes are best modeled similarly.[16] It would not be surprising if such mechanisms apply to all palladium SCS and PCP pincer complexes.[12,36d] Hence, we became much less enthusiastic about testing **10**-$R_{fn}$ as a recoverable catalyst or catalyst precursor for any type of aryl halide coupling. However, palladium PCP pincer complexes catalyze other types of reactions,[5b,29b,37] and here **10**-$R_{fn}$ remain viable candidates for recyclable molecular catalysts.

The mechanisms of alkane dehydrogenations catalyzed by iridium PCP pincer complexes have also been studied in detail.[14,34a,38] In contrast to some of the palladium systems described above, these are clearly molecular catalysts. However, monohydride chloride complexes such as **11**-$R_{f8}$ are not active. Rather, *di*hydride complexes such as **13**-$R_{f8}$ (Scheme 4) are commonly employed to enter the catalytic cycle. Although $LiEt_3BH$ is often used to displace such chloride ligands,[14,26b,34b] we were never able to effect a clean conversion to **13**-$R_{f8}$. NMR data suggested the formation of polyhydride species (*e.g.*, **14**-$R_{f8}$), and optimizations were limited by the quantity of **11**-$R_{f8}$ available.

As illustrated in Table 1, the new fluorous PCP pincer ligands and metal complexes are soluble in both fluorous and non-fluorous solvents. However, **10**-$R_{f8}$ and **11**-$R_{f8}$ have quite biased $CF_3C_6F_{11}$/toluene partition coefficients (>96 : <4), even though they contain an aryl ring, 2.5 $CH_2$ groups per $R_{f8}$ segment, and auxiliary ligands. These values are in the range of dimeric phosphapalladacycles that contain three $R_{f8}$ ponytails per arene ring.[13] Fluorophilicities might be further increased by incorporating additional ponytails, such as in the silyl-substituted complexes in Scheme 1, or by lengthening existing $R_{fn}$ segments, such as with $R_{f10}$ analogs. Partition coefficients for the pincer complexes in Scheme 1 are not available, but the palladium SCS species is easily recovered by a fluorous solid phase extraction.[10c]

In accord with the trend for **3**-$R_{f6}$ and **3**-$R_{f8}$ in Table 1, lengthening the $R_{fn}$ segments of our complexes is certain to decrease their absolute solubilities. Indeed, one very promising direction for fluorous catalysis involves thermomorphic species with very little or no solubility in non-fluorous solvents at room temperature, but appreciable solubilities at elevated temperatures.[39–42] This allows catalyst recovery by simple

liquid/solid phase separations. The highly temperature-dependent solubility of **10**-$R_{f8}$ in hexane suggests considerable promise for PCP pincer complexes derived from fluorous ligands **I**. Also, the high temperature required for alkane dehydrogenation by iridium PCP pincer complexes makes for an ideal test reaction.

In summary, expedient syntheses of fluorous PCP pincer ligands have been developed. However, in contrast to non-fluorous analogs, one low-yield step cannot be avoided. Nonetheless, palladium and iridium complexes have been prepared, and their structures and reactions characterized. Future papers will describe more readily accessible fluorous SCS pincer ligands that contain two ponytails per arene ring,[16] and palladium complexes that give non-molecular catalysts for Heck reactions, as noted for related species above.[12]

## Experimental

### General

Reactions were, unless noted otherwise, conducted under $N_2$ with glassware that had been oven-dried (110 °C), assembled while warm, and cooled under vacuum. Chemicals were treated as follows: THF, diethyl ether, hexanes, and toluene, distilled from Na/benzophenone; ethanol, distilled from $CaH_2$; $CF_3C_6F_5$, distilled from $P_2O_5$; $CF_3C_6F_{11}$ (ABCR) and $HNEt_2$ (Fluka), freeze–pump–thaw degassed; $H_2C{=}CHR_{f6}$, $H_2C{=}CHR_{f8}$, $Pd(O_2CCF_3)_2$ (3 × ABCR), 1,3-$C_6H_4(CH_2Br)_2$ (**2**), $LiAlH_4$, AIBN (3 × Aldrich), $BH_3$ (1 M in THF), *n*-BuLi (1.6 M in hexane), $C_6D_6$, [$D_8$]THF, [$D_6$]DMSO, (5 × Acros), and KOH (Grüssing Gmbh), used as received. Silica gel (Merck grade 9385, 230–400 mesh) was dried at 110 °C and 0.02 Torr (24 h).

NMR spectra were recorded on Bruker 300 or 400 MHz spectrometers at ambient probe temperature and referenced as follows: $^1$H, residual internal [$D_7$]THF ($\delta$ 1.73, 3.58) or $C_6D_5H$ ($\delta$ 7.16); $^{13}$C internal [$D_8$]THF ($\delta$ 25.37, 67.57) or $C_6D_6$ ($\delta$ 128.39); $^{31}$P, external $H_3PO_4$ ($\delta$ = 0.00 ppm); $^{19}$F, internal $C_6F_6$ ($\delta$ = −162.0 ppm). IR and mass spectra were recorded on ASI React-IR 1000 and Micromass Zabspec instruments, respectively. DSC and TGA data were recorded with a Mettler-Toledo DSC821 apparatus and treated by standard methods.[43] Elemental analyses were conducted on a Carlo Erba EA1110 instrument.

**1,3-$C_6H_4(CH_2PH_2)_2$ (1)[18].** A Schlenk flask was charged with $LiAlH_4$ (5.56 g, 147 mmol) and diethyl ether (25 mL) and cooled to −20 °C. Another Schlenk flask was charged with 1,3-$C_6H_4(CH_2P(=O)(OCH_2CH_3)_2)_2$ (22.00 g, 66.63 mmol)[18b] and diethyl ether (75 mL). This solution was slowly cannulated into the first flask with stirring. The mixture was allowed to warm to room temperature over several hours, stirred overnight, and cooled to 0 °C. A degassed solution of saturated aqueous NaOH was slowly added *via* cannula with vigorous stirring, until the formation of a white precipitate was complete. The ether layer was transferred under $N_2$ to a flask charged with $MgSO_4$. The white aqueous layer was further extracted with diethyl ether (2 × 50 mL). The ether layers were combined, dried ($MgSO_4$), and concentrated by oil pump vacuum. The crude opaque oil was distilled (Kugelrohr) to give **2** as a clear, strong-smelling oil (5.670 g, 33.35 mmol, 50%). Calcd for $C_8H_{12}P_2$: C, 56.48; H, 7.11. Found: C, 56.30; H, 7.34%. NMR ($\delta$, $C_6D_6$): $^1$H 2.44 (m, 4H, P$H_2$), 2.84 (td, $J_{HH}$ = 7.6 Hz, $J_{PH}$ = 191.7 Hz, 4H, ArC$H_2$), 6.75 (d, $J_{HH}$ = 5.6 Hz, 2H, Ar), 6.77 (s, 1H, Ar), 6.99 (t, $J_{HH}$ = 7.6 Hz, 1H, Ar); $^{13}$C{$^1$H} 20.9 (d, $J_{PC}$ = 11.2 Hz, Ar$C$H$_2$), 125.1 (s, Ar), 127.4 (t, $J_{PC}$ = 14 Hz, Ar), 128.8 (t, $J_{PC}$ = 16.4 Hz, Ar), 129.1 (s, Ar); $^{31}$P{$^1$H} − 121.9 (s).

**1,3-$C_6H_4(CH_2P(CH_2CH_2R_{f8})_2)_2$ (3-$R_{f8}$).**

*Method A.* A Schlenk flask was charged with **1** (1.079 g, 6.350 mmol), $H_2C{=}CHR_{f8}$, (17.0 g, 38.1 mmol), and AIBN (0.500 g, 3.045 mmol), and placed in a 75 °C bath. The mixture was stirred (6 h), cooled, and filtered through a silica gel plug (3.0 × 1.5 cm) that was rinsed with hexanes/$CF_3C_6H_5$ (4 : 1 v/v, 100 mL). The volatiles were removed from the filtrate by oil pump vacuum. The yellowish oil was chromatographed on silica gel (20 × 3 cm column; packed in hexanes) with hexanes/$CF_3C_6H_5$ (7 : 1 v/v, 800 mL; then 4 : 1 v/v, 500 mL).[19] The fractions were monitored by $^{31}$P NMR, and the solvents were removed by oil pump vacuum. The earlier cuts (300–450 mL) gave 1,3-$C_6H_4(CH_3)(CH_2P(CH_2CH_2R_{f8})_2)$ (**4**-$R_{f8}$; 2.204 g, 2.140 mmol, 35%), and the later cuts (550–1000 mL) **3**-$R_{f8}$ (0.510 g, 0.261 mmol, 4%), both as air sensitive white solids.

*Method B.* A photochemical immersion well reactor was charged with **1** (1.527 g, 8.980 mmol), $H_2C{=}CHR_{f8}$ (24.6 g, 56.0 mmol), and AIBN (0.100 g, 0.609 mmol). The mixture was irradiated with a Heraeus TQ 150 medium pressure mercury lamp (6 h). Workup as in method A gave **4**-$R_{f8}$ and **3**-$R_{f8}$ (0.851 g, 0.436 mmol, 5%).

*Method C.* A Schlenk flask was charged with HP-$(CH_2CH_2R_{f8})_2$ (**5**-$R_{f8}$;[21] 4.520 g, 4.880 mmol) and **2** (0.612 g, 2.32 mmol), which were intimately mixed. The flask was placed in a 55 °C oil bath, and warmed to 75 °C over 0.5 h. The mixture melted, and was stirred with a stir bar until it solidified again. The flask was warmed to 80 °C over a few minutes. After 1 h total, the mixture was cooled and THF (100 mL) was added. The solid product was triturated to a sand-like suspension and cooled to 0 °C. Then $LiAlH_4$ (0.0660 g, 1.74 mmol) was added with stirring. The mixture was slowly warmed to room temperature. After 3 h, the mixture was cooled to 0 °C and aqueous NaOH (3.0 M) was slowly added. After a few minutes, the mixture was filtered through $MgSO_4$. The solvent was removed by oil pump vacuum. Then $CF_3C_6H_5$ (5–10 mL) was added, and column chromatography as in method A gave **3**-$R_{f8}$ (0.938 g, 0.480 mmol, 20%).

*Data for* ***3***-$R_{f8}$. mp 63 °C. Calc. for $C_{48}H_{24}F_{68}P_2$: C 29.48; H 1.23; Found: C 29.74; H 1.14%. NMR ($\delta$, [$D_8$]THF): $^1$H 1.72 (m, 4H, C$H_2$CH$_2$CF$_2$), 2.22 (m, 4H, CH$_2$C$H_2$CF$_2$), 2.95 (s, 4H, ArC$H_2$), 7.06 (d, $J_{HH}$ = 7.6 Hz, 2H, Ar), 7.10 (s, 1H, Ar), 7.22 (t, $J_{HH}$ = 7.6 Hz, 1H, Ar); $^{13}$C{$^1$H} 17.8 (d, $J_{CP}$ = 16.1 Hz, $C$H$_2$CH$_2$CF$_2$), 28.6 (m, CH$_2$$C$H$_2$CF$_2$), 35.1 (d, $J_{CP}$ = 17.6 Hz, Ar$C$H$_2$), 127.8 (d, $J_{CP}$ = 5.1 Hz, Ar), 129.7 (s, Ar), 130.2 (t, $J_{CP}$ = 5.9 Hz, Ar), 138.1 (d, $J_{CP}$ = 2.9 Hz, Ar); $^{31}$P{$^1$H} −19.4 (s).

*Data for* ***4***-$R_{f8}$. mp 55 °C. Calc. for $C_{28}H_{17}F_{34}P$: C 32.64; H 1.66; Found: C 32.63; H 1.83%. NMR ($\delta$, $C_6D_6$): $^1$H 1.59 (m, 4H, C$H_2$CH$_2$CF$_2$), 2.04 (m, 4H, CH$_2$C$H_2$CF$_2$), 2.30 (s, 3H, ArC$H_3$), 2.70 (s, 2H, ArC$H_2$), 6.87 (d, $J_{HH}$ = 7.6 Hz, 2H, Ar), 6.91 (s, 1H, Ar), 7.07 (t, $J_{HH}$ = 7.6 Hz, 1H, Ar); $^{13}$C{$^1$H} 18.0 (d, $J_{CP}$ = 17.6 Hz, $C$H$_2$CH$_2$CF$_2$), 20.7 (s, Ar$C$H$_3$), 28.8 (m, CH$_2$$C$H$_2$CF$_2$), 35.3 (d, $J_{CP}$ = 17.6 Hz, Ar$C$H$_2$), 126.4 (d, $J_{CP}$ = 5.9 Hz, Ar), 127.6 (d, $J_{CP}$ = 2.9 Hz, Ar), 129.1 (s, Ar), 130.2 (d, $J_{CP}$ = 5.1 Hz, Ar), 137.1 (d, $J_{CP}$ = 3.7 Hz, Ar), 139.4 (d, $J_{CP}$ = 1.5 Hz, Ar); $^{31}$P{$^1$H} −22.0 (s). MS (FAB, 3-NBA), *m/z* (%):[23] 1031 (60) [M]$^+$, 611 (10) [M − $R_{f8}$]$^+$, 583 (10) [M − $CH_2CH_2R_{f8}$]$^+$.

**1,3-$C_6H_4(CH_2P(CH_2CH_2R_{f6})_2)_2$ (3-$R_{f6}$).** Compounds **1** (0.501 g, 2.94 mmol), $H_2C{=}CHR_{f6}$ (6.105 g, 17.65 mmol) and AIBN (0.121 g, 0.735 mmol) were reacted in a manner analogous to method A for **3**-$R_{f8}$. An identical filtration and chromatographic[19] workup gave 1,3-$C_6H_4(CH_3)(CH_2P(CH_2CH_2R_{f6})_2)$ (**4**-$R_{f6}$; 0.733 g, 0.882 mmol, 30%) and **3**-$R_{f6}$ (0.503 g, 0.324 mmol, 11%). as air sensitive clear colorless oils.

*Data for* ***3***-$R_{f6}$. NMR ($\delta$, $C_6D_6$): $^1$H 1.69 (m, 4H, C$H_2$CH$_2$CF$_2$), 2.11 (m, 4H, CH$_2$C$H_2$CF$_2$), 2.79 (s, 4H, ArC$H_2$), 7.02 (d, $J_{HH}$ = 7.6 Hz, 2H, Ar), 7.07 (s, 1H, Ar), 7.23 (t, $J_{HH}$ = 7.6 Hz, 1H, Ar); $^{13}$C{$^1$H} 17.5 (d, $J_{CP}$ = 16.1 Hz, $C$H$_2$CH$_2$CF$_2$), 28.4 (m, CH$_2$$C$H$_2$CF$_2$), 34.6 (d, $J_{CP}$ = 17.6 Hz, Ar$C$H$_2$), 127.7 (d, $J_{CP}$ = 5.1 Hz, Ar), 129.6 (s, Ar), 130.5 (t, $J_{CP}$ = 5.9 Hz, Ar), 138.1 (d, $J_{CP}$ = 2.9 Hz, Ar); $^{31}$P{$^1$H} −21.5 (s).

*Data for* ***4***-$R_{f6}$. NMR ($\delta$, $C_6D_6$): $^1$H 1.59 (m, 4H, C$H_2$CH$_2$CF$_2$), 2.04 (m, 4H, CH$_2$C$H_2$CF$_2$), 2.38 (s, 3H, ArC$H_3$),

2.75 (s, 2H, ArC$H_2$), 6.87 (d, $J_{HH}$ = 7.6 Hz, 2H, Ar), 6.91 (s, 1H, Ar), 7.07 (t, $J_{HH}$ = 7.6 Hz, 1H, Ar); $^{13}C\{^1H\}$ 18.0 (d, $J_{CP}$ = 17.6 Hz, $CH_2CH_2CF_2$), 20.7 (s, Ar$CH_3$), 29.0 (m, $CH_2CH_2CF_2$), 35.3 (d, $J_{CP}$ = 17.6 Hz, Ar$CH_2$), 126.4 (d, $J_{CP}$ = 5.9 Hz, Ar), 127.6 (d, $J_{CP}$ = 2.9 Hz, Ar), 129.1 (s, Ar), 130.2 (d, $J_{CP}$ = 5.1 Hz, Ar), 137.1 (d, $J_{CP}$ = 3.7 Hz, Ar), 139.5 (d, $J_{CP}$ = 1.5 Hz, Ar); $^{31}P\{^1H\}$ − 22.6 (s).

**(2,6,1-$C_6H_3(CH_2\overline{P(CH_2CH_2R_{f6})_2})_2$)$\overline{Pd(O_2CCF_3)}$ (10-$R_{f6}$).** A Schlenk flask was charged with **3**-$R_{f6}$ (0.275 g, 0.177 mmol), THF (10 mL) and $Pd(O_2CCF_3)_2$ (0.058 g, 0.18 mmol). The mixture was stirred. After 10 h, the solvent was removed by oil pump vacuum. The orange solid was chromatographed on silica gel (20 cm × 2 cm column packed in hexanes) with $CF_3C_6H_5$/hexanes (1 : 4 v/v). The solvent was removed from the product-containing fraction by oil pump vacuum to give **10**-$R_{f6}$ (0.250 g, 0.142 mmol, 80%) as a white solid.

*Data for* ***10****-$R_{f6}$.* mp 63 °C (capillary), 60.7 °C (DSC, endotherm, $T_e$). TGA, onset of mass loss 174.6 °C. Calc. for $C_{42}H_{24}F_{55}O_2P_2Pd$. C 28.44; H 1.36; Found: C 28.42; H 1.90%. NMR ($\delta$, $C_6D_6$): $^1H$ 1.63 (m, 4H, C$H$H′CHH′$CF_2$), 1.96 (m, 4H, CH$H$′CHH′$CF_2$), 2.44 (m, 4H, C$H$H′$CF_2$), 2.57 (m, 4H, CH$H$′$CF_2$), 2.71 (virtual t,[28] $J$ = 4.3 Hz, 4H, ArC$H_2$), 6.79 (d, $J_{HH}$ = 7.5 Hz, 2H, Ar), 6.94 (t, $J_{HH}$ = 8.0 Hz, 1H, Ar); $^{13}C\{^1H\}$ 17.3 (virtual t,[28] $J$ = 13.5 Hz, $CH_2CH_2CF_2$), 28.0 (m, $CH_2CH_2CF_2$), 38.3 (virtual t,[28] $J$ = 13.2 Hz, Ar$CH_2$), 124.4 (t, $J$ = 11.1 Hz, Ar), 127.2 (s, Ar), 149.3 (t, $J$ = 10.1 Hz, Ar), 152.7 (s, Ar); $^{31}P\{^1H\}$ 40.6 (s). MS (FAB, 3-NBA), $m/z$ (%):[23] 1659 (100), $[M - OCOCF_3]^+$.

**(2,6,1-$C_6H_3(CH_2\overline{P(CH_2CH_2R_{f8})_2})_2$)$\overline{Pd(O_2CCF_3)}$ (10-$R_{f8}$).** A Schlenk flask was charged with **3**-$R_{f8}$ (0.195 g, 0.100 mmol), THF (10 mL), and $Pd(O_2CCF_3)_2$ (0.034 g, 0.10 mmol). The mixture was warmed to 80 °C. After 5 h, the solution was cooled and the solvent removed by oil pump vacuum. The orange solid was dissolved in $CF_3C_6H_5$ and chromatographed on silica gel (20 cm × 2 cm column packed in 4 : 1 v/v $CF_3C_6H_5/CH_2Cl_2$) with $CF_3C_6H_5/CH_2Cl_2$ (1 : 1 v/v). The eluate was monitored by TLC. Solvent was removed from the product-containing fraction by oil pump vacuum to give spectroscopically pure **10**-$R_{f8}$ as a light yellow solid (0.200 g, 0.093 mmol, 90%). Recrystallization from hot hexanes gave **10**-$R_{f8}$ (0.099 g, 0.046 mmol, 46%) as colorless prisms.

*Data for* ***10****-$R_{f8}$.* mp 83 °C (capillary), 65.4 °C (DSC, endotherm, $T_e$). TGA, onset of mass loss 254.7 °C. Calc. for $C_{50}H_{23}F_{71}O_2P_2Pd$: C 27.65; H 1.07; Found: C 27.67; H 1.09%. IR ($cm^{-1}$, powder film): $\nu_{CO}$ 1690 (m). NMR ($\delta$, $C_6D_6$): $^1H$ 1.67 (m, 4H, C$H$H′CHH′$CF_2$), 2.01 (m, 4H, CH$H$′CHH′$CF_2$), 2.29 (m, 4H, C$H$H′$CF_2$), 2.50 (m, 4H, CH$H$′$CF_2$), 2.71 (virtual t,[28] $J$ = 4.3 Hz, 4H, ArC$H_2$), 6.83 (d, $J_{HH}$ = 7.5 Hz, 2H, Ar), 6.93 (t, $J_{HH}$ = 8.0 Hz, 1H, Ar); $^{13}C\{^1H\}$ 18.7 (m, $CH_2CH_2CF_2$), 27.7 (m, $CH_2CH_2CF_2$), 38.7 (virtual t,[28] $J_{CP}$ = 13.0 Hz, Ar$CH_2$), 124.2 (t, $J_{CP}$ = 11.0 Hz, Ar), 127.2 (s, Ar), 148.9 (t, $J_{CP}$ = 10.3 Hz, Ar), 151.4 (s, Ar); $^{31}P\{^1H\}$ 41.4 (s); $^{19}F$ −124.7 ($CF_2CF_3$), −122.0 ($CF_2CF_2CF_3$), −121.2 ($CF_2(CF_2)_2CF_3$, −120.3 ($CH_2CF_2(CF_2)_3$), −113.3 ($CH_2CF_2$), −79.4 ($CF_3$). MS (FAB, 3-NBA), $m/z$ (%):[23] 2059 (100) $[M - OCOCF_3]^+$.

**(2,6,1-$C_6H_3(CH_2\overline{P(CH_2CH_2R_{f8})_2})_2$)$\overline{Ir(Cl)(H)}$ (11-$R_{f8}$).**

*Method A.* A Schlenk flask was charged with **3**-$R_{f8}$ (0.1980 g, 0.1012 mmol), THF (12 mL), and argon. Then $[IrCl(COE)_2]_2$ (0.0580 g, 0.0668 mmol)[33] was added with stirring. After 0.5 h, the mixture was warmed to 80 °C. After 48 h, during which time some brown precipitate formed, the mixture was cooled and filtered. The solvent was removed from the filtrate by oil pump vacuum. The brownish solid (0.0890 g) was dissolved in $CF_3C_6F_{11}$ (3 mL). The solution was extracted with toluene (3 × 1.5 mL). The $CF_3C_6F_{11}$ was removed by oil pump vacuum to give **11**-$R_{f8}$ (0.0630 g, 0.0289 mmol, 29%) as an orange-yellow solid.

*Method B.* An NMR tube was charged with **3**-$R_{f8}$ (0.031 g, 0.055 mmol) and a solution of $[IrCl(COE)_2]_2$ (0.025 g, 0.030 mmol) in [$D_8$]THF (0.7 mL) in a glove box. The tube was tightly closed and immersed in an oil bath (80 °C). Data: Fig. 3.

*Data for* ***11****-$R_{f8}$.* mp 98 °C. Calc. for $C_{48}H_{24}ClF_{68}IrP_2$: C 26.40; H 1.10; Found: C 26.44; H 1.15%. IR ($cm^{-1}$, powder film): $\nu_{Ir-H}$ 2200 (vw). NMR ($\delta$, [$D_8$]THF): $^1H$ −25.3 (t, $J_{PH}$ = 14.6 Hz, 1H, Ir$H$), 2.17 (m, 4H, C$H_2$CH$_2$CF$_2$), 2.49 (m, 4H, C′$H_2$C′H$_2$C′F$_2$), 2.88 (m, 4H, C$H_2$CF$_2$), 3.02 (m, 4H, C′$H_2$C′F$_2$), 3.80 (d, $J_{PH}$ = 13.2 Hz, 4H, ArC$H_2$), 6.66 (t, $J_{HH}$ = 7.3 Hz, 1H, Ar), 6.82 (d, $J_{HH}$ = 7.3 Hz, 2H, Ar); $^{13}C\{^1H\}$ 17.1 (virtual t,[28] $J_{CP}$ = 13.2 Hz, $CH_2CH_2CF_2$), 18.3 (virtual t,[28] $J_{CP}$ = 15.5 Hz, $CH'_2CH'_2CF'_2$), 26.9 (t, $J_{CF}$ = 22.4 Hz, C‘H$_2$C′F$_2$), 27.9 (t, $J_{CF}$ = 22.6 Hz, C‘H$_2$C′F$_2$), 38.9 (virtual t,[28] $J_{CP}$ = 17.4 Hz, Ar$CH_2$), 123.0 (t, $J_{CP}$ = 8.5 Hz, Ar), 124.4 (s, Ar), 138.5 (m, Ar), 145.8 (t, $J_{CP}$ = 8.5 Hz, Ar) $^{31}P\{^1H\}$ 26.0 (s); $^{19}F$ −122.2 ($CF_2CF_3$), −119.5 ($CF_2CF_2CF_3$), −118.7 ($CF_2(CF_2)_2CF_3$, −117.7 ($CH_2CF_2(CF_2)_3$), −110.5 ($CH_2CF_2$), −77.1 ($CF_3$). MS (FAB, 3-NBA), $m/z$ (%):[23] 2181 (30) $[M]^+$, 2146 (75) $[M - Cl]^+$, 1987 (100) $[M - Ir]^+$.

## Partition coefficients

**Method A.** A 10 mL vial was charged with **10**-$R_{f8}$ (0.0112 g, 0.00515 mmol), $CF_3C_6F_{11}$ (2.000 mL), and toluene (2.000 mL), fitted with a mininert valve, and vigorously shaken (2 min). After 2 h (24 °C), a 0.200 mL aliquot of the fluorous phase and a 0.800 mL aliquot of the non-fluorous phase were removed. The solvents were evaporated and the residues dried by oil pump vacuum (1 h). Each residue was dissolved in $CF_3C_6F_{11}$/EtOH (9 : 1 v/v; 0.500 mL) and analyzed by HPLC (average of 5 injections, 200 × 4 mm Nucleosil 100 − 5 column, UV/visible detector). The relative peak intensities were, after normalization to the aliquot volumes, 96.4 : 3.6.

**Method B.** A 10 mL flask was charged with **11**-$R_{f8}$ (0.0620 g, 0.0284 mmol) and $CF_3C_6F_{11}$ (3.00 mL). After complete dissolution, toluene (3.00 mL) was added and the sample was vigorously shaken (20 min). After 48 h (25 °C), 0.500 mL aliquots were removed from each layer. The $CF_3C_6F_{11}$ aliquot was evaporated to dryness. A solution of the internal standard $C_6F_6$ (0.1010 g, 0.5430 mmol) in $CF_3C_6H_5$ (13.4448 g) was prepared. Portions of this solution were added gravimetrically to the aliquots ($CF_3C_6F_{11}$: 0.7150 g solution, 0.02870 mmol $C_6F_6$; toluene: 0.0633 g solution, 0.00254 mmol $C_6F_6$), followed by [$D_8$]THF (0.05 mL). $^{19}F$ NMR spectra were recorded. The area of the $(CF_2)_7CF_3$ signal was integrated *versus* that of $C_6F_6$. The procedure was repeated, giving an average partition coefficient of 98.0 : 2.0 (0.000189 g of **11**-$R_{f8}$ in 0.500 mL toluene; 0.00966 g of **11**-$R_{f8}$ in 0.0500 mL of $CF_3C_6F_{11}$). A 3.00/0.500 scale factor gave a mass recovery of 0.0591 g (95%).

## Crystallography

A nearly saturated solution of **10**-$R_{f8}$ in refluxing hexanes was allowed to cool to room temperature. After 1 day, a transparent colorless prism (0.25 × 0.20 × 0.20 mm) was taken to a Nonius KappaCCD area detector for data collection at 173(2) K ($\lambda$ 0.71073 Å). Cell parameters were obtained from 10 frames using a 10° scan and refined with 1242 reflections. Lorentz, polarization and empirical (Scalepack) absorption corrections[44] were applied. The space group was determined from systematic absences and subsequent least-squares refinement. The structure was solved by direct methods. The parameters were refined with all data by full-matrix-least-squares on $F^2$ using SHELXL-97.[45] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. The atom F46A showed some disorder, but this could not be resolved. Scattering factors were taken from the literature.[46]

**Crystal data.** Empirical formula: $C_{50}H_{23}F_{71}O_2P_2Pd$; Formula weight: 2173.02; Crystal system: monoclinic; Space group: $P2_1/n$; Unit cell dimensions: $a/b/c$ [Å] 19.2920(9)/19.3960(11)/20.5830(11), $\beta$ [°] 115.522(3), $V$ [Å$^3$] 6950.3(6); $Z$ 4; $D_c$ [Mg m$^{-3}$]: 2.077; Absorption coefficient [mm$^{-1}$]: 0.546; $F(000)$: 4216; $q$ limit [°]: 2.19 to 25.10; Index ranges ($h$, $k$, $l$): −22, 22; −22, 22; −24, 24; Reflections collected: 23414; Independent reflections: 12099 [$R$(int) = 0.0616]; Reflections [$I > 2\sigma(I)$]: 6854; Completeness to $\Theta$ = 25.10° (%): 97.7; Max. and min. transmission: 0.8986 and 0.8755; Data/restraints/parameters: 12099/67/1135; Goodness-of-fit on $F^2$: 1.037; Final $R$ indices [$I > 2\sigma(I)$]: $R1$ = 0.1124, $wR2$ = 0.2973; $R$ indices (all data): $R1$ = 0.1731, $wR2$ = 0.3413; Largest diff. peak and hole [e Å$^{-3}$]: 1.764/−1.096.

CCDC reference number 256984.

See http://www.rsc.org/suppdata/dt/b5/b502309b/ for crystallographic data in CIF or other electronic format.

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## References and notes

1 (*a*) M. Albrecht and G. van Koten, *Angew. Chem. Int. Ed.*, 2001, **40**, 3750; M. Albrecht and G. van Koten, *Angew. Chem.*, 2001, **113**, 3866; (*b*) M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759.

2 (*a*) W. T. S. Huck, F. C. J. M. van Veggel, B. L. Kropman, D. H. A. Blank, E. G. Keim, M. M. A. Smithers and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1995, **117**, 8293; (*b*) W. T. S. Huck, F. C. J. M. van Veggel and D. N. Reinhoudt, *J. Mater. Chem.*, 1997, **7**, 1213; (*c*) B.-H. Huisman, H. Schönherr, W. T. S. Huck, A. Friggeri, H.-J. van Manen, E. Menozzi, G. J. Vancso, F. C. J. M. van Veggel and D. N. Reinhoudt, *Angew. Chem. Int. Ed.*, 1999, **38**, 2248; B.-H. Huisman, H. Schönherr, W. T. S. Huck, A. Friggeri, H.-J. van Manen, E. Menozzi, G. J. Vancso, F. C. J. M. van Veggel and D. N. Reinhoudt, *Angew. Chem.*, 1999, **111**, 2385.

3 M. Q. Slagt, S.-E. Stiriba, H. Kautz, R. J. M. K. Gebbink, H. Frey and G. van Koten, *Organometallics*, 2004, **23**, 1525.

4 (*a*) M. D. Meijer, M. Rump, R. A. Gossage, J. H. T. B. Jastrzebski and G. van Koten, *Tetrahedron Lett.*, 1998, **39**, 6773; (*b*) M. D. Meijer, N. Ronde, D. Vogt, G. P. M. van Klink and G. van Koten, *Organometallics*, 2001, **20**, 3993.

5 (*a*) C. Pathmamanoharan, P. Wijkens, D. M. Grove and A. P. Philipse, *Langmuir*, 1996, **12**, 4372; (*b*) R. Chanthateyanonth and H. Alper, *Adv. Synth. Catal.*, 2004, **346**, 1375.

6 (*a*) D. E. Bergbreiter, P. L. Osburn and Y.-S. Liu, *J. Am. Chem. Soc.*, 1999, **121**, 9531; (*b*) D. E. Bergbreiter, P. L. Osburn, A. Wilson and E. M. Sink, *J. Am. Chem. Soc.*, 2000, **122**, 9058.

7 G. van Koten and J. T. B. H. Jastrzebski, *J. Mol. Catal. A.*, 1999, **146**, 317.

8 D. E. Bergbreiter and J. Li, *Chem. Commun.*, 2004, 42.

9 E. Mas-Marzá, A. M. Segarra, C. Claver, E. Peris and E. Fernandez, *Tetrahedron Lett.*, 2003, **44**, 6595.

10 (*a*) H. Kleijn, J. T. B. H. Jastrzebski, R. A. Gossage, H. Kooijman, A. L. Spek and G. van Koten, *Tetrahedron*, 1998, **54**, 1145; (*b*) P. Dani, B. Richter, G. P. M. van Klink and G. van Koten, *Eur. J. Inorg. Chem.*, 2001, 125; (*c*) D. P. Curran, K. Fischer and G. Moura-Letts, *Synlett.*, 2004, 1379.

11 *Handbook of Fluorous Chemistry*, ed. J. A. Gladysz, D. P. Curran and I. T. Horváth, Wiley/VCH, Weinheim, 2004.

12 (*a*) K. Yu, W. Sommer, J. M. Richardson, M. Weck and C. W. Jones, *Adv. Synth. Catal.*, 2005, **347**, 161; (*b*) D. E. Bergbreiter, P. L. Osburn and J. Frels, *Adv. Synth. Catal.*, 2005, **347**, 172.

13 (*a*) C. Rocaboy and J. A. Gladysz, *New J. Chem.*, 2003, **27**, 39; (*b*) C. Rocaboy and J. A. Gladysz, *Tetrahedron.*, 2002, **58**, 4007; (*c*) C. Rocaboy and J. A. Gladysz, *Org. Lett.*, 2002, **4**, 1993.

14 C. M. Jensen, *Chem. Commun.*, 1999, 2443.

15 J. A. Gladysz, C. Emnet and J. Rábai, in *Handbook of Fluorous Chemistry*, ed. J. A. Gladysz, D. P. Curran and I. T. Horváth, Wiley/VCH, Weinheim, 2004, ch. 6.

16 R. C. da Costa and J. A. Gladysz, manuscript in preparation.

17 (*a*) L. J. Alvey, D. Rutherford, J. J. J. Juliette and J. A. Gladysz, *J. Org. Chem.*, 1998, **63**, 6302; (*b*) A. Klose and J. A. Gladysz, *Tetrahedron: Asymmetry*, 1999, **10**, 2665; (*c*) L. J. Alvey, R. Meier, T. Soós, P. Bernatis and J. A. Gladysz, *Eur. J. Inorg. Chem.*, 2000, 1975.

18 (*a*) E. I. Musina, G. N. Nikonov, A. S. Balueva, E. F. Gubanov and E. V. Kovalenko, *Russ. J. Gen. Chem.*, 1999, **69**, 407; (*b*) We substitute 1,3-$C_6H_4(CH_2Br)_2$ for the dichloride and $P(OEt)_3$ for the $P(OBu)_3$ used in the preceding reference, as reported by N. A. Caplan, C. I. Pogson, D. J. Hayes and G. M. Blackburn, *J. Chem. Soc., Perkin Trans. I*, 2000, 421; (*c*) Since the final reduction step in our synthesis of **1** is technically new, full details are given in the Experimental section.

19 It is essential to conduct the column chromatography (Experimental section) under rigorous inert atmosphere conditions with degassed solvents. The highest yields were obtained when this was done in a glove box.

20 (*a*) D. G. Gusev, M. Madott, F. M. Dolgushin, K. A. Lyssenko and M. Y. Antipin, *Organometallics.*, 2000, **19**, 1734; (*b*) E. Hollink, J. C. Stewart, P. Wei and D. W. Stephan, *Dalton Trans.*, 2003, 3968; (*c*) J. C. Grimm, C. Nachtigal, H.-G. Mack, W. C. Kaska and H. A. Mayer, *Inorg. Chem. Commun.*, 2000, **3**, 511; (*d*) H. A. Y. Mohammad, J. C. Grimm, K. Eichele, H.-G. Mack, B. Speiser, F. Novak, M. G. Quintanilla, W. C. Kaska and H. A. Mayer, *Organometallics*, 2002, **21**, 5775; (*e*) D. Hermann, M. Gandelman, H. Rozenberg, L. J. W. Shimon and D. Milstein, *Organometallics*, 2002, **21**, 812.

21 (*a*) C. Emnet and J. A. Gladysz, *Synthesis*, 2005, 1012; (*b*) C. Emnet, R. Tuba and J. A. Gladysz, *Adv. Synth. Catal.*, submitted for publication.

22 J. A. Gladysz, in *Handbook of Fluorous Chemistry*, ed. J. A. Gladysz, D. P. Curran and I. T. Horváth, Wiley/VCH, Weinheim, 2004, ch. 5.

23 (*a*) All $m/z$ values represent the most intense peak of the isotope envelope; (*b*) Both **10**-$R_{f6}$ and **10**-$R_{f8}$ gave ions with masses corresponding to $[M + H_3O]^+$, but the intensities strongly depended upon the sample.

24 (*a*) W. J. Bailey and S. A. Buckler, *J. Am. Chem. Soc.*, 1957, **79**, 3567; (*b*) S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, 1961, 4263; (*c*) K. Sasse, *Houben-Weyl Methoden der Organischen Chemie*, Georg Thieme Verlag, Stuttgart, Germany, 1963, vol. XII, part 1, pp. 52–53.

25 In one experiment, the crude reaction mixture was suspended in THF and treated with NaOAc. A $^{31}$P NMR spectrum showed small quantities of the target pincer ligand **3**-$R_{f8}$, presumably formed by the deprotonation of **6**-$R_{f8}$.

26 (*a*) T. Imamoto, T. Kusumoto, N. Suzuki and K. Sato, *J. Am. Chem. Soc.*, 1985, **107**, 5301; (*b*) D. Morales-Morales, R. E. Cramer and C. M. Jensen, *J. Organomet. Chem.*, 2002, **654**, 44.

27 H. Lebel, S. Morin and V. Paquet, *Org. Lett.*, 2003, **5**, 2347.

28 (*a*) W. H. Hersch, *J. Chem. Educ.*, 1997, **74**, 1485; (*b*) The $^iJ_{CP}$ values given represent the apparent coupling between adjacent peaks of the triplet. They are half of the true values $|^iJ_{CP} + {}^{i+2}J_{CP}|$.

29 (*a*) R. J. Cross, A. R. Kennedy and K. W. Muir, *J. Organomet. Chem.*, 1995, **487**, 227 and earlier literature in Table 3 therein; (*b*) J. M. Longmire, X. Zhang and M. Shang, *Organometallics.*, 1998, **17**, 4374; (*c*) W. D. Cotter, L. Barbour, K. L. McNamara, R. Hechter and R. J. Lachicotte, *J. Am. Chem. Soc.*, 1998, **120**, 11016; (*d*) R. B. Bedford, S. M. Draper, P. N. Scully and S. L. Welch, *New. J. Chem.*, 2000, **24**, 745; (*e*) B. S. Williams, P. Dani, M. Lutz, A. L. Spek and G. van Koten, *Helv. Chim. Acta*, 2001, **84**, 3519; (*f*) R. Chanthateyanonth and H. Alper, *J. Mol. Catal. A*, 2003, **201**, 23; (*g*) M. R. Eberhard, S. Matsukawa, Y. Yamamoto and C. M. Jensen, *J. Organomet. Chem.*, 2003, **687**, 185; (*h*) A. Naghipour, S. J. Sabounchei, D. Morales-Morales, S. Hernández-Ortega and C. M. Jensen, *J. Organomet. Chem.*, 2004, **689**, 2494.

30 In *n*-perfluoroalkanes, global energy minima with *anti* F–C–C–F torsion angles of *ca.* 165° are commonly found. See (*a*) B. Albinsson and J. Michl, *J. Phys. Chem.*, 1996, **100**, 3418; (*b*) E. K. Watkins and W. L. Jorgensen, *J. Phys. Chem. A.*, 2001, **105**, 4118; (*c*) J. D. Dunitz, A. Gavezzotti and W. B. Schwiezer, *Helv. Chim. Acta.*, 2003, **86**, 4073.

31 (*a*) M.-A. Guillevic, C. Rocaboy, A. M. Arif, I. T. Horváth and J. A. Gladysz, *Organometallics*, 1998, **17**, 707; (*b*) J. Fawcett, E. G. Hope, R. D. W. Kemmitt, D. R. Paige, D. R. Russell, A. M. Stuart, D. J. Cole-Hamilton and M. J. Payne, *Chem. Commun.*, 1997, 1127; (*c*) C. M. Haar, J. Huang and S. P. Nolan, *Organometallics*, 1998, **17**, 5018; (*d*) D. C. Smith, E. D. Stevens, Jr. and S. P. Nolan, *Inorg. Chem.*, 1999, **38**, 5277; (*e*) R. T. Stibrany and S. M. Gorun, *J. Organomet. Chem.*, 1999, **579**, 217.

32 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

33 J. L. Herde, J. C. Lambert and C. V. Senoff, *Inorg. Synth.*, 1974, **15**, 18.

34 (*a*) I. Göttker-Schnetmann and M. Brookhart, *J. Am. Chem. Soc.*, 2004, **126**, 9330; (*b*) D. Morales-Morales, R. Rédon, C. Yung and C. M. Jensen, *Inorg. Chim. Acta*, 2004, **357**, 2953.
35 P. Osburn, Universität Erlangen-Nürnberg, unpublished results.
36 (*a*) J. Dupont, M. Pfeffer and J. Spencer, *Eur. J. Inorg. Chem.*, 2001, 1917; (*b*) M. Ohff, A. Ohff, M. E. van der Boom and D. Milstein, *J. Am. Chem. Soc.*, 1997, **119**, 11687; (*c*) K. Kiewel, Y. Liu, D. E. Bergbreiter and G. A. Sulikowski, *Tetrahedron Lett.*, 1999, **40**, 8945; (*d*) M. R. Eberhard, *Org. Lett.*, 2004, **6**, 2125.
37 (*a*) N. Solin, J. Kjellgren and K. J. Szabó, *Angew. Chem. Int. Ed.*, 2003, **42**, 3656; N. Solin, J. Kjellgren and K. J. Szabó, *Angew. Chem.*, 2003, **115**, 3784; (*b*) N. Solin, J. Kjellgren and K. J. Szabó, *J. Am. Chem. Soc.*, 2004, **126**, 7026.
38 K. B. Renkema, Y. V. Kissin and A. S. Goldman, *J. Am. Chem. Soc.*, 2003, **125**, 7770.
39 M. Wende and J. A. Gladysz, *J. Am. Chem. Soc.*, 2003, **125**, 5861.
40 (*a*) K. Ishihara, S. Kondo and H. Yamamoto, *Synlett.*, 2001, 1371; (*b*) K. Ishihara, A. Hasegawa and H. Yamamoto, *Synlett.*, 2002, 1299; (*c*) K. Mikami, Y. Mikami, H. Matsuzawa, Y. Matsumoto, J. Nishikido, F. Yamamoto and H. Nakajima, *Tetrahedron.*, 2002, **58**, 4015; (*d*) J. Otera, *Acc. Chem. Res.*, 2004, **37**, 288 and earlier work cited therein; (*e*) G. Maayan, R. H. Fish and R. Neumann, *Org. Lett.*, 2003, **5**, 3547.
41 J. A. Gladysz, R. C. da Costa, in *Handbook of Fluorous Chemistry*, ed. J. A. Gladysz, D. P. Curran and I. T. Horváth, Wiley/VCH, Weinheim, 2004, ch. 4.
42 L. V. Dinh and J. A. Gladysz, *Angew. Chem. Int. Ed.*, 2005, **44**, DOI: 10.1002/anie.200500237.
43 H. K. Cammenga and M. Epple, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1171; H. K. Cammenga and M. Epple, *Angew. Chem.*, 1995, **107**, 1284.
44 (*a*) *Collect data collection software*, Nonius B.V., Delft, The Netherlands, 1998; (*b*) "Scalepack" data processing software: Z. Otwinowski and W. Minor, *Methods in Enzymology*, Academic Press, New York, 1997, vol. 276 (Macromolecular Crystallography, Part A), p. 307.
45 G. M. Sheldrick, *SHELX-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
46 D. T. Cromer and J. T. Waber, in *International Tables for X-ray Crystallography*, ed. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, UK, 1974.