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Inorganica Chimica Acta 359 (2006) 4874–4884
Inorganica Chimica Acta
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Synthesis, structure, and reactivity of fluorous phosphorus/carbon/phosphorus pincer complexes derived from $P(CH_2)_5P$ backbones

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Received 28 June 2006; accepted 31 July 2006
Available online 10 August 2006

Dedicated to Professor Dr. Wolfgang A. Herrmann in appreciation of his many contributions to inorganic and organometallic chemistry.

Abstract

Reactions of the diphosphine $H_2P(CH_2)_5PH_2$ and fluorous alkenes $H_2C{=}CHR_{fn}$ (excess; $R_{fn} = (CF_2)_{n-1}CF_3$; n = **a**, 6; **b**, 8; **c**, 10) at 60 °C in the presence of AIBN give the precursors $(R_{fn}CH_2CH_2)_2P(CH_2)_5P(CH_2CH_2R_{fn})_2$ (**2a–c**; 68–74%). These react with $Pd(O_2CCF_3)_2$ in $CF_3C_6F_5$ at 80 °C to give the title complexes $(R_{fn}CH_2CH_2)_2P(CH_2)_2CH(CH_2)_2P(CH_2CH_2R_{fn})_2Pd(O_2CCF_3)$ (**5a–c**, 51–18%). Addition of LiCl to **5b** gives $(R_{f8}CH_2CH_2)_2P(CH_2)_2CH(CH_2)_2P(CH_2CH_2R_{f8})_2PdCl$ (**6b**, 97%); subsequent reaction with MeLi affords the corresponding methyl complex (97%). A solvate of **6b** is crystallographically characterized. The structure exhibits $CH_2CH_2R_{f8}$ groups with nearly anti C–C–C–C conformations, extending in parallel above and below the palladium square plane to create fluorous lattice domains. Reactions of **2b** and other metal complexes are described; in the cases of $(PhCN)_2PdCl_2$ or $(COD)_2PtCl_2$ ($CF_3C_6H_5$, room temperature), bimetallic species in which two MCl_2 moieties are bridged by two diphosphines appear to form. The $CF_3C_6F_{11}$/toluene partition coefficients of **2a–c** and **5a–c** establish high fluorophilicities; despite the lower fluorine weight%, those of **5a–c** are slightly greater ((97.4–99.7):(2.6–0.3) versus (95.3–99.3):(4.7–0.7)).

Keywords: Pincer; Fluorous; Radical addition; Palladium; Platinum; Iridium; Partition coefficient

1. Introduction

Pincer ligands and their complexes continue to play increasingly important roles in metal-catalyzed reactions [1]. Systems based upon aliphatic backbones [2–4] as opposed to the more usual arene-based tethers have provided several notable recent developments [2g,3e,4d]. A variety of approaches to recoverable pincer ligands and complexes have been reported [5–14]. These efforts have included fluorous derivatives [13,14], which can be recycled by a variety of liquid/liquid and liquid/solid biphasic techniques [15]. Representative examples are provided in Scheme 1 (**A–D**) [13,14]. However, to our knowledge there have been no attempts to immobilize pincer complexes with aliphatic backbones.

We have described several fluorous arene-based phosphorus/carbon/phosphorus or $PC(sp^2)P$ pincer ligands and metal complexes, as exemplified by **D** in Scheme 1 [14]. However, the ligands were much more difficult to prepare than their non-fluorous counterparts. New types of side-reactions were encountered, and significantly lower yields were obtained. Thus, our attention was drawn to analogs with aliphatic backbones. A variety of convenient protocols for synthesizing aliphatic fluorous phosphines

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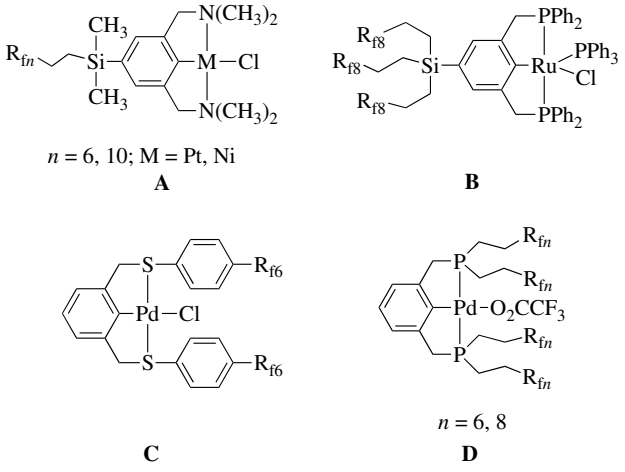
doi:10.1016/j.ica.2006.07.092



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

have been developed in our laboratory [16] and we were optimistic that these could be applied to pincer systems without difficulty.

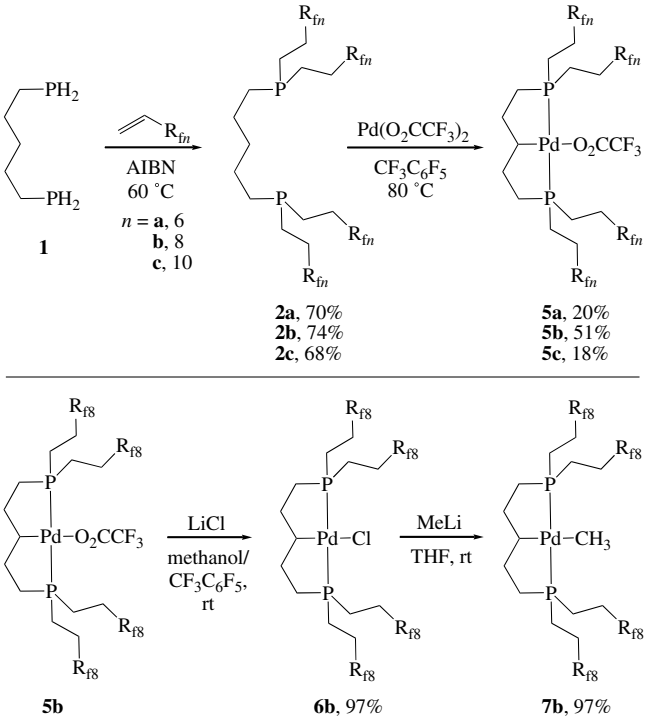
Accordingly, we set out to prepare fluorous 1,5-diphosphines of the formula $(R_{fn}CH_2CH_2)_2P(CH_2)_5P(CH_2CH_2R_{fn})_2$, and define their coordination chemistry. Analogous non-fluorous ligands have been used as springboards to a variety of PC(sp^3)P pincer complexes [2–4]. We report below (1) efficient high yield syntheses of such ligands, (2) their metalation to give fluorous palladium PC(sp^3)P pincer complexes, (3) subsequent substitution reactions, (4) preliminary data involving adducts of other metals, (5) the crystallographic characterization an R_{f8}-based palladium complex, and (6) key phase properties of the preceding compounds.

2. Results

2.1. Diphosphine synthesis and characterization

We and others have described many free radical chain additions of $R_{3-x}PH_x$ species to fluorous terminal alkenes $H_2C{=}CHR_{fn}$ [14,16]. Thus, the known diprimary 1,5-diphosphine $H_2P(CH_2)_5PH_2$ (**1**) was synthesized from the corresponding 1,5-dibromide by a convenient and easily scalable Arbuzov/reduction sequence [17]. As shown in Scheme 2 (top), **1** and excess $H_2C{=}CHR_{fn}$ (n = **a**, 6; **b**, 8; **c**, 10) were reacted neat at 60 °C in the presence of the radical initiator AIBN. Workups gave the fluorous ditertiary diphosphines $(R_{fn}CH_2CH_2)_2P(CH_2)_5P(CH_2CH_2R_{fn})_2$ (**2a**–**c**) as air sensitive liquids (**2a**) or solids (**2b**,**c**) in 68–74% yields on 3–5 g scales.

The diphosphines **2a**–**c** were characterized by microanalyses and NMR spectroscopy (^{1}H, ^{13}C, ^{19}F, ^{31}P), as summarized in Section 4. The chemical shifts and coupling constants associated with the $P(CH_2)_5P$ and $P(CH_2CH_2CF_2)$ segments closely resembled those reported for related compounds earlier [2a,16].



Scheme 2. Synthesis of fluorous pincer ligands and palladium complexes.

As summarized in Table 1, the diphosphine **2a** was very soluble in the fluorous solvent $CF_3C_6F_{11}$ (perfluoro(methylcyclohexane)), the hybrid solvent $CF_3C_6H_5$ [18], and the non-fluorous solvent $CF_3C_6F_5$ [18]. It was moderately soluble in THF and CH_2Cl_2. The homologs **2b** and **2c** exhibited progressively lower solubilities, consistent with R_{fn} length trends observed with other fluorous compounds [16a]. No dramatic changes in solubilities were noted at 60 °C. The $CF_3C_6F_{11}$/toluene partition coefficients were determined by ^{19}F NMR as described in Section 4. As summarized in Table 2, values ranged from 95.3:4.7 (**2a**) to 99.3:0.7 (**2c**), indicative of high fluorophilicities.

2.2. Diphosphine derivatization

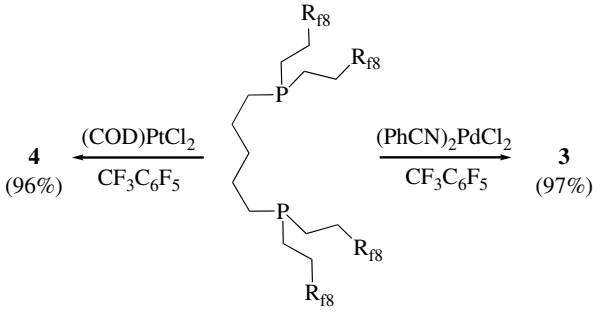
Reactions of non-fluorous 1,5-diphosphines $R_2P(CH_2)_5PR_2$ with L_2PdCl_2 or L_2PtCl_2 species often give bimetallic complexes of the type **E** (Scheme 3) [2a,2b]. These can be converted at elevated temperatures to monometallic PC(sp^3)P pincer complexes. Thus, **2b** and $(PhCN)_2PdCl_2$ were combined in $CF_3C_6F_5$ at room temperature. A ^{31}P NMR spectrum of the reaction mixture showed one signal, suggesting the clean formation of a single complex (**3**). Workup gave a seemingly homogeneous material (97%), but FAB mass spectra did not give informative ion patterns. The ^{13}C NMR spectrum showed virtual triplets [19] for the P*C*H$_2$CH$_2$CF$_2$ signals, suggesting a *trans* geometry. An analogous reaction of **2b** and $(COD)_2PtCl_2$ also appeared to give a single complex (**4**; 96%). The ^{31}P NMR spectrum showed one signal with a J_{PtP} value of 2680 Hz, diagnostic for $PtCl_2$ complexes with *trans*

Table 1
Qualitative solubility profile of palladium pincer ligands and complexes

	Room temperature					60 °C				
	$CF_3C_6F_{11}$	$CF_3C_6H_5$	$CF_3C_6F_5$	THF	CH_2Cl_2	$CF_3C_6H_5$	$CF_3C_6F_5$	hexane	THF	CH_2Cl_2
2a	high	high	high	moderate	moderate	high	high	moderate	moderate	moderate
2b	high	high	high	low	low	high	high	low	low	low
2c	high	high	high	v. low	v. low	high	high	v. low	v. low	v. low
5a	high	high	high	high	high	high	high	high	high	high
5b	moderate	high	high	moderate	v. low	high	high	moderate	moderate	moderate
5c	moderate	moderate	moderate	v. low	v. low	moderate	high	v. low	v. low	v. low

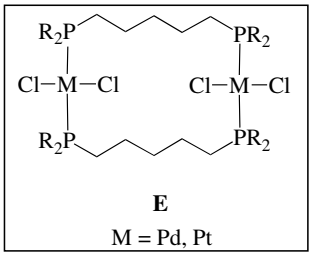
Table 2
$CF_3C_6F_{11}$/toluene partition coefficients of fluorous pincer ligands and palladium complexes (23 °C) measured by ^{19}F NMR

Compound	Partition coefficient
2a	95.3:4.7
2b	98.8:1.2
2c	99.3:0.7
5a	97.4:2.6
5b	99.3:0.7
5c	99.7:0.3



2a

proposed structures (**3**, **4**):



E

M = Pd, Pt

Scheme 3. Reaction of fluorous pincer ligand **2b** with L_2MCl_2 species.

phosphine ligands [20]. Hence, we suggest that **3** and **4** have structures of the type **E**. However, other possibilities cannot be rigorously excluded.

Complexes **3** and **4** were (a) heated as solids and (b) refluxed in trifluoroacetic acid for extended periods. Under these conditions, non-fluorous complexes of the type **E** are efficiently converted to palladium and platinum pincer complexes [2a,2b,2d]. However, **3** gave only black palladium metal. With **4**, no reaction was apparent (although some chloride/trifluoroacetate ligand exchange may have occurred with (b)).

Hence, alternative cyclometalation strategies were investigated. As shown in Scheme 2 (top), the palladium trifluoroacetate complex $Pd(O_2CCF_3)_2$ and **2a**–**2c** were combined in $CF_3C_6F_5$ at 80 °C. In accord with much precedent [1a,1b,1c,2e], workups gave the air-stable fluorous palladium pincer complexes **5a**–**5c** in 51–18% yields. These were characterized by NMR spectroscopy (^1H, ^{13}C, ^{31}P, ^{19}F) and mass spectrometry, as described in Section 4. Microanalyses suggested that **5b**,**c** crystallized with a molecule of $CF_3C_6H_5$ (used in the final silica gel filtration step). Mass spectra showed intense M^+–CF_3CO_2 peaks (100%), but no parent ions.

The ^{13}C NMR spectra of **5a**–**c** exhibited diagnostic signals for the metalated (Pd*C*H) carbon atoms at 56 ppm. The PdC*H* ^1H NMR resonance was obscured by other peaks. The ^{31}P NMR chemical shifts were ca. 35 ppm downfield from those of **2a**–**c**, consistent with the formation of five-membered phosphacycles [21]. In accord with the non-planar bicyclic PC(sp^3)P pincer cores, two P*C*H$_2$CH$_2$CF$_2$ ^{13}C signals were observed, corresponding to the ponytails *cis* and *trans* to the bridgehead PdC*H* hydrogen atom. The ^{19}F NMR spectra showed three sets of CH$_2$CH$_2$C*F*$_2$ signals (4:2:2, m/m/m), which is a logical consequence of the diastereotopic relationship of all geminal fluorine atoms in **5a**–**c**.

As summarized in Table 1, the pincer complexes **5a**–**c** exhibited solubility trends similar to those of the free ligands. Interestingly, the $CF_3C_6F_{11}$/toluene partition coefficients (Table 2) were slightly more biased than those of the free ligands, indicating enhanced fluorophilicity despite the diminished weight% of fluorine (e.g., 67.3% for **2b** versus 63.1% for **5b** (or 61.3% for **5b**·$CF_3C_6H_5$)). Similar phenomena have been documented with other metal complexes of fluorous ligands [22]. As would be expected, the fluorophilicity of **5b** was greater than that of its aromatic counterpart **D** in Scheme 1 (99.3:0.7 versus 96.4:3.6) [14].

2.3. Further chemistry

Extensions of the preceding reactions were attempted. First, **5b** and excess LiCl were combined in methanol/$CF_3C_6H_5$ at room temperature. As shown in Scheme 2 (bottom), workup gave the chloride complex **6b** as an analytically pure $CF_3C_6H_5$ monosolvate in 97% yield. Most spectroscopic properties were similar to those of **5a**–**c**.

No trace of **6b** was detected during the pyrolysis of **3** (above).

Certain methyl derivatives of palladium PC(sp^3)P pincer complexes have been reported to be effective catalyst precursors [2d]. Hence, **6b** was treated with MeLi (1.0 equiv.) in THF at room temperature (Scheme 2, bottom). Workup gave the crude methyl complex **7b** in 97% yield as an air stable white powder. However, it was quite labile in solution. After 4 h, a $CF_3C_6H_5$ solution showed substantial decomposition to two new species, as assayed by ^{31}P NMR. Hence, **7b** was only partially characterized. However, the Pd*C*H_3 ^{13}C NMR signal was very close to that reported for a non-fluorous analog (62.6 versus 62.2 ppm) [2d].

Adducts of other catalytically active metals were sought. Iridium PC(sp^2)P complexes see extensive use in carbon–hydrogen bond activation reactions [23], and the bis(cyclooctene) complex $[IrCl(COE)_2]_2$ [24] has often been used as a precursor [4b,14,23]. Thus, **2a** and $[IrCl(COE)_2]_2$ were reacted in THF at 80 °C. Workup gave a material that was pure by ^{31}P NMR and exhibited an upfield Ir*H* ^1H NMR signal (δ −28.18) that was furthermore coupled to phosphorus (t, $J_{HP} = 15.0$ Hz). This was tentatively assigned to the target molecule

$(R_{f8}CH_2CH_2)_2P(CH_2)_2CH(CH_2)_2P(CH_2CH_2R_{f8})_2IrHCl$ (**8b**).

However, ^1H and ^{13}C spectra of the reaction mixture showed that other species were present, and **8b** could only be isolated in 10% yield. Attempts to effect cyclometalations with $RhCl_3 \cdot 3H_2O$ analogous to protocols for non-fluorous systems [3a] were unsuccessful.

Table 3
Crystallographic data for **6b**·$CF_3C_6H_5$

Empirical formula	$C_{52}H_{30}ClF_{71}P_2Pd$
Formula weight	2207.55
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	*Pnma*
Unit cell dimensions	
a (Å)	11.555(2)
b (Å)	34.672(7)
c (Å)	18.721(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	7500(3)
Z	4
ρ_{calc} (Mg m^{-3})	1.955
μ (mm^{-1})	0.540
$F(000)$	4296
Crystal dimensions (mm)	0.35 × 0.30 × 0.25
θ Range (°)	1.17–25.00
Index ranges (h,k,l)	−13,13; −41,41; −22,22
Reflections collected	11 964
Independent reflections (R_{int})	6649 (0.0416)
Reflections ($I > 2\sigma(I)$)	4195
Completeness to $\theta = 27.51°$ (%)	98.6
Maximum and minimum transmission	0.8768 and 0.8334
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	6649/5/598
Goodness-of-fit on F^2	1.426
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1211$
	$wR_2 = 0.3440$
R indices (all data)	$R_1 = 0.1686$
	$wR_2 = 0.3788$
Largest difference in peak, hole [e Å^{-3}]	1.659, −0.881

2.4. Crystallography

In what remains somewhat of a rare event with fluorous molecules, single crystals of **6b**·$CF_3C_6H_5$ were obtained. They were of marginal quality, but X-ray data could be collected as described in Table 3 and Section 4. Refinement gave the structures shown in Figs. 1 and 2.

As illustrated in Fig. 2, the carbon atoms adjacent to the PdCH moiety were disordered in an up/up versus down/down sense about a crystallographic mirror plane. The plane runs vertically thought the structures in Fig. 1, contains all palladium-bound atoms, and requires a simultaneous disorder of the bridgehead hydrogen atom (not located). Analogous phenomena have been observed with other crystalline PC(sp^3)P pincer complexes [2f]. Several fluorine atoms in two of the ponytails were also disordered, as signaled by large thermal ellipsoids (bottom chains, top structure).

Key metrical parameters of **6b**·$CF_3C_6H_5$ are summarized in Table 4. Most bond lengths and angles are routine. The palladium atom exhibits a distorted square planar geometry, but with a P–Pd–P angle (168.1(1)°) larger than in similar non-fluorous complexes (166.2(1)°, P(t-Bu)$_2$/methyl analog [2d]; 165.9(7)°, PPh_2/chloride analog [2f]). 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 are nearly in van-der-Waals contact (Fig. 1, bottom).

It is now well-established that the lowest energy (anti) conformations of *n*-perfluoroalkanes and perfluoroalkyl groups exhibit C–C–C–C torsion angles somewhat less than those of *n*-alkanes (ca. 166° versus 180°) [25,26]. Accordingly, the C–C–C–C torsion angles within the R_{f8} segments of **6b**·$CF_3C_6H_5$ average 162.8° (high 167.8(12)°, low 157(2)°). This imparts a slight twist, which propagates in the same direction to give helical $(CF_2)_n$ moieties, as evident in Fig. 1 and exploited in two recent papers in other fluorous molecules [26].

As illustrated in Fig. 3, the crystal lattice is divided into fluorous and non-fluorous domains, with the ponytails of neighboring molecules nearly in van-der-Waals contact. Other square planar metal complexes with fluorous alkylphosphines crystallize similarly [14,27]. The van-der-Waals radius of fluorine is 1.40 Å [28], and the shortest intermolecular fluorine–fluorine distances (2.789–2.914 Å) are included in Table 4.

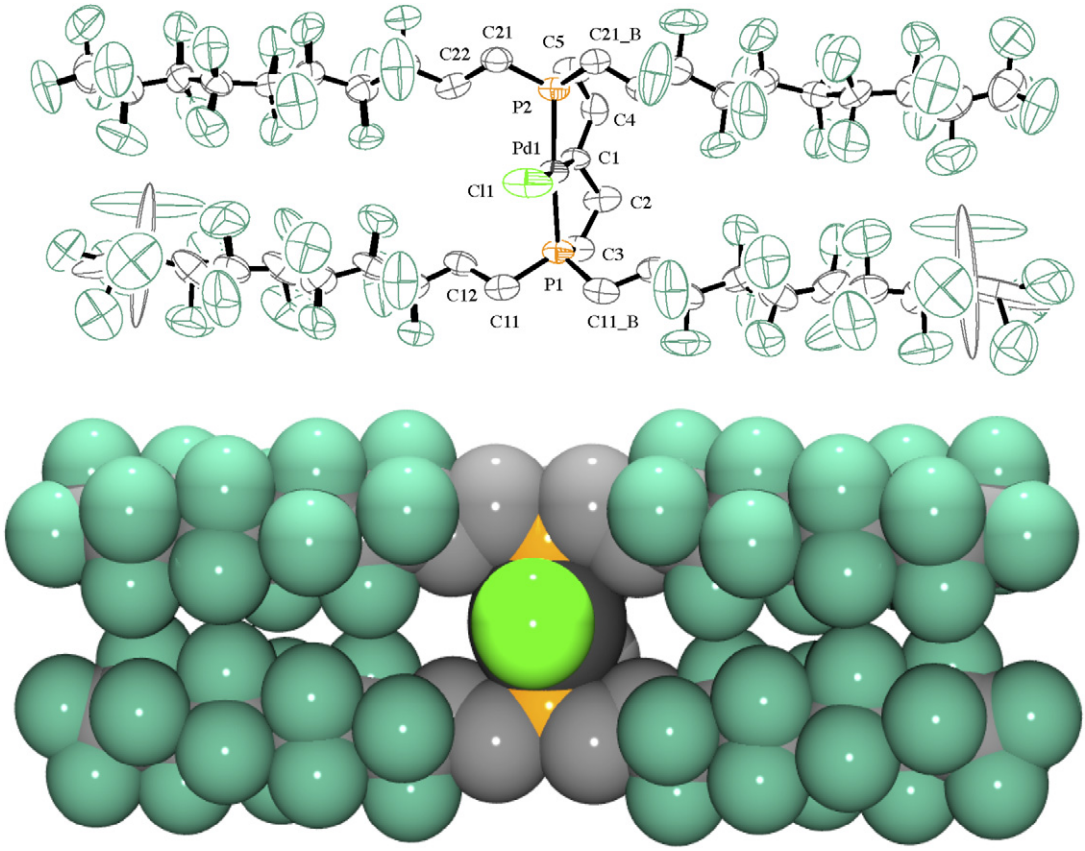


Fig. 1. Molecular structure of palladium pincer complex **6b**·$CF_3C_6H_5$, with the solvent omitted.

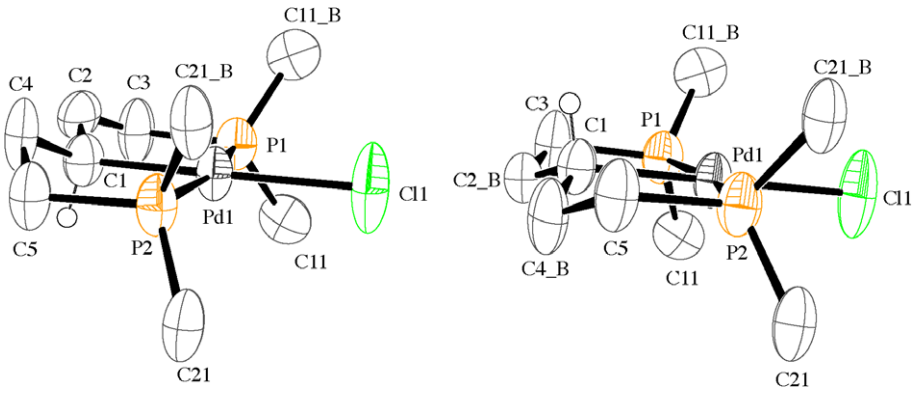


Fig. 2. Limiting structures for the disordered bicyclic core of **6b**·$CF_3C_6H_5$.

3. Discussion

The fluorous ditertiary 1,5-diphosphines **2a**–**c** are easily synthesized on 3–5 g scales as shown in Scheme 1. Under appropriate conditions, they can be converted to pincer complexes that feature aliphatic backbones. This is most readily accomplished with $Pd(O_2CCF_3)_2$ at elevated temperature. As illustrated by the partition coefficients in Table 2, the diphosphines and resulting palladium adducts **5a**–**c** exhibit appreciable fluorophilicities that will lead to high recoveries under fluorous/organic liquid/liquid biphase conditions. However, increasing numbers of fluorous catalysts and reagents are being recovered by fluorous/organic solid/liquid phase separations [29]. Towards this end, the much lower solubilities of **2c** and **5c** (Table 1) should prove advantageous.

Many palladium PCP pincer complexes are effective catalyst precursors for Heck alkenylations of aryl halides [1d,30,31]. However, it is increasingly appreciated that many of these merely serve as precursors for pincer-free palladium(0) nanoparticles or low-coordinate molecular species, which constitute the active catalysts [31]. Much

Table 4
Selected bond lengths (Å), bond angles (°), and intermolecular contacts (Å) for **6b**·$CF_3C_6H_5$

Bond lengths (Å)			
Pd(1)–C(1)	2.112(12)	C(1)–C(4)	1.48(2)
Pd(1)–P(1)	2.268(4)	C(1)–C(2)	1.497(13)
Pd(1)–P(2)	2.290(3)	C(2)–C(3)	1.397(10)
Pd(1)–Cl(1)	2.394(4)	P(2)–C(5)	1.828(13)
P(1)–C(11)	1.798(10)	P(2)–C(21)	1.835(17)
P(1)–C(3)	1.821(5)	C(4)–C(5)	1.57(2)
Bond Angles (°)			
C(1)–Pd(1)–P(1)	83.8(3)	C(4)–C(1)–C(2)	119.0(11)
C(1)–Pd(1)–P(2)	84.3(3)	C(4)–C(1)–Pd(1)	112.7(9)
P(1)–Pd(1)–P(2)	168.08(13)	C(2)–C(1)–Pd(1)	111.4(7)
C(1)–Pd(1)–Cl(1)	177.5(3)	C(3)–C(2)–C(1)	120.0(5)
P(1)–Pd(1)–Cl(1)	93.66(14)	C(5)–P(2)–Pd(1)	104.0(5)
P(2)–Pd(1)–Cl(1)	98.25(13)	C(2)–C(3)–P(1)	108.4(2)
C(11)–P(1)–C(3)	108.1(6)	C(1)–C(4)–C(5)	113.0(14)
C(3)–P(1)–Pd(1)	104.09(19)	C(4)–C(5)–P(2)	106.8(10)
Intermolecular contacts (Å)			
F17A–F26A	2.789	F26B–F16A	2.793
F19A–F28A	2.914	F26B–F18A	2.804
F14A–F29A	2.876		

data now support analogous pathways for Heck reactions catalyzed by palladium SCS pincer complexes [9c,9d], and other types of palladacycles [32–34]. Hence, during the course of this study we became much less enthusiastic about testing **5a**–**c** as recoverable catalysts or catalyst precursors for any type of aryl halide coupling reaction, which was originally a major impetus for this work.

Nonetheless, there are many other types of reactions catalyzed by pincer complexes that might be targeted in future efforts [1d,2d,3e,8b,35]. In this context, several issues are deserving of attention. First, the yields of **5a**–**c** are modest, that of the related iridium complex **8b** is lower still, and precursors of the types in Scheme 3 are ineffective. The development of functionalized fluorous 1,5-diphosphines that would undergo more ready cyclometalation would be especially helpful. Although some leads have been reported for non-fluorous systems [3c], one particularly appealing approach would involve the replacement of the central methylene group of **2** by a CHR_{fn} moiety. This might promote metalation while at the same time enhancing fluorophilicity. Alternatively, transmetalations [1a,1b,1c] involving **5b** (available in the highest yield, 51%) could be investigated.

Finally, this study has also expanded the modest range of crystallographically characterized fluorous metal complexes. Further examples will be reported in due course [36]. Additional efforts involving fluorous ligand development for catalytic reactions remain in progress [36b], and will be described in future publications.

4. Experimental

4.1. General data

Reactions were conducted under N_2 atmospheres unless noted. Chemicals were treated as follows: THF, ether, and toluene, distilled from Na/benzophenone; $CF_3C_6F_{11}$, $CF_3C_6F_5$, and $CF_3C_6H_5$ (3 × Fluorochem or ABCR), distilled from CaH_2; [d_6]DMSO (Deutero GmbH), $H_2C{=}CHR_{f6}$, $H_2C{=}CHR_{f8}$, $H_2C{=}CHR_{f10}$ (3 × ABCR), $(PhCN)_2PdCl_2$, $Pd(O_2CCF_3)_2$, $RhCl_3\cdot 3H_2O$ (3 × Strem, 99–97%), AIBN (Merck, >98%), and MeLi (Acros, 1.0 M in hexane), used as received.

NMR spectra were obtained on a Bruker 400 MHz spectrometer and referenced as follows: ^1H, external residual [d_5]DMSO ($\delta = 2.49$ ppm); ^{13}C, external [d_6]DMSO ($\delta = 39.5$ ppm); ^{19}F, internal C_6F_6 ($\delta = -162.0$ ppm); ^{31}P,

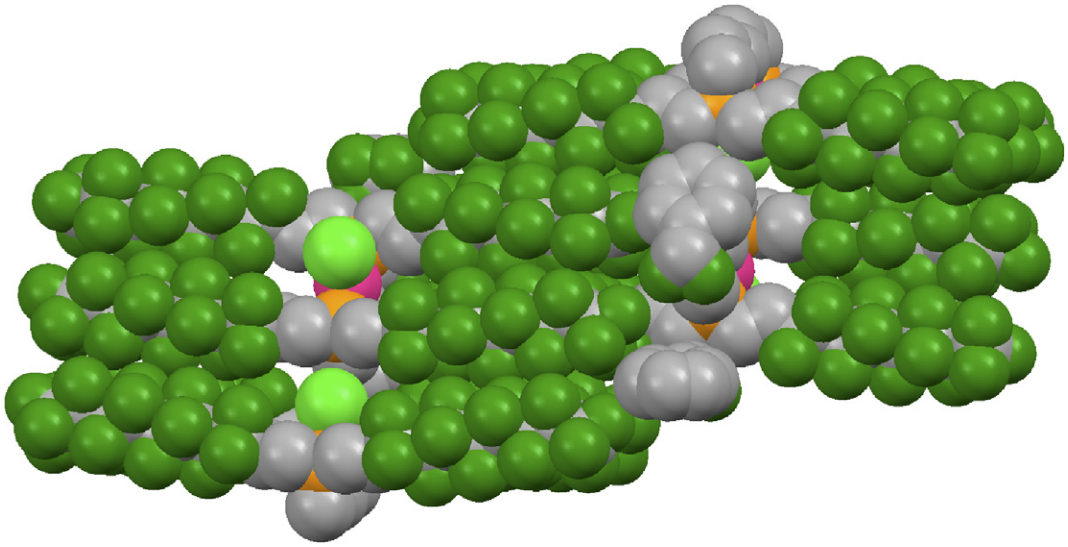


Fig. 3. Packing diagram for **6b**·$CF_3C_6H_5$.

external H_3PO_4 ($\delta = 0.00$ ppm). The highly coupled ^{13}C signals of the fluorinated carbons are not listed. Mass spectra were recorded on a Micromass Zabspec instrument.[1] DSC and TGA data were recorded with a Mettler-Toledo DSC821 instrument (heating rate, 10 °C/min) and treated by standard methods [37]. Microanalyses were conducted with a Carlo Erba EA1110 instrument.

4.2. $(R_{f6}CH_2CH_2)_2P(CH_2)_5P(CH_2CH_2R_{f6})_2$ (**2a**)

A Schlenk flask was charged with $H_2P(CH_2)_5PH_2$ (0.700 g, 5.14 mmol) [17], AIBN (0.100 g, 1.00 mmol), and $H_2C{=}CHR_{f6}$ (12.4 g, 36.0 mmol) in a glove box. The mixture was stirred at 65 °C (oil bath). After 4 h, a ^{31}P NMR spectrum of an aliquot showed the starting material to be consumed. Excess alkene was removed by oil pump vacuum. The oil was washed with CH_2Cl_2 to remove the remaining AIBN and dried by oil pump vacuum to give **2a** as a slightly yellow viscous liquid (5.42 g, 3.59 mmol, 70%). *Anal.* Calc. for $C_{37}H_{26}F_{52}P_2$: C, 29.26; H, 1.72. Found: C, 29.39; H, 1.71%.

NMR (δ, $CF_3C_6F_5$, [d_6]DMSO capillary): ^1H 1.62–1.44 (m, 4CH_2CF$_2$), 1.08–1.00 (m, 4PCH_2CH$_2$CF$_2$), 0.95–0.88 (m, 5CH_2); $^{13}C\{^1H\}$ 31.3 (t, $J_{CP} = 11.9$ Hz, PCH$_2$-CH$_2$*C*H$_2$), 26.2 (dt, $J_{CP} = 19.0$ Hz, $J_{CF} = 23.6$ Hz, *C*H$_2$CF$_2$), 25.1 and 23.7 (2 d, $J_{CP} = 13.4$ and 13.8 Hz, P*C*H$_2$*C*H$_2$CH$_2$), 15.0 (d, $J_{CP} = 16.0$ Hz, P*C*H$_2$CH$_2$CF$_2$); ^{19}F −84.6 (t, $J_{FF} = 10.4$ Hz, 12F, CF_3), −118.5 (m, 8F), −124.8 (m, 8F), −125.8 (m, 8F), −126.3 (m, 8F), −129.3 (m, 8F); $^{31}P\{^1H\}$ −26.8 (s).

4.3. $(R_{f8}CH_2CH_2)_2P(CH_2)_5P(CH_2CH_2R_{f8})_2$ (**2b**)

$H_2P(CH_2)_5PH_2$ (0.305 g, 2.24 mmol), AIBN (0.100 g, 1.00 mmol) and $H_2C{=}CHR_{f8}$ (7.01 g, 15.4 mmol) were combined in a procedure analogous to that for **2a**. Excess alkene was removed by oil pump vacuum. The yellow solid was extracted with $CF_3C_6H_5$. The extract was concentrated and cooled to 0 °C. The white solid was collected by filtration and dried by oil pump vacuum to give **2b** (3.16 g, 1.65 mmol, 74%), m.p. 42 °C (T_e, DSC). *Anal.* Calc. for $C_{45}H_{26}F_{68}P_2$: C, 28.14; H, 1.36. Found: C, 28.24; H, 1.09%.

NMR (δ, $CF_3C_6F_5$, [d_6]DMSO capillary): ^1H 1.68–1.50 (m, 4CH_2CF$_2$), 1.13–1.06 (m, 4PCH$_2$CH_2CF$_2$), 1.03–0.93 (m, 5CH_2); $^{13}C\{^1H\}$ 31.2 (t, $J_{CP} = 11.2$ Hz, PCH$_2$CH$_2$*C*H$_2$), 26.1 (dt, $J_{CP} = 19.8$ Hz, $J_{CF} = 23.2$ Hz, *C*H$_2$CF$_2$), 25.0 and 23.6 (2 d, $J_{CP} = 13.6$ and 13.9 Hz, P*C*H$_2$*C*H$_2$CH$_2$), 15.0 (d, $J_{CP} = 17.4$ Hz, P*C*H$_2$CH$_2$CF$_2$); ^{19}F −84.5 (t, $J_{FF} = 10.4$ Hz, 12F, 4CF_3), −118.3 (m, 8F), −124.6 (m, 24F), −125.5 (m, 8F), −126.2 (m, 8F), −129.1 (m, 8F); $^{31}P\{^1H\}$ −26.7 (s).

4.4. $(R_{f10}CH_2CH_2)_2P(CH_2)_5P(CH_2CH_2R_{f10})_2$ (**2c**)

$H_2P(CH_2)_5PH_2$ (0.442 g, 3.25 mmol), AIBN (0.100 g, 1.00 mmol) and $H_2C{=}CHR_{f10}$ (10.8 g, 19.6 mmol) were combined in a procedure analogous to that for **2b**. An identical workup gave **2c** as a light brown solid (5.11 g, 2.21 mmol, 68%), m.p. 73 °C (T_e, DSC). *Anal.* Calc. for $C_{56}H_{26}F_{84}P_2$: C, 27.43; H, 1.13. Found: C, 27.43; H, 1.09%.

NMR (δ, $CF_3C_6F_5$, [d_6]DMSO capillary): ^1H 1.70–1.50 (m, 4CH_2CF$_2$), 1.14–1.04 (m, 4PCH_2CH$_2$CF$_2$), 1.01–0.91 (m, 5CH_2); $^{13}C\{^1H\}$ 31.2 (t, $J_{CP} = 10.8$ Hz, PCH$_2$CH$_2$-*C*H$_2$), 26.2 (dt, $J_{CP} = 19.3$ Hz, $J_{CF} = 21.7$ Hz, *C*H$_2$CF$_2$), 25.0 and 23.6 (2 d, $J_{CP} = 13.6$ and 13.9 Hz, P*C*H$_2$*C*H$_2$CH$_2$), 14.9 (d, $J_{CP} = 16.0$ Hz, P*C*H$_2$CH$_2$CF$_2$); ^{19}F −84.5 (t, $J_{FF} = 10.4$ Hz, 12F, 4CF_3), −118.3 (m, 8F), −124.4 (m, 40F), −125.4 (m, 8F), −126.1 (m, 8F), −129.1 (m, 8F); $^{31}P\{^1H\}$ −26.6 (s).

4.5. *trans,trans*-$Cl_2Pd[(R_{f8}CH_2CH_2)_2P(CH_2)_5P(CH_2CH_2R_{f8})_2]_2PdCl_2$ (**3**)

A Schlenk flask was charged with **2b** (0.175 g, 0.0910 mmol), $(PhCN)_2PdCl_2$ (0.035 g, 0.091 mmol), and $CF_3C_6H_5$ (2 mL). The mixture was stirred for 4 h. The solvent was removed by rotary evaporation. The light yellow solid was extracted twice with hot THF. The solvent was removed by rotary evaporation to give **3**·$CF_3C_6H_5$ as a light yellow solid (0.185 g, 0.882 mmol, 97%), m.p. 92 °C (T_e, DSC, dec). *Anal.* Calc. for $C_{45}H_{26}Cl_2F_{68}P_2Pd\cdot CF_3C_6H_5$: C, 27.83; H, 1.39. Found: C, 27.83; H, 1.72%.

NMR (δ, $CF_3C_6F_5$, [d_6]DMSO capillary)[2]: ^1H 2.07–1.27 (br m); $^{13}C\{^1H\}$ 30.7 (t, $J_{CP} = 7.5$ Hz, PCH$_2$CH$_2$*C*H$_2$), 24.9 (t, $J_{CF} = 23.2$ Hz, *C*H$_2$CF$_2$), 22.1 and 21.2 (s and virtual t [19], $J_{CP} = 13.3$ Hz, P*C*H$_2$*C*H$_2$CH$_2$), 12.1 (virtual t, $J_{CP} = 12.9$ Hz, P*C*H$_2$CH$_2$CF$_2$); ^{19}F −84.6 (t, $J_{FF} = 10.3$ Hz, 12F, 4CF_3), −118.3 (m, 8F), −124.6 (m, 24F), −125.5 (m, 8F), −125.8 (m, 8F), −129.2 (m, 8F); $^{31}P\{^1H\}$ 12.3 (s).

4.6. *trans,trans*-$Cl_2Pt[(R_{f8}CH_2CH_2)_2P(CH_2)_5P(CH_2CH_2R_{f8})_2]_2PtCl_2$ (**4**)

A Schlenk flask was charged with **2b** (0.251 g, 0.131 mmol), $(COD)_2PtCl_2$ (0.059 g, 0.13 mmol) [38] and $CF_3C_6F_5$ (2 mL). The mixture was stirred for 4 h. The solvent was removed by oil pump vacuum to give **4** as a light yellow solid (0.216 g, 0.122 mmol, 96%). NMR (δ, $CF_3C_6F_5$, [d_6]DMSO capillary): $^{31}P\{^1H\}$ 8.6 (s, $^1J_{PPt} = 2680$ Hz).[3]

[1] The *m*/*z* values represent the most intense peak of the isotope envelope. The diphosphines **2a**–**c** exhibited only ions derived from the bis(oxides).

[2] The ^1H signals of the solvate are obscured by protic impurities in the $CF_3C_6F_5$ solvent, and the CH ^{13}C signals of the solvate are obscured by the CF signals of the solvent.

[3] This coupling represents a satellite (d; $^{195}Pt = 33.8\%$), and is not reflected in the peak multiplicity given.

4.7. $(R_{f6}CH_2CH_2)_2P(CH_2)_2CH(CH_2)_2P(CH_2CH_2R_{f6})_2Pd(O_2CCF_3)$ (**5a**)

A Schlenk tube was charged with **2a** (0.802 g, 0.527 mmol), $Pd(O_2CCF_3)_2$ (0.174 g, 0.523 mmol), and $CF_3C_6F_5$ (5 mL) in a glove box. The mixture was stirred at 80 °C for 2 d, during which time aliquots were assayed by ^{31}P NMR. The solvent was removed by oil pump vacuum and the brown residue extracted with 1:1 v/v CH_2Cl_2/hexane (3 × 5 mL). The solvents were removed from the extract by oil pump vacuum. The dark residue was filtered through silica using $CF_3C_6H_5$. The solvent was removed from the filtrate by oil pump vacuum to give **5a**·$CF_3C_6H_5$ as light yellow crystalline solid (0.180 g, 0.105 mmol, 20%), m.p. 87 °C (T_e, DSC).[4]

NMR (δ, $CF_3C_6F_5$, [d_6]DMSO capillary)[2]: ^1H 1.95–1.13 (br m); $^{13}C\{^1H\}$[5] 54.5 (s, Pd*C*H), 35.9 (virtual t [19], J_{CP} = 6.7 Hz, PCH_2CH_2CH), 25.8 (overlapping signals, PCH_2CH_2CH and CH_2CF_2), 15.8 (virtual t, J_{CP} = 11.9 Hz, 2C of $4PCH_2CH_2CF_2$), 15.1 (virtual t, J_{CP} = 11.8 Hz, 2C of $4PCH_2CH_2CF_2$); ^{19}F −78.7 (s, 3F, CO_2CF_3), −84.6 (t, J_{FF} = 10.1 Hz, 12F, $4CF_3$), −117.6 (m, 2F of $4PCH_2CH_2CF_2$), −117.9 (m, 2F of $4PCH_2CH_2CF_2$), −118.6 (m, 4F of $4PCH_2CH_2CF_2$), −124.7 (m, 8F), −125.6 (m, 8F), −125.9 (m, 8F), −129.3 (m, 8F); $^{31}P\{^1H\}$ 48.6 (s). MS (positive FAB, *m*/*z*)[1]: 1625 ([**5a**–CF_3CO_2]$^+$, 100%), 1278 ([**5a**–CF_3CO_2–$CH_2CH_2R_{f6}$]$^+$, 10%), 899 ([**5a**–CF_3CO_2–$P(CH_2CH_2R_{f6})_2$+H]$^+$, 40%).

4.8. $(R_{f8}CH_2CH_2)_2P(CH_2)_2CH(CH_2)_2P(CH_2CH_2R_{f8})_2Pd(O_2CCF_3)$ (**5b**)

Diphosphine **2b** (0.800 g, 0.416 mmol), $Pd(O_2CCF_3)_2$ (0.138 g, 0.416 mmol) and $CF_3C_6F_5$ (5 mL) were combined in a procedure analogous to that for **5a**. The brown residue extracted with hot THF (3 × 10 mL). The solvents were removed from the extract by oil pump vacuum. The dark residue was filtered through silica using $CF_3C_6H_5$. The solvent was removed from the filtrate by oil pump vacuum to give **5b**·$CF_3C_6H_5$ as a light yellow crystalline solid (0.455 g, 0.212 mmol, 51%), m.p. 123 °C (T_e, DSC). *Anal.* Calc. for $C_{47}H_{25}F_{71}O_2P_2Pd\cdot CF_3C_6H_5$: C, 28.38; H, 1.32. Found: C, 28.38; H, 1.27%.

NMR (δ, $CF_3C_6F_5$, [d_6]DMSO capillary)[2]: ^1H 1.91–0.99 (br m); $^{13}C\{^1H\}$[2] 54.5 (s, Pd*C*H), 36.0 (virtual t[1], J_{CP} = 6.9 Hz, PCH_2CH_2CH), 25.9 (overlapping signals, PCH_2CH_2CH and CH_2CF_2), 15.8 (virtual t, J_{CP} = 11.4 Hz, 2C of $4PCH_2CH_2CF_2$), 15.1 (virtual t, J_{CP} = 11.7 Hz, 2C of $4PCH_2CH_2CF_2$); ^{19}F −78.7 (s, 3F, CO_2CF_3), −84.5 (t, J_{FF} = 10.4 Hz, 12F, $4CF_3$), −117.5 (m, 2F of $4PCH_2CH_2CF_2$), −117.9 (m, 2F of $4PCH_2CH_2CF_2$), −118.5 (m, 4F of $4PCH_2CH_2CF_2$), −124.6 (m, 24F), −125.5 (m, 8F), −125.9 (m, 8F), −129.2 (m, 8F); $^{31}P\{^1H\}$ 48.4 (s). MS (positive FAB, *m*/*z*)[1]: 2026 ([**5b**–CF_3CO_2]$^+$, 100%), 1578 ([**5b**–CF_3CO_2–$CH_2CH_2R_{f8}$]$^+$, 10%), 1099 ([**5b**–CF_3CO_2–$P(CH_2CH_2R_{f8})_2$+H]$^+$, 60%).

4.9. $(R_{f10}CH_2CH_2)_2P(CH_2)_2CH(CH_2)_2P(CH_2CH_2R_{f10})_2Pd(O_2CCF_3)$ (**5c**)

Diphosphine **2c** (0.800 g, 0.345 mmol), $Pd(O_2CCF_3)_2$ (0.114 g, 0.345 mmol), and $CF_3C_6F_5$ (5 mL) were combined in a procedure analogous to that for **5a**. After 6 d at 80 °C, the solvent was removed by oil pump vacuum. The brown residue was filtered through silica using 1:1 v/v $CF_3C_6H_5$/$CF_3C_6F_5$. The solvent was removed from the filtrate by oil pump vacuum to give **5c**·$CF_3C_6H_5$ as a light yellow crystalline solid (0.159 g, 0.0621 mmol, 18%), m.p. 129 °C (capillary, dec), solid phase transition 105 °C (T_e, endotherm, DSC), m.p. 135 °C (T_e, endotherm, DSC). The TGA trace shows 3.7% mass loss at ca. 105 °C (calculated for $CF_3C_6H_5$ loss, 5.3%), with additional mass loss beginning gradually above 135 °C. *Anal.* Calc. for $C_{55}H_{25}F_{87}O_2P_2Pd\cdot CF_3C_6H_5$: C, 27.73; H, 1.13. Found: C, 27.83; H, 1.25%.

NMR (δ, $CF_3C_6F_5$, [d_6]DMSO capillary)[2]: ^1H 1.97–0.93 (br m); ^{19}F −78.7 (s, 3F, CO_2CF_3), −84.5 (t, J_{FF} = 10.2 Hz, 12F, $4CF_3$), −117.4 (m, 1F of $4PCH_2CH_2CF_2$), −117.8 (m, 4F of $PCH_2CH_2CF_2$), −118.1 (m, 1F of $4PCH_2CH_2CF_2$), −118.5 (m, 2F of $4PCH_2CH_2CF_2$), −124.4 (m, 40F), −125.4 (m, 8F), −125.9 (m, 6F), −126.4 (m, 2F), −129.1 (m, 8F); $^{31}P\{^1H\}$ 48.7 (s). MS (positive FAB, *m*/*z*)[1]: 2425 ([**5c**–CF_3CO_2]$^+$, 100%).

4.10. $(R_{f8}CH_2CH_2)_2P(CH_2)_2CH(CH_2)_2P(CH_2CH_2R_{f8})_2PdCl$ (**6b**)

A Schlenk flask was charged with **5b** (0.102 g, 0.0477 mmol), $CF_3C_6H_5$ (5 mL), and a solution of LiCl (0.0432 g, 0.935 mmol) in methanol (2 mL). The mixture was stirred for 4 h. The solvent was removed by oil pump vacuum. Then $CF_3C_6H_5$ was added, and the mixture filtered through a short plug of silica. The solvent was removed from the filtrate by oil pump vacuum to give **6b**·$CF_3C_6H_5$ as a white crystalline solid (0.0953 g, 0.0462 mmol, 97%), m.p. 105 °C (T_e, DSC). *Anal.* Calc. for $C_{45}H_{25}ClF_{68}P_2Pd\cdot CF_3C_6H_5$: C, 28.29; H, 1.37. Found: C, 28.38; H, 1.27%.

NMR (δ, $CF_3C_6F_5$, [d_6]DMSO capillary)[2]: ^1H 2.44–1.12 (br m); $^{13}C\{^1H\}$[5] 58.8 (s, Pd*C*H), 35.6 (virtual t [19], J_{CP} = 7.7 Hz, PCH_2CH_2CH), 27.0 (virtual t [19], J_{CP} = 11.5 Hz, PCH_2CH_2CH), 25.8 (m, CH_2CF_2), 14.5 (m, $PCH_2CH_2CF_2$); ^{19}F −84.5 (t, J_{FF} = 10.3 Hz, 12F, $4CF_3$), −117.6 (m, 2F of $4PCH_2CH_2CF_2$), −117.9 (m, 2F of $4PCH_2CH_2CF_2$), −118.5 (m, 4F of $4PCH_2CH_2CF_2$), −124.5 (m, 24F), −125.5 (m, 8F), −125.9 (m, 8F), −129.2 (m, 8F); $^{31}P\{^1H\}$ 47.7 (s). MS (positive FAB,

[4] The solvate is inferred from the related compounds (**5b**, **5c**, **6b**) that crystallize similarly. However, while the carbon analysis agreed with a monosolvate, the hydrogen analysis was too high.

[5] These signals were assigned by analogy of those of similar complexes in Ref. [2f].

m/*z*)[1]: 2025 ([**6**–Cl]$^+$, 100%), 1578 ([**6**–Cl–$CH_2CH_2R_{f8}$]$^+$, 5%), 1099 ([**6**–Cl–$P(CH_2CH_2R_{f8})_2$+H]$^+$, 67%).

4.11. $(R_{f8}CH_2CH_2)_2P(CH_2)_2CH(CH_2)_2P(CH_2CH_2R_{f8})_2PdCH_3$ (**7b**)

A Schlenk flask was charged with **6b** (0.173 g, 0.0839 mmol), ether (5 mL), and MeLi (0.84 mL, 1.0 M in hexane, 0.084 mmol). The mixture was stirred for 4 h. Degassed water was added (0.10 mL). The solvents were removed by oil pump vacuum. Then $CF_3C_6H_5$ was added, and the mixture was filtered using a cannula. The solvent was removed from the filtrate to give **7b** as a white crystalline solid (0.166 g, 0.0813 mmol, 97%).

NMR (δ, $CF_3C_6H_5$, [d_6]DMSO capillary): ^{1}H 2.13–0.4 (br m); ^{13}C{^{1}H} 62.6 (s, Pd*C*H$_3$)[6]; ^{19}F −84.5 (t, J_{FF} = 10.3 Hz, 12F, 4C*F*$_3$), −117.1 (br m, 4F of 4PCH$_2$CH$_2$C*F*$_2$), −118.6 (br m, 4F of 4PCH$_2$CH$_2$C*F*$_2$), −124.2 (br m, 24F), −125.5 (m, 8F), −126.0 (m, 8F), −129.2 (m, 8F); ^{31}P{^{1}H} 49.1 (s).

4.12. $(R_{f8}CH_2CH_2)_2P(CH_2)_2CH(CH_2)_2P(CH_2CH_2R_{f8})_2IrHCl$ (**8b**)

A Schlenk flask was charged with **2b** (0.798 g, 0.41 mmol), THF (2 mL), and [IrCl(COE)$_2$]$_2$ (0.140 g, 0.20 mmol) [24]. The mixture was stirred for 2 d under argon at 80 °C. The THF phase was removed and the resulting oil extracted twice with hot THF (much oil remained). The THF phases were combined, and solvent was removed by oil pump vacuum to give **8b** as a slightly yellow oil (0.081 g, 0.042 mmol, 10%).

NMR (δ, $CF_3C_6F_5$, [d_6]DMSO capillary): ^{1}H 2.22–1.19 (br m), −28.18 (t, IrH, J_{HP} = 15.0 Hz); ^{31}P{^{1}H} 27.2 (s). MS (positive FAB, *m*/*z*)[1]: 2111 ([**9**–HCl]$^+$, 100%).

4.13. Partition coefficients

The following is representative. A 10 mL vial was charged with **2b** (0.120 g, 0.0995 mmol), $CF_3C_6F_{11}$ (2.000 mL), and toluene (2.000 mL), fitted with a mininert valve, and gently heated until **2b** dissolved. The vial was vigorously shaken (2 min) to ensure good phase mixing, and kept in a darkened location at room temperature (24 h, 23 °C). An aliquot (0.500 mL) was removed from each layer and added to a stock solution of C_6F_6 in $CF_3C_6H_5$ (0.200 mL, 0.176 M). A [d_6]DMSO capillary was added, and ^{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 98.8:1.2 (0.0313 g of **2b** in 0.500 mL of $CF_3C_6F_{11}$; 0.000381 g of **2b** in 0.500 mL of toluene). The total amount of **2b** calculated from this data (0.127 g after a 2.000/0.500 scale factor) closely agrees with that utilized.

[6] It was not possible to assign other ^{13}C NMR signals due to the decomposition of **7b** during the acquisition time.

4.14. Crystallography

A nearly saturated $CF_3C_6H_5$ solution of **6b** was allowed to slowly concentrate at room temperature. After 2 weeks, a transparent colorless prism of **6b**·$CF_3C_6H_5$ was taken to a Nonius KappaCCD diffractometer for data collection as outlined in Table 3. Cell parameters were obtained from 10 frames using a 10° scan and refined with 4195 reflections. Lorentz, polarization and empirical (Scalepack) absorption corrections [39] 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 [40]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. The pincer chelate atoms C2 and C4 were disordered (50:50) about a crystallographic mirror plane. Several fluorine atoms of the ponytail extending from C21 to C30 were disordered, and could not be resolved. The CF_3 group of the solvate was disordered, but could be modeled by a set of four conformations, each with 75% occupancy. Scattering factors were taken from the literature [41].

5. Supporting information

Crystallographic data for **6b**·$CF_3C_6H_5$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 611620. Copies may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (DFG, GL 300/3-3), the Humboldt Foundation (fellowship to CSC), and Johnson Matthey PMC (precious metal loans) for support.

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