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Key indicators

Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.058
 wR factor = 0.174
Data-to-parameter ratio = 13.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**(*R*)-2,2'-Bis(diphenylphosphino)-6,6'-bis(tridecafluoro-*n*-hexyl)-1,1'-binaphthyl**

The molecule of the title compound, $\text{C}_{56}\text{H}_{30}\text{F}_{26}\text{P}_2$, is located on a twofold axis perpendicular to the central C—C bond of the binaphthyl group and the P atoms have the typical pseudotetrahedral geometry found for compounds of this type.

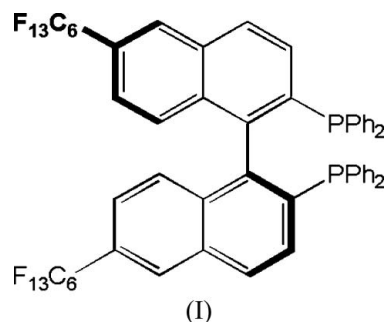
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Comment

We have probed the application of perfluoroalkylated phosphorus(III) ligands for catalysis in perfluorocarbon solvents as alternative reaction media to conventional organic solvents (Stuart *et al.*, 2000; Foster, Adams *et al.*, 2002; Foster, Gudmunsen *et al.*, 2002), including structural characterizations of a number of perfluoroalkylated phosphine coordination compounds (Fawcett *et al.*, 1997, 1998, 2001). More recently, we turned our attention to asymmetric catalysis, including the synthesis of (*R*)-2,2'-bis(diphenylphosphino)-6,6'-bis(tridecafluoro-*n*-hexyl)-1,1'-binaphthyl and (*R*)-2,2'-bis(diphenylphosphino)-6,6'-bis(1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl)-1,1'-binaphthyl, and their application in ruthenium-catalysed hydrogenation in methanol (Birdsall *et al.*, 2001) and dichloromethane with ligand recycling using fluorosilica gel (Hope *et al.*, 2004). Although we have previously structurally characterized perfluoroalkylated triphenylphosphine oxides (Bhattacharyya *et al.*, 2000; Croxtall *et al.*, 2002), there have been no previous single-crystal structure determinations of phosphine ligands with fluoros tails. We present here the crystal structure of the title such ligand, (I).



The molecular structure of (I), viewed down the C2—C2' pivot (Fig. 1), clearly shows the non-coplanar geometry of the two naphthyl ring systems, in which the perfluoroalkyl chains adopt conformations in the solid state that minimize their interactions with each other. The molecule is located on a twofold axis perpendicular to the C2—C2' bond of the binaphthyl group and the P atoms have the typical pseudotetrahedral geometry found for other structurally characterized BINAP complexes (Ozawa *et al.*, 1993). The P—C bond

distances are very similar to those found for metal-bound BINAP ligands, suggesting that any influence of the perfluoroalkyl unit does not manifest itself in the P–C(naphthyl) bond length. However, the C–P–C bond angles are all smaller [104.75 (13), 100.35 (12) and 103.01 (12)°, cf. 106.7 (5), 105.7 (4) and 105.1 (4)°], reflecting the stereochemical activity of the P lone pair.

The perfluoroalkyl unit is kinked (Fawcett *et al.*, 1998), with a single *gauche* conformation [C11–C12–C13–C14 –60.0 (4)°], as opposed to the more usual *trans* staggered conformation [C13–C14–C15–C16 167.7 (3)°] found for linear perfluoroalkyl chains.

Although within each individual molecule the perfluoroalkyl chains have no interactions, the molecular packing of (I) shows that the fluorinated groups and binaphthyl rings are stacked in alternate layers perpendicular to the *c* axis, to generate fluorine and hydrocarbon domains, characteristic of structural characterizations of fluorinated materials (Fawcett *et al.*, 1997, 1998).

Experimental

The title compound was synthesized by the literature route of Birdsall *et al.* (2001). Crystals of (I) suitable for structural characterization were grown by slow evaporation of a solution of the compound in a diethyl ether–hexane (1:6) mixture.

Crystal data

C₅₆H₃₀F₂₆P₂
M_r = 1258.74
 Monoclinic, C₂/c
a = 19.456 (3) Å
b = 8.2838 (9) Å
c = 31.886 (4) Å
 β = 101.212 (4)°
V = 5040.9 (11) Å³
Z = 4

D_x = 1.659 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 5639 reflections
 θ = 2.3–25.4°
 μ = 0.22 mm⁻¹
T = 150 (2) K
 Block, colourless
 0.34 × 0.16 × 0.14 mm

Data collection

Bruker APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.888, *T_{max}* = 0.982
 19219 measured reflections

4947 independent reflections
 4108 reflections with *I* > 2σ(*I*)
R_{int} = 0.031
 θ_{max} = 26.0°
 h = –23 → 23
 k = –10 → 10
 l = –39 → 39

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.058
wR (*F*²) = 0.174
S = 1.03
 4947 reflections
 379 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1018P)^2 + 8.8615P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 2.64 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.43 \text{ e } \text{Å}^{-3}$

A 2.6 e Å⁻³ residual electron-density peak located 1.3 Å from the unique P atom may be refined as a 20% occupancy O atom, due to partial oxidation to the phosphine oxide; by comparison, the electron density for a typical C atom is found to be 7.5 e Å⁻³. For the final refinement, however, the site was assumed to be occupied by a lone pair, and subsequent calculations of formula weight, density and

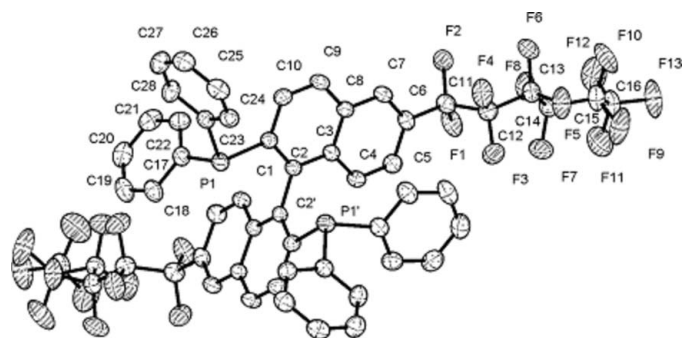


Figure 1

The molecular structure of (I), showing the atom-labelling scheme and with 50% probability displacement ellipsoids. H atoms have been omitted for clarity. The molecule is located on a twofold axis; primed atoms are generated by the symmetry operator (1 – *x*, *y*, $\frac{1}{2}$ – *z*).

absorption coefficient are based on this model. All H atoms were included in calculated positions as riding atoms, with C–H = 0.95 Å and *U_{iso}*(H) = 1.2*U_{eq}*(C).

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Sheldrick, 2000); software used to prepare material for publication: SHELXTL.

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