Journal of Fluorine Chemistry 131 (2010) 1187–1191

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

# The effect of trifluoromethyl groups in the para positions of a perfluoroaryl phosphine: A comparison of the structures of $[\{\eta^5,\kappa P\text{-}C_5Me_4CH_2C_6F_3X\text{-}5\text{-}P(C_6F_4X\text{-}4)\text{-}2\text{-}CH_2P(C_6F_4X\text{-}4)_2\}RhCl_2]$, X = F and $CF_3$

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ARTICLE INFO

*Article history:*
Received 13 April 2010
Received in revised form 23 June 2010
Accepted 24 June 2010
Available online 3 July 2010

*Keywords:*
Bis{bis(4-trifluoromethyltetrafluorophenyl)}phosphino}methane
Rhodium
Carbon–fluorine bond cleavage
Intramolecular dehydrofluorinative carbon–carbon coupling
Crystal structure

ABSTRACT

The complex $[\{\eta^5,\kappa P\text{-}C_5Me_4CH_2C_6F_3CF_3\text{-}5\text{-}P(C_6F_4CF_3\text{-}4)\text{-}2\text{-}CH_2P(C_6F_4CF_3\text{-}4)_2\}RhCl_2]$ (**2**) was formed by dehydrofluorinative carbon–carbon coupling in the reaction between bis{bis(4-trifluoromethyltetrafluorophenyl)phosphino}methane and $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$. The structure of **2** has been determined by single crystal X-ray diffraction and compared to that of the pentafluorophenyl analogue $[\{\eta^5,\kappa P\text{-}C_5Me_4CH_2C_6F_4P(C_6F_5)\text{-}2\text{-}CH_2P(C_6F_5)_2\}RhCl_2]$ (**3**). The presence of the trifluoromethyl groups, although not affecting the local structure about rhodium, disrupts the packing and consequently the structure of the two complexes is very different. The structure of **2** contains channels about 3-fold axes comprising fluoroaryl cavities separated by aliphatic constrictions arising from hexagonal rings of alternating enantiomers.

## 1. Introduction

The presence of fluorine atoms in aryl substituents of phosphines reduces the basicity of the phosphines and increases their bulk. This can have profound consequences on the properties of metal complexes, such as complex stability, reactivity and catalytic activity [1]. Although the trifluoromethyl group is bulkier than fluorine it exerts a similar electronic effect; the Hammett constants, $\sigma_m$ and $\sigma_p$, of the trifluoromethyl group (0.43 and 0.08) and fluorine (0.34 and 0.06) are similar [2]. However, the presence of the trifluoromethyl group is expected to affect the packing of the molecules in the solid state.

A number of intermolecular interactions involving polyfluorophenyl rings have been identified in the solid state [3]. $C\text{–}F\cdots H\text{–}C$ interactions are very weakly attractive [4], but are considered important in determining the structures of fluoroarenes [5]. Although they are optimal when the covalent bonds are colinear, the majority of structures possess reduced $F\cdots H\text{–}C$ angles, with the distribution maximum at 125°, probably as a consequence of other packing effects. The energy of the interaction, based on calculations on 1,3,5-trifluorobenzene, is estimated to be between 1 and 2 kJ $mol^{-1}$ [6]. $C\text{–}F\cdots\pi$ interactions are stronger, ca. 5–10 kJ $mol^{-1}$ [7]. There are a number of types of these interactions depending on the relative positions of the two rings. If they are perpendicular one fluorine atom of one may be close to the centre of the other (vertex-to-face) or two fluorine atoms of one may be close to two mutually para carbon atoms of the other (edge-to-face). If the rings are parallel they may have colinear normals (face-to-face), in which case the interaction is $\pi\cdots\pi$, or be offset by up to the $C_6$ ring's diameter (offset face-to-face) [4,7]. The nature of $F\cdots F$ interactions is ill-defined, but it has been concluded that the electrostatic repulsion between fluorine atoms is not an influential contribution to the total energy [7]. The interactions can give rise to 'embracing' [8], but this has yet to be observed in tris(pentafluorophenyl)phosphine or its complexes. In crystals where interactions involving fluorine atoms predominate, substitution of those fluorine atoms by trifluoromethyl groups is expected to cause a drastic change in the packing of the molecules.

As part of our on-going investigation into fluorinated arylphosphines we are investigating phosphines bearing 4-trifluoromethyltetrafluorophenyl substituents. These phosphines are expected to exert similar electronic effects on transition metals as the pentafluorophenyl analogues, and also similar steric effects because of identical cone angles [9]. Here we communicate the effect of introducing trifluoromethyl groups at the para positions of a perfluorophenyl substituted diphosphinomethane on the structure

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doi:10.1016/j.jfluchem.2010.06.016

of a rhodium complex of a tethered ligand formed by intramolecular dehydrofluorinative coupling.

## 2. Results and discussion

Bis{bis(4-trifluoromethyltetrafluorophenyl)phosphino}-methane, **1**, was prepared in 63% yield by treatment of bis(dichlorophosphino)methane with 4-trifluoromethyltetrafluorophenyl magnesium bromide. The $^1$H and $^{31}$P{$^1$H} NMR spectral data, a triplet at $\delta$ 3.90 ($^2J_{PH}$ = 5.7 Hz) and a virtual septet at $\delta$ −50.3 respectively, are similar to those of bis{bis(pentafluorophenyl)phosphino}methane ($\delta_H$ = 3.81, $\delta_P$ = −52.1) [10]. The $^{19}$F NMR spectrum displays a triplet at $\delta$ −57.22 ($^3J_{FF}$ = 21.8 Hz) and two symmetrical multiple line patterns at $\delta$ −128.1 and −138.02 consistent with the $A[[M]_2[N]_2[X_3]]_2$ spin system and with that of dimethyl{(4-trifluoromethyl)tetrafluorophenyl}phosphine ($\delta_F$ = −57.4 ($^3J_{FF}$ = 21.5 Hz), −131.4 and −142.1) [11]. Diphosphine **1** was further characterized by the oxidation of an NMR sample by hydrogen peroxide. The $^1$H and $^{31}$P{$^1$H} NMR spectra of the resulting dioxide, {(4-$CF_3C_6F_4)_2PO\}_2CH_2$, are similar to those of {$(C_6F_5)_2PO\}_2CH_2$ [12], and the $^{19}$F NMR spectrum is similar to that of **1**.

Treatment of [($\eta^5$-$C_5Me_5$)RhCl($\mu$-Cl)]$_2$ with **1** in refluxing benzene gave a mixture of compounds. The $^{31}$P{$^1$H} NMR spectrum displayed two predominant resonances: a doublet of multiplets at $\delta$ 43.3 and a doublet of quintets at $\delta$ −66.5 with a mutual coupling of 190 Hz. By comparison with the NMR data of [{$\eta^5$,κP-$C_5Me_4CH_2C_6F_4P(C_6F_5)$-2-$CH_2P(C_6F_5)_2$}$RhCl_2$], **3**, ($\delta$ 43.1 and −66.6, $^2J_{PP}$ = 185 Hz) these are assigned to the coordinated and non-coordinated phosphorus atoms respectively of [{$\eta^5$,κP-$C_5Me_4CH_2C_6F_3CF_3$-5-P($C_6F_4CF_3$-4)-2-$CH_2P(C_6F_4CF_3$-4$)_2$}$RhCl_2$], **2**. Unfortunately, although **2** was the major component of the mixture (>50% from the $^{31}$P{$^1$H} NMR spectrum), purification by repeated recrystallization from chloroform afforded only a small quantity of pure **2** as orange-red crystals (ca. 5% yield). The $^1$H and $^{19}$F NMR spectra are entirely consistent with the formulation of **2**. The $^1$H NMR spectrum shows two mutually coupled triplet resonances arising from the methylene group of the diphosphine at $\delta$ 5.28 and 4.32, two multiplet resonances at $\delta$ 3.83 and 3.77 arising from the methylene group linking the cyclopentadienyl ring to the trifluoromethyltetrafluorophenyl group, and four resonances arising from the non-equivalent methyl groups at $\delta$ 2.00, 1.94, 1.81 and 1.42. These data are similar to those of **3**. The $^{19}$F NMR spectrum displays four resonances at ca. $\delta$ −57 arising from the four non-equivalent trifluoromethyl groups, three resonances, each integrating for one fluorine atom, at $\delta$ −110.75, −120.30 and −133.99, which are assigned to the fluorine atoms of the trifluorophenyl ring, and four resonances, each integrating for three fluorine atoms at $\delta$ −126.83, −128.89, −136.81 and −138.17 arising from the three tetrafluorophenyl groups. The data indicate that there is hindered rotation about at least one P–$C_6F_4CF_3$ bond. The similarity between the $^{31}$P{$^1$H} NMR data of **2** and **3** strongly suggests that the electronic effects of the phosphine are similar in the two complexes.

The structure of **2**, which crystallized with 0.23 molecules of $CHCl_3$, was determined by single crystal X-ray diffraction (Fig. 1). Crystallographic data are given in Table 1. Selected bond distances and angles are given in Table 2. Compound **2** adopts a very similar conformation to **3** (CEJBEZ) [10,12]. Two fluoroaryl substituents are positioned such that they are twisted by 21.4° from coplanarity. The third 4-trifluoromethyltetrafluorophenyl ring lies almost perpendicular to these and is virtually parallel (deviation 5.4°) to the fluoroaryl ring of the tether. The conformation of the diphosphine fragment is similar to that adopted by bis{bis(pentafluorophenyl)phosphino}methane [12]. The bond distances and angles of **2** around rhodium are very similar to those of **3**, with both displaying a small degree of ring slippage: the two carbon atoms opposite to the tether are slightly further from the rhodium than the other three and the bond between them is shorter than the other C–C bond distances in the ring. P(2)–C(11) is identical to the P–$CH_2$ distances of **3**, but P(1)–C(11) is ca. 0.02 Å shorter. The similarity of the bond distances and angles about rhodium supports the argument that the difference between the steric and electronic effects exerted by fluorine and by trifluoromethyl in the para position is very small.

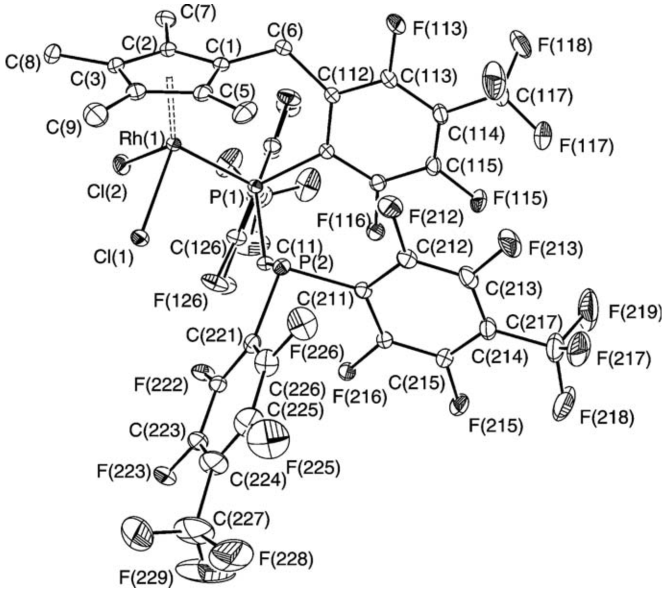

**Fig. 1.** Structure of the R enantiomer of [{$\eta^5$,κP-$C_5Me_4CH_2C_6F_3CF_3$-5-P($C_6F_4CF_3$-4)-2-$CH_2P(C_6F_4CF_3$-4$)_2$}$RhCl_2$] (**2**). Thermal ellipsoids are at the 30% probability level. Hydrogen atoms are omitted for clarity.

Although the molecular structures of **2** and **3** are similar, the packing of the molecules in the solid state is very different. Complex **3** crystallizes in an orthorhombic unit cell ($Pna2_1$) with a structure comprising columns of alternating enantiomers parallel to the *a* axis (Fig. 2a). Between the molecules there is a short (less than the sum of the van der Waals radii [13]) H· · ·Cl distance involving a hydrogen atom of the methylene (2.760 Å) group of the

**Table 1**
Crystallographic data for [{$\eta^5$,κP-$C_5Me_4CH_2C_6F_3CF_3$-5-P($C_6F_4CF_3$-4)-2-$CH_2$P-($C_6F_4CF_3$-4$)_2$}$RhCl_2$] (**2**).

| | |
|---|---|
| Formula | $C_{39}H_{16}Cl_2F_{27}P_2Rh{\cdot}0.23CHCl_3$ |
| Formula weight | 1260.32 |
| Crystal system | Trigonal |
| Space group | $R\bar{3}$ |
| $a$ (Å) | 44.0071(11) |
| $c$ (Å) | 12.7266(4) |
| $V$ (Å$^3$) | 21344.6(10) |
| $Z$ | 18 |
| $D_c$ (g cm$^{-3}$) | 1.765 |
| Crystal size (mm$^3$) | 0.76 × 0.43 × 0.30 |
| $\mu$ (mm$^{-1}$) | 0.715 |
| $\theta$ range (°) | 2.45 → 33.14 |
| Total reflections | 18,043 |
| Unique reflections ($R_{int}$) | 18,043 (0.0447) |
| Observed reflections [$I > 2\sigma(I)$] | 14,420 |
| Parameters | 661 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1$ 0.0436, $wR_2$ 0.1197 |
| $R$ indices (all data) | $R_1$ 0.0613, $wR_2$ 0.1376 |
| Weighting scheme | $w = 1/[\sigma^2(F_0^2) + \{0.0659(F_0^2 + 2F_c^2)/3\}^2 + 78.8270(F_0^2 + 2F_c^2)/3]$ |
| Max., min.$\Delta\rho$ (eÅ$^{-3}$) | 1.608, −0.872 |
| Goodness of fit on $F^2$ | 1.094 |

Estimated standard deviations are given in parentheses. Data were collected at 93(2) K with graphite monochromated Mo–K$_\alpha$ radiation ($\lambda$ = 0.71073 Å).

**Table 2**
Selected bond distances (Å) and angles (°) for [{$\eta^5$,$\kappa$P-$C_5Me_4CH_2C_6F_3CF_3$-5-P($C_6F_4CF_3$-4)-2-$CH_2P(C_6F_4CF_3\text{-}4)_2$}$RhCl_2$] (**2**).

| | | | |
|---|---|---|---|
| Rh–C(1) | 2.127(2) | Rh–C(2) | 2.138(2) |
| Rh–C(3) | 2.226(2) | Rh–C(4) | 2.247(2) |
| Rh–C(5) | 2.159(2) | Cp*–Rh | 1.801(2) |
| C(1)–C(2) | 1.442(3) | C(2)–C(3) | 1.446(4) |
| C(3)–C(4) | 1.414(4) | C(4)–C(5) | 1.445(3) |
| C(5)–C(1) | 1.434(4) | C(1)–(6) | 1.493(3) |
| C(6)–(112) | 1.522(3) | Mean C–$CH_3$ | 1.489(4) |
| Rh–Cl(1) | 2.4085(6) | Rh–Cl(2) | 2.3876(6) |
| Rh–P(1) | 2.2721(5) | P(1)–C(11) | 1.8326(19) |
| P(1)–C(111) | 1.846(2) | P(1)–P(121) | 1.834(2) |
| P(2)–C(11) | 1.851(2) | P(2)–C(211) | 1.854(2) |
| P(2)–C(221) | 1.851(2) | Mean C(aryl)–F | 1.338(4) |
| Cp*–Rh–P(1) | 127.19 | Cp*–Rh–Cl(1) | 121.95 |
| Cp*–Rh–Cl(2) | 123.69 | P(1)–Rh–Cl(1) | 92.852(18) |
| P(1)–Rh–Cl(2) | 90.07(2) | Cl(1)–Rh–Cl(2) | 91.14(2) |
| Rh–P(1)–C(11) | 111.77(7) | Rh-P(1)–C(111) | 115.69(7) |
| Rh–P(1)–C(112) | 116.81(7) | P(1)–C(11)–P(2) | 108.58(10) |

Estimated standard deviations are given in parentheses. Cp* represents the centroid of the $C_5$ ring.

cyclopentadienyl ring. There is also a short H···F distance (2.526 Å) involving a methyl group. Between adjacent molecules along the direction of the *b* axis there is an H···F distance of 2.473 Å involving a hydrogen atom of the methylene bridge of the diphosphine fragment and a para (to phosphorus) fluorine atom of the tetrafluorophenyl group of the tether (Fig. 2b). Between adjacent molecules along the direction of the *c* axis there is an H···F distance of 2.525 Å involving a hydrogen atom of a cyclopentadienyl ring methyl group and a meta fluorine atom of the uncoordinated phosphine fragment. There are also some intermolecular F···F distances less than the sum of the van der Waals radii (2.94 Å) involving para fluorine atoms, but the rings are not arranged in vertex-to-face, edge-to-face or face-to-face conformations (Fig. 2c).

Since the para fluorine atoms are involved in some of the short intermolecular distances in the structure of **3** it is expected that the introduction of trifluoromethyl groups at the para positions would disrupt this packing arrangement. Indeed this is the case. The molecules of **2** are arranged such that the two chlorine atoms of one molecule are close to the pentamethylcyclopentadienyl ring of a molecule of the other enantiomer (Cl···HC 2.641 Å, Cl···C 3.371 and 3.379 Å) resulting in hexagonal rings of alternating enantiomers. Between molecules parallel to the *c* axis there are three short C···F distances (3.033, 3.147 and 3.147 Å) involving one fluorine atom of the trifluoromethyl group of the 4-trifluoromethyltetrafluorophenyl substituent of the coordinated phosphine moiety and both 4-trifluoromethyltetrafluorophenyl substituents of the non-coordinated phosphine moiety. Between molecules of adjacent heaxagons there are short F···F($CF_3$) (2.833, 2.918, 2.930 Å), ($CF_3$)F···F($CF_3$) (2.855 Å), F···F (2.836, 2.901 Å), C···F($CF_3$) (3.163 Å) and C···F (3.025, 3.099 Å) distances. As with **3** the fluoroaryl rings are not arranged in vertex-to-face, edge-to-face or face-to-face conformations. The hexagonal rings define infinite channels along 3-fold axes parallel to the *c* axis (Fig. 3). The channels comprise cylindrical cavities separated by constrictions. The cavities have a diameter of ca. 14 Å and are bordered by six 4-trifluoromethyltetrafluorophenyl groups with the phenyl planes parallel to the 3-fold axis and tangential to the cylindrical cavity (Fig. 3b). The cavities are separated along the channels by constrictions with a diameter of ca. 4.2 Å resulting from the position of two methyl groups of each pentamethylcyclopentadienyl ring (Fig. 3a). The distance between constrictions along the channel is ca. 4.6 Å and the constrictions are ca. 8.2 Å long. The arrangement and dimensions of the cavities and constrictions are represented diagrammatically in Fig. 4. A free space of 1014 $Å^3$ (ca.

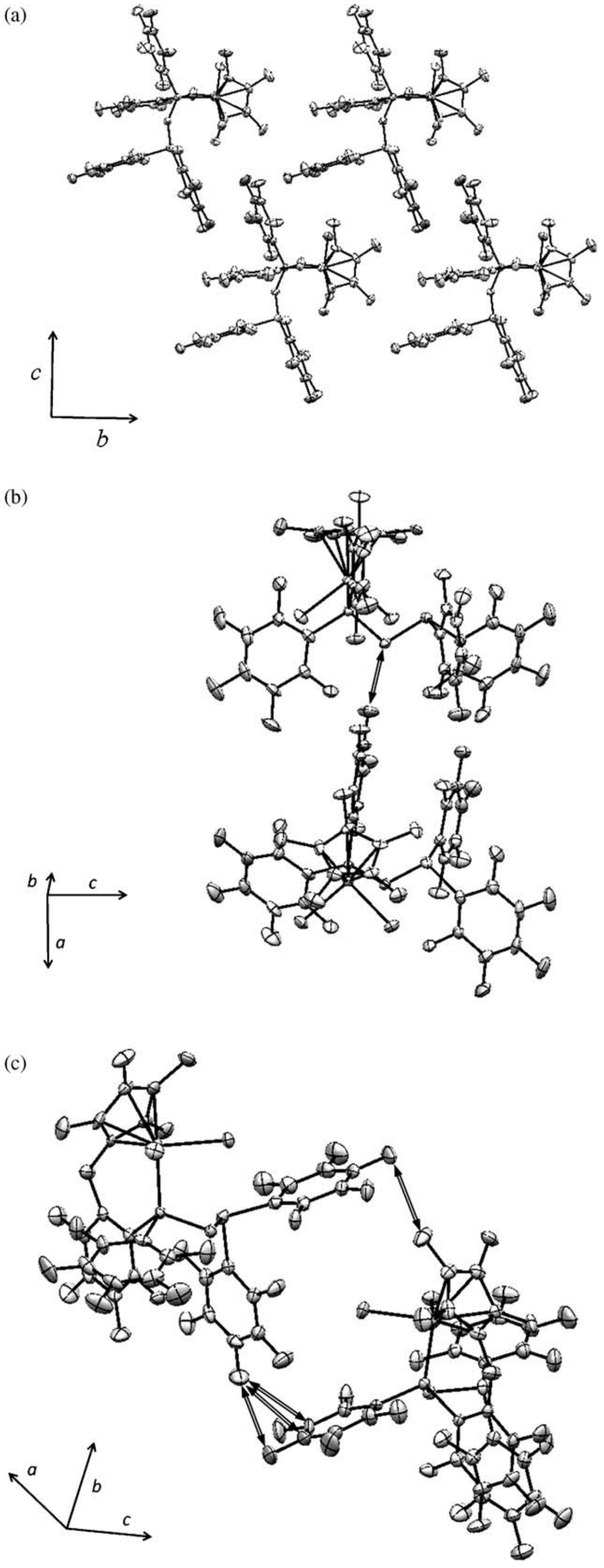

**Fig. 2.** A diagram showing the packing arrangement of [{$\eta^5$,$\kappa$P-$C_5Me_4CH_2C_6F_4P(C_6F_5)$-2-$CH_2P(C_6F_5)_2$}$RhCl_2$] (**2**). Hydrogen atoms are omitted for clarity: (a) showing arrangement of columns, viewed along the *a* axis, and showing short intermolecular distances involving para fluorine atoms (b) along the *b* axis and (c) along the *c* axis.

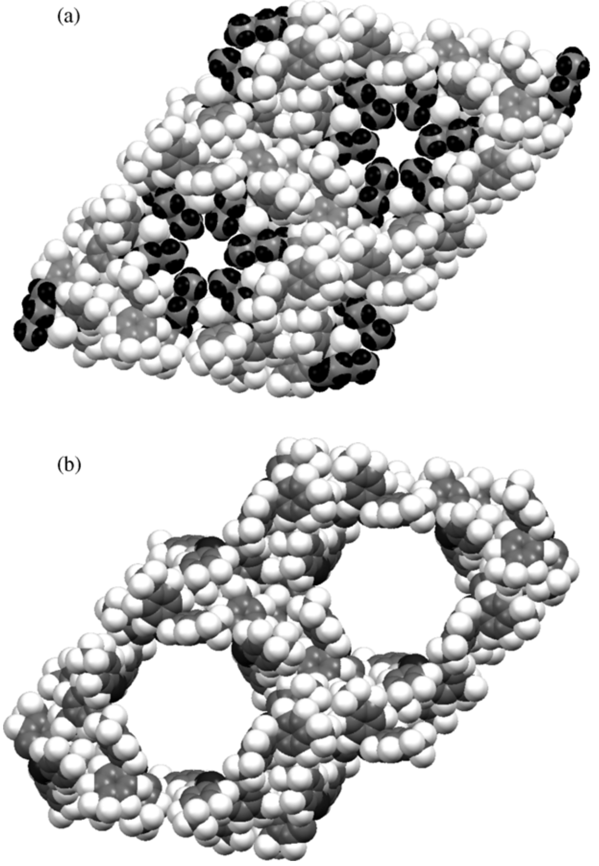

**Fig. 3.** A space-filling diagram of the unit cell of $[\{\eta^5,\kappa P\text{-}C_5Me_4CH_2C_6F_3CF_3\text{-}5\text{-}P(C_6F_4CF_3\text{-}4)\text{-}2\text{-}CH_2P(C_6F_4CF_3\text{-}4)_2\}RhCl_2]$ (**2**) viewed along the *c* axis. Chloroform molecules are omitted for clarity. Hydrogen atoms are black, fluorine atoms are white and all other atoms are grey: (a) showing the constrictions of the channels, and (b) with $(\eta^5\text{-}C_5Me_5)RhCl_2$ units omitted to reveal the cavities.

5% of the unit cell volume) accessible to solvent molecules was calculated for the structure, excluding the chloroform molecules, with the PLATON software package [14]. The chloroform sites, which are only 0.23 occupied, form a hexagonal ring with an external diameter of ca. 14 Å within the cavity. The distance between adjacent sites, Cl···Cl, is 2.574 Å, so clearly adjacent sites are not occupied. The closest Cl···Cl distance between alternate chloroform molecules is 4.348 Å, suggesting that the cavities can accommodate up to three molecules of chloroform. The occupancy of 0.23 indicates that between 19% and 38% of the cavities contain at least 2 molecules of chloroform. The shortest distance to **2**, Cl···H (Me), is 2.880 Å.

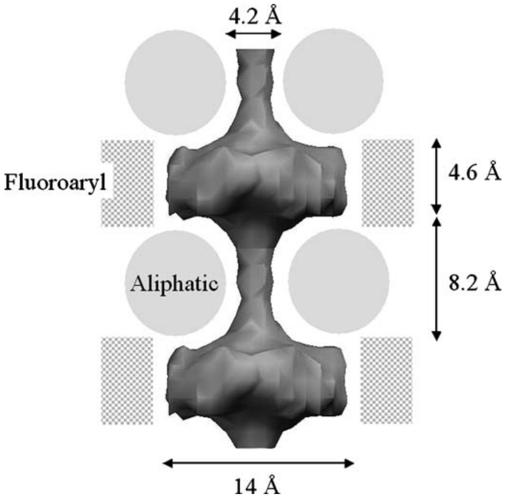

**Fig. 4.** A diagram showing the dimensions of the cavities and constrictions of $[\{\eta^5,\kappa P\text{-}C_5Me_4CH_2C_6F_3CF_3\text{-}5\text{-}P(C_6F_4CF_3\text{-}4)\text{-}2\text{-}CH_2P(C_6F_4CF_3\text{-}4)_2\}RhCl_2]$ (**2**) along the channels viewed perpendicular to the *c* axis.

A search of the Cambridge Structural Database revealed very few similar structures (those with channels surrounded by six pairs of methyl groups). Examples include L-leucyl-L-serine (JAZBOC) [15] and aqua(bis-2,2-dimethylpropyldiamine)copper metavanadate (POYNAT) [16] which have channels with diameters of 5.2 and 7.3 Å respectively, and an adduct of benzoxazole–chlorotetrahydrobenzoxanthene and toluic acid (WAGREC) [17]. The last possesses larger cavities with a diameter of 5.5 Å and surrounded by chlorine atoms, and smaller cavities with a diameter of 5 Å and surrounded by methyl groups. Most similar is the structure of β-bis(1,1,1-trifluoro-5,5-dimethyl-5-methoxyacetylacetonoato)copper (EDEMAB) [18,19], which possesses channels comprising alternating larger fluorous cavities of diameter 6.4 Å and smaller aliphatic cavities of diameter 5.3 Å. Extensive studies have revealed that small molecules, such as chloroform, acetone, tetrahydrofuran and benzene, can be reversibly accommodated in the channels [18–21].

## 3. Conclusion

The rhodium complex **2** was prepared by intramolecular dehydrofluorinative coupling between the diphosphine **1** and $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$. The NMR data and the bond distances and angles around rhodium support the argument that the substitution of the para fluorine atoms with trifluoromethyl groups has little electronic effect on the environment around the metal. In contrast there is a profound effect upon the packing of the molecules in the solid state. The crystal structure of **2** possesses infinite channels comprising cylindrical fluorous cavities and aliphatic constrictions. The cavities are able to accommodate at least two molecules of chloroform.

## 4. Experimental

### 4.1. Instrumentation

The $^1H$, $^{13}C\{^1H\}$, $^{19}F$ and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ using Bruker DRX300 or DPX400 spectrometers. $^1H$ (300.13 or 400.14 MHz) were referenced internally using the residual portion solvent resonance relative to $SiMe_4$ ($\delta$ 0), $^{13}C$ (100.61 MHz) externally to $SiMe_4$ ($\delta$ 0), $^{19}F$ (282.40 MHz) externally to $CFCl_3$ ($\delta$ 0) and $^{31}P$ (121.49 MHz) externally to 85% $H_3PO_4$ ($\delta$ 0). All chemical shifts are quoted in $\delta$ (ppm), using the high frequency positive convention, and coupling constants in Hz. Elemental analyses were carried out by the Campbell Microanalytical Laboratory, The University of Otago. The mass spectrum was recorded on a Bruker Daltonics micrOTOF spectrometer.

### 4.2. Materials

The compounds bis(dichlorophosphino)methane (Aldrich) and 4-bromotrifluoromethyltetrafluorobenzene (Apollo) were used as supplied. $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ was prepared as described [22]. Diethyl ether was dried by passage through activated alumina.

### 4.3. Preparation of $\{(4\text{-}CF_3C_6F_4)_2P\}_2CH_2$ (1)

Bis(dichlorophosphino)methane (0.8 $cm^3$, 0.0059 mol) was added by syringe, under nitrogen, to a solution of $4\text{-}CF_3C_6F_4MgBr$ in diethyl ether freshly prepared from 4-bromotrifluoromethyltetrafluorobenzene (10 g, 0.034 mol) and magnesium (0.62 g, 0.0255 mol). A milky precipitate formed after 5 min. The mixture was left at ambient temperature for 14 h, after which it was exposed to air and distilled water (20 $cm^3$) was added to destroy the excess of Grignard reagent. Ethyl acetate (200 $cm^3$) was added. The organic layer was separated and washed with water (40 $cm^3$). The solvent was removed by rotary evaporation to afford a brown oil, which was dissolved in dichloromethane and passed through deactivated alumina (4 cm). The solvent was removed by rotary evaporation to afford a yellow oil, which deposited a colourless waxy solid on drying in vacuo. Recrystallization from chloroform gave colourless crystals. Yield 3.53 g (63.4%). Anal. Calcd for $C_{29}H_2F_{28}P_2$: C, 36.9; H, 0.2. Found C, 37.1; H, 0.3%. MS (negative ion): $C_{29}HF_{28}P_2$ requires 942.9106; found: $[M{-}H]^-$ 942.9162. $^1H$ NMR: $\delta = 3.90$ (2H, t, $^1J_{PH} = 5.7$ Hz, $CH_2$). $^{13}C\{^1H\}$ NMR: $\delta = 147.6$ (ddquart, $^1J_{CF} = 267$, $^2J_{CF} = 13$, $^3J_{CF} = 5$, $C_{meta}$), 144.0 (dd, $^1J_{CF} = 265$, $^2J_{CF} = 19$ Hz, $C_{ortho}$), 120.3 (quart, $^1J_{CF} = 275$ Hz, $CF_3$), 116.9 (m, $C_{ipso}$), 112.8 (quartt, $^2J_{CF} = 35$ Hz, $^2J_{CF} = 13$ Hz, $C_{para}$), 18.0 (tm, $^1J_{CP} = 22$ Hz, $CH_2$). $^{19}F$ NMR: $\delta = -57.22$ (12F, t, $^3J_{FF} = 21.8$ Hz, $CF_3$), $-128.1$ (8F), $-138.02$ (8F) (X, M and N components respectively of an $A[[M]_2[N]_2[X_3]]_3$ spin system). $^{31}P\{^1H\}$ NMR: $\delta = -50.3$ (virtual septet, 17 Hz, a component of an $A[[M]_2[N]_2[X_3]]_3$ spin system).

A sample of **1** in $CDCl_3$ (ca. 1 $cm^3$) in an NMR tube was shaken with an equal volume of aqueous hydrogen peroxide (30%) to give the dioxide $\{(4\text{-}CF_3C_6F_4)_2PO\}_2CH_2$. $^1H$ NMR ($CDCl_3$): $\delta = 4.15$ (2H, t, $^1J_{PH} = 14.8$ Hz, $CH_2$). $^{19}F$ NMR: $\delta = -56.88$ (12F, t, $^3J_{FF} = 21.9$ Hz, $CF_3$), $-129.90$ (8F), $-135.45$ (8F) (X, M and N components respectively of an $[M]_2[N]_2[X_3]$ spin system). $^{31}P\{^1H\}$ NMR: $\delta = 7.85$ (unresolved multiplet).

### 4.4. *Preparation of* $[\{\eta^5,\kappa P\text{-}C_5Me_4CH_2C_6F_3CF_3\text{-}5\text{-}P(C_6F_4CF_3\text{-}4)\text{-}2\text{-}CH_2P(C_6F_4CF_3\text{-}4)_2\}RhCl_2]$ *(2)*

A slurry of $[\{(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)\}_2]$ (0.051 g, 0.08 mmol) and **1** (0.155 g, 0.16 mmol) in benzene (50 $cm^3$) was heated at reflux for 172 h. After cooling, the solvent was removed by rotary evaporation. Repeated recrystallizations of the orange powder yielded a small amount of orange-red crystals of **2**$\cdot 0.23CHCl_3$ (ca. 0.010 g, 5%). Anal. Calcd for $C_{39}H_{16}Cl_2F_{27}P_2Rh \cdot 0.23CHCl_3$: C, 37.4; H, 1.3. Found: C, 37.55; H, 1.4%. $^1H$ NMR: $\delta = 5.28$ (1H, dd, $^2J_{PH} = {}^2J_{HH'} = 14.9$ Hz, PCHH′P), 4.32 (1H, dd, $^2J_{PH'} = {}^2J_{HH'} = 14.9$ Hz, PCHH′P), 3.83 (1H, m, $C_5CHH'C_6F_3$), 3.77 (1H, m, $C_5CHH'C_6F_3$), 2.00 (3H, d, $^4J_{PH} = 7.5$ Hz, $CH_3$), 1.94 (3H, d, $^4J_{PH} = 5.6$ Hz, $CH_3$), 1.81 (3H, s, $CH_3$), 1.42 (3H, s, $CH_3$). $^{19}F$ NMR: $\delta = -56.59$ (3F, t, $^3J_{FF} = 21.0$ Hz, $CF_3$), $-56.66$ (3F, t, $^3J_{FF} = 21.0$ Hz, $CF_3$), $-57.09$ (3F, t, $^3J_{FF} = 22.0$ Hz, $CF_3$), $-57.29$ (3F, td, $^3J_{FF} = 22.4$ Hz, $J = 1.9$ Hz, $CF_3$), $-110.75$ (1F, m, $C_6F_3$), $-120.30$ (1F, quart, $^3J_{FF} = 18.8$ Hz, $C_6F_3$), $-126.83$ (3F, m), $-128.89$ (3F, m), $-133.99$ (1F, dquart, $^3J_{FF} = 22.9$, $^3J_{FF} = 22.9$ Hz, $C_6F_3$), $-136.81$ (3F, m), $-138.17$ (3F, m). $^{31}P\{^1H\}$ NMR: $\delta = 43.3$ (ddm, $^1J_{RhP} = 164$ Hz, $^2J_{PP} = 190$ Hz, PRh), $-66.5$ (dquint, $^2J_{PP} = 190$ Hz, $^3J_{PF} = 38$ Hz, $P(C_6F_4CF_3)_2$).

### 4.5. *X-ray crystallography*

Crystals of **2**$\cdot 0.23CHCl_3$ were grown from chloroform. Unit cell dimensions and reflection data were collected at the University of Canterbury on a Bruker Nonius Apex II CCD diffractometer at 93(2) K. Absorption corrections to the data were made by SADABS [23]. Crystal and refinement data for the complex are presented in Table 1. The structure was solved by direct methods using SHELXS-97 [24] and refined using SHELXL-97 [25] with all non-hydrogen atoms of 2 anisotropic, and the non-hydrogen atoms of CHCl3 isotropic. All H atoms were included in calculated positions. Crystallographic data (excluding structure factors) for the structure of 2 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 771467. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033 or e-mail: deposit@ccdc cam ac uk

## Acknowledgements

The author thanks the University of Waikato for financial support, Prof B.K. Nicholson for much assistance with the structure determination, and Dr Jan Wikaira (University of Canterbury) for the X-ray data set.

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