

Ronan M. Bellabarba, Mark
Nieuwenhuyzen and Graham
C. Saunders*School of Chemistry, Queen's University Belfast,
David Keir Building, Belfast BT9 5AG, Northern
Ireland

Correspondence e-mail: g.saunders@qub.ac.uk

Key indicators

Single-crystal X-ray study
 $T = 153$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.047
 wR factor = 0.109
Data-to-parameter ratio = 15.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.(Acetonitrile- κN){1,2-bis[bis(pentafluorophenyl)-
phosphino]ethane- $\kappa^2 P, P$ }(η^5 -pentamethylcyclo-
pentadienyl)ruthenium(II) hexafluorophosphate

The cation of the title salt, $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{NCMe})\{\text{(C}_6\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]^+\text{PF}_6^-$ or $[\text{Ru}(\text{C}_{10}\text{H}_{15})(\text{C}_{26}\text{H}_4\text{F}_{20}\text{P}_2)(\text{C}_2\text{H}_3\text{N})]\text{PF}_6^-$, has contacts with three anions. One lies close to the pentamethylcyclopentadienyl ring, such that three F atoms of the anion are *ca* 3.5 Å from two of the ring methyl C atoms of the cation and there is one $\text{H}\cdots\text{F}$ distance shorter than the sum of the van der Waals radii.

Comment

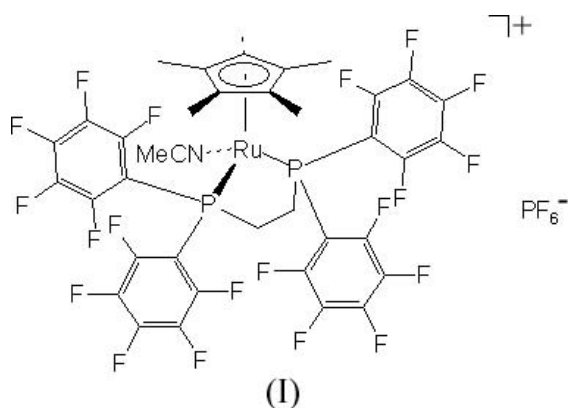
Salts of the cation $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\{\text{(C}_6\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]^+$ have been found to undergo intramolecular dehydrofluorinative C–C reactions on thermolysis or in the presence of a proton sponge or fluoride, to yield $[(\eta^5, \kappa P, \kappa P\text{-C}_5\text{Me}_4\text{CH}_2\text{C}_6\text{F}_4\text{-2-P}(\text{C}_6\text{F}_5)\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2)\text{RhCl}]^+$ and then $[(\eta^5, \kappa P, \kappa P\text{-C}_5\text{Me}_3[\text{CH}_2\text{C}_6\text{F}_4\text{-2-P}(\text{C}_6\text{F}_5)\text{CH}_2\text{-1,3})\text{RhCl}]^+$ (Atherton *et al.*, 1996; Bellabarba *et al.*, 2001). The thermolysis is dependent on the solvent and the anion. The reaction for the tetrafluoroborate salt occurs only in polar protic solvents, such as ethanol, whereas for chloride, hexafluorophosphate and tetraphenylborate salts, the reaction also occurs readily in non-polar aprotic solvents, such as benzene (Atherton *et al.*, 1999).

The structure of $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\{\text{(C}_6\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]\text{BF}_4^-$ revealed that a tetrafluoroborate anion is positioned close to the pentamethylcyclopentadienyl ligand, such that three F atoms of the anion form a plane almost parallel (5.1° deviation) to the C_5 plane, with a separation between the two planes of *ca* 3.19 Å. The anion is displaced slightly from the $(\eta^5\text{-C}_5\text{Me}_5)\text{-Rh}$ axis, giving rise to short $\text{F}\cdots\text{H}$ and $\text{F}\cdots\text{C}$ distances between the anion and the pentamethylcyclopentadienyl ligand of 2.4–2.7 and 3.1–3.3 Å, respectively (Atherton *et al.*, 1996). A similar positioning of the anion and cation is found in the related salts $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}\{\text{(C}_6\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]\text{BF}_4^-$ (Atherton *et al.*, 1996) and $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\{\text{(C}_6\text{H}_3\text{F}_2\text{-2,6})_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_3\text{F}_2\text{-2,6})_2\}]\text{BF}_4^-$ (Fawcett *et al.*, 1998). If $\text{BF}_4^-\cdots\text{C}_5\text{Me}_5$ interactions are present in aprotic solvents, then the absence of similar anion $\cdots\text{C}_5\text{Me}_5$ interactions in the salts of the other anions may provide the basis for an explanation for the difference in reactivity. Of particular relevance is the salt of the hexafluorophosphate anion, which is the most similar to the tetrafluoroborate anion. These two anions comprise a periphery of F atoms, with equilateral triangular faces with edges of *ca* 2.1–2.3 Å (Allen *et al.*, 1987; Atherton *et al.*, 1996; Fawcett *et al.*, 1998). Unfortunately, crystals suitable for single-crystal X-ray diffraction studies of the non-tetrafluoroborate salts of $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\{\text{(C}_6\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]^+$ have been elusive. However, the structure of the title isoelectronic ruthenium salt, $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{NCMe})\{\text{(C}_6\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2\}]\text{PF}_6^-$ (I), has now been determined and is presented here.

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The structure of (I) (Fig. 1) reveals that the hexafluorophosphate anion does not adopt a similar position to that of the tetrafluoroborate anion in $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}[(\text{C}_6\text{F}_5)_2\text{-PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2]]\text{BF}_4$ and $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}[(\text{C}_6\text{H}_3\text{F}_2\text{-2,6})_2\text{-PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_3\text{F}_2\text{-2,6})_2]]\text{BF}_4$. The cation shows contacts to three anions which are shorter than the sum of the van der Waals radii of the respective atoms. One anion position is close to the pentamethylcyclopentadienyl ligand, such that there is one $\text{F}\cdots\text{H}$ distance shorter than the sum of the van der Waals radii ($\text{F36}\cdots\text{H10C} = 2.626 \text{ \AA}$). The shortest inter-ion $\text{F}\cdots\text{C}(\text{C}_5\text{Me}_5)$ distances are between atoms F34 and C9 [3.493 (6) \AA], F36 and C10 [3.564 (7) \AA], and F32 and C10 [3.597 (7) \AA]. However, for this anion, the shortest inter-ion $\text{F}\cdots\text{C}$ distance of 3.028 (6) \AA is between atoms F36 and C2S of the acetonitrile. The distance between atoms C3S and F36 is 3.123 (5) \AA , with $\text{F36}\cdots\text{H3S2} = 2.609 \text{ \AA}$, and that between atoms C3S and F34 is 3.396 (7) \AA , with $\text{F34}\cdots\text{H3S2} = 2.481 \text{ \AA}$.

Another anion position gives three short contacts with a C_6F_5 ring ($\text{F32}\cdots\text{F26B} = 2.888 (6) \text{ \AA}$, $\text{F32}\cdots\text{C26B} = 2.964 (6) \text{ \AA}$ and $\text{F32}\cdots\text{C25B} = 3.110 (6) \text{ \AA}$) and a contact with a CH_2 H atom ($\text{F35}\cdots\text{H2A2} = 2.633 \text{ \AA}$). The third anion position gives a contact with a C_6F_5 ring ($\text{F31}\cdots\text{C14B} = 3.113 (7) \text{ \AA}$), a CH_2 H atom ($\text{F33}\cdots\text{H1A1} = 2.599 \text{ \AA}$) and an acetonitrile H atom ($\text{F35}\cdots\text{H3S1} = 2.428 \text{ \AA}$).

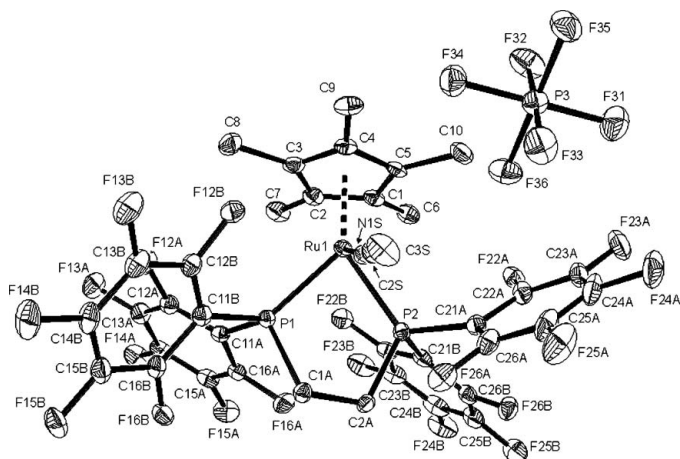


Figure 1

A view of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

Experimental

The title complex was obtained from the reaction of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{NCMe})_3]\text{PF}_6$ with $(\text{C}_6\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2$ in dichloromethane (10 ml) gave a yellow-green solution from which a small number of yellow crystals of (I) were obtained by cooling the reaction mixture to 273 K.

Crystal data

$[\text{Ru}(\text{C}_{10}\text{H}_{15})(\text{C}_{26}\text{H}_4\text{F}_{20}\text{P}_2)(\text{C}_2\text{H}_3\text{N})]\text{PF}_6$
 $M_r = 1180.55$
 Monoclinic, $P2_1/n$
 $a = 12.5380 (9) \text{ \AA}$
 $b = 10.6157 (8) \text{ \AA}$
 $c = 31.760 (2) \text{ \AA}$
 $\beta = 98.062 (2)^\circ$
 $V = 4185.4 (5) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.874 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 5351 reflections
 $\theta = 4\text{--}50^\circ$
 $\mu = 0.64 \text{ mm}^{-1}$
 $T = 153 (2) \text{ K}$
 Needle, red
 $0.42 \times 0.10 \times 0.08 \text{ mm}$

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.775$, $T_{\text{max}} = 0.951$
 37499 measured reflections

9479 independent reflections
 5575 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.098$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -16 \rightarrow 16$
 $k = -13 \rightarrow 13$
 $l = -41 \rightarrow 40$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.109$
 $S = 0.94$
 9479 reflections
 627 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0422P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.67 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.83 \text{ e \AA}^{-3}$

H atoms were added in idealized positions and a riding model with fixed displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the parent atom ($1.5U_{\text{eq}}$ for methyl H atoms)].

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2002); data reduction: SHELXTL (Bruker, 2001) and SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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