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Key indicators

 Single-crystal X-ray study
 T = 120 K
 Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
 Disorder in solvent or counterion
 R factor = 0.030
 wR factor = 0.074
 Data-to-parameter ratio = 44.8

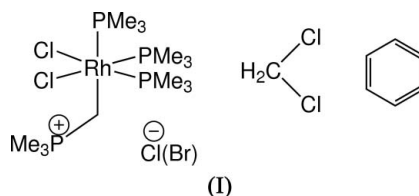
 For details of how these key indicators were
 automatically derived from the article, see
<http://journals.iucr.org/e>.

fac-Dichlorotrakis(trimethylphosphine)- (trimethylphosphoniomethyl)rhodium(III) chloride/bromide dichloromethane benzene solvate

 The title complex, $[\text{RhCl}_2(\text{C}_4\text{H}_{11}\text{P})(\text{C}_3\text{H}_9\text{P}_3)](\text{Br}_{0.12}/\text{Cl}_{0.88})\cdot\text{CH}_2\text{Cl}_2\cdot\text{C}_6\text{H}_6$, has an ionic structure with *fac*-octahedral coordination of Rh^{III} in the cation. The anion is a mixture of Cl and Br in a 7:1 ratio.

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Comment

 The *fac*- $[\text{RhCl}_2(\text{CH}_2\text{PMe}_3)(\text{PMe}_3)_3]\text{Cl}$ salt has been prepared by Marder, Fultz *et al.* (1987) *via* a reaction of dichloromethane (DCM) with a 16-electron Rh^{I} complex $[\text{RhCl}(\text{PMe}_3)_3]$, and characterized by an X-ray crystal structure analysis of its DCM monosolvate, (*Ia*). We report here a solvated mixed-anion salt analogue of (*Ia*), obtained as a by-product during our ongoing study of PMe_3 -containing rhodium-acetylide complexes (Zhu *et al.*, 2006; Rourke *et al.*, 2002; Rourke *et al.*, 1995, 2001; Fyfe *et al.*, 1991; Chow *et al.*, 1989; Zargarian *et al.*, 1989; Marder, Zargarian *et al.*, 1987).

 The asymmetric unit of (I) comprises one *fac*- $[\text{RhCl}_2(\text{CH}_2\text{PMe}_3)(\text{PMe}_3)_3]^+$ cation, one halide anion and one DCM molecule in general positions, and two half-molecules of benzene; the benzene rings lie on crystallographic inversion centres. The cation has a somewhat distorted *fac*-octahedral geometry, very similar to that of (*Ia*). The $\text{Rh}-\text{P}$ bond *trans* to Cl is *ca.* 0.1 \AA longer than the other two, indicating the strong *trans* influence of a σ -bonded C atom in comparison with the chloride ligands. The $\text{P1}-\text{Me}$ bond lengths in the phosphoniomethyl ligand average 1.793 (2) \AA , appreciably shorter than in the phosphine ligands [1.804 (2)–1.837 (2) \AA , average 1.818 (9) \AA].

 Initial treatment of the anion as purely Cl^- gave high residual electron density of 2.4 e \AA^{-3} and $R[\text{F}^2 > 2\sigma(\text{F}^2)] = 0.037$. Modelling the disorder between Cl^- and Br^- in a 7:1 ratio resulted in satisfactory refinement. The source of bromide was found to be an impure commercial sample of $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$, which contained a small amount of the bromo analogue, as confirmed later by spectroscopic analysis.

 The anion is surrounded by ten H atoms at distances of 2.74–3.17 \AA (2.70–3.09 \AA using C–H distances normalised to the neutron diffraction value of 1.08 \AA). The DCM molecules form hydrogen bonds to both chloro ligands of the cation, especially Cl1 (adjusted $\text{H}\cdots\text{Cl}$ distances of 2.54 and 2.74 \AA).

Experimental

Conversion of impure commercial $\text{RhCl}_3 \cdot 2\text{H}_2\text{O}$ to $\text{Rh}(\text{PPh}_3)_3\text{Cl}/\text{Br}$ was followed by reaction with PMe_3 (Jones *et al.*, 1980) which gave the salt, $[\text{Rh}(\text{PMe}_3)_4]^+ \cdot \text{Cl}^-/\text{Br}^-$, which subsequently reacted with DCM solvent to give a very small amount of the title complex. The absence of bromide at the rhodium centre shows that both halides which are coordinated to the metal originate from the DCM and that little, if any, exchange occurs between these and the outer-sphere halide ion.

Crystal data

$[\text{RhCl}_2(\text{C}_4\text{H}_{11}\text{P})(\text{C}_3\text{H}_9\text{P})_3]^-$
 $(\text{Br}_{0.12}/\text{Cl}_{0.88}) \cdot \text{CH}_2\text{Cl}_2 \cdot \text{C}_6\text{H}_6$
 $M_r = 696.17$
 Monoclinic, $P2_1/c$
 $a = 16.949$ (3) Å
 $b = 10.3396$ (15) Å
 $c = 18.424$ (3) Å
 $\beta = 105.07$ (1)°
 $V = 3117.7$ (9) Å³
 $Z = 4$

$D_x = 1.483$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 999 reflections
 $\theta = 12.1$ – 23.7 °
 $\mu = 1.34$ mm⁻¹
 $T = 120$ (2) K
 Block, colourless
 $0.40 \times 0.19 \times 0.13$ mm

Data collection

Bruker SMART 6K CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
 $T_{\min} = 0.685$, $T_{\max} = 0.845$
 55018 measured reflections

13203 independent reflections
 10300 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$
 $\theta_{\max} = 35.0$ °
 $h = -26 \rightarrow 26$
 $k = -16 \rightarrow 16$
 $l = -29 \rightarrow 29$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.074$
 $S = 1.04$
 13203 reflections
 295 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 0.4573P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 1.23$ e Å⁻³
 $\Delta\rho_{\min} = -0.82$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{C14}-\text{H141} \cdots \text{Cl1}$	0.99	2.60	3.498 (2)	150
$\text{C14}-\text{H142} \cdots \text{Cl2}^i$	0.99	2.81	3.6455 (19)	142

Symmetry code: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$.

Methyl groups were treated as rigid bodies ($\text{C}-\text{H} = 0.98$ Å) rotating around the $\text{P}-\text{C}$ bonds, with a common refined U_{iso} value for the three H atoms. Other H atoms were treated as riding on the attached C atoms [$\text{Csp}^2-\text{H} = 0.95$ Å and $\text{Csp}^3-\text{H} = 0.99$ Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.3U_{\text{eq}}(\text{C})$, respectively]. The maximum electron-density peak lies 0.05 Å from the Rh atom

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve

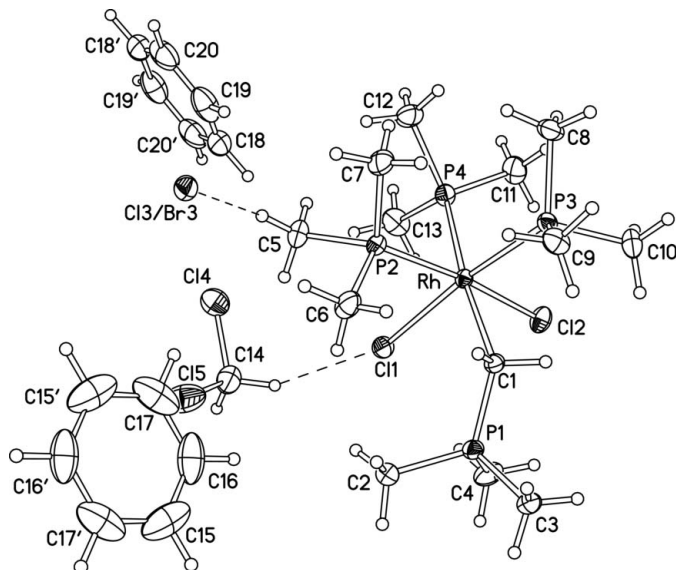


Figure 1

The molecular structure of (I). Atomic displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds.

structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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