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# Preparation and characterization of rhodium(III) complexes containing 1,1,1-tris(dimethylphosphinomethyl)ethane (tdmme). Structures of $[RhX_3(tdmme)]$ ($X = Cl$, Br or I), $[Rh(NH_3)_3(tdmme)]^{3+}$ and $[\{Rh(tdmme)\}_2(\mu\text{-}X)_3]^{3+}$ ($X = Cl$ or OH) in the solid state and in solution

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Several new rhodium(III) complexes containing a tripodal tridentate phosphine, $MeC(CH_2PMe_2)_3$ (tdmme), have been synthesized and their structures investigated both in the solid state and in solution. Single-crystal X-ray analyses revealed the smaller steric requirement and stronger *trans* influence of tdmme than those of the phenyl-substituted analogue, $MeC(CH_2PPh_2)_3$ (tdpme). The long Rh–Cl bond in the mononuclear trichloro complex, $[RhCl_3(tdmme)]$ **1**, due to the strong *trans* influence of tdmme, made the complex reactive in water; the structure of **1** in solution and its reaction products with some acids or bases were characterized. The triply chloro-bridged dinuclear complex, $[\{Rh(tdmme)\}_2(\mu\text{-}Cl)_3][BF_4]_3$, also showed structural change in water, while the mononuclear triammine complex, $[Rh(NH_3)_3(tdmme)][BF_4]_3$, and the triply hydroxo-bridged dinuclear complex, $[\{Rh(tdmme)\}_2(\mu\text{-}OH)_3][BF_4]_3$, were stable. The absorption spectra of the tdmme complexes suggested a stronger ligand field of tdmme to the rhodium(III) centre than those of corresponding didentate diphosphine ligands, in accordance with the short Rh–P bond lengths in **1** found by single-crystal X-ray analysis.

The chemistry of transition-metal complexes with the tripodal tridentate phosphine ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (tdpme) has been developed in the last two decades.[1] In particular, complexes containing a 'M(tdpme)' fragment (M = Re,[2,3] Ru,[4–6] Rh[7–11] or Ir[11–18]) have been studied extensively because they have shown interesting structural[1–3,15,18–22] and physical properties,[17,18] in addition to fascinating reactivities toward organic molecules[9–13] or metal cluster compounds.[6–8] In contrast, there have been only a limited number of complexes reported for 1,1,1-tris(dimethylphosphinomethyl)ethane (tdmme),[23–33] although it is known that the dimethylphosphino donor group has higher basicity and less steric bulk than the corresponding diphenylphosphino analogue. Further, the complexes with methyl-substituted phosphines would be more soluble in polar organic solvents and water than those of the corresponding phenyl-substituted phosphines, and hence would be advantageous to studies on the structure and reactivity in such solvents. In order to compare the structural features and reactivities of the tdmme complexes with those of the corresponding tdpme complexes we are investigating the syntheses, structures and reactivities of transition-metal complexes with tdmme. As the continuation of our preceding studies on the cobalt(III)[31,32] and iron(II)[33] complexes, we will describe here, the preparation of rhodium(III) complexes with tdmme and their structures both in the solid state and in solution. The complexes reported are the first examples of tdmme complexes of platinum-group metals {the complex $[RhMe_3(tdmme)]$ has been mentioned[34] but not fully reported to our knowledge}.

## Experimental

The ligand tdmme was prepared according to the literature[30] and handled under an atmosphere of argon until it formed air-stable rhodium(III) complexes. The $^{31}P$ NMR spectra were recorded at 23 °C on a JEOL GX400, GSX270 or EX270 spectrometer, using 85% $H_3PO_4$ as external reference, infrared spectra on a Perkin-Elmer System 2000 FT-IR or a Hitachi 270-30 spectrophotometer by the Nujol-mull method using polyethylene film or KRS-5 disc, and UV/VIS absorption spectra on a Hitachi U-3410 spectrophotometer at room temperature.

### Complex preparation

The complex *trans*-$[RhCl_2(py)_4]Cl{\cdot}5H_2O$ (py = pyridine) was prepared by the method described previously.[35]

**Trichloro[1,1,1-tris(dimethylphosphinomethyl)ethane]-rhodium(III) 1.** To a suspension of *trans*-$[RhCl_2(py)_4]Cl{\cdot}5H_2O$ (4.50 g, 7.31 mmol) in dry pyridine (15 cm$^3$) was added tdmme (2.01 g, 7.97 mmol) dropwise with stirring. The mixture was refluxed for 20 h and then cooled in an ice-bath for 30 min. The resulting white precipitate was filtered off, washed with dry pyridine (10 cm$^3$) and diethyl ether (50 cm$^3$), and then dried *in vacuo*. The crude product was dissolved in hot methanol (60 °C, 300 cm$^3$) and filtered while hot. The filtrate was cooled to room temperature and evaporated to *ca.* 10 cm$^3$ under reduced pressure, giving white needle *crystals* of

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complex **1**. These crystals were filtered off, washed with cold methanol (10 cm$^3$) and dried *in vacuo* (2.42 g, 71.7%) (Found: C, 28.65; H, 5.60. $C_{11}H_{27}Cl_3P_3Rh$ requires C, 28.65; H, 5.90%). $\tilde{\nu}_{max}$/cm$^{-1}$ (Nujol): 1300s, 1290s, 1224s, 1128m, 1096s, 1064m, 940vs, 916s, 892s, 862m, 854m, 840m, 814m, 746s, 722m, 696s, 582m (br), 494s, 438s, 374s, 336s, 318m, 287s, 277vs, 247vs, 230s, 213s, 159s and 142s.

**Tribromo[1,1,1-tris(dimethylphosphinomethyl)ethane]-rhodium(III) 2.** Hydrobromic acid (47%, 2.0 cm$^3$) was added to an aqueous solution (2.0 cm$^3$) of complex **1** (250 mg, 0.542 mmol), and the pale yellow clear mixture allowed to stand overnight. Pale yellow prismatic *crystals* were deposited, which were filtered off and dried *in vacuo* (225 mg, 69.8%) (Found: C, 22.4; H, 4.65. $C_{11}H_{27}Br_3P_3Rh$ requires C, 22.2; H, 4.55%). $\tilde{\nu}_{max}$/cm$^{-1}$ (Nujol): 490s, 437s, 371s, 338s, 304m, 238m, 218m, 170vs, 155vs and 127s.

**Triiodo[1,1,1-tris(dimethylphosphinomethyl)ethane]-rhodium(III) 3.** Hydroiodic acid (57%, 2.0 cm$^3$) was added dropwise with stirring to an aqueous solution (2.0 cm$^3$) of complex **1** (250 mg, 0.542 mmol), giving an orange precipitate immediately. The precipitate was filtered off and dried *in vacuo*. The crude product was dissolved in acetonitrile (500 cm$^3$), and the filtered solution concentrated to *ca.* 5 cm$^3$ by evaporation under reduced pressure. The orange *microcrystalline solid product* was filtered off, washed with dichloromethane (5 cm$^3$) and dried *in vacuo* (324 mg, 81.2%) (Found: C, 18.15; H, 3.75. $C_{11}H_{27}I_3P_3Rh$ requires C, 17.95; H, 3.70%). $\tilde{\nu}_{max}$/cm$^{-1}$ (Nujol): 486s, 436s, 368s, 334s, 303m, 275m, 236m, 150s, 130vs and 110vs.

**Tri-μ-chloro-bis{[1,1,1-tris(dimethylphosphinomethyl)-ethane]rhodium(III)} tris(tetrafluoroborate) 4a.** Tetrafluoroboric acid (6.3%, 0.5 cm$^3$) was added dropwise with stirring to an aqueous solution (2 cm$^3$) of complex **1** (382 mg, 0.828 mmol), giving a white precipitate within a few minutes. After stirring for 2 h the precipitate was filtered off and dried *in vacuo*. Recrystallization of the product from the minimum volume of hot water (80 °C) yielded colourless prismatic *crystals*, which were filtered off and dried in air (289 mg, 64.8%) (Found: C, 24.5; H, 4.70. $C_{22}H_{54}B_3Cl_3F_{12}P_6Rh_2$ requires C, 24.55; H, 5.05%). $\tilde{\nu}_{max}$/cm$^{-1}$ (Nujol): 1462vs, 1414m, 1378s, 1312s, 1302s, 1236s, 1050vs (br) ($BF_4^-$), 954s, 935s, 916s, 900s, 860m, 822m, 744m, 698m, 520m ($BF_4^-$), 494m and 436m.

**Tri-μ-chloro-bis{[1,1,1-tris(dimethylphosphinomethyl)-ethane]rhodium(III)} tris(perchlorate) 4b. CAUTION:** this perchlorate salt is potentially explosive and should be handled carefully. To perchloric acid (10%, 5 cm$^3$) was added complex **1** (400 mg, 0.867 mmol) with stirring. From the clear colourless solution a white precipitate was obtained within a few minutes. After stirring for 1 h the precipitate was filtered off and dried *in vacuo*. Recrystallization from the minimum volume of hot water (80 °C) yielded colourless needle *crystals* (330 mg, 68.3%). Owing to the danger of explosion the elemental analysis of this salt was not performed, but a structure similar to that of **4a** was suggested by the IR spectrum. $\tilde{\nu}_{max}$/cm$^{-1}$ (Nujol): 1460vs, 1412m, 1378s, 1312s, 1300s, 1234s, 1094vs (br) ($ClO_4^-$), 954s, 934s, 916s, 898s, 858m, 822m, 744m, 698m, 622s ($ClO_4^-$), 494m and 436m.

**Triammine[1,1,1-tris(dimethylphosphinomethyl)ethane]-rhodium(III) tris(tetrafluoroborate) 5a.** To a mixture of an aqueous solution (1.0 cm$^3$) of complex **1** (300 mg, 0.850 mmol) and concentrated aqueous ammonia (28%, 2.0 cm$^3$) was added an aqueous solution (1.0 cm$^3$) of $NaBF_4$ (500 mg, 4.55 mmol). The clear colourless solution was allowed to stand for 2 d. Colourless prismatic *crystals* of complex **5a**·$n$$H_2O$ were deposited and collected by filtration. Since the crystals were highly efflorescent the elemental analysis and spectroscopic measurements were performed with the sample completely dried *in vacuo* (336 mg, 59.6%) (Found: C, 20.0; H, 5.20; N, 6.25. $C_{11}H_{39}B_3F_{12}N_3P_3Rh$ requires C, 19.8; H, 5.45; N, 6.30%). $\tilde{\nu}_{max}$/cm$^{-1}$ (Nujol): 3344vs, 3292vs, 3224vs, 1636s (br), 1360vs, 1326vs, 1290s, 1238s, 940vs, 912s, 894s, 858m, 822m, 804s, 768s, 744s (br), 698m, 534vs, 493s, 432s, 365s, 340s, 285s (br) and 218s (br).

**Tri-μ-hydroxo-bis{[1,1,1-tris(dimethylphosphinomethyl)ethane]rhodium(III)} tris(tetrafluoroborate) 6a.** Moist silver oxide was prepared from sodium hydroxide (300 mg, 7.50 mmol) and silver nitrate (680 mg, 4.00 mmol) in water (20 cm$^3$), washed with water until free of NaOH,[36] and then added to an aqueous solution (50 cm$^3$) of complex **1** (461 mg, 1.00 mmol). The mixture was stirred for 4 h in the dark and filtered. The filtrate was concentrated to 5 cm$^3$ by evaporation under reduced pressure, and an aqueous solution (5 cm$^3$) of $NaBF_4$ (3.00 g) added to the concentrate to give a white precipitate, which was filtered off and dried *in vacuo*. The crude precipitate was dissolved in hot water (80 °C, 15 cm$^3$), filtered while hot, and cooled in a refrigerator to form colourless prismatic *crystals* of complex **6a**·4$H_2O$. The elemental analyses and spectroscopic measurements were performed with the sample completely dried *in vacuo* (383 mg, 75.0%) (Found: C, 25.45; H, 5.20. $C_{22}H_{57}B_3F_{12}O_3P_6Rh_2$ requires C, 25.85; H, 5.60%).

## Crystallography

Pale yellow prismatic crystals of complex **1** were obtained by diffusion of acetonitrile vapour into a concentrated aqueous solution, colourless prismatic crystals of **4a** by slow cooling of a saturated aqueous solution at 40 °C to room temperature. A crystal of each suitable for X-ray diffraction study was glued on top of a glass fibre with epoxy resin. A colourless prismatic crystal of **6a**·4$H_2O$ was obtained by a similar method to that of **4a** and sealed in a glass capillary tube to prevent efflorescence. The X-ray intensities were measured at 23 °C with graphite-monochromated Mo-Kα radiation ($\lambda$ = 0.710 73 Å) on an automated Rigaku four-circle diffractometer AFC-5 (for **1** and **4a**) or AFC-5R (for **6a**·4$H_2O$). The ω-scan technique was employed at a scan rate of 4° min$^{-1}$. Final lattice parameters were determined by least-squares treatment using setting angles of 25 reflections in the range $25 \leqslant 2\theta \leqslant 30°$. Three standard reflections were monitored every 150 and showed no serious decomposition $[|F_o|/(|F_o|)_{initial} > 98\%]$. The intensities collected for a $(+h,+k,+l)$ octant at $2\theta \leqslant 60°$ were corrected for Lorentz-polarization effects, and absorption corrections were made by the Gauss numerical integration method.[37] The observed independent reflections with $|F_o| > 5\sigma(|F_o|)$ were used for the structural calculations.

The structures were solved by the usual heavy-atom method. The function $\Sigma w||F_o| - |F_c||^2$, with $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$, was minimized by the full-matrix method using anisotropic thermal parameters for all non-hydrogen atoms (refined on $F$). Hydrogen atoms located by Fourier-difference syntheses were included in the structural calculations with isotropic thermal parameters. The other hydrogens of complexes **1** and **4a** were introduced at the theoretical positions and fixed in the refinements, but those of **6a**·4$H_2O$ were not included in the calculations. Complex neutral-atom scattering factors[38] were used. All the calculations were carried out on a Fujitsu IX-4 workstation using the XTAL 3.2 software package.[39]

**Complex 1.** Systematic absences ($h0l$, $h + l$ odd; $hk0$, $k$ odd) indicated the space group $P2_1nb$ or $Pmnb$. The Patterson function could be analysed based only on the former space group. The structure model with $P2_1nb$ cannot be transferred to that of the centrosymmetric space group $Pmnb$ because there is only one independent molecule ($Z$ = 4) and it has neither a centre of symmetry nor a mirror plane (Fig. 1). The *R* factors did not alter significantly for the inverted structure model ($x,y,z \longrightarrow -x,-y,-z$), therefore the polar direction of the *a* axis could not be assigned.

**Complexes 4a and 6a·4H$_2$O.** For both crystals systematic absences (0*kl*, *k* + *l* odd; *hk*0; *h* odd) indicated the space group $Pn2_1a$ or *Pnma*. Assuming the centrosymmetric space group *Pnma* the structures could be solved reasonably. There was a crystallographically imposed plane of symmetry for each crystal, and three bridging Cl atoms of **4a** and three bridging O atoms of **6a**·4H$_2$O lay on the plane, respectively. One of the $BF_4^-$ anions of **4a** [B(2), F(5)–F(8)] was found on the symmetrical plane, and the F(7) and F(8) atoms were positionally disordered. In **6a**·4H$_2$O there were three positions for the oxygen atoms of hydrated water, O(4w), O(5w) and O(6w); atom O(4w) was on the plane of symmetry, and O(6w) relatively close to the plane, the distance O(6w)···O(6w′) being 1.87(6) Å. Therefore, O(6w) was treated as a positionally disordered atom. The total number of hydrated water molecules per dinuclear complex was determined to be four. These disorders of **4a** and **6a**·4H$_2$O did not disappear with the space group $Pn2_1a$.

Crystal data are summarized in Table 1, selected bond lengths and angles in Table 2.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/181.

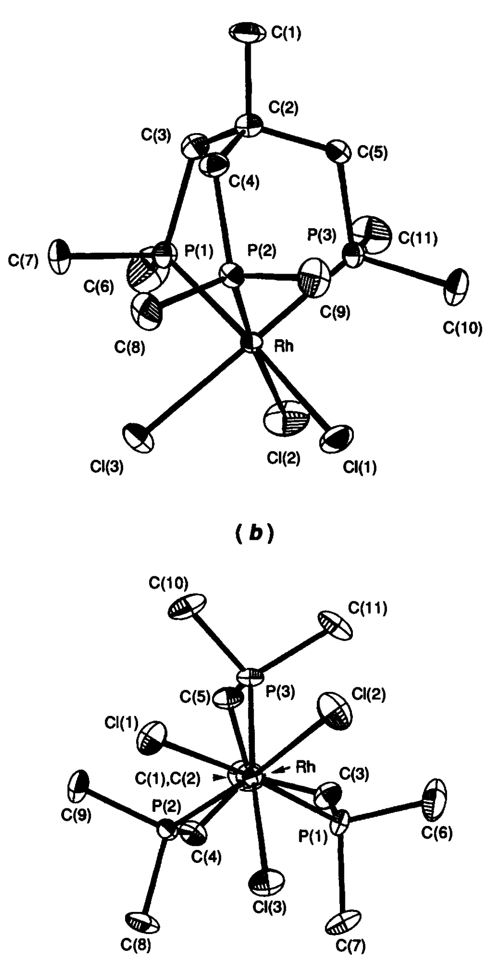


**Fig. 1** Perspective drawings of [RhCl$_3$(tdmme)] **1**: (*a*) a side view and (*b*) a view along a pseudo-$C_3$ axis

## Results and Discussion

### Synthesis and crystal structure of [RhCl$_3$(tdmme)] 1

The reaction of *trans*-[RhCl$_2$(py)$_4$]Cl·5H$_2$O with tdmme in a 1:1 molar ratio in dry pyridine gave a white precipitate. This was recrystallized either from hot methanol to give white needle crystals or from a mixture of water and acetonitrile to deposit pale yellow columnar crystals. The X-ray analysis revealed that the crystal is isomorphous to that of the analogous cobalt(III) complex, [CoCl$_3$(tdmme)],[32] and that the complex molecule has a mononuclear *facial* trichloro structure with the tripodal phosphine ligand, [RhCl$_3$(tdmme)] **1**. The perspective drawing of **1** is illustrated in Fig. 1. The co-ordination geometry around the Rh centre is nearly octahedral; three bite angles (P–Rh–P) of tdmme are close to a right angle, and three *trans* P–Rh–Cl bond angles are in the range 174.1–174.8°. All three arms of tdmme are twisted in the same direction [Fig. 1(*b*)]; the torsion angles of Rh–P–C–C(2) are in the range 24.3–27.6°.

The remarkable features of complex **1** are the Rh–P and Rh–Cl bond lengths; the Rh–P bond (average 2.254 Å) is one of the shortest in rhodium(III)–phosphine complexes,[40] while the Rh–Cl bond (average 2.444 Å) is one of the longest rhodium(III)–chloro (terminal) bonds.[40] The Rh–P (*trans* to Cl) bond in **1** is relatively shorter than those in the related rhodium(III)–mono- or di-dentate trialkylphosphine complexes, such as *fac*-[RhCl$_2$(CH$_2$PMe$_3$)(PMe$_3$)$_3$] (2.280 Å),[41] *cis*-[RhCl$_2$(dmpe)$_2$]PF$_6$ [2.291 Å; dmpe = 1,2-bis(dimethylphosphino)ethane] and *cis*-[RhCl$_2$(dmpp)$_2$]PF$_6$ [2.301 Å; dmpp = 1,3-bis(dimethylphosphino)propane].[35] The shortening of the Rh–P bond in **1** would result from reduction of steric crowding among the ligands around the Rh, in addition to the steric fitness and chelate effect of the tripodal phosphine ligand tdmme. The Rh–Cl (*trans* to P) bond in **1** is considerably longer than that in the structurally related complex, [RhCl$_3${(NC$_5$H$_4$)$_3$COH}]·MeOH (average 2.355 Å).[42] This elongation is due to the strong *trans* influence of tdmme ligand, the elongation being 0.06–0.12 Å (average 0.09 Å). In our previous study[35] it is reported that the elongations of the Rh–Cl (*trans* to P) bonds owing to the *trans* influences of dmpe and dmpp are 0.04–0.065 (average 0.06) and 0.06–0.09 (average 0.07 Å), respectively. Thus, it can be concluded that the *trans* influence of tdmme is stronger than those of dmpe and dmpp. The very weak Rh–Cl bond in **1** would be related to the structure and reactivity of **1** in solution as described below.

### Reaction of complex 1 in water and structural characterization of the products

Complex **1** is well soluble in water, slightly soluble in methanol and acetonitrile, and hardly soluble in other common organic solvents. Since the corresponding tdpme complex, [RhCl$_3$(tdpme)], is insoluble in water,[11] it is interesting to investigate the structure and reactivity of **1** in water.

Treatment of complex **1** with hydrobromic acid gave pale yellow crystals, and with hydroiodic acid gave orange microcrystals. These products were characterized to be [RhBr$_3$(tdmme)] **2** and [RhI$_3$(tdmme)] **3**, respectively, by elemental analysis and infrared spectroscopy. The infrared spectra of **2** and **3** were very similar to that of **1**, except the bands at 277 and 247 cm$^{-1}$ for **1**, 170 and 155 cm$^{-1}$ for **2**, 130 and 110 cm$^{-1}$ for **3**, which were reasonably assigned to ν(Rh–X).[43] In contrast, addition of tetrafluoroboric acid or perchloric acid to an aqueous solution of **1** gave a white precipitate of tetrafluoroborate or perchlorate salt of a triply chloro-bridged dinuclear complex, [{Rh(tdmme)}$_2$(μ-Cl)$_3$]$^{3+}$ **4**. The products obtained, **4a** and **4b**, afforded colourless prismatic and white needle crystals, respectively, by recrystallization from hot water. Since the infrared spectra of **4a** and **4b** coincided with each other except for the absorption bands due to the $BF_4^-$ and $ClO_4^-$ anions,[43] it is suggested that both **4a** and **4b** contain the

**Table 1** Crystallographic data for complexes **1**, **4a** and **6a**·4$H_2O$*

| | **1** | **4a** | **6a**·4$H_2O$ |
|---|---|---|---|
| Formula | $C_{11}H_{27}Cl_3P_3Rh$ | $C_{22}H_{54}B_3Cl_3F_{12}P_6Rh_2$ | $C_{22}H_{65}B_3F_{12}O_7P_6Rh_2$ |
| *M* | 461.52 | 1077.10 | 1093.82 |
| Crystal size/mm | 0.45 × 0.45 × 0.4 | 0.9 × 0.5 × 0.4 | 0.45 × 0.35 × 0.15 |
| Space group | $P2_1nb$ (alternative $Pna2_1$, no. 33) | *Pnma* (no. 62) | *Pnma* (no. 62) |
| $a$/Å | 13.549(1) | 17.741(3) | 18.584(5) |
| $b$/Å | 14.027(1) | 25.019(2) | 24.265(3) |
| $c$/Å | 9.400(2) | 9.538(3) | 10.037(5) |
| $U$/Å$^3$ | 1786.5(4) | 4234(2) | 4562(3) |
| $D_c$/Mg m$^{-3}$ | 1.72 | 1.69 | 1.60 |
| $F$(000) | 936 | 2160 | 2212 |
| μ(Mo-Kα)/mm$^{-1}$ | 1.66 | 1.27 | 1.02 |
| No. reflections measured | 2965 | 6860 | 7311 |
| Transmission factors | 0.476–0.608 | 0.528–0.716 | 0.727–0.848 |
| No. observed reflections | 2450 | 3778 | 2152 |
| $R,R'$ | 0.048, 0.074 | 0.052, 0.065 | 0.066, 0.083 |

* Details in common: orthorhombic; $Z = 4$; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$.

**Table 2** Selected bond lengths (Å), angles (°), non-bonded distances (Å) and dihedral angles (°) for complexes **1**, **4a** and **6a**·4$H_2O$

| | **1** | **4a** | **6a**·4$H_2O$ |
|---|---|---|---|
| Rh–P(1) | 2.248(3) | 2.259(2) | 2.235(4) |
| Rh–P(2) | 2.257(2) | 2.268(2) | 2.234(5) |
| Rh–P(3) | 2.254(3) | 2.258(2) | 2.246(5) |
| Rh–Cl(1) [Rh–O(1)] | 2.465(3) | 2.464(2) | [2.14(1)] |
| Rh–Cl(2) [Rh–O(2)] | 2.421(3) | 2.464(2) | [2.12(1)] |
| Rh–Cl(3) [Rh–O(3)] | 2.446(3) | 2.466(2) | [2.115(9)] |
| P(1)–Rh–P(2) | 89.0(1) | 89.86(8) | 88.5(2) |
| P(1)–Rh–P(3) | 88.4(1) | 88.37(7) | 89.7(2) |
| P(2)–Rh–P(3) | 89.85(9) | 88.96(8) | 87.9(2) |
| Cl(1)–Rh–Cl(2) [O(1)–Rh–O(2)] | 87.7(1) | 81.91(8) | [78.3(5)] |
| Cl(1)–Rh–Cl(3) [O(1)–Rh–O(3)] | 87.2(1) | 82.11(8) | [75.6(5)] |
| Cl(2)–Rh–Cl(3) [O(2)–Rh–O(3)] | 88.1(1) | 82.40(8) | [76.6(4)] |
| P(1)–Rh–Cl(1) [P(1)–Rh–O(1)] | 174.5(1) | 174.86(7) | [170.6(3)] |
| P(1)–Rh–Cl(2) [P(1)–Rh–O(2)] | 96.3(1) | 95.43(8) | [95.4(4)] |
| P(1)–Rh–Cl(3) [P(1)–Rh–O(3)] | 89.1(1) | 93.20(7) | [96.2(3)] |
| P(2)–Rh–Cl(1) [P(2)–Rh–O(1)] | 87.2(1) | 92.65(8) | [96.8(4)] |
| P(2)–Rh–Cl(2) [P(2)–Rh–O(2)] | 174.1(1) | 174.32(7) | [171.8(3)] |
| P(2)–Rh–Cl(3) [P(2)–Rh–O(3)] | 94.6(1) | 95.29(8) | [95.8(3)] |
| P(3)–Rh–Cl(1) [P(3)–Rh–O(1)] | 95.6(1) | 96.15(8) | [98.2(4)] |
| P(3)–Rh–Cl(2) [P(3)–Rh–O(2)] | 87.7(1) | 93.22(7) | [99.3(4)] |
| P(3)–Rh–Cl(3) [P(3)–Rh–O(3)] | 174.8(1) | 175.47(8) | [173.1(3)] |
| Rh–Cl(1)–Rh′ [Rh–O(1)–Rh′] | — | 81.35(9) | [87.3(6)] |
| Rh–Cl(2)–Rh′ [Rh–O(2)–Rh′] | — | 81.33(8) | [88.6(5)] |
| Rh–Cl(3)–Rh′ [Rh–O(3)–Rh′] | — | 81.25(9) | [88.8(5)] |
| Rh ··· Rh′ | — | 3.2114(8) | 2.958(1) |
| Rh–P(1)–C(3)–C(2) | 24.5(9) | 19.4(7) | 15(2) |
| Rh–P(2)–C(4)–C(2) | 24.3(9) | 24.9(8) | 18(2) |
| Rh–P(3)–C(5)–C(2) | 27.6(9) | 22.8(7) | 24(2) |

same cationic complex. The structure of **4a** was revealed by the single-crystal X-ray diffraction method, and a perspective view of the dinuclear complex cation is shown in Fig. 2.

When an aqueous solution of complex **1** was mixed with concentrated aqueous ammonia a triammine complex, $[Rh(NH_3)_3(tdmme)]^{3+}$ **5**, was formed and crystallized as the $BF_4^-$ salt **5a** by addition of a saturated aqueous $NaBF_4$ solution. The infrared spectrum showed absorption bands due to δ(N–Rh–N) [285m (br) cm$^{-1}$], the vibration based on the co-ordinated $NH_3$ [3344vs, 3292vs, 3224vs, 1636s (br), 1326vs (br) and 744s (br) cm$^{-1}$] and the vibration based on the $BF_4^-$ anion [1064vs (br) and 524 cm$^{-1}$].[43] The remaining bands were similar to those of **1**–**3**, indicating that the **5a** has also a mononuclear *facial*-triammine structure. In order to prepare a hydroxo complex of Rh(tdmme), **1** was treated with $Ag_2O$ in water. Concentration of the filtered reaction mixture did not give any crystalline material, but addition of $NaBF_4$ to the concentrate yielded white microcrystalline solids. The product was recrystallized from hot water to obtain colourless prismatic crystals, and the crystal structure determined by X-ray analysis as a triply hydroxo-bridged dinuclear complex, $[\{Rh(tdmme)\}_2(\mu\text{-}OH)_3][BF_4]_3\cdot 4H_2O$ **6a**·4$H_2O$. In Fig. 3 is shown a perspective view of the dinuclear complex cation, which is similar to the triply chloro-bridged one in **4a**.

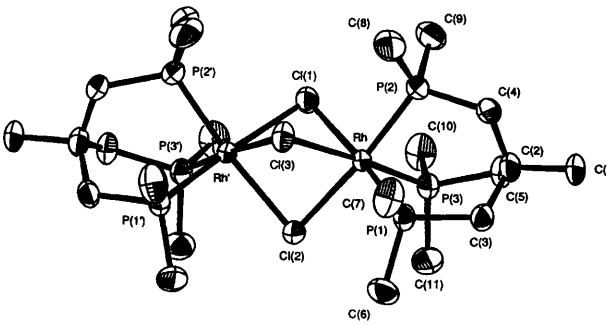


Fig. 2 Perspective drawing of the cationic complex $[\{Rh(tdmme)\}_2(\mu\text{-}Cl)_3][BF_4]_3$ **4a**

### Crystal structures of the dinuclear complexes 4a and 6a·4H₂O and comparisons of their structural parameters with those of the tdpme analogue

In complex **4a** (Fig. 2), there is a crystallographically imposed plane of symmetry, where the three bridging chloride ligands are in the plane. The tdmme ligand is co-ordinated to each Rh in a *facial* fashion, likewise in **1**; the Rh–P bond lengths (average 2.262 Å) and the bite angles of tdmme (average 89.1°) are comparable to those in **1**. Although the *trans* P–Rh–Cl bond angles in **4a** (average 174.9°) are very similar to those in **1**, the *cis* Cl–Rh–Cl angles are relatively smaller (average 82.14°) than those in **1** (average 87.7°).

The structural parameters of complex **4a**, particularly those in the trigonal bipyramid formed by two Rh and three bridging Cl atoms, reveal the steric characteristics of the tdmme ligand, as compared to those of $[\{Rh(tdpme)\}_2(\mu\text{-}Cl)_3][CF_3SO_3]_3$[44] (Table 3). The trigonal bipyramid in **4a** is relatively flatter than that in the tdpme complex; the Rh ··· Rh distance is relatively shorter (3.2114 Å in **4a** *vs.* 3.414 Å in the tdpme complex), the Rh–Cl–Rh angle narrower (average 81.31 *vs.* 87.3°) and the Cl–Rh–Cl angle wider (average 82.14 *vs.* 77.6°). These differences in structural parameters are due to the difference in steric requirements between the two tripod-type phosphine ligands (tdmme *vs.* tdpme) co-ordinated to both Rh in the dinuclear complexes. The two 'Rh(tdpme)' fragments in $[\{Rh(tdpme)\}_2(\mu\text{-}Cl)_3]^{3+}$ cannot be closer to each other because of the interligand steric repulsions between the phenyl

**Table 3** Comparison of the structural parameters (lengths in Å, angles in °)[a] between complex **4a** and $[\{Rh(tdpme)\}_2(\mu\text{-}Cl)_3][CF_3SO_3]_3$ [b]

| | **4a** | $[\{Rh(tdpme)\}_2(\mu\text{-}Cl)_3][CF_3SO_3]_3$ |
|---|---|---|
| Rh–P | 2.262 | 2.320 |
| Rh–Cl | 2.465 | 2.474 |
| P–Rh–P | 89.03 | 89.5 |
| Cl–Rh–Cl | 82.14 | 77.6 |
| *trans* P–Rh–Cl | 174.87 | 164.7 |
| *cis* P–Rh–Cl (larger) | 95.62 | 105.7 |
| (smaller | 93.02 | 88.4 |
| | 81.31 | 87.3(1) |
| Rh ··· Rh′ | 3.2114(8) | 3.414(4) |
| P–Rh ··· Rh′–P′ | 0 | 34.0(2) |

[a] Data without estimated standard deviations are averaged values. [b] Ref. 44.

substituents. In contrast, such steric repulsions are reduced in **4a** owing to the smaller methyl substituents on tdmme. The torsion angle P–Rh ··· Rh–P in **4a** is 0° (as required by the symmetrical plane), but that in the tdpme complex is 34.0°; the twisted structure of $[\{Rh(tdpme)\}_2(\mu\text{-}Cl)_3]^{3+}$ must also be related to such steric repulsions between the phenyl substituents. The fairly large difference in the Rh–P bond lengths (average 2.262 in **4a** *vs.* 2.320 Å in the tdpme complex) is attributable to the co-operative effect of the more basic and less bulky $PMe_2$ group compared with $PPh_2$. A similar difference in Rh–P bond lengths due to $PMe_2$ and $PPh_2$ groups has been found in *trans*(*Cl*,*Cl*), *cis*(*P*,*P*)-$[RhCl_2(edmp)_2]^+$ [average 2.252 Å; edmp = (2-aminoethyl)dimethylphosphine][45] and -$[RhCl_2(edpp)_2]^+$ [average 2.300 Å; edpp = (2-aminoethyl)-diphenylphosphine].[46] For the latter pair of complexes the difference in *trans* influences between $PMe_2$ and $PPh_2$ groups affects the *trans*-positioned Rh–N bond lengths (average 2.165 Å in the edmp and average 2.125 Å in the edpp complex).[45,46] However, there is no significant difference in the *trans*-positioned Rh-Cl bond lengths between **4a** (average 2.465 Å) and the tdpme complexes (average 2.474 Å). These Rh–Cl (bridge) bonds are originally very long, and may be little affected by the *trans* influence of the *trans*-positioned ligand.

In the crystal structure of complex **6a**·$4H_2O$ (Fig. 3) there are four water molecules of crystallization per dinuclear unit [O(6w) is positionally disordered]. All the water molecules hydrogen-bond to either bridging hydroxo ligands, $BF_4^-$ anions or other water molecules. The Rh–P bond lengths (average 2.238 Å) are slightly shorter than those in **1** and **4a**, and the bite angles of tdmme (average 88.7°) similar to those in **1** and **4a**. The Rh–O (bridge) bonds (average 2.12 Å) are shorter than the Rh–Cl (bridge) bonds in **4a**. This shorter bond for the bridging OH ligands results in a shortening of the Rh ··· Rh distance [2.958(1) Å]. Although the Rh ··· Rh distance is relatively shorter than those in other dinuclear rhodium(III) complexes, there seems to be no bonding interaction between the two Rh atoms in the complex cation, as supported by the spectroscopic measurements. In fact, the $^{31}P$ NMR spectrum of **6a** in $D_2O$ gives a doublet resonance, resulting from a coupling with only one Rh atom. Further, complex **6a** in the solid state and in solution gives no absorption bands in the visible region expected for metal–metal interaction.[47] The Rh–O (bridge) bond distances in **6a**·$4H_2O$ are much longer than those in $[\{Rh(tacn)(H_2O)\}_2(\mu\text{-}OH)_2][ClO_4]_4$ [average 2.041 Å; tacn = 1,4,7-triazacyclononane)],[48] indicating the stronger *trans* influence of tdmme than that of tacn.

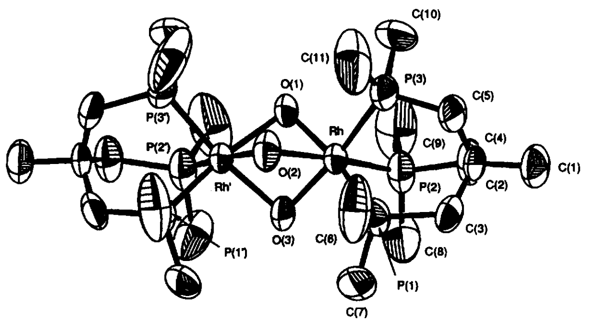
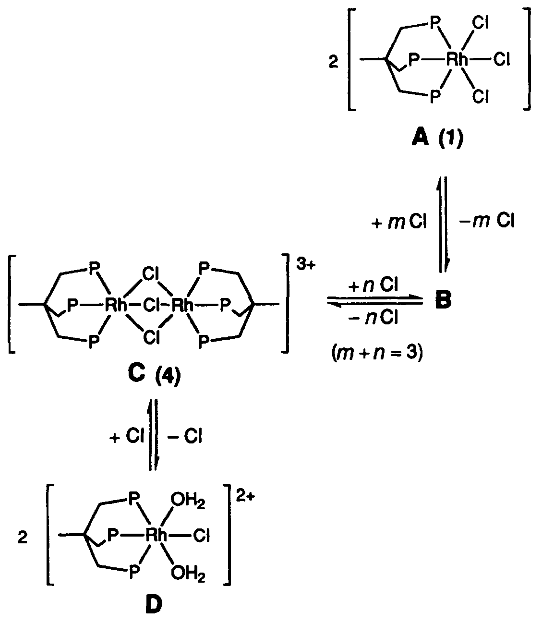


**Fig. 3** Perspective drawing of the cationic complex $[\{Rh(tdmme)\}_2(\mu\text{-}OH)_3][BF_4]_3$·$4H_2O$ **6a**.$4H_2O$



**Scheme 1**

## Structures of the complexes in solution

The $^{31}P$ NMR data for the complexes prepared are collected in Table 4. The triammine complex **5a** retains its mononuclear structure in water, giving a simple and sharp doublet peak at δ 12.5 [$^1J$(RhP) 91.9 Hz] in the $^{31}P$ NMR spectrum. In contrast, complexes **1** and **4a** display complicated equilibria due to the Rh–Cl bond dissociation and formation in water as shown in Scheme 1. Phosphorus-31 NMR spectroscopy is the most powerful method to reveal the equilibria in $D_2O$. Complex **1** in $D_2O$ (0.10 mol $dm^{-3}$) gave a $^{31}P$ NMR spectrum consisting of two kinds of doublet peaks (both due to the coupling between $^{31}P$ and $^{103}Rh$) at δ 22.1 [*J*(RhP) 101.3, **A**] and 33.2 [*J*(RhP) 103.8 Hz; **C**] and a very broad peak around δ 24.6 (**B**) [Fig. 4(*a*)]. When NaCl was added to the solution (1.0 mol $dm^{-3}$), the doublet peak **A** became larger and broader [Fig. 4(*b*)]. On the other hand, when the solution of **1** was diluted with $D_2O$ (0.010 mol $dm^{-3}$), resonances **A** and **B** diminished in intensity and another set of signals (**D**) appeared which consisted of a doublet of doublets at δ 32.1 [*J*(RhP) 106.8 and *J*(PP) 31.1 Hz] and a doublet of triplets at 24.0 [*J*(RhP) 101.3 and *J*(PP) 31.1 Hz] in the intensity ratio of 2:1 [Fig. 4(*c*)]. A saturated $D_2O$ solution of complex **4a** (3.3 mmol $dm^{-3}$) showed the same spectrum [Fig. 4(*d*)] as that of **1** in $D_2O$ (6.6 mmol $dm^{-3}$), consisting of resonances **C** and **D**. Complex **4a** showed the same spectral change as that for **1** in Fig. 4 with a change in the concentration of the $Cl^-$ ion. Doublet resonance **A** is assigned to the mononuclear trichloro complex **1**, since the signal intensity became larger as the concentration of $Cl^-$ increased, and since the simple resonance pattern must correspond to a highly symmetrical species {**1** shows only a sharp doublet peak at δ 18.6 [*J*(RhP) 100.8 Hz] in acetonitrile, retaining the mononuclear trichloro structure}. Doublet resonance **C**

**Table 4** Phosphorus 31 NMR data at room temperature

| Resonance | Solvent | Assignment | δ (*J*/Hz)[a] |
|---|---|---|---|
| A | $D_2O$ | **1** | 22.1 (d, 101.3) |
| B | $D_2O$ | Unassignable mixture | 24.6 (br) |
| C | $D_2O$ | **4a** | 33.2 (d, 103.8) |
| D | $D_2O$ | $[RhCl(tdmme)(H_2O)_2]^{2+}$ | 24.0 (dt, 101.3), 32.1 (dd, 106.8, 31.1) |
| E | $D_2O$ | **6a** | 24.7 (d, 103.8) |
| F | $D_2O$ | $[\{Rh(tdmme)\}_2(\mu\text{-}Cl)(\mu\text{-}OH)_2]^{3+}$ | 21.8 (dd, 99.8), 38.9 (dt, 112.9, 34.2) |
| G | $D_2O$ | $[\{Rh(tdmme)\}_2(\mu\text{-}Cl)_2(\mu\text{-}OH)]^{3+}$ | 22.3 (dt, 95.8), 34.6 (dd, 108.6, 33.0) |
|  | $D_2O$ | **7**[b] | 35.6 (d, 106.6) |
|  | $D_2O$ | **5a** | 12.5 (d, 91.9) |
|  | $CD_3CN$ | **1** | 18.6 (d, 100.8) |

[a] ${}^1J$(RhP) followed by ${}^2J$(PP). [b] The sample was prepared from complex **6a** by addition of aqueous $HBF_4$.

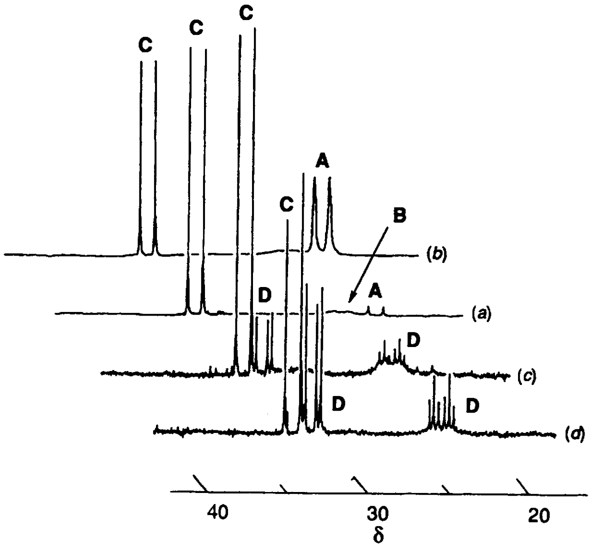


**Fig. 4** The ${}^{31}P$ NMR spectra of (*a*) a concentrated $D_2O$ solution of $[RhCl_3(tdmme)]$ **1** (0.10 mol $dm^{-3}$), (*b*) on addition of an excess of NaCl (1.0 mol $dm^{-3}$), (*c*) on diluting the solution with $D_2O$ ([**1**] = 0.010 mol $dm^{-3}$) and (*d*) a saturated $D_2O$ solution of $[\{Rh(tdmme)\}_2(\mu\text{-}Cl)_3][BF_4]_3$ **4a** (3.3 mmol $dm^{-3}$) at 23 °C

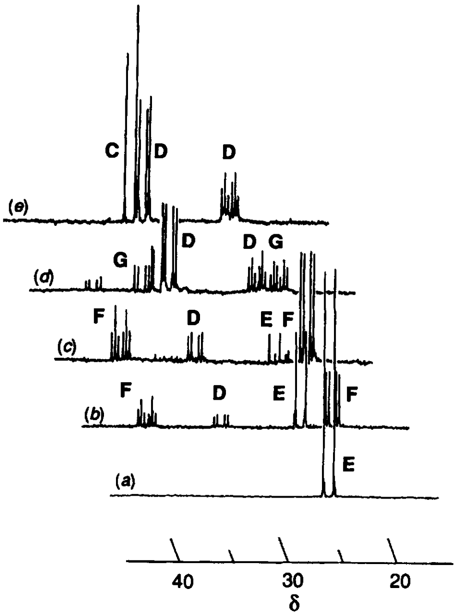
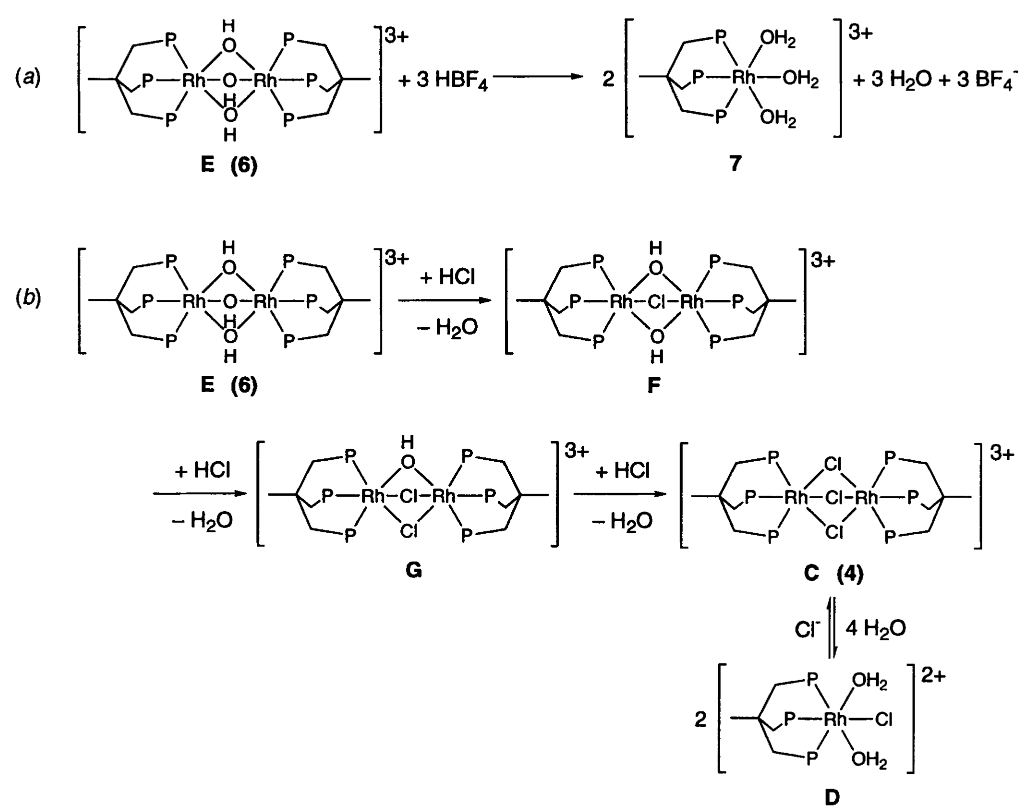


**Fig. 5** The ${}^{31}P$ NMR spectral changes of a saturated $D_2O$ solution of $[\{Rh(tdmme)\}_2(\mu\text{-}OH)_3][BF_4]_3$ **6a** on addition of HCl at 23 °C: (*a*) the spectrum in $D_2O$ (4.8 mmol $dm^{-3}$); (*b*) [**6a**] : [HCl] = 1 : 0.75, (*c*) 1 : 1.5, (*d*) 1 : 2.25 and (*e*) 1 : 3

coincides with that of **4a** in chemical shift and coupling constant, and is reasonably assigned to the triply chloro-bridged dinuclear species, $[\{Rh(tdmme)\}_2(\mu\text{-}Cl)_3]^{3+}$ **4**. The species corresponding to the very broad resonance **B** would be intermediates yielded during reactions from **1** to **4**, but we could not characterize them. The assignment of resonance **D** will be made after the NMR spectra of complex **6a** and its derivatives described below.

The triply hydroxo-bridged complex **6a** is stable in water; it gives a sharp doublet at δ 24.7 [*J*(RhP) 103.8 Hz, **E** in Fig. 5(*a*)] in the ${}^{31}P$ NMR spectrum, and the spectrum does not change upon addition of NaCl. However, the complex is unstable in tetrafluoroboric or hydrochloric acid. When an excess of tetrafluoroboric acid is added to a $D_2O$ solution of **6a**, the ${}^{31}P$ doublet is shifted to δ 35.6 [*J*(RhP) 106.6 Hz], which corresponds to $[Rh(tdmme)(H_2O)_3]^{3+}$ **7** [Scheme 2(*a*)]. In the case of the reaction with hydrochloric acid the triply chloro-bridged complex **4** is formed as the final product through intermediate products by a stepwise Rh–Cl bond formation as seen in Scheme 2(*b*). The reaction with hydrochloric acid was followed by means of ${}^{31}P$ NMR spectroscopy (Fig. 5). At first signals **F** were observed, and signals **D** and **G** appeared upon further addition of hydrochloric acid. Signals **F** or **G** consist of a doublet of doublets and a doublet of triplets in the intensity ratio of 2 : 1, and suggest that the corresponding species have two kinds of magnetically non-equivalent phosphorus atoms. It is reasonable to assume that the chemical shift values of the P atoms *trans* to the bridging OH and bridging Cl ligands are similar to those of the triply hydroxo-bridged complex **6** (signal **E**) and the triply chloro-bridged complex **4** (signal **C**), respectively. Therefore, signals **F** and **G** are assigned to $[\{Rh(tdmme)\}_2(\mu\text{-}Cl)(\mu\text{-}OH)_2]^{3+}$ and $[\{Rh(tdmme)\}_2(\mu\text{-}Cl)_2(\mu\text{-}OH)]^{3+}$, respectively. The spectral patterns and the intensity ratios satisfy the symmetry requirement for the complexes.

From the above discussion the P atom of the tdmme ligand *trans* to a bridging Cl or terminal $H_2O$ ligand gives the resonance around δ 35 as seen for complex **4** or **7**, while the P atom *trans* to a terminal Cl or bridging OH ligand resonates around δ 23 as mentioned before for **1** or **6a**. Resonance **D** consists of a doublet of doublets at δ 32.1 and a doublet of triplets at δ 24.0 with 2 : 1 intensity ratio. Since the corresponding species exists in a solution acidified with HCl and would not have a bridging OH ligand, the doublet of triplets peak can be assigned to a P atom *trans* to a terminal Cl ligand. The doublet of doublets is assignable to a P atom *trans* to either a bridging Cl or a terminal $H_2O$ ligand. The latter is more probable, because the intensity of resonance **D** increases with decreasing concentration of $Cl^-$ [Fig. 4(*d*) and Scheme 1]. Thus, the species giving resonance **D** is probably a mononuclear monochlorodiaqua complex, $[RhCl(tdmme)(H_2O)_2]^{2+}$. Schemes 1 and 2 summarize the reactions and equilibria of complexes **1**, **4a** and **6a** in $D_2O$ solutions as found by ${}^{31}P$ NMR spectral measurements.



Scheme 2

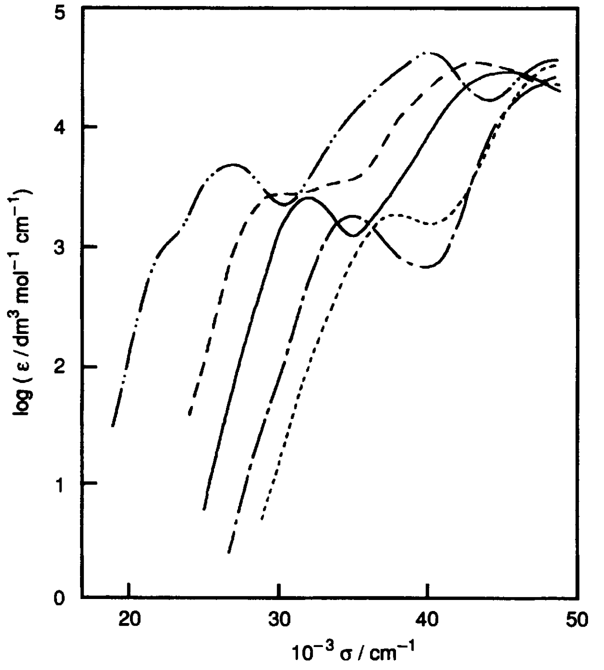


**Fig. 6** Absorption spectra of complex **1** in acetonitrile (——), **2** in acetonitrile (– – – –), **3** in acetonitrile (— · · —), **5a** in water (· · · ·) and **7** (prepared from **6a**) in 0.01 mol $dm^{-3}$ aqueous $HBF_4$ (— · — ·) at room temperature

**Table 5** Absorption spectral data for $[RhX_3(tdmme)]^{n+}$ (X = Cl, Br or I, $n = 0$; X = $NH_3$ and $H_2O$, $n = 3$) complexes

| Complex | Solvent | $10^{-3}\ \sigma/cm^{-1}$ (log $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) |
|---|---|---|
| **1** | MeCN | 31.86 (3.42), 45.22 (4.51) |
| **2** | MeCN | 29.8 (sh) (3.45), 33.6 (sh) (3.6), 42.93 (4.56) |
| **3** | MeCN | 22.6 (sh) (3.0), 27.00 (3.72), 40.01 (4.65) |
| **5a** | Water | 37.88 (3.29), 48.64 (4.61) |
| **7** | 0.01 mol $dm^{-3}$ aqueous $HBF_4$ | 34.88 (3.28), 48.08 (4.39) |

## Absorption spectra

In Fig. 6 the absorption spectra of mononuclear $[RhX_3(tdmme)]^{n+}$ ($n = 0$ for X = Cl, Br or I; $n = 3$ for X = $NH_3$ or $H_2O$) complexes are shown, and corresponding data are given in Table 5. For each complex, the first d–d band is clearly observed in the 25 000–40 000 $cm^{-1}$ region. The intensity of these bands [log ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) ≈ 3.5] are greater by an order of magnitude than those of related centrosymmetric rhodium(III)–phosphine complexes, such as *trans*-$[RhCl_2(L\text{–}L)_2]^+$ (L–L = dmpp or dmpe) [log ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) ≈ 2.5].[35] The high intensities of the present complexes are due to the lack of centrosymmetry. The trichloro complex **1** shows the d–d band at 31 860 $cm^{-1}$. The differences in position between this band and those of the other tdmme complexes are compatible with the expected values from the related complexes[31,49,50] and Shimura's semiempirical estimation.[51] From the absorption data for **1** and Shimura's parameters [$m_{Rh^{III}} = 1.56$, $\alpha([Rh^{III}P_3Cl_3]) = 0.94$ and $d(Cl^-) = 12\ 500\ cm^{-1}$],[49] the spectrochemical *d* value for the tdmme ligand, *d*(tdmme), is estimated to be 30 900 $cm^{-1}$. This value is relatively larger than those of dmpp [*d*(dmpp) = 25 300 $cm^{-1}$] and dmpe [*d*(dmpe) = 26 000 $cm^{-1}$], and accords well with the fact that the Rh–P bond lengths in **1** are shorter than those in the dmpp and dmpe complexes. The iodo complex **3** shows a shoulder at 22 600 $cm^{-1}$, owing to a spin-forbidden transition. For the halogeno complexes **1**–**3** there are very intense absorption bands [log ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) ≈ 4.5] around 40 000–45 200 $cm^{-1}$, which are due to the metal–halide charge-transfer bands.

## Conclusion

The smaller steric requirement and higher electron-donating property (stronger *trans* influence) of tdmme in the rhodium(III) complexes are demonstrated in this study. The characteristic properties of tdmme are closely related to the structure and reactivity of complex **1** in water, which result from easy dissociation of the Rh–Cl bond. The results described suggest that further interesting co-ordination and organometallic chemistry will be found for the platinum-group metal complexes of tdmme.

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