

## An organometallic Rh<sup>III</sup> complex with a distorted octahedral structure: (acetonitrile- $\kappa$ N)dimethyl(1,4,7-trimethyl-1,4,7-triazacyclononane- $\kappa^3$ N,N',N'')rhodium(III) tetraphenylborate

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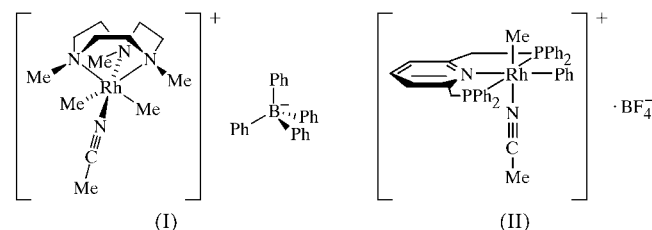
In the title compound,  $[\text{Rh}(\text{CH}_3)_2(\text{C}_2\text{H}_3\text{N})(\text{C}_9\text{H}_{21}\text{N}_3)](\text{C}_{24}\text{H}_{20}\text{B})$ , the geometry around the Rh<sup>III</sup> centre is distorted octahedral, with elongated Rh—N bonds *trans* to the metal-bonded methyl groups. The metal-containing cations are located in channels formed by an anionic supramolecular mesh, in which aromatic  $\pi$ – $\pi$  interactions between anionic  $[\text{B}(\text{Ph})_4]^-$  units play a major role.

### Comment

Recent years have seen an increasing interest in hard non- $\pi$ -interacting ligands for organometallic and inorganic coordination compounds, azacrown compounds being one group of interest (Chaudhuri & Wieghardt, 1987; Reichenbach-Klinke & König, 2002). In this respect, the Cn\* ligand present in the title compound, (I)  $[\text{Cn}^*$  is 1,4,7-trimethyl-1,4,7-triazacyclononane, according to the notation suggested by Flood *et al.* (2000)], represents a six-electron, and thus isoelectronic, alternative to the more conventional ligand systems, such as cyclopentadienyl (Cp and Cp\*;  $\eta^5\text{-C}_5\text{R}_5$ , R = H or Me), tris-(pyrazolyl)borate and tridentate phosphine ligands. Azacrown ligands are devoid of back-bonding capabilities, commonly yielding highly electron-rich metal centres (Flood, Sowa *et al.*, 1996).

A range of group 9 organometallic compounds have been shown to exhibit catalytic activity in a variety of reactions, such as C—H activation and olefin polymerization (for recent reviews, see Shilov & Shul'pin, 1997; Britovsek *et al.*, 1999). In some instances (*i.e.* polymerization), late-metal compounds might represent robust alternatives to early-metal catalysts,

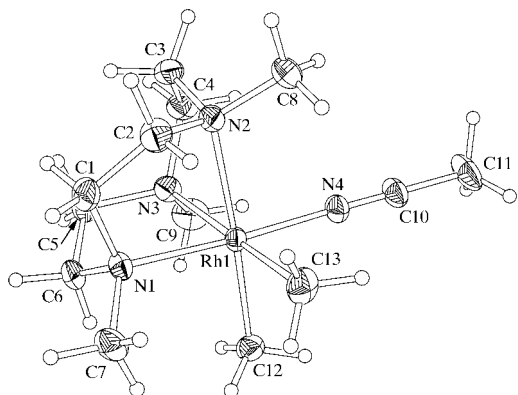
which tend to be highly sensitive towards polar functional groups, air and water. In fact,  $\text{Cn}^*\text{Rh}(\text{H}_2\text{O})(\text{Me})(\text{OH})^+$ , a complex closely related to (I), has been reported to polymerize ethene using water as solvent (Flood *et al.*, 1993).



Compound (I) was synthesized as part of a general study of electron-transfer-induced reactions of certain group 9 organometallic complexes (Fooladi & Tilset, 1997; Fooladi *et al.*, 2002, and references therein). Oxidation of the trimethyl complex  $\text{Cn}^*\text{RhMe}_3$ , previously reported by Flood, Wang *et al.* (1996), in acetonitrile solvent resulted in the spontaneous elimination of ethane, yielding a mixture of the two solvento complexes  $[\text{Cn}^*\text{Rh}(\text{Me})(\text{NCMe})_2]^{2+}$  and (I). The oxidatively induced simultaneous cleavage of two  $M$ —C bonds to yield ethane resembles the reactivity of other Rh<sup>III</sup> compounds  $[\text{Cp}^*\text{Rh}(\text{Me}_2\text{SO})\text{Me}_2$  and  $\text{Cp}^*\text{Rh}(\text{PPh}_3)\text{Me}_2]$ , but contrasts with the reactivity of related Ir compounds  $[\text{Cp}^*\text{Ir}(\text{Me}_2\text{SO})\text{Me}_2$  and  $\text{Cp}^*\text{Ir}(\text{PPh}_3)\text{Me}_2]$ , in which bond formation (Ir—Ir bond formation and insertion of Ir into a  $\text{Cp}^*\text{C—H}$  bond) is involved in the primary reactions, presumably due to the relatively different  $M$ —C and  $M$ —M bond strengths of second- versus third-row metals (Fooladi *et al.*, 2002).

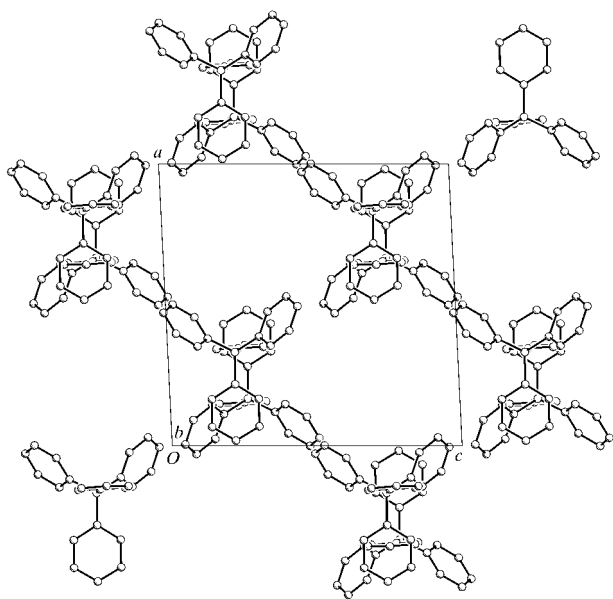
The structure of the Rh<sup>III</sup> cation in (I) is shown in Fig. 1. The three N—Rh—N bond angles within the Cn\* ligand exhibit a marked deviation from the ideal value of 90° for octahedral coordination, with values lying between 80.95 (3) and 83.08 (4)°. Also, the acetonitrile and the two Rh-bound methyl ligands are forced slightly towards one another, but less than for the cyclononane ligand. In both cases, the bond angles closely resemble those observed in the corresponding trimethyl analogue  $\text{Cn}^*\text{RhMe}_3$  [N—Rh—N 80.2 (2) and 80.0 (3)°, and Me—Rh—Me 87.6 (3) and 87.2 (5)°; Flood, Wang *et al.* (1996)]. A noticeable *trans* influence is reflected in the Rh—N(Cn\*) bond distances, as the two Rh—N bonds *trans* to the Rh-bound methyl groups are markedly elongated [2.2135 (9) and 2.2258 (9) Å] compared with the Rh—N bond *trans* to the acetonitrile ligand [2.0942 (8) Å]. This elongation also affects the Cn\* ligand, in that the N—Rh—N angle *trans* to the two methyl groups is smaller relative to the angles involving the shorter Rh—N bond, as would be expected according to a valence-shell electron-pair repulsion argument: a shorter bond results in more steric congestion close to the metal centre, thus resulting in a wider N—Rh—N bond angle.

To our knowledge, only one other X-ray crystal structure of a rhodium acetonitrile alkyl compound has been reported, namely that of the octahedral compound  $[\text{Rh}(\text{PNP})(\text{Ph})(\text{Me})(\text{NCMe})](\text{BF}_4)$ , (II), in which PNP is the tridentate ligand 2,6-bis(diphenylphosphanymethyl)pyridine (Hahn *et al.*,


**Figure 1**

A view of the molecular structure of the cation in (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

1999). The Rh–N bond of the acetonitrile ligand in (II) is slightly longer [2.142 (3) Å] than the corresponding bond in (I). This elongation is presumably due to a stronger *trans* influence of the methyl group compared with the Cn\* N atom. In (I), the end-on coordinated acetonitrile molecule exhibits a nearly linear arrangement [Rh1–N4–C10 = 176.31 (11)° and N4–C10–C11 = 179.08 (15)°], as observed in (II) and other related compounds (Hahn *et al.*, 1999, and references therein). Furthermore, a related tetranuclear Cn\* acetonitrile complex, [(Cn\*Rh(NCMe)Cl<sub>2</sub>)<sub>3</sub>Ag](OSO<sub>2</sub>CF<sub>3</sub>), was recently published (Südfeld & Sheldrick, 2000). Unfortunately, the characterization is insufficient for a detailed discussion of the structural properties of the compound.


**Figure 2**

A packing diagram for (I), viewed along the *b* axis, showing the anionic channel-forming network in which the metal-containing cations are confined.

As far as the crystal packing of (I) is concerned, it should be noted that numerous  $\pi$ – $\pi$ -stacking interactions between adjacent [B(Ph)<sub>4</sub>]<sup>–</sup> anions play a major role in the solid-state phase of this complex. These interactions are typically in the range 2.9–3.2 Å, where the distance is between the aromatic H atoms and the C atoms of neighbouring molecules. Furthermore, the [B(Ph)<sub>4</sub>]<sup>–</sup> anions form a mesh with channels when looking along the *b* axis in the crystal. The metal-containing cations are confined within these channels (Fig. 2).

## Experimental

The synthesis of (I) was carried out according to the procedure reported previously by Fooladi & Tislet (1997). A solution of HBF<sub>4</sub>·Et<sub>2</sub>O (51 mg, 0.31 mmol) in acetonitrile (1 ml) was added dropwise to a stirred solution of Cn\*RhMe<sub>3</sub> (100 mg, 0.31 mmol) in acetonitrile–dichloromethane (2:1, 6 ml) at 259 K. The mixture was warmed to ambient temperature and stirred for another 1.5 h, followed by removal of the solvent *in vacuo*. The resulting oily residue was washed with benzene (2 ml) in order to remove any remaining Cn\*RhMe<sub>3</sub>, dissolved in dichloromethane, filtered through Celite and recrystallized by slow addition of ether, giving [Rh(CH<sub>3</sub>)<sub>2</sub>–(C<sub>2</sub>H<sub>3</sub>N)(C<sub>9</sub>H<sub>21</sub>N<sub>3</sub>)](BF<sub>4</sub>) (yield 108 mg, 81%). The title compound, (I), was obtained by ion exchange with NaBPh<sub>4</sub>. The Rh complex (21 mg, 0.05 mol) was dissolved in acetonitrile (2 ml) and a solution of NaBPh<sub>4</sub> (17 mg, 0.05 mol) in acetonitrile was added with stirring. The mixture was stirred overnight, filtered through a frit, and the solvent removed *in vacuo*. The product was extracted with cold dichloromethane (2 ml). Crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of (I) in dichloromethane under a nitrogen atmosphere over a period of nine months.

### Crystal data

[Rh(CH<sub>3</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>N)(C<sub>9</sub>H<sub>21</sub>N<sub>3</sub>)]<sup>–</sup>  
(C<sub>24</sub>H<sub>20</sub>B)  
*M<sub>r</sub>* = 664.53  
Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 14.2560 (3) Å  
*b* = 16.6074 (3) Å  
*c* = 14.6189 (3) Å  
 $\beta$  = 92.789 (1)°  
*V* = 3457.0 (1) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.277 Mg m<sup>–3</sup>  
Mo *K*α radiation  
Cell parameters from 8192 reflections  
 $\theta$  = 2.3–40.4°  
 $\mu$  = 0.52 mm<sup>–1</sup>  
*T* = 150 (2) K  
Block, yellow  
0.6 × 0.4 × 0.3 mm

### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
Absorption correction: empirical (SADABS; Sheldrick, 1996)  
*T*<sub>min</sub> = 0.73, *T*<sub>max</sub> = 0.85  
55 207 measured reflections

20 545 independent reflections  
17 370 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.017  
 $\theta$ <sub>max</sub> = 40.4°  
*h* = –25 → 25  
*k* = –29 → 30  
*l* = –25 → 26

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.032  
*wR*(*F*<sup>2</sup>) = 0.077  
*S* = 1.21  
20 545 reflections  
388 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 1.41P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
( $\Delta/\sigma$ )<sub>max</sub> = 0.003  
 $\Delta\rho$ <sub>max</sub> = 0.74 e Å<sup>–3</sup>  
 $\Delta\rho$ <sub>min</sub> = –0.64 e Å<sup>–3</sup>

**Table 1**

Selected geometric parameters (Å, °).

|            |            |             |             |
|------------|------------|-------------|-------------|
| Rh1—N1     | 2.0942 (8) | Rh1—N4      | 1.9888 (9)  |
| Rh1—N2     | 2.2135 (9) | Rh1—C12     | 2.0941 (11) |
| Rh1—N3     | 2.2258 (9) | Rh1—C13     | 2.0633 (12) |
|            |            |             |             |
| N1—Rh1—N2  | 82.84 (3)  | N4—Rh1—C13  | 87.04 (5)   |
| N1—Rh1—N3  | 83.08 (4)  | C12—Rh1—C13 | 86.08 (5)   |
| N2—Rh1—N3  | 80.95 (3)  | Rh1—N4—C10  | 176.31 (11) |
| N4—Rh1—C12 | 88.33 (4)  | N4—C10—C11  | 179.08 (15) |

All H atoms were placed in calculated positions, with C—H distances in the range 0.95–0.99 Å, and refined isotropically riding on their parent atoms.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1087). Services for accessing these data are described at the back of the journal.

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