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(η^6-Benzene)bis(η^6-*p*-cymene)tri-μ-hydrido-μ_3-oxo-triruthenium hexafluorophosphate

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Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.007 Å
Disorder in main residue
R factor = 0.033
wR factor = 0.078
Data-to-parameter ratio = 14.1

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

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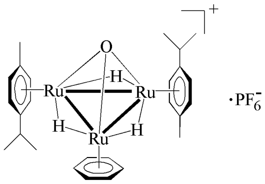
The trinuclear arene–ruthenium cluster cation $[H_3Ru_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_2(\mu_3\text{-}O)]^+$has been synthesized and crystallized as the hexafluorophosphate salt. The cation possesses a mirror plane through the (η^6-benzene)ruthenium moiety and the μ_3-O atom, and is disordered over a perpendicular mirror plane that includes the three Ru atoms.

Comment

In 1999 we found that the water-soluble cluster cation $[H_3Ru_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)]^+$ catalyses the hydrogenation of benzene to give cyclohexane under biphasic conditions (Faure *et al.*, 1999). Searching for more active derivatives, we synthesized the analogous trinuclear arene–ruthenium cluster cation $[H_3Ru_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_2(\mu_3\text{-}O)]^+$, where the two hexamethylbenzene ligands have been replaced by *p*-cymene ligands. The cation is found to be active for the hydrogenation of benzene under biphasic conditions. However, the metallic core appears to be unstable under catalytic conditions (catalyst/substrate ratio 1:1000, 383 K, 60 bar H_2, 4 h) giving rise to mono-, di-, and tetranuclear species, as observed by mass spectrometry. In order to rationalize the stability of the cation under catalytic conditions, a single-crystal structure analysis was performed.



(I)

The trinuclear arene–ruthenium cluster cation $[H_3Ru_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_2(\mu_3\text{-}O)]^+$, isolated and characterized as the hexafluorophosphate salt, (I), has been synthesized from the dinuclear precursor $[Ru_2(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_2(\mu_2\text{-}H)_3]^+$ (Bennett & Ennett, 1992), and the mononuclear complex $[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3]^{2+}$ (Stebler-Röthlisberger *et al.*, 1988) formed *in situ* from the dimer $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ (Bennett & Smith, 1974) in aqueous solution. The bond distances and angles are similar to those observed in other $[H_3Ru_3(\eta^6\text{-arene})_3(\mu_3\text{-}O)]^+$ cluster cations, *viz*. $[H_3Ru_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)]^+$ (Faure *et al.*, 1999), $[H_3Ru_3(\eta^6\text{-}C_6Me_4)_3(\mu_3\text{-}O)]^+$ (Meister *et al.*, 1994), $[H_3Ru_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_2Me_4)_2(\mu_3\text{-}O)]^+$ (Vieille-Petit *et al.*, 2003*a*), and $[H_3Ru_3(\eta^6\text{-}C_6H_5(CH_2)_2OH)(\eta^6\text{-}C_6Me_6)_2(\mu_3\text{-}O)]^+$ (Vieille-Petit *et al.*, 2003*b*).

The metal core consists of three Ru atoms, with Ru–Ru distances in accordance with a metal–metal single bond. The

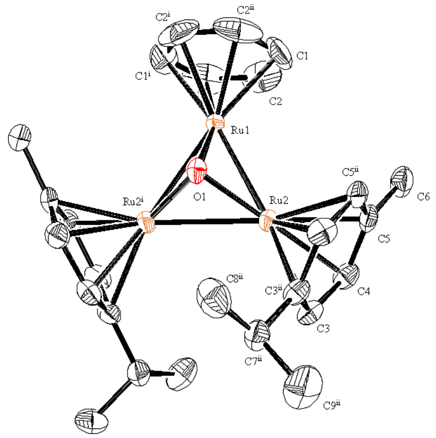


Figure 1
The molecular structure of (I). H atoms, the PF_6^- anion and one component of the disorder have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x, \frac{1}{2} - y, z$; (ii) $x, \frac{1}{2} - y, z$.]

three Ru atoms are capped by a μ_3-oxo ligand which is almost symmetrically coordinated. The three hydrido ligands bridging the three Ru—Ru bonds could be located, and were constrained in the refinement. The μ_3-oxo cap, as well as the three hydrido ligands, are disordered, occupying equivalent positions above and below the Ru_3 plane, with occupancy factors of 0.5. Therefore, the methyl and isopropyl substituents of the two adjacent *p*-cymene ligands are also disordered over two equivalent positions. The *p*-cymene ligands adopt a staggered configuration, to minimize the contacts between the isopropyl groups. Complex (I) possesses two perpendicular mirror planes intersecting at Ru1; atoms Ru1, Ru2 and C1 lie in the first one, and atoms Ru1 and O1 in the second. No meaningful interactions between the cation and the hexafluorophosphate anion were observed, other than normal coulombic attractions.

Experimental

A mixture of $[RuCl_2(\eta^6\text{-}C_6H_4MePr^i\text{-}p)]_2$ (400 mg, 0.6 mmol) and Ag_2SO_4 (376 mg, 1.2 mmol) in water (40 ml) was stirred in the dark for 1 h. During this period, the mixture was treated several times with ultrasound, until the orange solid was completely dissolved. The white precipitate (AgCl) was removed by filtration from the yellow solution containing $[Ru(\eta^6\text{-}C_6H_4MePr^i\text{-}p)(H_2O)_3]^{2+}$. To this yellow solution, an aqueous solution containing $NaBH_4$ (100 mg, 2.6 mmol, 10 ml H_2O) was added dropwise. The solution turned dark-red due to the formation of $[Ru_2(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_2(\mu_2\text{-}H)_3]^+$. After filtration, solid $[RuCl_2(C_6H_6)]_2$ (280 mg, 0.56 mmol) was added. The mixture was heated to 333 K for 50 h in a closed-pressure Schlenk tube. The resulting red solution was filtered and an excess of KPF_6 was added to precipitate $[H_3Ru_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_4MePr^i\text{-}p)_2(\mu_3\text{-}O)](PF_6)$. The precipitate was centrifuged, dissolved in CH_2Cl_2, filtered on celite to eliminate excess KPF_6 and purified on silica-gel plates (eluent: CH_2Cl_2/acetone 2:1). Yield: 136 mg (28%). ^1H NMR (400 MHz, $CDCl_3$): δ 5.60 (*s*, 6H, C_6H_6), 5.48 (*m*, 8H, C_6H_4), 2.52 [*hept*, 2H, ^3J = 6.82 Hz, $CH(CH_3)_2$], 2.23 [*s*, 6H, $(C_6H_4)CH_3$], 1.28 [*d*, 12H, ^3J = 6.82 Hz, $CH(CH_3)_2$], −18.67 (*d*, 2H, ^2J = 4.05 Hz, Ru-hydride), −18.86 (*t*, 1H, ^2J = 4.05 Hz, Ru—hydride); MS (ESI positive mode, acetone): m/z 669 $[M + H]^+$. Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of an acetone/hexane solution.

Crystal data

$C_{26}H_{37}ORu_3^+ \cdot PF_6^-$
$M_r = 813.74$
Orthorhombic, *Imma*
$a = 19.522\ (4)$ Å
$b = 10.738\ (2)$ Å
$c = 13.628\ (3)$ Å
$V = 2856.8\ (10)$ Å^3
$Z = 4$
$D_x = 1.892$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 6951 reflections
$\theta = 1.8\text{–}25.9^\circ$
$\mu = 1.68$ mm^{-1}
$T = 153\ (2)$ K
Block, red
0.40 × 0.15 × 0.15 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: none
9851 measured reflections
1505 independent reflections
1162 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.085$
$\theta_{\rm max} = 25.9^\circ$
$h = -23 \rightarrow 23$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.078$
$S = 0.92$
1505 reflections
107 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.82$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.79$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—Ru2	1.924 (5)	Ru1—Ru2	2.7536 (8)
O1—Ru1	1.945 (7)	Ru2—Ru2^{i}	2.7917 (11)
Ru2—O1—Ru2^{i}	93.0 (3)	Ru2^{i}—Ru1—Ru2	60.92 (3)
Ru2—O1—Ru1	90.7 (2)	Ru1—Ru2—Ru2^{i}	59.542 (14)

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

Data collection: *EXPOSE* (Stoe & Cie, 2000); cell refinement: *CELL* (Stoe & Cie, 2000); data reduction: *INTEGRATE* (Stoe & Cie, 2000); program(s) used to solve structure: *SHELXS*-97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*99 (Spek, 1990); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997).

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