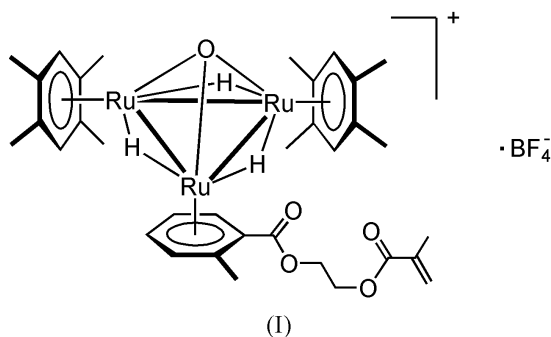


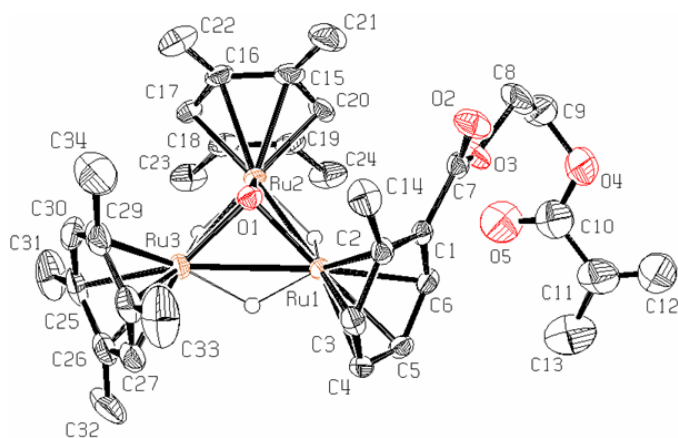
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Key indicators

Single-crystal X-ray study
T = 153 K
Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
Disorder in solvent or counterion
R factor = 0.039
wR factor = 0.087
Data-to-parameter ratio = 18.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>. $[\eta^6\text{-2-(2-Methylbenzoyloxy)ethyl methacrylate}]$ -
 $\text{bis}(\eta^6\text{-1,2,4,5-tetramethylbenzene})\text{tri-}\mu\text{-hydrido-}\mu_3\text{-}$
 $\text{oxo-triruthenium(II)}(3 \text{ Ru}-\text{Ru}) \text{ tetrafluoroborate}$ The trinuclear arene-ruthenium cluster cation, $[\text{Ru}_3\text{H}_3(\text{O})(\text{C}_{10}\text{H}_{14})_2(\text{C}_{14}\text{H}_{16}\text{O}_4)]^+$, has been synthesized and crystallized as the tetrafluoroborate (BF_4^-) salt. The cations form, along the *b* axis, infinite one-dimensional chains through π -stacking interactions.

Comment

In view of the potential advantages of heterogeneous, as opposed to homogeneous, catalysts, several methods to immobilize arene-ruthenium complexes have been investigated (Polborn & Severin, 2000; Opstal *et al.*, 2001; Akiyama & Kobayashi, 2002; Wendicke *et al.*, 2003). In 1999, we found that the water-soluble cluster cation $[\text{Ru}_3\text{H}_3(\text{O})(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2]^+$, used as its tetrafluoroborate salt, catalyses the hydrogenation of benzene to give cyclohexane under biphasic conditions (Faure *et al.*, 1999). Therefore, in order to provide an anchor to immobilize the cationic cluster for catalytic applications, we synthesized the analogous trinuclear arene-ruthenium cluster cation $[\text{Ru}_3\text{H}_3(\text{O})(\text{arene})(1,2,4,5\text{-C}_6\text{H}_2\text{Me}_4)_2]^+$ (1) [arene = 2-(2-methylbenzoyloxy)ethyl methacrylate], in which the two hexamethylbenzene groups and the benzene ligand are replaced by 1,2,4,5-tetramethylbenzene ligands (durene) and by an arene ligand containing a polymerizable side chain, respectively.The trinuclear ruthenium cluster cation, (1), isolated and characterized as its tetrafluoroborate salt, has been synthesized from the dinuclear precursor $[\text{Ru}_2\text{H}_3(1,2,4,5\text{-C}_6\text{H}_2\text{Me}_4)_2]\text{BF}_4$ (Bennett & Ennett, 1992; Vieille-Petit *et al.*, 2003*a*), and the chloro-bridged arene ruthenium dimer $[\text{Ru}(\text{arene})\text{Cl}_2]_2$ (arene as above) (Wendicke *et al.*, 2003) in aqueous solution. Cation (1) is chiral, due to the planar chirality of the arene-ruthenium moiety. This is reflected in the ^1H NMR spectrum, where (1) gives rise to three hydride signals showing up as pseudo-triplets instead of the expected double-doublets. $[(1)]\text{BF}_4$, hereinafter (I), is the racemic mixture of both enantiomers.Received 4 November 2004
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Figure 1

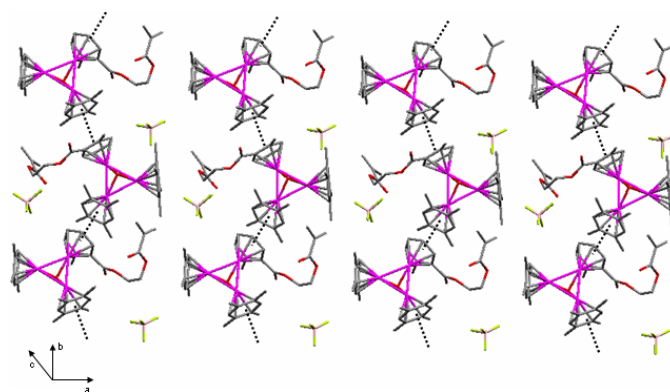
ORTEP-3 drawing (Farrugia, 1997) of (I), showing the atomic numbering scheme. H atoms and the tetrafluoroborate anion have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

A single-crystal X-ray structure analysis of (I) has been performed. The metal core consists of three Ru atoms, with an average Ru–Ru distance of 2.75 Å, which is in accordance with a metal–metal single bond. This value, as well as the other bond distances and angles, are similar to those found in other trinuclear arene complexes, $[\text{Ru}_3\text{H}_3(\text{O})(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2]^+$ (Faure *et al.*, 1999), $[\text{Ru}_3\text{H}_3(\text{O})(\text{C}_6\text{H}_6)(1,2,4,5\text{-C}_6\text{H}_2\text{Me}_4)_2]^+$ (Vieille-Petit *et al.*, 2003a) and $[\text{Ru}_3\text{H}_3(\text{O})(\text{C}_6\text{Me}_6)(\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OH})_2]^+$ (Vieille-Petit *et al.*, 2003b). The flexible methacrylate side chain points away from the metallic core and shows only weak interactions with neighbouring molecules. Furthermore, no meaningful interactions between the trinuclear cation and the tetrafluoroborate anion were observed, other than normal Coulombic attractions.

However, in the crystal packing of (I), π -stacking interactions are observed between one durene ligand and the benzene ring of the methacrylate ligand. The π -stacking interacting system forms a series of one-dimensional supramolecular multimers along the *b* axis (Fig. 2). The centroid–centroid distance between the benzene rings of the arene ligands is 3.483 Å. This is in good agreement with the theoretical value calculated for a strong parallel π -stacking mode (Tsuzuki *et al.*, 2002).

Experimental

In a Schlenk pressure tube, to a solution of $[\text{Ru}_2\text{H}_2(1,2,4,5\text{-C}_6\text{H}_2\text{Me}_4)_2]\text{BF}_4$ (165 mg, 0.29 mmol) in acetone (50 ml) and water (30 ml) was added $[\text{RuCl}_2(\text{arene})]_2$ [arene = 2-(2-methylbenzoyloxy)ethyl methacrylate] (186 mg, 0.22 mmol). The mixture was stirred under about 1.5 bar of N_2 for 4 d at room temperature. The resulting red solution was evaporated to dryness; the residue was dissolved in 5 ml of CH_2Cl_2 and subjected to preparative thin-layer chromatography on silica-gel using CH_2Cl_2 /acetone (2/1) as eluant. The pure compound was extracted with acetone from the main red band. Evaporation of acetone under vacuum gave 96 mg of (I) as a red powder (36% yield). Crystals suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into an acetone solution. ^1H NMR (400 MHz, acetone- d_6): 6.63 (*d*, 1H, $J = 5.8$ Hz,


Figure 2

The molecular packing of (I) in the *ab* plane, showing, along the *b* axis, the one-dimensional π -stacking chains (MERCURY; Bruno *et al.*, 2002).

$\text{H}_{\text{aromatic}}$, 6.14 (*s*, 1H, C=CH), 6.11 (*t*, 1H, $J = 5.8$ Hz, $\text{H}_{\text{aromatic}}$), 5.72 (*s*, 2H, $\text{C}_6\text{H}_2\text{Me}_4$), 5.71 (*s*, 1H, C=CH), 5.69 (*s*, 2H, $\text{C}_6\text{H}_2\text{Me}_4$), 5.66 (*t*, $J = 5.8$ Hz, 1H, $\text{H}_{\text{aromatic}}$), 5.55 (*d*, $J = 5.8$ Hz, 1H, $\text{H}_{\text{aromatic}}$), 4.73–4.55 (*m*, 4H, OCH_2), 2.62 (*s*, 3H, $\text{H}_3\text{C}-\text{C}=\text{CH}$), 2.24 [*s*, 6H, $\text{C}_6\text{H}_2(\text{CH}_3)_4$], 2.22 [*s*, 6H, $\text{C}_6\text{H}_2(\text{CH}_3)_4$], 2.21 [*s*, 6H, $\text{C}_6\text{H}_2(\text{CH}_3)_4$], 2.20 [*s*, 6H, $\text{C}_6\text{H}_2(\text{CH}_3)_4$], 1.96 (*s*, 3H, Ar-CH₃), –18.51 (*t*, 1H, $J = 3.8$ Hz, hydride), –18.77 (*t*, 1H, $J = 3.8$ Hz, hydride), –18.85 (*t*, 1H, $J = 3.8$ Hz, hydride); MS (ESI positive mode, acetone): m/z 838 [M]⁺.

Crystal data

$[\text{Ru}_3\text{H}_3(\text{O})(\text{C}_{10}\text{H}_{14})_2(\text{C}_{14}\text{H}_{16}\text{O}_4)]\text{-BF}_4$
 $M_r = 925.74$
 Monoclinic, $P2_1/c$
 $a = 13.592$ (3) Å
 $b = 17.817$ (4) Å
 $c = 15.066$ (4) Å
 $\beta = 100.238$ (3)°
 $V = 3590.4$ (15) Å³
 $Z = 4$

$D_x = 1.713$ Mg m^{−3}
 Mo $K\alpha$ radiation
 Cell parameters from 8000 reflections
 $\theta = 1.8\text{--}28.5^\circ$
 $\mu = 1.31$ mm^{−1}
 $T = 153$ (2) K
 Block, orange
 0.24 × 0.18 × 0.14 mm

Data collection

Stoe IPDS diffractometer
 φ scans
 Absorption correction: none
 30 927 measured reflections
 8673 independent reflections
 5034 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.074$
 $\theta_{\text{max}} = 28.7^\circ$
 $h = -18 \rightarrow 18$
 $k = -23 \rightarrow 24$
 $l = -17 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.087$
 $S = 0.90$
 8673 reflections
 461 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0313P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.25$ e Å^{−3}
 $\Delta\rho_{\text{min}} = -0.65$ e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

O1–Ru1	1.979 (3)	Ru1–Ru3	2.7476 (7)
O1–Ru3	1.982 (3)	Ru1–Ru2	2.7672 (8)
O1–Ru2	1.991 (3)	Ru2–Ru3	2.7508 (7)
Ru3–Ru1–Ru2	59.842 (14)	Ru1–Ru3–Ru2	60.43 (2)
Ru3–Ru2–Ru1	59.725 (15)		

The BF_4 molecule is disordered over two positions, in which the B atom and one F atom remain with full occupancy. The three remaining F atoms were treated as disordered with partial occupancy factors of 0.5. H atoms were included in calculated positions and treated as riding atoms, with C–H distances in the range 0.95–0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and Ru–H distances in the range 1.56–1.74 Å and $U_{\text{iso}}(\text{H}) = 0.05 \text{ \AA}^2$. Residual electron density greater than 1 e \AA^{-3} is observed around the O3 atom at a distance of 1.9 Å.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* for Windows (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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