

[Ru₄(CO)₇(μ-CO)₂(η²,η⁵,η²-indenyl)(η⁵-dihydroindenyl)]:† a Novel Planar Cluster with a Three-way Bridging Indenyl Ligand

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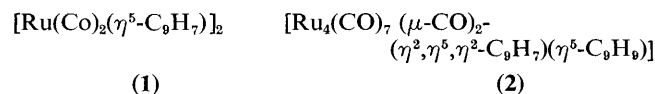
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The novel tetranuclear planar cluster [Ru₄(CO)₇(μ-CO)₂(η²,η⁵,η²-indenyl)(η⁵-dihydroindenyl)] was prepared by the reaction of indene with Ru₃(CO)₁₂ and its structure determined by a single crystal X-ray diffraction study.

The reaction of indene with Ru₃(CO)₁₂ in boiling heptane was reported¹ to give the (η⁵-indenyl)ruthenium carbonyl dimer [Ru(CO)₂(η⁵-C₉H₇)₂] (1), in an unspecified yield. A repeat of this reaction in refluxing methylcyclohexane revealed a low yield of conversion into (1) (*ca.* 9.4%) as well as the presence of a second product which was ultimately characterized as a tetranuclear cluster (2; 9.6% yield). While the preparation of (1) can be significantly improved (*ca.* 65%) if carried out in boiling methyl isobutyl ketone, the yield of (2) (*ca.* 5%) appears to remain exceptionally low irrespective of the reaction conditions. The structure of (2), a novel planar tetranuclear cluster, is described here.

Appropriate equidimensional (0.4 × 0.4 × 0.4 mm) deep-red crystals of (2) [m.p. decomp. >230 °C; i.r. (CHCl₃) 2051(s), 2002(vs), 1990(vs), 1955(s), 1944(sh), and 1762(s) cm⁻¹] were obtained by slow evaporation of a 1,2-dichloroethane solution of the complex. The structure was resolved from the X-ray diffraction analysis. *Crystal data*: for (2): C₂₇H₁₆O₉Ru₄, *M* = 888.7, orthorhombic, space group *Pbn*2₁,

a = 10.992(2), *b* = 13.897(3), and *c* = 16.813(6) Å, *U* = 2568.3 Å³, *D*_c = 2.30 g cm⁻³, and *Z* = 4. Data were collected on a computer-controlled CAD-4 diffractometer [λ(Cu-Kα) = 1.5405 Å] at 20 °C. The structure was solved by direct methods using 2542 unique reflection with *F*_o > 3σ(*F*_o). Block diagonal least-squares refinement converged to *R* = 0.06.‡



The molecular structure of (2) is illustrated in Figure 1 along with some representative interatomic bond distances and angles. This tetranuclear cluster consists of a *triangulo*-triruthenium [Ru(1), Ru(2), and Ru(3)] unit with Ru(4) being bonded to Ru(3). The near planarity of the Ru₄ skeleton is best illustrated by the slight displacement (*ca.* 0.07 Å) of Ru(3) from the plane defined by the remaining metal atoms.

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

† η²,η⁵,η²≡4-5-η;1-3a(7a)-η;6-7-η-bonding; η⁵≡1-3a(7a)-η-bonding throughout this communication.

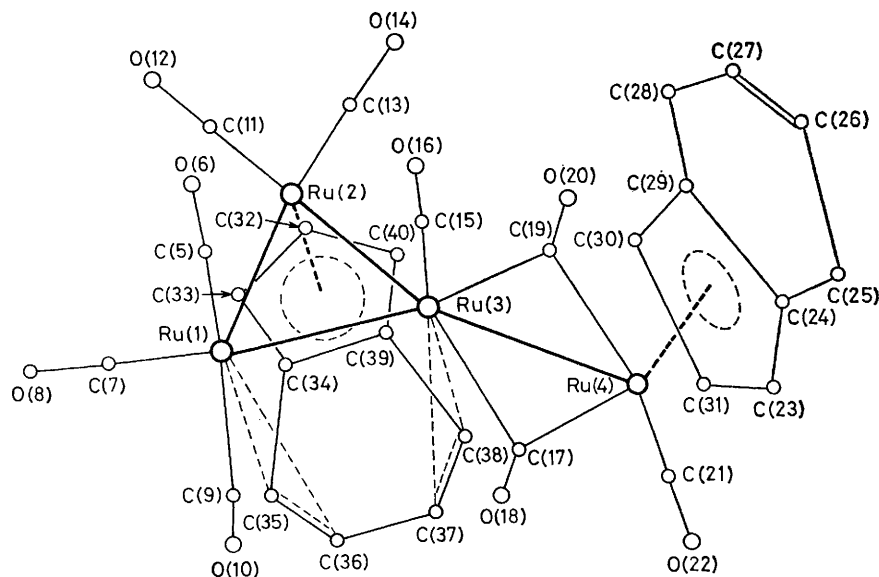


Figure 1. The molecular structure of $[\text{Ru}_4(\text{CO})_7(\mu\text{-CO})_2(\eta^5, \eta^5, \eta^2\text{-indenyl})(\eta^5\text{-dihydroindenyl})]$ (**2**) (hydrogen positions are omitted for clarity). Ru(1)–Ru(2), 2.845(3); Ru(2)–Ru(3), 2.972(3); Ru(1)–Ru(3), 2.819(3); Ru(3)–Ru(4), 2.765(2) Å; Ru(1)–Ru(2)–Ru(3), 57.9 (1.0); Ru(2)–Ru(3)–Ru(4), 144.1 (1.0); Ru(1)–Ru(3)–Ru(4), 156.8 (1.0)°. Ru–carbonyl groups (terminal, average): Ru–C, 1.88(3); C–O, 1.16(3) Å; Ru–C–O, 173.6(2.6)°; bridging, average: Ru–C, 2.05(2); C–O, 1.17(1) Å; Ru–C–O, 137.5(1.3); Ru(3)–C(O)–Ru(4), 84.7(0.6)°. Indenyl (η^5 -dienyl): Ru(2)–C(32–34, 39, 40) (average), 2.26(1) Å; η^2, η^2 -benzo moiety: Ru(1)–C(35), 2.28(3); Ru(1)–C(36), 2.41(3); Ru(3)–C(38), 2.29(3); Ru(3)–C(37), 2.36(3) Å. Dihydroindenyl (η^5 -dienyl): Ru(4) to C(23), 2.25(3); C(24), 2.34(3); C(29), 2.39(3); C(30), 2.30(3); C(31), 2.28(3) Å.

Intermetallic distances clearly indicate single Ru–Ru bonds. The alignment of the exocyclic Ru(4) atom is somewhat off-symmetry with respect to the *triangulo*-triruthenium unit as is evident from the appropriate skeleton bond angles. The organic ligands in (**2**) consist of seven terminal carbonyls [$\text{Ru}(1)(\text{CO})_3$, $\text{Ru}(2)(\text{CO})_2$, $\text{Ru}(3)(\text{CO})$, and $\text{Ru}(4)(\text{CO})$], two bridging carbonyls [$\text{Ru}(3)(\text{CO})_2\text{Ru}(4)$], three-way bridging indenyl [η^2, η^5, η^2 -Ru(1), Ru(2), and Ru(3), respectively], and dihydroindenyl [η^5 -Ru(4)]. Bond distances and angles associated with the terminal and bridging (symmetrical) carbonyls in (**2**) appear in their normal ranges. Bonding of the three-way bridging indenyl involves an η^5 -cyclopentadienyl and an η^2, η^2 -dieno(benzo) unit. A dihedral angle of 171.7° is found between the dienyl and dieno planes. Angles between the normal to the *triangulo*-triruthenium plane and those of the dienyl (1.42°) and dieno (9.65°) planes imply a nearly parallel arrangement. The bonding of the η^5 -dihydroindenyl ligand to the Ru(4) atom involves two out of five significantly longer Ru–C bond distances and this might suggest an isolated η^2, η^3 -ligand system. With the exception of the isolated olefinic bond [C(26)–C(27)], the remaining carbon–carbon distances in both the five- and six-membered fused rings of the dihydroindenyl ligand are quite similar. This ligand is planar within ± 0.03 Å except for the *exo*-displacement (*ca.* 0.1 Å) of the olefinic C(26) atom.

The structural features of (**2**) are of interest from several points of view. In the first place, planar tetranuclear clusters are rather rare.^{2,3} According to the skeletal electron pair (SEP) theory,³ eight electrons (4-SEP) are available for intermetallic bonding in (**2**). Formal distribution of these electrons [2e–Ru(1); 1e–Ru(2); 4e–Ru(3); 1e–Ru(4)] implies that the formation of the Ru(2)–Ru(3) bond involves an interaction between a 'filled donor orbital' on Ru(3) and a 'vacant acceptor orbital' on Ru(2). This bond, where the electron density appears to be unevenly distributed, is significantly longer (0.13–0.15 Å) than the remaining *triangulo*-triruthenium

distances which are compatible with those reported for $\text{Ru}_3(\text{CO})_{12}$.⁴ The shortest intermetallic distance in (**2**), that of the carbonyl bridged Ru(3)(CO)₂Ru(4) unit, is similar to the distance characterized in $[\text{Ru}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2$.⁵ Another noteworthy feature in (**2**) is the three-way bridging indenyl ligand, a bonding mode which had not been observed hitherto. Bond distances and angles observed for the indenyl and dihydroindenyl ligands in (**2**) are quite similar to those reported for bis(η^5 -indenyl)ruthenium.⁶ The presence of η^5 -indenyl instead of η^5 -dihydroindenyl in some of the clusters could explain the greater disorder [rather large, anisotropic temperature factors of C(25)–C(28)] observed in the data of the latter ligand.

The formation of (**2**) is also of interest from the standpoint of the chemistry of clusters. The presence of a three-way bridging indenyl in hydrido-containing cluster intermediates suggests intramolecular hydrogen transfer processes during the formation of the η^5 -dihydroindenyl ligand in (**2**). Moreover, the presence of the $[\text{Ru}(\text{CO})_2(\eta^5\text{-dihydroindenyl})]$ unit in (**2**) suggests the possible role of cluster-extended intermediates during the formation of dinuclear products [*e.g.*, (**1**)] from $\text{Ru}_3(\text{CO})_{12}$.

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