Synthesis and Characterisation of $[Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2]$: the First Example of Cyclohexa-1,4-diene in a Bridging Coordination Mode

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The molecular structure of the square-pyramidal cluster $[Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2]$ has been established by single crystal X-ray analysis; the coordination mode is unique for the two cyclohexa-1,4-diene ligands, each bridging two ruthenium atoms.

There are numerous examples of cyclohexa-1,3-diene ligands coordinated to mononuclear transition metal complexes which have been characterised by both spectroscopic methods and single crystal X-ray analysis.[1] For ruthenium the 1,3-form usually results regardless of whether a 1,3- or 1,4-diene was used in the synthesis. There are comparatively few examples of transition metal clusters in which cyclohexadiene ligates, and in most cases the ligand maintains an η^4-coordination mode to one metal centre.[2] The bridging $\mu_2\text{-}\eta^2\text{:}\eta^2$-coordination mode for cyclohexa-1,3-diene has been reported in two examples, $[Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,3)]$ being one of these.[3]

The first examples of 1,4-dienes to be characterised by spectroscopic techniques were found for the 1-methoxy- and 1-ethyl-cyclohexa-1,4-diene in cobalt complexes.[4] More recently, an η^4-dihydrohexamethylcyclohexa-1,4-diene has been elucidated by X-ray crystallography in a monoruthenium complex,[5] the cyclohexa-1,4-diene ring in this complex is clearly 'boat-shaped'. To our knowledge $[Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2]$ is the first species to contain bridging cyclohexa-1,4-diene ligands which has been fully characterised by single crystal X-ray diffraction.

The synthetic approach adopted in the preparation of $[Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2]$ involves a two-stage chemical activation route. The oxidative decarbonylation reagent trimethylamine *N*-oxide (Me_3NO) is added dropwise to the square-pyramidal cluster $[Ru_5C(CO)_{15}]$ in cyclohexa-1,4-diene–CH_2Cl_2, yielding $[Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)]$[†] as the major product. Further treatment of this cluster with Me_3NO, also in cyclohexa-1,4-diene–CH_2Cl_2 affords the *bis*-cyclohexa-1,4-diene cluster $[Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2]$.[‡] Both this cluster and the intermediate are isolated from the reaction mixture by TLC using CH_2Cl_2 (30%)–hexane (70%) as eluent.

The molecular structure of $[Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2]$[§] is shown in Fig. 1 together with the labelling scheme and some relevant structural parameters. There are two 'half' molecules in the asymmetric unit related to the other respective halves by a crystallographic mirror plane. Both C_6H_8 ligands are bisected by the symmetry plane, which also passes through the apical Ru atom, one of its CO ligands and the C carbido atom. The metal framework consists of a square pyramid common to the majority of cyclohexadiene and benzene derivatives of $[Ru_5C(CO)_{15}]$.[3] The most important structural feature is the presence of the two $1,4\text{-}C_6H_8$ ligands μ_2-bridging two opposite Ru–Ru bonds in the square base. With respect to the parent cluster $[Ru_5C(CO)_{15}]$, one ligand formally replaces two radial CO ligands on two contiguous Ru atoms, while the second ligand formally replaces two axial ligands. The reason for this different choice of coordination site is probably found in the unfavourable interactions that could arise between the three apical carbonyl ligands and the two cyclohexadiene moieties. The observed arrangement clearly minimises these steric interactions. Localisation of multiple bond character within the C_6 ring is clearly recognisable in the four independent ligands with 'short' [mean 1.37(1) Å] C=C bonds involved in the π-interactions. The C_6H_8 ligands adopt a boat conformation. Metal–metal bonds within the two independent cluster units are strictly comparable with those of the $1,3\text{-}C_6H_8$ derivative.

[†] *Spectroscopic data* for $[Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2]$: ($CH_2Cl_2$) ν(CO)/cm^{-1}: 2084m, 2051s, 2033m,sh, 2016vs, 1983w,br, 1942w,br; ^{1}H NMR ($CDCl_3$): δ 5.08 (m, 1H), 4.56 (m, 1H), 2.03 (s, 2H); positive fast atom bombardment mass spectrum M$^+$ obs. 962 (calc. 962).

[‡] *Spectroscopic data* for $[Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2]$: ($CH_2Cl_2$) ν(CO)/cm^{-1}: 2048m, 2017vs, 1984m,br, 1935w,br; ^{1}H NMR ($CDCl_3$) 235 K: δ 5.13 (d, 2H), 4.84 (d, 1H), 4.67 (d, 2H), 4.55 (d, 1H), 4.24 (d, 2H), 4.12 (d, 2H), 3.81 (d, 1H), 3.67 (d, 2H), 3.47 (d, 1H), 2.98 (d, 1H), 2.49 (d, 1H), (all signals are broad at room temp.); positive fast atom bombardment mass spectrum M$^+$ obs. 985 (calc. 985).

[§] *Crystal data for* $[Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2]$: $C_{24}H_{16}O_{11}Ru_5$, M = 985.7, orthorhombic, space group *Pbam*, a = 31.469(9), b = 13.572(4), c = 12.682(5) Å, U = 5416.5 Å^3, Z = 8, D_c = 2.42 g cm^{-1}, $F(000)$ = 3744, μ(Mo-Kα) = 27.3 cm^{-1}, T = 293K, $3 < \theta < 25°$, final R value 0.052 due to the low quality of the crystal for 4591 independent reflections [$I > 2\sigma(I)$]. Two independent half molecules are present in the asymmetric unit, each one lying on a crystallographic mirror plane. Diffraction data collected by the ω–2θ scan method. The structure was solved by direct methods and refined by full-matrix least-squares.[7] Absorption correction was applied by the Walker and Stuart method. All non-hydrogen atoms were allowed to vibrate anisotropically. The H-atoms were added in calculated positions (C–H 0.97 Å for the methylenic and 0.92 Å for the aromatic ones) and refined 'riding' on their respective C atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

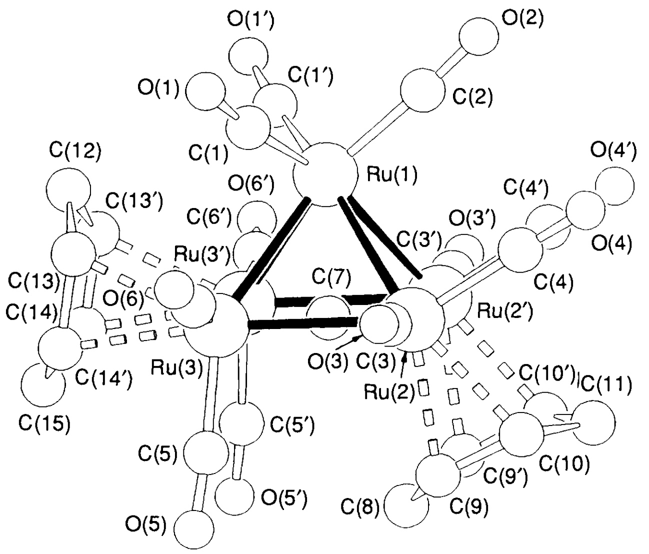

Fig. 1 The molecular structure of only one of the two independent molecules is shown, primed atoms are generated by the crystallographic mirror plane passing through the mid-point of the Ru(2)–Ru(2′) and Ru(2)–Ru(3′) bonds and comprising the apical Ru(1) atom and one of its carbonyl ligands. Relevant structural parameters are given as pairs of chemically equivalent bonds (Å). Ru(1)–Ru(2) 2.807(2), 2.828(2); Ru(1)–Ru(3) 2.855(2), 2.867(2); Ru(2)–Ru(3) 2.844(2), 2.841(2); Ru(2)–Ru(2′) 2.842(2), 2.840(2); Ru(3)–Ru(3′) 2.794(2), 2.808(2); C(8)–C(9) 1.51(1), 1.54(1); C(9)–C(10) 1.36(1), 1.38(1); C(10)–C(11) 1.52(1), 1.52(1); C(12)–C(13) 1.52(1), 1.50(1); C(13)–C(14) 1.37(1), 1.37(1); C(14)–C(15) 1.52(1), 1.52(1); Ru(1)–C(7) 2.10(1), 2.07(1); Ru(2)–C(7) 2.01(1), 2.02(1); Ru(3)–C(7) 2.00(1), 1.99(1).

The fact that cyclohexadiene coordinates to two ruthenium atoms in the 1,4-form is somewhat surprising, since in the related chemistry of the hexaruthenium carbidocarbonyl cluster [$Ru_6C(CO)_{17}$], only 1,3-products are obtained regardless of the diene used.[6]

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