

The cluster–surface analogy: the interaction of norbornene and norbornadiene with low-nuclearity ruthenium carbonyl clusters

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The thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with norbornene (nbe) and norbornadiene (nbd) leads to the tri- and tetra-ruthenium clusters, $[(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-C}_7\text{H}_8)]$ **1** and $[\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\eta^2\text{-C}_7\text{H}_6)]$ **2**, respectively; the molecular structures of both clusters show organo-cluster interactions similar to the proposed organo-surface adsorption modes found on the Pt(111) surface, in which the bicyclic ring straddles a trimetallic face, coordinating through one alkenic bond and an agostic C–H...M interaction.

The chemical and structural characterisation of molecular clusters bearing organic ligands has led to a clearer understanding of the bonding modes adopted by organic species chemisorbed on metal surfaces.¹ Surface chemists now frequently employ comparisons of the vibrational spectra of adsorbed species with those of molecular metal clusters as a means of determining the structures of adsorbates on the surface.² A key example is the interaction of benzene with the Rh(111) surface,³ and the trinuclear carbonyl clusters $[\text{M}_3(\text{CO})_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-C}_6\text{H}_6)]$ (M = Ru, Os).⁴ It has recently been proposed that norbornene (nbe) and norbornadiene (nbd) may bind to the Pt(111) surface *via* one double bond and an agostic interaction of the C–H bond of the bridging CH_2 unit (Fig. 1),^{5,6} however, previously characterised mono- and polynuclear organometallic complexes have involved interaction of the ligand with a single metal atom only.⁷

Here we report the synthesis and structural characterisation of the two cluster compounds $[(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-C}_7\text{H}_8)]$ **1** and $[\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\eta^2\text{-C}_7\text{H}_6)]$ **2**, which exhibit an analogous bonding mode to that proposed for nbe and nbd adsorbed on the Pt(111) surface, and may shed light on the reaction mechanisms involved in their conversion to benzene on a metal surface.^{5,6,8}

When a suspension of $[\text{Ru}_3(\text{CO})_{12}]$ in cyclohexane containing an excess of nbe is heated to reflux (80 °C), one major product is obtained. Compound **1** has been fully characterised as the triruthenium cluster $[(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-C}_7\text{H}_8)]$, both in solution by spectroscopic methods, and in the solid state by single-crystal X-ray diffraction (Fig. 2).[†] Alternatively, if a hexane solution of $[\text{Ru}_3(\text{CO})_{12}]$ containing excess nbd is heated (69 °C) for 4 h, the major product is the tetranuclear butterfly cluster $[\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}\eta^2\text{-C}_7\text{H}_6)]$ **2**.[†] Again, **2** has been fully characterised by spectro-

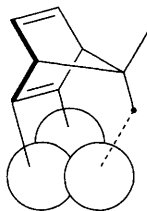


Fig. 1 Proposed bonding mode of nbd on a Pt(111) surface

scopy, and its molecular structure determined by a single-crystal X-ray diffraction analysis (Fig. 3).[‡]

Compound **1** consists of a triangular ruthenium core with an nbe moiety interacting through its alkenic bond in the well established face-capping di- σ and π manner. An agostic C–H...Ru interaction between H(7Na) and Ru(3) [3.072 Å, all C–H bonds normalised to the neutron diffraction distance of 1.08 Å] completes the bonding mode. The cluster also carries nine terminal carbonyl groups arranged with two equatorial and one apical ligand on each metal atom, and two hydrido atoms situated on the two longest edges of the metal triangle [Ru(1)–Ru(2) 3.015(1), Ru(2)–Ru(3) 2.882(1) Å]. Compound **1** may therefore be considered as an organometallic cluster analogue of nbe chemisorbed on a Pt(111) surface. The main evidence for the agostic interaction is the chemical shift in the solution ¹H NMR spectrum of **1**. In free nbe, the bridgehead CH_2 protons give a signal at δ 1.55, whereas upon coordination signals appear at δ 1.35 and 0.65; this shift is a clear indication that the proton is deshielded by the ruthenium atom. Further evidence is provided by IR spectroscopy; a C–H stretching frequency appears at the lower value of 2360 cm^{-1} consistent with that expected for a C–H...M agostic interaction.

Compound **2** consists of a tetra-ruthenium butterfly framework, with the nbd unit coordinated to the cluster through both double bonds. One alkenic bond 'straddles' the hinge of the butterfly forming two σ -interactions with the hinge ruthenium

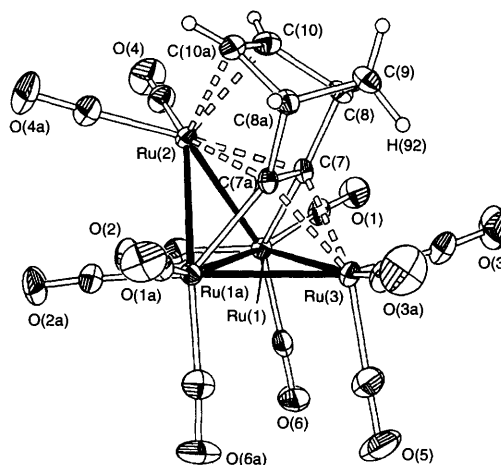


Fig. 2 Solid-state molecular structure of $[(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-C}_7\text{H}_8)]$ **1**, showing atomic labelling scheme; C atoms of CO groups bear the same numbering as the corresponding O atoms. Relevant bond lengths (Å) and angles (°): Ru(1)–Ru(2) 3.015(1), Ru(1)–Ru(3) 2.741(1), Ru(2)–Ru(3) 2.882(1), Ru(1)–C(1N) 2.073(9), Ru(2)–C(2N) 2.10(1), Ru(3)–C(1N) 2.233(9), Ru(3)–C(2N) 2.30(1), Ru(3)–H(7Na) 3.072, C(1N)–C(2N) 1.32(1), C(1N)–C(6N) 1.55(1), C(2N)–C(3N) 1.53(2), C(3N)–C(4N) 1.48(2), C(3N)–C(7N) 1.51(2), C(4N)–C(5N) 1.60(2), C(5N)–C(6N) 1.54(2), C(6N)–C(7N) 1.53(2), mean Ru–C_(CO) 1.92(1), mean C–O 1.13(1), Ru(1)–H(1) 1.801, Ru(2)–H(1) 1.621, Ru(2)–H(2) 1.936, Ru(3)–H(2) 1.934; Ru(1)–H(1)–Ru(2) 123.5, Ru(2)–H(2)–Ru(3) 96.3.

atoms and π -interactions with the two wingtip atoms. The second alkenic unit bonds to a single wingtip ruthenium atom [Ru(2)] in an η^2 -manner. A similar coordination mode has been reported for cycloocta-1,5-diene in $[\text{Ru}_4(\text{CO})_{11}(\text{C}_8\text{H}_{10})]$.⁹

The molecule may be viewed as a model for nbd chemisorbed at a surface step-site. Again ¹H NMR data show a shift in frequency for the bridgehead protons of the nbd moiety from δ 1.99 in the free ligand to δ 2.27 and 0.43 upon coordination, providing strong evidence for an agostic interaction. Both alkenic bonds of the nbd ligand interact with Ru(2) in the chelating fashion,⁷ and two further agostic interactions are apparent [C(10)–H(10)···Ru(2) 2.672 Å].

Agostic interactions are usually observed in electron deficient systems.¹⁰ We have recently reported an example where two isomeric butterfly clusters exist as either 60 or 62 electron systems.¹¹ In this system it appears that 'saturation' is achieved by varying electron donation from the ligand to the cluster. Since **2** is formally electron deficient, it is possible that the three agostic interactions may provide additional electron density.

An investigation into the coordination of nbe and nbd to a number of clusters with differing nuclearities and frameworks is in progress, and may help in an understanding of the reaction mechanisms involved in the conversion of nbe and nbd to benzene on a metal surface.

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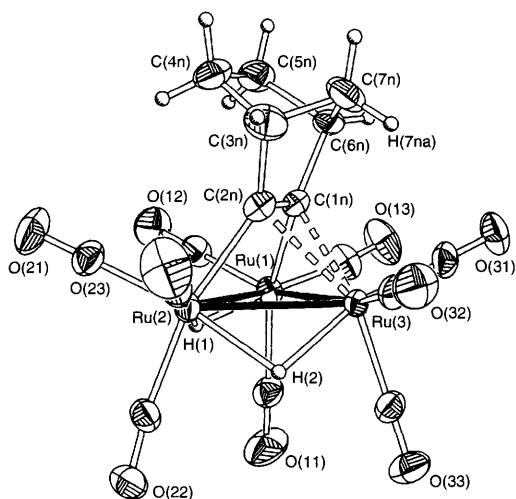


Fig. 3 Solid-state molecular structure of $[\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-}\eta^1:\eta^1:\eta^2\text{-}\eta^2\text{-C}_7\text{H}_8)]$ **2**, showing atomic labelling scheme; C atoms of CO groups bear the same numbering as the corresponding O atoms. Relevant bond lengths (Å): Ru(1)–Ru(1a) 2.851(1), Ru(1)–Ru(2) 2.734(1), Ru(1)–Ru(3) 2.755(1), Ru(1)–C(7) 2.096(5), Ru(2)–C(7) 2.188(8), Ru(2)–C(10) 2.219(8), Ru(3)–C(7) 2.181(8), Ru(3)–H(92) 2.765, C(7)–C(7a) 1.49(1), C(7)–C(8) 1.541(8), C(8)–C(9) 1.529(9), C(8)–C(10) 1.56(1), C(10)–C(10a) 1.38(2), mean Ru–C_(CO) 1.90(1), mean C–O 1.14(1).

Footnotes

† *Crystal data*: for $[(\mu\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-C}_7\text{H}_8)]$ **1**: crystallises with two molecules per asymmetric unit; yellow crystal, $\text{C}_{16}\text{H}_{10}\text{O}_9\text{Ru}_3$, $0.35 \times 0.35 \times 0.10 \text{ mm}^3$, $T = 293 \text{ K}$, $M = 649.45$, triclinic, space group $P\bar{1}$, $a = 14.498(2)$, $b = 16.087(3)$, $c = 10.142(2) \text{ Å}$, $\alpha = 104.50(2)$, $\beta = 93.57(2)$, $\gamma = 116.49(1)^\circ$, $U = 2007.9(6) \text{ Å}^3$, $Z = 4$, $D_c = 2.148 \text{ Mg m}^{-3}$, $\lambda = 0.71073 \text{ Å}$, $F(000) = 1240$, $R1 = 0.0509$ [6966 reflections with $F_o > 4\sigma(F_o)$], $wR = 0.3799$ for 7048 independent reflections corrected for adsorption [$\mu(\text{Mo-K}\alpha) = 2.272 \text{ mm}^{-1}$] and 517 parameters (all non-H atoms anisotropic). For $[\text{Ru}_4(\text{CO})_{11}(\mu_4\text{-}\eta^1:\eta^1:\eta^2\text{-}\eta^2\text{-C}_7\text{H}_8)]$ **2**: black crystal, $\text{C}_{18}\text{H}_6\text{O}_{11}\text{Ru}_4$, $0.22 \times 0.18 \times 0.05 \text{ mm}^3$, $T = 293 \text{ K}$, $M = 802.51$, orthorhombic, space group $Pnma$, $a = 17.241(4)$, $b = 12.588(2)$, $c = 10.038(4) \text{ Å}$, $U = 2178.5(11) \text{ Å}^3$, $Z = 4$, $D_c = 2.447 \text{ Mg m}^{-3}$, $\lambda = 0.71073 \text{ Å}$, $F(000) = 1512$, $R1 = 0.0323$ [2731 reflections with $F_o > 4\sigma(F_o)$], $wR2 = 0.1047$ for 2738 independent reflections corrected for adsorption [$\mu(\text{Mo-K}\alpha) = 2.778 \text{ mm}^{-1}$] and 171 parameters (all non-H atoms anisotropic). The structures were solved by direct methods,¹² and a series of difference Fourier maps were used to locate all light atoms except the H atoms. The positions of the bridging hydrido atoms in **1** were located using the program HYDEX,¹³ and the remaining H atoms were added in calculated positions (C–H 0.96 Å) riding on the respective C atoms. All other calculations were performed using SHELX93.¹⁴ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/88.

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