The Synthesis and Characterisation of $Ru_6(\mu_3\text{-}H)(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^5\text{-}C_5H_4Me)$—an Example of Cluster Mediated Ring Contraction

Scott L. Ingham,[a] Brian F. G. Johnson,*[a] Caroline M. Martin[a] and David Parker[b]

[a] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*
[b] *ICI Group R & T Affairs, P.O. Box 90, Wilton Centre, Middlesbrough, Cleveland, UK TS90 8JE*

Reaction of cyclohexene with $Ru_3(CO)_{12}$ leads primarily to dehydrogenation with products based on C_6H_8 and C_6H_6, however the formation of the cluster complex $Ru_6(\mu_3\text{-}H)(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^5\text{-}C_5H_4Me)$ **1**, has revealed that C–C activation and ring contraction is also a significant reaction pathway.

The catalytic transformation of C_6 and C_8 hydrocarbons is of considerable importance and it is well established that metals such as platinum are highly effective in activating both C–H and C–C bonds of organic molecules.[1] Studies of the adsorption and subsequent reactions of cyclic C_6 hydrocarbons such as cyclohexane, cyclohexene and cyclohexadiene have revealed that on a Pt(111) surface the dominating chemistry is their dehydrogenation to benzene.[2] One of the primary objectives of our current work is to mimic such behaviour on related cluster surfaces and in a series of experiments we have found that similar behaviour occurs on the surface of deltahedral clusters of ruthenium and osmium atoms.[3] Significantly we have been able to isolate model compounds corresponding to the adsorption and successive dehydrogenation of cyclohexene, cyclohexadiene and benzene. A feature of this work has been the formation of both enyl and alkynyl derivatives corresponding to the cleavage of both saturated and unsaturated C–H bonds respectively.[4] We now wish to report a further novel reaction which involves the conversion of coordinated cyclohexene (C_6H_{10}) to a methylcyclopentadienyl ($C_5H_4CH_3$) derivative which involves the activation of both C–H and C–C bonds within this C_6 hydrocarbon.

We have observed that the thermolysis of $Ru_3(CO)_{12}$ in octane in the presence of cyclohexene affords a variety of C_6-hydrocarbon containing clusters with nuclearities ranging from four to eight,[5] *e.g.* $Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_6H_6)$, $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$ and $H_4Ru_8(CO)_{18}(\eta^6\text{-}C_6H_6)$, in which the integrity of the C_6 ring has been retained.† However, we have also isolated the hexaruthenium cluster $Ru_6(\mu_3\text{-}H)(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^5\text{-}C_5H_4Me)$ **1** from this same reaction. This novel compound has been characterised by spectroscopy‡ and its molecular structure determined by a single crystal X-ray diffraction analysis.§

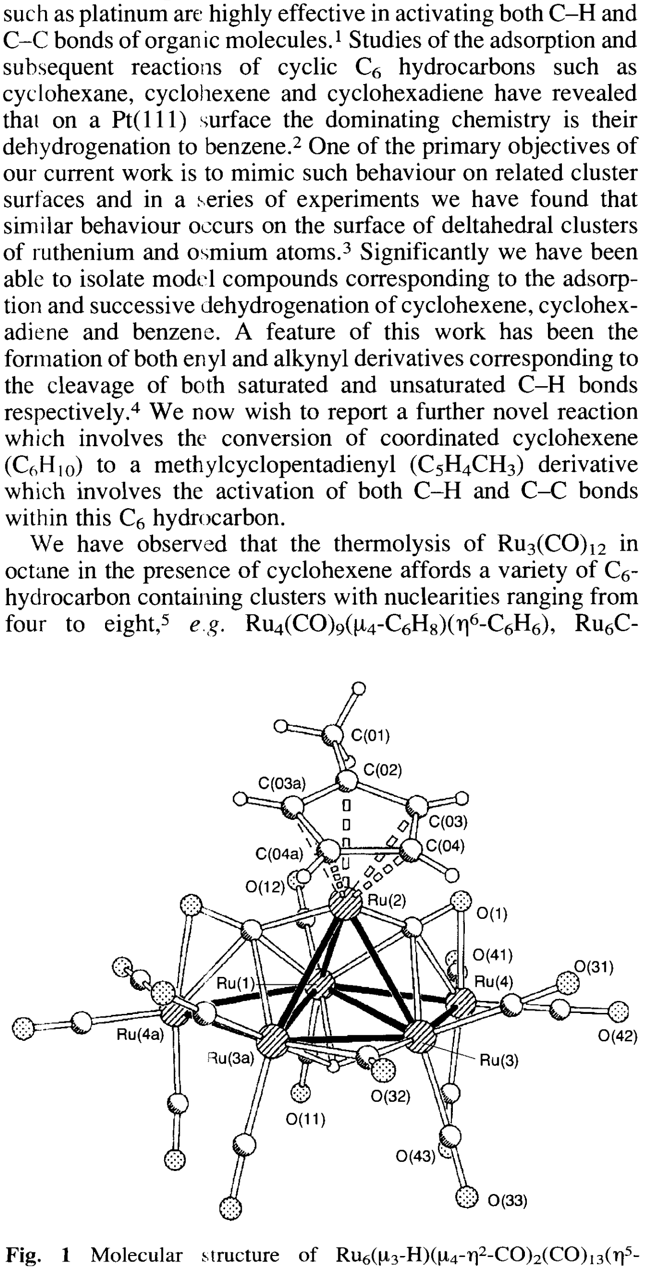
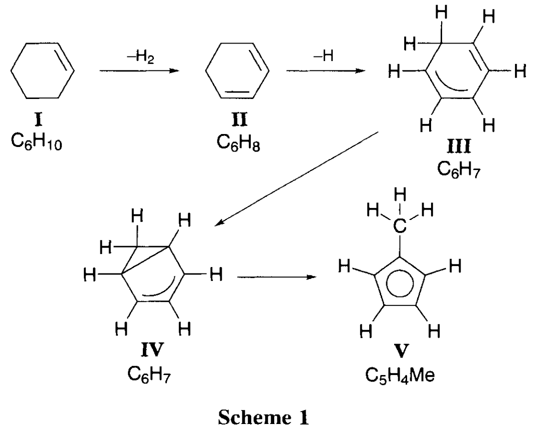


Fig. 1 Molecular structure of $Ru_6(\mu_3\text{-}H)(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^5\text{-}C_5H_4Me)$ **1**, showing the labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Principal bond distances (Å) are: Ru(1)–Ru(2) 2.759(2), Ru(1)–Ru(3) 2.8440(13), Ru(1)–Ru(4) 2.8433(10), Ru(2)–Ru(3) 2.7798(11), Ru(3)–Ru(3a) 2.717(2), Ru(3)–Ru(4) 2.7666(12), mean Ru–C(COterminal) 1.90(1), mean C–O(COterminal) 1.14(2), Ru(3)–C(32) 2.126(10), C(32)–O(32) 1.14(2), Ru(1)–C(1) 2.219(9), Ru(2)–C(1) 1.936(9), Ru(3)–C(1) 2.267(8), Ru(4)–C(1) 2.290(8), Ru(4)–O(1) 2.139(5), C(1)–O(1) 1.232(10), mean Ru–C(ring) 2.23(1), mean C–C(ring) 1.41(2), C(01)–C(02) 1.50(2), mean Ru–H(μ_3) 1.9(1).

The solid state molecular structure of **1** is shown in Fig. 1 together with some relevant structural parameters. The metal framework of **1** consists of a tetrahedral Ru_4 arrangement with two edge-bridging ruthenium atoms. The Ru–Ru bond distances range from 2.8440(13) to 2.717(2) Å, the longest edges of the tetrahedron being those bridged by the two remaining Ru atoms *i.e.* Ru(1)–Ru(3) and Ru(1)–Ru(3a), and the shortest being the unique basal edge which is spanned by a symmetrically bridging (μ_2) carbonyl ligand, Ru(3)–Ru(3a). This metal core geometry has previously only been observed for a related mesitylene containing cluster $Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)$,[6] and both compounds require 88 valence shell electrons. The methylcyclopentadienyl ligand in **1** adopts the conventional η^5-terminal coordination mode and is bonded to the only tetrahedron vertex not associated the bridged edges. There are two, four electron donating, π-bonded ($\mu_4\text{-}\eta^2\text{-}$) carbonyl ligands situated in the two Ru_4 'butterflies' created by the bridging Ru atoms and the faces of the metal tetrahedron. The C–O bond lengths of the η^2-bonded carbonyl ligands are considerably lengthened relative to the terminally coordinated ligands [1.232(10) *vs.* mean 1.14(2) Å] which may be attributed to electron donation from the C–O π-bond, and increased electron density in the C–O π* orbital due to the $d_\pi\text{–}p_\pi$ bonding from three metals. The triply bridging (μ_3-) hydride atom has been located experimentally beneath the basal plane, Ru(1)–Ru(3)–Ru(3a), of the central Ru tetrahedron.

As aforementioned, compound **1** is similar to the mesitylene complex $Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)$, which can be converted quantitatively, by thermolysis in mesitylene, to the cluster complex $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$, demonstrating that it is a precursor in the formation of the hexaruthenium carbido-cluster from $Ru_3(CO)_{12}$. ^{13}C labelling experiments have established that the carbido-atom in $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$ is derived from a carbonyl ligand and it would therefore seem



Scheme 1

likely that the transformation of $Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)$ into the carbido-cluster occurs *via* the thermally induced cleavage of one of the activated (μ_4-η^2-CO) ligands, with the ejection of CO_2. However, all attempts to repeat the analogous chemistry and convert compound **1** into the carbido-cluster $Ru_6(\mu_3\text{-}H)C(CO)_{14}(\eta^5\text{-}C_5H_4Me)$ have been unsuccessful. The reasons for this unexpected behaviour are not clear but in other work we have established that the transfer of the O-atom from one coordinated CO to another may not be simple and may, for example, involve the initial transference to a bonded organo-fragment.[7]

As yet, we have been unable to establish the mechanism by which this ring contraction process occurs. A likely mechanism is illustrated in Scheme 1 and involves the initial dehydrogenation of the cyclohexene to a cluster stabilised cyclohexenyl (C_6H_7) fragment. At this stage the transannular addition followed by hydrogen transfer provide a plausible possibility. In our work we have observed and fully characterised derivatives of the C_6H_{10} **I**, C_6H_8 **II** and C_6H_7 **III** fragments, however not unexpectedly, a derivative of **IV** has yet to be isolated. As far as we are aware such behaviour has not been observed on adsorption of cyclooctene on the Pt(111) surface but ring contraction is not an uncommon phenomenon and certainly C_8 cyclic alkenes are known to produce benzene and acetylene.[8]

In view of the high degree of interest currently shown in the transformation of cyclic C_6 alkenes on metal surfaces, this observation must be regarded as significant. It would appear that the chemistry of these hydrocarbons on the cluster surface is, like that on the metal [Pt(111)], dominated by C–H activation and dehydrogenation reactions, but that the activation of C–C bonds is also of importance.

We would like to thank the EPSRC, ICI (Wilton) (C. M. M) and The University of Edinburgh for financial support.

Received, 3rd October 1994; Com. 4/06027J

Footnotes

† *Experimental details*: $Ru_3(CO)_{12}$ (100 mg) was suspended in octane (30 ml). Excess cyclohexene (2 ml) was added, and the reaction mixture was heated to reflux for 6 h. The solvent was removed *in vacuo* and the products separated by tlc, using a solution of dichloromethane–hexane (3 : 7) as eluent. Several bands were isolated and characterised, in order of elution, as $Ru_4(CO)_{12}(\mu_4\text{-}C_6H_8)$ (red, 18%), $Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_6H_6)$ (red, 6%), $Ru_6(\mu_3\text{-}H)(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^5\text{-}C_5H_4Me)$ **1** (brown, 15%), $Ru_8(\mu\text{-}H)_4(CO)_{18}(\eta^6\text{-}C_6H_6)$ (brown, 12%) and $Ru_6C(CO)_{14}((\eta^6\text{-}C_6H_6)$ (red, 14%).

‡ *Spectroscopic data* for $Ru_6(\mu_3\text{-}H)(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^5\text{-}C_5H_4Me)$ **1**: IR (CH_2Cl_2) $\nu_{(CO)}$/cm^{-1}: 2093w, 2080m, 2066vs, 2034m, 2022m, 1965w, 1920w; (KBr disc) $\nu_{(CO)}$/cm^{-1}: 1431s, 1388m; ^1H NMR ($CDCl_3$): δ 5.44 (m, 2H), 5.31 (m, 2H), 2.10 (s, 3H) and −17.81 (s, 1H); Positive fast atom bombardment mass spectrum M$^+$ obs 1106 (calc. 1107).

§ *Crystal data* for $Ru_6(\mu_3\text{-}H)(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^5\text{-}C_5H_4Me)$ **1**: $Ru_6O_{15}C_{21}H_8$, monoclinic, space group $P2_1/m$, a = 9.910(3), b = 16.963(4), c = 24.936(9) Å, β = 100.26(3)°, M = 1106.69, U = 4125(2) Å^3, Z = 6, D_c = 2.673 g cm^{-3}, T = 150 K, $F(000)$ = 3108, $R1$ = 0.0409 [5185 reflections with $F_o > 4\sigma(F_o)$], w$R2$ = 0.1134 for 6282 independent reflections corrected for absorption [μ(Mo-Kα) = 3.284 mm^{-1}] and 620 parameters. Atomic coordinates bond lengths and angles, and thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 G. A. Somorjai, *Chemistry in Two Dimensions: Surfaces*, Cornell University Press, Ithaca, 1981, ch. 9.

2 M. C. Tsai, C. M. Friend and E. L. Muetterties, *J. Am. Chem. Soc.*, 1982, **104**, 2539; M. E. Bussell, F. C. Henn and C. T. Campbell, *J. Phy. Chem.*, 1992, **96**, 5978; F. C. Henn, A. L. Diaz, M. E. Bussell, M. B. Hugenschmidt, M. E. Domagala and C. T. Campbell, *J. Phys. Chem.*, 1992, **96**, 5965; M. B. Hugenschmidt, A. L. Diaz and C. T. Campbell, *J. Phys. Chem.*, 1992, **96**, 5974.

3 See for example: A. J. Canty, A. J. P. Domingos, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1973, 2056; B. F. G. Johnson, A. J. Blake, C. M. Martin, D. Braga, E. Parisini and H. Chen, *J. Chem. Soc., Dalton Trans.*, 1994, 2167; P. J. Dyson, B. F. G. Johnson, J. Lewis, M. Martinelli, D. Braga and F. Grepioni, *J. Am. Chem. Soc.*, 1993, **115**, 9062; P. J. Dyson, B. F. G. Johnson, D. Reed, D. Braga, F. Grepioni and E. Parisini, *J. Chem. Soc., Dalton Trans.*, 1993, 2817.

4 M. A. Gallop, B. F. G. Johnson, J. Lewis, A. McCamley and R. N. Perutz, *J. Chem. Soc., Chem. Commun.*, 1988, 1071.

5 B. F. G. Johnson, C. M. Martin, D. Braga, F. Grepioni and E. Parisini, *J. Chem. Soc., Chem. Commun.*, 1994, 1253; D. Braga, F. Grepioni, P. J. Dyson, B. F. G. Johnson and C. M. Martin, *J. Chem. Soc., Dalton Trans.*, submitted for publication.

6 C. E. Anson, P. J. Bailey, G. Conole, B. F. G. Johnson, J. Lewis, M. McPartlin and H. R. Powell, *J. Chem. Soc., Chem. Commun.*, 1989, 442; P. J. Bailey, M. J. Duer, B. F. G. Johnson, J. Lewis, G. Conole, M. McPartlin, H. R. Powell and C. E. Anson, *J. Organomet. Chem.*, 1990, **383**, 441.

7 P. J. Dyson, B. F. G. Johnson, C. M. Martin, D. Reed, D. Braga and F. Grepioni, *J. Am. Chem. Soc.*, submitted for publication.

8 M. J. Hostetler, L. H. Dubois, R. G. Nuzzo and G. S. Girolami, *J. Am. Chem. Soc.*, 1993, **115**, 2044; M. J. Hostetler, R. G. Nuzzo, G. S. Girolami and L. H. Dubois, *J. Phys. Chem.*, 1994, **98**, 2952.