The Preparation and Solid-state Structure of $Ru_5C(CO)_{13}(\eta^4-C_4Ph_4)$: The First Cluster to Carry a Cyclobutadiene Ring

Philip J. Bailey, Alexander J. Blake, Paul J. Dyson, Scott L. Ingham and Brian F. G. Johnson*

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ

The new organometallic pentaruthenium cluster $Ru_5C(CO)_{13}(\eta^4-C_4Ph_4)$ has been prepared from the redox mediated ligand transfer reaction between $[Ru_5C(CO)_{14}]^{2-}$ and $[Pd(\eta^4-C_4Ph_4)(acetone)_3]^{2+}$ during which the four-membered ring transfers from the palladium cation to a cluster ruthenium atom; the cluster has been characterised by single-crystal X-ray diffraction.

There now exists a wide and diverse chemistry of benzene-metal clusters.[1] Benzene and its close relatives such as toluene, xylene and mesitylene have been shown to bond in the conventional η^6 terminal mode, the former two also in the less conventional μ_3 facial mode.[2] Other arenes with unsaturated side-chains have also been characterised in the face-capping mode.[1] Interconversion between the two coordination modes has been observed,[2,3] and there are now several examples of C–H bond activation to generate benzyne derivatives.[4] However, to date these phenomena have been restricted almost exclusively to six-membered aromatic systems, although C_5-dienyl ring systems also show terminal and facial bonding to clusters.[5] Here we report a new synthetic method which gives easy access to clusters with bonded cyclobutadiene moieties. We believe this reaction to be general and to offer a potential route into a wide variety of C_4-cluster systems.

The ligand transfer reaction between $[Pd(\eta^4-C_4Ph_4)Br]_2$ and $Fe(CO)_5$ to yield the organometallic complex $Fe(CO)_3(\eta^4-C_4Ph_4)$ is well documented.[6] In this work we have adopted a similar approach to our cluster systems but with an important modification, *viz* the use of the highly active solvated species $[Pd(\eta^4-C_4Ph_4)(acetone)_3]^{2+}$ which may be prepared in high yield from the reaction of the chloro-bridged dimeric species $[Pd(\eta^4-C_4Ph_4)Cl]_2$ with 2 equivalents of $AgBF_4$ in acetone. Redox mediated ligand transfer occurs on reaction of the pentanuclear dianionic cluster, $[Ru_5C(CO)_{14}]^{2-}$, added in a dropwise fashion to a slight excess of the cationic palladium complex in dichloromethane, followed by heating to reflux for 30 min. This affords, after purification by filtration through a short silica column, the new neutral cluster $Ru_5C(CO)_{13}(\eta^4-C_4Ph_4)$ **1** in virtually quantitative yield.

Characterisation of **1** is based on spectroscopic data,† and a single-crystal X-ray diffraction study;‡ the results from these analyses being in complete agreement. The molecular structure of **1** is depicted in Fig. 1 together with relevant bond parameters. The ruthenium atoms form a square-based pyramidal geometry, similar to that found in the parent cluster, $Ru_5C(CO)_{15}$ but somewhat more distorted.[7] We believe this to be due to the presence of the C_4Ph_4 ligand. The Ru–Ru bond lengths range from 2.790(2)–2.948(2) Å [mean = 2.846(2) Å] [*cf.* $Ru_5C(CO)_{15}$, 2.800(2)–2.882(2) Å, mean = 2.840(2) Å]. The Ru–C(carbide) distances do not show much variance within the square base ranging from 2.012(9)–2.059(9) Å; however, the interaction with the apical ruthenium atom, Ru(5), is longer [2.254(10) Å] so that the carbide is displaced by 0.251 Å out of the basal plane. The most important feature of compound **1** is the presence of the C_4Ph_4 group which is η^4 bonded to a basal metal atom [Ru(1)–C(1l) 2.239(9), Ru(1)–C(2l) 2.202(9), Ru(1)–C(3l) 2.193(9) and Ru(1)–C(4l) 2.271(10) Å]. Within the C_4-square, the mean C–C bond length is 1.472(14) Å, which is typical of those found in four-membered ring systems. The four phenyl groups (1, 2, 3 and 4) exhibit dihedral angles of 60.2(5), 15.3(7), 81.5(4) and 20.5(7)°, respectively, thus alternate rings show similar degrees of torsion, two being almost flat and two almost perpendicular to the square plane. The phenyl groups also bend out of the square plane away from the cluster, the mean elevation of the *ipso*-carbon atoms above this plane being 0.33 Å. The presence of this ring alters the topology of the carbonyl groups which range from terminal groups to bridging ligands so as to give essentially a homogeneous electron distribution of six electrons to each metal atom like that found in the parent molecule which has three terminal carbonyl groups attached to each ruthenium atom.[7]

Our approach to the transfer of the cyclobutadiene ligand requires both the oxidation of the cluster dianion and the expulsion of one carbonyl group. A possible mechanism for this transformation involves the formation of a hexanuclear intermediate in which the palladium unit bonds to the base of the ruthenium cluster forming $Ru_5PdC(CO)_{14}(\eta^4-C_4Ph_4)$ in the first instance. The IR spectrum of the post reaction mixture is markedly different from that of **1**, hence corroborating the above statement, and the slippage of the C_4Ph_4 ring to a basal ruthenium atom must then follow together with the expulsion of palladium metal affording the neutral product **1**. We are currently attempting to substantiate these proposals in more detail, and we have also found that a similar reaction occurs between the hexanuclear cluster, $[Ru_6C(CO)_{16}]^{2-}$, and $[Pd(\eta^4-C_4Ph_4)(acetone)_3]^{2+}$ to afford a similar cyclobutadiene-containing product, the explusion of the palladium occurring at a much faster rate in this case. We are applying this high yielding synthesis to a number of other dianionic clusters.

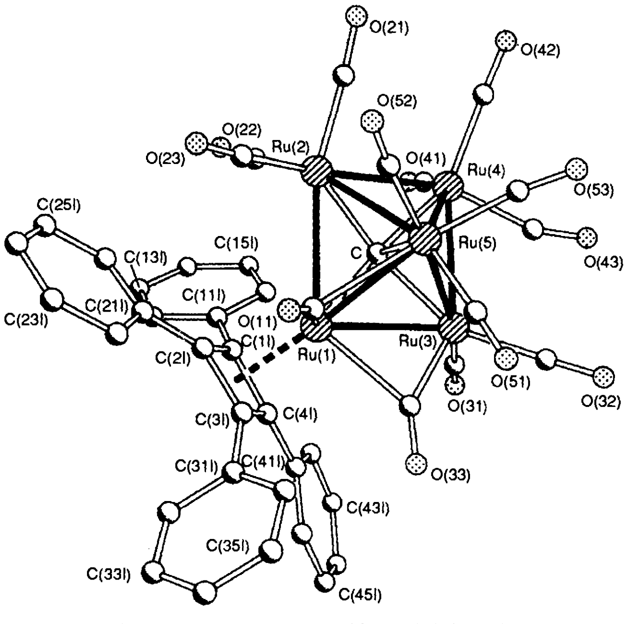

Fig. 1 The molecular structure of $Ru_5C(CO)_{13}(\eta^4-C_4Ph_4)$ **1** in the solid state. Principal bond parameters (Å); Ru(1)–Ru(2) 2.948(2), Ru(1)–Ru(3) 2.8319(14), Ru(1)–Ru(5) 2.862(2), Ru(2)–Ru(4) 2.831(2), Ru(2)–Ru(5) 2.803(2), Ru(3)–Ru(4) 2.790(2), Ru(3)–Ru(5) 2.8026(14), Ru(4)–Ru(5) 2.898(2). Ru–$C_{carbide}$; Ru(1)–C 2.025(9), Ru(2)–C 2.026(9), Ru(3)–C 2.059(9), Ru(4)–C 2.012(9), Ru(5)–C 2.254(10). Ru(1)–C_{ring}; Ru(1)–C(1l) 2.239(9), Ru(1)–C(2l) 2.202(9), Ru(1)–C(3l) 2.193(9), Ru(1)–C(4l) 2.271(10). C_{ring}–C_{ring}; C(1L)–C(2L) 1.491(13), C(2L)–C(3L) 1.467(13), C(3L)–C(4L) 1.468(14), C(4L)–C(1L) 1.460(14).

We would like to thank the EPSRC, The University of Edinburgh and NATO for financial support.

Received, 15th July 1994; 4/04360J

Footnotes

† *Spectroscopic data* for $Ru_5C(CO)_{13}(\eta^4\text{-}C_4Ph_4)$: ν(CO)/cm^{-1} (CH_2Cl_2) 2080m, 2060s, (sh) 2046vs, 2028s, (sh), 1967w, br, 1906w, br, 1792vw, br; ^{1}H NMR ($CDCl_3$) multiplet resonances are observed between δ 7.12 and 7.94, assigned to the protons of the four phenyl rings; MS $M^+ = 1237$ (calc. = 1237.9) and ions consistent with weights corresponding to the sequential loss of 13 carbonyl groups.

‡ *Crystal data* for $Ru_5C(CO)_{13}(\eta^4\text{-}C_4Ph_4)$ **1**: $O_{13}Ru_5C_{42}H_{20}$, monoclinic, space group $P2_1/c$, $a = 16.604(6)$, $b = 15.926(5)$, $c = 15.743(4)$ Å, $\beta = 95.39(6)°$, $M = 1237.93$, $U = 4125(2)$ Å^3, $Z = 4$, $D_c = 1.984$ g cm^{-3}, $T = 295$ K, $F(000) = 2384$, $R1 = 0.0473$ [3737 reflections with $F_o > 4\sigma(F_o)$], $wR2 = 0.0755$ for 5121 independent reflections corrected for absorption [μ(Mo-Kα) = 1.845 mm^{-1}] and 541 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 H. Wadepohl, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 247; D. Braga, P. J. Dyson, F. Grepioni and B. F. G. Johnson, *Chem. Rev.*, in the press.

2 D. Braga, F. Grepioni, E. Parisini, P. J. Dyson, B. F. G. Johnson, D. Reed, D. S. Shephard, P. J. Bailey and J. Lewis, *J. Organomet. Chem.*, 1993, **462**, 301.

3 P. J. Dyson, B. F. G. Johnson and D. Braga, *Inorg. Chim. Acta*, 1994, **222**, 299, and references therein.

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

5 E. O. Fischer, O. S. Mills, E. F. Paulus and H. Wawersik, *J. Chem. Soc., Chem. Commun.*, 1967, 643; O. S. Mills and E. F. Paulus, *J. Organomet. Chem.*, 1968, **11**, 587; A. J. Blake, P. J. Dyson, B. F. G. Johnson, D. Reed and D. S. Shephard, *J. Chem. Soc., Chem. Commun.*, 1994, 1347.

6 P. M. Maitlis and A. Efraty, *J. Am. Chem. Soc.*, 1963, **85**, 1887; D. F. Pollock and P. M. Maitlis, *J. Organomet. Chem.*, 1971, **26**, 407.

7 B. F. G. Johnson, J. Lewis, J. N. Nicholls, J. Puga, P. R. Raithby, M. J. Rosales, M. McPartlin and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1983, 277.