New linked and threaded cluster compounds

Brian F. G. Johnson,*[a] Catherine M. G. Judkins,[a] Justin M. Matters,[a] Douglas S. Shephard[a] and Simon Parsons[b]

[a] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW.*
E-mail: bfgj1@cam.ac.uk
[b] *Dept. of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*

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The linked cluster species $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4C_{10}H_{20}O_6)]_2[H_3N(CH_2)_8NH_3][BF_4]_2$ 2 and the threaded derivative $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4C_{12}H_{24}O_8C_6H_4)][PhCH_2NH_2CH_2Ph]PF_6$ 4 have been prepared and fully characterised by single crystal X-ray analysis; these compounds are valuable precursors in the formation of nanoparticle devices.

For some time we have been investigating the potential of metal clusters to act as precursors in the formation of nanoparticle arrays for use in catalysis[1] and in the production of electronic devices.[2] A primary objective of our work has been the preparation of polymer precursors which lead to materials with cluster units bonded either within the polymer backbone [Fig. 1(a)] or as pendants, suspended from a polymeric backbone [Fig. 1(b)].

In each case clear advantages have become apparent.[3,4] Recently, we have established a route to “electron-hopping” materials which permit the production of linked nanoparticle arrays such as chains or wires. In this work we report a new and valuable route to linked and threaded clusters which has enabled us to investigate the potential of adopting such methods in the formation of polymers bearing discrete cluster units.

Several years ago we demonstrated[5] that arene clusters of the type $[(\eta^6\text{-arene})Ru_6C(CO)_{14}]$ and later $[(\mu_3\text{-arene})Ru_6C(CO)_{14}]$ could easily be prepared.[6] With this knowledge in mind, attempts were made to establish a range of derivatised arenes coordinated to cluster units. More recently, we have been able to attach benzocrown ethers to hexaruthenium clusters by direct thermolysis and this has generated our interest into the potential use of such complexes as molecular sensors.[7,8] Preliminary investigations into such applications have been conducted and the compound $[Ru_6C(CO)_{14}(\eta^6\text{-}C_{16}H_{24}O_6)]$ **1** shown to encapsulate either the NH_4^+ ion or metal ions such as K^+ and Na^+.[8]

Building on these observations, we have investigated the use of such non-covalent interactions to link two or more clusters and have developed a simple route to both linked and threaded cluster systems.

Compound **1** may be readily prepared according to the reaction sequence outlined in Scheme 1.[7] It has been fully characterised by the usual spectroscopic techniques and by single crystal X-ray analysis† (Fig. 2). The arene ring is coordinated in an η^6 fashion to a single ruthenium atom, with the average Ru–arene bond distance being 2.26 Å. In each of these cluster/crown complexes the interstitial carbon atom is displaced slightly from the centre of the cluster towards the arene ring and there is one bridging carbonyl ligand on the cluster. The oxygen atoms are tilted up at an angle to the plane of the arene ring and the undistorted cavity allows an ideal site for host–guest chemistry.

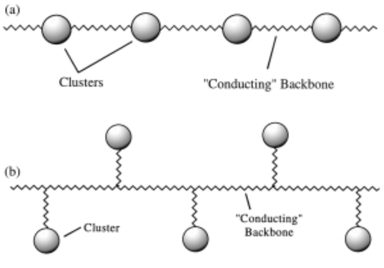
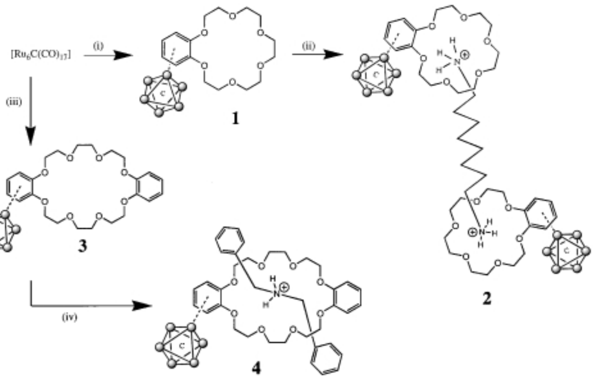


Fig. 1 (a) Polymer with cluster units within polymer backbone and (b) with cluster units as pendants.



Scheme 1 Preparation of **2** and **4**: *Reagents and conditions*: (i) di-*n*-butyl ether, benzo-18-crown-6, 16 h reflux, N_2; (ii) CH_2Cl_2 + few drops MeOH, stir 24 h; (iii) di-*n*-butyl ether, dibenzo-24-crown-8, 16 h reflux, N_2; (iv) stir 24 h in CH_2Cl_2.

Treatment of **1** with the diprotonated diamine $[H_3N(CH_2)_8NH_3]^{2+}$ yields the new linked cluster system **2** (yield *ca*. 76%) in which the two quaternary ammonium units are embraced at either end by the polycyclic ether bonded to a cluster unit. This novel compound has been fully characterised by IR and NMR spectroscopy, elemental analysis and its molecular structure established by single crystal X-ray analysis. This is shown in Fig. 3, together with some relevant bond distances. As expected, the cluster units arrange themselves in a *trans*-configuration relative to the diammonium octane ‘linker,’ with the $–NH_3^+$ function lying *ca*. 1.3217 Å above the least squares mean plane of oxygen atoms. Two of the hydrogen atoms on each of the ammonium species interact with two of the oxygen atoms of the crown and have N–H···O bond distances of 2.970(5) and 2.967(5) Å (in each of which the N–H distances

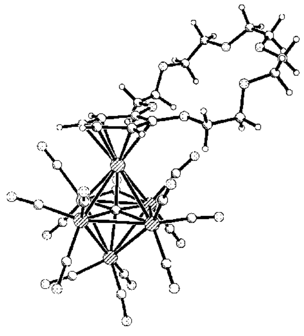


Fig. 2 Molecular structure of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4C_{10}H_{20}O_6)]$ **1**.

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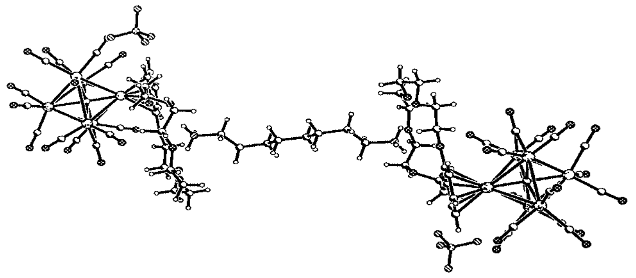

Fig. 3 Molecular structure of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4C_{10}H_{20}O_6)]_2\text{-}[H_3N(CH_2)_8NH_3][BF_4]_2$ **2** Average ruthenium–arene bond length = 2.26 Å; N–O distances range from 2.952(4) to 3.231(4) Å.

are 0.91 Å). The third hydrogen of the ammonium species points in the direction of one of the oxygen atoms of the crown but is aimed above the plane and displays a long range interaction of 3.205(4) Å.

In a separate experiment, compound **3**, a relative of **1** but containing the dibenzo-24-crown-8 ligand was prepared as outlined in Scheme 1 and a crystal suitable for X-ray analysis† obtained (Fig. 4). The crown is approximately planar with the mean deviation from the plane of oxygen atoms being 0.0747 Å. The larger macrocyclic cavity size which is suitable for "threading" reactions (in which the molecules are actually threaded through the hole) to yield *pseudo*rotaxanes[9] can clearly be seen.

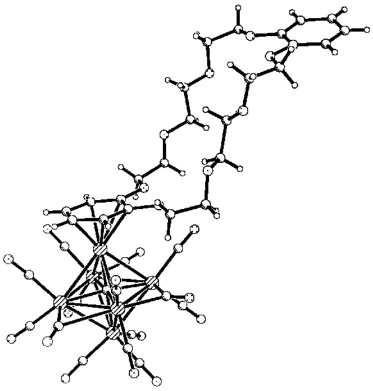

Fig. 4 Molecular structure of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4C_{12}H_{24}O_8C_6H_4)]$ **3**. Average ruthenium–arene bond length = 2.26 Å.

When **3** was reacted with the protonated amine $[PhCH_2NH_2CH_2Ph]^+$ in dichloromethane, the *pseudo*rotaxane **4** was produced (yield *ca*. 70%). The amine has threaded through the macrocyclic cavity attached to the cluster to generate the classic 'bead on a string configuration.' This compound has also been fully characterised by single crystal X-ray analysis† and the molecular structure is shown in Fig. 5. In contrast to analogous organic compounds[9] in which the two arene rings of the crown ether are widely separated, the macrocycle in **4** has bent to display a π-stacking arrangement between the two arene units of the crown and one of the phenyl units of the thread. The two hydrogen atoms of the ammonium group display short range interactions with two of the oxygen atoms of the crown, with approximate distances of 2.019 and 2.131 Å. They also display longer range interactions with two further oxygen atoms of the crown (distances *ca*. 2.4–2.6 Å) and there are also several long range interactions between the hydrogen atoms of the methylene group nearest to the arene involved in the π-stack and the macrocyclic oxygen atoms.

These new materials open up a new and important route to cluster polymer precursors which, in other systems, have been shown to serve as valuable intermediates in the formation of nanoparticle materials for use in electron devices.[10]

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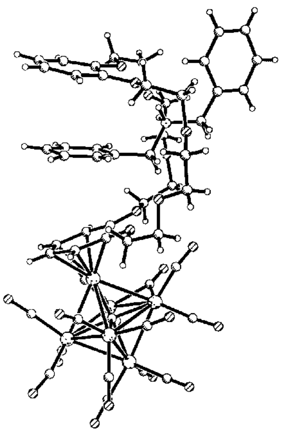

Fig. 5 Molecular structure of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4C_{12}H_{24}O_8C_6H_4)]\text{-}[PhCH_2NH_2CH_2Ph]PF_6$ **4**. Distance between planes 1 and 2 = 4.105 Å, distance between planes 2 and 3 = 3.820 Å. Angle between planes 1 and 2 = 22.5°, angle between planes 2 and 3 = 8.5°. Average N···O separation = 2.9595 Å, average H···O separation = 2.075 Å.

Notes and references

† *Crystal data*: $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4C_{10}H_{20}O_6)]$ **1**: M = 1322.94, orthorhombic, a = 19.1672(8), b = 14.8037(6), c = 27.0061(8) Å, U = 7662.9(5) Å^3, T = 180 K, space group $Pca2_1$, Z = 8, μ(Mo-Kα) = 2.387 mm^{-1}, 30683 reflections collected, 12064 unique (R_{int} = 0.0571) which were used in all calculations. Final $R1$ (observed) was 0.0682. Single crystals of **1** were recrystallised from CH_2Cl_2–hexane. Some atoms of the crown ether moieties are not well resolved: isotropic temperature factors and extensive bond distance restraints were applied to these atoms.

$[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4C_{10}H_{20}O_6)]_2[H_3N(CH_2)_8NH_3][BF_4]_2$ **2**: M = 2965.76, triclinic, a = 10.1350(2), b = 15.0310(4), c = 16.4410(5) Å, U = 2413.39(11) Å^3, T = 180 K, space group $P1$, Z = 1, μ(Mo-Kα) = 1.921 mm^{-1}, 29071 reflections collected, 8467 unique (R_{int} = 0.0354) which were used in all calculations. Final $R1$ (observed) was 0.0286. Single crystals of **2** were recrystallised from acetone–pentane. Some atoms of the crown are not well resolved and there is disorder over two sites. Isotropic temperature factors and bond distance restraints were applied to these atoms.

$[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4C_{12}H_{24}O_8C_6H_4)]$ **3**: M = 1459.09, triclinic, a = 9.9611(5), b = 16.6690(10), c = 18.2217(11) Å, U = 2695.1(3) Å^3, T = 230 K, space group $P1$, Z = 2, μ(Mo-Kα) = 1.711 mm^{-1}, 16205 reflections collected, 12081 unique (R_{int} = 0.0371) which were used in all calculations. Final $R1$ (observed) was 0.0692. Single crystals of **3** were recrystallised from CH_2Cl_2–hexane. Some atoms of the crown ether moieties are not well resolved: isotropic temperature factors and extensive bond distance restraints were applied to these atoms.

$[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4C_{12}H_{24}O_8C_6H_4)][PhCH_2NH_2CH_2Ph]PF_6$ **4**: M = 1802.34, monoclinic, a = 12.312(5), b = 9.580(7), c = 52.612(16) Å, U = 6188 (6) Å^3, T = 220 K, space group $P2_1/c$, Z = 4, μ(Mo-Kα) = 1.547 mm^{-1}, 8463 reflections collected, 7964 unique (R_{int} = 0.0445) which were used in all calculations. Final $R1$ (observed) was 0.1290.

CCDC 182/1707. See http://www.rsc.org/suppdata/cc/b0/b003291n/ for crystallographic files in .cif format.

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