

Difunctionalised arene Ru₆C cluster compounds with electron-withdrawing groups

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Thermolysis of [Ru₆C(CO)₁₇] **1** with dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate [C₆H₆(CO₂Me)₂-1,4] in dibutyl ether gave two isomeric cluster compounds [Ru₆C(CO)₁₄(η⁶-C₆H₄(CO₂Me)₂-1,4)] **2** and [Ru₆C(CO)₁₄(μ₃-η²:η²:η²-{C₆H₄(CO₂Me)₂-1,4})] **3**. The solid-state molecular structures of **2** and **3** have been established by low-temperature single-crystal X-ray diffraction analysis. These constitute the first example of co-ordination isomerism for the Ru₆C(CO)₁₄ unit with respect to a specific arene. In **2** the arene is η⁶ bonded to a single ruthenium atom whereas in **3** the arene is bonded in the μ₃ mode to a triangular Ru₃ face of the octahedral cluster unit. The solid-state structure of **3** is comprised of two rotamers along with two molecules of dichloromethane solvate. The solid-state architectures of **2** and **3** were also examined. The bifunctionalised arene ligand in **2** and **3** has the potential for further organic chemistry at these sites including possible copolymerisation with primary/secondary diamines.

The synthesis of materials with useful properties in the field of organometallic chemistry is of growing interest.¹ Clusters have long been known to possess various interesting characteristics. Redox activity,² for instance, is known to increase with cluster nuclearity.³ Optical work on the hexanuclear bicapped tetrahedral cluster [Os₆(CO)₁₈] has suggested semiconductor properties.⁴ We have recently shown that [Ru₆C(CO)₁₇] can act as an electron acceptor with 'tuneable' redox activity.⁵ The solid-state architecture of bis(arene) clusters is notable in that one-dimensional arrays are produced through intermolecular arene-arene 'graphite-like' interactions.⁶ The ability of clusters to activate both C-H and C-C bonds is also a valuable characteristic. We have therefore extended our work on cluster-co-ordinated carbocycles to include study of functionalised arenes, which may, by simple organic reactions, be incorporated in organometallic networks.⁷ The electronic/steric influences that dictate the co-ordination modes of cluster-bound arenes are still unclear. Hence, the examination of co-ordinated arene derivatives containing strong electron donating/withdrawing effects is attractive and may shed light on some fundamental questions concerning cluster co-ordination. The chemistry reported in this paper is therefore both an extension of our work on the cluster-arene bond and a foray into the synthesis of higher-nuclearity cluster-containing materials.

Results and Discussion

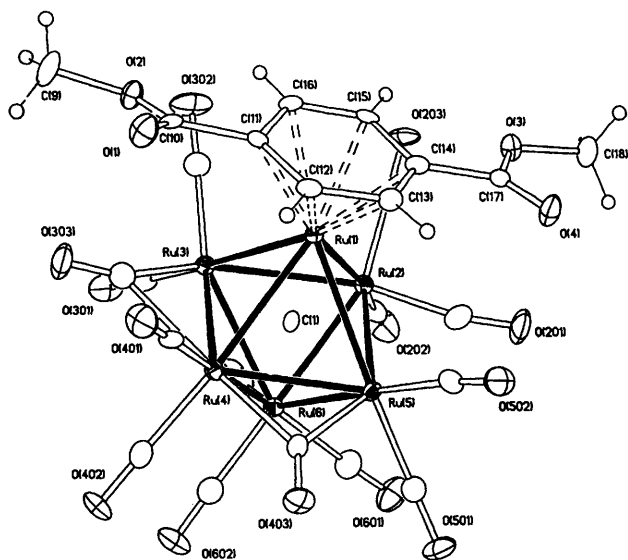
Thermolysis of [Ru₆C(CO)₁₇] **1** with a two-fold excess of dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate C₆H₆(CO₂Me)₂-1,4 in dibutyl ether for 4 h yields the two cluster compounds **2** and **3** as the major products. Separation of these products was achieved by TLC using dichloromethane-ethyl acetate-hexane (2:1:7 v/v) as eluent. Brown **2** and the red **3** were tentatively characterised in the first instance on the basis of their positive-ion fast atom bombardment mass spectra, which exhibit a parent peak at *m/z* 1205, in each case, and their solution infrared spectra. The cluster-bound carbonyl stretching energies for **2** and **3** are higher (*ca.* 6 cm⁻¹) than those observed for [Ru₆C(CO)₁₄(η⁶-C₆H₆)]⁸ and [Ru₆C(CO)₁₄(μ₃-C₁₆H₁₆)]⁹ respectively, and may be taken to indicate a reduced degree of M→CO π-back donation as a result of reduced electron density in the cluster core. This in turn may be attributable to a poorer

donor ability of the co-ordinated arene and/or an enhanced π-acceptor ability resulting in a net reduction of electron density transferred to the cluster core. Hence, in this instance, the carbonyl stretching energies act as a probe into the cluster-core electron density and thus the nature of the arene-cluster bond. The ester carbonyl stretch absorption of **3** is lower in energy than that of **2**. This is perhaps due to a simple electron-withdrawing effect of the π-deficient arene or through some form of hyperconjugation operating in the facial co-ordination mode of **3**. The ¹H NMR solution spectra of **2** and **3** in CDCl₃ solution each show two signals of relative integrals 4:6 at δ 6.41, 3.88 and 4.81, 3.95 respectively. The presence of only two signals in each case indicates that at ambient temperature the arene is free to rotate. It may also be assumed that steric impedence of the methyl carboxylate groups is insufficient to significantly hinder rotation. The spectra were redetermined several days later, after storage of the NMR solution samples at ambient temperature. No change was observed indicating that interconversion of **2** and **3** is an unfavourable process under these conditions. The large difference in the resonant frequency of the singlet signal assigned to the four aryl protons (1.6 ppm) may be attributed to a stronger cluster-arene interaction in **3**. These observations are consistent with the results from extended-Hückel molecular orbital calculations which show a stronger arene-cluster interaction for the facial co-ordination mode.⁶

The molecular structure of compound **2**, as determined by single-crystal X-ray diffraction, is shown in Fig. 1 and some key structural parameters in Table 1. An octahedron of six ruthenium metal atoms encapsulates a carbido atom at the centre, an architecture shared by many derivatives of **1**. The carbido atom is shifted toward the arene-carrying metal [Ru(1)-C(1) 1.938(7) Å]. All intermetallic contacts fall within the normal range [2.8125(12)-3.0312(13) Å]. Two bridging and twelve terminal carbonyls constitute the co-ordination sphere for metals Ru(2)-Ru(6) of the cluster. The μ-CO are bound to Ru(3), Ru(4) and Ru(5) with Ru(4) being common to both. Of primary importance to the aims of this study is the apically co-ordinated arene. The Ru(1)-arene bond lengths lie in the range 2.224(7)-2.270(7) Å. Two electron-withdrawing methyl carboxylate groups occupy the *para* positions, and are approximately coplanar with the C₆ ring. Carbons C(10) and C(17) are planar

Table 1 Bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) for compound **2**

Ru(1)–C(1)	1.937(8)	Ru(1)–C(14)	2.224(7)	Ru(1)–C(12)	2.243(7)		
Ru(1)–C(15)	2.246(7)	Ru(1)–C(11)	2.253(7)	Ru(1)–C(16)	2.267(7)		
Ru(1)–C(13)	2.270(7)	Ru(1)–Ru(2)	2.8375(12)	Ru(1)–Ru(3)	2.8499(10)		
Ru(1)–Ru(5)	2.8616(11)	Ru(1)–Ru(4)	2.8895(12)	Ru(2)–C(202)	1.893(9)		
Ru(2)–C(203)	1.901(9)	Ru(2)–C(201)	1.927(9)	Ru(2)–C(1)	2.049(7)		
Ru(2)–Ru(6)	2.8165(12)	Ru(2)–Ru(5)	2.9712(12)	Ru(2)–Ru(3)	3.0312(13)		
Ru(3)–C(302)	1.881(9)	Ru(3)–C(301)	1.904(10)	Ru(3)–C(303)	1.972(9)		
Ru(3)–C(1)	2.051(7)	Ru(3)–Ru(4)	2.8556(12)	Ru(3)–Ru(6)	2.8968(12)		
Ru(4)–C(401)	1.884(8)	Ru(4)–C(402)	1.888(9)	Ru(4)–C(403)	2.083(8)		
Ru(4)–C(1)	2.091(7)	Ru(4)–C(303)	2.446(9)	Ru(4)–Ru(5)	2.8125(12)		
Ru(4)–Ru(6)	2.9755(13)	Ru(5)–C(501)	1.882(8)	Ru(5)–C(502)	1.891(9)		
Ru(5)–C(403)	2.048(8)	Ru(5)–C(1)	2.070(7)	Ru(5)–Ru(6)	2.8953(10)		
Ru(6)–C(601)	1.897(9)	Ru(6)–C(603)	1.905(9)	Ru(6)–C(602)	1.921(9)		
Ru(6)–C(1)	2.069(8)	O(1)–C(10)	1.215(9)	O(2)–C(10)	1.307(9)		
O(2)–C(9)	1.459(9)	O(3)–C(17)	1.334(9)	O(3)–C(18)	1.456(9)		
O(4)–C(17)	1.199(9)	C(10)–C(11)	1.493(10)	C(11)–C(12)	1.418(10)		
C(11)–C(16)	1.423(10)	C(12)–C(13)	1.396(10)	C(13)–C(14)	1.416(10)		
C(14)–C(15)	1.420(10)	C(14)–C(17)	1.495(10)	C(15)–C(16)	1.392(10)		
C(201)–O(201)	1.144(10)	C(202)–O(202)	1.132(10)	C(203)–O(203)	1.145(10)		
C(301)–O(301)	1.139(10)	C(302)–O(302)	1.140(10)	C(303)–O(303)	1.135(10)		
C(401)–O(401)	1.142(9)	C(402)–O(402)	1.146(9)	C(403)–O(403)	1.158(9)		
C(501)–O(501)	1.129(9)	C(502)–O(502)	1.134(10)	C(601)–O(601)	1.131(10)		
C(602)–O(602)	1.126(10)	C(603)–O(603)	1.142(10)				
C(10)–O(2)–C(9)	116.3(6)	C(17)–O(3)–C(18)	115.2(6)	C(13)–C(14)–C(15)	119.5(7)	C(13)–C(14)–C(17)	118.2(7)
O(1)–C(10)–O(2)	126.3(7)	O(1)–C(10)–C(11)	120.9(7)	C(15)–C(14)–C(17)	122.2(7)	C(16)–C(15)–C(14)	120.7(7)
O(2)–C(10)–C(11)	112.8(6)	C(12)–C(11)–C(16)	118.4(7)	C(15)–C(16)–C(11)	120.2(7)	O(4)–C(17)–O(3)	125.2(7)
C(12)–C(11)–C(10)	120.6(6)	C(16)–C(11)–C(10)	120.8(6)	O(4)–C(17)–C(14)	123.5(7)	O(3)–C(17)–C(14)	111.2(6)
C(13)–C(12)–C(11)	121.8(7)	C(12)–C(13)–C(14)	119.2(7)				

**Fig. 1** Solid-state molecular structure of compound **2**

to within experimental error. The carbon–oxygen bond lengths C(10)–O(2) and C(17)–O(3) are shorter than their corresponding values in comparable unco-ordinated aryl carboxylates, perhaps suggesting an increased bonding interaction between the O atoms and their electron-deficient neighbours. The strong electron-withdrawing nature of the cluster provides a driving force for such a structural feature. Correlation of substituent parameters with the metal carbonyl stretching force constant in arenetricarbonylchromium complexes suggests that the overall electronic substituent effect transmitted to the carbonyl groups involves both mesomeric and inductive mechanisms. Within the restricted domain, including substituent group and arene, transmission proceeds largely by resonance, with a minor inductive (through-bond and field) effect operative in the same domain. Further transmission from the substituted arene ring to the metal atom predominantly involves an inductive mechanism. This suggests appreciable participation of the ring-

carbon σ framework in the formation of the metal–ring bond.¹⁰ This description is consistent with the above structural and spectral observations. A representation of the dimethyl cyclohexadiene-1,4-dicarboxylate framework bond lengths of **2** in the solid state is given in Fig. 2.

The solid-state molecular structure of compound **3** has also been determined by X-ray crystallography. The asymmetric unit contains two molecules that differ in the orientation of a carboxylate group, along with two molecules of dichloromethane solvate. Representations of the *anti* (**3**) and *syn* (**3'**) structures are given in Fig. 3(a) and 3(b) respectively. Selected structural parameters are given in Tables 2 and 3. Compound **3** is one of the few examples of a facially co-ordinated arene on a higher-nuclearity cluster. Six Ru atoms encapsulating a carbon atom constitute the octahedral cluster core in **3** and **3'**. The metal–metal contacts for **3** and **3'** lay in the ranges 2.799(2)–3.011(14) and 2.7900(14)–3.012(2) Å respectively. In each cluster core the carbido atom is slightly inclined towards the arene-co-ordinated ruthenium triangle. Metal to C₆ ring distances in **3** and **3'** lie in the ranges 2.151(7)–2.411(7) and 2.170(8)–2.381(7) Å respectively. The carbon–carbon bond lengths of the C₆ rings in each compound show little inclination to the hypothetical cyclohexatriene 'short-long' deformation previously observed for benzene on ruthenium and osmium triangular faces (Fig. 2).¹¹ This is understandable simply on grounds of symmetry and electronic effects. The local C_{3v} symmetry previously observed is not available to a *para*-substituted arene, whilst electron-withdrawing substituents in these positions have an unequal effect on the individual metal η^2 interactions. The planarity of the C₆ rings in **3** and **3'** is significantly less than that observed in **2**. The room-mean-square (r.m.s.) deviation for C(11')–C(16') from their least-squares plane is 0.044, greatest deviations being shown by C(15') and C(16') at 0.074(5) and 0.062(5) respectively, whilst the r.m.s. deviation for C(11)–C(16) from their least-squares plane is 0.027, greatest deviations being shown by C(15) and C(14) at 0.045(5) and 0.031(5) Å respectively.

The methyl carboxylate substituent carbons C(10), C(17), C(10') and C(17') in compounds **3** and **3'** are significantly bent out of the plane of the C₆ ring by 27.9(7), 15.3(8), 26.9(7) and

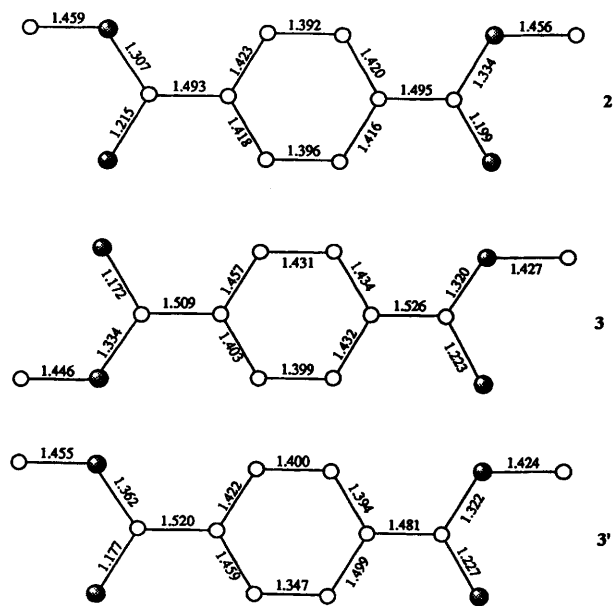


Fig. 2 Representation of the dimethyl cyclohexadiene-1,4-dicarboxylate framework bond lengths of compounds 2, 3 and 3' in the solid state

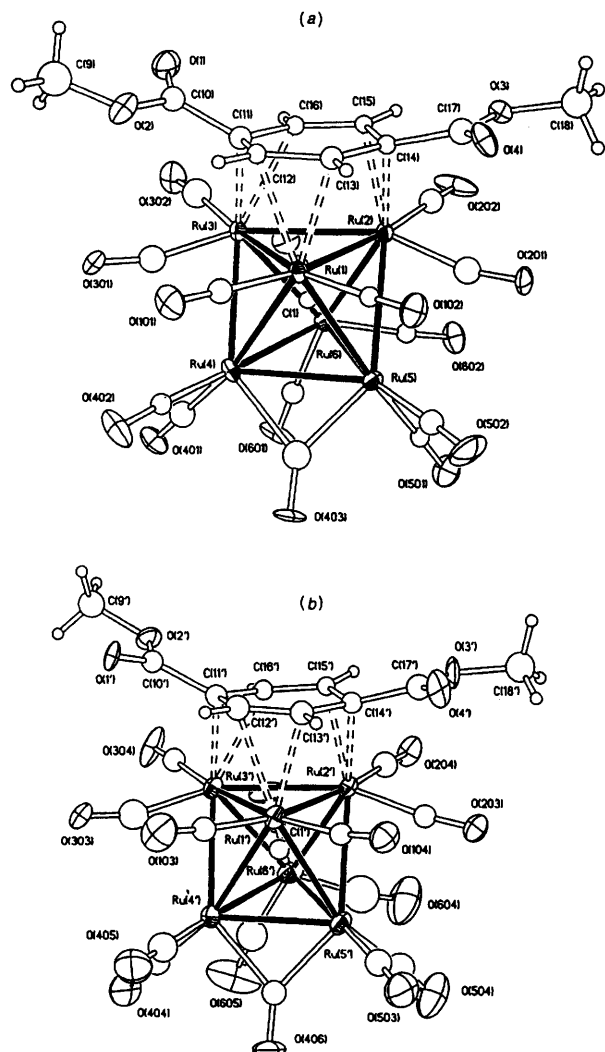


Fig. 3 Solid-state molecular structures of compounds 3 (a) and 3' (b)

18.0(7)° respectively. This indicates a radically different hybridisation of the co-ordinated carbon atoms in 2 and 3, the geometry of carbons C(11), C(14), C(11'), C(14') in 3 indicating a greater inclination toward sp^3 hybridisation. It is interesting

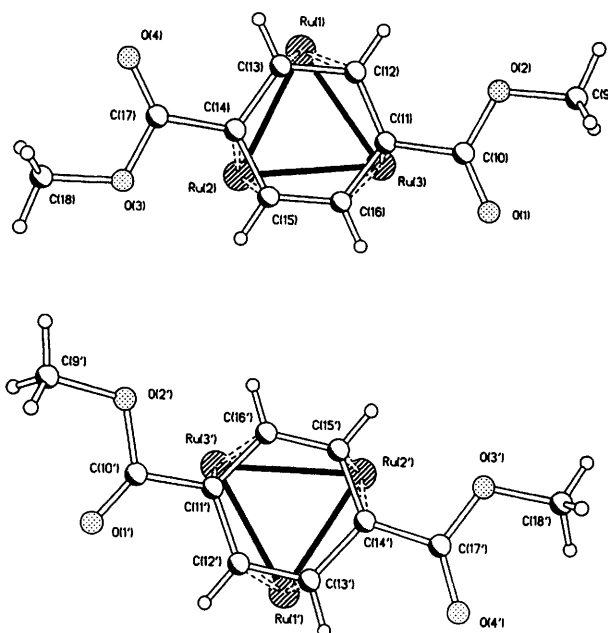


Fig. 4 The arene-triruthenium conformations in compounds 3 and 3' projected through the C_6 ring plane

that the pairs of angles for each molecule in 3 are markedly different. Since 3 and 3' show very different packing motifs it is unlikely this large difference is solely the result of solid-state interactions. Hence this arrangement appears to be a conformational energy minimum for both the *syn* and *anti* forms in the solid state. The remaining co-ordination spheres of 3 and 3' are made up of thirteen terminal CO and a μ -CO bridging Ru(5) and Ru(4) in both rotamers.

The solid-state arene- Ru_3 orientations of compounds 3 and 3', projected through the C_6 ring plane, are shown in Fig. 4. In each molecule the orientation deviates from a regular staggered C_{3v} conformation. The rotation axes of the Ru_3 triangle and C_6 ring are not collinear. The wide range of Ru-C bond lengths in 3 and 3' is due to a long-short dihapto arrangement giving a near-eclipsed conformation in both molecules. The solid-state architectures of 2 and 3 show some interesting intermolecular interactions. Compound 2 shows a single short contact of the type terminal carbonyl oxygen to ring hydrogen [O(501) \cdots H(15) 2.475 Å]; 3 and 3', however, show a highly complex packing motif. Central to the solid-state ordering of 3 is the relation of two *anti*-molecules about a centre of inversion [Fig. 5(a)]. This molecular pairing of the *anti* rotamers is maintained by the interaction of the ketonic oxygen O(4) with the ring hydrogen H(13) [O(4) \cdots H(13) 2.491 Å]. The nature of this interaction is unclear although an admixture of dipole-dipole and hydrogen-bonding interactions may serve as an adequate description. The second pair of ketonic oxygens show a further interaction with two dichloromethane solvate molecules [O(1) \cdots H(20a) 2.434 Å] also related by the centre of inversion. The 3' molecules are not paired in similar interactions but produce chains or 'snakes' in a nose-to-tail arrangement also involving close contacts of the H \cdots O type [O(406) \cdots H(16a) 2.580 and H(9'b) \cdots O(403) 2.554 Å] [Fig. 6(b)]. Packing motifs such as 'carbonyl interlocking,' previously seen in carbonyl compounds, are also present in 2 and 3.⁶

In conclusion, it is of particular interest that in this case the arene ligand may adopt either the η^6 - or the μ_3 - η^2 : η^2 : η^2 bonding mode giving the two isomeric forms 2 and 3. There are few examples of the μ_3 mode for systems based on the Ru_6C unit, arenes in general preferring to adopt the more usual η^6 mode. It is tempting to suggest that in this case, because of the electron-withdrawing abilities of the two CO_2Me groups, the μ_3 mode is available for electronic reasons. This is in accordance

Table 2 Bond lengths (Å) and angles (°) with e.s.d.s for compound 3

Ru(1)–C(101)	1.884(8)	Ru(1)–C(102)	1.907(6)	Ru(1)–C(1)	1.982(7)		
Ru(1)–C(13)	2.249(7)	Ru(1)–C(12)	2.335(6)	Ru(1)–Ru(2)	2.8210(14)		
Ru(1)–Ru(3)	2.828(2)	Ru(1)–Ru(5)	2.9011(14)	Ru(1)–Ru(4)	2.9399(13)		
Ru(2)–C(201)	1.866(8)	Ru(2)–C(202)	1.905(8)	Ru(2)–C(1)	2.054(8)		
Ru(2)–C(15)	2.189(6)	Ru(2)–C(14)	2.295(7)	Ru(2)–Ru(6)	2.8199(13)		
Ru(2)–Ru(3)	2.937(2)	Ru(2)–Ru(5)	3.0111(14)	Ru(3)–C(301)	1.866(9)		
Ru(3)–C(302)	1.890(7)	Ru(3)–C(1)	2.023(6)	Ru(3)–C(11)	2.151(7)		
Ru(3)–C(16)	2.411(7)	Ru(3)–Ru(4)	2.8589(13)	Ru(3)–Ru(6)	2.9224(14)		
Ru(4)–C(401)	1.882(8)	Ru(4)–C(402)	1.902(7)	Ru(4)–C(1)	2.070(8)		
Ru(4)–C(403)	2.114(7)	Ru(4)–Ru(5)	2.799(2)	Ru(4)–Ru(6)	2.972(2)		
Ru(5)–C(501)	1.911(7)	Ru(5)–C(502)	1.924(6)	Ru(5)–C(403)	2.044(9)		
Ru(5)–C(1)	2.064(6)	Ru(5)–Ru(6)	2.863(2)	Ru(6)–C(602)	1.905(8)		
Ru(6)–C(601)	1.906(8)	Ru(6)–C(603)	1.906(6)	Ru(6)–C(1)	2.064(7)		
O(1)–C(10)	1.223(8)	O(2)–C(10)	1.320(10)	O(2)–C(9)	1.427(10)		
O(3)–C(17)	1.334(9)	O(3)–C(18)	1.446(10)	O(4)–C(17)	1.172(8)		
C(10)–C(11)	1.526(10)	C(11)–C(16)	1.432(11)	C(11)–C(12)	1.434(8)		
C(12)–C(13)	1.431(10)	C(13)–C(14)	1.457(11)	C(14)–C(15)	1.403(8)		
C(14)–C(17)	1.509(11)	C(15)–C(16)	1.399(10)	C(101)–O(101)	1.146(9)		
C(102)–O(102)	1.142(7)	C(201)–O(201)	1.153(9)	C(202)–O(202)	1.122(9)		
C(301)–O(301)	1.143(10)	C(302)–O(302)	1.157(8)	C(401)–O(401)	1.147(10)		
C(402)–O(402)	1.130(9)	C(403)–O(403)	1.134(9)	C(501)–O(501)	1.126(9)		
C(502)–O(502)	1.118(8)	C(601)–O(601)	1.129(9)	C(602)–O(602)	1.142(10)		
C(603)–O(603)	1.131(7)						
C(10)–O(2)–C(9)	114.1(5)	C(17)–O(3)–C(18)	115.3(5)	O(101)–C(101)–Ru(1)	178.4(7)	O(102)–C(102)–Ru(1)	176.7(6)
O(1)–C(10)–O(2)	126.2(7)	O(1)–C(10)–C(11)	122.3(7)	O(201)–C(201)–Ru(2)	165.8(7)	O(202)–C(202)–Ru(2)	177.4(7)
O(2)–C(10)–C(11)	111.5(5)	C(16)–C(11)–C(12)	118.7(7)	O(301)–C(301)–Ru(3)	165.9(6)	O(302)–C(302)–Ru(3)	173.4(8)
C(16)–C(11)–C(10)	116.5(5)	C(12)–C(11)–C(10)	116.9(6)	O(401)–C(401)–Ru(4)	179.1(7)	O(402)–C(402)–Ru(4)	176.3(6)
C(13)–C(12)–C(11)	118.3(7)	C(12)–C(13)–C(14)	121.7(5)	O(403)–C(403)–Ru(5)	139.7(7)	O(403)–C(403)–Ru(4)	135.4(7)
C(15)–C(14)–C(13)	118.1(6)	C(15)–C(14)–C(17)	124.0(7)	O(501)–C(501)–Ru(5)	177.6(5)	O(502)–C(502)–Ru(5)	178.1(7)
C(13)–C(14)–C(17)	114.9(5)	C(14)–C(15)–C(16)	120.3(7)	O(601)–C(601)–Ru(6)	176.9(8)	O(602)–C(602)–Ru(6)	177.3(5)
C(15)–C(16)–C(11)	122.4(5)	O(4)–C(17)–O(3)	124.9(8)	O(603)–C(603)–Ru(6)	171.8(7)		
O(4)–C(17)–C(14)	126.0(8)	O(3)–C(17)–C(14)	109.1(5)				

Table 3 Bond lengths (Å) and angles (°) with e.s.d.s for compound 3'

Ru(1')–C(104)	1.889(8)	Ru(1')–C(103)	1.905(6)	Ru(1')–C(1')	2.015(7)		
Ru(1')–C(13')	2.181(8)	Ru(1')–C(12')	2.330(9)	Ru(1')–Ru(2')	2.8146(14)		
Ru(1')–Ru(3')	2.8309(13)	Ru(1')–Ru(5')	2.9125(13)	Ru(1')–Ru(4')	2.9735(14)		
Ru(2')–C(203)	1.852(8)	Ru(2')–C(204)	1.878(8)	Ru(2')–C(1')	2.041(6)		
Ru(2')–C(15')	2.204(8)	Ru(2')–C(14')	2.253(7)	Ru(2')–Ru(6')	2.7900(14)		
Ru(2')–Ru(3')	2.943(2)	Ru(2')–Ru(5')	3.012(2)	Ru(3')–C(303)	1.895(7)		
Ru(3')–C(304)	1.939(9)	Ru(3')–C(1')	2.028(8)	Ru(3')–C(11')	2.170(8)		
Ru(3')–C(16')	2.381(7)	Ru(3')–Ru(4')	2.858(2)	Ru(3')–Ru(6')	2.9124(13)		
Ru(4')–C(405)	1.833(8)	Ru(4')–C(404)	1.866(8)	Ru(4')–C(1')	2.065(6)		
Ru(4')–C(406)	2.072(9)	Ru(4')–Ru(5')	2.774(2)	Ru(4')–Ru(6')	2.978(2)		
Ru(5')–C(503)	1.888(9)	Ru(5')–C(504)	1.900(9)	Ru(5')–C(406)	2.025(7)		
Ru(5')–C(1')	2.064(8)	Ru(5')–Ru(6')	2.9027(13)	Ru(6')–C(605)	1.847(9)		
Ru(6')–C(606)	1.881(8)	Ru(6')–C(604)	1.907(10)	Ru(6')–C(1')	2.053(7)		
O(1')–C(10')	1.177(8)	O(2')–C(10')	1.362(10)	O(2')–C(9')	1.455(10)		
O(3')–C(17')	1.322(8)	O(3')–C(18')	1.424(9)	O(4')–C(17')	1.227(10)		
C(10')–C(11')	1.520(11)	C(11')–C(16')	1.422(9)	C(11')–C(12')	1.459(11)		
C(12')–C(13')	1.347(10)	C(13')–C(14')	1.499(9)	C(14')–C(15')	1.394(11)		
C(14')–C(17')	1.481(10)	C(15')–C(16')	1.400(9)	C(103)–O(103)	1.160(8)		
C(104)–O(104)	1.168(9)	C(203)–O(203)	1.155(9)	C(204)–O(204)	1.185(9)		
C(303)–O(303)	1.140(8)	C(304)–O(304)	1.104(10)	C(404)–O(404)	1.177(10)		
C(405)–O(405)	1.145(10)	C(406)–O(406)	1.181(10)	C(503)–O(503)	1.141(11)		
C(504)–O(504)	1.095(11)	C(604)–O(604)	1.170(12)	C(605)–O(605)	1.180(11)		
C(606)–O(606)	1.172(10)						
C(10')–O(2')–C(9')	113.6(5)	C(17')–O(3')–C(18')	116.2(7)	O(3')–C(17')–C(14')	110.0(7)	O(103)–C(103)–Ru(1')	174.6(7)
O(1')–C(10')–O(2')	126.7(7)	O(1')–C(10')–C(11')	124.2(8)	O(104)–C(104)–Ru(1')	172.5(7)	O(203)–C(203)–Ru(2')	172.9(7)
O(2')–C(10')–C(11')	109.1(5)	C(16')–C(11')–C(12')	116.5(6)	O(204)–C(204)–Ru(2')	176.3(7)	O(303)–C(303)–Ru(3')	163.7(8)
C(16')–C(11')–C(10')	122.7(7)	C(12')–C(11')–C(10')	114.3(6)	O(304)–C(304)–Ru(3')	177.3(7)	O(404)–C(404)–Ru(4')	178.3(7)
C(13')–C(12')–C(11')	121.8(6)	C(12')–C(13')–C(14')	121.7(7)	O(405)–C(405)–Ru(4')	176.4(7)	O(406)–C(406)–Ru(5')	140.7(6)
C(15')–C(14')–C(17')	125.5(6)	C(15')–C(14')–C(13')	114.7(6)	O(406)–C(406)–Ru(4')	134.0(5)	O(503)–C(503)–Ru(5')	178.2(6)
C(17')–C(14')–C(13')	115.3(6)	C(14')–C(15')–C(16')	123.3(6)	O(504)–C(504)–Ru(5')	175.1(9)	O(604)–C(604)–Ru(6')	172.3(11)
O(4')–C(17')–O(3')	126.5(6)	O(4')–C(17')–C(14')	123.5(6)	O(605)–C(605)–Ru(6')	173.2(9)	O(606)–C(606)–Ru(6')	178.7(7)

with observations made in bis(arene) Ru₆C systems,^{9,12} where electron-rich arenes such as mesitylene and xylene are restricted to apical sites whereas benzene and toluene have been found to occupy both facial and apical positions. Until now, only paracyclophane¹³ and the pseudo-arenes 6,6-diphenyl¹⁴ and

6,6-dimethyl-fulvene¹⁵ have been identified as μ₃-co-ordinated species on the Ru₆C(CO)₁₄ cluster moiety.

As determined by X-ray crystallography, the carboxylate carbons are in positions such that they are susceptible to nucleophilic attack. Their electrophilic character may also be

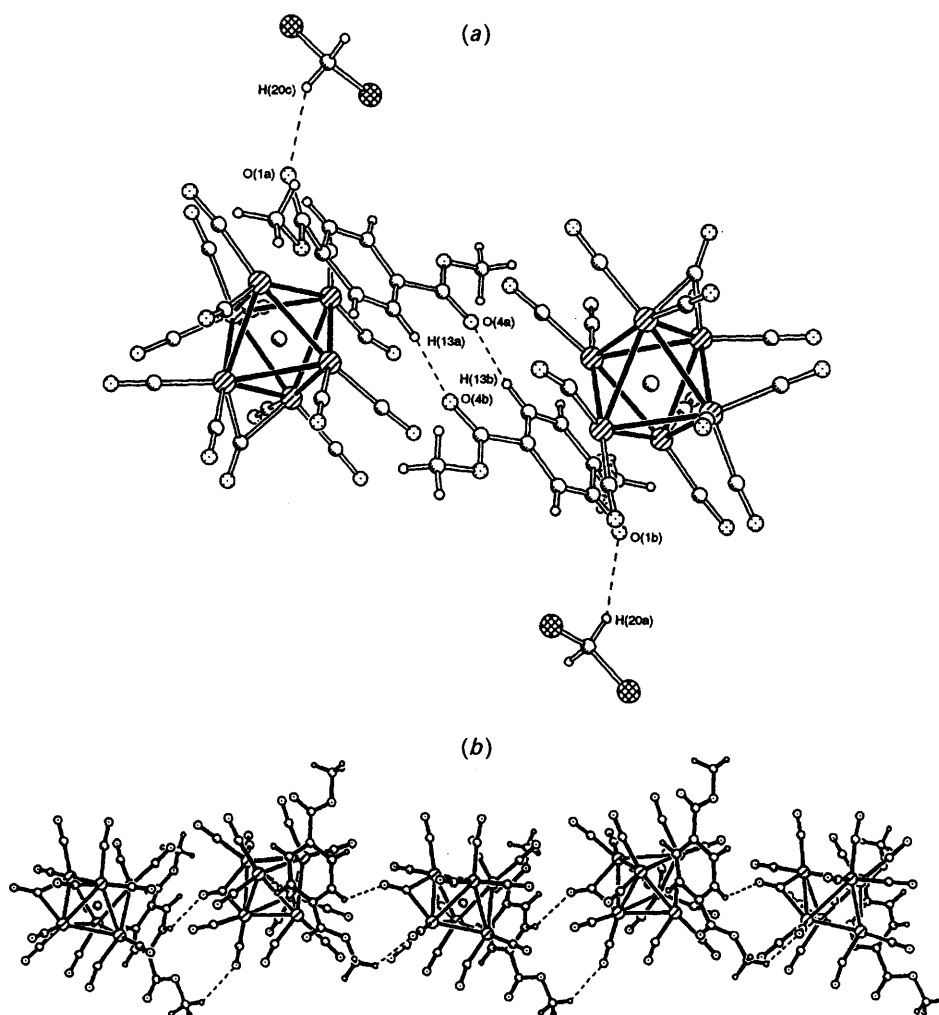


Fig. 5 Solid-state packing between molecules of compound 3 (a) and molecules of 3' (b)

taken to be enhanced by the electron-withdrawing effect of the cluster. Preliminary investigations into the reactivity of compounds 2 and 3 with primary diamines have yielded encouraging results, and dark brown materials, apparently polymers, have been formed. We are now in the process of characterising the cluster-containing polyamides produced and completing an electrochemical study of the precursors.

Experimental

All reactions were carried out with the exclusion of air using solvents distilled under an atmosphere of nitrogen. Subsequent work-up of products was achieved without precautions to exclude air. Infrared spectra were recorded on a Perkin-Elmer 1710 series FTIR instrument in CH_2Cl_2 using NaCl cells (0.5 mm path length), positive-ion fast atom bombardment mass spectra using a Kratos MS50TC spectrometer with CsI as calibrant and ^1H NMR spectra in CDCl_3 using a Bruker AM 360 instrument, referenced to internal SiMe_4 . Products were separated by thin-layer chromatography (TLC) using plates supplied by Merck (0.25 mm layer of Kieselgel 60 F₂₅₄). The compound $[\text{Ru}_6\text{C}(\text{CO})_{17}]^{16}$ was prepared by the literature procedure. Dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate and dibutyl ether were obtained from Aldrich and used without further purification.

Preparation of compounds 2 and 3

Compound 1 (1.00 g) was placed in a dry round-bottom flask

(50 cm^3) equipped with a magnetic follower. Dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate (2 g) and dibutyl ether (20 cm^3) were added and the mixture was refluxed under N_2 for 4 h. The flask was allowed to cool to ambient temperature under N_2 , after which the solvent was removed *in vacuo*. The products were separated by silica column chromatography. Elution with hexane gave a white residue of unreacted dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate and some 1. Further elution with dichloromethane–hexane (1:3 v/v) gave a brown and a red band, as the only major products, 2 (190 mg) and 3 (270 mg) respectively. Elution purely with dichloromethane gave small amounts of a dark and as yet uncharacterised product. Compounds 2 and 3 were initially characterised on the basis of their infrared and positive-ion fast atom bombardment spectra. Crystals of 2 suitable for X-ray structural determination were grown by layering hexane on a concentrated solution in dichloromethane and allowing slow diffusion to occur at ambient conditions in the absence of light, while single crystals of 3 were grown from dichloromethane solution by slow diffusion of pentane at 248 K.

Compound $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_4(\text{CO}_2\text{Me})_{2-1,4})]$ 2: IR (CH_2Cl_2) $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$ 2080m, 2068s, 2037 (sh), 2031vs, 1821w (br) and 1736m; ^1H NMR (CDCl_3) δ 6.41 (s, 4 H) and 3.88 (s, 6 H); FAB mass spectrum m/z 1205 (1205, M^+). Compound $[\text{Ru}_6\text{C}(\text{CO})_{14}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_4(\text{CO}_2\text{Me})_{2-1,4})]$ 3: IR (CH_2Cl_2) $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$ 2084m, 2048vs, 2035vs, 1825w (br) and 1718s; ^1H NMR (CDCl_3) δ 4.81 (s, 4 H) and 3.95 (s, 6 H); FAB mass spectrum m/z 1205 (1205, M^+) [Found (Calc. for $\text{C}_{25}\text{H}_{10}\text{O}_{18}\text{Ru}_6$): C, 24.95 (24.9); H, 0.85 (0.85)%].

Crystallography

Crystal data for compound 2. $C_{25.50}H_{11}ClO_{18}Ru_6$, $M = 1247.21$, triclinic, space group $P\bar{1}$, $a = 9.933(2)$, $b = 10.396(2)$, $c = 15.885(3)$ Å, $\alpha = 87.52(3)$, $\beta = 89.50(3)$, $\gamma = 82.26(3)^\circ$, $U = 1623.9(5)$ Å³, $Z = 2$, $D_c = 2.551$ Mg m⁻³, $\lambda = 0.71073$ Å, $T = 150.0(2)$ K, $\mu = 2.882$ mm⁻¹.

Data were collected on a Stöe-Stadi four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device,¹⁷ using a crystal of dimensions $0.13 \times 0.19 \times 0.08$ mm, mounted directly from solution, by the θ - ω method ($3 < 2\theta < 50^\circ$). Of a total of 5699 reflections collected, 5697 were independent ($R_{int} = 0.010$). Data were corrected for absorption using ψ scans ($T_{max} = 0.548$, $T_{min} = 0.427$).¹⁸ The structure was solved by direct methods (SHELXTL PLUS)¹⁹ and refined by full-matrix least-squares analysis on F^2 with $R1 [F > 4\sigma(F)]$ and $wR2$ (all data) 0.0376 and 0.0878, respectively. Hydrogen atoms were placed in calculated positions and allowed to refine 'riding' on their C atoms. Largest peak and hole in final difference map $+1.256$ and -0.985 e Å⁻³.

Crystal data for compound 3. $C_{26}H_{12}Cl_2O_{18}Ru_6$, $M = 2579.34$, monoclinic, space group $P2_1/c$, $a = 20.449(9)$, $b = 19.875(9)$, $c = 18.578(9)$ Å, $\beta = 115.09(3)^\circ$, $U = 6838(5)$ Å³, $Z = 8$, $D_c = 2.503$ Mg m⁻³, $\lambda = 0.71073$ Å, $T = 150.0(2)$ K, $\mu = 2.818$ mm⁻¹. Data were collected on a crystal of dimensions $0.20 \times 0.15 \times 0.50$ mm as above. Of a total of 9251 reflections collected, 8991 were independent ($R_{int} = 0.224$). Data were corrected for absorption ($T_{max} = 0.536$, $T_{min} = 0.139$) and the structure solved and refined as above to $R1$ and $wR2$ of 0.0656 and 0.1497, respectively. Hydrogen atoms were placed in fixed calculated positions. Largest peak and hole in final difference map $+0.979$ and -1.050 e Å⁻³.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/194.

Acknowledgements

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