Synthesis and Characterisation of Precursors to Organometal Cluster Networks†

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Thermolysis of triruthenium dodecacarbonyl in the presence of the appropriate dicyclic ligand $C_6H_5(CH_2)_nPh$ in octane afforded organometallic clusters with the general formula $[Ru_6C(CO)_{14}\{\eta^6\text{-}C_6H_5(CH_2)_nPh\}]$. The molecular structures of the three octahedral cluster compounds (n = 0 **1**, 1 **2** or 2 **3**) have been established by single-crystal X-ray analysis. In all three the ligand occupies an apical position formally replacing three carbonyl units on a single metal site of $[Ru_6C(CO)_{17}]$. Studies of the ^1H NMR spectra of compounds **1**–**3** have revealed a trend in electronic inductive effects. Thermolysis of $[Ru_6C(CO)_{17}]$ in the presence of an excess of *trans*-stilbene afforded **3** and *trans*-$[Ru_6C(CO)_{14}\{\eta^6\text{-}C_6H_5(CH)_2Ph\}]$ **4** in good yield.

We are currently investigating the chemistry of arene clusters and for some time have been particularly interested in the formation of systems containing η^6- and μ_3-η^2:η^2:η^2-bonded units. We have been able to devise a number of systematic routes to cluster systems containing from three to eight metal atoms and which contain a diverse range of arene-bonded units.[1-4] Of special interest has been the observation that many of these cluster compounds adopt crystallographic forms that maximise the interaction between the arene moieties on adjacent cluster units. The interactions which occur (η^6–η^6 and μ_3-η^2:η^2:η^2–μ_3-η^2:η^2:η^2) have been deemed to be graphite-like with interarene distances of about 3.5 Å. Following this work we are now exploring the possibility of producing self-organising polymeric units in which redox-active cluster units are linked through conducting polycyclic organic units. In this paper we report the synthesis and full characterisation of the four key precursor compounds $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Ph)]$ **1**, $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5CH_2Ph)]$ **2**, $[Ru_6C(CO)_{14}\{\eta^6\text{-}C_6H_5(CH_2)_2Ph\}]$ **3** and $[Ru_6C(CO)_{14}\{\eta^6\text{-}C_6H_5(CH)_2Ph\}]$ **4**.

Inter-ring interactions of multicyclic ligands have previously been observed in cluster-cyclophane compounds by NMR spectroscopy.[5] We have found a comparable electronic effect across a range of compounds. The study of the electronic nature of the monomeric species is of great import to the properties of potential polymeric materials.

Results and Discussion

The compounds **1**–**3** have been prepared from the reaction of $[Ru_3(CO)_{12}]$ with an excess of the appropriate polyarene in octane under reflux, method A. In all cases the reaction proceeds to give moderate yields of the required product together with small amounts of $[Ru_6C(CO)_{17}]$. The compounds were purified by thin-layer chromatography (TLC) on silica plates, using dichloromethane–hexane (30 : 70) as eluent. In each case crystals suitable for X-ray diffraction analysis were grown by slow evaporation from dichloromethane solution.

Compound **3** was made in improved yield by an alternative method B along with a second product **4** formed by direct reaction of the parent cluster $[Ru_6C(CO)_{17}]$ with *trans*-stilbene in an autoclave. Single crystals of **4** were grown from dichloromethane, however due to solvent loss at ambient temperature and a phase transition on cooling to 150 K data collection was not possible. Hence, the proposed molecular structure is shown in Fig. 1. The new compounds were initially characterised on the basis of their positive-ion fast atom bombardment mass spectra and IR spectra. The source of the hydrogen in the hydrogenation step required to give **3** has not been established. The possibility of trace water being involved is unlikely in view of the results of deuterium-labelling experiments carried out on a similar system.[6] The activation of hydrocarbon solvent would appear to be one alternative hydrogenation pathway, as would dehydrogenation of the stilbene.

^1H *NMR Spectra of Compounds* **1**–**4**.—The ^1H NMR spectra of compounds **1**–**3** due to ring protons are shown in Fig. 2. On examination of the *ortho* doublet of the unco-ordinated phenyl ring (δ 7.32, 7.10 and 6.97 for **1**, **2** and **3** respectively) it is apparent that as the number of CH_2 linkage units is reduced from two to none there is an increase in the chemical shift. This can be attributed to the effect of ^1H deshielding caused by the withdrawal of electron density from the unco-ordinated to the co-ordinated phenyl ring. It is greatest when there is no aliphatic bridge. On examination of the *ortho* resonances for the co-ordinated phenyl ring a similar trend (δ 5.91, 5.62 and 5.27 for **1**, **2** and **3** respectively) is found but of greater magnitude. This may be explained by considering two effects which act upon the proton environments. First, there is a deshielding effect caused by co-ordination to the metal cluster which is in part compensated for by the inductive effect of the attached phenyl group. The extent to which this inductive compensatory process

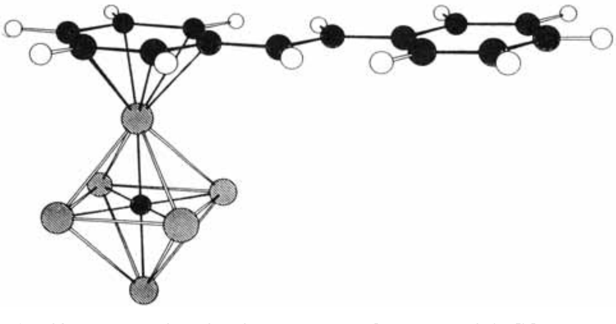

Fig. 1 The proposed molecular structure of compound **4** (CO groups are omitted)

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

takes place is related to the number of aliphatic linkages. Secondly, since there is a reduction in π-electron density associated with the co-ordinated phenyl ring, there is a concomitant reduction in the ring current and the subsequent field enhancement associated with it.[7] However, the unco-ordinated phenyl has a ring current which will be experienced by protons proximal to it, hence this effect on the co-ordinated ring protons is also related to the number of aliphatic linkages by their displacement of the two phenyl groups in space.

Compound **4** is of interest since the two rings are linked by an unsaturated *trans*-ethylene group. (An observed H–H coupling of 16 Hz is consistent with this.) Such a compound could be expected to 'transmit' electronic effects along the π system and indeed the NMR evidence suggests this is so. The *ortho* resonance for the co-ordinated ring observed at δ 5.81 implies a greater electronic inductive effect than for either **1** or **2**. A pointer to the possible reactivity of this moiety is the polarity observed across the double bond due to the electron-withdrawing effect of the cluster. This effect is manifest in a chemical shift difference of 0.54 ppm between the olefinic doublets. Such a property is akin to that of a Michael acceptor.[8]

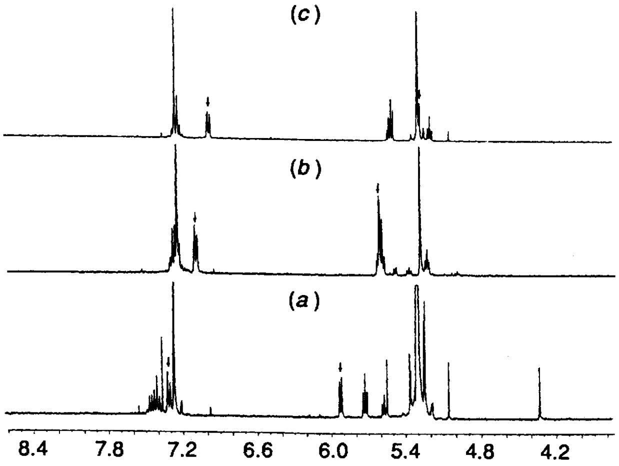

Fig. 2 The 360 MHz ^1H NMR spectra of compounds **1**(*a*), **2**(*b*) and **3**(*c*). The arrows indicate the *o*-proton resonances

Solid-state Molecular Structures of Compounds **1**–**3**.—The solid-state molecular structures of compounds **1**–**3** are shown in Figs. 3–5 and selected bond lengths are presented in Tables 1–3. In each compound the metal framework of the octahedral cluster resembles that of the parent cluster $[Ru_6C(CO)_{17}]$ containing an interstitial C(carbido) atom. The cluster geometry experiences small but significant electronic effects due to the electron-donating capacity of the co-ordinated arene. Owing to the complex nature of the CO stretching region of the IR spectra and the 'dilution effect' of so many carbonyls, it was not possible to make a meaningful comparison of CO stretching frequency and electronic effects with variation of substituent groups on the co-ordinated arene. Correlations of substituent parameters with the carbonyl stretching force constant in arenetricarbonyl-chromium complexes suggest 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.[9]

The thirteen terminal carbonyl ligands in compound **1** exhibit M–C–O angles deviating from linearity by 19(2) to 1(2)°. The μ-CO on **1** gives a M–C–M angle of 88.0(8)°. The biphenyl ligand experiences a twist angle of 34.2° between the two averaged phenyl planes. Deviations from linearity of metal–carbonyl groups in **2** from range 15.1(11) to 0.6(12)°. It also shows a single bridging carbonyl with a M–C–M angle of

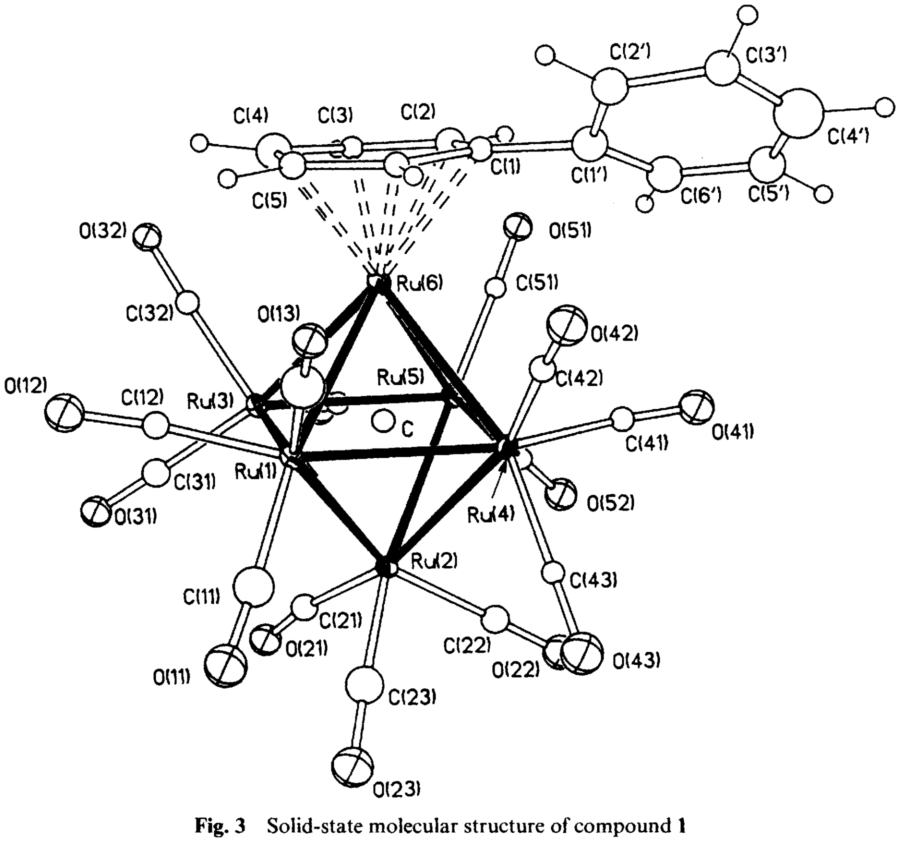

Fig. 3 Solid-state molecular structure of compound **1**

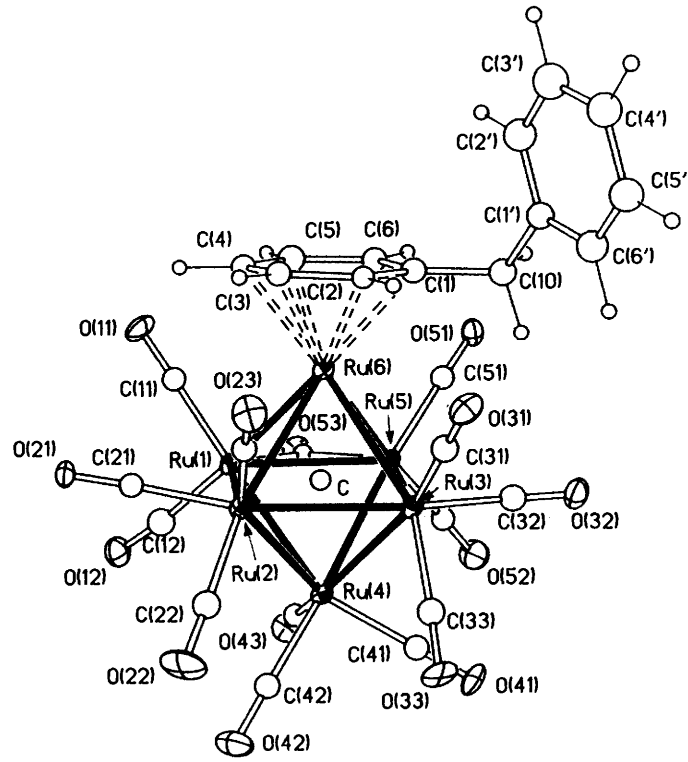

Fig. 4 Solid-state molecular structure of compound **2**

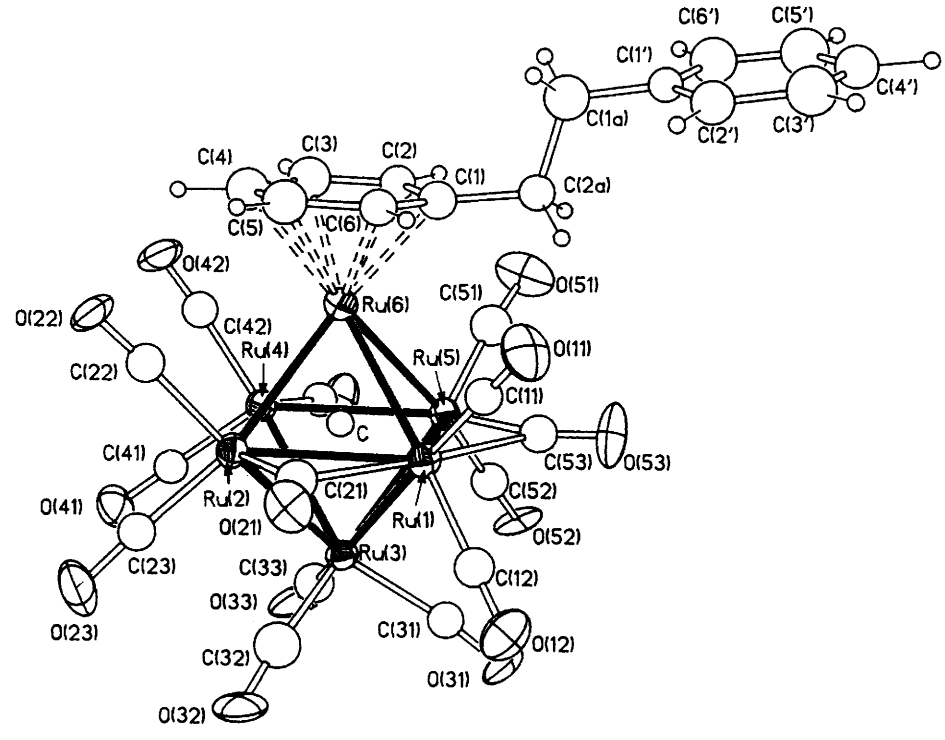

Fig. 5 Solid-state molecular structure of compound **3**

88.2(5)°. An angle of 52.2° is produced between the two averaged planes determined by the phenyl groups. In contrast to **1** and **2**, compound **3** shows twelve terminal carbonyl ligands and two μ-CO ligands bridging metals Ru(2), Ru(1) and Ru(5) [Ru(1) being the common atom]. The terminal carbonyls deviate from linearity by 13(3) to 2(3)°. The two bridging carbonyls give M–C–M angles of 84.1(11) and 84.0(11)°, both smaller than in **1** and **2**. Within estimated error, the aliphatic carbons C(2a) and C(1a) adopt an ideal staggered conformation.

The relative solid-state orientations of the arenes in the cluster compounds **1**–**3** are shown in Fig. 6. It is apparent that

Table 1 Selected bond lengths Å with standard deviations for compound **1**

Ru(1)–Ru(2)	2.9074(24)	Ru(6)–C	1.940(21)
Ru(1)–Ru(3)	2.9135(23)	Ru(6)–C(3)	2.192(20)
Ru(1)–Ru(4)	2.8565(23)	Ru(6)–C(4)	2.259(23)
Ru(1)–Ru(6)	2.8714(23)	Ru(6)–C(5)	2.217(21)
Ru(1)–C	2.057(21)	Ru(6)–C(6)	2.243(20)
Ru(2)–Ru(3)	2.9467(24)	C(1)–C(2)	1.43(3)
Ru(2)–Ru(4)	2.8542(24)	C(1)–C(6)	1.46(3)
Ru(2)–Ru(5)	2.8717(24)	C(1)–C(1′)	1.50(3)
Ru(2)–C	2.099(21)	C(2)–C(3)	1.42(3)
Ru(3)–Ru(5)	2.8430(23)	C(3)–C(4)	1.40(3)
Ru(3)–Ru(6)	2.8955(23)	C(4)–C(5)	1.40(3)
Ru(3)–C	2.126(21)	C(5)–C(6)	1.41(3)
Ru(4)–Ru(5)	3.0633(23)	C(1′)–C(2′)	1.39(3)
Ru(4)–Ru(6)	2.8668(23)	C(1′)–C(6′)	1.37(3)
Ru(4)–C	2.013(21)	C(2′)–C(3′)	1.43(3)
Ru(6)–C(1)	2.331(20)	C(3′)–C(4′)	1.37(4)
Ru(6)–C(2)	2.249(22)	C(4′)–C(5′)	1.39(4)
Ru(5)–Ru(6)	2.8967(23)	C(5′)–C(6′)	1.39(3)
Ru(5)–C	2.074(21)		

Table 2 Selected bond lengths (Å) with standard deviations for compound **2**

Ru(1)–Ru(2)	2.9089(14)	Ru(6)–C(2)	2.230(12)
Ru(1)–Ru(4)	2.8989(14)	Ru(6)–C(3)	2.275(13)
Ru(1)–Ru(5)	2.8504(13)	Ru(6)–C(4)	2.231(13)
Ru(1)–Ru(6)	2.8693(13)	Ru(6)–C(5)	2.264(15)
Ru(1)–C	2.057(11)	Ru(6)–C(6)	2.289(13)
Ru(2)–Ru(3)	2.8367(14)	C(1)–C(2)	1.469(18)
Ru(2)–Ru(4)	2.9359(15)	C(1)–C(6)	1.388(19)
Ru(2)–Ru(6)	2.8743(14)	C(1)–C(10)	1.474(20)
Ru(2)–C	2.048(11)	C(2)–C(3)	1.371(17)
Ru(3)–Ru(4)	2.8562(14)	C(3)–C(4)	1.445(18)
Ru(3)–Ru(5)	3.0220(13)	C(4)–C(5)	1.368(20)
Ru(3)–Ru(6)	2.8813(13)	C(5)–C(6)	1.474(20)
Ru(3)–C	2.059(11)	C(1′)–C(2′)	1.376(22)
Ru(4)–Ru(5)	2.8299(14)	C(1′)–C(6′)	1.355(21)
Ru(4)–C	2.091(11)	C(1′)–C(10)	1.555(20)
Ru(5)–Ru(6)	2.8493(13)	C(2′)–C(3′)	1.367(24)
Ru(5)–C	2.059(11)	C(3′)–C(4′)	1.401(24)
Ru(6)–C	1.929(11)	C(4′)–C(5′)	1.331(24)
Ru(6)–C(1)	2.272(13)	C(5′)–C(6′)	1.364(23)

the arene ligands achieve similar local conformations within the constraints of the crystal-packing forces. The figure also shows no correlation between the position of the bridging CO and the orientation of the substituent group.

Conclusion

We have been able to demonstrate that potential precursors to polymers containing the highly redox-active cluster unit Ru_6C may be readily prepared. Studies of the ^1H NMR spectra of the derivatives so formed have revealed a possible method of direct electron-density transfer through the organic moiety. More detailed studies of these and related systems are currently underway.

Experimental

All reactions were carried out with the exclusion of air using solvents freshly 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 1600 series FTIR spectrometer in CH_2Cl_2 using NaCl cells, positive-ion fast atom bombardment mass spectra using a Kratos MS50TC spectrometer using CsI as calibrant and ^1H NMR spectra in $CDCl_3$ using a Bruker 360 MHz instrument and referenced to internal $SiMe_4$. Separation of products was accomplished with Merck TLC plates as supplied (0.25 mm layer of Kieselgel 60 F_{254}). The compounds $[Ru_3(CO)_{12}]$ and $[Ru_6C(CO)_{17}]$ were prepared by the literature procedures.[10,11] Biphenyl, diphenylmethane,

Table 3 Selected bond lengths (Å) with standard deviations for compound **3**

Ru(1)–Ru(2)	2.856(3)	Ru(6)–C(3)	2.27(3)
Ru(1)–Ru(3)	2.883(3)	Ru(6)–C(4)	2.25(3)
Ru(1)–Ru(5)	2.894(3)	Ru(6)–C(5)	2.23(3)
Ru(1)–Ru(6)	2.879(3)	Ru(6)–C(6)	2.25(3)
Ru(1)–C	2.084(23)	C(1)–C(2)	1.46(4)
Ru(2)–Ru(3)	2.920(3)	C(1)–C(6)	1.40(4)
Ru(2)–Ru(4)	2.925(3)	C(1)–C(2a)	1.50(4)
Ru(2)–Ru(6)	2.869(3)	C(2)–C(3)	1.39(4)
Ru(2)–C	2.074(23)	C(3)–C(4)	1.47(5)
Ru(3)–Ru(4)	2.875(3)	C(4)–C(5)	1.42(5)
Ru(3)–Ru(5)	2.846(3)	C(5)–C(6)	1.38(4)
Ru(3)–C	2.141(23)	C(1a)–C(2a)	1.53(4)
Ru(4)–Ru(5)	2.944(3)	C(1a)–C(1′)	1.48(4)
Ru(4)–Ru(6)	2.871(3)	C(1′)–C(2′)	1.41(4)
Ru(4)–C	2.033(23)	C(1′)–C(6′)	1.40(4)
Ru(5)–Ru(6)	2.869(3)	C(2′)–C(3′)	1.41(5)
Ru(5)–C	2.041(23)	C(3′)–C(4′)	1.33(5)
Ru(6)–C	1.887(23)	C(4′)–C(5′)	1.36(5)
Ru(6)–C(1)	2.23(3)	C(5′)–C(6′)	1.37(5)
Ru(6)–C(2)	2.24(3)		

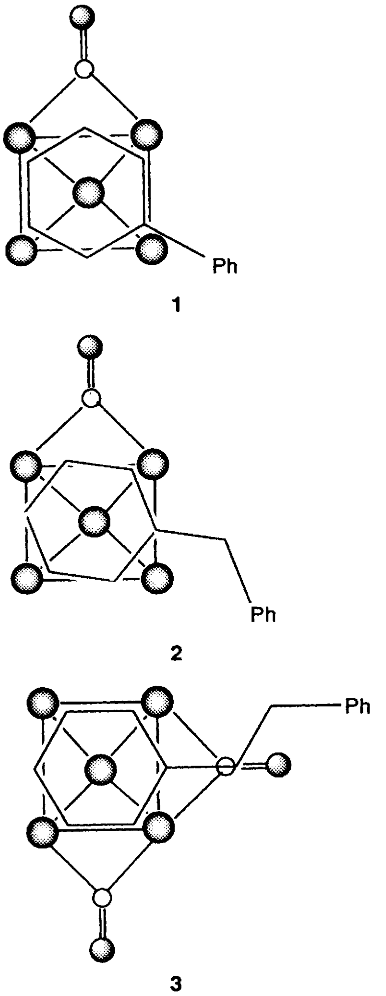

Fig. 6 The solid-state orientations of the dicyclic ligands in compounds **1**–**3**

Table 4 Crystal data and details of structure determinations for compounds **1**–**3**

	1	**2**	**3**
Formula	$C_{27}H_{10}O_{14}Ru_6$	$C_{28}H_{12}O_{14}Ru_6$	$C_{29}H_{14}O_{14}Ru_6$
M	1164.79	1178.81	1192.84
Crystal size/mm	1.10 × 1.00 × 0.02	1.50 × 0.80 × 0.40	1.60 × 1.90 × 0.10
a/Å	9.458(13)	15.130(14)	9.272(5)
b/Å	12.248(16)	9.623(9)	9.595(5)
c/Å	26.155(25)	22.714(21)	37.69(3)
β/°	100.10(12)	107.19(8)	91.05(5)
U/Å^3	2983	3159	3353
F(000)	2192	2224	2256
D_c/g cm^{-3}	2.593	2.478	2.363
μ(Mo-Kα)/mm^{-1}	2.978	2.814	2.653
Measured reflections	3321	3951	3402
Unique observed reflections $[I_o > 2\sigma(I_o)]$	2685	3637	2607
No. refined parameters	219	294	298
Highest peak in final difference synthesis/e Å^{-3}	2.9	1.6	1.1
R, R', S	0.0693, 0.0843, 0.976	0.0698, 0.1196, 1.92	0.0660, 0.0883, 1.498
g In weighting scheme $w = \sigma^2(F) + gF^2$	0.0006	0.0050	0.0

* Details in common: monoclinic, space group $P2_1/c$; $Z = 4$; λ(Mo-Kα) = 0.710 73 Å; θ range = 2.5–22.5°

Table 5 Fractional coordinates of atoms with standard deviations for compound **1**

Atom	x	y	z
Ru(1)	0.075 20(16)	0.212 52(13)	0.207 52(7)
Ru(2)	0.267 23(17)	0.037 32(13)	0.188 85(7)
Ru(3)	−0.009 76(16)	0.068 51(13)	0.118 79(7)
Ru(4)	0.342 81(16)	0.259 97(13)	0.175 94(7)
Ru(5)	0.253 19(16)	0.107 03(13)	0.083 25(7)
Ru(6)	0.079 47(16)	0.290 86(13)	0.104 33(7)
C	0.170 5(20)	0.170 0(16)	0.145 4(9)
C(1)	0.130 3(20)	0.459 6(16)	0.070 5(8)
C(2)	0.086 8(21)	0.381 7(17)	0.030 1(9)
C(3)	−0.042 5(19)	0.320 6(16)	0.026 3(8)
C(4)	−0.137 5(23)	0.342 4(19)	0.060 4(10)
C(5)	−0.095 4(21)	0.412 0(16)	0.102 9(9)
C(6)	0.034 9(20)	0.470 2(16)	0.108 3(9)
C(1′)	0.265 2(23)	0.526 5(18)	0.076 7(10)
C(2′)	0.251 5(23)	0.633 8(18)	0.092 3(10)
C(3′)	0.373 8(22)	0.702 5(18)	0.092 8(9)
C(4′)	0.500(3)	0.661 6(22)	0.081 3(12)
C(5′)	0.505 1(24)	0.554 8(18)	0.063 5(10)
C(6′)	0.384 1(22)	0.489 0(19)	0.058 9(10)
C(11)	0.103 0(24)	0.169 8(20)	0.278 4(11)
O(11)	0.113 6(16)	0.148 9(13)	0.322 6(7)
C(12)	−0.118 2(21)	0.167 6(16)	0.195 9(9)
O(12)	−0.239 5(16)	0.156 5(13)	0.201 5(7)
C(13)	0.050(3)	0.359 1(21)	0.223 5(11)
O(13)	0.036 6(14)	0.449 6(12)	0.234 4(6)
C(21)	0.185 1(21)	−0.107 1(17)	0.178 3(9)
O(21)	0.152 4(15)	−0.194 6(12)	0.176 5(6)
C(22)	0.453 2(21)	−0.009 5(17)	0.183 7(9)
O(22)	0.569 8(16)	−0.038 2(12)	0.181 8(7)
C(23)	0.305 9(25)	0.012 7(20)	0.261 0(10)
O(23)	0.337 0(17)	−0.008 1(13)	0.306 8(7)
C(31)	−0.109 1(22)	−0.056 3(17)	0.136 6(9)
O(31)	−0.170 8(14)	−0.128 7(12)	0.147 7(6)
C(32)	−0.174 7(20)	0.090 4(16)	0.069 9(9)
O(32)	−0.275 7(14)	0.107 0(11)	0.038 5(6)
C(41)	0.485 1(20)	0.264 5(16)	0.133 5(8)
O(41)	0.581 6(15)	0.275 8(12)	0.113 3(6)
C(42)	0.331 6(20)	0.414 6(16)	0.187 4(8)
O(42)	0.330 2(16)	0.503 4(13)	0.196 8(7)
C(43)	0.468 3(19)	0.238 5(16)	0.239 4(8)
O(43)	0.545 5(16)	0.226 6(13)	0.280 0(7)
C(51)	0.245 9(19)	0.160 3(16)	0.015 0(9)
O(51)	0.238 4(14)	0.188 5(12)	−0.026 0(6)
C(52)	0.401 1(20)	0.009 4(16)	0.070 0(8)
O(52)	0.489 3(16)	−0.046 5(12)	0.063 1(7)
C(53)	0.097 6(20)	−0.006 2(16)	0.065 5(8)
O(53)	0.075 5(15)	−0.086 4412)	0.040 1(6)

bibenzyl, *trans*-stilbene and octane were obtained from Aldrich Chemicals and used without further purification.

Preparation of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Ph)]$ **1**, $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5CH_2Ph)]$ **2** *and* $[Ru_6C(CO)_{14}\{\eta^6\text{-}C_6H_5(CH_2)_2Ph\}]$ **3**. *Method A*.—The compound $[Ru_3(CO)_{12}]$ (1.00 g) was refluxed in octane (40 cm^3) with the appropriate bis(arene) (200 mg) for 6 h. Infrared spectroscopy indicated complete consumption of the starting material. The solvent was removed *in vacuo* and the residue separated by TLC using dichloromethane–hexane (30:70) as eluent. The major red-brown band was extracted and characterised (average yield: 17%).

Preparation of Compounds **3** *and* $[Ru_6C(CO)_{14}\{\eta^6\text{-}C_6H_5(CH)_2Ph\}]$ **4**. *Method B*.—The compound $[Ru_6C(CO)_{17}]$ (0.25 g) was placed in an autoclave (200 cm^3) along with hexane (20 cm^3) and *trans*-stilbene (1.00 g) and sealed under N_2. The vessel was then heated for 6 h at 433 K. After cooling to room temperature the solvent was removed *in vacuo* and the residue separated by TLC using dichloromethane–hexane (30:70) as eluent. The two major red-brown bands were extracted and characterised (average yields: **3**, 24%; **4**, 32%).

Spectroscopic Data.—Compound **1**: IR (CH_2Cl_2) ν(CO) 2076m, 2060m, 2035(sh), 2026vs and 1988w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.41 (3 H, m), 7.29 (2 H, m), 5.91 (2 H, m), 5.72 (2 H, m) and 5.56 (1 H, m); mass spectrum m/z = 1167 (calc. 1165 for M^+). Compound **2**: IR (CH_2Cl_2) ν(CO) 2077m, 2054m, 2034(sh), 2027vs and 1988w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.27 (3 H, m), 7.10 (2 H, m), 5.62 (4 H, m), 5.26 (1 H, m) and 3.52 (2 H, s); mass spectrum m/z = 1179 (calc. 1179 for M^+). Compound **3**: IR (CH_2Cl_2) ν(CO) 2075m, 2034(sh), 2025vs, 1985w and 1819w (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.23 (3 H, m), 6.97 (2 H, m), 5.50 (2 H, m), 5.27 (2 H, m), 5.19 (1 H, m), 2.86 (2 H, m) and 2.51 (2 H, m); mass spectrum m/z = 1193 (calc. 1193 for M^+). Compound **4**: IR (CH_2Cl_2) ν(CO) 2075m, 2034sh, 2025vs, 1985w and 1819w (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.23 (3 H, m),

Table 6 Fractional coordinates of atoms with standard deviations for compound **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.931 29(6)	0.168 29(9)	0.867 30(4)	C(21)	0.883 1(8)	0.399 7(12)	0.794 0(6)
Ru(2)	0.772 47(7)	0.282 35(9)	0.773 97(5)	O(21)	0.933 4(6)	0.485 9(8)	0.797 0(4)
Ru(3)	0.657 61(6)	0.063 22(10)	0.791 80(4)	C(22)	0.746 9(10)	0.308 5(14)	0.687 5(7)
Ru(4)	0.826 81(7)	−0.008 91(9)	0.767 79(5)	O(22)	0.732 0(10)	0.330 6(13)	0.636 2(5)
Ru(5)	0.821 57(6)	−0.054 76(9)	0.889 78(5)	C(23)	0.679 9(9)	0.415 4(13)	0.773 9(6)
Ru(6)	0.762 36(6)	0.224 51(9)	0.895 96(4)	O(23)	0.622 7(7)	0.490 4(9)	0.773 2(5)
C	0.793 6(7)	0.116 9(10)	0.833 2(5)	C(31)	0.553 7(9)	0.166 9(14)	0.795 8(7)
C(1)	0.669 7(9)	0.213 6(12)	0.958 4(6)	O(31)	0.490 4(7)	0.229 3(9)	0.798 7(5)
C(2)	0.648 2(8)	0.337 6(11)	0.919 0(5)	C(32)	0.621 6(9)	−0.102 9(13)	0.824 4(6)
C(3)	0.713 9(9)	0.435 8(12)	0.919 1(6)	O(32)	0.589 7(7)	−0.200 7(9)	0.839 1(5)
C(4)	0.808 9(9)	0.411 9(13)	0.954 8(6)	C(33)	0.600 4(9)	0.028 2(13)	0.703 8(7)
C(5)	0.832 5(10)	0.299 3(14)	0.993 0(7)	O(33)	0.567 5(7)	0.011 5(10)	0.653 5(4)
C(6)	0.760 2(9)	0.199 0(13)	0.995 7(6)	C(41)	0.762 6(9)	−0.178 6(13)	0.741 1(6)
C(1′)	0.508 8(9)	0.182 6(13)	0.967 5(6)	O(41)	0.727 2(7)	−0.282 6(8)	0.727 2(5)
C(2′)	0.515 3(11)	0.276 1(16)	1.014 4(8)	C(42)	0.832 3(9)	0.038 6(13)	0.686 9(7)
C(3′)	0.437 4(11)	0.341 3(17)	1.019 2(8)	O(42)	0.838 8(8)	0.056 6(11)	0.639 0(5)
C(4′)	0.352 8(12)	0.320 0(16)	0.973 9(8)	C(43)	0.942 8(9)	−0.100 0(13)	0.788 4(6)
C(5′)	0.348 3(12)	0.227 8(16)	0.929 4(8)	O(43)	1.009 3(7)	−0.166 2(9)	0.802 0(5)
C(6′)	0.426 0(11)	0.163 0(16)	0.924 5(8)	C(51)	0.813 8(9)	−0.099 8(13)	0.969 3(7)
C(10)	0.597 6(9)	0.112 2(14)	0.960 4(7)	O(51)	0.810 9(6)	−0.132 1(9)	1.015 9(4)
C(11)	0.993 5(9)	0.285 7(13)	0.932 3(7)	C(52)	0.838 8(9)	−0.242 9(14)	0.877 7(6)
O(11)	1.032 1(7)	0.359 3(11)	0.970 4(5)	O(52)	0.849 7(9)	−0.358 6(10)	0.869 3(6)
C(12)	1.035 6(10)	0.161 8(14)	0.840 3(7)	C(53)	0.960 0(8)	−0.012 9(11)	0.917 2(6)
O(12)	1.105 6(7)	0.160 4(11)	0.829 0(5)	O(53)	1.027 9(6)	−0.069 8(9)	0.948 1(5)

Table 7 Fractional coordinates of atoms with standard deviations for compound **3**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.381 02(22)	0.649 24(23)	0.130 56(6)	C(21)	0.204(3)	0.524(3)	0.157 2(8)
Ru(2)	0.074 77(22)	0.624 45(24)	0.123 82(6)	O(21)	0.212 7(21)	0.436 0(19)	0.179 0(5)
Ru(3)	0.254 61(21)	0.595 01(23)	0.061 48(6)	C(22)	−0.066(3)	0.676(3)	0.159 2(8)
Ru(4)	0.069 63(22)	0.834 04(23)	0.067 45(6)	O(22)	−0.152 2(20)	0.709 5(21)	0.176 2(6)
Ru(5)	0.385 12(22)	0.858 42(22)	0.075 28(6)	C(23)	−0.054(3)	0.484(3)	0.110 7(8)
Ru(6)	0.202 19(22)	0.893 66(23)	0.135 20(6)	O(23)	−0.129 3(24)	0.388(3)	0.102 9(8)
C	0.224 6(24)	0.754 2(24)	0.100 5(6)	C(31)	0.442(3)	0.534(3)	0.048 1(8)
C(1)	0.338(3)	1.028(3)	0.170 8(8)	O(31)	0.549 3(21)	0.484 3(22)	0.039 6(6)
C(2)	0.257(3)	1.117(3)	0.145 8(7)	C(32)	0.182(4)	0.415(4)	0.063 2(10)
C(3)	0.109(3)	1.111(4)	0.141 3(9)	O(32)	0.143(3)	0.300 1(24)	0.062 8(6)
C(4)	0.029(4)	1.011(3)	0.163 3(9)	C(33)	0.196(3)	0.628(4)	0.011 8(10)
C(5)	0.109(3)	0.932(3)	0.188 4(9)	O(33)	0.162(3)	0.640(3)	−0.015 2(6)
C(6)	0.257(3)	0.939(3)	0.192 4(7)	C(41)	−0.078(3)	0.742(3)	0.042 2(8)
C(1a)	0.521(3)	1.161(4)	0.207 0(9)	O(41)	−0.168 1(22)	0.681(3)	0.027 1(6)
C(2a)	0.495(3)	1.055(3)	0.177 3(7)	C(42)	−0.066(3)	0.975(3)	0.077 8(8)
C(1′)	0.675(3)	1.186(3)	0.216 6(7)	O(42)	−0.153 2(23)	1.052 4(21)	0.085 4(6)
C(2′)	0.749(3)	1.095(3)	0.239 9(8)	C(43)	0.147(3)	0.943(3)	0.031 0(8)
C(3′)	0.896(4)	1.128(4)	0.245 3(10)	O(43)	0.170 0(22)	1.009(3)	0.005 3(6)
C(4′)	0.968(3)	1.233(3)	0.230 4(9)	C(51)	0.439(4)	1.038(4)	0.078 1(10)
C(5′)	0.892(4)	1.318(4)	0.207 9(10)	O(51)	0.481(3)	1.155 5(25)	0.076 6(6)
C(6′)	0.748(4)	1.296(4)	0.200 9(10)	C(52)	0.474(3)	0.836(3)	0.032 1(8)
C(11)	0.468(3)	0.678(3)	0.175 0(8)	O(52)	0.531 3(22)	0.824 6(23)	0.004 3(5)
O(11)	0.523 8(23)	0.701(3)	0.202 1(6)	C(53)	0.552(3)	0.788(3)	0.103 4(8)
C(12)	0.489(3)	0.487(3)	0.127 0(8)	O(53)	0.672 8(22)	0.792(3)	0.110 2(7)
O(12)	0.553 8(22)	0.387(3)	0.125 7(6)				

6.97 (2 H, m), 5.50 (2 H, m), 5.27 (2 H, m), 5.19 (1 H, m), 2.86 (2 H, m) and 2.51 (2 H, m); mass spectrum m/z = 1191 (calc. 1191 for M^+) (Found: C, 28.95; H, 1.10. $C_{29}H_{12}O_{14}Ru_6$ requires C, 29.25; H, 1.00%).

Crystal Structure Determinations of Compounds **1**–**3**.—Crystallographic information and details of measurements are summarised in Table 4. Diffraction intensities for compounds **1** and **2** at 150 K and **3** at 298 K were collected on a Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[12] The structures were solved by direct methods (Ru)[13] and refined by full-matrix least squares.[14] Data were corrected for absorption, initially by means of ψ scans and finally using DIFABS.[15] Ruthenium and oxygen atoms were allowed to vibrate anisotropically. The H atoms were added in calculated positions (C–H 0.97 Å for the methylenic and 0.92 Å for the aromatic atoms) and refined 'riding' on their respective carbon atoms. Fractional atomic coordinates for **1**–**3** are listed in Tables 5–7 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 B. F. G. Johnson, R. D. Johnson and J. Lewis, *J. Chem. Soc. A*, 1968, 2865.

2 P. J. Bailey, B. F. G. Johnson, J. Lewis, M. McPartlin and H. R. Powell, *J. Organomet. Chem.*, 1989, **377**, C17.

3 P. J. Bailey, M. J. Duer, B. F. G. Johnson and J. Lewis, *J. Organomet. Chem.*, 1990, **383**, 441.

4 D. Braga, F. Grepioni, E. Parisini, P. J. Dyson, A. J. Blake and B. F. G. Johnson, *J. Chem. Soc., Dalton Trans.*, 1993, 2951.

5 B. F. G. Johnson, C. M. Martin, P. J. Dyson, D. Braga and F. Grepioni, *Organometallics*, 1994, **13**, 2113.

6 D. S. Shephard, unpublished work, University of Edinburgh

7 Ch. Elschenbroich, *Chem. Ber.*, 1984, **117**, 3165.

8 E. D. Bergmann, D. Ginsburg and R. Pappo, *Org. React. (N.Y.)*, 1959, **10**, 179.

9 E. W. Neuse, *J. Organomet. Chem.*, 1975, **99**, 287.

10 B. F. G. Johnson, R. D. Johnson, J. Lewis and B. H. Robinson, *J. Chem. Soc. A*, 1968, 2856.

11 J. N. Nicholls, M. D. Vargas, J. Hriljac and M. Sailor, *Inorg. Synth.*, 1989, **28**, 280.

12 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.

13 SHELXS 86, G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

14 SHELX 76, G. M. Sheldrick, University of Cambridge, 1976.

15 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

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