

Synthesis and characterisation of hexa- and hepta-ruthenium carbido carbonyl clusters containing arenes derived from 1,1-diphenylethene

Brian F. G. Johnson,^{*,a} Douglas S. Shephard,^a Dario Braga,^b Fabrizia Grepioni^b and Simon Parsons^c

^a Department of Chemistry, The University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW

^b Dipartimento di Chimica 'G. Ciamician', dell'Università di Bologna, Via Selmi 2, 40126 Bologna, Italy

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

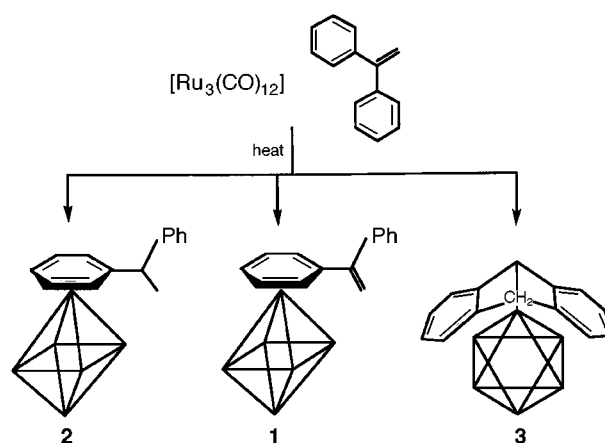
The three ruthenium arene clusters $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-PhCHMePh})]$ **1**, $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-PhC=CH}_2\text{Ph})]$ **2** and $[\text{Ru}_7\text{C}(\text{CO})_{14}(\mu_3\text{-}\kappa\text{:}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4)]$ **3** have been synthesized by reaction of 1,1-diphenylethene with triruthenium dodecacarbonyl in octane under reflux. Compound **1** is a 1,1-diphenylethene hexaruthenium carbido cluster (Ru_6C) derivative wherein the organo-group, hydrogenated at the olefinic centre, is bound to the cluster by a single phenyl ring in an η^6 manner. Compound **2** is a similar Ru_6C derivative wherein the 1,1-diphenylethene ligand remains unsaturated, whilst the third, and minor, product is the first example of a metal carbonyl cluster chelated by a diphenyl ligand and is one of the few examples of an Ru_7C 'spiked' octahedron. The subtle electronic effects of the Ru_6C co-ordination in **2** have been probed by ^1H NMR spectroscopy. The solid-state structures of both the hydrogenated derivative **1** and the Ru_7C 'spiked' octahedral cluster **3** have been determined by single-crystal X-ray analysis. The supramolecular architecture of **3** has been examined in depth.

Further to our continuing interest in the construction of organometal cluster networks and arene clusters, we have synthesized and fully characterised several compounds containing hydrocarbon frameworks derived from the ligand 1,1-diphenylethene. In the design of these potentially interesting materials we wish to introduce an unsaturated link between redox-active cluster centres thus increasing electronic communication between the metal-containing units. Dehydrogenation (and hydrogenation) of alkenes of the type $\text{RCH=CHR}'$ in thermolysis reaction of $[\text{Ru}_3(\text{CO})_{12}]$ is a commonly observed phenomenon, usually yielding alkyne moieties co-ordinated to clusters of various nuclearities.^{1a} Hence, for the synthesis of $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-Ph}(\text{CH}_2)_2\text{Ph})]$ a direct carbonyl substitution reaction on the parent cluster $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ was chosen.^{1b} To avoid these problems in the thermolysis reaction and still produce an unsaturated linking group connecting the arene rings 1,1-diphenylethene was used in the production of a further group of Ru_6C (arene) type compounds (Scheme 1).

Results and Discussion

The three Ru_6C derivatives **1**, **2** and **3** respectively were prepared from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with an excess of 1,1-diphenylethene in *n*-octane under reflux. The reaction proceeded to give moderate yields of the three products together with a small amount of $[\text{Ru}_6\text{C}(\text{CO})_{17}]$. No evidence was found for the production of hydrocarbon-linked clusters. The cluster compounds were purified by TLC on silica plates, using an eluent based on the mixture 30% dichloromethane–70% hexane. Crystals of **1** and **3** suitable for X-ray determination were nucleated from dichloromethane–pentane slow diffusion.

The three derivatives **1**, **2** and **3** were observed as red-brown, black and brown-black bands on the thin-layer chromatographic plates respectively. After separation the yields of **1** and **2** were similar and substantially higher than that of **3** which could only be isolated in small amounts. The IR spectra of **1** and **2** in the CO region were consistent with that of an Ru_6C



Scheme 1 Thermolysis products of 1,1-diphenylethene and $[\text{Ru}_3(\text{CO})_{12}]$

(arene) compound bound in an η^6 mode. The FAB mass spectra of **1**, **2** and **3** showed molecular ion peaks at m/z 1192 (calc. 1193), 1190 (1191) and 1290 (1291) respectively, with a carbonyl regression typical of these systems, showing the loss of several CO units.

^1H NMR spectra of compounds **1** and **2**

The ^1H NMR spectrum of compound **1** in CDCl_3 under ambient conditions showed a more complex set of proton resonances than previously observed for similar systems. A multiplet centred at δ 7.26 and a doublet at δ 7.05 correspond to the *plm*- and *o*-protons of the unco-ordinated phenyl ring respectively. At lower frequencies a set of five signals due to the co-ordinated ring protons may be identified. A series of decoupling experiments identified the origins of the resonances. The *ortho* signals, at δ 5.89 and 5.34, are in distinct environments. While the *meta* signals are also differentiated at δ 5.56 and 5.51. The *para* resonance overlaps with the low-frequency

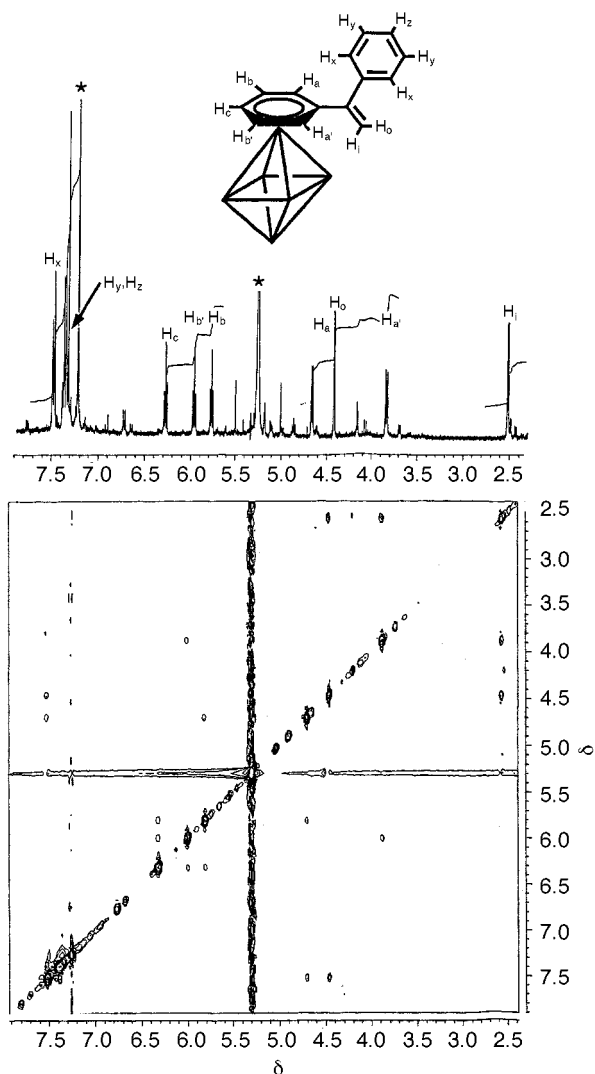


Fig. 1 The NOE NMR spectrum of compound 2; * = solvent

ortho signal and is centred at δ 5.32. The existence of these individual proton environments is a consequence of the proximal chiral centre, which (whether in its *R* or *S* form) denies mirror symmetry to the co-ordinated phenyl. The aliphatic protons show two signals: a quartet centred at δ 3.84 corresponding to a single hydrogen attached to the tertiary carbon and a doublet at δ 1.43 due to a methyl group. This led us to conclude that the double bond in the 1,1-diphenylethene ligand had undergone hydrogenation during the thermolysis reaction. This was later confirmed by the solid-state structure as determined by a single-crystal X-ray diffraction study. The source of the hydrogen remains unclear, but was postulated as being from small amounts of water in the reaction mixture. Therefore in order to evaluate this hypothesis an experiment was undertaken. The reactants were further purified; $[\text{Ru}_3(\text{CO})_{12}]$ was sublimed prior to use, 1,1-diphenylethene distilled and octane distilled from Na/K alloy. The reaction was then repeated as before with added D_2O (0.5 cm^3). Isolation of the products showed a greater degree of breakdown to metallic ruthenium than usual and reduced yields of the products. A ^1H NMR spectrum of **1** in CDCl_3 under ambient conditions together with a positive-ion FAB mass spectrum showed no decrease in the presence of ^1H at the site of hydrogenation.

The ^1H NMR spectrum of compound **2** in CDCl_3 under ambient conditions showed that the ligand had remained unsaturated, consistent with the positive-ion FAB mass spectrum, although the C=C stretch could not be conclusively identified from the solution IR spectrum. The nuclear Overhauser effect NOE NMR spectrum of **2** along with the spin assign-

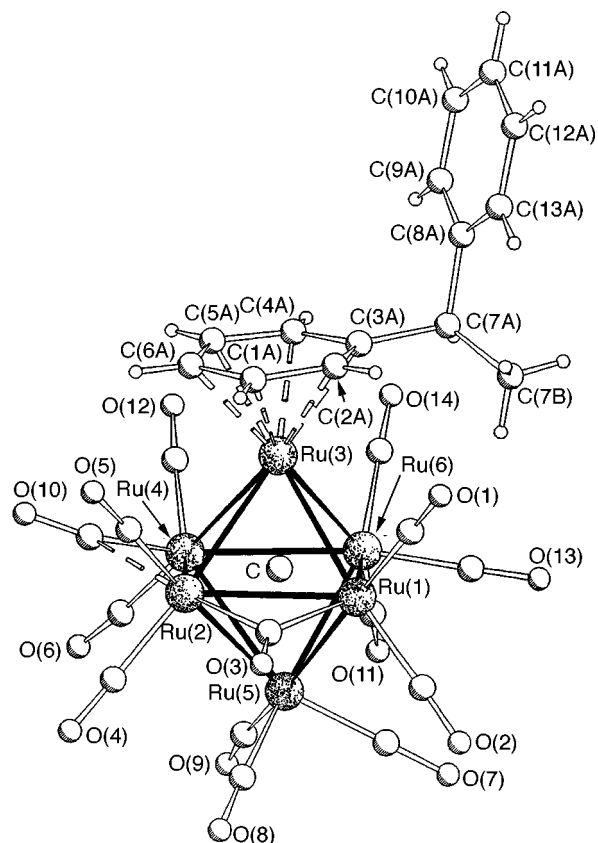


Fig. 2 Solid-state molecular structure of compound **1**, showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as that of the corresponding O atoms

ments is shown in Fig. 1. As in **1** five separate environments can be identified for the co-ordinated arene protons. However they span a much greater frequency range (*ca.* 2.5 ppm). The large chemical shift difference between the protons H_1 and H_0 indicates very different environments for them. This is probably due to the steric control exercised by the C=C double bond, holding H_1 close to the carbonyl cluster and H_0 away from it. Equivalence of the H_x hydrogen atoms suggests the pendant phenyl is free to rotate. However, rotation is hindered according to the NOE data, about the $\text{Ph}_{\text{coor}}\text{-C}$ axis. This may be due to the steric requirements of the ligand or due to some hyperconjugative effect involving the Ph_{coor} and the alkene π system. There is evidence in the IR spectrum to suggest this may be so. A shift to lower energy of the two principal absorptions (*cf.* **1**), indicates a larger degree of $\text{M}\rightarrow\text{CO}$ π^* back donation and therefore increased electron density in the cluster core.

Solid-state molecular structure of compound **1**

The solid-state structure of compound **1** is shown in Fig. 2 and some structural parameters are in Table 1. In common with the other compounds the cluster core consists of an octahedral arrangement of ruthenium metal atoms encapsulating the interstitial carbido atom. The substituted arene is co-ordinated in an η^6 mode which is predominant in compounds of this type. Fourteen carbonyl ligands make up the remaining co-ordination sphere of the hexaruthenium cluster.

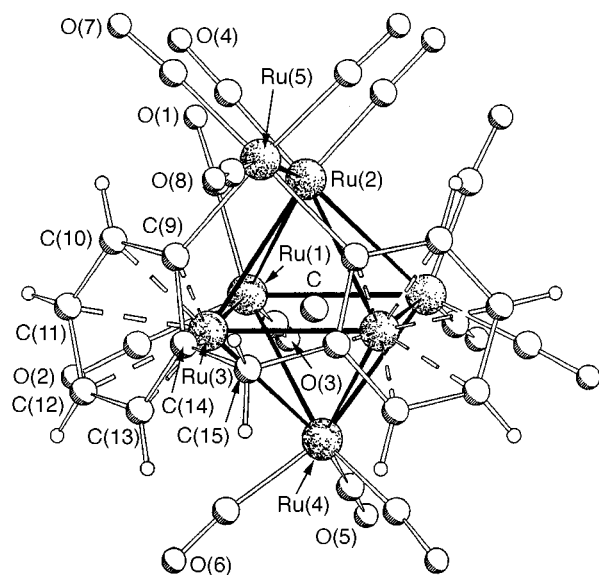
The twelve ruthenium contacts lie in the range Ru(2)–Ru(4) 2.799(1) to Ru(1)–Ru(6) 3.143(1) Å. This is a similarly wide range to that observed in the parent cluster $[\text{Ru}_6\text{C}(\text{CO})_{17}]$. The shortest Ru–C (carbide) distance is to the metal carrying the arene [Ru(3)–C 1.921(8) Å], a phenomenon commonly observed in these systems. The Ru(3)–C (arene) distances vary little and lie in the range Ru(3)–C(1A) 2.21(1) to Ru(3)–C(3A) 2.28(1) Å whilst the co-ordinated arene carbon–carbon distances lie in the range C(4A)–C(5A) 1.38(1) to C(3A)–C(4A)

Table 1 Selected bond distances (Å) with estimated standard deviations (e.s.d.s) for compound 1

Ru(1)–Ru(2)	2.823(1)	Ru(1)–Ru(5)	2.844(1)	Ru(1)–Ru(3)	2.888(1)	Ru(1)–Ru(6)	3.143(1)
Ru(2)–Ru(4)	2.799(1)	Ru(2)–Ru(3)	2.883(1)	Ru(2)–Ru(5)	2.967(1)	Ru(3)–Ru(4)	2.856(1)
Ru(3)–Ru(6)	2.862(1)	Ru(4)–Ru(6)	2.907(1)	Ru(4)–Ru(5)	2.923(1)	Ru(5)–Ru(6)	2.811(1)
Ru(1)–C	2.045(9)	Ru(2)–C	2.092(9)	Ru(3)–C	1.921(8)	Ru(4)–C	2.084(9)
Ru(5)–C	2.084(8)	Ru(6)–C	2.052(9)	Ru(3)–C(1A)	2.21(1)	Ru(3)–C(2A)	2.25(1)
Ru(3)–C(3A)	2.28(1)	Ru(3)–C(4A)	2.23(1)	Ru(3)–C(5A)	2.24(1)	Ru(3)–C(6A)	2.24(1)
C(3A)–C(7A)	1.52(1)	C(8A)–C(7A)	1.53(1)	C(7B)–C(7A)	1.52(1)	C(1A)–C(6A)	1.40(1)
C(1A)–C(2A)	1.41(1)	C(2A)–C(3A)	1.40(1)	C(3A)–C(4A)	1.44(1)	C(4A)–C(5A)	1.38(1)
C(5A)–C(6A)	1.43(1)						

Table 2 Selected bond distances (Å) with e.s.d.s for compound 3

Ru(1)–Ru(1 ¹)	2.9042(10)	Ru(1)–Ru(2)	3.0486(9)	Ru(1)–Ru(3)	2.8497(11)
Ru(1)–Ru(4)	2.8425(9)	Ru(2)–Ru(3)	2.8599(9)	Ru(2)–Ru(5)	2.9174(12)
Ru(3)–Ru(4)	2.8491(9)	Ru(3)–Ru(3 ¹)	2.7832(10)	Ru(1)–C	2.068(6)
Ru(2)–C	2.079(8)	Ru(3)–C	1.961(6)	Ru(4)–C	2.095(8)
Ru(1)–C(1)	1.894(7)	Ru(1)–C(2)	1.917(7)	Ru(1)–C(3)	1.887(7)
Ru(2)–C(4)	1.837(7)	Ru(4)–C(5)	1.950(11)	Ru(4)–C(6)	1.907(6)
Ru(5)–C(7)	1.957(7)	Ru(5)–C(8)	1.882(12)	C(1)–O(1)	1.146(8)
C(2)–O(2)	1.132(7)	C(3)–O(3)	1.145(9)	C(4)–O(4)	1.157(8)
C(5)–O(5)	1.107(11)	C(6)–O(6)	1.137(7)	C(7)–O(7)	1.132(8)
C(8)–O(8)	1.144(13)	Ru(3)–C(9)	2.187(6)	Ru(5)–C(9)	2.113(6)
Ru(3)–C(10)	2.196(6)	Ru(3)–C(11)	2.246(6)	Ru(3)–C(12)	2.219(6)
Ru(3)–C(13)	2.216(6)	Ru(3)–C(14)	2.198(6)		

**Fig. 3** Solid-state molecular structure of compound 3. Details as in Fig. 2

1.44(1) Å. Of importance in this determination is the structural confirmation of the hydrogenation of the olefinic part of the 1,1-diphenylethene ligand. The chiral centre C(7A) displays a distorted tetrahedral geometry consistent with that of a saturated hydrocarbon together with three bond lengths to C(3A), C(8A) and C(7B) of single-bond character. However, no enantiomeric excess is observed since the space group is centrosymmetric. This may not however be the case for the bulk compound although no measurements were undertaken to ascertain this. Twelve carbonyls show terminal bonding with bond parameters typical of this type. Whilst CO(3) displays a bridging mode triangulating the Ru(1)–Ru(2) vector and CO(10) occupies a semibridging mode to Ru(4) and Ru(2) [Ru(2)–C(10) 2.37(1), Ru(4)–C(10) 1.99(1) Å].

Solid-state molecular structure of compound 3

The solid-state structure of compound 3 is shown in Fig. 3 and some structural parameters are in Table 2. A crystallographic mirror plane passes through Ru(5), Ru(2) and Ru(4), making the two phenyl rings and their cluster interaction identical. The

arrangement of the seven ruthenium metal atoms may be described as a 'spiked' octahedron, produced by the addition of a single ruthenium carbonyl fragment to the more orthodox hexaruthenium carbido cluster core. This arrangement of metal atoms is relatively rare, the only examples displaying stabilisation of the ruthenium 'spike' in an unsaturated metallocycle.² The 'spike' Ru(5) is σ co-ordinated to both C₆ rings along with three carbonyls, which including the interaction with the cluster core produces an essentially octahedral co-ordination geometry. It is immediately apparent that the 1,1-diphenylethene ligand has been substantially transformed. The C=C bond has been cleaved and the remaining 'carbene' [C(15)] hydrogenated to give a simple CH₂ link between the C₆ rings. Hydrogens at both C(9) positions have been replaced by an orthometallation by Ru(5) at these sites. The hydrocarbon moiety spans two *cis*-ruthenium cluster core atoms with each C₆ ring displaying co-ordination in an η^6 mode.

The cluster-core metal–metal contacts span a large range. The smallest of these is between Ru(3) and its symmetry-equivalent Ru(3¹) (2.7832 Å), which is spanned by the hydrocarbon ligand. Whilst the longest, Ru(1)–Ru(2) 3.0486(11) Å, is an unbridged edge between an equatorial metal and the apical metal with a metal connectivity of five, which is repeated twice, due to symmetry. The 'spike' bond length lies in the normal range for a ruthenium metal–metal bond [Ru(2)–Ru(5) 2.9174(12) Å]. Of the metal–carbide distances, the smallest is that to the arene carrying Ru(3) at 1.961(6) Å.

The bonding mode of the hydrocarbon ligand is novel. The chelating diphenylmethane donates a total of fourteen electrons: twelve π electrons to the cluster core and a further two in σ co-ordination to Ru(5). These σ bonds to the ruthenium 'spike' are the shortest metal–ligand interaction at 2.113(6) Å and produce an angle of 87.3(3)° at Ru(5). The η^6 -co-ordinated C₆ rings are closely bound to the cluster core and give a range of metal–carbon bond lengths; Ru(3)–C(9) 2.187(6) to Ru(3)–C(11) 2.246(6) Å. The C₆ rings are essentially planar and produce a dihedral angle of 110.3(8)° at C(15). A representation of the hydrocarbon bond lengths is given in Fig. 4. The shortest C–C bond is between carbons C(11) and C(12) which, at the same time, have the longest cluster–arene bond lengths. Fourteen terminal carbonyl ligands make up the remaining co-ordination sphere of the cluster core and 'spike' and donate a total of 28e⁻ to the system. Together with the electrons donated by the hydrocarbon ligand this gives a total electron count of

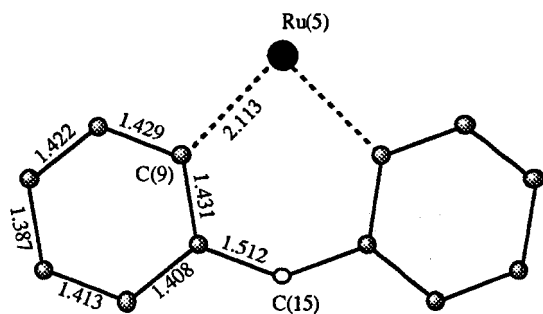


Fig. 4 Representation of the carbon framework in compound **3**; bond lengths in Å

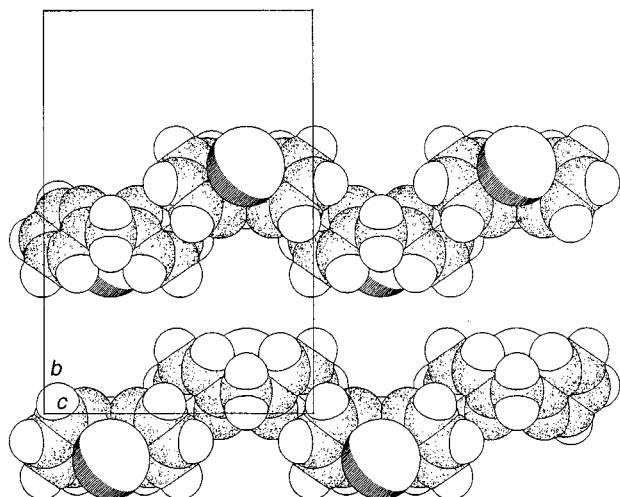


Fig. 5 Solid-state architecture of compound **3**. The carbonyls have been removed for clarity and cluster cores are represented by large spheres positioned by their centre of mass

102 for the 'spiked' octahedron, which is in accordance with the rules for condensed polyhedra $[86(\text{Oh.}closo) + 34(\text{M}_2) - 18(\text{one vertex shared}) = 102e^-]$.³

It is apparent that in the formation of compound **3** hydrogenolysis of the C=C bond has occurred. A source of hydrogen for such a reaction is orthometallation of the phenyl groups and may in turn be transferred to the olefinic bond. We may exclude the possibility of **3** being the result of adventitious diphenylmethane since no **3** was isolated in the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with diphenylmethane.^{1b} We are presently undertaking experiments which should shed more light upon this fascinating mechanism.

Solid-state supramolecular architecture of compound **3**

The solid-state architecture of compound **3** also shows some interesting intermolecular interactions. A projection through the *bc* plane shown in Fig. 5 shows a packing motif constructed of interlocking snakes of molecules displaying two dominant interactions which extend along the *a* axis. First, there is a 'graphitic' interaction between arenes of adjacent molecules; Fig. 6 shows a projection through the aligned C₆ rings displaying the type of overlap produced. The distance between the two planes in this interaction is 3.45 Å, which is comparable to values previously observed in similar bis(arene) systems.⁴ Secondly, there is a short contact of the CO...H-C type between the snake-like chains of the previously mentioned 'graphitic' interactions. Owing to the high symmetry of the crystal structure this short contact is repeated four times for each molecule. The O...H distance is quite short for interactions of this type, falling in the lower range of C-H...O_{CO} 'hydrogen bonds'. The multibonded network thus produced is shown in Fig. 7 along with a summary of the interaction parameters. The 'snake' arrangement closely resembles that observed in the

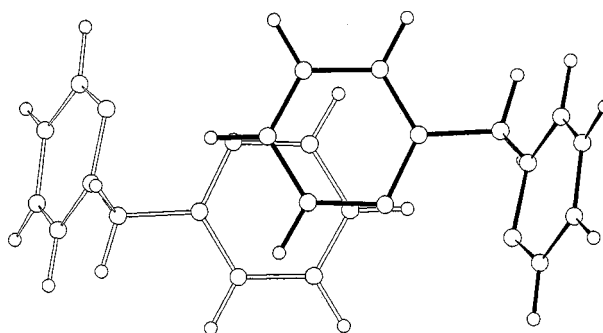


Fig. 6 Projection through the C₆ rings in compound **3** showing the overlap geometry [interplanar angle 0(2)° with an offset distance of 1.88(4) Å]

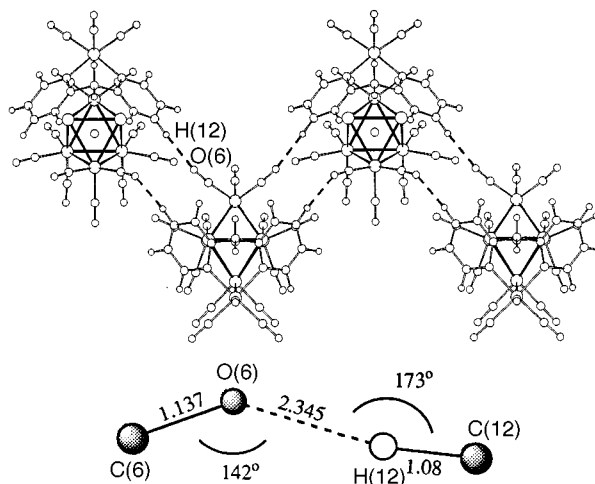


Fig. 7 The CO...H-C type interactions between molecules of compound **3**; distances in Å

solid-state structure of $[\text{Ru}_6\text{C}(\text{CO})_{11}(\eta^6\text{-C}_6\text{H}_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_6\text{H}_6)]$. The geometry of the two ligands with respect to the cluster, albeit very different from that of **3**, generates similar steric requirements and makes the molecules very similar in shape hence in packing requirements.

Conclusion

Compound **1** is an interesting example of metal carbonyl-mediated hydrogenation. Whilst the source of the hydrogen has not been pinpointed it is likely that reforming-type reactions may take place with the hydrocarbon solvent even at this low temperature. Compound **2** may serve as a precursor to a cluster network connected by the unsaturated C=C link. Compound **3** is the first example of a chelating diphenyl ligand on a carbonyl cluster; it is also one of a very rare collection of spiked octahedral cluster compounds.

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 CH₂Cl₂ using NaCl cells (0.5 nm path length). Positive-ion fast atom bombardment mass spectra were obtained using a Kratos MS50TC spectrometer, with CsI as calibrant, ¹H NMR spectra in CDCl₃ using a Bruker AM400 instrument, referenced to internal SiMe₄. Products were separated by thin-layer chromatography using plates supplied by Merck (0.25 mm layer of Kieselgel 60 F₂₅₄). The compound $[\text{Ru}_3(\text{CO})_{12}]$ was prepared by the literature procedure.⁵ 1,1-Diphenylethylene from Aldrich was used without further purification.

Synthesis and characterisation of [Ru₆C(CO)₁₄(η⁶-PhCHMe-Ph)] **1, [Ru₆C(CO)₁₄(η⁶-Ph=CH₂Ph)] **2** and [Ru₇C(CO)₁₄(μ₃-κ: η⁶: η⁶-C₆H₄CH₂C₆H₄)] **3****

The compound [Ru₃(CO)₁₂] (1.00 g) was refluxed in *n*-octane (40 cm³) with 1,1-diphenylethene (300 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 (3:7) as eluent. Two major red-brown bands and a minor darker band were extracted with dichloromethane and characterised (average yields) (75 **1**), (100 **2**) and (*ca.* 5 mg **3**).

Spectroscopic data: **1**, IR (CH₂Cl₂) ν(CO) 2076m, 2035 (sh), 2025vs, 1985w, 1968w and 1816w (br) cm⁻¹; ¹H NMR (CDCl₃) δ 7.26 (m, 3 H), 7.05 (m, 2 H), 5.89 (m, 1 H), 5.56 (m, 1 H), 5.51 (m, 1 H), 5.34 (m, 1 H), 5.32 (m, 1 H), 3.84 (q, 1 H) and 1.43 (d, 3 H); *m/z* 1192 (*M*⁺; calc. 1193) (Found: C, 30.1; H, 1.2. Calc. for C₂₉H₁₄O₁₄Ru₆: C, 29.2; H, 1.18%); **2**, IR (CH₂Cl₂) ν(CO) 2070m, 2033 (sh), 2023vs, 1996m (br) and 1816w (br) cm⁻¹; ¹H NMR (CDCl₃): δ 7.52 (m, 2 H), 7.39 (m, 3 H), 6.31 (m, 1 H), 6.01 (m, 1 H), 5.81 (m, 1 H), 4.71 (m, 1 H), 4.47 (m, 1 H), 3.88 (m, 1 H) and 2.57 (m, 1 H); *m/z* 1190 (*M*⁺, calc. 1191) (Found: C, 31.2; H, 1.15. Calc. for C₂₉H₁₂O₁₄Ru₆: C, 29.25; H, 1.02%); **3**, IR (CH₂Cl₂) ν(CO) 2067m, 2055 (sh), 2023vs and 1970s cm⁻¹; *m/z* 1278 (*M*⁺, calc. 1279).

Crystallography

Crystal data for compound 1. C₂₉H₁₂O₁₄Ru₆, *M* = 1192.82, monoclinic, space group *P*2₁/*a*, *a* = 11.644(4), *b* = 16.546(3), *c* = 17.650(2) Å, β = 105.56(3)°, *U* = 3275.8(13) Å³, *Z* = 4, *D*_c = 2.419 Mg m⁻³, λ = 0.710 73 Å, *T* = 150(2) K, μ = 2.764 mm⁻¹.

Data were collected on a Stoe-Stadi four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device, using a crystal of dimensions 0.16 × 0.20 × 0.15 mm, mounted directly from solution, by the θ–ω method (3 < 2θ < 50°). Of a total of 6127 reflections collected, 5740 were independent (*R*_{int} = 0.0397). Data were corrected for absorption using ψ scans (*T*_{max} = 0.659, *T*_{min} = 0.559).⁶ The structure was solved by direct methods (SHELXTL PLUS)⁷ and refined by full-matrix least-squares analysis on *F*² with *R*1 [*F* > 4σ(*F*)] and *wR*2 (all data) to 0.0499 and 0.0946, respectively. The pendant phenyl [C(8A) to C(13A)] shows considerable disorder over several positions. Since a satisfactory model could not be produced the AFIX 66 command was used to fit

the C atoms with a regular hexagon in the highest-occupancy orientation. Hydrogen atoms were placed in fixed calculated positions. Largest peak and hole in final difference map +2.033 and –1.671 e Å⁻³. The residual peaks were all in the proximity of the metal atoms, indicating an only partially successful experimental absorption correction.

Crystal data for compound 3. C₂₈H₁₀O₁₄Ru₇, *M* = 1277.85, orthorhombic, space group *Pbcm*, *a* = 9.664(3), *b* = 21.556(6), *c* = 14.748(3) Å, *U* = 3072.3(14) Å³, *Z* = 4, *D*_c = 2.763 Mg m⁻³, λ = 0.710 73 Å, *T* = 150(2) K, μ = 3.419 mm⁻¹.

Data were collected as for compound **1** using a crystal of dimensions 0.10 × 0.12 × 0.15 mm. Of a total of 4622 reflections collected, 2108 were independent (*R*_{int} = 0.0607). The structure was solved and refined as for **1** to *R*1 and *wR*2 0.0336 and 0.0912, respectively. The H atoms were placed in fixed calculated positions. Largest peak and hole in final difference map +0.850 and –1.495 e Å⁻³.

CCDC reference number 186/772.

Acknowledgements

We gratefully acknowledge financial support from NATO, EPSRC and The University of Edinburgh.

References

- (a) C. M. Martin, Ph.D. Thesis, University of Edinburgh, 1995 and refs. therein; J. Wang, M. Sabat, L. J. Lyons and D. F. Shriver, *Inorg. Chem.*, 1991, **30**, 382; (b) A. J. Blake, P. J. Dyson, B. F. G. Johnson, D. Reed and D. S. Shephard, *J. Chem. Soc., Dalton Trans.*, 1995, 843.
- D. Braga, F. Grepioni, E. Parisini, P. J. Dyson, D. Reed, P. E. Gaede, J. J. Byrne and B. F. G. Johnson, *Organometallics*, 1995, **14**, 4892; A. J. Blake, P. J. Dyson, P. E. Gaede, D. Braga, E. Parisini and B. F. G. Johnson, *J. Chem. Soc., Dalton Trans.*, 1995, 3431.
- D. M. P. Mingos, *J. Chem. Soc., Chem. Commun.*, 1983, 706.
- D. Braga, P. J. Dyson, F. Grepioni, B. F. G. Johnson and M. J. Calhorda, *Inorg. Chem.*, 1994, **33**, 3218.
- B. F. G. Johnson, J. Lewis and P. A. Kilty, *J. Chem. Soc. A*, 1968, 2859.
- A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
- G. M. Sheldrick, SHELXTL PLUS, Siemens Analytical Instruments, Madison, WI, 1990.

Received 6th October 1997; Paper 7/07179E