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# The synthesis and characterisation of some indenylophane clusters $[M_4H(CO)_9(L - H)]$ (M = Ru or Os)

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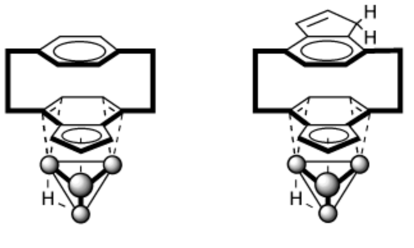
In a study concerning the reactivity of the $[M_3(CO)_{12}]$ (M = Ru or Os) clusters towards the [2.2]parabenzoindenophane ($L^1$) and *anti*-[2.2]indenophane ($L^2$) ligands, the molecular structures of three new compounds $[Ru_4H(CO)_9(L^1 - H)]$ **1**, $[Os_4H(CO)_9(L^1 - H)]$ **2** and $[Ru_4H(CO)_9(L^2 - H)]$ **3** were established by single crystal X-ray diffraction analyses. In all cases it was observed that the ligand had undergone C–H bond activation with the resultant indenyl and hydride fragments retained upon the metal cluster in the facial $\mu_3$-$\eta^5:\eta^2:\eta^2$ and edge-bridging $\mu$ modes, respectively. Surprisingly, despite possessing two indene faces for cluster association, $L^2$ also appears only to be able to utilise one of them.

## Introduction

The interaction of the cyclophanes with transition metals has fascinated chemists for several decades.[1] Research in this field was initiated by the isolation of the mono- and bis-$[Cr(CO)_3]$ complexes of the parent compound [2.2]paracyclophane.[2,3] The potential use of the cyclophane moiety as a monomer group for organometallic sandwich based polymers was quickly recognised and the initial study extended to encompass virtually all of the transition metals. These efforts culminated elegantly upon the unification of three metal ions by two cyclophane ligands much later.[4,5] More recently, an evolution of cyclophane and of arene cluster chemistry has been the attempt to bring together transition metal carbonyl clusters in an analogous manner.[6] Although we have only achieved limited success with the [2.2.2]paracyclophane ligand unit so far,[7] our investigation into the combination of a wide variety of cyclophane ligands and transition metal carbonyls has provided us with much useful information about the bonding mode and geometrical preferences in such systems.

Of the many cyclophanes cited in the literature, two interesting condensed species, namely [2.2]parabenzoindenophane ($L^1$)[8] and *anti*-[2.2]paraindenophane ($L^2$),[5] stand out. Although the ferrocene type chemistry of the $L^1$ and $L^2$ ligands had been developed, there was no work concerning their interaction with transition metal clusters.[5,8–10] The compound $L^1$ was of particular interest to us because we wished to establish whether a cluster would display an affinity for an indene group over a benzene group. When that was proved to be the case, $L^2$ then became of interest because of its greater potential than the parent compound, [2.2]paracyclophane, to link cluster units together. To this end the reaction of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ with [2.2]parabenzoindenophane and *anti*-[2.2]paraindenophane was investigated, the results of which are shown in Fig. 1.



**1 and 2** **3**

**Fig. 1** The compounds $[Ru_4H(CO)_9(L^1 - H)]$ **1**, $[Os_4H(CO)_9(L^1 - H)]$ **2** and $[Ru_4H(CO)_9(L^2 - H)]$ **3**.

## Results and discussion

The thermolysis of [2.2]parabenzoindenophane ($L^1$) with three molar equivalents of $[Ru_3(CO)_{12}]$ in heptane under reflux over a 4 h period affords only one new complex, namely $[Ru_4H(CO)_9(\mu_3\text{-}\eta^5:\eta^2:\eta^2\text{-}C_{19}H_{17})]$ **1**. Similarly, analogous reactions between $L^1$ and $[Os_3(CO)_{12}]$ in nonane over 6 h and between *anti*-[2.2]paraindenophane ($L^2$) and $[Ru_3(CO)_{12}]$ in heptane over 4 h afford $[Os_4H(CO)_9(\mu_3\text{-}\eta^5:\eta^2:\eta^2\text{-}C_{19}H_{17})]$ **2** and $[Ru_4H(CO)_9(\mu_3\text{-}\eta^5:\eta^2:\eta^2\text{-}C_{22}H_{19})]$ **3**, respectively. In any case, compounds **1**, **2** and **3** may be separated from the starting materials and binary metal carbonyl by-products by column/thin layer chromatography.

The molecular structure of compounds **1**, **2** and **3** was determined using single crystals obtained from concentrated dichloromethane–toluene solutions at −20 °C. Crystalline **1** and **2** were found to be both isomorphous and isostructural, with two independent molecules co-crystallised with one molecule of dichloromethane in the asymmetric unit. The molecular structure of compound **1** (both molecules **A** and **B**) is illustrated in Fig. 2 with alternative views in Fig. 3 (molecule **B** only). The molecular structure of **2** has not been illustrated due to its similarity to that of **1**. Relevant bond distances are shown in Tables 1, 2 and 3 for both compounds **1** and **2**, and for molecules **A** and **B**, while crystal data and measurement details are given in the Experimental section. Both independent molecules in crystalline **1** and **2** are characterised by the same kind of coordination of the cyclophane ligand to the cluster. The metal framework consists of a closed tetrahedron with an indenyl group lying over one triangular face and a hydride ligand bridging one metal–metal edge. The most obvious difference between the two independent molecules **A** and **B** is in the position of the hydride upon the cluster core with respect to the upright orientation of the cyclophane ligand (see Fig. 2). In molecule **A** of

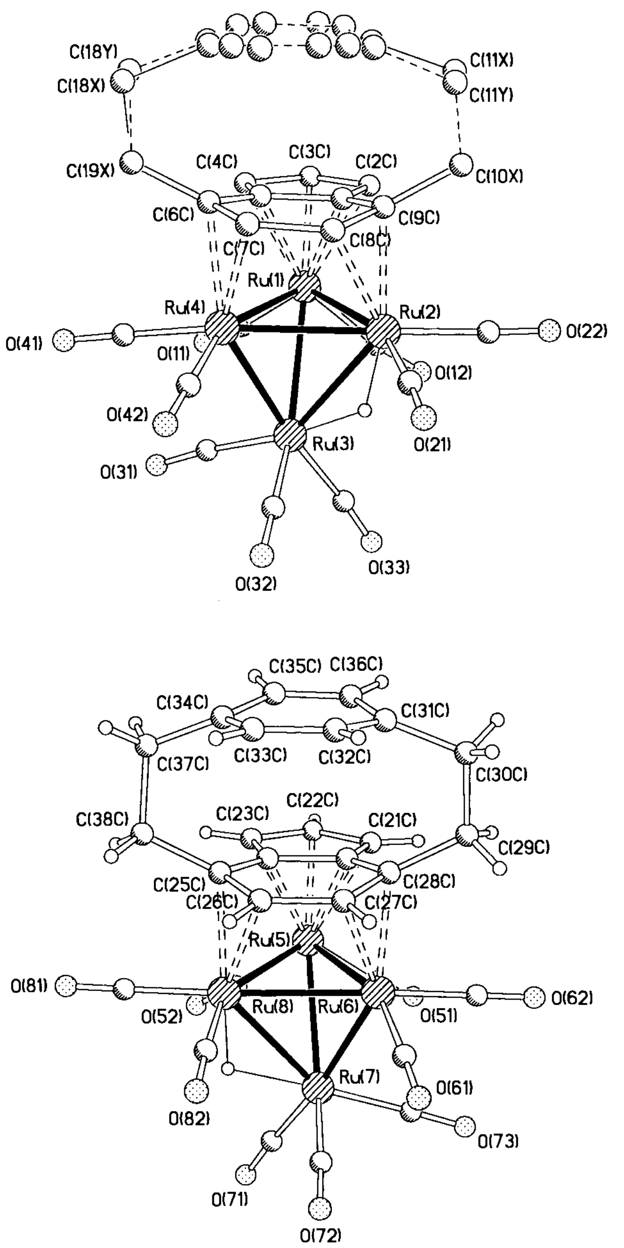


**Fig. 2** The two independent molecules in the crystalline structure of compound **1**: **A** (top) and **B** (bottom).

compound **1** part of the cyclophane ligand was disordered over two positions in a 55:45 ratio. The crystallographic data, however, were not good enough to establish a similar disorder in the corresponding molecule of **2**.

Owing to the close analogy between the cyclophane clusters in both compounds **1** and **2**, and also between molecules **A** and **B**, only the structural features of **1B** will be described in detail. Since all nine carbon atoms of the indenyl group {C(20c) through C(28c)} interact with the trimetallic face {Ru(5)–Ru(6)–Ru(8)} there are two possible bonding modes that the cyclophane may adopt. These are the $\mu_3$-$\eta^5$:$\eta^2$:$\eta^2$ cyclopentadienyl-diene and the $\mu_3$-$\eta^3$:$\eta^3$:$\eta^3$ tris-allyl modes. The analysis of the metal–carbon bond lengths has given an insight into the type of bonding interaction present (see Fig. 4). For example, the Ru(8)–C(24c) and Ru(8)–C(26c) contact distances were found to be 2.699(9) and 2.338(9) Å, respectively, while the Ru(8)–C(25c) distance was found to be only 2.212(9) Å. This clearly suggests that Ru(8) interacts with an olefinic moiety {C(25c)–C(26c)} rather than an allylic one {C(24c)–C(25c)–C(26c)}. Since the same pattern is demonstrated in the corresponding the Ru(5)–ligand carbon contact distances it may be concluded that the cyclophane is bound to the cluster in the former cyclopentadienyl-diene mode. However, since Ru(8)–C(26c) is significantly longer than Ru(8)–C(25c) by more than 0.1 Å {and Ru(5)–C(27c) longer than Ru(5)–C(28c)} it appears that the $\mu_3$-$\eta^5$:$\eta^2$:$\eta^2$ bonding mode has slipped significantly toward $\mu_3$-$\eta^3$:$\eta^3$:$\eta^3$. A large $C_5$ ring slippage parameter† of 0.045 Å {*cf.* with 0.005 Å in the related 1,3-diethylindenyl cluster [$Os_4H(CO)_9(\eta^5$:$\eta^2$:$\eta^2$-$C_{13}H_{15})$][11]} supports this conclusion. This slippage effect is possibly due to the distorted nature of the ligand. Whereas the indenyl ligand in [$Os_4H(CO)_9(\eta^5$:$\eta^2$:$\eta^2$-$C_{13}H_{15})$] is planar,[11] the indenyl moiety in [$Ru_4H(CO)_9(\eta^5$:$\eta^2$:$\eta^2$-$C_{19}H_{17})$] **1** is folded with the {C(28c)-

**Table 1** M–C Distances (Å) in crystalline compounds **1** and **2** (M = Ru for **1** and Os for **2**)

| | **1** | **2** |
|---|---|---|
| M(1)–C(1C) | 2.29(1) | 2.25(4) |
| M(1)–C(2C) | 2.25(1) | 2.22(4) |
| M(1)–C(3C) | 2.24(1) | 2.28(3) |
| M(1)–C(4C) | 2.24(1) | 2.27(4) |
| M(1)–C(5C) | 2.295(9) | 2.34(4) |
| M(2)–C(8C) | 2.35(1) | 2.36(3) |
| M(2)–C(9C) | 2.19(1) | 2.24(3) |
| M(4)–C(6C) | 2.21(1) | 2.24(3) |
| M(4)–C(7C) | 2.242(9) | 2.22(3) |
| M(5)–C(20C) | 2.307(9) | 2.32(3) |
| M(5)–C(21C) | 2.241(9) | 2.28(4) |
| M(5)–C(22C) | 2.23(1) | 2.25(3) |
| M(5)–C(23C) | 2.234(9) | 2.17(3) |
| M(5)–C(24C) | 2.257(9) | 2.25(3) |
| M(6)–C(27C) | 2.249(9) | 2.24(4) |
| M(6)–C(28C) | 2.195(9) | 2.15(3) |
| M(8)–C(25C) | 2.212(9) | 2.22(4) |
| M(8)–C(26C) | 2.338(9) | 2.34(4) |

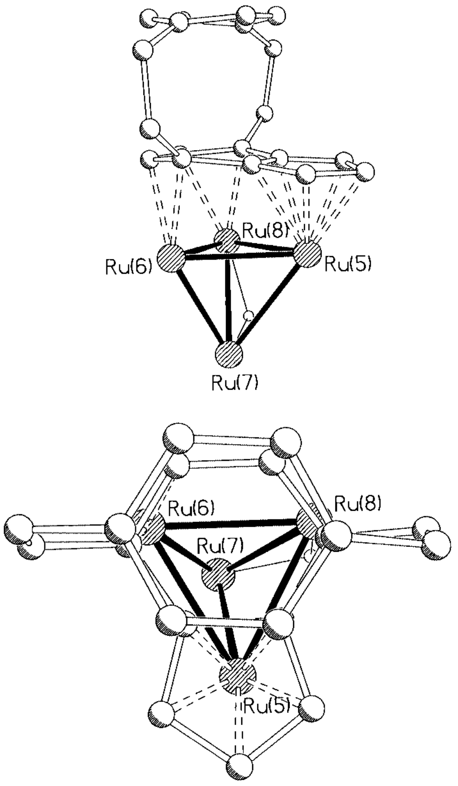


**Fig. 3** Alternative views of the molecular structure of [$Ru_4H(CO)_9(\mu_3$-$C_{19}H_{17})$] **1**.

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† The ring slippage parameter is an indicator of the $\eta^3$ or $\eta^5$ character of a co-ordinated cyclopentadienyl ring. In the case of compound **1** it is calculated from [{Ru(5)–C(20c) + Ru(5)–C(24c)}/2 − {Ru(5)–C(21c) + Ru(5)–C(23c)}/2].[11]

**Table 2** C–C Distances (Å) in crystalline compounds **1** and **2** (M = Ru for **1** and Os for **2**)

| | **1** | **2** |
|---|---|---|
| C(1C)–C(2C) | 1.47(1) | 1.41(5) |
| C(1C)–C(5C) | 1.43(1) | 1.49(5) |
| C(1C)–C(9C) | 1.48(1) | 1.45(5) |
| C(2C)–C(3C) | 1.40(2) | 1.42(5) |
| C(3C)–C(4C) | 1.42(2) | 1.49(5) |
| C(4C)–C(5C) | 1.44(1) | 1.49(5) |
| C(5C)–C(6C) | 1.45(1) | 1.41(5) |
| C(6C)–C(7C) | 1.43(1) | 1.43(4) |
| C(7C)–C(8C) | 1.42(1) | 1.42(4) |
| C(8C)–C(9C) | 1.41(2) | 1.47(4) |
| C(10C)–C(9C) | 1.52(1) | 1.54(4) |
| C(10C)–C(11C) | 1.62(3) | 1.45(7) |
| C(11C)–C(12C) | 1.52(4) | 1.45(7) |
| C(12C)–C(13C) | 1.3900 | 1.41(6) |
| C(12C)–C(17C) | 1.40(4) | 1.41(6) |
| C(13C)–C(14C) | 1.43(3) | 1.42(6) |
| C(14C)–C(15C) | 1.42(4) | 1.34(5) |
| C(15C)–C(16C) | 1.3900 | 1.44(5) |
| C(15C)–C(18C) | 1.56(5) | 1.48(5) |
| C(16C)–C(17C) | 1.41(3) | 1.38(5) |
| C(18C)–C(19C) | 1.61(4) | 1.49(5) |
| C(19C)–C(6C) | 1.50(1) | 1.51(4) |
| C(20C)–C(21C) | 1.43(1) | 1.49(5) |
| C(20C)–C(24C) | 1.46(1) | 1.45(5) |
| C(20C)–C(28C) | 1.46(1) | 1.47(5) |
| C(21C)–C(22C) | 1.43(1) | 1.49(5) |
| C(22C)–C(23C) | 1.41(1) | 1.36(5) |
| C(23C)–C(24C) | 1.41(1) | 1.46(4) |
| C(24C)–C(25C) | 1.45(1) | 1.38(5) |
| C(25C)–C(26C) | 1.42(1) | 1.40(5) |
| C(25C)–C(38C) | 1.54(1) | 1.60(4) |
| C(26C)–C(27C) | 1.44(1) | 1.48(5) |
| C(27C)–C(28C) | 1.40(1) | 1.47(5) |
| C(28C)–C(29C) | 1.53(1) | 1.46(5) |
| C(29C)–C(30C) | 1.54(1) | 1.56(6) |
| C(30C)–C(31C) | 1.50(2) | 1.48(6) |
| C(31)C–C(36C) | 1.38(2) | 1.40(5) |
| C(31C)–C(32C) | 1.39(2) | 1.35(5) |
| C(32C)–C(33C) | 1.39(2) | 1.39(5) |
| C(33C)–C(34C) | 1.37(2) | 1.39(5) |
| C(34C)–C(35C) | 1.40(2) | 1.39(5) |
| C(34C)–C(37C) | 1.48(2) | 1.54(5) |
| C(35C)–C(36C) | 1.38(2) | 1.34(5) |
| C(37C)–C(38C) | 1.58(2) | 1.59(4) |

**Table 3** M–M and M–H distances (Å) in crystalline compounds **1** and **2** (M = Ru for **1** and Os **2**)

| | **1** | **2** |
|---|---|---|
| M(1)–M(2) | 2.895(1) | 2.909(2) |
| M(1)–M(3) | 2.911(2) | 2.947(2) |
| M(1)–M(4) | 2.901(1) | 2.926(2) |
| M(2)–M(3) | 2.863(1) | 2.872(2) |
| M(2)–M(4) | 2.786(1) | 2.810(2) |
| M(3)–M(4) | 2.667(1) | 2.667(2) |
| M(2)–H(1) | 1.7(1) | 1.7(1) |
| M(3)–H(1) | 1.5(1) | 1.6(1) |
| M(5)–M(6) | 2.889(1) | 2.918(2) |
| M(5)–M(7) | 2.913(1) | 2.939(2) |
| M(5)–M(8) | 2.873(1) | 2.882(2) |
| M(6)–M(7) | 2.662(1) | 2.671(2) |
| M(6)–M(8) | 2.760(1) | 2.790(2) |
| M(7)–M(8) | 1.859(1) | 2.858(2) |
| M(7)–H(2) | 1.7(1) | 1.7(1) |
| M(8)–H(2) | 1.8(1) | 1.9(1) |

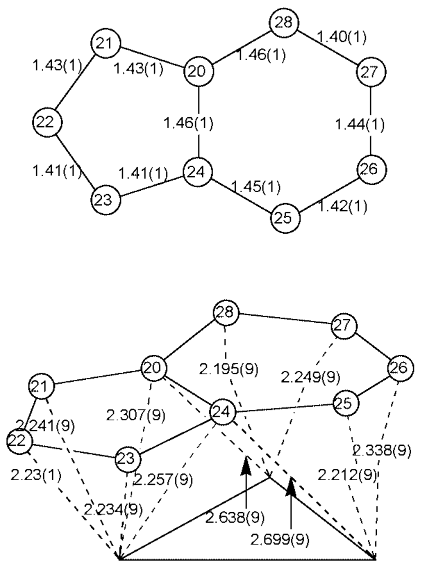

**Fig. 4** Selected structural parameters (Å) for the molecular structure of [$Ru_4H(CO)_9(\mu_3\text{-}\eta^5:\eta^2:\eta^2\text{-}C_{19}H_{17})$] **1** (molecule **B**).

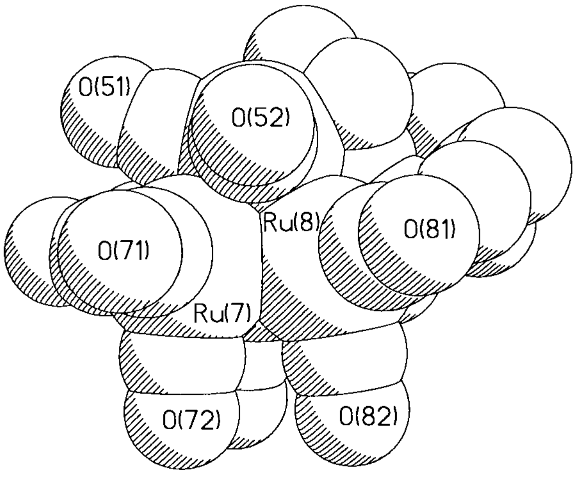

**Fig. 5** The space-filling representation of the molecular structure of compound **1** which shows the vacancy in the ligand sphere that is occupied by a hydride ligand.

C(20c)C(24c)C(25c)} plane meeting the {C(25c)C(26c)C(27c)-C(28c)} and the {C(20c)C(21c)C(22c)C(23c)C(24c)} planes at angles of +12.3 and −3.3°, respectively. This non-planarity effect is also apparent from the angle at which the {C(28c)-C(20c)C(24c)C(25c)} plane lies with respect to the underlying metal triangle (8.1°), which is almost twice that observed in [$Os_4H(CO)_9(\eta^5:\eta^2:\eta^2\text{-}C_{13}H_{15})$].[11] The analysis of the carbon–carbon bond distances is not as revealing as the metal–carbon since no significant pattern can be discerned especially in the light of estimated standard deviations.

It is therefore concluded that a single metal atom, Ru(5), interacts with five cyclopentadienyl carbon atoms, C(20c) through C(24c), at an average distance of 2.254(9) Å in molecule **1B** while two single metal atoms, namely Ru(6) and Ru(8), each interact with a pair of olefinic carbon atoms, C(27c)–C(28c) and C(25c)–C(26c), respectively, at an average distance of 2.249(9) Å. Nine terminal and essentially linear carbonyl ligands occupy the cluster periphery. Finally, the co-ordination sphere is completed by a hydride ligand. This could not be located directly, but a vacancy on the cluster framework at the Ru(7)–Ru(8) edge (see Fig. 5) and the alignment of CO(71) and CO(81) away from that edge (compared to the analogous carbonyl ligands on the Ru(6)–Ru(7) edge) suggest that the hydride resides there. Furthermore, the longest metal–metal bonds in the cluster involve Ru(5) (the metal atom formally richest in electrons) with the exception of the Ru(7)–Ru(8) edge {2.859(1) Å}. This observation is consistent with the edge-lengthening effect of a bridging hydride. Indeed, potential energy calculations (XHYDEX) confirm this prediction.[12] The cluster therefore has a total valence electron count of sixty which, using the PSEPT (polyhedral skeletal electron pair

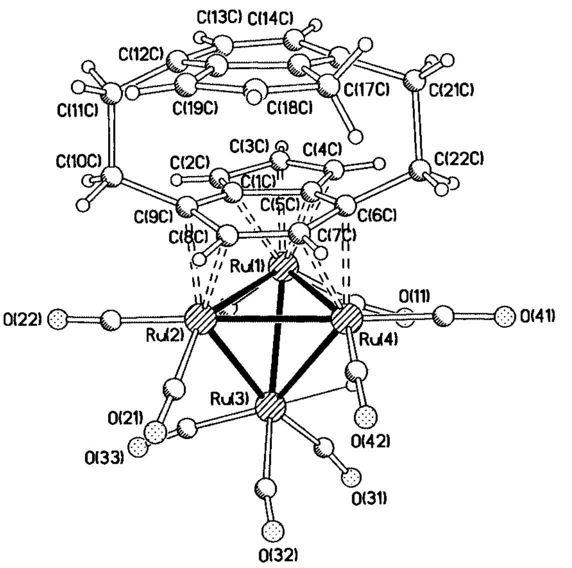

**Fig. 6** The molecular structure of $[Ru_4H(CO)_9(\mu_3\text{-}C_{22}H_{19})]$ **3**.

theory) method of electron counting, is consistent with the observed tetrahedral metal geometry.

The $^1$H NMR spectrum of compound **1** can be divided into four distinct sets of resonances. The protons of the free benzene ring resonate at $\delta$ 7.52 and 6.78 with no coupling observed between them. Presumably the lower field resonance corresponds to the protons H(35c) and H(36c) which are thrust out over the face of the cyclopentadienyl ring and as such are deshielded by ring current to a greater extent than H(32c) and H(33c). The protons of the bound indenyl ring resonate at $\delta$ 5.66 (H22a), 4.48 {H(26c) and H(27c)} and 3.96 {H(21c) and H(23c)}. The triplet at $\delta$ 5.66 and doublet at 3.96 (with coupling constants of $J$ 2.9 Hz) clearly belong to the cyclopentadienyl ring while the singlet at $\delta$ 4.48 is consistent with that observed for a facially bound arene, being some 2.02 ppm upfield of the corresponding resonance of the "free" ligand.[8] It should be noted, however, that the chemical shifts of the protons of the bound rings in the face-capped [2.2]paracyclophane clusters $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$[13] and $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$[14] are $\delta$ 3.76 and 3.40, respectively, which may suggest that the bound six-membered ring in compound **1** is more olefinic and less aromatic in character. The protons of the ethano bridges were observed as broad multiplets in the range $\delta$ 3.26–3.00 and 2.83–2.69. This is because each proton of the ethano bridges is distinct from and couples to its three neighbours. Finally, the hydride ligand was observed at $\delta$ −10.78.

The $^1$H NMR spectrum of compound **2** was similar in appearance to that of **1**. Only minor differences are apparent such as the free ring proton signals of **2** being displaced at least 0.1 ppm further downfield and the bound ring proton signals 0.1 ppm further upfield relative to compound **1**. The hydride is also observed further upfield at $\delta$ −13.67. Such observations are consistent with the spectra of other ruthenium and osmium analogues.[15,16]

The molecular structure of compound **3** is shown in Fig. 6 with alternative views in Fig. 7. Relevant bond distances are shown in Table 4 with the crystal data and measurement details given in the Experimental section. The metal framework in compound **3** again consists of a closed tetrahedron with an indenyl group lying over one triangular face and a hydride ligand bridging the Ru(3)–Ru(4) edge. Owing to structural similarities of compounds **3** and **1**, the cyclophane ligand in **3** was also assigned the $\mu_3$-$\eta^5:\eta^2:\eta^2$ bonding mode despite possessing an even larger ring slippage parameter (of 0.10 Å). It is clear that only one of the condensed faces of the cyclophane ligand in compound **3** is involved in cluster co-ordination and that the cyclopentadiene ring of the second face remains protonated.

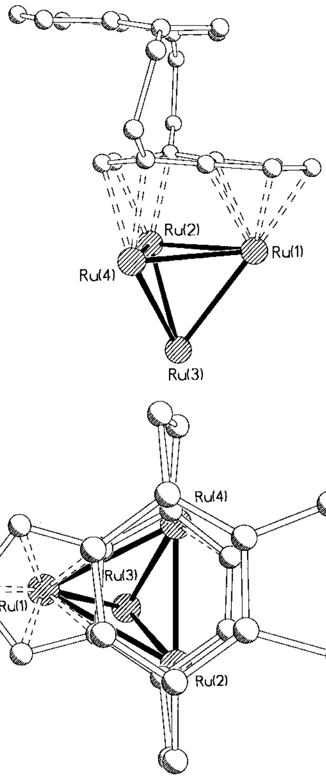

**Fig. 7** Alternative views of the molecular structure of $[Ru_4H(CO)_9(\mu_3\text{-}C_{22}H_{19})]$ **3**.

We believe that this proton was the cause of severe band streaking problems encountered during chromatographic separation. Over the course of development **3** streaks from the baseline. This may be attributable to the transfer of this proton from the cyclopentadiene ring to the silica gel. Thus the compound becomes anionic and binds tightly to the substrate. Surprisingly, the *anti*-[2.2]indenophane ligand in compound **3** does not show any inclination to accept a second cluster unit despite its apparent acidity, nor does it acquire monometallic fragments such as $[Mo(CO)_4]^+$ and $[FeCp]^+$ or even show reactivity toward $FeCl_2 \cdot 2THF$.

Another notable feature of the molecular structure of compound **3** is that the co-ordinated $C_6$ ring of the cyclophane ligand is more distorted than the unco-ordinated. The planes {C(6c)C(7c)C(8c)C(9c)} and {C(9c)C(1c)C(5c)C(6c)} meet each other at 13.9° while {C(12c)C(13c)C(14c)C(15c)} and {C(12c)C(20c)C(16c)C(15c)} meet each other at 11.1° This behaviour has been noted previously in other [2.2]paracyclophane cluster complexes,[17] and is similar to that observed for the cyclophane derivatives **1** and **2**. Finally, the cluster's co-ordination sphere is completed with nine terminal carbonyl ligands.

The satisfactory assignment of the $^1$H NMR spectrum of compound **3** could not be achieved without reference to a correlation (COSY) spectrum (see Figs. 8 and 9 and Table 5). The resonances attributable to the protons of the free indene ring are observed at $\delta$ 7.24 (A), 6.89 (B), 6.70 (C), 6.58 (D) and 3.73–3.61 (H). The COSY spectrum clearly shows that signals {A, B and H} and {C and D} are observed to couple. Signals A and B belong to the olefinic protons {H(19) and H(18)} and H to the methylene protons {H(17a) and H(17b)} of the free cyclopentadiene ring (although H strictly relates to two protons in different environments that are not differentiable).

On the basis of the assignment of protons in free indene, signal A is assigned as the olefinic proton next to the six membered ring and B the nearest to the methylene protons.[18] The signals C and D belong to those protons of the free six membered ring which protrude out over the bound cyclopentadienyl

**Table 4** Important bond distances (Å) in crystalline compound **3**

| | |
|---|---|
| Ru(1)–C(1C) | 2.33(3) |
| Ru(1)–C(2C) | 2.21(3) |
| Ru(1)–C(3C) | 2.24(3) |
| Ru(1)–C(4C) | 2.23(3) |
| Ru(1)–C(5C) | 2.30(3) |
| Ru(2)–C(8C) | 2.21(4) |
| Ru(2)–C(9C) | 2.19(3) |
| Ru(4)–C(6C) | 2.22(3) |
| Ru(4)–C(7C) | 2.33(3) |
| C(1C)–C(2C) | 1.38(4) |
| C(1C)–C(5C) | 1.52(4) |
| C(1C)–C(9C) | 1.37(5) |
| C(2C)–C(3C) | 1.44(4) |
| C(3C)–C(4C) | 1.39(5) |
| C(4C)–C(5C) | 1.49(5) |
| C(5C)–C(6C) | 1.40(4) |
| C(6C)–C(7C) | 1.36(5) |
| C(6C)–C(22C) | 1.54(4) |
| C(7C)–C(8C) | 1.31(5) |
| C(8C)–C(9C) | 1.47(5) |
| C(9C)–C(10C) | 1.52(5) |
| C(10C)–C(11C) | 1.58(5) |
| C(11C)–C(12C) | 1.38(5) |
| C(12C)–C(13C) | 1.33(5) |
| C(12C)–C(20C) | 1.37(5) |
| C(13C)–C(14C) | 1.34(5) |
| C(14C)–C(15C) | 1.45(5) |
| C(15C)–C(16C) | 1.37(5) |
| C(15C)–C(21C) | 1.44(4) |
| C(16C)–C(17C) | 1.45(5) |
| C(16C)–C(20C) | 1.45(5) |
| C(17C)–C(18C) | 1.47(6) |
| C(18C)–C(19C) | 1.44(6) |
| C(19C)–C(20C) | 1.49(6) |
| C(21C)–C(22C) | 1.64(4) |
| Ru(1)–Ru(2) | 2.912(4) |
| Ru(1)–Ru(3) | 2.901(4) |
| Ru(1)–Ru(4) | 2.853(4) |
| Ru(2)–Ru(3) | 2.671(4) |
| Ru(2)–Ru(4) | 2.758(4) |
| Ru(3)–Ru(4) | 2.840(4) |
| Ru(3)–H(1) | 1.7(1) |
| Ru(4)–H(1) | 1.8(1) |

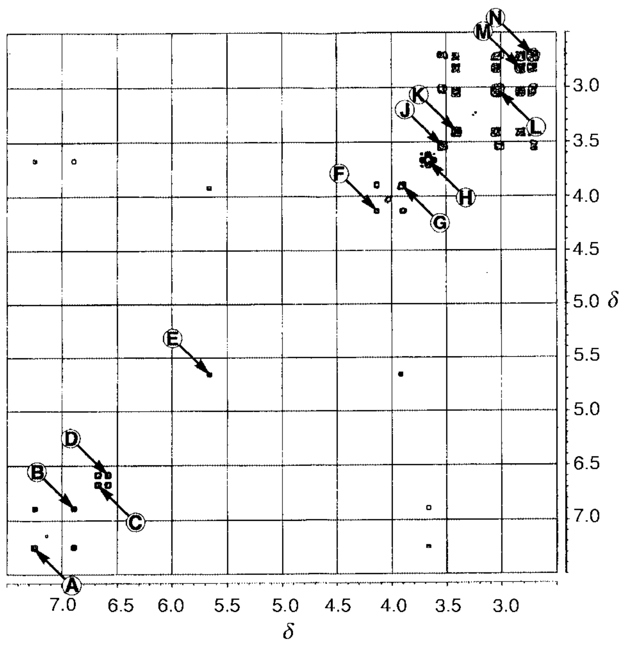

**Fig. 8** The COSY NMR spectrum of $[Ru_4H(CO)_9(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^2\text{-}C_{22}H_{19})]$ **3**. Refer to Fig. 9 and Table 5 for assignments.

**Table 5** The correlation of labels, chemical shifts and atom labels for compound **3**

| Signal | δ | Assignment |
|---|---|---|
| A | 7.24 | H(19) |
| B | 6.89 | H(18) |
| C | 6.70 | H(13) |
| D | 6.58 | H(14) |
| E | 5.66 | H(3) |
| F | 4.14 | H(8) |
| G | 3.92–3.89 | {H(2) and H(4)} and H(7) |
| H | 3.73–3.61 | H(17a) and H(17b) |

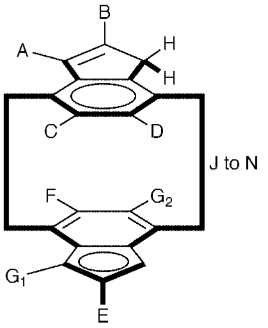

**Fig. 9** The assignment of signals in the COSY NMR spectrum of $[Ru_4H(CO)_9(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^2\text{-}C_{22}H_{19})]$ **3**.

ring. These two protons are in different chemical environments (in contrast to those of the corresponding protons in compounds **1** and **2**) due to the asymmetry of the molecule. Using the same justifications as before, C is assigned as the proton on the opposite side {H(13)} of the molecule from the methylene protons and D as those on the same side {H(14)}.

The signals corresponding to the protons of the bound indenyl moiety are observed at δ 5.66 (E), 4.14 (F) and 3.92–3.89 (G). Signals {E and $G_1$} and {F and $G_2$} are observed to couple with constants *J* 2.6 and 6.8 Hz, respectively. Doublet signals F and $G_2$ belong to the protons of the bound six membered ring and are assigned in the same manner as before, respectively. Triplet signal E {H(3)} and doublet signal $G_1$ {H(2) and H(4)} with integral ratio 1 : 2 clearly belong to the bound cyclopentadienyl ring. It should be noted that the two protons constituting signal $G_1$ are not split as for other pairs of similar environment protons, presumably because of their distance from the asymmetry.

The resonances attributed to the protons of the ethano bridges are observed at δ 3.56–3.51 (J), 3.44–3.39 (K), 3.08–2.99 (L), 2.86–2.80 (M) and 2.67–2.07 (N). Although the signals for these protons cannot be assigned definitively on the basis of the COSY experiment, this spectrum clearly shows that there are two sets of four inter-coupling protons {J, $L_2$, $N_2$ and $N_3$} and (K, $L_1$, M and $N_1$}. Finally the hydride was observed at δ −10.82.

## Conclusion

The reaction of the indenophanes $L^1$ and $L^2$ with $[M_3(CO)_{12}]$ (M = Ru or Os) results in C–H activation of the ligand to give a hydrido-indenyl tetranuclear species. As such, the cluster co-ordinates to the face of the ligand that is richest in π electron density *via* an $\eta^9$-cyclopentadienyl-diene interaction rather than *via* the benzene ring. Despite this predisposition of the indene face, *anti*-[2.2]paraindenophane has also been shown to co-ordinate only to a single cluster unit, even though it possesses two indene rings suitable for cluster co-ordination. This is possibly due to through space deactivation effects.

## Experimental

### Synthesis and characterisation

All syntheses were performed with the exclusion of air using solvents dried by conventional procedures. The compound $[Ru_3(CO)_{12}]$ and the cyclophane ligands were prepared by literature procedures without modification.[5,8–10] Other chemicals were purchased from Sigma-Aldrich Ltd. Infrared spectra were recorded in dichloromethane using NaCl cells (0.5 mm path length) on a Perkin-Elmer 1600 Series FTIR spectrometer, FAB mass spectra on a Kratos MS890 spectrometer in the positive mode using a 3-nitrobenzyl alcohol matrix, $^1H$ NMR spectra on a Bruker DPX-250 FT instrument, using 5 mm 528-PP quartz tubes, and proton–proton COSY NMR spectra on a Bruker DRX-500 FT instrument. Diffraction intensities were collected on a Rigaku AFC7r diffractometer equipped with a graphite monochromator (Mo-Kα radiation, $\lambda = 0.71069$) and an Oxford Cryosystem low temperature device.

### Synthesis of $[Ru_4H(CO)_9(\mu_3\text{-}\eta^5:\eta^2:\eta^2\text{-}C_{19}H_{17})]$ 1

A suspension of $[Ru_3(CO)_{12}]$ (770 mg, 1.2 mmol) in heptane (20 ml) containing [2.2]parabenzoindenophane (98 mg, 400 μmol) was heated to reflux. Heating was discontinued after 4 h and the solvent removed *in vacuo*. The residue was separated into its components by column chromatography using dichloromethane–hexane (1 : 1, v/v) as eluent. The $[Ru_4H(CO)_9(\mu_3\text{-}\eta^5:\eta^2:\eta^2\text{-}C_{19}H_{17})]$ **1** (red, yield: 76 mg, 84 μmol, 21%) was then purified by TLC eluting with the same solvent ratio before characterisation. The syntheses of compounds **2** and **3** were affected in a similar manner using $[Os_3(CO)_{12}]$ (1.09, 1.2 mmol) and $L^1$ (98 mg, 400 μmol) in refluxing nonane (20 ml) over 6 h, and $[Ru_3(CO)_{12}]$ (770 mg, 1.2 mmol) and $L^2$ (114 mg, 400 μmol) in refluxing heptane (20 ml) over 4 h, respectively (**2**: orange, yield: 92 mg, 61 μmol, 16%. **3**: red, yield 73 mg, 78 μmol, 20%).

### Spectroscopic data

**Compound 1.** IR($CH_2Cl_2$): $\tilde{\nu}_{CO}/cm^{-1} = 2060$vs, 2001vs, 1975 (sh) and 1938m. FAB-MS: $m/z = 904$ (calc. 902) with the loss of all nine CO observed; the largest peak was observed at $m/z = 848$ corresponding to the loss of two CO groups. $^1H$ NMR ($CDCl_3$): $\delta$ 7.52 (s, 2 H), 6.78 (s, 2 H), 5.66 (t, $J = 2.9$, 1 H), 4.48 (s, 2 H), 3.96 (d, $J = 2.9$, 2 H), 3.26–3.00 (m, 4 H), 2.83–2.69 (m, 4 H) and −10.78 (s, 1 H).

**Compound 2.** IR($CH_2Cl_2$): $\tilde{\nu}_{CO}/cm^{-1} = 2063$s, 2015s, 1997vs and 1969m. FAB-MS: $m/z = 1260$ (calc. 1259) with the loss of all nine CO observed. $^1H$ NMR ($CDCl_3$): $\delta$ 7.76 (s, 2 H), 6.87 (s, 2 H), 5.54 (t, $J = 2.9$, 1 H), 4.22 (s, 2 H), 4.06 (d, $J = 2.9$ Hz, 2 H), 3.26–3.01 (m, 4 H), 2.74–2.59 (m, 4 H) and −13.67 (s, 1 H).

**Compound 3.** IR($CH_2Cl_2$): $\tilde{\nu}_{CO}$ / $cm^{-1} = 2061$s, 2001s, 1976 (sh), 1937w and 1918w. FAB-MS: $m/z = 943$ (calc. 940) with the loss of all nine CO observed; the largest was observed at $m/z = 887$ corresponding to the loss of two CO groups. $^1H$ NMR ($CDCl_3$): $\delta$ 7.24 (m, 1 H), 6.89 (m, 1 H), 6.70 (d, $J = 3.8$ 1 H), 6.58 (d, $J = 3.8$, 1 H), 5.66 (t, $J = 2.6$, 1 H), 4.14 (d, $J = 2.6$ Hz, 1 H), 3.92–3.89 (m, 3 H), 3.73–3.61 (m, 2 H), 3.56–3.51 (m, 2 H), 3.44–3.39 (m, 1 H), 3.08–2.99 (m, 2 H), 2.86–2.80 (m, 1 H) 2.67–2.07 (m, 3 H) and −10.82 (s, 1 H).

### Crystal structure determinations

**Crystal data.** *Compound 1*. $C_{29}H_{20}Cl_2O_9Ru_4$, $M = 987.63$, monoclinic, space group $P2_1/c$, $a = 19.764(4)$, $b = 14.943(6)$, $c = 20.738(5)$ Å, $\beta = 104.26(2)°$, $V = 5936(3)$ Å$^3$, $Z = 8$, $T = 150(2)$ K, $D_c = 2.210$ g cm$^{-3}$, $\mu = 2.231$ mm$^{-1}$, 12308 reflections measured, refinement on $F^2$ (10116 independent reflections) for 798 parameters; $wR(F^2$, all reflections$) = 0.156$, $R1 = 0.056$, $S = 1.013$; crystal size 0.40 × 0.30 × 0.10 mm, $F(000) = 3808$; $\theta$ range 3.5–25.0°.

*Compound 2*. $C_{29}H_{20}Cl_2O_9Os_4$, $M = 1344.15$, monoclinic, space group $P2_1/c$, $a = 19.704(4)$, $b = 14.900(6)$, $c = 20.990(4)$ Å, $\beta = 104.64(2)°$, $V = 5962(3)$ Å$^3$, $Z = 8$, $T = 150(2)$ K, $D_c = 2.995$ g cm$^{-3}$, $\mu = 17.227$ mm$^{-1}$, 7790 reflections measured, refinement on $F^2$ (7790 independent reflections) for 402 parameters; $wR(F^2$, all reflections$) = 0.212$, $R1 = 0.077$, $S = 1.019$; crystal size 0.10 0.10 × 0.10 mm, $F(000) = 4832$; $\theta$ range 2.5–22.5°.

*Compound 3*. $C_{31}H_{19}O_9Ru_4$, $M = 939.74$, orthorhombic, space group $P2_12_12_1$, $a = 12.650(5)$, $b = 24.045(5)$, $c = 11.864(4)$ Å, $V = 3609(2)$ Å$^3$, $Z = 4$, $T = 150(2)$ K, $D_c = 1.730$ g cm$^{-3}$, $\mu = 1.687$ mm$^{-1}$, 4921 reflections measured, refinement on $F^2$ (3430 independent reflections) for 242 parameters; $wR(F^2$, all reflections$) = 0.269$, $R1 = 0.097$, $S = 1.076$; crystal size 0.20 × 0.10 × 0.08 mm, $F(000) = 1812$; $\theta$ range 3.5–22.5°.

**Solution and refinement.** The computer programs SHELXS 86[19a] and SHELXL 97[19b] were used for structure solution and refinement. Hydrogen atoms were added in calculated positions and refined riding on their respective C atoms. For compound **1**, all non-H atoms were refined anisotropically, with the exception of some of the carbon atoms belonging to the disordered cyclophane ligands, and the atoms on the disordered carbonyl ligand. Owing to the poor quality of crystals of **2** and **3**, only the osmium atoms in crystalline **2**, and the ruthenium atoms and the oxygens in **3** were refined anisotropically.

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