The Preparation, Characterisation and Low-temperature Solid-state Structure of the Dinuclear Complex Ru2(CO)6(μ-η3 : η3-C16H16)

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The new [2.2]paracyclophane (C16H16) complex Ru2(CO)6(μ-η3 : η3-C16H16) has been prepared and characterised by X-ray diffraction methods at 150 K; the aromatic ring bridges the two metals *via* two enyl interactions.

We and others have observed that in metal–arene compounds the η6 bonding mode dominates over all alternative coordination types. Nonetheless other simple bonding modes are known (*e.g.* σ, η2, η3, and η4) in addition to more elaborate bridging configurations (*viz* μ-η2 : η2, μ-η3 : η3, μ-η4 : η4 and μ-η6 : η6).[1] In clusters the face-bridging μ3-η2 : η2 : η2 mode is now common, with a favourable interaction between the hexagonal ring and the metal deltahedron; it has been observed for M3 (M = Co,[2] Rh,[3] Ru,[4] Os[5]), Ru5,[6] and M6 (M = Ru,[5,7] Os[8]) systems. In several ruthenium and osmium clusters face-bridged arenes have been found to undergo migration to a terminal η6 site.[6,9] Such migration can be initiated by thermal, photochemical or chemical influences. We have confirmed that this process occurs by an intramolecular mechanism,[10] and consider that the bonding of the arene in the intermediate involves a μ-η3 : η3 interaction. This provides an attractive model for the established surface chemistry of benzene. We now report the synthesis and full characterisation of a compound that acts as an excellent model for our proposed intermediate.

The diruthenium species Ru2(CO)6(μ-η3 : η3-C16H16) 1 has been prepared in modest yields from the degradation of the trinuclear complex, Ru3(CO)9(μ3-η2 : η2 : η2-C16H16), which bears a triply-bridging paracyclophane fragment, by reaction with 3-molecular equivalents of trimethylamine N-oxide (Me3NO) in dichloromethane. Isolation of the dinuclear product, in approximately 10% yield, is achieved chromatographically on silica eluting with dichloromethane–hexane (1 : 4, v/v). Me3NO has been widely used *in situ* in the presence of an appropriate ligand as a method of oxidatively replacing CO groups by that ligand. In this case, no ligand was present, and removal of CO as CO2 brings about cluster degradation and the formation of the new dinuclear complex as the primary product. Compound 1 has been fully characterised by both spectroscopy† and an X-ray diffraction analysis.‡

The molecular structure of the new diruthenium complex 1 is depicted in Fig. 1. It can be seen that the molecule contains a paracyclophane moiety bridging two metal centres; each ruthenium atom interacting with three carbon atoms of the 'bonded' ring and three CO ligands. An important feature of this structure is the unusual bonding of the ring to the Ru2 dimeric unit. A related bonding mode has been observed on one previous occasion in the compound Rh2(η5-C5H5)2-(μ-η3 : η3-C6H6).[3] These two compounds are strikingly similar in the sense that the η3 : η3 arenes both adopt a boat conformation: the angle between the two enyl planes defined by C(1c)–C(6c)–C(5c) and C(2c)–C(3c)–C(4c) is 56° in Ru2(CO)6(μ-η3 : η3-C16H16), and is of a similar magnitude (53°) in Rh2(η5-C5H5)2(μ-η3 : η3-C6H6). Although the rings in free [2.2]paracyclophane also adopt boat conformations,[11] the angle between the two enyl planes is only 23°, indicating a dramatic change on coordination which is rather unusual for aromatic systems. It would appear from these observations that in order to construct a stable η3 : η3 bond between the organic ring and the two metal atoms, significant deviations from planarity and hence different hybridisation states of the ring C-atoms is essential. In this connection it is also worth pointing out that the mean C–C bond lengths of the enyl sections of the ring, *viz.* C(1c)–C(6c), C(5c)–C(6c), C(2c)–C(3c) and C(3c)–C(4c) are shorter than the C–C bonds linking the two enyl units, *viz.* C(1c)–C(2c) and C(4c)–C(5c) (see Fig. 2). In the free ligand and for the unattached ring in Ru2(CO)6(μ-η3 : η3-C16H16) there is no recognisable pattern of long and short C–C bond lengths, the mean distance for all C–C bonds in the ring being 1.385 and 1.390(11) Å, respectively. In this work the high quality of the low-temperature X-ray data has made it possible to locate the ring hydrogen positions and for the coordinated ring all four hydrogen atoms are observed to bend out of the plane defined by C(1c), C(2c), C(4c) and C(5c) and away from the ruthenium atoms. The mean deviation from the plane is 0.20(8) Å.

The distortions described above for the ring attached to the two ruthenium atoms are not apparent in the unattached ring, or are even reversed. For example, the ring is almost planar.
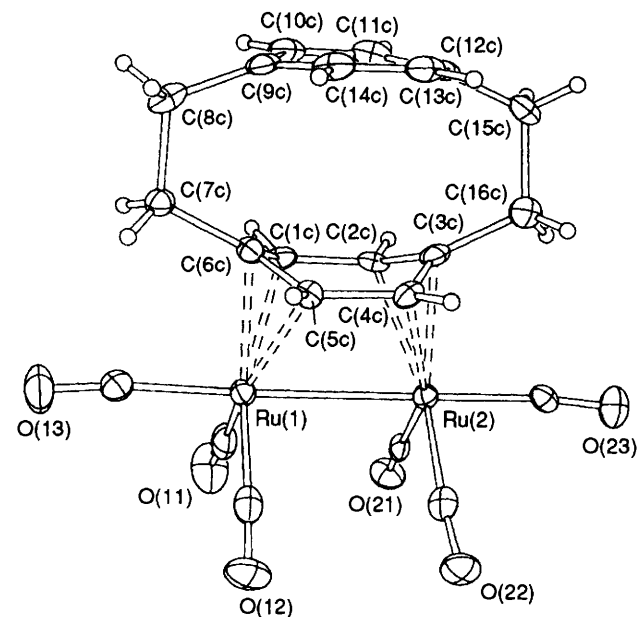
Fig. 1 The molecular structure of Ru2(CO)6(μ-η3 : η3-C16H16) in the solid state. Principal bond parameters (Å): Ru(1)–Ru(2) 2.838(3), mean Ru–C(CO) 1.916, mean C–O(CO) 1.145, Ru(1)–C(1c) 2.264, Ru(1)–C(5c) 2.295(7), Ru(1)–C(6c) 2.191(7), Ru(2)–C(2c) 2.278(7), Ru(2)–C(3c) 2.187(7), Ru(2)–C(4c) 2.253(7). Coordinated ring C–C distances, C(1c)–C(2c) 1.481(10), C(2c)–C(3c) 1.399(10), C(3c)–C(4c) 1.412(10), C(4c)–C(5c) 1.486(10), C(5c)–C(6c) 1.408(10), C(6c)–C(1c) 1.437(10). Uncoordinated ring C–C distances, C(9c)–C(10c) 1.393(11), C(10c)–C(11c) 1.380(12), C(11c)–C(12c) 1.408(11), C(12c)–C(13c) 1.389(11), C(13c)–C(14c) 1.372(11), C(14c)–C(9c) 1.398(11). Linkage C–C distances, C(6c)–C(7c) 1.529(10), C(7c)–C(8c) 1.569(10), C(8c)–C(9c) 1.505(11) C(12c)–C(15c) 1.498(11), C(15c)–C(16c) 1.564(10), C(16c)–C(3c) 1.541(10).
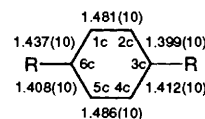
Fig. 2 Plan view of the coordinated ring showing the distribution of bond lengths: C–C bonds within the enyl groups are shorter than those linking the two enyl-units

The angle between the two enyl planes is 18°, less than in the free ligand itself. Also the hydrogen atoms are nearly in the plane defined by C(10c), C(11c), C(13c) and C(14c) [mean deviation = 0.05(8) Å].

However, the interpretation of these various features is not easy: as we have pointed out before,[12] the two rings seem to act in synchrony. The ^1H NMR spectrum of the compound also tends to concur with this hypothesis. In free $C_{16}H_{16}$ a singlet resonance is observed at δ 6.5 for the ring protons. On coordination this degeneracy is lost due to the asymmetry introduced into the molecule, the ring protons affording singlets at δ 3.59 and 7.06 for the attached and unattached rings, respectively. While the change in chemical shift experienced by the coordinated ring is not unexpected, and is in keeping with observations for more simple arenes,§ the signal derived from the unattached ring is not easily reconciled, but has been observed in cluster systems containing the [2.2]paracyclophane ligand.[12,13]

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Footnotes

† *Spectroscopic data* for $Ru_2(CO)_6(\mu-\eta^3:\eta^3-C_{16}H_{16})$: ν_{CO} (CH_2Cl_2) 2060s, 2022vs, 1993s, 1950w (sh); ^1H NMR ($CDCl_3$) δ 7.06 (s, 4H), 3.59 (s, 4H), 2.93 (m, 4H) and 2.56 (m, 4H); MS M^+ = 579 (calc. = 579).

‡ *Crystal data* for $Ru_2(CO)_6(\mu-\eta^3:\eta^3-C_{16}H_{16})$: $C_{22}H_{16}O_6Ru_2$: M = 578.5, monoclinic, space group $P2_1/n$, a = 9.183(10), b = 21.912(10), c = 10.366(10) Å, β = 106.84(10)°, V = 1996(3) Å^3, Z = 4, D_c = 1.925 g cm^{-3}, μ = 1.550 mm^{-1}. Diffraction data were collected on a Stoë Stadi-4 four-circle diffractometer employing graphite-monochromated Mo-Kα X-radiation, ω–2θ scan mode and real time profile fitting (W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22). The crystal used (0.30 × 0.15 × 0.10 mm) was held at 150.0(2) K in the cold stream of an Oxford Cryosystems low-temperature device (J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105): 2605 independent reflections were collected to 2θ_{max} = 45° and corrected for the effects of absorption by means of ψ scans (A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351). Automatic direct methods (G. M. Sheldrick, SHELXS-86, *Acta Crystallogr., Sect. A*, 1990, **46**, 467) identified the positions of the metal atoms and iterative cycles of least-squares refinement (on F^2) and difference Fourier synthesis located the remaining non-hydrogen atoms. All non-H atoms were refined anisotropically; ring H atoms were refined subject only to the constraint that the C–H distances were 0.96(1) Å, those in the –C_2H_4– linkages were included in fixed, calculated positions. Refinement on F^2 (G. M. Sheldrick, SHELX-93, *J. Appl. Crystallogr.*, in the press) against 2563 data led to final convergence with $R1$ [$I > 2\sigma(I)$] = 0.0363, $wR2$ (all data) = 0.1301, S = 1.063 for 296 refined parameters and the final ΔF synthesis showed no peaks above ±0.79 e Å^{-3}.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Informaton for Authors, Issue No. 1.

§ The protons on a face-capping benzene in a variety of different clusters afford singlet resonances in the range δ 4.0–4.5, this value is lower than that observed for terminal benzene ligands.

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