Coordination of an anthracene-derived ligand through eight carbon atoms in the pentaruthenium bow-tie cluster $[Ru_5(CO)_{13}(\mu_5\text{-}\eta^1:\eta^2:\eta^3:\eta^3\text{-}C_{14}H_8\text{-}\eta^1\text{-}PPh)]$

Antony J. Deeming* and Caroline M. Martin

Department of Chemistry, University College London, 20 Gordon Street, London, UK WC1H 0AJ

The new pentaruthenium phenylphosphidoanthracene bow-tie cluster, $[Ru_5(CO)_{13}(\mu_5\text{-}\eta^1:\eta^2:\eta^3:\eta^3\text{-}C_{14}H_8\text{-}\eta^1\text{-}PPh)]$, is prepared from the thermolysis of $[Ru_3(CO)_{12}]$ and (9-anthracyl)diphenylphosphine, the crystal structure of which reveals a unique μ_5-interaction of the ligand with the ruthenium cluster.

Research into the incorporation of aromatic hydrocarbons into clusters has largely been stimulated by their potential to serve as models for chemisorption on a metal surface, and by a wish to modify arene structure and reactivity.[1] Studies of polymetallic–polyaromatic compounds are hindered by the difficulty of introducing the polyaromatic component into the coordination sphere of the metal, and as a result very few complexes have been reported. To our knowledge all past studies on the coordination chemistry of anthracene have centred on mono- and bi-nuclear species and anthracene has been found to exist as the dianion in $[Mg(C_{14}H_{10})(thf)_3]$,[2] or to be coordinated by π-complexation mainly through bis-allylic η^3 interactions, *e.g.* $[Fe_2(CO)_6(\mu\text{-}\eta^3:\eta^3\text{-}C_{14}H_{10})]$ and $[(\eta^5\text{-}C_5Me_5)_2Sm]_2[\mu\text{-}\eta^3:\eta^3\text{-}C_{14}H_{10}]$.[3,4]

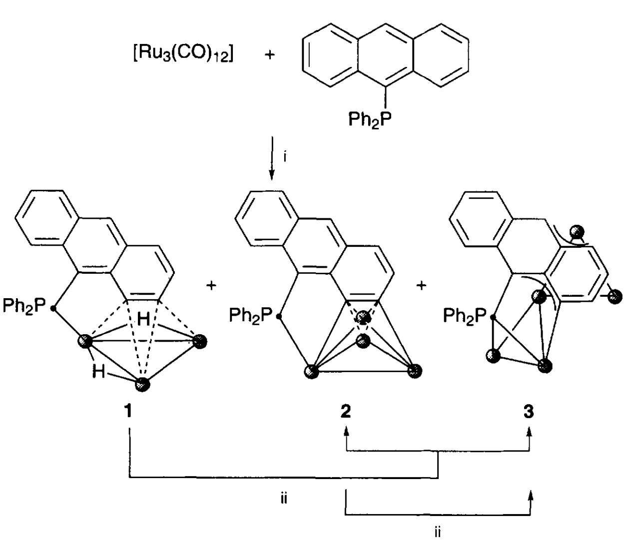
We set out to investigate the interaction of anthracene with transition-metal clusters by introducing the ligand using a well established synthetic route involving degradation of a tertiary phosphine. This communication reports the reaction of $[Ru_3(CO)_{12}]$ with diphenyl(9-anthracyl)phosphine,[5] and the isolation of the pentaruthenium phenylphosphidoanthracene cluster, $[Ru_5(CO)_{13}(\mu_5\text{-}\eta^1:\eta^2:\eta^3:\eta^3\text{-}C_{14}H_8\text{-}\eta^1\text{-}PPh)]$. This complex is unique in that it contains an unprecedented mode of activation for the anthracene moiety, and also, as far as we are aware, represents the first example of a ruthenium cluster adopting a bow-tie configuration.

When a suspension of $[Ru_3(CO)_{12}]$ and a slight excess of diphenyl(9-anthracyl)phosphine in octane is heated to reflux at 125 °C for four hours, several products are obtained in moderate yield which may be readily isolated by TLC.† These products include the yellow trinuclear cluster $[Ru_3(\mu\text{-}H)_2(CO)_8(\mu_3\text{-}C_{14}H_7PPh_2)]$ **1** and the purple tetraruthenium butterfly complex, $[Ru_4(CO)_{11}(\mu_4\text{-}C_{14}H_7PPh_2)]$ **2**; both anthracyne complexes being derived *via* double metallation of one of the unsubstituted rings, and also the dark purple pentaruthenium bow-tie cluster, $[Ru_5(CO)_{13}(\mu_5\text{-}\eta^1:\eta^2:\eta^3:\eta^3\text{-}C_{14}H_8\text{-}\eta^1\text{-}PPh)]$ **3** (see Scheme 1). Furthermore, treatment of the trinuclear species **1** with 1 molecular equivalent of $[Ru_3(CO)_{12}]$ under thermal conditions (refluxing octane) results in cluster build-up with the formation of the tetra- and penta-ruthenium species **2** and **3**. Likewise, the thermolysis of **2** with $[Ru_3(CO)_{12}]$ also leads to **3**.

Compounds **1** and **2** have been identified from spectroscopic data‡ and by comparisons with the naphthyl analogues for which the molecular structures have been determined by X-ray crystallography.[6] Compound **3**, an air-stable, black crystalline solid, has also been fully characterised by spectroscopy‡ and its molecular structure determined by single-crystal X-ray diffraction (see Fig. 1).§

Complex **3** consists of two triangular Ru_3 groupings which share the central metal atom Ru(1), a bow-tie arrangement previously observed in several osmium clusters including the binary carbonyl $[Os_5(CO)_{19}]$.[7] The Ru–Ru bond lengths range from 2.768(1) to 3.068(1) Å, the shortest [Ru(4)–Ru(5)] carrying a symmetrical edge-bridging carbonyl ligand. The remaining twelve carbonyls are terminal and essentially linear. The anthracene unit may be regarded as consisting of an isolated C=C double bond at one end [C(4a)–C(5a)] coordinated to Ru(5), two allyl groups [C(1a)–C(2a)–C(3a) and C(6a)–C(7a)–C(8a)] coordinated to Ru(1) and Ru(4) respectively, and a benzene ring at the other end [C(9a)–C(14a)] which does not coordinate to the metal framework. The anthracene system therefore interacts with the Ru(1)Ru(4)Ru(5) triangle in a μ_3-$\eta^2:\eta^3:\eta^3$ manner. C–H bond activation results in a σ interaction between C(3a) and one of the metal atoms from the second triangular unit, Ru(2). Ru(2) is also bound to phosphorus, which having lost a phenyl group, probably as benzene, forms a three-electron donating phosphido bridge between Ru(2) and Ru(3). The ligand as a whole therefore donates twelve electrons to the cluster framework which, together with the thirteen carbonyl ligands, gives the cluster an electron count of 78, the number required for an electron-precise bow-tie cluster.

The two triangular Ru_3 units are not coplanar, but are skewed with respect to each other so that the dihedral angle between the Ru(1)Ru(2)Ru(3) and Ru(1)Ru(4)Ru(5) planes is 38.9°. This twisting between the two planes is common in bow-tie structures, *cf.* 21.2 and 24.8° in $[Os_5(CO)_{19}]$ and $\{Os_5(CO)_{16}\}P(OMe)_3]_3)$, respectively,[7] and the larger angle found in **3** is presumably a consequence of the steric constraints imposed on Ru(2) from the σ interaction with C(3a) of the anthracene moiety. Atom Ru(2) lies 1.579 Å above the Ru(1)Ru(4)Ru(5) plane and almost in the plane of the anthracene, while Ru(3) almost sits in the Ru(1)Ru(4)Ru(5) plane. Thus there are two



Scheme 1 Products from the thermolysis of $[Ru_3(CO)_{12}]$ with $PPh_2C_{14}H_9$. *Reagents and conditions*; i, heat, octane; ii, heat, octane, 1 mol. equiv. $[Ru_3(CO)_{12}]$.

parallel sheets of atoms: Ru(2), C(1a)–C(14a) and Ru(1), Ru(3), Ru(4), Ru(5) and one could envisage larger molecules in which these parallel sheets of carbon and metal atoms are extended [see Fig. 2(*a*)]. Fig. 2(*b*) shows a similar situation in the compound $[Ru_5(CO)_{13}(C_6H_4)(PPh)]$, reported by Knox *et al.*,[8] where just one C_6 ring is bound to the metal framework. The Ru(2)–C(3a) bond, together with the P(1)–C(1a) bond, also account for the significant differences between the two allylic interactions; the Ru(1)–C bond lengths are shorter than the corresponding Ru(4)–C distances, and the Ru(1)–C(3a) π interaction [2.177(8) Å] is comparable to a σ bond [*cf.* Ru(2)–C(3a) 2.121(9) Å]. There is some difference in C–C bond length between the coordinated and the uncoordinated sections of the anthracene moiety (mean 1.43 *vs.* 1.40 Å) which is consistent with the donation of π-electron density to the cluster, and this loss of aromaticity is also apparent from the slight buckling of the anthracene across the C(3a)–C(6a) and C(2a)–C(7a) axes (162.4 and 169.2°, respectively).

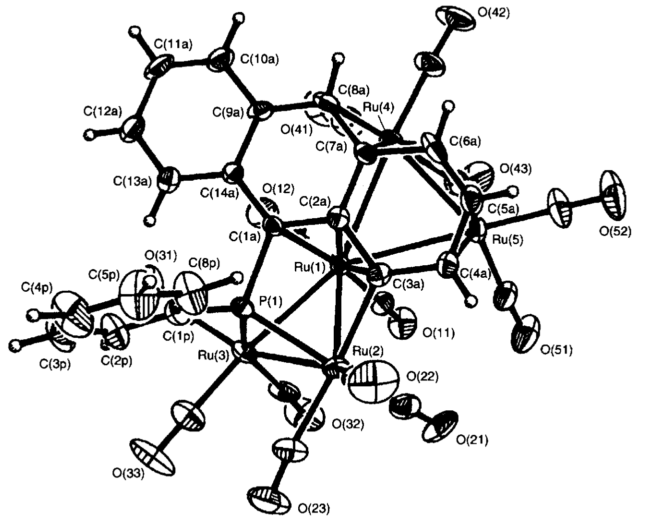
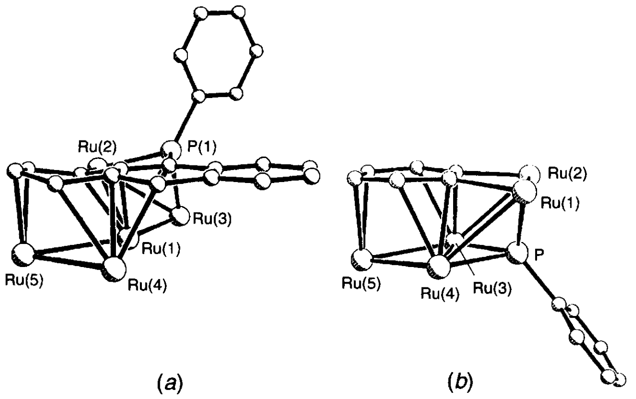


Fig. 1 Molecular structure of $[Ru_5(CO)_{13}(\mu_5\text{-}\eta^1:\eta^2:\eta^3:\eta^3\text{-}C_{14}H_8\text{-}\eta^1\text{-}PPh)]$ **3**, showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Relevant bond distances (Å) and angles (°) are: Ru(1)–Ru(2) 2.837(1), Ru(1)–Ru(3) 2.823(1), Ru(1)–Ru(4) 2.963(1), Ru(1)–Ru(5) 3.068(1), Ru(2)–Ru(3) 2.863(1), Ru(4)–Ru(5) 2.768(1), Ru(2)–P(1) 2.305(2), Ru(3)–P(1) 2.284(2), Ru(1)–C(1a) 2.363(8), Ru(1)–C(2a) 2.205(8), Ru(1)–C(3a) 2.177(8), Ru(2)–C(3a) 2.121(9), Ru(4)–C(6a) 2.50(1), Ru(4)–C(7a) 2.276(8), Ru(4)–C(8a) 2.358(9), Ru(5)–C(4a) 2.301(9), Ru(5)–C(5a) 2.26(1), P(1)–C(1a) 1.815(8), P(1)–C(1p) 1.799(9), C(1a)–C(2a) 1.40(1), C(1a)–C(14a) 1.45(1), C(2a)–C(3a) 1.44(1), C(2a)–C(7a) 1.46(1), C(3a)–C(4a) 1.49(1), C(4a)–C(5a) 1.41(1), C(5a)–C(6a) 1.40(2), C(6a)–C(7a) 1.43(1), C(7a)–C(8a) 1.41(1), C(8a)–C(9a) 1.43(1), C(9a)–C(10a) 1.41(1), C(9a)–C(14a) 1.42(1), C(10a)–C(11a) 1.34(2), C(11a)–C(12a) 1.42(2), C(12a)–C(13a) 1.39(1), C(13a)–C(14a) 1.40(1), Ru(4)–C(43) 2.05(1), Ru(5)–C(43) 2.06(1). Dihedral angles (°): Ru(1)Ru(2)Ru(3)–Ru(1)Ru(4)Ru(5) 38.9, C(3a)(C4a)-C(5a)C(6a)–C(2a)C(3a)C(6a)C(7a) 162.4, C(2a)C(3a)C(6a)C(7a)–C(1a)-C(2a)C(7a)C(8a) 169.2.



(*a*) (*b*)

Fig. 2 Molecular structure (*a*) of $[Ru_5(CO)_{13}(C_{14}H_8PPh)]$ **3**, showing the two parallel sheets of atoms Ru(2), C(1a)–C(14a) and Ru(1), Ru(3), Ru(4), Ru(5) (CO ligands and H atoms are omitted for clarity). The similarity with the structure of the reported compound $[Ru_5(CO)_{13}(C_6H_4)(PPh)]$ (*b*) is apparent.

The characterisation of further products from this reaction are currently in hand which may shed light on the mechanisms involved in the formation of such complexes.

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Footnotes

† *Experimental*: a solution of $[Ru_3(CO)_{12}]$ (100 mg, 0.157 mmol) and $PPh_2(C_{14}H_9)$ (60 mg, 0.166 mmol) in octane (30 ml) was heated to reflux for 4 h. The solvent was removed *in vacuo* and the mixture separated by TLC using a solution of dichloromethane–hexane (3 : 7) as eluent. Several bands were isolated and characterised in order of elution as unreacted starting material $[Ru_3(CO)_{12}]$ (5%), $[Ru_3(\mu\text{-}H)_2(CO)_8(\mu_3\text{-}C_{14}H_7PPh_2)]$ **1** (30%), $[Ru_4(CO)_9(\mu_4\text{-}C_{14}H_7PPh_2)]$ **2** (15%) and $[Ru_5(CO)_{13}(\mu_5\text{-}\eta^1:\eta^2:\eta^3:\eta^3\text{-}C_{14}H_8\text{-}\eta^1\text{-}PPh)]$ **3** (5%). Several other minor products are currently under investigation.

‡ *Spectroscopic data* for **1**: IR (cyclohexane) ν_{CO} 2081s, 2049vs, 2037m, 2010vs, 2003m, 1991w, 1984sh cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.51 (d, 1 H), 8.16 (d, 1 H), 7.95 (d, 1 H), 7.92 (d, 1 H), 7.90 (dd, 1 H), 7.53 (dd, 1 H), 7.43 (dd, 1 H), 7.51–7.17 (m, 10 H), −15.98 (dd, 1 H), −19.44 (dd, 1 H); positive FAB MS, M^+ obs. 889 (calc. 890).

For **2**: IR (cyclohexane) ν_{CO} 2079m, 2058s, 2044w, 2035w, 2025s, 2014vs, 1993m, 1961w (br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.34 (d, 1 H), 8.07 (d, 1 H), 8.04 (d, 1 H), 7.57 (m, 4 H), 7.47 (d, 1 H), 7.44 (m, 6 H), 7.42 (d, 1 H), 7.24 (ddd, 1 H), 6.71 (dd, 1 H); positive FAB MS, M^+ obs. 1074 (calc. 1073).

For **3**: IR (cyclohexane) ν_{CO} 2084m, 2057vs, 2042m, 2027vs, 2014s, 1994m, 1984w, 1974w, 1870w (br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.53 (m, 2 H^{Ph}), 7.46 (d, 1 $H^{10/13}$), 7.43 (m, 3 H^{Ph}), 7.36 (d, 1 $H^{10/13}$), 7.14 (t, 1 $H^{11/12}$), 7.07 (d, 1 H^4), 6.89 (t, 1 $H^{11/12}$), 5.60 (t, 1 H^5), 5.58 (s, 1 H^8), 2.51 (d, 1 H^6); positive FAB MS, M^+ obs. 1154 (calc. 1154); found (calc.), C 34.22 (34.35), H 1.20 (1.14)%.

§ *Crystal data* for $[Ru_5(CO)_{13}(\mu_5\text{-}\eta^1:\eta^2:\eta^3:\eta^3\text{-}C_{14}H_8\text{-}\eta^1\text{-}PPh)]$ **3**: dark red–black crystal, $C_{36.5}H_{17}O_{13}PRu_5$ (including 0.5 molecule of toluene solvent), 0.48 × 0.40 × 0.18 mm^3, M = 1199.85, monoclinic, space group $P2_1/n$, $a = 11.763(2)$, $b = 16.157(5)$, $c = 19.107(5)$ Å, $\beta = 98.38(2)°$, $U = 3593(2)$ Å^3, $Z = 4$, $D_c = 2.22$ g cm^{-3}, $\lambda = 0.71073$ Å, μ(Mo-Kα) = 21.26 cm^{-1}, $F(000) = 2300$. Nicolet R3v/m diffractometer, direct methods (SHELXTL-PLUS), 5128 unique absorption-corrected data in the range $5 \leqslant 2\theta \leqslant 50°$ and with $I_o \geqslant 3\sigma(I_o)$ used in the refinement, 470 parameters (all non-H atoms anisotropic), final $R = 0.0470$ and $R_w = 0.0543$, with $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ and $w = 1/[\sigma^2(F_o) + 0.00063\ F_o^2]$.. H-atoms added in calculated positions (C–H 0.96 Å) riding on the respective C atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre. See Information for Authors, Issue No. 1.

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