π-Coordination of *ortho*-Benzoquinone: Synthesis and Structure of $[\{Ru_2(\eta^4\text{-}\mu_2\text{-}o\text{-}C_6H_4O_2)(CO)_4(AsPh_3)\}_2]$ and $[Ru_2(\eta^4\text{-}\mu_2\text{-}o\text{-}C_6H_4O_2)(CO)_4(\mu_2\text{-}I)I]$

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The coordination polymer prepared by treating $[Ru_3(CO)_{12}]$ with catechol can be cleaved with either a Lewis base or iodine to give products containing η^4-*ortho*-benzoquinone ligands, two of which, $[\{Ru_2(\eta^4\text{-}\mu_2\text{-}o\text{-}C_6H_4O_2)(CO)_4(AsPh_3)\}_2]$ and $[Ru_2(\eta^4\text{-}\mu_2\text{-}o\text{-}C_6H_4O_2)(CO)_4(\mu_2\text{-}I)I]$ are structurally characterized by X-ray diffraction.

The dioxolenes *ortho*- and *para*-benzoquinone are recognised as having markedly different π-coordination chemistries; although *para*-benzoquinones commonly form 1,4-diene complexes as in A,[1] the η^4-coordination of an *ortho*-benzoquinone as a 1,3-diene, **B** has not been reported.[2,3] Typically *ortho*-quinones bind as an η^2-chelate to transition metals, and the formal description of the amphoteric metal–quinone interaction is in terms of the quinone, semiquinone, or catecholate contributions **C–E**.[4,5] In the course of our related studies to examine the oxidative-addition chemistry of simple oxygen-containing substrates such as carboxylic and phosphinic acids,[6] formyl ylides,[7] aldehydes[8] and phenol[9] to metallo-carbonyl clusters we have observed that $[Ru_3(CO)_{12}]$ and catechol condense in *o*-xylene under reflux to form an insoluble precipitate (Scheme 1). This paper reports (*i*) the preparation and characterization of this unusual coordination polymer, (*ii*) its fragmentation reactions with Lewis bases and iodine, and (*iii*) the structural characterization of these derivatives, which contain the first examples of η^4-π-coordinated *ortho*-benzoquinone.

When $[Ru_3(CO)_{12}]$ and an excess of catechol are heated to relux in *o*-xylene an air-stable, yellow–orange microcrystalline precipitate forms in 94% yield, Scheme 1. The elemental analyses,† IR spectra,‡ fragmentation reactions and insolubility of this product are consistent with the oligomeric formula $[\{Ru_2(C_6H_4O_2)(CO)_4\}_n]$, **1**. Unlike the previously known catecholate bridged dimer $[\{Ru(\mu_2\text{-}o\text{-}O_2C_6Cl_4)(CO)_2(PPh_3)\}_2]$,[10] which is readily cleaved by a wide variety of Lewis bases, L, to return the mononuclear complexes $[Ru(\eta^2\text{-}o\text{-}O_2C_6Cl_4)(CO)_2(PPh_3)L^n]$, (L = PPh_3, $AsPh_3$, $P(OPh)_3$, pyridine; $n = 0$; Cl^-, Br^-, and I^-, $n = -1$), the fragmentation

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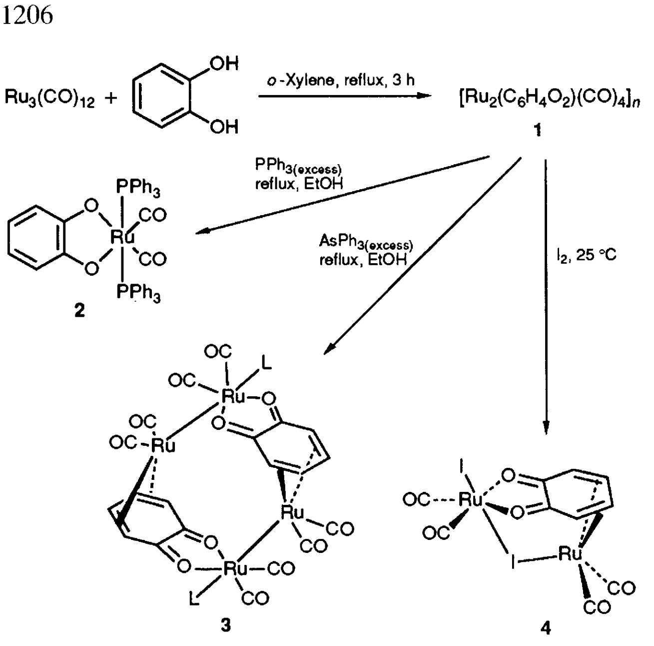
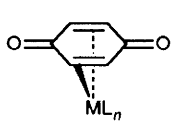
† Satisfactory elemental analyses for C and H have been obtained for all new compounds **1–4**.

‡ *Selected IR spectroscopic data*: (KBr, ν/cm^{-1}) all bands strong unless otherwise noted: **1** 2051, 2006, 1965, 1956, 1336, 1322, 1252; **2** 2029, 1965, 1257; **3** 2049w, 2025m, 2013, 1981, 1929, 1921, 1351m, 1334, 1305w; **4** 2089w, 2080m, 2056, 2025, 1991, 1505, 1329w.

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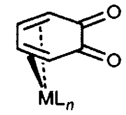
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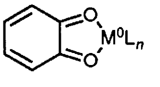
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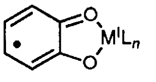
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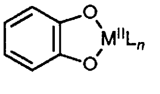
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of **1** depends markedly upon the base. For example, treating **1** with an excess of triphenylphosphine returns a modest yield of the mononuclear η^2-*o*-$O_2C_6H_4$ containing complex $[Ru(\eta^2\text{-}o\text{-}O_2C_6H_4)(CO)_2(PPh_3)_2]$, **2** while an excess of triphenylarsine results in a high conversion to the tetranuclear complex $[\{Ru_2(\eta^4\text{-}\mu_2\text{-}o\text{-}C_6H_4O_2)(CO)_4AsPh_3)\}_2]$, **3**, which contains a π-bound bridging *ortho*-benzoquinone ligand. Mild oxidants also fragment **1**, and a dinuclear derivative, $[Ru_2(\eta^4\text{-}\mu_2\text{-}o\text{-}C_6H_4O_2)(CO)_4(\mu_2\text{-}I)I]$, **4** is derived in 95% yield by treating **1** with a slight excess of iodine at room temperature.

The structures of **2**–**4** have been determined by X-ray crystallography,§ ORTEP views of **3** and **4** are depicted in Figs. 1 and 2. Important trends in the metrical data include: (*i*) a skewing of the metal away from the α-dicarbonyl fragment towards the 1,3-diene subunit of the *ortho*-benzoquinone in both π-bound structures **3** and **4**; (*ii*) intermediate C–O bond lengths for the π-bound *ortho*-quinone species in **3** and **4** compared with the correspondingly long {*d*(C–O) = 1.347(4) Å} catecholate-like bond lengths in **2**; (*iii*) the planarity of the $C_6H_4O_2$ ligand and the metal in structures **2** and **3**, but not in **4** where there is a dihedral angle of 156° between the planes defined by the *ortho*-quinone ligand and the $\{Ru(CO)_2\}$ fragment in both independent molecules **A** and **B** in the unit cell.

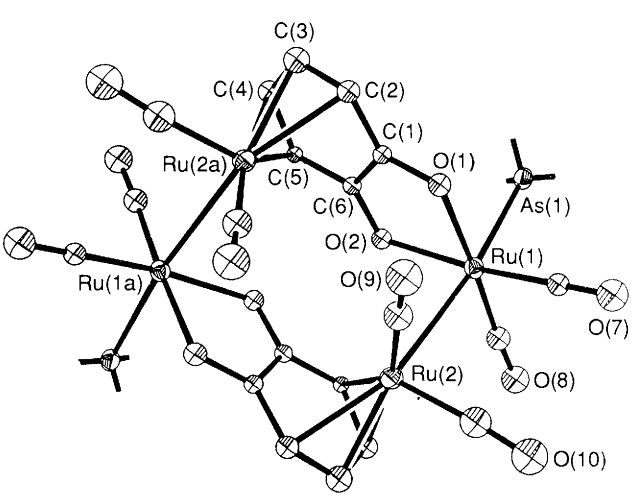

Fig. 1 Molecular structure of **3**. Hydrogen atoms and phenyl rings of triphenylarsine ligands omitted for clarity, selected bond lengths (Å): Ru(2)···C(1) 2.577(14); Ru(2a)–C(2) 2.321(14); Ru(2a)–C(3) 2.235(15); Ru(2a)–C(4) 2.259(15); Ru(2a)–C(5) 2.356(14); Ru(2a)···C(6) 2.583(4); C(1)–O(1) 1.303(18); C(6)–O(2) 1.302(17); Ru(1)–O(1) 2.114(10); Ru(1)–O(2) 2.106(10); Ru(1)–Ru(2) 2.821(2); Ru(1)–As(1) 2.495(2).

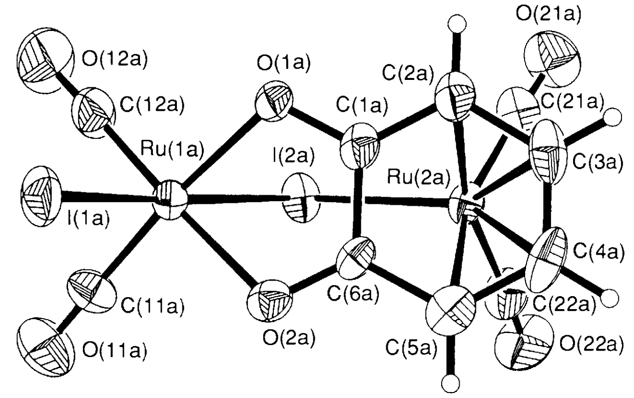

Fig. 2 Molecular structures for molecule A, one of the two independent molecules in the unit cell of **4**. Views perpendicular to *ortho*-benzoquinone plane. Average bond lengths (Å) for molecule A and B: Ru(2)···C(1) 2.458(9); Ru(2)–C(2) 2.294(9); Ru(2)–C(3) 2.205(12); Ru(2)–C(4) 2.225(11); Ru(2)–C(5) 2.314(9); Ru(2)···C(6) 2.480(8); C(1)–O(1) 1.284(12); C(6)–O(2) 1.270(12); Ru(1)–O(1) 2.100(5); Ru(1)–O(2) 2.101(6); Ru(1)–I(1) 2.665(1); Ru(1)–I(2) 2.774(1); Ru(2)–I(2) 2.723(1).

Two other π-bound η^n-complexes containing the $C_6H_4O_2$ fragment have recently been described. In $[Pd_4(\eta^3\text{-}\mu_2\text{-}o\text{-}O_2C_6H_4)_4]$[11] a semiquinone binds as an η^3-allyl anion, which has markedly different C–O bond lengths, consistent with the structure **D**. In $[(Pr^i{}_2PCH_2)_2Rh\{(\eta^6\text{-}C_6H_4O_2)B(O_2C_6H_4)\}]$[12] the dicatecholborate anion has a single η^6-π-bound $C_6H_4O_2$ substituent with relatively long C–O and Rh–C bond distances

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§ *Crystal data* for **3** (from CH_2Cl_2–ethanol): $C_{56}H_{38}As_2O_{12}Ru_4$, M = 1457.0, orthorhombic space group *Pbcn*, a = 16.412(3), b = 20.624(3), c = 15.483(3) Å, U = 5240.7(16) Å^3, Z = 4, D_c = 1.847 g cm^{-3}, μ(Mo-*K*α) = 2.421 mm^{-1}, $F(000)$ = 2848, T = 173 K. Anisotropic refinement of the heavy atoms Ru and As, and isotropic refinement of all other non-hydrogen atoms (Hs fixed; 164 variables) using 1636 reflections with $F > \sigma(F)$, from 4654 unique data collected on a Siemens R3m/V diffractometer by the ω scan method ($4.0 < 2\theta < 50.0$), gave R = 0.048, R_w = 0.045.

For **4** (from CH_2Cl_2–ethanol): $C_{10}H_4I_2O_6Ru_2\cdot\frac{1}{2}CH_2Cl_2$, M = 761.02, triclinic space group $P\bar{1}$, a = 10.222(2), b = 12.418(2), c = 14.621(2) Å, α = 107.970(10), β = 102.590(10), γ = 93.870(10)°, U = 1704.7(5) Å^3, Z = 2, D_c = 2.800 g cm^{-3}, μ(Mo-*K*α) = 5.503 mm^{-1}, $F(000)$ = 1308, T = 296 K. Anisotropic refinement for all non-hydrogen atoms (Hs fixed; 388 variables) using 3946 reflections with $F > 6\sigma(F)$, from 5380 unique data collected by the ω-scan method ($4.0 < 2\theta < 48.0$), gave R = 0.033, R_w = 0.042.

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

throughout. Taken together these structural results illustrate that each formal electronic description of *ortho*-benzoquinone complexes, **C–E**, can π-bond to a transition metal in a unique manner. Significantly, each example above has the two oxygens involved in a five-membered chelate ring. Reported attempts to prepare a purely π-bound complex such as in **A** have failed.[2,3]

Dioxolene-bridged polymers are of interest as redox active materials; two examples that contain μ_2-O bound *para*-benzoquinones have been recently reported.[13,14] The polymer **1** is unusual in that it contains an *ortho*-benzoquinone bridging group. Furthermore, based on the fragmentation reactions and the number and intensity of the terminal ν(C–O) bands in the IR spectra of **1**,[15] we propose that the *ortho*-benzoquinone ligands bridge $[(OC)_2Ru–Ru(CO)_2]$ metal–metal bonded units by chelating to one ruthenium and π-bonding to the other. A second dimension may be added to this chain by the μ_2-coordination of a chelating benzoquinone oxygen. Powder diffraction experiments are currently underway to confirm this proposed unit-cell constitution.

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