Inorg. Chem. **1993**, *32*, 4173–4174

Structural and Reactivity Patterns in π-Complexes of *o*-Benzoquinone

D. Scott Bohle,[*,†] **A. Nørlund Christensen,**[‡] **and Patricia A. Goodson**[†]

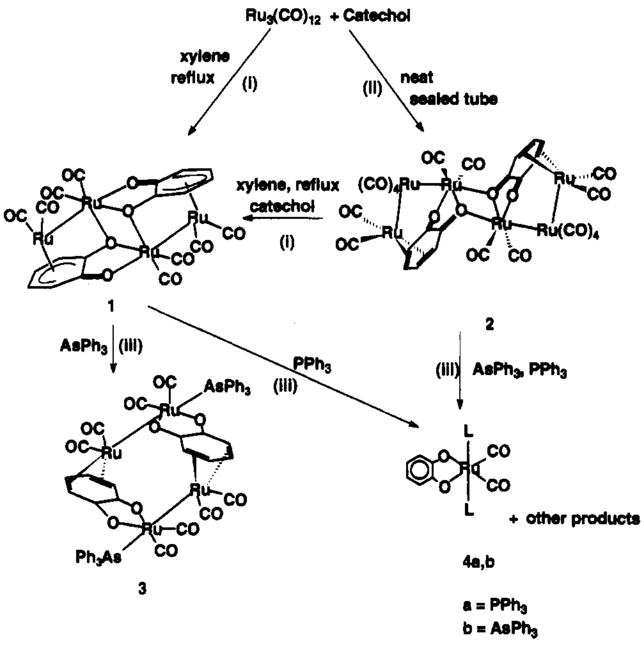
Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838, and Chemistry Department, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark

Received May 18, 1993

The recent isolation of π-complexes containing η^3-semi-*o*-benzoquinone,[1] η^4-*o*-benzoquinone,[2] and η^6-catecholate[3] fragments augments the extensive π-coordination chemistry of η^4-*p*-benzoquinones.[4] Although our structural understanding of π-bound metalloquinones is now well developed, information concerning the reactivity and electronic structures of π-bound *o*- and *p*-quinones is limited.[5] The recognition of metalloquinone π-interactions in the copper containing metalloquinoid proteins[6] galactose oxidase[7] and the amine oxidases,[8] which contain tyrosyl-(4-thioether)[9] and topaquinone[10] residues, respectively, suggest that the metal–quinoid cofactor π-interaction may be rather common[6a] and critical to enzymatic turnover.[11] When contrasted with the detailed understanding of the electronic structure of the η^3-O-chelate bound quinoids,[5a,12] there is a conspicuous lack of experimental and theoretical data for the π-bound complexes. This paper concerns one end of the scale of possible metalloquinone π-interactions, that characterized by strong back-bonding to the quinone and relatively short metal-carbon bonds.

Depending upon the specific conditions employed, Scheme I, the oxidative addition of catechol to triruthenium dodecacarbonyl yields either $\{Ru_2(\eta^2,\mu_2,\eta^n\text{-}O_2C_6H_4)(CO)_4\}_2$ (**1**), which precipitates in high yield as an air-stable pale yellow microcrystalline insoluble diamagnetic solid, or the dimeric edge opened complex $\{Ru_3(\eta^2,\mu_2,\eta^n\text{-}O_2C_6H_4)(CO)_8\}_2$ (**2**). It is possible to convert **2** in high yield to **1** by treating it with additional catechol under the conditions (i) in Scheme I. The insolubility of **1** in organic solvents and the microcrystallinity of this preparation led to its initial characterization by powder diffraction techniques.[13] The unit cell for this product is identical to that determined subsequently for a product of a lower temperature preparation, which gave crystals suitable for single-crystal X-ray diffraction.[16]

Scheme I[a]



[a] Conditions: (i) xylene, reflux, 3 h; (ii) neat catechol, sealed tube, 157 °C, 16 h; (iii) ethanol, reflux, 2 h.

Although the π-*o*-benzoquinone ligands in **1** and **2** are in comparable environments in that they are both π-bound to a $Ru(CO)_2$ fragment and are involved in η^2-O chelate ring formation to a second as well as bridging to a third ruthenium, there are notable differences in the two structures. In the structure of **1**, Figure 1, there is a significant difference in the two quinone C–O bond lengths for the bridging [C(1)–O(1) = 1.351(3) Å] and nonbridging [C(6)–O(2) = 1.292(3) Å] oxygens,[17] while in the structure of **2**, Figure 2,[18] the corresponding C–O bond lengths are not significantly different. The ruthenium–carbon bond lengths also indicate that ring slippage in the two structures differ in that in **1** there is a single long Ru–C bond length,

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[†] University of Wyoming.

[‡] Aarhus University.

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(9) Derived from the covalent linkage of the cysteinyl sulfur in cys 228 to the four position of the phenyl ring in tyr 272.[7]

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(13) Crystal data for **1**: The X-ray powder pattern of $[Ru_2(O_2C_6H_4)(CO)_4]_2$ was recorded on a Nonius Guinier camera at 25 °C with Si (a = 5.43050 Å) as an internal standard and Cu Kα_1 radiation (λ = 1.540 598 Å). The position of the diffraction lines were measured on a photometer, and the powder pattern was indexed using the program FZON,[14] with a triclinic cell a = 6.584 Å, b = 8.809 Å, c = 10.717 Å, α = 99.31°, β = 105.64°, γ = 110.71°, and $M(20)$ = 16.4 (the figure of merit). From the indexed powder pattern the unit cell parameters were refined by a least squares procedure using the program CELLKANT.[15] The values obtained in the refinements were a = 6.584(2) Å, b = 8.810(2) Å, c = 10.726(3) Å, α = 99.31(2)°, β = 105.65(2)°, and γ = 108.65(2)° using 52 lines of the pattern.

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(16) A sample suitable for single-crystal X-ray diffraction was obtained by treating 30 mg of $Ru_3(CO)_{12}$ with a 20-fold excess of catechol in 10 mL of *o*-xylene at 127 °C for 46 h. Single-crystal diffraction data for **1**: $[C_{10}H_4O_6Ru_2]_2$, M = 422.3, triclinic group $P\bar{1}$, a = 6.585(2) Å, b = 8.813(2) Å, c = 10.416(2) Å, α = 99.31(3)°, β = 105.65(3)°, γ = 108.92(3)°, V = 529.7(2) Å^3, Z = 1, D_c = 2.648 g cm^{-3}, μ(Mo Kα) = 2.867 mm^{-1}, $F(000)$ = 400, T = 295 K. Anisotropic refinement for all non-hydrogen atoms (H's fixed; 179 variables) using 2503 reflections with $F > 6\sigma(F)$, from 3097 unique data collected on a Siemens R3m/V diffractometer by the Wyckoff scan method ($4.0 \leq 2\theta \leq 60.0$), gave R = 0.021 and R_w = 0.029.

(17) For comparison the carbon–oxygen bond lengths in the η^3-containing semibenzoquinone complex $Pd_2\{Pd(\eta^2\text{-}\eta^3\text{-}(DBSQ)\}$ (DBSQ = 3,5-*tert*-butyl-1,2-benzosemiquinone) are 1.280(17) and 1.354(17) Å.[1]

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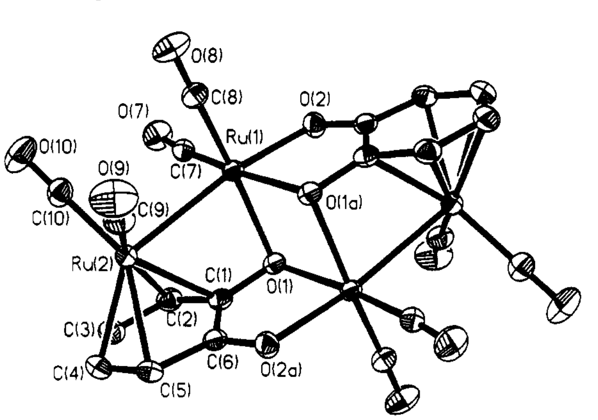

Figure 1. Molecular structure of **1**. Selected bond lengths (Å): Ru(2)–C(1) = 2.319(3); Ru(2)–C(2) = 2.313(4); Ru(2)–C(3) = 2.302(4); Ru(2)–C(4) = 2.300(3); Ru(2)–C(5) = 2.325(3); Ru(2)···C(6) = 2.402(3); C(1)–O(1) = 1.351(3); C(6)–O(2a) = 1.292(3); Ru(1)–O(1) = 2.192(2); Ru(1)–O(2) = 2.097(2); Ru(1)–O(1a) = 2.206(2); Ru(1)–Ru(2) = 2.775(1). Hydrogen atoms not shown.

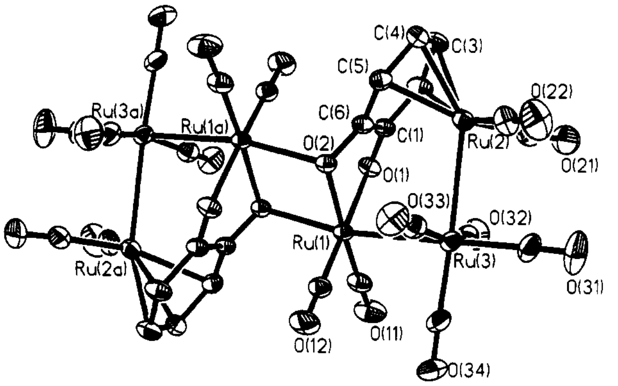

Figure 2. Molecular structure of **2**. Selected bond lengths (Å): Ru(2)···C(1) = 2.396(6); Ru(2)–C(2) = 2.271(7); Ru(2)–C(3) = 2.249(7); Ru(2)–C(4) = 2.247(7); Ru(2)–C(5) = 2.311(6); Ru(2)···C(6) = 2.420(6); C(1)–O(1) = 1.306(6); C(6)–O(2) = 1.316(6); Ru(1)–O(1) = 2.105(4); Ru(1)–O(2) = 2.121(3); Ru(1)–O(2a) = 2.295(4); Ru(1)–Ru(3) = 2.830(1); Ru(2)–Ru(3) = 2.881(1). Catechol solvate and hydrogen atoms not shown.

[Ru(2)···C(6) = 2.402(3) Å],[19] while in **2** the metal has shifted toward the 1,3-diene moiety of the benzoquinone. In addition, while the benzoquinone ligand in **2** is planar,[20] the nonbridging oxygen in **1** is bent 0.14 Å out of the plane defined by the remainder of the benzosemiquinone ligand. These structural trends suggest that **1** is best described as a η^5-*o*-benzoquinone complex. The profound insolubility of **1**, which precipitates from xylene at reflux, can be attributed to the close intermolecular π-stacking; the eclipsed six membered rings of the stacked η^5-benzosemiquinone ligands have an average intermolecular carbon–carbon distance of 3.596 Å.[21] This distance is at the lower end of the range 3.61–3.87 Å found for η^2-chelate quinone structures in the Cambridge Structural Database (version 5) which have π-stacked tetrachloro-*o*- and phenanthroquinones.[5a,22] The stabilization offered by π-stacking may account for some of the uniqueness of **1**; efforts to prepare substituted analogues of **1** which contain sterically hindered halo- and alkyl-substituted catechols have been unsuccessful.[23] The diffuse reflectance electronic spectrum for **1** has an intense band at 404.6 nm and a weaker band at 690 nm. Although the high energy band is common to all the complexes **1**–**3**,[24] the weak lower energy transition is unique to **1**, and is most likely associated with an intermolecular charge transfer transition.[25]

Lewis bases readily add to **1** or **2** to give products which depend markedly upon the base employed. The π-bound $Ru(CO)_2$ fragments in **1** and **2** are cleaved upon treatment with excess triphenylphosphine to give **4a** in modest yield. On the other hand, treatment of **1** and **2** with less basic donors such as triphenylarsine results in markedly different behavior to give either the mononuclear η^2-chelate **4b** from **2** or the tetranuclear π-complex **3** from **1**.[2] The addition of triphenylarsine to **1** cleaves the bridging oxygens *only* and coordinates the new ligand *trans* to the metal–metal bond in the opened cyclic structure found in **3**.

Electrochemical characterization of **2** and **3** by cyclic voltammetry illustrates the strong perturbation that the π-binding of the quinone has on the redox potential for this ensemble. While the η^2-O bound catecholate in **4a** has a reversible couple at −354 mV,[26] which is assigned to a ligand-based oxidation [$Ru^{II}(cat^{2-})/Ru^{II}(sbq^{1-})$],[27] the π-*o*-benzoquinone complex **2** undergoes an irreversible oxidation at 585 mV. Future work will attempt to resolve the question of the degree to which the metal–quinone separation and the strength of the π-binding perturbs quinone redox potential and, concomitantly, how the metalloquinone ensemble functions as a two-electron oxidation catalyst in the metalloquinoproteins.[11b]

Acknowledgment. We would like to gratefully acknowledge financial support from the donors of the Petroleum Research Fund (Grant 25141-63), administered by the American Chemical Society, and the assistance of Dr. Susan Swapp of the University of Wyoming Geology Department in acquiring preliminary X-ray powder diffraction results.

Supplementary Material Available: Tables giving summaries of the X-ray crystallographic results for **1** and **2**, positional and thermal parameters, and bond distances and angles (10 pages). Ordering information is given on any current masthead page.

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(18) Crystal data for **2** (from catechol melt): $C_{17}H_4O_{10}Ru_3$, $M = 671.42$, monoclinic space group $P2_1/n$, $a = 8.869(1)$ Å, $b = 9.804(2)$ Å, $c = 23.437(5)$ Å, $\beta = 92.400(10)°$, $V = 2036.0(6)$ Å^3, $Z = 4$, $D_c = 2.248$ g cm^{-3}, μ(Mo Kα) = 2.213 mm^{-1}, $F(000) = 1312$, $T = 296$ K. The compound crystallizes with half a catechol per triruthenium unit. The catechol molecule is disordered between two orientations related by a 60° rotation of the plane of the molecule which refine to occupancy factors of 32.9 and 17.%. Final anisotropic refinement for all non-hydrogen atoms (H's fixed; 342 variables) using 3153 reflections with $F > 6\sigma(F)$, from 4699 unique data collected by the 2θ–θ scan method ($4.0 \leq 2\theta \leq 55.0$), gave $R = 0.032$ and $R_w = 0.048$.

(19) The range of ruthenium–carbon bond lengths for (η^6-arene)Ru complexes in the Cambridge Structural Database (version 5) is 2.16–2.29 Å.

(20) For comparison, the largest out of plane deviations in complexes with η^4-*o*-benzoquinone ligands are 0.019 Å by the nonbridging oxygen O(1) in **2**, and 0.040 Å by C(6) in [$Ru_2(\eta^4,\mu_2,\eta^2\text{-}o\text{-}C_6H_4O_2)(CO)_4(\mu_2\text{-}I)I$].[2]

(21) Note that similar π-stacking interactions are not found in any of the other π-bound *o*-quinone structures.[2]

(22) For example the quinone length in [$Pt(dmso)_2(\eta^2\text{-}O_2C_6Cl_4)$]^a and [Pd(phenanthroquinone)(9,10-dimethylphenanthrene)]^b form eclipsed stacked dimers with an average intermolecular carbon–carbon distance of 3.70 and 3.71 Å respectively. (a) Khodashova, T. S.; Porai-Koshits, M. A.; Rudii, R. I.; Cherkashima, N. V.; Moiseev, I. I. *Koord. Khim.* **1984**, *10*, 850. (b) Yanovskii, A. I.; Zagorodnikov, V. P.; Struchkov, Yu. T. *Koord. Khim.* **1986**, *12*, 336.

(23) The reaction of $Ru_3(CO)_{12}$ with either 2,3,4,5-tetrachlorocatechol or 4-methylcatechol under the conditions (i) in Scheme I does not result in a microcrystalline precipitate similar to **1**.

(24) Solution phase UV–vis data for related complexes (λ_{max} (log ϵ), nm) in dichloromethane at 25 °C: **2**, 446 sh (3.9); **3**, 438 sh (4.1), 467 (4.1); **4a**, 482 (3.3).

(25) Self-donor–acceptor complexes such as **1** have been reviewed: McGlynn, S. P. *Chem. Rev.* **1958**, *58*, 1113.

(26) Electrochemical measurements were performed in dry oxygen-free dichloromethane with a 0.1 M tetrakis(*n*-butyl)ammonium hexafluorophosphate electrolyte, a platinum working electrode, and Ag/AgCl reference electrode. The potentials are given relative to an internal ferrocene/ferrocenium couple.

(27) For related electrochemical results see: (a) Connelly, N. G.; Manners, I.; Protheroe, J. R. C.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1984**, 2713. (b) Balch, A. L. *J. Am. Chem. Soc.* **1973**, *95*, 2723. (c) Girgis, A. L.; Sohn, Y. S.; Balch, A. L. *Inorg. Chem.* **1975**, *14*, 2327. (d) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1991**, *31*, 35. (e) Haga, M.; Isobe, K.; Boone, S. R.; Pierpont, C. G. *Inorg. Chem.* **1990**, *29*, 3795. (e) Haga, M.; Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1986**, *25*, 447.