# Rational Syntheses of Novel Linear Chain Rhodium(I)–Semiquinonato Complexes Using Redox Reaction of $Rh_4(CO)_{12}$ Cluster with *o*-Benzoquinone Derivatives

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Redox reactions of dodecacarbonyltetrarhodium(0), $Rh_4(CO)_{12}$, with 9,10-phenanthraquinone derivatives gave novel one-dimensional rhodium(I)–semiquinonato complexes. Two typical linear chain structures with direct Rh–Rh contacts were determined by X-ray crystal structure analyses of the compounds.

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Materials with highly one-dimensional (1-D) character in the crystal and electronic structures have attracted much attention among chemists and physicists.[1–3] $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ (KCP(Br)) is a typical example of such materials, in which a partially filled conduction band is formed by the partial oxidation of platinum atoms by bromine. In such a compound, band-filling control after crystallization is difficult since the oxidation numbers of the central metal atoms are fixed by the number of counter anion and their positions. Therefore, if further functionality would be developed for those compounds, an alternative approach should be introduced to produce the partially oxidized or mixed-valence compounds.

Redox-active dioxolene derivatives are possible to take redox isomers of benzoquinone, semiquinonate and catecholate by the two steps one electron transfer as shown in Figure 1.

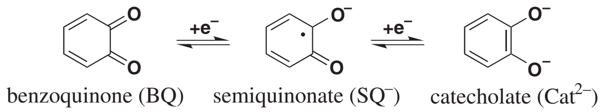

**Figure 1.** Redox characteristics of dioxolene derivative.

Several transition-metal complexes containing such dioxolene ligands are known to have very close energy levels between frontier orbitals of metal d and dioxolene ligand $\pi$, and to exhibit intramolecular electron transfer between metal and ligand under conditions of the thermal equilibrium.[4] In addition, rhodium(I)–semiquinonato complex, $[Rh(3,6\text{-DBSQ})(CO)_2]$ (3,6-DBSQ = 3,6-di-*tert*-butyl-1,2-benzosemiquinonato), was reported to form a linear chain structure with direct Rh–Rh bonds.[5] Though this compound is an insulator, the energy levels of electron-rich Rh(I) core and electron-deficient semiquinonato ligand are considered to be comparatively close to each other. If the frontier orbitals of the metal d and ligand $\pi$ orbitals could be adjusted to the same or closely related energy levels by the chemical modification, a rhodium(I,II) mixed-valence or partially oxidized state would be achieved by the intramolecular electron transfer between metals and ligands. This approach may be essential for developing novel type of 1-D conductors based on metal complexes. As for the literature method,[6] this compound is synthesized by the reaction of Tl(3,6-DBSQ) with $[RhCl(CO)_2]_2$ in toluene. However, this preparation method should be avoided since disposal of thallium waste is hard in this country. We have found the novel rational synthetic method of rhodium(I)–semiquinonato complex by the redox reaction of dodecacarbonyltetrarhodium(0), $Rh_4(CO)_{12}$, with *o*-benzoquinone derivatives.

Here we report the crystal structures and solid-state properties of novel linear chain rhodium(I)–semiquinonato complexes $[Rh(PhenSQ)(CO)_2]$ (PhenSQ = 9,10-phenanthrasemiquinonato) (**1**) and $[Rh(2,6\text{-DBPhenSQ})(CO)_2]$ (2,6-DBPhenSQ = 2,6-di-*tert*-butyl-9,10-phenanthrasemiquinonato) (**2**) together with the rational preparation method of these compounds.

The redox reaction of $Rh_4(CO)_{12}$ with 9,10-phenanthraquinone or 2,6-di-*tert*-butyl-9,10-phenanthraquinone at room temperature in THF or *n*-pentane led to the compounds **1** or **2**, respectively.[7,8] We have also succeeded in the synthesis of $[Rh(3,6\text{-DBSQ})(CO)_2]$ using this preparation method.

Compounds **1** and **2** crystallized in monoclinic space groups $Cc$ and $C2/c$, respectively and ORTEP diagrams are shown in Figures 2 and 3, respectively.[9,10] Compound **1** consists of linear-chains of $[Rh(PhenSQ)(CO)_2]$ stacked in the slipped-stack arrangement. There are four crystallographically independent 1-D chain structures in the unit cell. In each 1-D chain, there are two types of intermolecular distance between central six-membered rings of PhenSQ molecules (3.14(9)–3.25(6) Å and 3.51(6)–3.56(9) Å), indicating that semiquinonato ligands form dimerized structure. Intradimer Rh–Rh distances are 3.117(1)–3.335(2) Å, while interdimer Rh–Rh distances are 3.741(2)–3.963(1) Å. The 1-D columnar stack with eclipsed conformation is considered to be mainly formed by the overlap of $\pi$ orbitals of PhenSQ ligands, since interdimer Rh–Rh distances are longer than the corresponding interplaner distances between the ligands. Because average C–O bond length (1.30(3) Å) of PhenSQ ligand is consistent with the value observed for the semiquinonato complexes (1.272(11)–1.312(7) Å),[11] dioxolene ligand takes semiquinonato form and, therefore the oxidation number of the rhodium ion is +1.

Compound **2** consists of zig-zag chain structure of dimerized $[Rh(2,6\text{-DBPhenSQ})(CO)_2]$ molecules stacked in the staggerd conformation, and the $Rh1^a$–Rh1–$Rh1^b$ angle is 147.97(2)°. Intradimer Rh–Rh distance is 3.1233(8) Å, while interdimer Rh–Rh distance is 3.6414(8) Å. The C–O bond distances of dioxolene ligand are 1.294(5) and 1.302(5) Å, which indicates semiquinonate form of the dioxolene ligand. The complex molecules are overlapped so as to avoid steric hindrance between *tert*-butyl groups and to increase the overlap between the central six-memberded rings of 2,6-DBPhenSQ. The distance between central six-membered rings is 3.1 (2) Å. Since there is no short contact distance of semiquinionato ligands between the 1-D chains in **1** and **2**, the electronic structures of these compounds are considered to be pseudo 1-D.

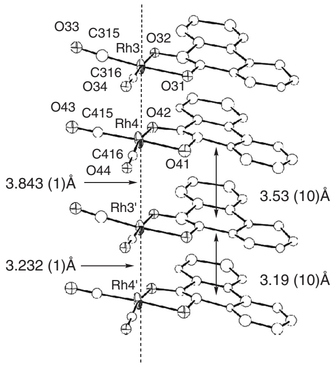

**Figure 2.** 1-D chain structure of **1**. Selected interatomic distances (Å): Rh1–Rh2 3.117(1), Rh1–Rh2′ 3.963(1), Rh3–Rh4 3.232(1), Rh3–Rh4′ 3.843(1), Rh5–Rh6 3.741(2), Rh5–Rh6′ 3.335(2), Rh7–Rh8 3.121(1), Rh7–Rh8′ 3.962(1) Å. Symmetry operation: $'-1 + x, y, z$.

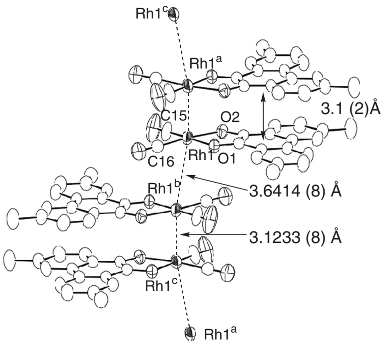

**Figure 3.** 1-D zig-zag chain structure of **2**. Methyl carbon atoms of *tert*-butyl groups have been omitted. Selected interatomic distances (Å): Rh1–Rh1$^a$ 3.1233(8), Rh1–Rh1$^b$ 3.6414(8), Rh1–O1 2.053(3), Rh1–O2 2.036(3), Rh1–C15 1.812(6), Rh1–C16 1.825(5) Å. Symmetry operations: $^a 1 - x, y, 1/2 - z$; $^b 1 - x, -y, 1 - z$; $^c x, -y, 1/2 + z$.

Temperature dependence of magnetic susceptibility of crystalline samples of **1** and **2** was measured in the range of 5–380 K under a magnetic field of 1 T using a SQUID magnetometer. In the compound **1**, the magnetic behavior originated from the thermally excited spins was observed above 260 K. The magnetic susceptibility data was analyzed based on the singlet–triplet model ($H = -JS_1 \cdot S_2$) containing a Curie spin term. The magnetic parameters can be estimated as $J/k_B = -2141$ K and the Curie spin concentration $\rho$ is 0.13%. This result indicates that the spins on the dimeric semiquinonato ligands strongly coupled antiferromagnetically. Whereas, only the impurity spin ($\rho = 0.08\%$) was observed in the compound **2** and thermally excited spin was not observed. This result indicates that the unpaired electron on each semiquinonato ligand in **2** is in the singlet state due to the dimerization. The eclipse conformation seems to be suitable for forming the uniform column structure, because the strong dimerization of the semiquinonato ligands in **2** can be weakened according to the interdimer interaction of the ligands in **1**.

Electric conductivity of the compound **1** was measured by four-prove method using a single crystal under high pressure. Electric conductivity at room temperature increases from $7.5 \times 10^{-6}$ S cm$^{-1}$ at 3.0 GPa to $4.2 \times 10^{-3}$ Scm$^{-1}$ at 8.2 GPa with increasing pressure. The compound shows typical semiconducting behavior in the temperature range measured and the activation energy is 239 meV at 8.2 GPa.

In summary, we have demonstrated that the redox reaction of $Rh_4(CO)_{12}$ with *o*-benzoquinone derivative is very useful for preparation of the novel rhodium(I)–semiquininato complexes. Using this preparation method, the synthetic research to produce a Rh(I,II) mixed-valence linear chain compound by controlling the energy level of metal d and ligand $\pi$ orbitals is now in progress.

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## References and Notes

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7 Synthesis of **1**: Compound **1** was prepared by the redox reaction of $Rh_4(CO)_{12}$ (80 mg, 0.11 mmol) with 9,10-phenanthraquinone (89 mg, 0.43 mmol) in 55 mL of THF at room temperature: yield 96 mg (61%). Anal. Found: C, 52.16; H, 2.12; O, 17.88%. Calcd for **1**: C, 52.34; H, 2.20; O, 17.43%. Vis-NIR (KBr, nm): 425, 750 (sh), 934 (sh).

8 Synthesis of **2**: Compound **2** was prepared by the similar procedure of **1** using *n*-pentane as solvent: yield 73%. Anal. Found: C, 59.96; H, 4.95; O, 13.30%. Calcd for **2**: C, 60.14; H, 5.05; O, 13.35%. Vis-NIR (KBr, nm): 385 (sh), 467 (sh), 762.

9 X-ray diffraction experiment of **1** was performed using the synchrotron radiation ($\lambda = 0.6165$ Å) at the BL02B1 beamline of the SPring-8 facility. Crystallographic data for **1** at 155 K: $C_{16}H_8O_4Rh$, fw = 367.13, dark green, monoclinic, space group *Cc*, $a = 7.072$ (1) Å, $b = 50.487$ (9) Å, $c = 27.459$ (3) Å, $\beta = 91.265$ (6)°, $V = 9802$ (2) Å$^3$, $Z = 32$. The final $R1$ factor was 0.0657 for 5494 reflections $|F_o| > 4\sigma(F_o)$ ($wR2 = 0.2257$ for 11268 all reflections). GOF = 0.982. Deposited in CCDC 236578.

10 Crystallographic data for **2** at 292 K: $C_{24}H_{24}O_4Rh$, fw = 479.36, dark brown, monoclinic, space group $C2/c$, $a = 16.728(4)$ Å, $b = 20.177(4)$ Å, $c = 12.945(3)$ Å, $\beta = 96.424$ (5)°, $V = 4342$ (2) Å$^3$, $Z = 8$. The final $R1$ factor was 0.0483 for 2939 reflections $|F_o| > 4\sigma(F_o)$ ($wR2 = 0.1038$ for 4915 all reflections). GOF = 0.933. Deposited in CCDC 236579.

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