Chain Complexes of Rhodium(II) Pivalate Dimers Formed by Ligation of C=C Double Bond and Carbonyl Oxygen of *p*-Quinone $[\{Rh_2(O_2CCMe_3)_4(p\text{-}Q)_2\}\{Rh_2(O_2CCMe_3)_4\}]_n$, *p*-Q = 1,4-Benzoquinone and 1,4-Naphthoquinone

Makoto Handa,*,[1a] Tadahiro Nakao,[1a] Masahiro Mikuriya,*,[1b] Takanori Kotera,[1b] Ryoji Nukada,[1b] and Kuninobu Kasuga[1a]

Department of Material Science, Interdisciplinary Faculty of Science and Engineering, Shimane University, Nishikawatsu, Matsue 690, Japan, and Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662, Japan

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Introduction

Tetrakis(μ-carboxylato)dimetal complexes ($M_2(O_2CR)_4X_m$; M = Cr, Mo, W, Tc, Re, Ru, Os, Rh, etc., m = 0−2) have been studied extensively from the standpoint of the unique properties conferred by the direct metal−metal bonds within their molecules.[2] Recently, there have been a number of investigations into the use of the dimetal complexes as building blocks in combination with the ligands of organic acceptors such as tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) to produce hybrid donor/acceptor polymers incorporating metal−metal bonds.[3] We have been engaged in preparing chain complexes with alternated alignment of the M_2 dimers and a kind of organic acceptor *p*-quinone formed by the axial coordination of the carbonyl oxygens to $M_2(O_2CCF_3)_4$ (M = Mo^{II} and Rh^{II}).[4] In the previous paper, we reported the chain complexes $[Rh_2(O_2CCF_3)_4(p\text{-}Q)]_n$ (*p*-Q = *p*-quinone: 1,4-benzoquinone (1,4-bq), 1,4-naphthoquinone (1,4-nq), and 2,3-dimethyl-1,4-benzoquinone) in which the *p*-quinones link the Rh_2 dimers by their carbonyl groups.[4c] We have since been interested in the effect of changing the substituent group R of the $Rh_2(O_2CR)$ dimer on the chain structure. By employing $Rh_2(O_2CCMe_3)_4$, we have found a novel coordination of the C=C double bond of the quinone to the Rh_2 dimer. Here, we present the crystal structures and properties of the chain complexes $[\{Rh_2(O_2CCMe_3)_4(p\text{-}Q)_2\}\{Rh_2(O_2CCMe_3)_4\}]_n$ (*p*-Q = 1,4-bq and 1,4-nq). A preliminary report has been published for $[\{Rh_2(O_2CCMe_3)_4(1,4\text{-}bq)_2\}\{Rh_2(O_2CCMe_3)_4\}]_n$.[5]

* Address correspondence to M. Handa (fax, +81 (852) 32-6429; e-mail, handam@riko.shimane-u.ac.jp) or to M. Mikuriya (fax, +81 (798) 51-0914; e-mail, junpei@kwansei.ac.jp).

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Table 1. Crystal Data and Data Collection Details

	1	2
empirical formula	$Rh_2O_{10}C_{26}H_{40}$	$Rh_2O_{10}C_{30}H_{42}$
fw	718.41	768.47
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	11.745(5)	10.973(5)
b/Å	15.164(7)	12.037(4)
c/Å	9.862(4)	14.112(9)
α/deg	101.52(2)	73.19(4)
β/deg	98.91(2)	76.12(4)
γ/deg	110.25(3)	73.59(3)
V/Å^3	1565.9(12)	1686.0(15)
Z	2	2
D_c/g cm^{-3}	1.52	1.52
D_m/g cm^{-3}	1.55	1.48
cryst size/mm	0.35 × 0.30 × 0.20	0.65 × 0.38 × 0.30
μ(Mo Kα)/cm^{-1}	10.8	10.1
2θ range/deg	1.0−48.0	1.0−48.0
no. of reflcns measd	4892	5266
no. of unique reflcns with $I > 3\sigma(I)$	3956	4231
R	0.026	0.056
R_w	0.032	0.070

Experimental Section

Synthesis of $[\{Rh_2(O_2CCMe_3)_4(1,4\text{-}bq)_2\}\{Rh_2(O_2CCMe_3)_4\}]_n$ (1). A solution of 1,4-bq (10 mg, 0.09 mmol) in hexane (10 mL) was added to a solution of $Rh_2(O_2CCMe_3)_4$[6] (50 mg, 0.08 mmol) in hexane (10 mL) under Ar, and the mixture was stirred for 5 h at room temperature. The precipitate was filtered off, washed with hexane, and dried under vacuum to give a blackish violet powder. The yield was 90% based on $Rh_2(O_2CCMe_3)_4$. Found: C, 43.73; H, 5.56. Calcd for $C_{13}H_{20}RhO_5$: C, 43.47; H, 5.61. IR (in KBr) ν/cm^{-1}: ν(CO) for 1,4-bq, 1630 (m) and 1660 (m); ν(COO) for $^-O_2CCMe_3$, 1420 (s) and 1580 (s).

Synthesis of $[\{Rh_2(O_2CCMe_3)_4(1,4\text{-}nq)_2\}\{Rh_2(O_2CCMe_3)_4\}]_n$ (2). This compound was obtained as a brown powder by the reaction of $Rh_2(O_2CCMe_3)_4$ (50 mg, 0.08 mmol) with 1,4-nq (14 mg, 0.09 mmol) in hexane using a method similar to that of **1**. The yield was 90% based on $Rh_2(O_2CCMe_3)_4$. Found: C, 46.57; H, 5.46. Calcd for $C_{15}H_{21}RhO_5$: C, 46.89; H, 5.51. IR (in KBr) ν/cm^{-1}: ν(CO) for 1,4-nq, 1630 (m) and 1670 (m); ν(COO) for $^-O_2CCMe_3$, 1420 (s) and 1580 (s).

Measurements. Elemental analyses for carbon and hydrogen were carried out using a Yanako CHN CORDER MT-5. Electronic spectra and infrared spectra (KBr pellets) were measured with Shimadzu UV-3100 and Hitachi 260-50 spectrometers, respectively. NMR spectra were recorded using a JEOL-GX 270 spectrometer at 270 MHz. The chemical shifts were determined in ppm using TMS as the internal standard. Cyclic voltammograms were obtained with a Hokuto Denko HA-501 potentiostat and an HB-104 function generator using a glassy carbon disk working electrode (3 mm diameter), a Pt coil counter, and a saturated calomel reference electrode (SCE). The concentration values for the complexes were based on the mole amounts of $Rh_2(O_2CCMe_3)_4$ in the solutions.

X-ray Crystal Structure Analysis. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation at 25 ± 1 °C. Crystal data and details concerning data collection are given in Table 1. The lattice constants were determined by a least-squares refinement based on 25 reflections with 20 ≤ 2θ ≤ 30°. The intensity data were corrected for Lorentz−polarization effects. The structures were solved by the heavy-atom methods. Refinements were carried out by the full-matrix least-squares methods. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The methyl carbon atoms on a *tert*-butyl group

(6) $Rh_2(O_2CCMe_3)_4\cdot 2H_2O$ was prepared by a literature method described in ref 8. The water molecules were removed by heating under vacuum.

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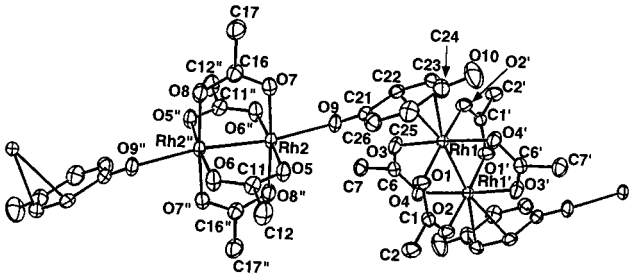

Figure 1. ORTEP drawing of **1**. Hydrogen atoms and CH_3 groups of the pivalate ions are omitted for clarity.

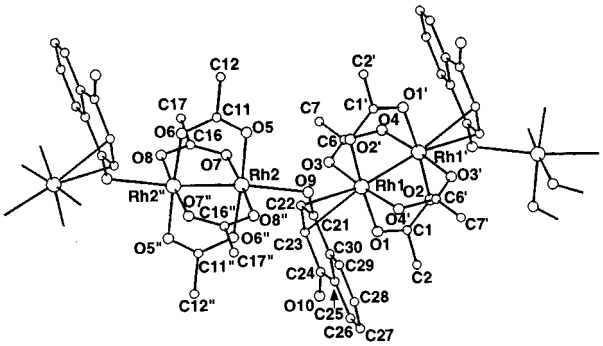

Figure 2. PLUTO drawing of **2**. Hydrogen atoms and CH_3 groups of the pivalate ions are omitted for clarity.

of pivalate for **1** were included in the full-matrix refinement with a disordered model. Hydrogen atoms were fixed at their calculated positions. The weighting scheme, $w = 1/[\sigma^2(|F_o|) + (0.02|F_o|)^2 + 1.0]$, was employed. The final discrepancy factors, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$, are listed in Table 1. All of the calculations were carried out on a micro VAX station 4000 90A computer using a MolEN program package.[7]

Results and Discussion

The crystal structures of **1** and **2** are shown in Figures 1 and 2, respectively. The chain structures are formed by alternated arrangement of Rh_2 dimers and *p*-quinone molecules (1,4-bq and 1,4-nq). It should be noted that *p*-quinone is coordinated to the Rh_2 dimer with the C═C double bond as well as the carbonyl oxygen. This coordination mode of *p*-quinone is different from that of the previously reported chain complexes $[M_2(O_2CCF_3)_4(p\text{-Q})]_n$ (M = Mo^{II} and Rh^{II}, *p*-Q = 1,4-bq, 1,4-nq, 2,3-dimethyl-1,4-benzoquinone, 2,6-dimethyl-1,4-benzoquinone, and 9,10-anthraquinone), in which only the two carbonyl oxygens participate in axial coordination.[4]

The bond distances and angles for the Rh_2 skeleton for **1** and **2** are listed in Table 2. In the case of **1**, a carbonyl oxygen of 1,4-bq is coordinated to the Rh_2 core with a distance of 2.293(2) Å. This value is 0.045 Å larger than the distance for $[Rh_2(O_2CCF_3)_4(1,4\text{-bq})]_n$[4c] and almost comparable to the axial Rh−O distance observed for $Rh_2(O_2CCMe_3)_4(H_2O)_2$ (2.295(2) Å).[8] The other carbonyl oxygen of 1,4-bq does not participate in the coordination. Rather, a C═C double bond of 1,4-bq is coordinated to the neighboring Rh_2 dimer with Rh−C distances of 2.435(4) and 2.486(5) Å. Such a crystallographically recognized coordination of a C═C double bond to an Rh_2 dimer has been reported only for the compound $Rh_2(O_2CCF_3)_4$((−)-*trans*-caryophyllene)$_2$.[9] The Rh−C distances were 2.46(1), 2.62(1), and 2.63(1) Å.[9] The first value is comparable to those for **1**.

Table 2. Selected Bond Distances (Å) and Angles (deg) Concerning Rh_2 Cores for **1** and **2** with Their Estimated Standard Deviations in Parentheses

Compound **1**[a]			
Rhl−Rhl′	2.3996(4)	Rh2−Rh2″	2.3768(4)
Rhl−O1	2.020(3)	Rh2−O5	2.029(3)
Rhl−O2′	2.033(3)	Rh2−O6″	2.026(4)
Rhl−O3	2.024(3)	Rh2−O7	2.020(3)
Rhl−O4′	2.028(3)	Rh2−O8″	2.045(3)
Rhl−C22	2.435(4)	Rh2−O9	2.293(2)
Rhl−C23	2.486(5)		
O1−Rhl−O2′	175.3(1)	O6″−Rh2−O7	90.3(1)
O1−Rhl−O3	92.0(1)	O6″−Rh2−O8″	90.2(1)
O1−Rhl−O4′	88.5(1)	O6″−Rh2−O9	86.1(1)
O2′−Rhl−O3	87.8(1)	O7−Rh2−O8″	176.3(1)
O2′−Rhl−O4′	91.3(1)	O7−Rh2−O9	85.5(1)
O3−Rhl−O4′	175.0(1)	O8″−Rh2−O9	98.2(1)
O5−Rh2−O6″	176.4(1)	Rh1′−Rh1−C22	162.1(1)
O5−Rh2−O7	89.7(1)	Rh1′−Rh1−C23	165.9(1)
O5−Rh2−O8″	89.5(1)	Rh2″−Rh2−O9	171.9(1)
O5−Rh2−O9	97.6(1)	Rh2−O9−C21	133.4(3)
Compound **2**[b]			
Rhl−Rhl′	2.402(1)	Rh2−Rh2″	2.367(1)
Rhl−Ol	2.013(7)	Rh2−O5	2.035(6)
Rhl−O2′	2.020(7)	Rh2−O6″	2.036(6)
Rhl−O3	2.012(9)	Rh2−O7	2.010(8)
Rhl−O4′	2.028(9)	Rh2−O8″	2.019(8)
Rhl−C22	2.486(8)	Rh2−O9	2.338(7)
Rh2−C23	2.479(9)		
O1−Rhl−O2′	175.0(2)	O6″−Rh2−O7	91.5(3)
O1−Rhl−O3	91.2(3)	O6″−Rh2−O8″	87.7(3)
O1−Rhl−O4′	89.2(3)	O6″−Rh2−O9	85.8(3)
O2′−Rhl−O3	88.8(3)	O7−Rh2−O8″	176.6(3)
O2′−Rhl−O4′	90.5(3)	O7−Rh2−O9	95.7(3)
O3−Rhl−O4′	175.4(2)	O8″−Rh2−O9	87.5(3)
O5−Rh2−O6″	176.6(3)	Rhl′−Rh1−C22	164.2(2)
O5−Rh2−O7	88.2(3)	Rhl′−Rh1−C23	162.8(3)
O5−Rh2−O8″	92.3(3)	Rh2″−Rh2−O9	173.1(2)
O5−Rh2−O9	97.6(2)	Rh2−O9−C21	113.2(6)

[a] Primes and double primes refer to the equivalent positions (−*x*, −*y*, −*z*) and (1 − *x*, 1 − *y*, 1 − *z*), respectively. [b] Primes and double primes refer to the equivalent positions (−*x*, −*y*, 1 − *z*) and (1 − *x*, −*y*, −*z*), respectively.

In the case of **2**, the carbonyl oxygen is coordinated to the dimer core (designated as Rh2−Rh2″) with a distance of 2.338(7) Å, while the other Rh_2 unit (designated as Rh1−Rh1′) is axially coordinated by C═C double bonds with Rh−C distances of 2.486(8) and 2.479(9) Å.

The Rh−Rh bond distances of **1** and **2** in the oxygen-coordinated Rh_2 cores are almost comparable to that of $Rh_2(O_2CCMe_3)_4(H_2O)_2$ (2.371(1) Å).[8] However, the Rh−Rh distances of the Rh_2 core with the C═C double bonds at their axial positions are ca. 0.03 Å longer than that for $Rh_2(O_2CCMe_3)_4(H_2O)_2$.[8]

In Table 3, bond distances for *p*-quinone moieties are listed with the data for the free 1,4-bq and 1,4-nq molecules.[10] It is clearly shown that the C═C double bond is lengthened on coordination, though without any accompanying significant difference in C═O bond distance.

In Figure 3, the diffuse reflectance spectra of **1** and **2** are shown with that of $Rh_2(O_2CCMe_3)_4$. $Rh_2(O_2CCMe_3)_4$ shows two distinctive bands at 680 nm (band A) and 430 nm (band B). Band A has been assigned as the $\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$

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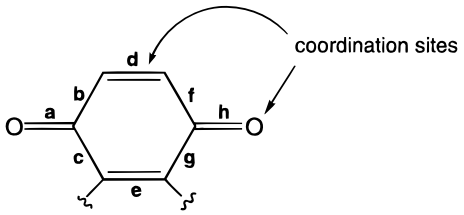
Table 3. Bond Distances of the *p*-Quinone Moieties for **1** and **2** and Free 1,4-bq and 1,4-nq (Å)



complex	a	b	c	d	e	f	g	h	ref
1	1.219(7)	1.472(8)	1.468(6)	1.346(7)	1.326(7)	1.488(5)	1.452(7)	1.226(5)	this work
2	1.22(2)	1.47(2)	1.48(2)	1.37(1)	1.38(2)	1.45(2)	1.45(2)	1.22(1)	this work
1,4-bq	1.218(8)	1.467(6)	1.467(6)	1.312(8)	1.312(8)	1.467(6)	1.467(6)	1.218(8)	10a
1,4-nq[a]	1.21	1.48	1.43	1.31	1.39	1.45	1.46	1.22	10b

[a] Estimated standard deviations for the bond lengths are not described in the literature.

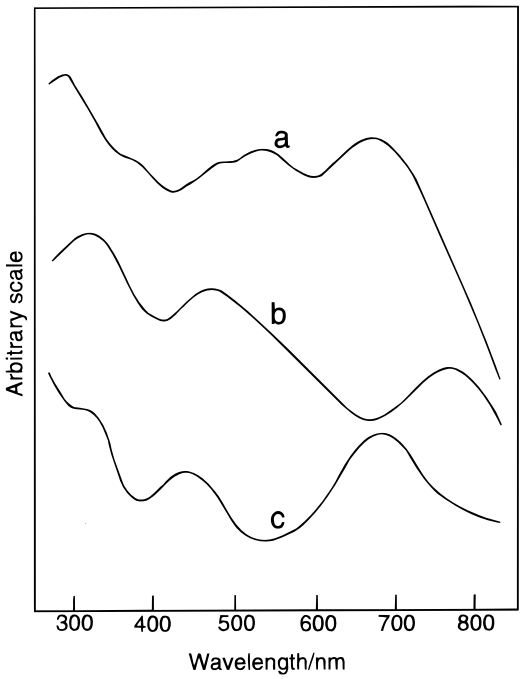


Figure 3. Reflectance spectra of **1** (a), **2** (b), and $Rh_2(O_2CCMe_3)_4$ (c).

transition and band B as the π(Rh−O) → σ*(Rh−O) transition.[2,11] In the corresponding visible regions, **1** and **2** have three absorption bands, respectively, *i.e.*, 480, 530, and 670 nm for **1** and 470, ca. 550 (the shoulder is obscure, but the spectral shape is indicative of this approximate absorption), and 760 nm for **2**. Since the position of band B is insensitive to the axial ligation, and since the n → π* transition bands of 1,4-bq and 1,4-nq at 420−460 nm (ϵ < 35 mol^{-1} dm^3 cm^{-1})[12] are much weaker than the B band (ϵ = 195 mol^{-1} dm^3 cm^{-1} (in CH_2Cl_2) for $Rh_2(O_2CCMe_3)_4$), the band at 470−480 nm observed for both of the complexes can be assigned as the π(Rh−O) → σ*(Rh−O) transition. The other two bands might be assigned as the π*(Rh_2) → σ*(Rh_2) transitions. The band positions may be correlated with the strength of the axial interactions; there are two types of Rh_2 units in the crystal: //−(Rh−Rh)−// and C═O−(Rh−Rh)−O═C. However, it is strange that a band appears at 760 nm in **2**, because an axial interaction generally results in a blue shift of the π*(Rh_2) → σ*(Rh_2) transition band.[13] The possibility of a significant bathochromic shift of the n → π* transition band of the *p*-quinone perturbed by coordination (which may enhance the band strength) or of the appearance of the new band in this region due to the charge transfer between the *p*-quinone and the Rh_2 dimer cannot be excluded.

These complexes are soluble even in solvents with low solvating ability, such as benzene or dichloromethane. The absorption spectra of **1** and **2** were measured in dichloromethane. The spectral features are dependent on the concentration of the complexes. **1** has absorption bands at 420, 550, and 670 nm when the concentration is 1×10^{-2} M. The band positions are almost identical to those observed in the reflectance spectrum. However, the spectral feature is quite similar to that of $Rh_2(O_2CCMe_3)_4$ when the concentration is 1×10^{-3} M. Equilibrium between the dimer and the polymer species probably exists in the solution, which may be the reason for the concentration dependence of the spectrum. The concentration dependence of **2** was not as remarkable as that of **1**.

^{1}H-NMR spectra (in $CDCl_3$) have shown the concentration dependence of chemical shifts for the olefinic protons of the *p*-quinone for both the complexes: 6.82 ppm at 1×10^{-3} M and 7.02 ppm at 1×10^{-2} M for **1**; 7.04 ppm at 1×10^{-3} M and 7.28 ppm at 1×10^{-2} M for **2**. On taking into account that the free quinone molecules have the signals at 6.79 ppm for 1,4-bq and 6.99 ppm for 1,4-nq, the low-field shifts are small compared with the corresponding value for $Rh_2(O_2CCF_3)_4$((−)-*trans*-caryophyllene)$_2$, of which the signal for the olefinic proton is shifted from 5.2−5.4 ppm (free ligand) to 7.1 ppm (the complex). Furthermore, the ^{13}C-NMR spectrum of **1**, which was measured in $CDCl_3$ at a concentration of 2×10^{-2} M, showed that the chemical shifts of the carbonylic carbon (188.8 ppm) and the olefinic carbon (134.6 ppm) were almost identical to those of the free 1,4-bq molecule itself (187.0 ppm for the carbonylic carbon and 136.4 ppm for the olefinic carbon).[14] These results reveal that the interactions of the carbonyl oxygens and the C═C double bonds of the quinones to the dimer are essentially weak.

The cyclic voltammograms (CVs) were measured for **1** and **2** in *o*-dichlorobenzene at a concentration of 1×10^{-3} M. Two redox processes were observed in the reducing direction (for **1**, $E_{1/2}$ (= (E_{pa} + E_{pc})/2) = −0.44, −0.96 V vs SCE; for **2**, $E_{1/2}$ =

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−0.66, −1.05 V vs SCE) at the same potentials as the corresponding redox processes of each *p*-quinone molecule itself.[15] New redox process were detected at positive sides of the first reductions of the free quinones (−0.25 V vs SCE for **1** and −0.54 V vs SCE for **2**) at a concentration of 3×10^{-3} M, which may be due to an increase of the amount of the dimer species coordinated by the *p*-quinone molecules in the solution.

In summary, a novel coordination of the C═C double bond to the Rh_2 dimer has been found in the chain complexes $[\{Rh_2(O_2CCMe_3)_4(p\text{-}Q)_2\}\{Rh_2(O_2CCMe_3)_4\}]_n$ (*p*-Q = 1,4-bq and 1,4-nq). The coordination of the C═C double bond and the carbonyl oxygen is essentially weak, which leads to considerable dissociation of the quinone molecules from the dimers in the solution.

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic thermal parameters, and bond lengths and angles and figures showing IR spectra in the carbonyl region and absorption spectra and CVs for **1** and **2** at various concentrations (17 pages). Ordering information is given on any current masthead page.

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