doi:10.1246/cl.2012.357
Published on the web March 17, 2012

Benzenedithiolate-bridged Rh_2W and RhW Cluster Complexes: Synthesis, Properties, and Formation Mechanism

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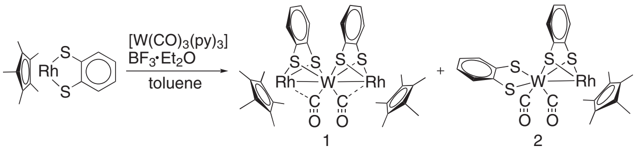
$[\{Cp^*Rh(S_2C_6H_4)\}_2W(CO)_2]$ (Cp^*: η^5-C_5Me_5) (**1**) and $[\{Cp^*Rh(S_2C_6H_4)\}(S_2C_6H_4)W(CO)_2]$ (**2**) were synthesized by the reaction of rhodadithiolene $[Cp^*Rh(S_2C_6H_4)]$ with $[W(CO)_3(py)_3]$, and their crystal structures and physical properties were investigated. The formation mechanism of **2** from **1** was pursued by ^{1}H NMR spectroscopy. **1** reacted with an excess amount of $BF_3 \cdot Et_2O$ to furnish **2**, indicating that a Lewis acid assisted the demetalation reaction.

Transition-metal cluster complexes have received much attention from chemists. Their properties and reactivities depend on the number of metal atoms, the structures, and the oxidation states.[1] The nature of the ligand groups also affects the characteristics of metal cluster complexes. Metal cluster complexes exhibit interesting properties attributable to the delocalization of d electrons over the metal atoms, which, for example, facilitates multistep electron transfer. Because of these features, transition-metal cluster complexes constitute an important research field in catalytic chemistry and bioinorganic chemistry.[2,3] Synthetic methods for preparing metal cluster complexes may be categorized into five types:[4] ligand substitution, addition, condensation, bridge-assisted reaction, and metal–metal exchange. Metal cluster complexes have not yet been synthesized at one's own will due to a shortage of methodologies. New synthetic methods are needed for the preparation of metal cluster complexes that yield designed structures.

Recently, we have developed a series of trinuclear cluster complexes through metal–metal bond formation reactions supported by benzenedithiolato ligands.[5–7] A metalladithiolene ring containing late transition metals forms a planar five-membered ring.[8] The presence of three canonical structures indicates that the ring is quasi-aromatic. Several metalladithiolene rings feature metal centers with 16 electrons, indicative of coordination unsaturation. This electron deficiency has proven to be advantageous for the formation of multinuclear metalladithiolenes. Our previous work exploited metal–metal bond formation reactions between group 9 metals and group 6 metals. All reactions solely generated neutral trinuclear cluster complexes (Co–Mo–Co, Co–W–Co, and Rh–Mo–Rh).[5,6] Here, we report a one-pot reaction that generates a novel dinuclear heterometal cluster complex **2** featuring Rh–W bond, as well as a Rh–W–Rh trinuclear complex **1** (Scheme 1). Here we also investigate the formation mechanism of **2** from **1** by ^{1}H NMR spectroscopy and determine that demetalation proceeds in the presence of a Lewis acid, $BF_3 \cdot Et_2O$. We note that Jin et al. studied metal–metal bond formation reactions that gave rise to dinuclear clusters in carborane–dichalcogenolene complexes.[8g,9] The difference between their system and **2** is that **2** features a bis(dithiolene) motif that plays a vital role in biological catalysis.[10]

The mixed-metal trinuclear cluster complex **1** was synthesized by a reaction of rhodadithiolene $[Cp^*Rh(S_2C_6H_4)]$ and $[W(CO)_3(py)_3]$ (Cp^*: η^5-C_5Me_5, py: pyridine) in the presence of $BF_3 \cdot Et_2O$ in toluene (Scheme 1, see the Supporting Information for details).[17] The combination of $[W(CO)_3(py)_3]$ and BF_3 was effective in generating a reactive $[W(CO)_3]$ fragment.[11] Surprisingly, the mixed-metal dinuclear cluster complex **2** was also obtained as a by-product. Our previous studies have never identified a mixed-metal benzenedithiolato dinuclear cluster complex similar to **2**.

The molecular structures of **1** and **2** were determined by single-crystal X-ray diffraction analysis (Figures 1, 2 and Tables S1, S2).[12,17] The structural features of **1** resembled those of $[\{Cp^*Rh(S_2C_6H_4)\}_2Mo(CO)_2]$ (**3**).[6] In **1**, the Rh–W distances were slightly longer than the sulfide-bridged Rh–W cluster complexes[8,13] but were shorter than the sum of the covalent radii (Rh: 1.42 Å; W: 1.62 Å).[14] Thus, **1** included direct Rh–W single bonds. The Rh–W bonds were supported by bridging benzenedithiolato ligands. The rhodadithiolene plane lost its planarity; the mean dihedral angle between the benzenedithiolato ligands and the S–Rh–S planes was 39.1°, and the angle between the benzenedithiolato ligands and the S–W–S planes was 59.7°. The



Scheme 1. Synthesis of **1** and **2**.

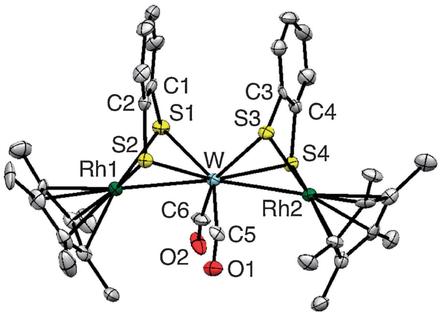


Figure 1. ORTEP drawing of **1** with a thermal ellipsoid set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1–W 2.897(2), Rh2–W 2.931(2), W–C6 1.95(1), W–C5 1.85(1), Rh1–C6 2.78(1), Rh2–C5 2.88(1), C6–O2 1.16(2), C5–O1 1.11(1), Rh1–W–Rh2 165.13(3), W–C6–O2 172.6(11), W–C5–O1 167.3(10).

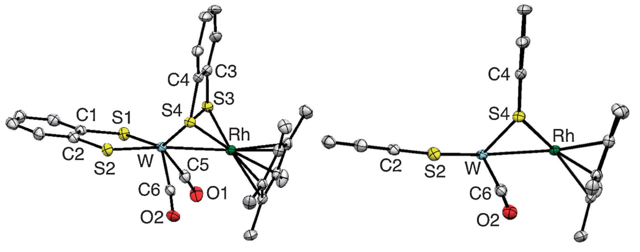


Figure 2. ORTEP drawing of **2** (oblique view: left, side view: right) with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh–W 2.7090(4), W–C5 2.000(4), W–C6 2.002(4), C5–O1 1.147(5), C6–O2 1.141(4), W–C5–O1 175.7(3), W–C6–O2 174.8(3).

two benzenedithiolato planes were twisted 39.8° relative to one another. The average bond length between the carbonyl groups and the W center (1.90 Å) was shorter than the C–Mo bond length (1.96 Å) in **3**. The average W–C–O angle was 170°. The coordination mode of the carbonyl groups was semibridging with a weak bonding interaction between the carbonyl groups and the Rh atoms. The IR spectrum of **1** in a KBr pellet showed two strong bands at 1800 and 1868 cm^{-1} that were assigned to the stretching vibrations of the carbonyl groups associated with the semibridging coordination bonds (Figure S1).[17] This result supports the notion that the π backdonation was contributed by both W and Rh atoms.

Figure 2 shows an ORTEP drawing of **2** in which the Rh–W bond distance is only slightly shorter than that in **1**, suggesting the presence of a single bond. The dihedral angle between the benzenedithiolato ligand comprising S3 and S4 and the S3–Rh–S4 plane was 48.7°, and that between the benzenedithiolato ligand comprising S3 and S4 and the S3–W–S4 plane was 41.9°. Thus, the rhodadithiolene ring lost its planarity upon formation of a bridging structure involving a W atom. On the other hand, the dihedral angle between the benzenedithiolato ligand containing S1 and S2 and the S1–W–S2 plane was 5.5°, indicating that the WS_2C_2 ring was planar and quasi-aromatic. The ^1H NMR spectrum in dichloromethane-d_2 confirmed this quasi-aromaticity (Figure S2).[17] The signals derived from the RhS_2C_2 ring were observed at 6.82 and 7.26 ppm, whereas those stemming from the WS_2C_2 ring emerged at 7.43 and 8.06 ppm. The W center was ligated by two carbonyl groups. The W–C–O angles approached 180°, suggesting that the coordination mode of these carbonyl groups was terminal. The IR spectrum of **2** featured two strong bands at 1897 and 1956 cm^{-1} that could be classified as terminal carbonyl groups. The structural features of **2** were similar to those of the diselenolene cluster complex, $[\{CpCo(Se_2C_6H_4)\}(Se_2C_6H_4)W(CO)_2]$ (**4**), which was previously synthesized in our laboratory.[5b]

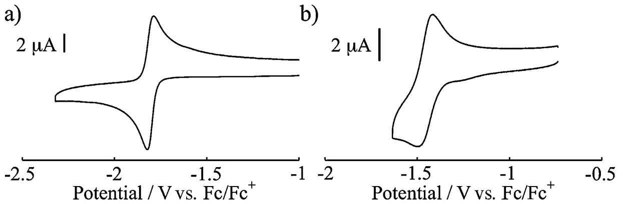


Figure 3. Cyclic voltammograms of **1** (left, a) and **2** (right, b) at 100 $mV\,s^{-1}$ in 0.1 M n-Bu_4NClO_4–MeCN/toluene (1:1 v/v) at 253 K.

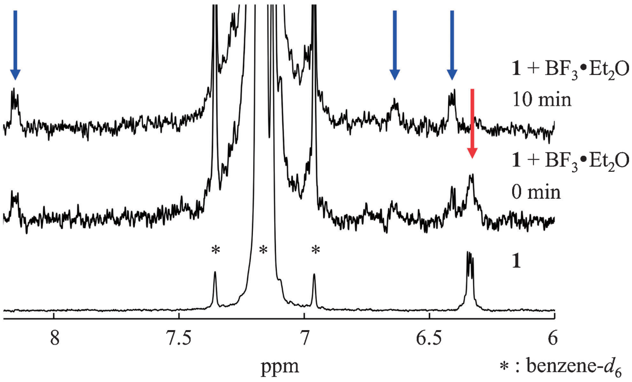


Figure 4. ^1H NMR spectral changes in the course of a conversion from **1** to **2** in benzene-d_6. The signals of **1** and **2** are denoted by red and blue arrows, respectively. The reaction time is described in each chart.

Cyclic voltammograms of **1** and **2** in 0.1 M n-Bu_4NClO_4–MeCN/toluene (1:1, v/v) at 253 K are shown in Figure 3. **1** displayed one reversible redox wave at $E^{0\prime} = -1.78$ V vs. ferrocenium/ferrocene (Fc^+/Fc) (Figure 3a). The peak potential difference, ΔE_p ($= E_{pa} - E_{pc}$), was 37 mV, smaller than that of an ideal reversible $1e^-$ redox reaction (50 mV at this temperature).[15] This redox process, therefore, was a one-step $2e^-$ redox reaction. DFT calculations (Figure S3)[17] predicted that the LUMO and LUMO+1 were antibonding orbitals with respect to the Rh–W bonds, suggesting that the $2e^-$ reduction could weaken the Rh–W bonds. The reduction potential of the Rh centers in **1** was shifted toward positive values compared with the corresponding value for **3** (−1.87 V).[6] On the other hand, **2** displayed one reversible redox wave (Figure 3b). A ΔE_p value of 65 mV suggested that **2** underwent a reversible one-electron reduction. This redox reaction can be regarded as an electron donation to the antibonding orbital of the Rh–W bond (Figure S4).[17]

Considering that the favored products of our metal-integrating reaction were the trinuclear cluster complexes, including **1**, **1** was conjectured as being an precursor in the preparation of **2**. The formation mechanism of **2** was examined by observing the conversion from **1** to **2** in toluene-d_8 or benzene-d_6 using ^1H NMR. **1** was stable under reflux conditions under an inert atmosphere for 4 days. To **1** were added excess 2,2′-bipyridine, 1,2-bis(diphenylphosphino)ethane, and 1,5-cyclooctadiene as neutral Lewis bases, with the expectation that these additives reacted with the electron-deficient Rh centers; however, **1** did not convert to **2**. Surprisingly, the reaction of **1** with the Lewis acid, $BF_3{\cdot}Et_2O$, enabled the conversion to **2** (Figure 4). We note that diethyl ether did not give rise to **2** alone. These results strongly suggest that the presence of BF_3 was indispensable to the formation of **2**. During this formation process, BF_3 may interact with the dithiolene moiety of **1** to facilitate Rh–W bond cleavage. We note that Pigge et al. previously reported the influence of a Lewis acid on the demetalation of ruthenium complexes.[16] In the course of the transformation from **1** to **2**, elimination of the [Cp*Rh] fragment should occur. In the Cp* region of the ^1H NMR spectra

(Figure S5),[17] several peaks were observed after the reaction. These peaks might be derived from the [Cp*Rh] fragment; however, we have not identified them thus far.

In conclusion, the heterometal cluster complexes **1** and **2** were synthesized through a metal–metal bond formation reaction of $[Cp^*Rh(S_2C_6H_4)]$ with $[W(CO)_3(py)_3]$, and the physical properties of these complexes were investigated. The demetalation of **1** was observed by ^1H NMR spectroscopy to determine that **1** reacted with an excess amount of $BF_3 \cdot Et_2O$ to give rise to **2**. This type of demetalation reaction has not previously been reported and, therefore, provides a new synthetic method for the preparation of cluster complexes.

The authors acknowledge Grants-in-Aid from MEXT of Japan (Nos. 20245013 and 21108002, area 2107, Coordination Programming), a JSPS Research Fellowship for Young Scientists, and the Global COE Program for Chemistry Innovation for financial support.

References and Notes

1 a) *The Chemistry of Metal Cluster Complexes*, ed. by D. F. Shriver, H. D. Kaesz, R. D. Adams, Wiley-VCH, **1990**. b) G. González-Moraga, *Cluster Chemistry: Introduction to the Chemistry of Transition Metal and Main Group Element Molecular Clusters*, Springer-Verlag, **1993**. c) *Metal Clusters in Chemistry*, ed. by P. Braunstein, L. A. Oro, P. R. Raithby, Wiley-VCH, **1999**, Vols. 1–3. d) P. J. Dyson, J. S. McIndoe, *Transition Metal Carbonyl Cluster Chemistry*, Gordon and Breach Science, **2000**.

2 a) Z. Li, Y. Ohki, K. Tatsumi, *J. Am. Chem. Soc.* **2005**, *127*, 8950. b) S. Tanino, Z. Li, Y. Ohki, K. Tatsumi, *Inorg. Chem.* **2009**, *48*, 2358. c) B. E. Barton, C. M. Whaley, T. B. Rauchfuss, D. L. Gray, *J. Am. Chem. Soc.* **2009**, *131*, 6942. d) C. Tard, C. J. Pickett, *Chem. Rev.* **2009**, *109*, 2245. e) C. Tard, X. Liu, S. K. Ibrahim, M. Bruschi, L. De Gioia, S. C. Davies, X. Yang, L.-S. Wang, G. Sawers, C. J. Pickett, *Nature* **2005**, *433*, 610. f) D. Chen, R. Scopelliti, X. Hu, *J. Am. Chem. Soc.* **2010**, *132*, 928. g) *Catalysts for Nitrogen Fixation: Nitrogenases, Relevant Chemical Models and Commercial Processes*, ed. by B. E. Smith, R. L. Richards, W. E. Newton, Kluwer Academic Publishers, Dordrecht, **2004**.

3 *Catalysis by Di- and Polynuclear Metal Cluster Complexes*, ed. by R. D. Adams, F. A. Cotton, Wiley-VCH, **1998**.

4 R. D. Adams, *Heteronuclear Metal–Metal Bonds* in *Comprehensive Organometallic Chemistry II*, ed. by E. W. Abel, F. G. A. Stone, G. Wilkinson, Pergamon, Oxford, U.K., **1995**, Vol. 10, Chap. 1, pp. 1–22. doi:10.1016/B978-008046519-7.00085-X.

5 a) M. Nihei, T. Nankawa, M. Kurihara, H. Nishihara, *Angew. Chem., Int. Ed.* **1999**, *38*, 1098. b) M. Murata, S. Habe, S. Araki, K. Namiki, T. Yamada, N. Nakagawa, T. Nankawa, M. Nihei, J. Mizutani, M. Kurihara, H. Nishihara, *Inorg. Chem.* **2006**, *45*, 1108. c) B.-H. Zhu, Y. Shibata, S. Muratsugu, Y. Yamanoi, H. Nishihara, *Angew. Chem., Int. Ed.* **2009**, *48*, 3858.

6 a) S. Muratsugu, K. Sodeyama, F. Kitamura, M. Sugimoto, S. Tsuneyuki, S. Miyashita, T. Kato, H. Nishihara, *J. Am. Chem. Soc.* **2009**, *131*, 1388. b) S. Muratsugu, K. Sodeyama, F. Kitamura, S. Tsukada, M. Tada, S. Tsuneyuki, H. Nishihara, *Chem. Sci.* **2011**, *2*, 1960.

7 a) N. Nakagawa, T. Yamada, M. Murata, M. Sugimoto, H. Nishihara, *Inorg. Chem.* **2006**, *45*, 14. b) N. Nakagawa, M. Murata, M. Sugimoto, H. Nishihara, *Eur. J. Inorg. Chem.* **2006**, 2129.

8 a) *Dithiolene Chemistry: Synthesis, Properties, and Applications in Progress* in *Inorganic Chemistry*, ed. by E. I. Stiefel, John Wiley & Sons, Inc., Hoboken, NJ, USA, **2004**, Vol. 52. doi:10.1002/0471471933. b) S. J. Lippard, R. Eisenberg, in *Progress in Inorganic Chemistry*, Wiley, **1970**, Vol. 12, p. 295. doi:10.1002/9780470166130.ch4. c) R. P. Burns, C. A. McAuliffe, *Adv. Inorg. Chem.* **1979**, *22*, 303. d) M. Fourmigué, *Coord. Chem. Rev.* **1998**, *178–180*, 823. e) A. Sugimori, T. Akiyama, M. Kajitani, T. Sugiyama, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 879. f) R. Kato, *Chem. Rev.* **2004**, *104*, 5319. g) S. Liu, Y.-F. Han, G.-X. Jin, *Chem. Soc. Rev.* **2007**, *36*, 1543.

9 a) S. Cai, G.-X. Jin, *Organometallics* **2005**, *24*, 5280. b) S. Cai, Y. Lin, G.-X. Jin, *Dalton Trans.* **2006**, 912. c) S. Cai, J.-Q. Wang, G.-X. Jin, *Organometallics* **2005**, *24*, 4226.

10 Reviews: a) R. H. Holm, *Coord. Chem. Rev.* **1990**, *100*, 183. b) M. K. Johnson, D. C. Rees, M. W. W. Adams, *Chem. Rev.* **1996**, *96*, 2817. c) E. I. Stiefel, S. J. N. Burgmayer, *Dithiolene Chemistry: Synthesis, Properties, and Applications* in *Progress in Inorganic Chemistry*, ed. by E. I. Stiefel, John Wiley & Sons, Inc., Hoboken, NJ, USA, **2003**, Vol. 52, p. 491. doi:10.1002/0471471933.ch9. d) H. Sugimoto, H. Tsukube, *Chem. Soc. Rev.* **2008**, *37*, 2609.

11 A. N. Nesmeyanov, V. V. Krivykh, V. S. Kaganovich, M. I. Rybinskaya, *J. Organomet. Chem.* **1975**, *102*, 185.

12 CCDC 860809 (**1**) and 860810 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

13 a) K. E. Howard, T. B. Rauchfuss, A. L. Rheingold, *J. Am. Chem. Soc.* **1986**, *108*, 297. b) K. E. Howard, T. B. Rauchfuss, S. R. Wilson, *Inorg. Chem.* **1988**, *27*, 3561. c) H. Seino, N. Iwata, N. Kawarai, M. Hidai, Y. Mizobe, *Inorg. Chem.* **2003**, *42*, 7387.

14 B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* **2008**, 2832.

15 A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., Wiley, NY, **2001**.

16 F. C. Pigge, J. J. Coniglio, N. P. Rath, *Organometallics* **2005**, *24*, 5424.

17 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.