Cluster Compounds

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A Cyclic Hexanuclear Heterometalladithiolene Cluster $[\{(Cp^*Rh)_2Mo(\mu\text{-}CO)_2(CO)\}_2(S_2C_6H_2S_2)_2]$ with Two π-Conjugated $S_2C_6S_2$ Bridges: Synthesis, Crystal Structure, and Properties**

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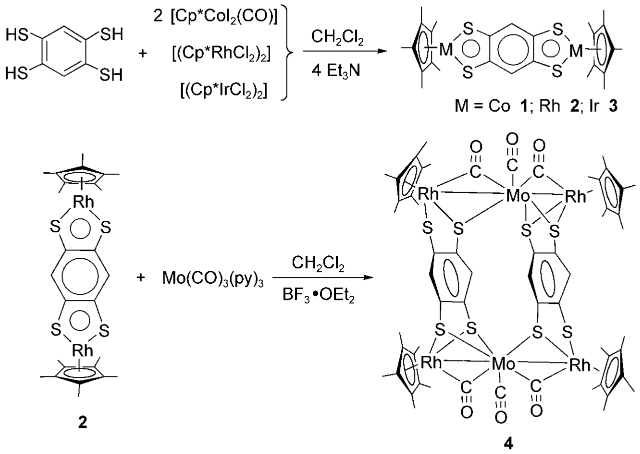
Recent attention has focused on metalladithiolenes of late transition metals that contain planar MS_2C_2 rings because of their redox activity, magnetic properties, deep color, and the addition reactions derived from the quasi aromaticity and electronic unsaturation of the metalladithiolene ring.[1] The metalladichalcogenolene rings can be used as building blocks for metal cluster complexes owing to the electron deficiency of the metal center.[2] We previously described the first example of a metal–metal bond formation reaction using a metalladithiolene complex.[2a] In that reaction, a trinuclear heterometal cluster $[\{CpCo(S_2C_6H_4)\}_2\ Mo(CO)_2]$ ($Cp = \eta^5\text{-}C_5H_5$), which possesses a slightly bent Co-Mo-Co unit and extremely deformed cobaltadithiolene rings, was synthesized from a metalladithiolene complex, $[CpCo(S_2C_6H_4)]$, and from $[Mo(CO)_3(py)_3]$ (py = pyridine). Interestingly, the Co⋯Co electronic interaction could be transmitted by the molybdenum atom. Another attractive possibility, the formation of heteronuclear metal–metal bonds by dinuclear metalladithiolene complexes, has yet to be explored.

To extend the metal–metal bond formation reaction to a system of two electron-deficient metal centers, two new π-conjugated dinuclear metalladithiolene complexes, $[Cp^*MS_2C_6H_2S_2MCp^*]$ ($Cp^* = \eta^5\text{-}C_5Me_5$, M = Rh **2**, Ir **3**), were synthesized and characterized (Scheme 1). It should be noted the analogue of cobalt complex **1** was recently reported by Nomura and Fourmigué.[1g] In exploring the reactivity of the dinuclear rhodadithiolene complex **2** with two $16e^-$ rhodium centers towards the molybdenum carbonyl complex, we discovered the formation of a double Rh-Mo-Rh trinuclear heterometalladithiolene cluster in which two $S_2C_6H_2S_2$ planes act as the bridges. Herein, we report the synthesis, structure, and properties of the two π-conjugated dinuclear complexes, **2** and **3**, and the first cyclic hexanuclear heterometalladithiolene cluster with two π-conjugated bridges, $[\{(Cp^*Rh)_2Mo(\mu\text{-}CO)_2(CO)\}_2(S_2C_6H_2S_2)_2]$ (**4**), as obtained from the dinuclear complex **2** by reaction with $[Mo(CO)_3(py)_3]$ and BF_3.



Scheme 1. Synthesis of compounds **1**–**4**.

Complexes **2** and **3** were obtained by complexation of 1,2,4,5-benzenetetrathiol with $[\{Cp^*RhCl_2\}_2]$ and $[\{Cp^*IrCl_2\}_2]$, respectively, under basic conditions at room temperature in dichloromethane. A similar reaction of $C_6H_2(SH)_4$ with $[Cp^*CoI_2(CO)]$ afforded **1** in a higher yield (65 %) than that reported previously (33 %).[1g] Complex **2** reacts with one equivalent of $[Mo(CO)_3(py)_3]$ in the presence of more than three equivalents of $BF_3{\cdot}OEt_2$ in dichloromethane at room temperature to give cluster **4** as a brown crystalline solid. This compound may be regarded as two π-conjugated dinuclear rhodadithiolene complexes bridged by two molybdenum tricarbonyl moieties. Consistent with this, one terminal and two bridging carbonyl absorptions are observed in the IR spectrum of **4** at 1924, 1830, and 1817 cm^{-1}. The combination of $[Mo(CO)_3(py)_3]$ and BF_3 is an effective way to generate a reactive $[Mo(CO)_3]$ fragment.[2,3] Only the molybdenum dicarbonyl unit, however, was observed in our first Co-Mo-Co trinuclear cluster[2a] and in the analogue obtained by Jin et al.[2b] We assume that $[Mo(CO)_3]$ adds to **2** to give a 1:1 complex with a Rh–Mo bond and two Rh–S–Mo linkages; however, because this complex has an odd number of electrons at molybdenum and another $16e^-$ rhodium center, two such molecules react together in a head to tail mode to form a closed 1:1 double trinuclear cluster with two

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Rh–Mo bonds and three Rh–S–Mo linkages, rather than losing one CO to form four Rh–S–Mo linkages.

The molecular structures of $\mathbf{3}\cdot CH_3OH$ and **4** were determined by single crystal X-ray analysis.[4] The structure of the iridium dinuclear complex **3** reveals that the $C_6H_2S_4M_2$ moieties are planar and that intermolecular π–π interactions occur between the Cp* rings and the C_6H_2 rings, as the interplane distances are 3.55 Å (see the Supporting Information, Figure S1 and Table S1). Similar π–π interactions have been observed in the structure of the cobalt complex **1**.[1g] In the structure of **4** (Figure 1), two molybdenum centers are eight-coordinate with dodecahedral geometry, and the coordination environments of the molybdenum centers are different from that of the previous trinuclear Co-Mo-Co cluster.[2] Only three sulfur atoms bond to each molybdenum center, and the $\{Mo(CO)_3\}$ fragment retains its three carbonyl groups during the metal addition reaction rather than losing one CO to form four Mo–S bonds. This kind of coordination mode causes the chemical environments of the two protons of each C_6H_2 ring and the two Cp* groups of each Rh-Mo-Rh trinuclear unit to be inequivalent. These differences were also confirmed by the observation of two sets of aryl and methyl signals at $\delta = 7.03$, 6.50, and 1.77, 1.60 ppm, respectively, in the ^1H NMR spectrum of **4**. The Rh1–Mo bond length (2.8983(7) Å) is 0.1577 Å longer than the Rh2–Mo bond length (2.7406(9) Å), with an Rh2-Mo-Rh1 angle of 150.18(2)°. The carbonyl C9O3 can be regarded as semi-bridging because the asymmetric parameter α is 0.24.[5] The quasi-aromatic systems of the dinuclear rhodadithiolene heterocycle **2** are changed in **4**; the dihedral angles at the S···S vector in the $Rh1S_2C_2$ and $Rh2S_2C_2$ rings are 14.0° and 129.8°, respectively. The $Rh1S_2C_2$ ring is slightly deformed, indicating that its quasi-aromaticity is largely retained after the formation of the Rh–Mo bond. This result is in contrast to the cases of the linear metalladichalcogenolene trinuclear clusters, $[\{CpCo(S_2C_6H_4)\}_2Mo(CO)_2]$,[2a,e] $[\{Cp^*Rh(S_2C_6H_4)\}_2Mo(CO)_2]$,[8] and $[\{Cp^*Ir(Se_2C_2(B_{10}H_{10})\}_2Mo(CO)_2]$,[2b] the quasi-aromaticities of which were lost after the creation of the metal–metal bonds. The two $S_2C_6H_2S_2$ planes are parallel to each other, with the separation of 3.266 Å, thus revealing the presence of intramolecular π–π interactions between the two planes. The number of carbonyl ligands and their coordination mode in **4** are different from the linear metalladithiolene trinuclear clusters to make the two $S_2C_6H_2S_2$ planes parallel because the $S_2C_6H_4$ planes in the trinuclear clusters were not parallel.[2a,e,8] The total number of valence electrons around the two Rh_2Mo cores is 100; six sulfur atoms each contribute three electrons, and the other two sulfur atoms each contribute one electron.

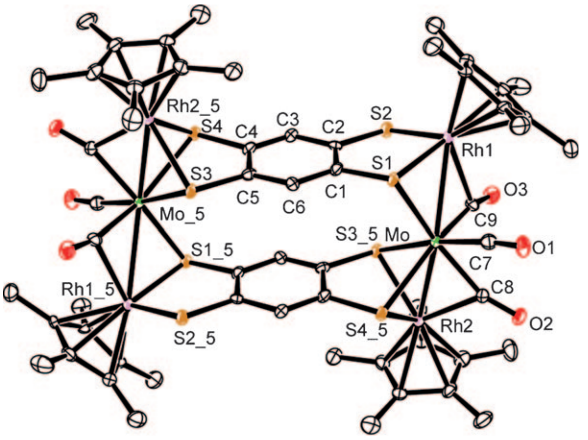

Figure 1. ORTEP of **4** with ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1–Mo 2.8983(7), Rh2–Mo 2.7406(9), Rh1–S1 2.3081(14), Rh1–S2 2.3280(15), Rh2–S3_5 2.3653(15), Rh2–S4_5 2.3877(16), Rh1–C9 2.483(6), Rh1–C8 2.210(6), Mo–C7 1.988(6), Mo–C9 2.004(6), Mo–C8 2.039(6), Mo–S1 2.4957(15), Mo–S3_5 2.5242(15), Mo–S4_5 2.5549(15), C1–C2 1.408(8), C2–C3 1.417(8), C3–C4 1.380(8), C4–C5 1.407(8), C6–C5 1.374(8), C1–C6 1.405(8); Rh2-Mo-Rh1 150.18(2), S1-Mo-Rh1 49.99(3), S2-Rh1-Mo 90.48(4), S3_5-Mo-Rh2 53.20(4), S4_5-Mo-Rh2 53.46(4), Mo-C8-Rh2 80.22(19), Mo-C9-Rh1 79.7(2).

UV/Vis-NIR absorption spectra of **1**–**3** show strong absorption bands at 678 (similar to the reported value),[1g] 586, and 474 nm, respectively (Figure 2a), which are assigned to the ligand–metal charge transfer (LMCT) band from dithiolene to metal that is usually observed for metalladithiolene complexes. The blue shift of the LMCT band with an increase in atomic number is attributed to the increase in the d-orbital energy level of the metal. For cluster **4**, the absorption spectrum has three visible absorption bands at 411, 465, and 574 nm, and one near-infrared absorption band at 756 nm (Figure 2b). To assign these absorption bands, we carried out an excited-state calculation by the time-dependent DFT method,[6] which has been successfully applied to coordination compounds,[2c,7] based on the molecular structure of **4** (see the Supporting Information, Figure S2 and Table S2). The calculation indicates that the band at 411 nm

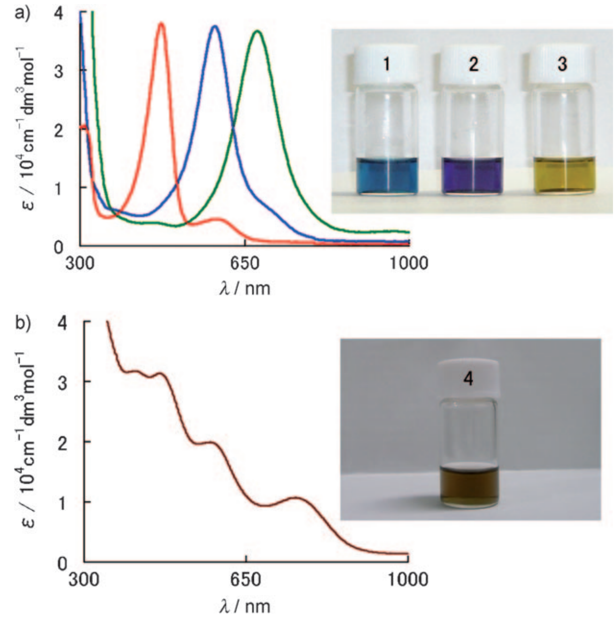

Figure 2. UV/Vis-NIR absorption spectra in dichloromethane of a) **1** (green), **2** (blue), and **3** (red), and b) **4**.

can be attributed to the mixed charge transfer of the metal–metal charge transfer (MMCT) from molybdenum to rhodium and the LMCT from dithiolene to molybdenum and rhodium, the band at 465 nm could be caused by the MMCT from molybdenum to rhodium rather than the LMCT, the band at 574 nm can be assigned to the LMCT band from dithiolene to rhodium, and the lowest energy absorbance band at 756 nm could be attributed primarily to the mixed excitations from the HOMO to the LUMO and the HOMO−1 to the LUMO+1 (Figure 3).

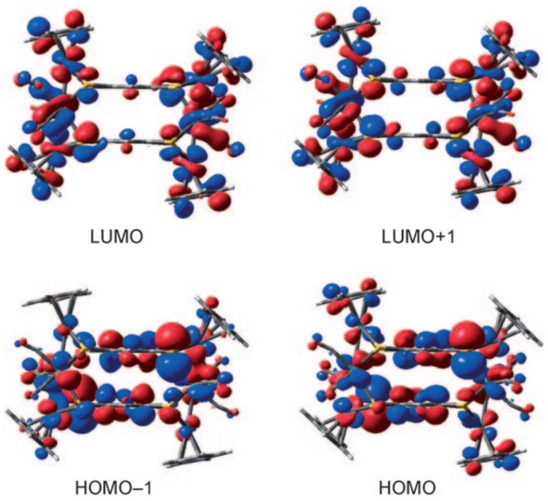

Figure 3. Molecular orbitals of **4** calculated with the TD-DFT(B3LYP) method in dichloromethane. Methyl groups are replaced by hydrogen for simplificity.

Electrochemical measurements on the dinuclear complexes **1–3** and the hexanuclear cluster **4** were carried out in 0.1 M Bu_4NClO_4 in benzonitrile. The differential pulse voltammograms of complexes **1–3** and the cyclic voltammogram (CV) of cluster **4** are shown in Figure 4. All the dinuclear complexes exhibit two-step, one-electron redox processes. The reductions of the two metal centers from M^{III} to M^{II} appeared as two one-electron waves, indicating the formation of a mixed-valence state $[M^{II}–M^{III}]$. Unexpectedly, the cyclic scan for cluster **4** between −1.0 and −2.2 V versus Fc^+/Fc shows only two couples of reduction and reoxidation waves at $E^{0\prime} = -1.58$ and −1.78 V. This result implies that cluster **4** may be undergoing a two-step, two-electron reversible redox process. This interpretation is also supported by our study on the linear Rh-Mo-Rh trinuclear cluster $[\{Cp^*Rh(S_2C_6H_4)\}_2Mo(CO)_2]$, which undergoes a one-step two-electron reduction process accompanied by a change in carbonyl bond mode from semibridging to bridging.[8] Detailed studies on the electrochemical properties of **4** are in progress.

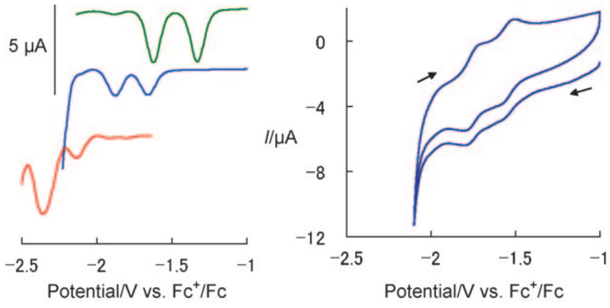

Figure 4. Differential pulse voltammograms at 0.02 V s^{-1} of dinuclear complexes. a) **1** (green), **2** (blue), and **3** (red), and b) the cyclic voltammogram of **4**, at a glassy carbon electrode and with a scan rate of 0.1 V s^{-1} in 0.1 mol dm^{-3} Bu_4NClO_4/C_6H_5CN.

In conclusion, we have presented a direct metal–metal bond formation reaction using the π-conjugated dinuclear metalladithiolene complex with two electron-deficient metal centers as building blocks. A novel cyclic hexanuclear heterometalladithiolene cluster **4** with two π-conjugated bridges was obtained by reaction of the dinuclear rhodadithiolene complex **2** with the Group 6 metal carbonyl complex $[Mo(CO)_3(py)_3]$. The hexanuclear heterometal cluster is unique because of its novel coordination mode of the molybdenum centers, maintenance of planarity of the rhodaditholene rings, intramolecular π–π interactions between the two parallel $S_2C_6H_2S_2$ bridges, and redox properties.

Experimental Section

Reactions were performed under an inert atmosphere of nitrogen using standard Schlenk techniques. **4**: $BF_3{\cdot}OEt_2$ (0.033 mL, 95 %, 0.3 mmol) was added dropwise to a stirred solution of **2** (34 mg, 0.05 mmol) and $[Mo(CO)_3(py)_3]$ (24 mg, 0.05 mmol) in dichloromethane (60 mL) at room temperature, and the suspension was stirred for 18 h. The solvent was evaporated under vacuum, and the components of the residue were separated by thin-layer chromatography on silica gel with dichloromethane/hexane (6/1) as eluent. The component in the second band was eluted with dichloromethane to give brown **4**, yield 7.9 % (3.4 mg). Elemental analysis (%), calculated for $C_{58}H_{64}O_6S_8Rh_4Mo_2{\cdot}CH_2Cl_2$: C 39.25, H 3.69; found: C 38.82, H, 4.25. ^1H NMR(400 MHz, $CDCl_3$): $\delta = 7.03$ (s, 2 H, Ar-H), 6.50 (s, 2 H, Ar-H), 5.30 (s, CH_2Cl_2), 1.77 (s, 30 H, Cp*), 1.60 ppm (s, 30 H, Cp*. IR (KBr disk): $\tilde{\nu} = 1924$, 1830, 1817 cm^{-1} (CO). ESI-MS: m/z 1717.64 [M^+]. For further experimental details, see the Supporting Information.

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