Thermochromic Triangular [MCo$_2$] (M = Rh, Ir, Ru) Clusters Containing a Planar Metalladithiolene Ring in η^3 Coordination

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The first series of triangular cluster complexes of [MCo$_2$] (M = Rh, Ir, Ru) with a planar metalladithiolene ring coordinating in the η^3-bonding mode were synthesized, and the crystal structures, spectral and electrochemical properties, and thermochromism of these complexes were revealed.

Late-transition-metal dithiolato complexes with planar ring structures (**A** in Chart 1) have attracted much attention because of both their properties and reactivities, which include redox activity, deep color, and addition reactions derived from the quasi-aromaticity and electronic unsaturation of the metalladithiolene ring.[1] We have previously reported the first direct metal−metal bond formation reaction using a metalladithiolene complex.[2] In this reaction, the group 9−6−9 trinuclear heterometal complex, [{CpCo(S$_2$C$_6$H$_4$)}$_2$-Mo(CO)$_2$], which has a linear metal−metal bond framework, was synthesized from a metalladithiolene complex, [CpCo-(S$_2$C$_6$H$_4$)], and Mo(CO)$_3$(py)$_3$. In this complex, the metalladithiolene ring is bent because of the donation of lone-pair electrons on S, thus leading to the loss of the aromaticity of the ring (**B** in Chart 1). All other metalladithiolene-derived compounds with a metal atom bound to the two sulfur atoms of the metalladithiolene ring also lose the planarity of the ring.[3] We report here the syntheses of triangular heterometal cluster complexes, [{(η^5-C$_5$Me$_5$)Rh(S$_2$C$_6$H$_4$)}Co$_2$(CO)$_5$] (**4**),

Chart 1
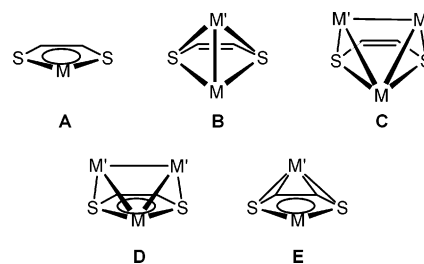
[{(η^5-C$_5$Me$_5$)Ir(S$_2$C$_6$H$_4$)}Co$_2$(CO)$_5$] (**5**), and [{(η^6-C$_6$Me$_6$)-Ru(S$_2$C$_6$H$_4$)}Co$_2$(CO)$_5$] (**6**), from mononuclear metalladithiolene complexes **1**−**3**, respectively. Recently, Jin and co-workers reported a similar triangular cluster complex containing a carborane dithiolato ligand, [{(η^5-C$_5$Me$_5$)Ir-(S$_2$C$_2$B$_{10}$H$_{10}$)}Co$_2$(CO)$_5$] (**7**),[4] the metalladithiolene ring of which was bent (**C** in Chart 1), but we carried independent investigations of the syntheses, structures, and properties of **4**−**6**.[5] These compounds are the first series of dithiolene-bridged trinuclear cluster complexes in which the planarity of the metalladithiolene ring is maintained (**D** in Chart 1). The complexes presented here indicate a novel mode of metalladithiolene bonding to metals. The molecular structures, physical properties, electronic structures, and thermochromism of the cluster complexes are presented in this paper.

One equivalent of dicobalt octacarbonyl was allowed to react with 1 equiv of each metalladithiolene complex, LM-(SSC$_6$H$_4$) (**1**, L = η^5-C$_5$(CH$_3$)$_5$, M = Rh; **2**, L = η^5-C$_5$(CH$_3$)$_5$, M = Ir; **3**, L = η^6-C$_6$(CH$_3$)$_6$, M = Ru) in the presence of 3 equiv of trimethylamine *N*-oxide in toluene at room temperature. This reaction yielded the following mixed-metal cluster complexes: RhCo$_2$ (**4**) from **1**, IrCo$_2$ (**5**) from **2**, and RuCo$_2$ (**6**) from **3**, as shown in Scheme 1. All of these complexes (i.e., **4**−**6**) were air- and moisture-stable in the crystalline state.

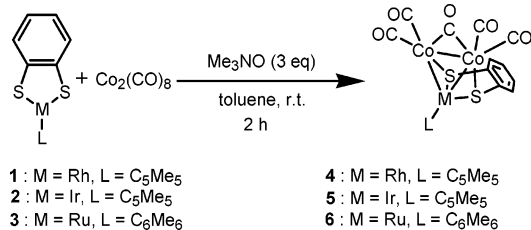* To whom correspondence should be addressed. E-mail: nisihara@chem.s.u-tokyo.ac.jp.
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Scheme 1. Synthesis of Triangular Cluster Complexes

1 : M = Rh, L = C$_5$Me$_5$
2 : M = Ir, L = C$_5$Me$_5$
3 : M = Ru, L = C$_6$H$_6$

4 : M = Rh, L = C$_5$Me$_5$
5 : M = Ir, L = C$_5$Me$_5$
6 : M = Ru, L = C$_6$H$_6$

The molecular structures of **4−6** were determined by single-crystal X-ray diffraction analyses (Figures 1 and S1 in the Supporting Information).[6] The shapes of the three cluster complexes were found to be very similar to each other. The average distances between Co and M in cluster complex **4** (M = Rh), **5** (M = Ir), and **6** (M = Ru) were 2.609, 2.608, and 2.619 Å, respectively, which are nearly identical with those of Co−M bonds in other cluster complexes;[7−9] therefore, the cluster complexes described here were considered to have direct Co−M bonds. The metal framework is that of an isosceles triangle, and two Co−M bonds are bridged with S atoms of the metalladithiolene ring. The dihedral angles of the metalladithiolene framework, MSSC$_6$H$_4$, are in the region between 4.6 and 5.7° for **4−6**, and the metalladithiolene rings are almost planar, indicating that their quasi-aromaticities remain after the formation of cluster complexes. This result is in contrast to the case of the linear metalladithiolene cluster complex, [{CpCo-(S$_2$C$_6$H$_4$)}$_2$Mo(CO)$_2$], the quasi-aromaticity of which was lost after the creation of metal−metal bonds. It should be noted that the metalladithiolene ring of cluster complex **7**, which contained Ir and Co, was bent; however, we concluded that this conformation was the result of steric hindrance of the ligand. The interatom distances between Co and M (2.61−2.63 Å) and between Co and S (2.24−2.29 Å) are short enough for direct bonds to exist, but those between Co and C of the metalladithiolene ring (3.20−3.23 Å) are too long for direct Co−C bonds to exist; these features indicate that the metalladitholene rings coordinate to Co$_2$ in the η^3-bonding mode. There have been reports on Ru−Ru dinuclear complexes with a planar metalladithiolene framework involving the SCCS η^4 coordination of a metalladithiolene ring to a
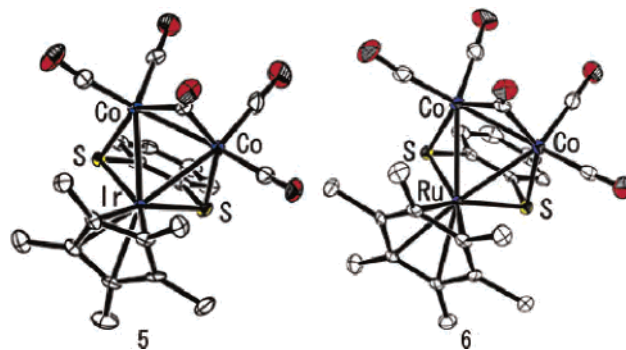
Figure 1. ORTEP drawing of cluster complexes **5** and **6** (50% probability).

metal complex and a long metal−metal distance (2.98−2.99 Å; **E** in Chart 1).[10] However, no previous examples of SMS η^3 coordination of a planar metalladithiolene moiety to a dinuclear complex moiety have been made available to date.

Variable-temperature ^{13}C NMR studies of **4−6** showed two peaks that were attributed to the carbon atoms of carbonyl groups around 200 ppm at 190 K; however, no peaks were observed in this region at 290 K (Figure S2 in the Supporting Information). These results indicate that the carbonyl groups move too rapidly to be observed by ^{13}C NMR at 290 K, although at 190 K, the decreased mobility of the carbonyl groups allows observation of these functional groups.

The IR spectra of **4−6** in the solid state showed two different types of carbonyl group absorbance peaks (Figure S3 in the Supporting Information). One such type was observed in the region from 1950 to 2030 cm^{-1}, which is generally attributed to terminal carbonyl groups, and the other type was in the region from 1780 to 1800 cm^{-1}, which is generally attributed to bridging carbonyl groups. These findings provide supportive evidence for the structures revealed by the X-ray crystallographic analyses. All of the carbonyl peaks of **6** were shifted to lower wavenumbers than those of **4** and **5**. The reason for this difference might be outlined as follows. The Ru atom of **6** is bound to a η^6-C$_6$-Me$_6$ ligand, which has greater electron donation ability than η^5-C$_5$Me$_5$ on the Rh (**4**) and Ir (**5**) atoms; therefore, the Co atoms of **6**, which directly bond to the Ru atom, receive more electron density than those of **4** and **5** connected with the Rh and Ir atoms, and the π-back-donations from the Co atoms to the carbonyl groups at cluster complex **6** are greater than those at cluster complexes **4** and **5**.

Theoretical calculations using the density functional theory (DFT) method were carried out for **5** (M = Ir, L = C$_5$Me$_5$) and **6** (M = Ru, L = C$_6$Me$_6$), based on the molecular structures determined by X-ray crystallography; their highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are shown in Figure 2. The LUMOs of **5** and **6** were found to be similar, but their respective HOMOs differed. The HOMO-1 of **5** (Ir−Co bonding) was very similar to the HOMO of **6** (Ru−Co bonding), and the HOMO-1 of **6** (Co−S bonding) was

(6) For **4**: C$_{21}$H$_{19}$Co$_2$O$_5$RhS$_2$, mol wt = 636.3, monoclinic, a =16.950-(3) Å, b = 14.6500(7) Å, c = 19.6300(5) Å, V = 4757.5(6) Å^3, space group $P2_1/c$, Z = 8, d_{calcd} = 1.777 g cm^{-3}, R1 [$I > 2\sigma(I)$] = 0.038, wR2 (all data) = 0.066. For **5**: C$_{21}$H$_{19}$Co$_2$IrS$_2$, mol wt = 725.6, monoclinic, a = 16.794(6) Å, b = 14.423(5) Å, c = 19.569(7) Å, V = 4625(3) Å^3, space group $P2_1/c$, Z = 8, d_{calcd} = 2.084 g cm^{-3}, R1 [$I > 2\sigma(I)$] = 0.021, wR2 (all data) = 0.029. Residual density located around the iridium atom. For **6**: C$_{23}$H$_{22}$Co$_2$O$_5$RuS$_2$, mol wt = 661.5, monoclinic, a = 10.096(4) Å, b = 16.310(6) Å, c = 15.174(6) Å, V = 2432(2) Å^3, space group $P2_1/n$, Z = 4, d_{calcd} = 1.807 g cm^{-3}, R1 [$I > 2\sigma(I)$] = 0.027, wR2 (all data) = 0.048.
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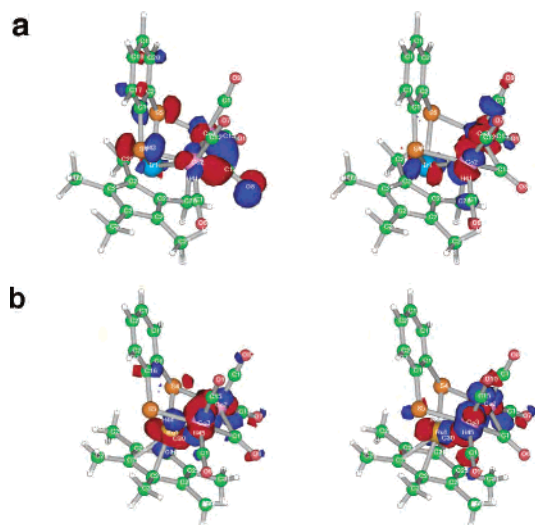
Figure 2. HOMOs (left) and LUMOs (right) of cluster complexes **5** (part a; M = Ir, L = C_5Me_5) and **6** (part b; M = Ru, L = C_6Me_6) calculated with the DFT(B3LYP) method. The core electrons of Co, Ru, and Ir were replaced with the effective core potential, and their valence orbitals were described with the LANL2DZ basis set. To the other atoms, the all-electron 6-31G basis set was applied.

identical with the HOMO of **5** (Co–S bonding); moreover, similar HOMO and HOMO-1 energy levels were observed in both compounds (see Figure S5 in the Supporting Information). To assign absorption bands in UV–vis–near-IR spectra, we carried out excited-state calculations by the time-dependent DFT,[11] which has been successfully applied to coordination compounds.[12] It has been shown that this method is reasonably accurate in comparison with refined post-Hartree–Fock methods.[12c] The calculations reproduced the obtained UV–vis–near-IR spectra fairly well (Figures S4 and S5 and Table S1 in the Supporting Information), and the lowest energy absorbance maximum in the UV–vis–near-IR spectrum [at 924 nm in dichloromethane (found), and at 1007 nm (calcd)] of **5** could be attributed primarily to the excitation from the HOMO to the LUMO. With regards to **6**, the lowest energy absorbance band was observed at 876 nm in dichloromethane and the absorbance maximum obtained from the theoretical calculations was at 893 nm, which could also be attributed primarily to the excitation from the HOMO to the LUMO.

In the cyclic voltammograms of **4–6** in Bu_4NClO_4–MeCN, one quasi-reversible $1e^-$ reduction wave was observed in the region between -1.04 and -1.14 V vs that of ferrocenium/ferrocene (Fc^+/Fc) (Table S2 and Figure S6 in the Supporting Information). These reduction potentials are located between those of the metalladithiolenes and **1–3** (-1.58 and -2.00 V in dichloromethane; $1e^-$, reversible) and the reduction potential of a related compound $[Co_2(CO)_8$, -0.42 V in THF; $1e^-$, irreversible]. The LUMOs of **5** and

6 shown in Figure 2 are for the most part localized around the Co_2 moiety and are less localized around the metalladithiolene; this environment is consistent with the position of the reduction potentials. The difference of the redox potentials around **4–6** was only 0.1 V; however, the difference of the mononuclear complexes **1–3** exceeded 0.4 V.

Thermochromism was observed in the case of **5** (Figure S7 in Supporting Information). The color of a solution of **5** in EtOH–MeOH–dimethylformamide (DMF) was dark brown at 300 K, but it turned to green at 77 K. Similar color changes were observed when **5** was dissolved in other solvents such as CH_2Cl_2 and when **5** was in the form of a KBr pellet. The UV–vis–near-IR spectrum of **5** in the form of a KBr pellet at 6 K revealed that several absorbance peaks shifted to the shorter wavelength and these peaks became sharper than those at 300 K. In addition, the IR spectrum of **5** in a KBr pellet at 300 K showed one broad peak attributed to $\nu(CC)$ and $\delta(CH)$ of a cyclopentadienyl ring around 1000 cm^{-1},[13] but several peaks appeared in the spectrum at 4 K, indicating that the rotation of the cyclopentadienyl ring stops when the temperature decreases. The peaks attributed to ν-($C\equiv O$) of the carbonyl groups also shifted and were sharper at 4 K than those at 300 K. These results indicate that the origin of thermochromism in the case of **5** is not a drastic change in the chemical structure but rather increased rigidity of the framework in accordance with the decrease in temperature, as mentioned above in the discussion of the variable-temperature ^{13}C NMR spectra. It should be noted that **4** and **6** also exhibited similar changes in the UV–vis–near-IR and IR spectra with decreases in temperature (Figures S8 and S9 in the Supporting Information).

In summary, we synthesized the first series of triangular cluster complexes of metalladithiolenes possessing a μ-S-bridged planar metalladithiolene ring. These cluster complexes are unique because of the maintenance of the planarity of the metalladitholene rings, despite the coordination of these rings to Co_2 in the η^3 mode. One possible explanation for this phenomenon is that two Co atoms are located just above the S atoms of the metalladithiolene rings, and the $p\pi$ orbitals of the S atoms can interact effectively with those of the Co atoms without perturbing the sp^2 configuration of the S atoms. In addition, these cluster complexes showed thermochromism with decreases in temperature.

Supporting Information Available: Details regarding the synthesis, characterization, ^1H and ^{13}C NMR spectra, UV–vis–near-IR spectra, and X-ray crystallography of **4–6**; an ORTEP drawing of **4**; DFT calculation results for **5** and **6**; and cyclic voltammograms of **4–6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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