

Dithiolato-Bridged [MRu₂] (M = Rh, Ir, Ru) Triangular 50e[−] Cluster Complexes Synthesized by Complete Metal Framework Reconstruction

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A method for synthesizing triangular dithiolene-bridged trinuclear cluster complexes $[\{LM(S_2C_6H_4)\}Ru_2(CO)_4(S_2C_6H_4)]$ [M = Rh, L = (η^5 -C₅Me₅); M = Ir, L = (η^5 -C₅Me₅); M = Ru, L = (η^6 -C₆Me₆)] by complete reconstruction of the metal framework was developed. The complexes thus obtained have 50

electrons around the metal atoms, indicating 3c4e[−] bonds; their molecular structures were determined by X-ray diffraction analyses and theoretical calculations.

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There have been various reports about syntheses of transition-metal cluster complexes and their unique properties, and the finding of a new metal–metal bond formation reaction and a new metal–metal bond character can lead to the creation of valuable metal cluster materials with novel chemical functions (including catalytic reactivity) and with novel optical, magnetic, and electronic properties.^[1] We have recently reported the synthesis of a triangular trinuclear heterometal cluster complex $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{S}_2\text{C}_6\text{H}_4)\}\text{Co}_2(\text{CO})_5]$ (**3**), a rare example containing a planar metalladithiolene ring.^[2] The number of the electrons around the trimetal framework in **3** is 48, adjusted to make three metal–metal single bonds in a triangle. We report here the unique reactivity of **3** and $[\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{S}_2\text{C}_6\text{H}_4)\}\text{Co}_2(\text{CO})_5]$ (**4**) [*p*-cymene = *p*-(Me₂CH)-C₆H₄Me], with mononuclear complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{S}_2\text{C}_6\text{H}_4)]$ (**1**) and $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{S}_2\text{C}_6\text{H}_4)]$ (**2**) to give new triangular cluster complexes composed of other metals. These reactions show the first complete reconstruction of the trimetal framework caused by successive metal–metal bond scission and formation reactions. The obtained complexes $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{S}_2\text{C}_6\text{H}_4)\}\text{Ru}_2(\text{CO})_4(\text{S}_2\text{C}_6\text{H}_4)]$ (**5**), $[\{(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{S}_2\text{C}_6\text{H}_4)\}\text{Ru}_2(\text{CO})_4(\text{S}_2\text{C}_6\text{H}_4)]$ (**6**), and $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{S}_2\text{C}_6\text{H}_4)\}\text{Ru}_2(\text{CO})_4(\text{S}_2\text{C}_6\text{H}_4)]$ (**7**) have triangular metal frameworks with 50 electrons around the trimetal framework, indicating that they belong to electron-rich compounds. Their unusual metal–metal bond properties

were clarified by X-ray crystallography and molecular orbital calculations.

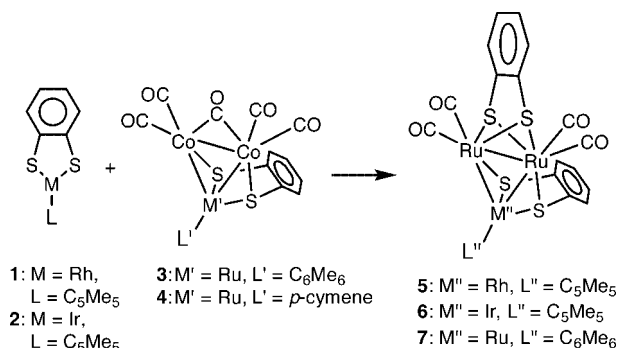
The reactions of the cluster complexes **3** and **4** with the mononuclear complexes **1** and **2** are summarized in Scheme 1 and Table 1. Scheme 1 shows the formation of the cluster complexes by transmetallation; products **5–7** were synthesized from another cluster complex consisting of completely different transition metals. There have been reports on syntheses of cluster complexes by transmetallation,^[1d] but the syntheses of cluster complexes by complete metal framework reconstruction is new. A mixture of **1** and **3** in a 1:1 molar ratio was refluxed in 1,4-dioxane to afford a red compound **5** in 41% yield based on the Ru cluster **3** (Entry 1). Product **5** seems to be generated from 1 equiv. of **1** and 2 equiv. of **3**; when the same reaction of **1** and **3** was performed in a 1:2 molar ratio, the same product **5** formed, however in a lower yield (24%). Similarly, the reaction of **2** with **3** gave the red compound **6** in 10% yield as a major product and a trace amount of **7** (Entry 2). The same cluster complexes **5** and **6** were obtained when **4** was used instead of **3**, but in relatively low yields (Entries 3 and 4). The trinuclear complexes **5–7** did not appear to be air- or moisture-sensitive either in the crystalline state or in solution, irrespective of their unusual electronic configuration (vide infra). In these reactions, a black powder precipitated which contained Co, but unfortunately it could not be characterized because of the insolubility in common solvents.

The molecular structures of **5**, **6**, and **7** were determined by single-crystal X-ray diffraction analysis, and an ORTEP drawing of **5** is shown in Figure 1.^[3] The metal frameworks of **5–7** are those of isosceles triangles, and the bond lengths and angles of **5–7** are similar to each other (Figure 1; Figures S1 and S2, Supporting Information). There are two benzenedithiolato ligands in **5**; one of them bridges two Ru atoms, and the other one bridges Rh and Ru atoms. The dihedral angle of the SRuS plane vs. the SCCS plane in the

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Scheme 1. Reactions of the mononuclear complexes **1** and **2** with the trinuclear cluster complexes **3** and **4**.

Table 1. Reactions of **1** and **2** with **3** and **4**.

Entry	Starting compounds	Products	Yield
1	1 + 3	5	41 %
2	2 + 4	6 (major) and 7 (minor)	10 % (for 6)
3	1 + 3	5	28 %
4	2 + 4	6	4 %

ruthenadithiolene in **5**, which bridges two Ru atoms, is 48.5°, indicating that the planarity of the metalladithiolene is lost; in contrast, the dihedral angle in the rhodiadithiolene, which bridges Rh and Ru atoms, is 15.5°, indicating that the planarity and thus the quasi-aromaticity of the metalladithiolene ring are not totally lost after coordination of S to Ru. The maintenance of the planarity of the metalladithiolene ring with the coordination of S to other metal atoms is rare but is found in some cases like **3**, [$\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{S}_2\text{C}_6\text{H}_4)\}\text{Co}_2(\text{CO})_5$] (**8**), and [$\{(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{S}_2\text{C}_6\text{H}_4)\}\text{Co}_2(\text{CO})_5$] (**9**), the structures of which are similar to each other.^[2] As mentioned above, an intriguing difference in the electronic structure of the trinuclear complexes between the starting materials **3** or **4** and the products **5–7** is the number of electrons around the three metal atoms; in **3** or **4** this number is 48, satisfying the 18-electron rule at each metal atom for three metal–metal single bonds in a triangle, which is common in transition-metal cluster complexes containing three metals in a triangular arrangement,^[4,5] whereas in **5–7** this number is 50. We have previously reported that the molecular structure of **3** as determined by X-ray crystallography is actually consistent with the existence of three metal–metal single bonds (Figure 2, closed form A).^[2] In contrast, the existence of two excess electrons around the trimetal framework in **5–7** suggests that some of the metal–metal bonds should be weaker than a single bond. Most trinuclear 50e[−] complexes are known to have linear or bent metal frameworks with two direct metal–metal single bonds (Figure 2, open form B),^[6] while some triangular cluster complexes exist that have more than 48 electrons around their metal frameworks and longer metal–metal bonds than the usual single metal bonds (Figure 2, closed form C).^[7] Compounds **5–7** are new examples of 50e[−] closed triangle complexes for which the Ru–Ru distance is 2.7648(4) Å, which is nearly equal to a single Ru–

Ru bond in other complexes.^[8] The average Rh–Ru distance is 3.019 Å, which is apparently longer than a single bond.

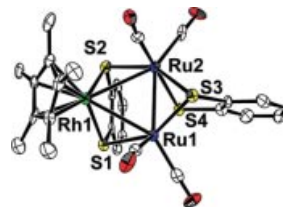


Figure 1. ORTEP drawing of **5** with 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1–Ru1 3.0062(4), Rh1–Ru2 3.0308(4), Ru1–Ru2 2.7648(4), Rh1–S1 2.2910(8), Rh1–S2 2.2968(8), Ru1–S1 2.3838(8), Ru1–S3 2.3862(9), Ru1–S4 2.4531(9), Ru2–S2 2.3832(9), Ru2–S3 2.3693(9), Ru2–S4 2.4555(9); Ru1–Rh1–Ru2 54.511(9), Rh1–Ru1–Ru2 63.198(9), Rh1–Ru2–Ru1 62.29(1).

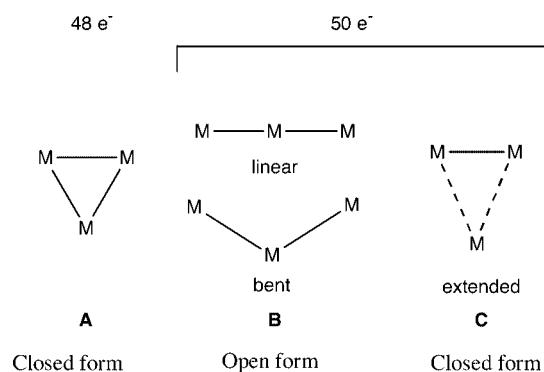


Figure 2. The metal frameworks of a trinuclear 48e[−] cluster complex and trinuclear 50e[−] cluster complexes.

To clarify the metal–metal bond characters in these 50e[−] triangle complexes, theoretical calculations were carried out for **5** using the DFT(B3LYP) method based on the molecular structures determined by X-ray crystallography. The HOMO of **5**, is drawn in Figure 3, together with the frontier orbitals of the molecular fragments, ($\eta^5\text{-C}_5\text{Me}_5$)Rh(S₂C₆H₄) and Ru₂(S₂C₆H₄)(CO)₄. The result shows that the HOMO of the Rh fragment is primarily the Rh d_{z²} orbital directing the midpoint of the Ru–Ru bond, and the LUMO of the Ru₂ fragment is the Ru–Ru π -bonding orbital primarily made up of d_{z²} orbitals of two Ru atoms. The HOMO of **5** is a bonding orbital among three metal atoms that includes π -electron donation from the HOMO of the Ru₂ fragment to the LUMO of the Rh fragment. Therefore, the trimetal framework is composed of one Ru–Ru single bond and one coordination bond from Ru₂ to Rh, and thus the trimetal bonding character in **5** is a three-centers-four-electrons (3c4e[−]) bond. This finding is consistent with the longer Ru–Rh distances than that observed for a regular Ru–Rh single bond. Compounds **6** and **7** can be elucidated to have similar 3c4e[−] characteristics according to their similarity in structure and in the bond length distribution to **5**.

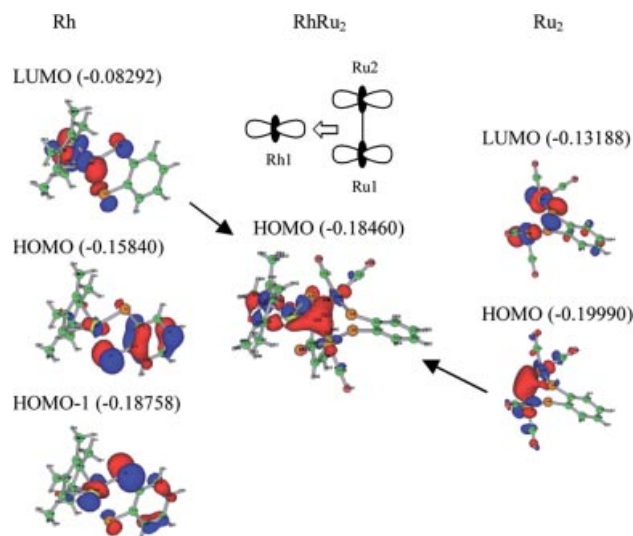


Figure 3. HOMO of **5** and frontier orbitals of the Ru₂ fragment and the Rh fragment calculated by the DFT(B3LYP) method. The core electrons of Ru and Rh have been replaced with the effective core potential, and their valence orbitals are described with the LANL2DZ basis set. To the other atoms, the all-electron 6-31G basis set was applied. Energy values of the orbitals in eV are given in the parentheses. The HOMO of **5** was composed of the interaction of an Ru–Ru π -bonding orbital (HOMO of the Ru₂ fragment) and an Rh orbital (LUMO of the Rh fragment).

UV/Vis/NIR spectra of **5** and **6** show no absorption peak around 900 nm, whereas **3**, **8**, and **9** have peaks attributable to the excitation from the HOMO to the LUMO.^[2] This result indicates that the energy gaps between the HOMO and the LUMO in 50e⁻ trinuclear cluster complexes **5–7** are larger than those in 48e⁻ trinuclear cluster complexes **3**, **4**, **8**, and **9** because the metal–metal bonds in **5–7** are weaker than those in **3**, **4**, **8**, and **9**. Cyclic voltammetry of **5–7** in Bu₄NClO₄ in CH₂Cl₂ showed an irreversible reduction peak at –1.79 V vs. ferrocenium/ferrocene, while metalladithiolene cluster complexes **3**, **4**, **8**, and **9** underwent reversible 1e⁻ reduction.^[2] This result indicates that the metal frameworks of **5–7** would be corrupted when electrons are added to the LUMO, the antibonding orbital of metal atoms.

Contrary to the reactions of **1** (Rh) or **2** (Ir) with **3** (RuCo₂) or **4** (RuCo₂), a mixture of **1** (Rh) and **9** (IrCo₂) in a 1:1 molar ratio was refluxed in 1,4-dioxane to give a 1:1 mixture of **8** (RhCo₂) and **9** (IrCo₂). The same result was obtained by the reaction of **2** (Ir) with **8** (RhCo₂). The differences in reactivity of the cluster complexes were thought to be due to the leaving ability of the ligands; neutral η^6 ligands, C₆Me₆ and *p*-cymene, on Ru cluster complexes **3** and **4**, have a higher leaving ability than C₅Me₅, an anionic η^5 ligand on Rh cluster complex **8** and Ir cluster complex **9**.

In summary, we have found a novel synthetic method for cluster complexes involving complete reconstruction of the trimetal framework. The cluster complexes obtained have 50 electrons around the trimetal framework, which is explained by a 3c4e⁻ bond character supported by bond lengths and theoretical calculation of molecular orbitals.

Supporting Information (see the footnote on the first page of this article): Synthesis, characterization of **8**, **9**, and **10**, ¹H and ¹³C NMR spectra and UV/Vis/NIR spectra of **8** and **9**, X-ray crystallography of **9** and **10**, DFT calculation results for **8**, and a cyclic voltammogram of **8**.

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