Inorganic Chemistry

Communication

pubs.acs.org/IC

# $Ir_3Co_6$ and $Co_3Fe_3$ Dithiolene Cluster Complexes: Multiple Metal–Metal Bond Formation and Correlation between Structure and Internuclear Electronic Communication

Satoru Tsukada,[†] Yusuke Shibata,[†] Ryota Sakamoto,[†] Tetsuya Kambe,[†] Tomoji Ozeki,[‡] and Hiroshi Nishihara*,[†]

[†]Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

[‡]Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551, Japan

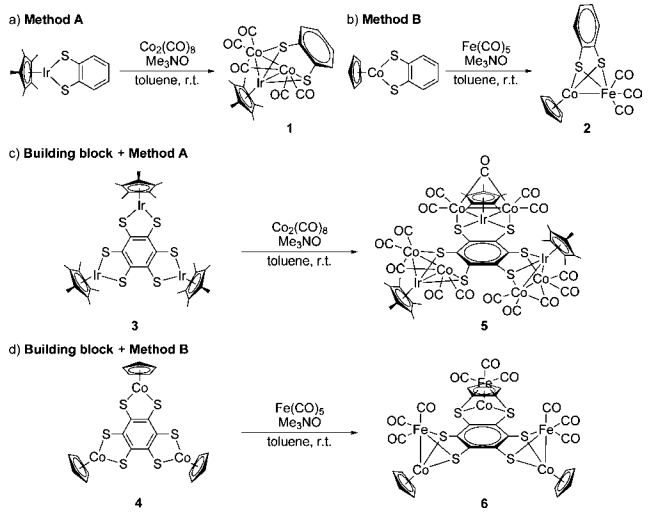
Supporting Information

**ABSTRACT:** π-Conjugated trinuclear iridium and cobalt dithiolenes undergo multiple metal–metal bond formation with $Co_2(CO)_8$ and $Fe(CO)_5$, giving rise to $Ir_3Co_6$ nonanuclear and $Co_3Fe_3$ hexanuclear cluster complexes **5** and **6**, respectively. **5** retains a planar framework and intense π conjugation across the three iridadithiolenes and the phenylene bridge, which results in intense electronic communication among the three $Co_2(CO)_5$ units in reduced mixed-valent states.

An important feature of metalladithiolenes is the quasi-aromaticity of the metal-containing five-membered ring.[1] The peculiar electronic structure can stabilize a $16e^-$ unsaturated coordination state at the metal center. This electron deficiency proved to be advantageous in an investigation of multinucleation of metalladithiolenes.[2−4] A major portion of this work exploited metal–metal bond formation reactions with low-valent metal molecules;[2,3] for example, we[3] and Jin et al.[5] independently synthesized neutral trinuclear $MCo_2$ metalladithiolene clusters (M = $Rh^{3+}$, $Ir^{3+}$, $Ru^{2+}$): The synthetic procedure for preparing the $IrCo_2$ cluster **1** is illustrated in Scheme 1a (method A). The main feature of this metal integration methodology was that the planarity of the metalladithiolene ring was retained, which preserved its quasi-aromaticity.[3a] On the other hand, a reaction of $CpCo(S_2C_6H_4)$ with $Fe(CO)_5$ produced a dinuclear CoFe cluster complex **2** (Method B, Scheme 1b),[2b] in which the metalladithiolene ring was bent, leading to a loss of the quasi-aromaticity.[2]

Another approach to the multinucleation of metalladithiolenes has used hexamercaptobenzene as a source of dithiolato ligands, which enables the fabrication of trinuclear metalladithiolene complexes featuring highly developed π conjugation.[4] The π-conjugated system in this series of complexes containing group 8–10 metals, such as **3** and **4** (Building Blocks, Scheme 1c,d), displayed intense electronic communication among the three dithiolene units in mixed-valent (MV) states. These findings stimulated a further question: Could the π-conjugated trinuclear dithiolene framework provide MV interactions among other redox-active sites? Given the background elaborated above, here we describe the fabrication of neutral nonanuclear and hexanuclear dithiolene cluster complexes **5** and **6** (Scheme 1c,d) in combination with the Building Blocks using Methods A and B, respectively. We disclose the single-crystal X-ray structures of **5** and **6** and focus on how altering the planarity of the trinuclear metalladithiolene backbone via metal–metal bond formation influences internuclear electronic communication in reduced MV states.

**Scheme 1. Multinucleation Methodologies for Metalladithiolenes**




Two potential structural isomers have syn and anti configurations, where the three $[Co_2]$ or [Fe] units all trend in the same direction and one of them faces away from the rest, respectively ($[Co_2]$ = $Co_2(CO)_5$ and [Fe] = $Fe(CO)_3$). The configurations were successfully identified by single-crystal X-ray structure analysis. **5** exclusively showed the anti structure (Figure 1a and Tables S1 and S2 in the Supporting Information, SI). The methyl groups on the Cp rings were split by a ratio of 2:1 in the $^1H$ NMR spectrum in chloroform-$d_1$ (Figure S1 in the SI), which also assured the anti configuration in solution. The absence of the syn isomer might be attributed to steric hindrance among the bulky $[Co_2]$ units. The Co–Ir distances (average: 2.610 Å) were nearly

**Received:** November 25, 2011
**Published:** January 26, 2012





dx.doi.org/10.1021/ic202548g | Inorg. Chem. 2012, 51, 1228–1230

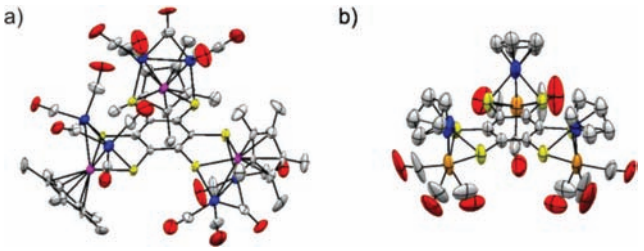



**Figure 1.** ORTEP drawings of (a) **5** and (b) **6** with thermal ellipsoids at the 50% probability level. Hydrogen atoms and crystal solvents are omitted for clarity. Color code: white, C; red, O; yellow, S; blue, Co; magenta, Ir; orange, Fe.

identical with those of Co−Ir bonds in other cluster complexes.[3a,6] Therefore, **5** included direct Co−Ir bonds. The interatomic distances between Co and S were short enough to permit direct bond formation. On the other hand, the Co−C distances were too large to possess direct bonds (Table S2 in the SI). These features indicated that the [$Co_2$] units were appended in an $\eta^3$-coordination fashion with one iridium and two sulfur atoms. The plane comprising the three iridadithiolene rings and the central phenylene bridge was slightly bent to form a bowl-like framework, but the extent of the bending was insignificant (the average S−C−C−S torsion angle was 5.72°). The shorter C−C bonds of the central phenylene belonged to the metalladithiolene five-membered rings, whereas the longer ones linked the rings together. The maximum difference among the C−C bond lengths was less than 0.06 Å [shortest, 1.36(2) Å; longest, 1.42(2) Å]. This difference was smaller than that of **3** (0.12 Å),[4b] indicating that the central phenylene of **5** was more strongly aromatic than that of **3**. In total, $\pi$ conjugation in **5**, which spanned the three iridadithiolene rings and the phenylene bridge, was expected to remain, even upon attachment of the [$Co_2$] units.

On the other hand, single-crystal X-ray structure analysis of **6** clarified the syn structure (Figures 1b and S12 in the SI). The protons on the Cp rings were all equivalent in a $^1$H NMR spectrum, which ensured the syn structure in solution. The Co−Fe distance in the crystal structure of **6** was 2.381 Å. This was nearly identical with other cluster complexes with direct Co−Fe bonds,[2b,7] indicating that the CpCo moiety and [Fe] unit were connected by a single Co−Fe bond. The sulfur atoms of the benzenehaxathiolato ligand constructed coordination bonds with both cobalt and iron (average bond distances: Co−S, 2.306 Å; Fe−S, 2.190 Å). On the other hand, the Co−C (average: 3.169 Å) and Fe−C distances (average: 3.115 Å) were too large to possess direct bonds. The dihedral angles between the benzenehaxathiolato ligand and the S−Co−S and S−Fe−S planes were 48.69° and 40.66°, respectively: Through incorporation of the [Fe] units, the planarity of the $CoS_2C_2$ rings was lost (Figure S12 in the SI), which also occurred in the previously described cluster complex **2**.[2b]

Figure 2 shows the representative frontier orbitals of **5** and **6** estimated by density functional theory (DFT) calculations; see Figures S4 and S11 in the SI for the rest of the orbitals]. In **5**, LUMO to LUMO+2 were mainly based on the [$Co_2$] units, with contributions from the iridium and sulfur atoms (Figures 2a and S4 in the SI). This agreed with the study of **1**,[3a] and assured that reductions in **5** initially occurred at the [$Co_2$] units. Above these three orbitals lay iridadithiolene($\pi^*$) orbitals (LUMO+3 to LUMO+5; Figure S4 in the SI), to which the iridium atoms provided the greatest contribution. On the other hand, HOMO−2 to HOMO contributed to the iridadithiolene-($\pi$) orbitals (Figures 2b and S4 in the SI). Here, the sulfur and carbon atoms contributed more electron density than iridium.

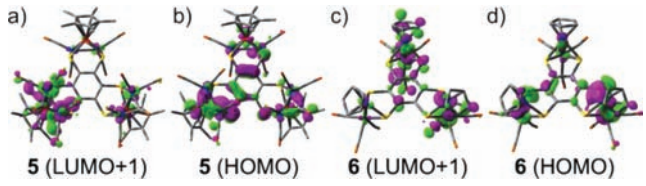



**Figure 2.** Representative frontier orbitals of **5** and **6** estimated by DFT calculations.

LUMO to LUMO+2 of **6** chiefly originated from the [Fe] units (Figures 2c and S11 in the SI): Therefore, the reduction should initially occur at the [Fe] units. LUMO+3 to LUMO+5 mainly stemmed from the cobalt ions, with small contributions from carbon and sulfur atoms comprising the dithiolene ring (Figure S11 in the SI). On the other hand, HOMO−2 to HOMO of **6** were based on both [Fe] units and cobalt ions (Figures 2d and S11 in the SI) by DFT calculations. This result contrasted sharply with the case of **5**, in which iridadithiolene-($\pi$) orbitals played a central role in HOMO−2 to HOMO (Figures 2b and S4) and could be rationalized by the fact that the $\pi$ system comprising the cobaltadithiolenes in **6** was disrupted by the bent structure.

Differential pulse voltammetry of **5** and **6** with respect to reductions was carried out (Figure S5 in the SI), and the numerical data are collected in Table 1, along with the data for

**Table 1. Electrochemical Data and Comproportionation Constant**

| | potential/V vs ferrocenium/ferrocene | | | comproportionation constant | |
|---|---|---|---|---|---|
| | $E^{\circ\prime}(\mathbf{X}^{2-}/\mathbf{X}^{3-})$ | $E^{\circ\prime}(\mathbf{X}^{2-}/\mathbf{X}^{2-})$ | $E^{\circ\prime}(\mathbf{X}/\mathbf{X}^{-})$ | log $K_c(\mathbf{X}^{2-})$ | log $K_c(\mathbf{X}^{-})$ |
| **5**[a] | −1.57 | −1.38 | −1.22 | 3.2 | 2.7 |
| **1**[b] | | | −1.27 | | |
| **6**[c] | −1.20 | −1.20 | −1.06 | 0.0 | 2.4 |
| **2**[d] | | | −1.48 | | |

[a]In 0.1 M $Bu_4NClO_4$−PhCN. [b]In 0.1 M $Bu_4NClO_4$−$CH_3CN$. Reference 3a. [c]In 0.1 M $Bu_4NClO_4$−PhCN/toluene (1:1 v/v). [d]In 0.1 M $Bu_4NClO_4$−$CH_3CN$. Reference 2b.

the related compounds **1** and **2**. **5** underwent three reversible one-electron reductions. Judging from the DFT calculations (Figures 2a,b and S4 in the SI), these redox waves could be assigned to electron donation to the three [$Co_2$] units. These three reductions in **5** occurred in a stepwise fashion, and these splits were assigned to electronic communication in the MV states. The comproportionation constant, $K_c$, which is one of the most convenient indicators of electronic communication, is defined as follows:[8]

$$K_c(\mathbf{X}^{-}) = [\mathbf{X}^{-}]^2/[\mathbf{X}][\mathbf{X}^{2-}] = \exp\{[E^{\circ\prime}(\mathbf{X}^{-}/\mathbf{X}^{-}) - E^{\circ\prime}(\mathbf{X}^{-}/\mathbf{X}^{2-})]F/RT\} \quad (1)$$

$$K_c(\mathbf{X}^{2-}) = [\mathbf{X}^{2-}]^2/[\mathbf{X}^{-}][\mathbf{X}^{3-}] = \exp\{[E^{\circ\prime}(\mathbf{X}^{-}/\mathbf{X}^{2-}) - E^{\circ\prime}(\mathbf{X}^{2-}/\mathbf{X}^{3-})]F/RT\} \quad (2)$$

where $[\mathbf{X}^{n-}]$ is the concentration of the chemical species $\mathbf{X}^{n-}$ and $E^{\circ\prime}(\mathbf{X}^{n-}/\mathbf{X}^{(n-1)-})$ is the formal potential of the $\mathbf{X}^{n-}/\mathbf{X}^{(n-1)-}$ redox couple. The log $K_c(\mathbf{5}^{-})$ and log $K_c(\mathbf{5}^{2-})$ values are


dx.doi.org/10.1021/ic202548g | Inorg. Chem. 2012, 51, 1228−1230

tabulated in Table 1. **5** yielded large values of log $K_c$, even in 0.1 M $NaBPh_4$/THF (Figure S6 and Table S3 in the SI), in which strong ion-pairing effects were present, and the Coulombic contribution to $K_c$ was consequently reduced.[9a,b] This assured that the contribution of electronic communication dominated the large $K_c$ of **5**. Astruc and co-workers have reported a contrastive molecular system that features no electronic communication among redox sites: In this system, the splits of the formal potentials of the redox sites have diminished in electrolyte solution with a strong ion-pairing ability.[9c] We note that the anti $[Co_2]$ unit experienced a chemical environment different from that of the other two counterparts, which could induce heterogeneous formal potentials. In the case of **5**, however, the heterogeneity was expected to be trivial: The platform for the $[Co_2]$ units, **4**, featured pseudo-$D_{3h}$ symmetry. Therefore, the $[Co_2]$ units received the same bonding fashion and experienced a similar extent of electronic communication, irrespective of the direction of the bond formation. A similar discussion had been applied toward the phenylene-annulated ferrocenyl trimer, in which electronic communication was observed, even in the anti isomer.[10] On the other hand, splits in the formal potentials upon reductions of **6** were less prominent than those of **5** (Figure S5b in the SI), even in less polar media, for example, a mixture of toluene and PhCN, which could enhance the Coulombic contribution. Considering the DFT calculations (Figures 2 and S4 and S11 in the SI), a plausible mechanism for electronic communication in **5** and **6** was electron superexchange via vacant orbitals or iridium or cobalt metalladithiolene $\pi^*$ orbitals (LUMO+3 to LUMO+5). This mechanism could well explain the experimental fact that **6** displayed weaker electronic communication because the $\pi^*$ orbitals were disrupted in **6** by the structural distortion, as observed in the X-ray structure (Figure 1b).

In conclusion, we synthesized nonanuclear $Ir_3Co_6$ and hexanuclear $Co_3Fe_3$ dithiolene metal cluster complexes **5** and **6** by means of our multinucleation methodologies applied to the $\pi$-conjugated trinuclear metalladithiolenes. **5** and **6** featured Co−Ir and Fe−Co metal−metal bonds, although the planar framework of the phenylene-bridged three metalladithiolenes was retained only in **5**. This planar configuration and the resultant $\pi$-conjugated electronic structure yielded strong electronic communication in the reduced MV states among the three $[Co_2]$ units in **5**. In sharp contrast, **6** displayed a far weaker interaction among the [Fe] units because of the bent metalladithiolene rings and the accompanying disrupted $\pi$ conjugation. Our methodology to build up gigantic multinuclear heterometal cluster complexes can contribute to one of the immature regions of chemistry: precise syntheses of metal-containing molecules. Also, this strategy involving the expression of distant electronic communication, utilization of $\pi$-conjugated metal complex bridges and metal−metal bond formation, and its controllability via structural changes in the bridge has provided new insight into MV chemistry.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details, crystallographic data of **5** and **6** (Tables S1, S2 and S4), $^1$H NMR spectrum of **5** (Figure S1), IR spectra of **5** and **6** (Figures S2 and S8), XPS of **5** and **6** (Figures S3 and S9), DFT calculations (Figures S4 and S11), cyclic voltammograms of **5** (Figures S5 and S6 and Table S3), and UV−vis spectra of **5** and **6** (Figures S7 and S10). This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION


### Corresponding Author

*E-mail: nisihara@chem.s.u-tokyo.ac.jp.


### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS


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


## ■ REFERENCES


(1) (a) Stiefel, E. I., Ed. Dithiolene Chemistry; Synthesis, Properties, and Applications. *Progress in Inorganic Chemistry*; Wiley: Hoboken, NJ, 2004; Vol. 52. (b) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295−369. (c) Burns, R. P.; McAullife, C. A. *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 303−348. (d) Fourmigue, M. *Coord. Chem. Rev.* **1998**, *178*−*180*, 823−864. (e) Sugimori, A.; Akiyama, T.; Kajitani, M.; Sugiyama, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 879−908. (f) Liu, S.; Han, Y.-F.; Jin, G.-X. *Chem. Soc. Rev.* **2007**, *36*, 1543−1560. (g) Meng, X.; Wang, F.; Jin, G.-X. *Coord. Chem. Rev.* **2010**, *254*, 1260−1272.

(2) (a) Nihei, M.; Nankawa, T.; Kurihara, M.; Nishihara, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1098−1100. (b) Murata, M.; Habe, S.; Araki, S.; Namiki, K.; Yamada, T.; Nakagawa, N.; Nankawa, T.; Nihei, M.; Mizutani, J.; Kurihara, M.; Nishihara, H. *Inorg. Chem.* **2006**, *45*, 1108−1116. (c) Zhu, B.-H.; Shibata, Y.; Muratsugu, S.; Yamanoi, Y.; Nishihara, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 3858−3861. (d) Muratsugu, S.; Sodeyama, K.; Kitamura, F.; Sugimoto, M.; Tsuneyuki, S.; Miyashita, S.; Kato, T.; Nishihara, H. *J. Am. Chem. Soc.* **2009**, *131*, 1388−1389. (e) Muratsugu, S.; Sodeyama, K.; Kitamura, F.; Tsukada, S.; Tada, M.; Tsuneyuki, S.; Nishihara, H. *Chem. Sci.* **2011**, *2*, 1960−1968.

(3) (a) Nakagawa, N.; Yamada, T.; Murata, M.; Sugimoto, M.; Nishihara, H. *Inorg. Chem.* **2006**, *45*, 14−16. (b) Nakagawa, N.; Murata, M.; Sugimoto, M.; Nishihara, H. *Eur. J. Inorg. Chem.* **2006**, 2129−2131.

(4) (a) Nishihara, H.; Okuno, M.; Kogawa, N.; Aramaki, K. *J. Chem. Soc., Dalton Trans.* **1998**, *120*, 2651−2656. (b) Shibata, Y.; Zhu, B.-H.; Kume, S.; Nishihara, H. *Dalton Trans.* **2009**, 1939−1943. (c) Kambe, T.; Tsukada, S.; Sakamoto, R.; Nishihara, H. *Inorg. Chem.* **2011**, *50*, 6856−6858.

(5) Wang, J.-Q.; Hou, X.; Weng, L.; Jin, G.-X. *Organometallics* **2005**, *24*, 826−830.

(6) (a) Herrmann, W. A.; Barnes, C. E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1985**, *4*, 172−180. (b) Hörlein, R.; Herrmann, W. A.; Barnes, C. E.; Weber, C.; Krüger, C.; Ziegler, M. L.; Zahn, T. *J. Organomet. Chem.* **1987**, *321*, 257−272. (c) Livotto, F. S.; Vargas, M. D.; Grepioni, F.; Braga, D. *J. Organomet. Chem.* **1993**, *452*, 197−203. (d) Chen, J.; Daniels, L. M.; Angelici, R. J. *Organometallics* **1996**, *15*, 1223−1229. (e) Chen, J.; Young, V. G.; Angelici, R. J. *Organometallics* **1996**, *15*, 1414−1421.

(7) (a) Mathur, P.; Sekar, P.; Satyanarayana, C. V. V.; Mahon, M. F. *J. Organomet. Chem.* **1996**, *522*, 291−295. (b) Manning, A. R.; McAdam, C. J.; Palmer, A. J.; Robinson, B. H.; Simpson, J. *Dalton Trans.* **2003**, 4472−4481. (c) Cai, S.; Hou, X.-F.; Chen, Y.-Q.; Jin, G.-X. *Dalton Trans.* **2006**, 3736−3741.

(8) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1−73 and references cited therein.

(9) (a) Barrière, F.; Geiger, W. E. *J. Am. Chem. Soc.* **2006**, *128*, 3980−3989. (b) Geiger, W. E.; Barrière, F. *Acc. Chem. Res.* **2010**, *43*, 1030−1039. (c) Diallo, A. K.; Absalon, C.; Ruiz, J.; Astruc, D. *J. Am. Chem. Soc.* **2011**, *133*, 629−641.

(10) Santi, S.; Orian, L.; Donoli, A.; Bisello, A.; Scapinello, M.; Benetollo, F.; Ganis, P.; Ceccon, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 5331−5334.