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## Heterometallic Complexes

# Efficient Synthesis of One- and Two-Dimensional Multimetallic Gold–Bis(dithiolene) Complexes

Michihisa Murata*[a] Shoji Kaji,[a] Hidetaka Nishimura,[a] Atsushi Wakamiya,[a] and Yasujiro Murata*[a]

**Abstract:** Multimetallic complexes having π-conjugated dithiolate ligands have recently received attention because of their unique solid-state properties. Reported herein are efficient and versatile routes for the synthesis of structurally well-defined multimetallic gold–bis(dithiolene) complexes. A dichlorogold(III) complex having a benzene-1,2-dithiolate ligand was prepared as a key terminal unit. A one-dimensional dimetallic gold complex was synthesized in good yield by using benzene-1,2,4,5-tetrathiolate as a bridging ligand. Furthermore, by using benzenehexathiolate as a bridging ligand, this strategy was applied to the synthesis of a two-dimensional trimetallic complex with a starburst structure. The solid-state structures of the anionic complexes were unambiguously confirmed by X-ray diffraction analyses.

## Introduction

One-dimensional (1D) polymers[1] and two-dimensional (2D) nanosheets[2] consisting of π-conjugated metal–bis(dithiolene) units have received significant attention because of their unique properties, which include high conductivity and magnetism, as well as their potential use in organic thermoelectric materials.[1h,1j,3] Whereas the relationship between the solid-state structure and the electronic properties of the monometallic bis(dithiolene) complexes with identical π-conjugated units (denoted as **A** for **1** in Figure 1) have been deeply studied from experimental and theoretical standpoints,[4] research on multimetallic complexes has remained largely unexplored thus far, owing in large part to the lack of an efficient and versatile route for their synthesis.

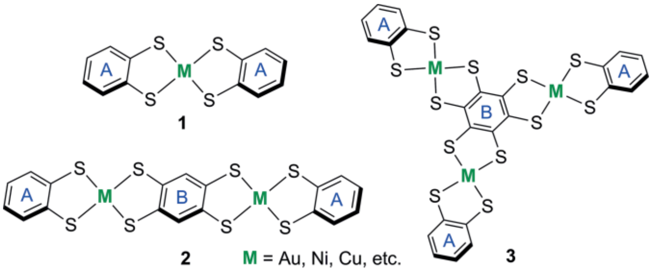

Figure 1. The structures of mono-, di-, and trimetallic bis(dithiolene) complexes **1**–**3**.

Over the past decades, di- and trimetallic bis(dithiolene) complexes have been mostly prepared with tetrathiooxalate (tto) ligand(s) as the linking bridge,[5] albeit in suppressed yields. For example, Kitagawa and co-workers recently reported the preparation of the dianion of the dimetallic nickel–bis(dithiolene) complex with the tto ligand in 3.4 % yield.[5f] Kato and co-workers reported the synthesis of a trimetallic nickel–bis(dithiolene) complex by using the tto ligands in ca. 5 % yield.[5e] Therefore, it is of great importance to establish a synthetic strategy from which a wide variety of π-conjugated multimetallic complexes can be realized. Herein, we report the development of a rational route for the synthesis of di- and trimetallic complexes that leads to the creation of not only 1D rod-shaped structure **2** but also 2D starburst structure **3** as potential precursors for molecular conductors. Whereas the structure of **3** is a segment of a multimetallic nanosheet,[2] this is the first example of the selective synthesis of the structurally well-defined 2D trimetallic complex. Gold complexes were selected not only because of their potential for molecular conductors[4] by oxidation but also because of the moderate stability against air oxidation, which permits characterization of the anionic complexes by NMR spectroscopy.

## Results and Discussion

For the preparation of multimetallic gold complexes **2** and **3**, which include two different π-conjugated ligands denoted as **A** and **B** for the terminal and bridging units (Figure 1), respectively, we anticipated that a dichlorogold(III) complex having a π-conjugated dithiolate ligand could be used as a key terminal unit. Thus, dichlorogold complex **5** with a benzene-1,2-dithiolate ligand was prepared as an air-stable green powder from dimethyltin complex **4** (Scheme 1).[6] The structure of dichlorogold complex **5** was unambiguously confirmed by single-crystal X-ray diffraction analysis (see the Supporting Information). Then, we studied the synthesis of the bridging ligands. Because unprotected 1,2,4,5-benzenetetrathiol was reported to

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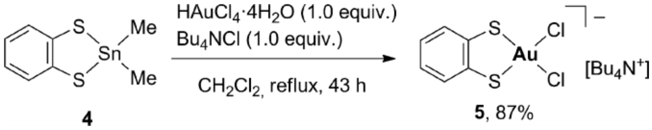
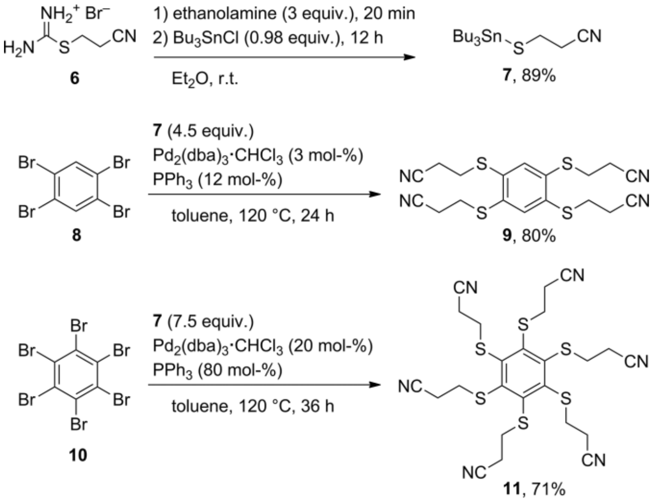
[a] *Institute for Chemical Research, Kyoto University,*
*Uji, Kyoto 611-0011, Japan*
*E-mail: mmurata@scl.kyoto-u.ac.jp*
*yasujiro@scl.kyoto-u.ac.jp*
*http://www.scl.kyoto-u.ac.jp/~kouzou/index.html*

*Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/ejic.201600595.*

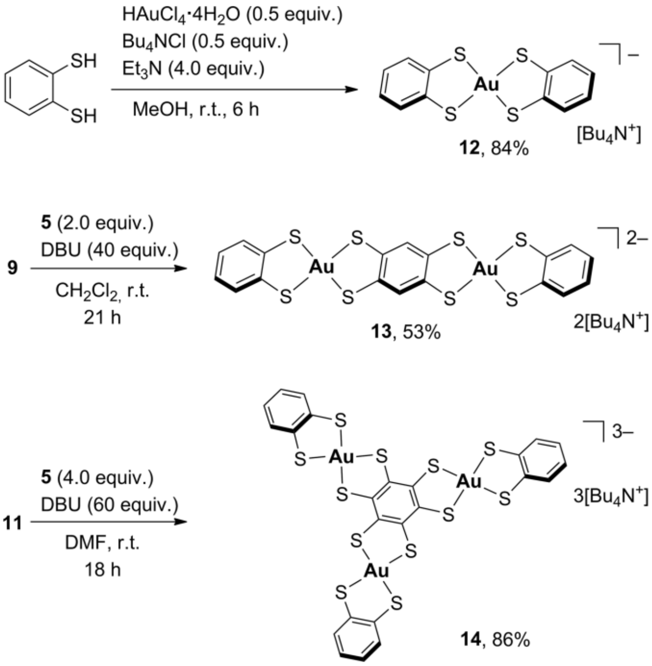
be air sensitive,[7] we developed routes for the synthesis of precursors **9** and **11**, in which the thiol groups were fully protected with cyanoethyl groups, by Stille coupling (Scheme 2).[8] Notably, we developed a useful method for the one-pot synthesis of tributylstannyl reagent **7**. This allowed us to isolate **7** in 89 % yield readily by extractions, whereas the conventional two-step synthesis includes isolation of 2-cyanoethanethiol with extreme stench by distillation and subsequent stannylation to give **7** only in 25 % overall yield.[9]



Scheme 1. Synthesis of dichlorogold(III) complex **5** as a terminal unit.



Scheme 2. Synthesis of **9** and **11** as the precursors for the bridging units; dba = dibenzylideneacetone.



Scheme 3. Synthesis of mono-, di-, and trimetallic complexes **12**–**14**.

We first performed the synthesis of simple monometallic complex **12**[10] by using triethylamine as the base and isolated **12** in 84 % yield as a green solid (Scheme 3). Then, the synthesis of the 1D dimetallic complex was examined with complex **5** and precursor **9** as the terminal and bridging units, respectively. Although the reaction did not proceed if triethylamine was employed, dimetallic complex **13** was synthesized efficiently in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). By simply washing the resulting precipitate with chloroform, **13** was obtained in 53 % yield as an air-stable yellowish green solid. Furthermore, this method could be applied to the synthesis of a 2D trimetallic complex with a starburst structure. Thus, reaction of **5** with precursor **11** under similar conditions gave trimetallic complex **14** in 86 % yield as an air-stable brown solid. Complexes **13** and **14** are well soluble in solvents such as dichloromethane, acetonitrile, DMF, and PhCN to degrees similar to that of monometallic complex **12**.

The structures of these complexes were characterized by $^1$H NMR and $^{13}$C NMR spectroscopy, mass spectrometry, as well as single-crystal X-ray diffraction analyses (Figures 2 and 3). Dimetallic and trimetallic complexes **13** and **14** were found to possess a slightly twisted structure; the twist angle between the terminal and central benzene rings is 6.1° for **13** and 4.0–6.6° for **14** (see the Supporting Information). The data for trimetallic complex **14** show that the Au–S bonds between Au and the central benzenehexathiolate ligand [2.305(1) Å[11] as an average for the inner six bonds] is slightly shorter than those between Au and the terminal benzene-1,2-dithiolate ligand [2.315(1) Å[11] as an average for the outer six bonds], whereas such a trend is not clearly seen in the structure of **13**. According to the results of the DFT calculations[12] [CAM-B3LYP/6-31G*, SDD (Au)], **13** and **14** optimized without countercations should have a planar structure. Thus, the twisted geometries in the solid state can be ascribed to the effect of the countercations and the crystal-packing forces, and this is indicative of the conformational flexibility of these complexes. In addition, the bond lengths of the inner Au–S bonds (2.34 Å) were calculated to be shorter than the outer Au–S bonds (2.38 Å), probably owing to the electron-rich character of the central ligand.

To clarify the electronic properties, we conducted cyclic voltammetry (CV) experiments for di- and trimetallic complexes **13** and **14** together with monometallic complex **12** for comparison (Table 1). Complexes **13** and **14** exhibit irreversible oxidation waves presumably as a result of adsorption phenomena on the electrode, as reported for monometallic complexes.[4h,5a,5b] The oxidation potentials [$E_{\text{onset,ox}}$ = –0.30 V vs. ferrocene/ferrocenium (Fc/Fc$^+$) for **13** and –0.42 V for **14**] are shifted to more negative values by $\Delta E_{\text{onset,ox}}$ = –0.58 and –0.70 V, respectively, with reference to the oxidation potential of **12** ($E_{\text{onset,ox}}$ = +0.28 V).[13] The data indicate that di- and trimetallic complexes **13** and **14** are markedly more electron rich than monometallic complex **12**. In the reduction process, **13** and **14** show irreversible reduction waves ($E_{\text{onset,red}}$ = –1.99 V for **13** and –2.04 V for **14**), and the potential is shifted to more negative values by $\Delta E_{\text{onset,red}}$ = –0.17 and –0.22 V, respectively, relative to that of

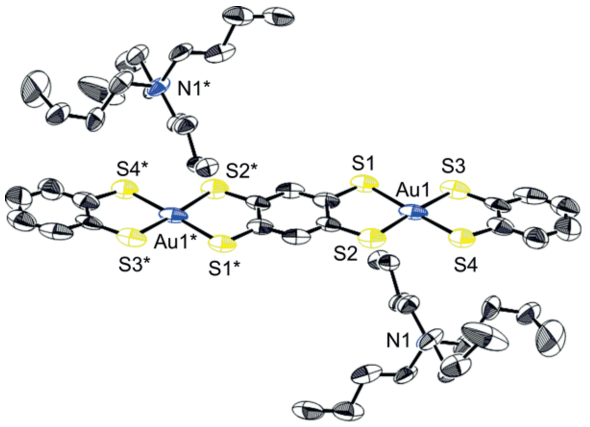


Figure 2. ORTEP drawing (50 % probability for thermal ellipsoids) of dimetallic complex **13**. Selected bond lengths [Å] and angles [°]: Au1–S1 2.323(4), Au1–S2 2.317(4), Au1–S3 2.323(4), Au1–S4 2.321(5), S1–Au1–S2 89.88(16), S1–Au1–S3 91.07(17), S2–Au1–S4 89.57(16), S3–Au1–S4 89.67(18).

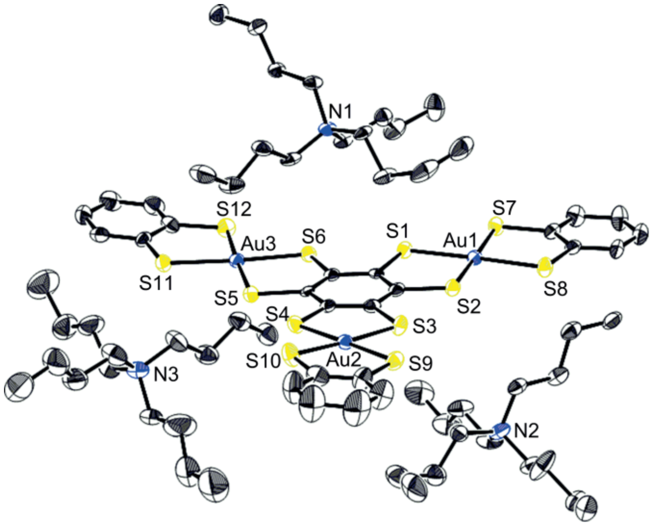


Figure 3. ORTEP drawing (50 % probability for thermal ellipsoids) of trimetallic complex **14**. Selected bond lengths [Å] and angles [°]: Au1–S1 2.304(2), Au1–S2 2.307(2), Au1–S7 2.314(2), Au1–S8 2.310(2), S1–Au1–S2 89.93(8), S1–Au1–S7 89.63(8), S2–Au1–S8 90.39(8), S7–Au1–S8 90.08(8).

**12**. The electron-rich characters of **13** and **14** were also demonstrated in bulk powder by means of photoelectron spectroscopy, which shows that the ionization potentials (IPs, HOMO levels) of the multimetallic complexes (–5.02 and –5.09 eV for **13** and **14**, respectively) are elevated relative to that of **1** (–5.51 eV), in good agreement with the results of the CV measurements. DFT calculations (see the Supporting Information) indicate that di- and trimetallic complexes **13** and **14** have well-delocalized π-orbitals (HOMO) and Au/ligand σ* orbitals (LUMO), both of which are doubly degenerate in the case of **14**, and this is indicative of the removal of an electron from the π orbital upon oxidation (Figure 4).

Monometallic complex **12** exhibits a weak absorption band with a maximum wavelength ($\lambda_{abs}$) at 637 nm in DMF. According to previous reports,[10] this band can be attributed to a symmetry-forbidden transition from the π orbital (HOMO) to the Au/ligand σ* orbital (LUMO) with charge-transfer character.

Table 1. Electrochemical and optical data.

| | Oxidation potential[a] $E_{onset,ox}$ [V] | Reduction potential[a] $E_{onset,red}$ [V] | HOMO[b] [eV] | $\lambda_{abs}$[c] [nm] (log ε) |
|---|---|---|---|---|
| **12** | +0.28 | –1.82 | –5.38 | 637 (1.75) |
| **13** | –0.30 | –1.99 | –4.80 | 685 (2.39) |
| **14** | –0.42 | –2.04 | –4.68 | 695 (2.58) |

[a] Onset potentials of the first oxidation peak measured by cyclic voltammetry in PhCN with $[Bu_4N^+][PF_6^-]$ (0.1 M) as a supporting electrolyte at a scan rate of 100 mV s$^{-1}$ by using Fc/Fc$^+$ as an internal standard. [b] HOMO levels estimated from the oxidation potentials by using the following equation: HOMO [eV] = $-(E_{onset,ox} + 5.1)$.[14] [c] Absorption maxima measured in DMF ($10^{-5}$ M), ε = absorption coefficient.

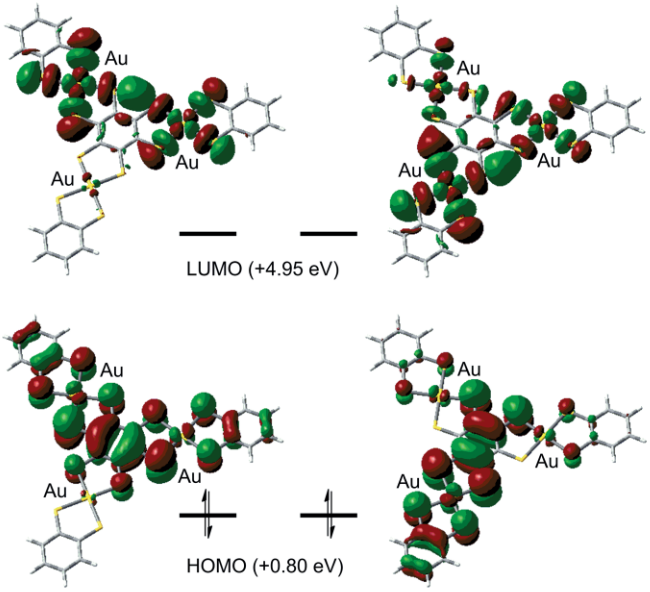


Figure 4. Pictorial representation of the frontier orbitals of trimetallic complex **14**. Geometry optimization was performed at the CAM-B3LYP/6-31G* (SDD for Au) level with no countercations.

Di- and trimetallic complexes **13** and **14** exhibit similar absorption bands at $\lambda_{abs}$ = 685 and 695 nm, respectively (Figure 5). It is notable that an intense absorption band is observed at $\lambda_{abs}$ =

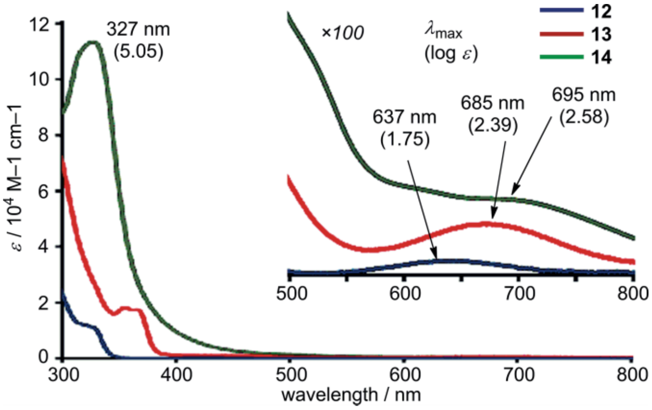


Figure 5. UV/Vis absorption spectra of **12**–**14** in DMF with their absorption maxima and logarithm of absorption coefficient. Inset shows the expanded spectra.

327 nm with a tail up to 460 nm for **14**. Single-point time-dependent DFT calculations [TD-CAM-B3LYP/6-31G*, SDD (Au), see the Supporting Information] for **13** and **14** indicate that the absorption bands in the visible region maintain the $\pi$–$\sigma^*$ character in a manner similar to that of **12**. The intense absorption band ($\lambda_{\mathrm{abs}}$ = 327 nm) observed for **14** is attributed to a transition having significant $\sigma$–$\sigma^*$ character (HOMO–8→LUMO, see the Supporting Information). Judging from the systematic comparison of the absorption spectra of the mono-, di-, and trimetallic complexes, the redshift in the $\sigma$–$\sigma^*$ transition band is remarkable, and a further redshift in this band can be expected upon increasing the number of gold–bis(dithiolene) segments.

## Conclusions

In summary, we demonstrated efficient and versatile methods for the synthesis of 1D and 2D multimetallic gold–bis(dithiolene) complexes with well-defined structures by using a dichlorogold(III) complex having a benzene-1,2-dithiolate ligand as a terminal unit. By using benzene-1,2,4,5-tetrathiolate as a bridging unit, a 1D rod-shaped dimetallic complex was synthesized in good yield. Furthermore, on the basis of this synthetic strategy, we prepared a 2D trimetallic complex with a starburst structure by using a benzenehexathiolate bridging unit. The solid-state structures of the anionic complexes were unambiguously revealed by X-ray diffraction analyses. The multimetallic complexes were shown to possess HOMO(s) that were elevated relative to that of the monometallic complex. The new synthetic methods can offer a way to prepare a wide variety of unprecedented 1D and 2D multimetallic gold–bis(dithiolene) complexes. Further studies on the structures and properties of the oxidized states as well as replacing gold with nickel or copper are currently underway in our group.

## Experimental Section

**Dimetallic Gold–Bis(dithiolene) Complex 13:** 1,8-Diazabicyclo-[5,4,0]-7-undecene (1.4 mL, 9.9 mmol) was added to a solution of **9** (100 mg, 0.239 mmol) and **5** (310 mg, 0.477 mmol) in dry $CH_2Cl_2$ (10 mL) under an argon atmosphere. After stirring for 21 h at room temperature, $CH_2Cl_2$ (100 mL) was added and the insoluble material was removed by filtration. The solvent was evaporated under reduced pressure, and the solid residue was washed with $CHCl_3$ to give **13** (173 mg, 0.127 mmol) in 53 % yield as a yellowish green solid, m.p. 257–259 °C (dec.). $^1H$ NMR (500 MHz, [D$_6$]acetone): $\delta$ = 7.06 (dd, $J$ = 6.0, 3.5 Hz, 4 H), 6.82 (s, 2 H), 6.73 (dd, $J$ = 6.0, 3.5 Hz, 4 H), 3.39 (m, 16 H), 1.78 (m, 16 H), 1.42 (m, 16 H), 0.96 ($t$, $J$ = 7.5 Hz, 24 H) ppm. $^{13}C$ NMR (126 MHz, [D$_6$]DMSO): $\delta$ = 141.59, 136.94, 127.88, 124.28, 123.09, 57.60, 23.11, 19.25, 13.55 ppm. HRMS (ESI-TOF–): calcd. for $C_{34}H_{40}NS_8Au_2$ [M – $Bu_4N^+$]$^-$ 1118.0732; found 1118.0751.

**Trimetallic Gold–Bis(dithiolene) Complex 14:** 1,8-Diazabicyclo-[5,4,0]-7-undecene (0.65 mL, 4.6 mmol) was added to a solution of **11** (45.0 mg, 76.4 µmol) and **5** (200 mg, 0.307 mmol) in dry DMF (4.5 mL) under an argon atmosphere. After stirring for 18 h, the mixture was quenched with aqueous $NH_4Cl$ and extracted with $CH_2Cl_2$. The solution was dried with $Na_2SO_4$, filtered, and evaporated under reduced pressure. The solid residue was dissolved in $CH_2Cl_2$ and then MeOH was added. The resultant precipitate was collected by filtration to give **14** (131 mg, 65.5 µmol) in 86 % yield as a brown solid, m.p. 151–152 °C (dec.). $^1H$ NMR (500 MHz, [D$_6$]acetone): $\delta$ = 7.09 (dd, $J$ = 6.0, 3.5 Hz, 6 H), 6.73 (dd, $J$ = 6.0, 3.5 Hz, 6 H), 3.30 (m, 24 H), 1.71 (m, 24 H), 1.41 (m, 24 H), 0.94 (t, $J$ = 7.5 Hz, 36 H) ppm. $^{13}C$ NMR (126 MHz, [D$_6$]acetone): $\delta$ = 140.59, 125.39, 124.40, 59.16, 24.09, 19.83, 13.51 ppm. HRMS (ESI-TOF–): calcd. for $C_{56}H_{84}N_2S_{12}Au_3$ [M – $Bu_4N^+$]$^-$ 1759.2285; found 1759.2218.

CCDC 1476788 (for **5**), 1476786 (for **13**), and 1476787 (for **14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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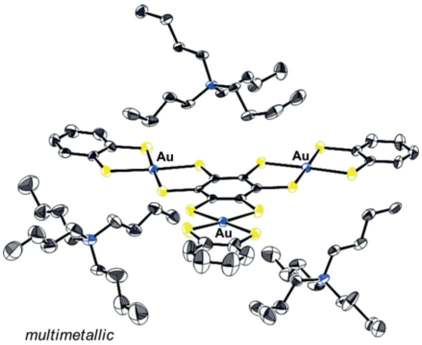
**Heterometallic Complexes**



multimetallic gold–bis(dithiolene) complex

We establish efficient and versatile methods for the synthesis of multimetallic gold–bis(dithiolene) complexes with well-defined structures. A two-dimensional trimetallic complex with a starburst structure is prepared and isolated in high yield. The solid-state structures of the complexes are unambiguously revealed by X-ray diffraction analyses.

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