# Unexpected Formation of the Novel Pentanuclear Heterodimetallic Metallamacrocycle $\{p\text{-}[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}Ph_4Sn_3S_3$

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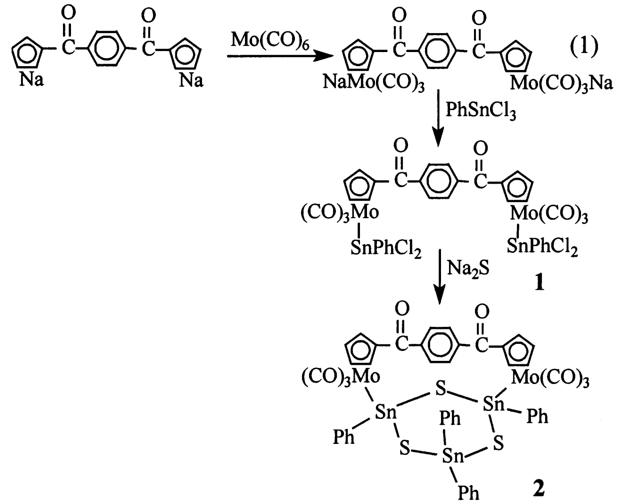
*Summary: Reaction of the dianion* $\{p\text{-}[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}^{2-}$ *with* $PhSnCl_3$ *yields the tetranuclear heterodimetallic complex* $p\text{-}[(PhCl_2Sn)(CO)_3MoC_5H_4C(O)]_2C_6H_4$ *(**1**). Treatment of complex **1** with* $Na_2S{\cdot}9H_2O$ *in boiling ethanol results in the novel pentanuclear heterodimetallic metallamacrocyclic complex* $\{p\text{-}[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}Ph_4Sn_3S_3$ *(**2**), which fuses a cyclic* $Sn_3S_3$ *system.*

## Introduction

Homo- and heteronuclear complexes have been widely investigated because of their interesting structural and reactive features as well as their potential utility as polyfunctional catalysts, or precursors for preparing other polynuclear heterogeneous catalysts,[1] and their chemistry has continued to be an active research area in organometallic chemistry in recent years. Among these complexes, heterodimetallic complexes with a directed polar metal−metal bond have attracted particular interest owing to their strikingly different reactivity and potential catalytic activity possibly for the sake of the cooperation effects of two metals.[2] Thus, a great number of heterometallic complexes containing the transition-metal−tin bond have been synthesized and characterized,[3] and some of them have proved to be very active and selective catalysts in many catalytic and stoichiometric processes.[3,4] We recently became interested in studying transition-metal−tin-bonded heterodimetallic complexes owing to their unusual structural features and reactivity.[5] In this paper we present a novel mode of reactivity of a transition-metal−tin-bonded heteronuclear complex. Reaction of $p\text{-}[(PhCl_2Sn)(CO)_3MoC_5H_4C(O)]_2C_6H_4$ with $Na_2S{\cdot}9H_2O$ yielded a novel pentanuclear heterodimetallic metallamacrocycle fusing a cyclic $Sn_3S_3$ system.

## Results and Discussion

Reaction of the dianion $\{p\text{-}[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}^{2-}$, prepared from the reaction of $Na_2\{p\text{-}[C_5H_4C(O)]_2C_6H_4\}$ with $Mo(CO)_6$ in situ, with $PhSnCl_3$ yielded the tetranuclear heterodimetallic complex $p\text{-}[(PhCl_2Sn)(CO)_3MoC_5H_4C(O)]_2C_6H_4$ (**1**), even with an excess of dianions, as shown in eq 1. No polymeric or cyclic products were obtained, and only one chloride on the tin atom was replaced by the metallic anion, indicating that the electron-withdrawing carbonyl groups on cyclopentadienyl rings possibly significantly decrease the nucleophilicity of cyclopentadienylmetal anions.[6]



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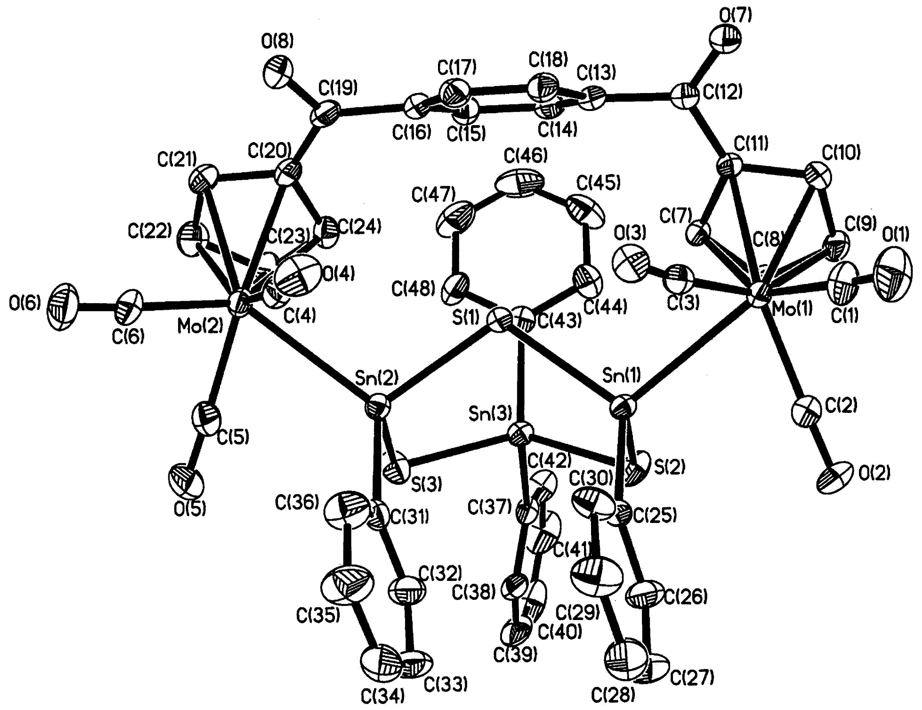

**Figure 1.** Molecular structure of **2**. Thermal ellipsoids are drawn at the 30% probability level.

Treatment of complex **1** with $Na_2S{\cdot}9H_2O$ in boiling ethanol resulted in the novel pentanuclear heterodimetallic metallamacrocyclic complex $\{p\text{-}[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}Ph_4Sn_3S_3$ (**2**), which was characterized by $^1H$ NMR spectroscopy, IR spectra, and elemental analyses, as well as by X-ray structural analysis. As shown in Figure 1, the molecule of **2** consists of a novel pentanuclear heterodimetallic metallamacrocyclic ring system, which simultanously fuses a cyclic $Sn_3S_3$ unit. It is noted that each tin atom in complex **1** is coordinated by only one phenyl group, while in complex **2** a new $SnPh_2$ unit is formed and linked to the sulfur atom with the salt elimination reaction. The formation of the $SnPh_2$ unit is not entirely clear, which is perhaps related to the redistribution reaction of the organotin moiety from the partial decomposition or reductive elimination of complex **1** under reductive conditions.[7]

In the molecule of **2** the two molybdenum centers adopt a 3:4 four-legged piano stool–square pyramidal structure, respectively, as calculated by Kubacek for $CpML_4$ complexes.[8] The average Mo–Sn bond distance is 2.799(1) Å (Table 1), which is within the normal range for Mo–Sn bonds.[3a] The average Sn–S bond distance is 2.417 Å, which is also comparable to the corresponding Sn–S bond distances in the six-membered rings of $(Ph_2SnS)_3$ (2.401 Å),[9] $[(PhSSn)_2(CH_2)_3]_2$ (2.403 Å),[10] $C_4H_7(PhSnS)_3$ (2.408 Å),[11] and $[Cp(CO)_2Fe]_2Sn_4S_6$ (2.426 Å),[12] respectively. However, the average ∠Sn–S–Sn of **2** (108.09°) is significantly larger than those in $(Ph_2SnS)_3$ (104.8°),[9] $[(PhSSn)_2(CH_2)_3]_2$ (99.62°),[10] and $C_4H_7(PhSnS)_3$ (94.3°),[11] respectively. It is interesting that O(7) and C(12) are nearly located coplanarly with the cyclopentadienyl plane but markedly deviate from the C(13)–C(18) phenyl plane, which are only 0.0025 (O(7)) and −0.0111 Å (C(12)) from the C(7)–C(11) cyclopentadienyl plane, but 0.0922 (O(7)) and −0.0723 Å (C(12)) from the C(13)–C(18) phenyl plane, respectively. The torsion angles of ∠C(10)–C(11)–C(12)–O(7) (2.2(11)°) and ∠O(7)–C(12)–C(13)–C(18) (−48.1(10)°) also indicate that the carbonyl group $\pi$-system is coplanar with the adjacent cycylopentadienyl ring system. The C(19)O(8) carbonyl group has also analogous coplanarity with the C(20)–C(24) cyclopentadienyl plane, compared with the C(12)O(7) carbonyl group. It is also noteworthy that

**Table 1. Selected Structural Parameters in Complex 2**

Bond Distances (Å)

| | | | |
|---|---|---|---|
| Mo(1)–Sn(1) | 2.8006(11) | Mo(2)–Sn(2) | 2.7903(11) |
| Sn(1)–S(1) | 2.4172(19) | Sn(1)–S(2) | 2.435(2) |
| Sn(2)–S(1) | 2.425(2) | Sn(2)–S(3) | 2.437(2) |
| Sn(3)–S(3) | 2.389(2) | Sn(3)–S(2) | 2.399(2) |
| Sn(1)–C(25) | 2.149(7) | Sn(2)–C(31) | 2.159(7) |
| Sn(3)–C(37) | 2.141(7) | Sn(3)–C(43) | 2.145(7) |

Bond Angles (deg)

| | | | |
|---|---|---|---|
| C(11)–C(12)–C(13) | 118.0(6) | C(25)–Sn(1)–S(1) | 114.8(2) |
| C(25)–Sn(1)–Mo(1) | 113.95(19) | S(1)–Sn(1)–Mo(1) | 105.22(5) |
| C(31)–Sn(2)–Mo(2) | 119.18(19) | C(31)–Sn(2)–S(3) | 103.1(2) |
| S(3)–Sn(3)–S(2) | 117.69(8) | C(37)–Sn(3)–S(2) | 101.6(1) |
| Sn(1)–S(1)–Sn(2) | 110.09(7) | Sn(3)–S(2)–Sn(1) | 106.90(7) |
| Sn(3)–S(3)–Sn(2) | 107.29(8) | | |

Torsion Angles (deg)

| | |
|---|---|
| C(10)–C(11)–C(12)–O(7) | 2.2(11) |
| C(17)–C(16)–C(19)–O(8) | 34.7(10) |
| S(1)–Sn(1)–S(2)–Sn(3) | −6.79(10) |
| O(7)–C(12)–C(13)–C(18) | −48.1(10) |
| O(8)–C(19)–C(20)–C(21) | 9.5(11) |
| Mo(1)–Sn(1)–S(1)–Sn(2) | −175.16(5) |

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some angles around the three tin atoms (such as ∠C(25)−Sn(1)−S(1) = 114.8(2)°, ∠C(31)−Sn(2)−Mo(2) = 119.18(19)°, and ∠S(3)−Sn(3)−S(2) = 117.69(8)°, respectively) significantly deviate from the tetrahedral geometry of the $sp^3$-hybridized tin centers.

Reaction of organotin halides[9] or bridged organotin halides, such as $CH_2(SnPhCl_2)$[13] and $CH(CH_2SnPhI_2)_3$,[11] with sulfide, yielding Sn−S-bonded ring or cage complexes, is well-known. The reaction of organotin halides containing transition-metal−tin bonds, such as $Cp(CO)_2FeSnCl_3$,[13] $[Cp(CO)_2Fe]_2SnCl_2$,[14] $[Cp(CO)_3Mo]_2SnCl_2$,[14] and $[(CO)_4Co]_2SnCl_2$,[15] with sulfide also yielded ring and adamantane structures. The rings or cages usually contain four to six members; no macrocyclic structures have been formed. In comparison with organotin halides containing transition-metal−tin bonds,[12−15] the present results exhibit a different mode of reactivity, which give a novel organometallic metallamacrocycle instead of an adamantane-like structure.[16] The bulky rigid terephthaloyl bridge as well as the incorporation of metal−metal bonds into the molecular entity possibly significantly affects the reactive pathway. Organotin heterocycles containing transition metals are well-known; these usually form small rings and fuse together to form more complex aggregates.[17] Organotin macrocycles containing transition metals have been less well explored,[18] and such macrocyclic complexes are also expected to have different reactivities and potential applications in host−guest chemistry for their selective recognition. The present investigation also shows that the introduction of heteroatoms and polar metal−metal bonds into the ring may induce distinctive reactivities. The structure of complex **2** also is a rare example of an organotin metallamacrocycle involving metal−metal bonds as integral parts of the molecular architecture and simultanously fusing a small heterocycle. Our research is continuing on properties of this metallamacrocycle and extensions to other bridged heteronuclear complexes and heteroatoms.

## Experimental Section

**General Considerations.** All reactions were carried out under an atmosphere of argon. Solvents were dried and distilled according to standard procedures. $^1H$ NMR spectra were recorded on a Bruker AC-P 200 spectrometer. IR spectra were recorded as KBr pellets on a Nicolet FT-IR 170SX spectrometer. Element analyses were carried out on a Perkin-Elmer 240C analyzer.

**Preparation of Complex 1.** $Na_2[p\text{-}C_5H_4C(O)]_2C_6H_4$ (1.1 mmol) was added to the solution of $Mo(CO)_6$ (2.0 mmol) in 30 mL of THF under Ar. The mixture was stirred and refluxed for 20 h to obtain a black-red solution of $Na_2[p\text{-}(CO)_3MoC_5H_4C(O)]_2C_6H_4$. After the mixture was cooled to room temperature, $PhSnCl_3$ (2.0 mmol) was added to the above solution by syringe, and the reaction mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and the residue was extracted with $CH_2Cl_2$. The extracted solution was passed through a short neutral alumina column eluted with $CH_2Cl_2$ to obtain a green-yellow solution. After the solvent was removed, the residue was recrystallized from $CH_2Cl_2$/hexane to yield green-yellow crystals of **1**. Yield: 42%. Anal. Found: C, 37.71; H, 2.06. Calcd for $C_{36}H_{22}Cl_4Mo_2O_8Sn_2$: C, 37.44; H, 1.91. IR (cm$^{-1}$): 2019.8 vs, 1965.8 s, 1935.1 vs ($\nu$(CO)); 1665.7 m ($\nu$(C=O)). $^1H$ NMR ($CDCl_3$): $\delta$ 7.82 (m, 4H, $C_6H_4$), 7.60 7.39, (m, m, 4H, 6H, $C_6H_5$), 6.02, 5,68 (t, t, 4H, 4H, $C_5H_4$). The same product was obtained when $Na_2[p\text{-}(CO)_3MoC_5H_4C(O)]_2C_6H_4$ reacted with $PhSnCl_3$ in a 1:1 ratio.

**Preparation of Complex 2.** $Na_2S{\cdot}9H_2O$ (0.2 mmol) was added to the solution of complex **1** (0.1 mmol) in 15 mL of ethanol under Ar. The mixture was stirred and refluxed for 4 h. After this mixture was cooled to room temperature, the solvent was removed under reduced pressure and the residue was extracted with $CH_2Cl_2$. The extracted solution was passed through a short neutral alumina column eluted with $CH_2Cl_2$ to obtain a yellow solution. After the solvent was removed, the residue was recrystallized from $CH_2Cl_2$/hexane to yield yellow crystals of **2**. Yield: 11%. Anal. Found: C, 41.36; H, 2.03. Calcd for $C_{48}H_{32}Mo_2O_8S_3Sn_3$: C, 41.71; H, 2.32. IR (cm$^{-1}$): 2013.2 vs, 1950.5 s, 1914.0 vs ($\nu$(CO)); 1662.2 m ($\nu$(C=O)). $^1H$ NMR ($CDCl_3$): $\delta$ 7.91 (m, 4H, $C_6H_4$), 7.48−6.67 (m, 20H, $C_6H_5$), 5.98, 5,66 (t, t, 4H, 4H, $C_5H_4$).

**X-ray Crystallographic Determination of 2.** Yellow crystals of **2** suitable for X-ray analysis were grown by slow diffusion of hexane into the $CH_2Cl_2$ solution of **2** at 277 K. Crystal data for **2**$\cdot 1.5CH_2Cl_2 \cdot 0.5H_2O$: $C_{49.5}H_{36}Cl_3Mo_2O_{8.5}S_3Sn_3$, $M_r = 1517.26$, triclinic, space group $P\bar{1}$, $a = 12.800(4)$ Å, $b = 14.624(5)$ Å, $c = 17.632(6)$ Å, $\alpha = 84.342(6)°$, $\beta = 71.524(5)°$, $\gamma = 64.114(5)°$, $V = 2813.3(16)$ Å$^3$, $Z = 2$, $D_{calcd} = 1.791$ g cm$^{-3}$, $T = 293$ K. A total of 9867 unique reflections were used for refinement ($R_{int} = 0.025$); final $R$ indices ($I > 2\sigma(I)$) were R1 = 0.0415 and wR2 = 0.0859.

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**Supporting Information Available:** Tables of crystallographic data, atom coordinates, thermal parameters, and bond distances and angles for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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