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Journal of Organometallic Chemistry 669 (2003) 57–63

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Tetranuclear heterodimetallic metallamacrocyles with M–Sn(IV) (M = Mo or W) bonds. Crystal structures of $\{p\text{-}[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}\{(Ph_2Sn)_2S\}$ and $\{p\text{-}[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}\{(Ph_2Sn)_2CH_2\}$

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Received 21 October 2002; received in revised form 5 December 2002; accepted 16 December 2002

Abstract

The dianions $\{[p\text{-}(CO)_3MC_5H_4C(O)]_2C_6H_4\}^{2-}$ reacted with Ph_2SnBr_2 in a 1:2 or 1:1 ratio to give tetranuclear heterodimetallic complexes $p\text{-}[(Ph_2BrSn)(CO)_3MC_5H_4C(O)]_2C_6H_4$ (M = Mo (**1**) or W (**2**), respectively), and with $CH_2(SnPhBr_2)_2$ to yield tetranuclear heterodimetallic metallamacrocycles $\{p\text{-}[(CO)_3MC_5H_4C(O)]_2C_6H_4\}\{(Ph_{2-n}Br_nSn)_2CH_2\}$ ($n = 1$, M = Mo (**5**) and W (**6**); $n = 0$, M = Mo (**7**) and W (**8**), respectively). Only one bromide on the tin atom was replaced by the metallic anions owing to the electron-withdrawing groups on the cyclopentadienyl rings greatly decreasing the nucleophilicity of the metallic anions. Treatment of complexes **1** and **2** with $Na_2S\cdot 9H_2O$ yielded the novel metallamacrocyclic complexes $\{p\text{-}[(CO)_3MC_5H_4C(O)]_2C_6H_4\}\{(Ph_2Sn)_2S\}$ (M = Mo (**3**) and W (**4**), respectively). All compounds have been characterized by elemental analyses, IR and ^1H-NMR spectra. The crystal structures of complexes **3** and **7** determined by X-ray crystallography indicate a novel 14-membered organometallic metallamacrocyclic ring system in which two Mo–Sn units are linked by the bridging cyclopentadienyl ligand and the sulfur or carbon atom. In addition, the carbonyl group π-system is coplanar with the adjacent cyclopentadienyl ring system, but markedly deviates from the bridging phenyl plane.

Keywords: Metallamacrocycle; Cyclopentadienyl; Molybdenum; Tungsten; Tin

1. Introduction

The metallamacrocyclic compounds have been extensively studied owing to their potential application in many aspects such as catalysis, sensing, molecular electronics, host–guest chemistry, and so on [1]. Among these compounds, the design and formation of organometallic metallamacrocyclic compounds have attracted particular interest owing to their fascinating structural features as well as molecular recognition and host–guest interactions [2]. Although numerous organometallic macrocycles with metal–metal bonds have been synthesized and characterized, such as those containing Ga–Ga [3], Rh–Rh [4], Fe–Fe [5], Mo/W–Co [6], Mo–Fe [7], few of organometallic macrocycles with transition metal–main group metal bonds have been reported. Organotin metallamacrocyclic compounds have been known for some time and found to be effective molecular hosts for anions and certain aromatic compounds [8–12]. However, organotin metallamacrocycles containing transition metals, especially involving metal–metal bonds as integral parts of the molecular architecture, are rare [13].

Our recent investigation on the transition metal–tin bonded heterodimetallic complexes displays that these complexes can be used as the construction of novel heteronuclear organometallic macrocycles [14]. Now we continue our investigation of heteronuclear metallamacrocyclic complexes with metal–metal bonds for the construction of the ring. Herein we report the synthesis of a series of tetranuclear heterodimetallic metallama-

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doi:10.1016/S0022-328X(02)02217-9

crocyles involving transition metal–tin bonds as integral parts of the molecular architecture.

2. Experimental

Diglyme, hexane and THF were distilled from sodium and benzophenone ketyl prior to use. All reactions were carried out under an argon atmosphere using standard Schlenk and Cannula techniques. The ^{1}H-NMR spectra were obtained with a Bruker AC-P 200 spectrometer, and the chemical shifts were reported in ppm with respect to the references. IR spectra data were obtained from a Nicolet FT-IR 170SX spectrometer using KBr discs. Element analyses were carried out on a Perkin–Elmer 240C analyzer. $CH_2(SnPh_2Br)_2$ and $CH_2(SnPhBr_2)_2$ were prepared by the published method [15].

2.1. Preparation of *p*-$[(Ph_2BrSn)(CO)_3MoC_5H_4C(O)]_2C_6H_4$ (**1**)

$Na_2[p\text{-}C_5H_4C(O)]_2C_6H_4$ (0.34 g, 1.1 mmol) was added to the solution of $Mo(CO)_6$ (0.53 g, 2.0 mmol) in 30 ml of THF. The mixture was stirred and heated at reflux for 20 h to obtain a black–red solution of $Na_2[p\text{-}(CO)_3MoC_5H_4C(O)]_2C_6H_4$. After cooling to room temperature (r.t.), Ph_2SnBr_2 (0.86 g, 2.0 mmol) was added to the above solution, and the reaction mixture was stirred overnight at r.t. The solvent was removed under a reduced pressure and the residual solid 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 removing the solvent, the residual solid was recrystallized from CH_2Cl_2–hexane to yield green–yellow crystals of **1**. Yield: 34%. ^{1}H-NMR ($CDCl_3$): δ 7.80 (m, 4H, C_6H_4), 7.61, 7.37 (m, m, 8H, 12H, C_6H_5), 5.99, 5.54 (t, t, 4H, 4H, C_5H_4). IR: $\nu_{CO} = 2019.9$ (vs), 1955.8 (s), 1925.1 (vs); $\nu_{C=O} = 1661.3$ (s) cm^{-1}. Anal. Calc. For $C_{48}H_{32}Br_2Mo_2O_8Sn_2.0.5CH_2Cl_2$: C, 42.53; H, 2.41. Found: C, 42.13; H, 2.52%. The same product was obtained when $Na_2[p\text{-}(CO)_3MoC_5H_4C(O)]_2C_6H_4$ reacted with Ph_2SnBr_2 in a 1:1 ratio.

2.2. Preparation of *p*-$[(Ph_2BrSn)(CO)_3WC_5H_4C(O)]_2C_6H_4$ (**2**)

$Na_2[p\text{-}C_5H_4C(O)]_2C_6H_4$ (0.34 g, 1.1 mmol) was added to the solution of $W(CO)_6$ (0.7 g, 2.0 mmol) in 20 ml of diglyme. The mixture was stirred and heated at reflux for 6 h to obtain a black–red solution of $Na_2[p\text{-}(CO)_3WC_5H_4C(O)]_2C_6H_4$. After cooling to r.t., Ph_2SnBr_2 (0.86 g, 2.0 mmol) was added to the above solution, and the reaction mixture was stirred overnight at r.t. After similar work-up employed for the isolation of **1**, green–yellow crystals of **2** were obtained. Yield: 36%. ^{1}H-NMR ($CDCl_3$): δ 7.80 (m, 4H, C_6H_4), 7.57, 7.35 (m, m, 8H, 12H, C_6H_5), 6.03, 5.65 (t, t, 4H, 4H, C_5H_4). IR: $\nu_{CO} = 2014.5$ (vs), 1947.3 (vs), 1916.2 (vs); $\nu_{C=O} = 1664.9$ (s) cm^{-1}. Anal. Calc. For $C_{48}H_{32}Br_2O_8Sn_2W_2.0.5CH_2Cl_2$: C, 37.68; H, 2.14. Found: C, 37.75; H, 2.39%. The same product was obtained when $Na_2[p\text{-}(CO)_3WC_5H_4C(O)]_2C_6H_4$ reacted with Ph_2SnBr_2 in a 1:1 ratio.

2.3. Preparation of {*p*-$[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}\{(Ph_2Sn)_2S\}$ (**3**)

$Na_2S\cdot 9H_2O$ (0.036 g, 0.15 mmol) was added to the solution of **1** (0.21 g, 0.15 mmol) in 20 ml of ethanol. The mixture was stirred and heated at reflux for 2 h. After cooling to r.t., the solvent was removed under a reduced pressure and the residual solid 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 removing the solvent, the residual solid was recrystallized from CH_2Cl_2–hexane to yield yellow crystals of **3**. Yield: 46%. ^{1}H-NMR ($CDCl_3$): δ 7.91 (s, 4H, C_6H_4), 7.81–7.06 (m, 20H, C_6H_5), 6.23, 5.65 (t, t, 4H, 4H, C_5H_4). IR: $\nu_{CO} = 1998.0$ (vs), 1937.5 (s), 1914.3 (sh), 1906.6 (vs); $\nu_{C=O} = 1665.2$ (m) cm^{-1}. Anal. Calc. For $C_{48}H_{32}Mo_2O_8SSn_2$: C, 48.08; H, 2.67. Found: C, 48.34; H, 2.94%.

2.4. Preparation of {*p*-$[(CO)_3WC_5H_4C(O)]_2C_6H_4\}\{(Ph_2Sn)_2S\}$ (**4**)

Compound **4** was obtained similarly using $Na_2S\cdot 9H_2O$ to react with compound **2** as described above for **3**. After similar work-up, yellow crystals of **4** were obtained. Yield: 48%. ^{1}H-NMR ($CDCl_3$): δ 7.90 (s, 4H, C_6H_4), 7.79–7.03 (m, 20H, C_6H_5), 6.26, 5.71 (t, t, 4H, 4H, C_5H_4). IR: $\nu_{CO} = 1994.5$ (vs), 1928.6 (s), 1914.3 (sh), 1894.7 (vs); $\nu_{C=O} = 1669.5$ (m) cm^{-1}. Anal. Calc. For $C_{48}H_{32}O_8SSn_2W_2$: C, 41.96; H, 2.35. Found: C, 41.56; H, 2.81%.

2.5. Preparation of {*p*-$[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}\{(PhBrSn)_2CH_2\}$ (**5**)

Compound **5** was obtained similarly using $CH_2(SnPhBr_2)_2$ (0.73 g, 1 mmol) to react with $Na_2[p\text{-}(CO)_3MoC_5H_4C(O)]_2C_6H_4$ (1 mmol) as described above for **1**. After similar work-up, yellow crystals of **5** were obtained. Yield: 43%. ^{1}H-NMR (DMSO-d_6): δ 7.76, 7.45 (m, m, 8H, 6H, C_6H_4 and C_6H_5), 5.62, 5.22 (t, t, 4H, 4H, C_5H_4). IR: $\nu_{CO} = 2017.6$ (vs), 1952.5 (vs), 1894.7 (vs); $\nu_{C=O} = 1668.9$ (s) cm^{-1}. Anal. Calc. For $C_{37}H_{24}Br_2Mo_2O_8Sn_2$: C, 37.44; H, 2.02. Found: C, 37.50; H, 1.91%.

2.6. Preparation of {p-$[(CO)_3WC_5H_4C(O)]_2C_6H_4\}\{(PhBrSn)_2CH_2\}$ (**6**)

Compound **6** was obtained similarly using $CH_2(SnPhBr_2)_2$ (0.73 g, 1 mmol) to react with Na_2[*p*-$(CO)_3WC_5H_4C(O)]_2C_6H_4$ (1 mmol) as described above for **2**. After similar work-up, yellow crystals of **6** were obtained. Yield: 38%. ^{1}H-NMR (CD_3COCD_3): δ 7.80 (m, 4H, C_6H_4), 7.59, 7.35 (m, m, 4H, 6H, C_6H_5), 6.03, 5.65 (t, t, 4H, 4H, C_5H_4). IR: $\nu_{CO}=2017.7$ (vs), 1952.1 (vs), 1894.3 (vs); $\nu_{C=O}=1668.5$ (s) cm^{-1}. Anal. Calc. For $C_{37}H_{24}Br_2O_8Sn_2W_2$: C, 32.60; H, 1.76. Found: C, 32.83; H, 1.95%.

2.7. Preparation of {p-$[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}\{(Ph_2Sn)_2CH_2\}$ (7)

Compound **7** was obtained similarly using $CH_2(SnPh_2Br)_2$ (0.72 g, 1 mmol) to react with Na_2[*p*-$(CO)_3MoC_5H_4C(O)]_2C_6H_4$ (1 mmol) as described above for **1**. After similar workup, green–yellow crystals of **7** were obtained. Yield: 37%. ^{1}H-NMR (DMSO-d_6): δ 7.83(s, 4H, C_6H_4), 7.80, 7.40 (m, m, 8H, 12H, C_6H_5), 5.62, 5.22 (t, t, 4H, 4H, C_5H_4). IR: $\nu_{CO}=2018.6$ (vs), 1951.8 (s), 1914.3 (sh), 1896.7 (vs); $\nu_{C=O}=1669.3$ (m) cm^{-1}. Anal. Calc. For $C_{49}H_{34}Mo_2O_8Sn_2$: C, 49.83; H, 2.98. Found: C, 50.13; H, 2.64%.

2.8. Preparation of {p-$[(CO)_3WC_5H_4C(O)]_2C_6H_4\}\{(Ph_2Sn)_2CH_2\}$ (**8**)

Compound **8** was obtained similarly using $CH_2(SnPh_2Br)_2$ (0.72 g, 1 mmol) to react with Na_2[*p*-$(CO)_3WC_5H_4C(O)]_2C_6H_4$ (1 mmol) as described above for **2**. After similar workup, green–yellow crystals of **8** were obtained. Yield: 36%. ^{1}H-NMR (DMSO-d_6): δ 7.85 (s, 4H, C_6H_4), 7.79, 7.38 (m, m, 8H, 12H, C_6H_5), 5.65, 5.23 (t, t, 4H, 4H, C_5H_4). IR: $\nu_{CO}=2008.4$ (vs), 1931.1 (s), 1903.5 (vs); $\nu_{C=O}=1668.0$ (m) cm^{-1}. Anal. Calc. For $C_{49}H_{34}O_8Sn_2W_2$: C, 43.36; H, 2.51. Found: C, 43.58; H, 2.82%.

2.9. X-ray crystallography

Crystals of **3** and **7** suitable for X-ray analysis were obtained from a CH_2Cl_2–hexane solution at −10 °C. Intensity data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo–K_α radiation ($\lambda=0.71073$ Å) using the $\omega/2\theta$ scan technique. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. A summary of the fundamental crystal data for **3** and **7** is listed in Table 1.

Table 1
Crystal data and refinement parameters for compounds **3** and **7**

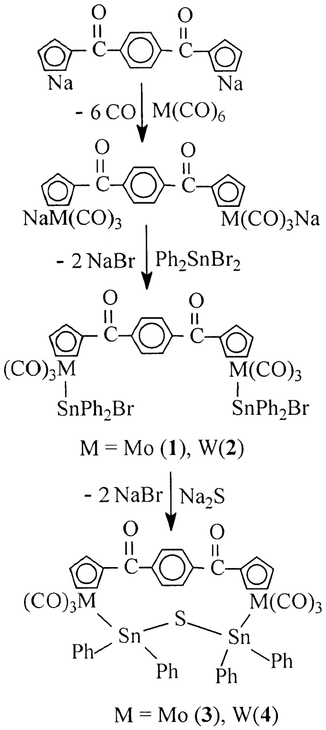
Compound	**3**	**7**
Formula	$C_{48}H_{32}Mo_2O_8SSn_2$	$C_{49}H_{34}Mo_2O_8Sn_2$
Formula weight	1198.06	1180.02
Crystal size (mm^3)	0.30 × 0.25 × 0.20	0.15 × 0.10 × 0.05
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*n*	*P*2(1)/*n*
Unit cell dimensions		
a (Å)	11.114(3)	17.444(9)
b (Å)	21.246(6)	11.965(6)
c (Å)	19.955(6)	25.838(13)
β (°)	102.887(5)	102.365(12)
V (Å)^3	4593(2)	5268(5)
Z	4	4
T (K)	293	293
D_{calc} (g cm^{-3})	1.732	1.488
F(000)	2336	2304
λ(Mo–K_α) (Å)	0.71073	0.71073
μ (mm^{-1})	1.705	1.448
No. of reflections measured	18941	21421
No. of reflections observed	8127 ($I\geq 2\sigma(I)$)	9258 ($I\geq 2\sigma(I)$)
No. of parameters	550	550
Residuals R, R_w	0.0323, 0.0607	0.0544, 0.1026
Goodness-of-fit on F^2	0.970	0.976

3. Results and discussion

3.1. Synthesis of sulfur-bridged organometallic metallamacrocyclic complexes

Treatment of the dianions of {[*p*-$(CO)_3MC_5H_4$-$C(O)]_2C_6H_4\}^{2-}$, prepared from the reaction of Na_2\{*p*-$[C_5H_4C(O)]_2C_6H_4\}$ with $M(CO)_6$ (M = Mo or W) in situ, with diphenyltin dibromide yielded only tetranuclear heterodimetallic complexes **1** and **2** in reasonable yield even with an excess of dianions (Scheme 1). No cyclic or polymeric products were obtained, indicating that the electron-withdrawing carbonyl groups on cyclopentadienyl rings significantly decrease the nucleophilicity of the cyclopentadienyl metallic anions. Complexes **1** and **2** were stable in air, and they were moderately soluble in chlorinated solvents. Although complexes **1** and **2** have six metal carbonyls and two ketone carbonyls, their IR spectra show only three typical metal carbonyl stretching bands in the range of 2020–1920 cm^{-1} and one absorption band of ketone carbonyl on ca. 1660 cm^{-1}, indicating that they may be symmetrical. Their ^{1}H-NMR spectra also exhibit the expected proton signals and two equivalent cyclopentadienyl rings. The Cp ring resonances appear as two triplets, which are separated by ca. 0.4–0.5 ppm.

Reaction of organotin halides containing transition metal–tin bonds, such as $Cp(CO)_2FeSnCl_3$ [16], $[Cp(CO)_2Fe]_2SnCl_2$ [17], $[Cp(CO)_3Mo]_2SnCl_2$ [17] and $[(CO)_4Co]_2SnCl_2$ [18] with sulfide, yielding Sn–S bonded ring or cage complexes, is well-known. The rings or cages usually contain four to six members; no macro-



Scheme 1.

cyclic structures have been formed. In the present work, the reaction of complexes **1** and **2** with $Na_2S \cdot 9H_2O$ in refluxing ethanol solution yielded novel organometallic metallamacrocyclic complexes **3** and **4**, which were characterized spectroscopically and by X-ray crystal structure analyses. The IR spectra of complexes **3** and **4** are similar with those in complexes **1** and **2**, with the exception of the metal carbonyls in complexes **3** and **4** significantly shifting toward lower wave numbers. This may be attributed to the donor property of sulfur as well as its smaller electronegativity compared with that of bromine weakening the d–d interactions of Sn–Mo, in turn strengthening metal–carbonyl back bonding. The replacement of the bromine in complexes **1** and **2** by the sulfur atom also results in the larger separation of the Cp ring resonances, which is ca. 0.5–0.6 ppm in complexes **3** and **4**.

The crystal structure of complex **3** determined by X-ray structure analyses is presented in Fig. 1. Selected bond lengths and angles are shown in Table 2. As shown in Fig. 1, the molecule of compound **3** consists of a novel 14-membered organometallic metallamacrocyclic ring system, in which two Mo–Sn units are linked by the bridging cyclopentadienyl ligand and the sulfur atom.

The molybdenum centers adopt a 3:4 four-legged piano stool–square pyramidal structure, as calculated by Kubacek for $CpML_4$ complexes [19]. The average Sn–Mo bond distance is 2.829(1) Å, which is similar with that in the acetylcyclopentadienyl complex $CH_3COC_5H_4Mo(CO)_3SnPh_2Cl$ (2.7683(6) Å) [20] and in the bridging cyclopentadienyl complex $[(Me_2SnCl)(CO)_3MoC_5H_4C(O)CH_2]_2$ (2.7755(3) Å) [21], p-$[(Ph_3Sn)(CO)_3MoC_5H_4C(O)]_2C_6H_4$ (0.28202(6) Å) [22] and $\{p\text{-}[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}Ph_4Sn_3S_3$ (2.799(1) Å) [14], respectively, but longer than that in 2,4-$(NO_2)_2C_6H_3NHN{=}C(CH_3)C_5H_4Mo(CO)_3SnCl_3$ (2.7040(7) Å) [23]. The average Sn–S bond distance is 2.426(1) Å, which is compared to those in $(Ph_2SnS)_3$ (2.401 Å) [24], $[(PhSSn)_2(CH_2)_3]_2$ (2.403 Å) [25], $C_4H_7(PhSnS)_3$ (2.408 Å) [26], $[Cp(CO)_2Fe]_2Sn_4S_6$ (2.426 Å) [16] and $\{p\text{-}[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}Ph_4Sn_3S_3$ (2.417 Å) [14], respectively. The dihedral angle between two cyclopentadienyl planes is 88.14°, indicating that they are nearly perpendicular to each other. The dihedral angle formed by the C(11)–C(15) cyclopentadienyl plane and the C(17)–C(22) phenyl plane is 51.11°, larger than the dihedral angle formed by the C(24)–C(28) cyclopentadienyl plane and the C(17)–C(22) phenyl plane (41.79°). It is interesting that O(7) and C(23) are nearly located coplanarly with the cyclopentadienyl plane, but markedly deviate from the C(17)–C(22) phenyl plane, which are only −0.0254 (O(7)) and 0.018 Å (C(23)) from the C(24)–C(28) cyclopentadienyl plane and 0.4305 (O(7)) and −0.1591 Å (C(23)) from the C(17)–C(22) phenyl plane, respectively. The torsion angles of ∠O(7)–C(23)–C(24)–C(28) (1.9(9)°) and ∠C(21)–C(20)–C(23)–O(7) (37.4(9)°) have also indicated that the carbonyl group π-system is coplanar with the adjacent cyclopentadienyl ring system. The C(16)O(8) carbonyl group has also analogous coplanarity with the C(11)–C(15) cyclopentadienyl plane, compared with the C(23)O(7) carbonyl group.

3.2. Synthesis of carbon-bridged organometallic metallamacrocyclic complexes

The reaction of the metallic dianions of $\{[p\text{-}(CO)_3MC_5H_4C(O)]_2C_6H_4\}^{2-}$ with bis(dibromophenylstannyl)methane or bis(bromodiphenylstannyl)methane yielded novel organometallic metallamacrocyclic complexes **5**–**8** (Scheme 2), which were also characterized spectroscopically and confirmed by X-ray crystal structure analyses. Complexes **5**–**8** were stable in air. They were slightly soluble in chlorinated solvents when precipitated out from the solvents. Their IR and ^1H-NMR spectra were similar, and analogous to those of complexes **1**–**4**.

The crystal structure of complex **7** determined by X-ray structure analyses is presented in Fig. 2. Selected bond lengths and angles are shown in Table 3. The overall view of **7** is analogous to that of complex **3**, but the sulfur bridge in complex **3** replaced by a carbon bridge. The configuration of two molybdenum centers is analogous to that in complex **3**. The average Sn–Mo bond distance is 2.852(1) Å, which is also compared with that in **3**. The average Sn–C(sp^3) bond distance (2.166

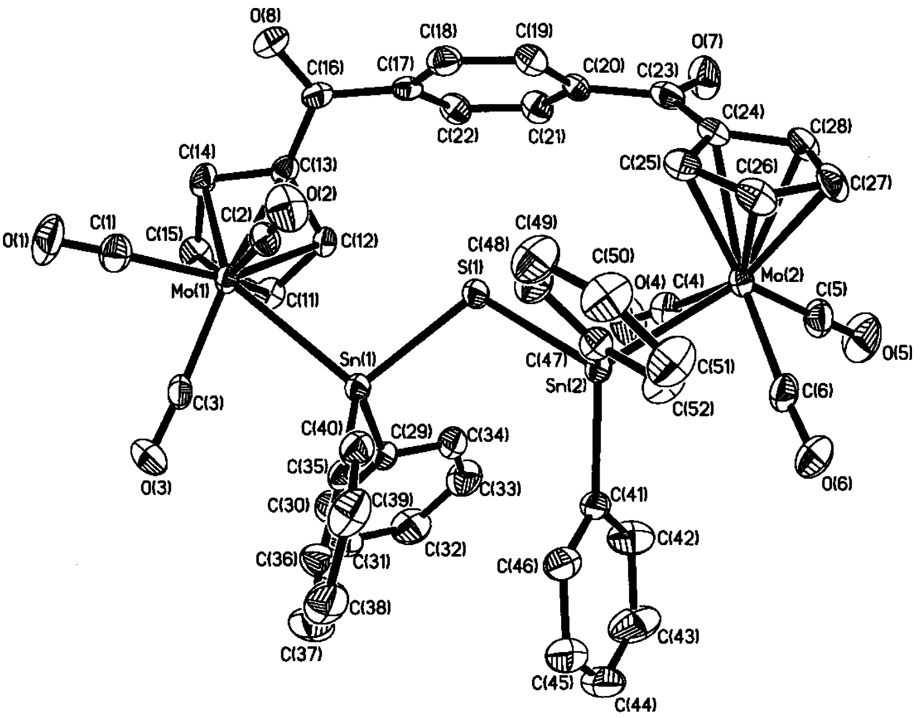
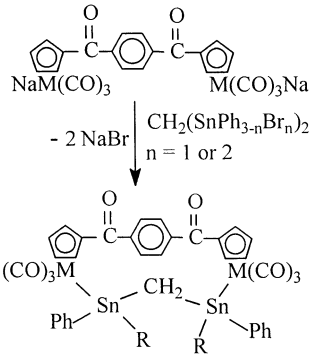


Fig. 1. The molecular structure of complex **3**. The thermal ellipsoids are drawn at the 30% probability level.

Å) is compared with that in $[(PhSSn)_2(CH_2)_3]_2$ (2.143 Å) and $[PhSn(S_2CNEt_2)]_2(S)(CH_2)_3$ (2.143 Å) [25], respectively. Two carbonyl group π-systems (C(12)O(7) and C(19)O(8)) are coplanarly arranged with their adjacent cyclopentadienyl ring systems like those in **3**. The torsion angles of ∠(7)–C(11)–C(12)–O(7) and ∠

Table 2
Selected bond lengths (Å) and bond angles (°) for **3**

Bond lengths			
Sn(1)–C(35)	2.149(6)	C(16)–C(17)	1.490(8)
Sn(1)–C(29)	2.162(6)	C(20)–C(23)	1.498(8)
Sn(1)–S(1)	2.427(1)	C(23)–C(24)	1.488(8)
Sn(1)–Mo(1)	2.823(1)	C(13)–C(16)	1.496(8)
Sn(2)–C(47)	2.153(6)	O(7)–C(23)	1.212(7)
Sn(2)–C(41)	2.161(6)	O(8)–C(16)	1.212(7)
Sn(2)–S(1)	2.425(1)	Sn(2)–Mo(2)	2.834(1)
Bond angles			
C(35)–Sn(1)–C(29)	109.8(2)	C(4)–Mo(2)–Sn(2)	73.0(1)
C(35)–Sn(1)–S(1)	110.4(1)	C(3)–Mo(1)–Sn(1)	71.9(1)
C(29)–Sn(1)–S(1)	106.4(1)	C(1)–Mo(1)–Sn(1)	131.5(1)
C(35)–Sn(1)–Mo(1)	118.7(1)	C(2)–Mo(1)–Sn(1)	72.9(1)
C(29)–Sn(1)–Mo(1)	107.0(1)	Sn(2)–S(1)–Sn(1)	110.9(6)
S(1)–Sn(1)–Mo(1)	103.7(4)	C(12)–C(13)–C(16)	129.3(5)
C(47)–Sn(2)–C(41)	108.0(2)	O(8)–C(16)–C(17)	121.7(6)
C(47)–Sn(2)–S(1)	104.8(1)	O(8)–C(16)–C(13)	120.7(6)
C(41)–Sn(2)–S(1)	114.3(1)	C(17)–C(16)–C(13)	117.6(6)
C(47)–Sn(2)–Mo(2)	105.8(1)	C(18)–C(17)–C(16)	119.1(6)
C(41)–Sn(2)–Mo(2)	116.7(1)	O(7)–C(23)–C(24)	120.0(6)
S(1)–Sn(2)–Mo(2)	106.4(4)	C(24)–C(23)–C(20)	119.5(5)
C(5)–Mo(2)–Sn(2)	129.6(2)	C(28)–C(24)–C(23)	122.5(5)
C(6)–Mo(2)–Sn(2)	72.1(1)	C(25)–C(24)–C(23)	130.2(6)
Torsion angles			
O(7)–C(23)–C(24)–C(28)	1.9(9)	O(7)–C(23)–C(24)–C(25)	−176.2(6)
C(19)–C(20)–C(23)–O(7)	−142.4(7)	C(21)–C(20)–C(23)–O(7)	37.4(9)
O(8)–C(16)–C(17)–C(22)	−138.8(7)	O(8)–C(16)–C(17)–C(18)	42.3(9)
C(12)–C(13)–C(16)–O(8)	−165.0(6)	C(14)–C(13)–C(16)–O(8)	11.8(9)



R = Br, M = Mo (**5**), W (**6**)
R = Ph, M = Mo (7), W (**8**)

Scheme 2.

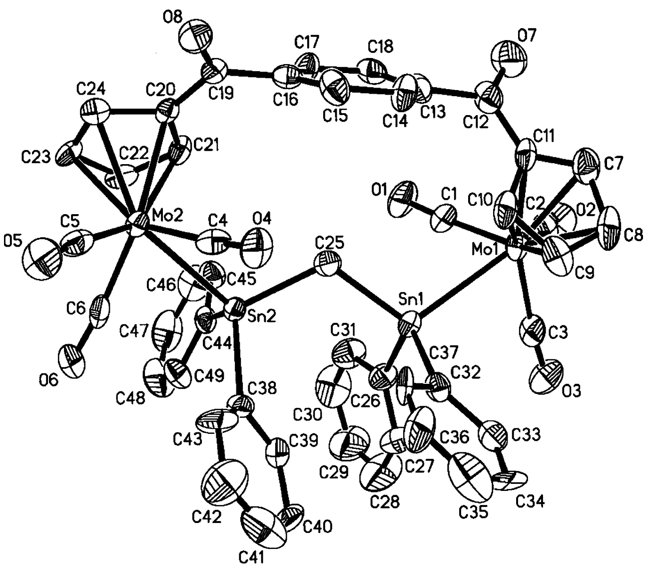


Fig. 2. The molecular structure of complex **7**. The thermal ellipsoids are drawn at the 30% probability level.

O(8)–C(19)–C(20)–C(24) are 1(2)° and 2.1(19)°, respectively. The replacement of the sulfur bridge by a carbon bridge has also led to some remarkable structural difference between complexes **7** and **3**. The dihedral angle between two cyclopentadienyl planes in **7** is 101.6°, which is larger than that in **3** (88.14°). The angle ∠Sn–C–Sn (117.8(5)°) in **7** is larger than the angle ∠Sn–S–Sn (110.91(6)°) in **3**, and significantly away from the tetrahedral geometry of the sp^3 hybridized carbon, indicating that the ring strain maybe exists in **7**. In addition, the angles ∠Mo(1)–Sn(1)–C(25) (109.9(3)°) and ∠Mo(2)–Sn(2)–C(25) (110.2(3)°) in **7** are in agreement with the tetrahedral tin center, while the angles ∠Mo(1)–Sn(1)–S(1) (103.769(4)°) and ∠Mo(2)–Sn(2)–S(2) (106.41(4)°) in **3** are slightly away from the tetrahedral tin center.

Table 3
Selected bond lengths (Å) and bond angles (°) for **7**

Bond lengths			
Mo(1)–Sn(1)	2.855(1)	C(19)–C(20)	1.480(15)
Mo(2)–Sn(2)	2.849(1)	O(7)–C(12)	1.209(14)
Sn(1)–C(32)	2.146(12)	O(8)–C(19)	1.192(12)
Sn(1)–C(26)	2.150(13)	C(11)–C(12)	1.438(18)
Sn(1)–C(25)	2.185(11)	C(12)–C(13)	1.506(18)
Sn(2)–C(25)	2.147(11)	C(16)–C(19)	1.500(16)
Sn(2)–C(44)	2.135(12)	Sn(2)–C(38)	2.144(13)
Bond angles			
C(1)–Mo(1)–Sn(1)	69.0(4)	C(6)–Mo(2)–Sn(2)	69.0(4)
C(2)–Mo(1)–Sn(1)	125.8(4)	C(4)–Mo(2)–Sn(2)	69.7(3)
C(3)–Mo(1)–Sn(1)	72.2(4)	C(5)–Mo(2)–Sn(2)	126.2(4)
O(7)–C(12)–C(11)	120.9(15)	C(32)–Sn(1)–C(26)	111.8(5)
O(7)–C(12)–C(13)	119.4(16)	C(32)–Sn(1)–C(25)	108.5(5)
C(11)–C(12)–C(13)	119.6(14)	C(26)–Sn(1)–C(25)	108.9(5)
C(18)–C(13)–C(12)	120.1(14)	C(32)–Sn(1)–Mo(1)	105.0(3)
C(14)–C(13)–C(12)	119.7(14)	C(26)–Sn(1)–Mo(1)	112.7(4)
C(15)–C(16)–C(19)	116.5(12)	C(25)–Sn(1)–Mo(1)	109.9(3)
O(8)–C(19)–C(20)	122.4(13)	C(44)–Sn(2)–C(38)	109.7(5)
O(8)–C(19)–C(16)	120.6(13)	C(44)–Sn(2)–C(25)	108.7(5)
C(20)–C(19)–C(16)	116.9(11)	C(38)–Sn(2)–C(25)	109.7(5)
Sn(2)–C(25)–Sn(1)	117.8(5)	C(44)–Sn(2)–Mo(2)	106.8(3)
C(25)–Sn(2)–Mo(2)	110.2(3)	C(38)–Sn(2)–Mo(2)	111.6(4)
Torsion angles			
C(7)–C(11)–C(12)–O(7)	1.0(2)	C(10)–C(11)–C(12)–O(7)	−173.2(14)
O(7)–C(12)–C(13)–C(18)	41.6(19)	O(7)–C(12)–C(13)–C(14)	−133.3(15)
O(8)–C(19)–C(20)–C(21)	−179.0(12)	O(8)–C(19)–C(20)–C(24)	2.1(19)
C(15)–C(16)–C(19)–O(8)	43.4(18)	C(17)–C(16)–C(19)–O(8)	−133.4(13)

In conclusion, a series of organometallic metallamacrocyclic complexes involving metal–metal bonds as the integral parts of the molecular architecture can be easily obtained by the convenient salt elimination reaction.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 195145 and 195146 for compounds **3** and **7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work is supported by the National Natural Science Foundation of China (no. 20172029) and the State Key Laboratory of Elemento-Organic Institute of Nankai University.

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