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Bridging cyclopentadienyl M–Sn(IV) bonded polymetallic complexes: X-ray crystal structures of $[(Me_2SnCl)(CO)_3MoC_5H_4C(O)CH_2]_2 \cdot CH_2Cl_2$ and $[(Ph_3Sn)(CO)_3WC_5H_4C(O)CH_2]_2 \cdot 3H_2O$

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Abstract

The dianions $[(CO)_3MC_5H_4C(O)CH_2]_2^{2-}$ reacted with R_nSnX_{4-n} in a 1:2 or 1:1 ratio to give tetranuclear complexes $[(R_nSnX_{3-n})(CO)_3MC_5H_4C(O)CH_2]_2$ (M = Mo or W; R = Ph or Me; X = Cl or Br; $n = 2$ or 3), which have been characterized by elemental analysis, ^{1}H NMR and IR spectroscopy. The electron-withdrawing groups on the cyclopentadienyl rings greatly decrease the nucleophilicity of the metallic anions. Thus, only one halogen atom on tin was replaced by the metallic anion when the dianions reacted with SnR_2X_2. The crystal structures of complexes **4** (M = Mo; R = Me; X = Cl; $n = 2$) and **5** (M = W; R = Ph; $n = 3$) were determined by X-ray crystallography, indicating that both Mo and W atoms adopt a 3:4 piano stool structure, and the Sn–M bond length is 2.7755(3) Å in complex **4** (Sn–Mo) and 2.8154(7) Å in complex **5** (Sn–W). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cyclopentadienyl; Molybdenum; Tungsten; Tin; X-ray crystal structure

1. Introduction

The chemistry of M–Sn(IV) bonded complexes has been the object of extensive studies owing to their applications in many catalytic and stoichiometric processes [1–4]. These complexes have direct bonding between different metals and hence may show different reactivities from those of mononuclear complexes [5,6]. The synthesis and reactivity of such compounds constitute an active area in organometallic chemistry. There are several synthetic methods for obtaining such complexes, such as oxidative addition and nucleophilic displacement reactions.

The cyclopentadienyl ligand has played an important role in the development of transition metal chemistry. As the electronic and steric characteristics of the ligand can easily be controlled by varying the substituents on the ring, the reactivity and physical properties of substituted cyclopentadienyl complexes are also very different from the unsubstituted analogues [7]. Many M–Sn bonded complexes containing the cyclopentadienyl ligand have also been prepared by salt elimination reactions in good yields [8], some of which have proved to be very active and selective for catalyzed olefin metathesis [9]. Our group has been interested in studying the M–Sn bonded bimetallic complexes in recent years [10,11]. We found that the electronic effect of substituents on cyclopentadienyl ligands has a great influence on the nucleophilicity of cyclopentadienyl metal anions [12]. In this paper, we describe the extension of the previous work and report the synthesis of bridging cyclopentadienyl M–Sn (M = Mo or W) bonded polynuclear complexes. The dianions $[(CO)_3MC_5H_4C(O)CH_2]_2^{2-}$ reacted with R_nSnX_{4-n} to give tetranuclear complexes $[(R_nSnX_{3-n})(CO)_3M\text{–}C_5H_4C(O)CH_2]_2$ (M = Mo or W; R = Ph or Me; X = Cl or Br; $n = 2$ or 3).

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2. Experimental

All reactions were carried out under an argon atmosphere using standard Schlenk and cannula techniques. Diglyme, hexane and THF were distilled from sodium and benzophenone ketyl prior to use. Element analyses were carried out on a Perkin–Elmer 240C analyzer. The ^{1}H NMR spectra were obtained with a Bruker AC-P 200 MHz spectrometer using $CDCl_3$ as solvent unless otherwise noted. 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. 1,4-Bis(cyclopentadienyl sodium)-1,4-butadione was prepared by published method [13].

2.1. Preparation of $[Na(CO)_3MoC_5H_4C(O)CH_2]_2$

1,4-Bis(cyclopentadienylsodium)-1,4-butadione (0.28 g, 1.1 mmol) was added to a solution of $Mo(CO)_6$ (0.26 g, 1.0 mmol) in 20 ml of THF. The mixture was stirred and refluxed for 20 h to obtain a blue black solution of $[Na(CO)_3MoC_5H_4C(O)CH_2]_2$. After cooling to room temperature, the solution was ready for subsequent use.

2.2. Preparation of $[(Ph_3Sn)(CO)_3MoC_5H_4C(O)CH_2]_2$ ***(1)***

To the above solution of $[Na(CO)_3MoC_5H_4C(O)CH_2]_2$ in THF, Ph_3SnCl (0.77 g, 2.0 mmol) was added and 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 yellow solution. After removing the solvent, the residue was recrystallized from CH_2Cl_2–hexane to yield yellow crystals of **1**. Yield: 38%. *Anal.* Found: C, 51.95; H, 3.48. Calc. for $C_{56}H_{42}Mo_2O_8Sn_2\cdot 1/2CH_2Cl_2$: C, 51.58; H, 3.27%. ^{1}H NMR: δ 7.52 (m, 12H); 7.34 (m, 18H); 5.77 (t, 4H); 5.32 (t, 4H); 2.78 (s, 4H) ppm. IR: ν (CO) 2001.4 (vs), 1935.8 (sh), 1892.4 (vs); ν (ketone CO) 1690.2 (m) cm^{-1}.

2.3. Preparation of $[(Ph_2SnCl)(CO)_3MoC_5H_4C(O)CH_2]_2$ ***(2)***

Compound **2** was obtained similarly using Ph_2SnCl_2 instead of Ph_3SnCl to react with the dianion. After a similar workup as employed for the isolation of **1**, yellow crystals of **2** were obtained. Yield: 43%. *Anal.* Found: C, 41.24; H, 2.61. Calc. for $C_{44}H_{32}Cl_2Mo_2O_8Sn_2\cdot 3/2CH_2Cl_2$: C, 41.47; H, 2.65%. ^{1}H NMR: δ 7.64–7.38 (m, 20H); 5.97 (t, 4H); 5.57 (t, 4H); 2.86 (s, 4H) ppm. IR: ν (CO) 1996.8 (s), 1925.8 (m), 1898.2 (s); ν (ketone CO) 1657.2 (m) cm^{-1}. The same product was obtained when the dianion was reacted with Ph_2SnCl_2 in a 1:1 ratio.

2.4. Preparation of $[(Ph_2SnBr)(CO)_3MoC_5H_4C(O)CH_2]_2$ ***(3)***

Compound **3** was obtained similarly using Ph_2SnBr_2 to react with the dianion as described above for **1**. After a similar workup, yellow crystals of **3** were obtained. Yield: 32%. *Anal.* Found: C, 40.85; H, 2.51. Calc. for $C_{44}H_{32}Br_2Mo_2O_8Sn_2$: C, 41.34; H, 2.50%. ^{1}H NMR: δ 7.64 (m, 8H); 7.38 (m, 12H); 5.93 (t, 4H); 5.46 (t, 4H); 2.85 (s, 4H) ppm. IR: ν (CO) 2021.7 (s), 1962.9 (s), 1919.5 (vs); ν (ketone CO) 1692.1 (m) cm^{-1}.

2.5. Preparation of $[(Me_2SnCl)(CO)_3MoC_5H_4C(O)CH_2]_2$ ***(4)***

Compound **4** was obtained similarly using Me_2SnCl_2 to react with the dianion as described above for **1**. After a similar workup, yellow crystals of **4** were obtained. Yield: 34%. *Anal.* Found: C, 29.51; H, 2.36. Calc. for $C_{24}H_{24}Cl_2Mo_2O_8Sn_2\cdot CH_2Cl_2$: C, 29.23; H, 2.53%. ^{1}H NMR: δ 5.97 (t, 4H); 5.49 (t, 4H); 2.98 (s, 4H); 0.95 (s, 12H) ppm. IR: ν (CO) 2003.5 (s), 1974.5 (s), 1928.4 (vs); ν (ketone CO) 1686.1 (m) cm^{-1}.

2.6. Preparation of $[Na(CO)_3WC_5H_4C(O)CH_2]_2$

1,4-Bis(cyclopentadienylsodium)-1,4-butadione (0.28 g, 1.1 mmol) was added to a solution of $W(CO)_6$ (0.35 g, 1.0 mmol) in 20 ml of diglyme. The mixture was stirred and refluxed for 6 h to obtain a blue–black solution of $[Na(CO)_3WC_5H_4C(O)CH_2]_2$. After cooling to room temperature, the solution was ready for subsequent use.

2.7. Preparation of $[(Ph_3Sn)(CO)_3WC_5H_4C(O)CH_2]_2$ ***(5)***

Ph_3SnCl (0.77 g, 2.0 mmol) was added to the above solution of $[Na(CO)_3WC_5H_4C(O)CH_2]_2$ in diglyme, and the mixture was stirred overnight at room temperature. Water (30 ml) was added to the mixture to precipitate out a black solid. After filtering and drying, the solid was dissolved in CH_2Cl_2 and passed through a short neutral alumina column eluted with CH_2Cl_2 to obtain a yellow solution. After removing the solvent, the residue was recrystallized from CH_2Cl_2–hexane to yield yellow crystals of **5**. Yield: 45%. *Anal.* Found: C, 45.27; H, 2.96. Calc. for $C_{56}H_{42}O_8Sn_2W_2\cdot 3H_2O$: C, 44.74; H, 3.20%. ^{1}H NMR: δ 7.48–7.33 (m, 30H); 5.80 (t, 4H); 5.42 (t, 4H); 2.77 (s, 4H) ppm. IR: ν (CO) 2006.9 (vs), 1943.9 (s), 1893.1 (vs); ν (ketone CO) 1688.1(m) cm^{-1}.

2.8. Preparation of $[(Ph_2SnCl)(CO)_3WC_5H_4C(O)CH_2]_2$ (**6**)

Compound **6** was obtained by a similar method as described for **5**. Yield: 45%. *Anal.* Found: C, 37.34; H, 2.42. Calc. for $C_{44}H_{32}Cl_2O_8Sn_2W_2\cdot CH_2Cl_2$: C, 37.24; H, 2.34%. ^1H NMR: δ 7.53–7.38 (m, 20H); 5.97 (t, 4H); 5.57 (t, 4H); 2.86 (s, 4H) ppm. IR: ν (CO) 1993.2 (s), 1891.8 (vs, br); ν (ketone CO) 1652.8 (m) cm^{-1}.

2.9. Preparation of $[(Ph_2SnBr)(CO)_3WC_5H_4C(O)CH_2]_2$ (**7**)

Compound **7** was obtained by a similar method as described for **5**. Yield: 38%. *Anal.* Found: C, 36.45; H, 2.42. Calc. for $C_{44}H_{32}Br_2O_8Sn_2W_2$: C, 36.31; H, 2.20%. ^1H NMR: δ 7.65 (m, 8H); 7.41 (m, 12H); 5.97 (t, 4H); 5.57 (t, 4H); 2.85 (s, 4H) ppm. IR: ν (CO) 2017.4 (s), 1955.3 (s), 1905.2 (vs); ν (ketone CO) 1692.5 (m) cm^{-1}.

2.10. Preparation of $[(Me_2SnCl)(CO)_3WC_5H_4C(O)CH_2]_2$ (**8**)

Compound **8** was obtained by a similar method as described for **5**. Yield: 36%. *Anal.* Found: C, 24.98; H, 2.10. Calc. for $C_{24}H_{24}Cl_2O_8Sn_2W_2\cdot CH_2Cl_2$: C, 24.95; H, 2.16%. ^1H NMR: δ 6.01 (t, 4H); 5.60 (t, 4H); 2.98 (s, 4H), 0.95 (s, 12H) ppm. IR: ν (CO) 2000.8 (s), 1973.5 (s), 1895.7 (s); ν (ketone CO) 1678.7 (m) cm^{-1}.

2.11. Preparation of $[(SnCl_3)(CO)_3MoC_5H_4C(O)CH_2]_2$ (**9**)

Compound **1** (0.64 g, 0.5 mmol) was dissolved in 20 ml of CH_2Cl_2 and the solution was cooled to −15°C. Dry HCl gas was continuously bubbled into the solution, the color of the solution slowly turned from light yellow to orange. After 30 min, the solvent was removed and the residue was recrystallized from CH_2Cl_2–hexane to afford yellow crystals of **9**. Yield: 88%. *Anal.* Found: C, 23.23; H, 1.61. Calc. for $C_{20}H_{12}Cl_6Mo_2O_8Sn_2$: C, 23.46; H, 1.17%. ^1H NMR: δ 6.13 (t, 4H); 5.76 (t, 4H); 3.00 (s, 4H) ppm. IR: ν (CO) 2046.6 (vs), 1966.5 (s), 1940.7 (s); ν (ketone CO) 1692.8 (m) cm^{-1}.

Table 1
Crystal data for **4** and **5**

Compound	$4\cdot CH_2Cl_2$	$5\cdot 3H_2O$
Formula	$C_{25}H_{26}Cl_4Mo_2O_8Sn_2$	$C_{56}H_{48}O_{11}Sn_2W_2$
M_r	1025.52	1502.02
Crystal size (mm)	0.10 × 0.25 × 0.30	0.20 × 0.25 × 0.30
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
Cell parameters		
a (Å)	37.712(3)	21.055(2)
b (Å)	7.1073(6)	19.761(2)
c (Å)	13.148(1)	15.924(2)
β (°)	103.327(2)	114.580(2)
V (Å^3)	3429.1(5)	6024.9(12)
Z	4	4
Reflections measured	6866	12481
Reflections observed	3038 $[I \geq 2\sigma(I)]$	4016 $[I \geq 2\sigma(I)]$
Parameters	189	330
Goodness-of-fit	1.026	1.088
Residuals R, R_w	0.023, 0.057	0.035, 0.12

2.12. Preparation of $[(SnCl_3)(CO)_3WC_5H_4C(O)CH_2]_2$ (**10**)

This compound was obtained by a similar method as described for **9**. Yield: 90%. *Anal.* Found: C, 20.32; H, 1.35. Calc. for $C_{20}H_{12}Cl_6O_8Sn_2W_2$: C, 20.02; H, 1.00%. ^1H NMR: δ 6.12 (t, 4H); 5.75 (t, 4H); 3.00 (s, 4H) ppm. IR: ν (CO) 2044.5 (s), 1967.5 (s), 1940.4 (s); ν (ketone CO) 1693.1 (m) cm^{-1}.

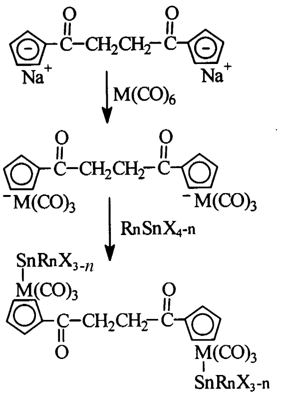
2.13. X-ray crystallography

Crystals of **4** and **5** 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 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 25°C to a maximum 2θ value of 50°. An empirical absorption correction was applied to intensity data. The structure was solved by direct methods and refined by full-matrix least-squares. The non-hydrogen atoms were refined anisotropically. The data collection and refinement parameters are summarized in Table 1.

3. Results and discussion

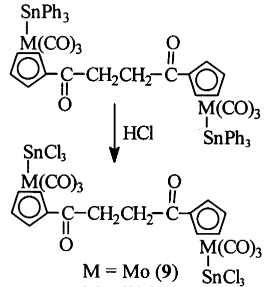
3.1. Synthesis and properties of complexes

Using the convenient salt elimination method, we have previously carried out the reaction of the anion of tricarbonyl cyclopentadienyl (or methylcyclopentadienyl) tungsten with diorganotin(IV) halides to afford W–Sn–W bonded trimetallic complexes. It was difficult to control the stepwise replacement of tin halide to form bimetallic complexes [14]. However, the reaction of the anion of tricarbonyl formyl [15] or acetylcyclopentadienyl [12] tungsten (molybdenum) with diorganotin(IV) halides only yielded Sn–M bonded bimetallic complexes, even with an excess of metal anions. In the present work, analogous results were obtained. The reactions of the dianions $[(CO)_3MC_5H_4C(O)CH_2]_2^{2-}$ with organotin(IV) halides yielded tetranuclear complexes **1**–**8** in reasonable yield, and only one halide atom of diorganotin dihalide was



R = Ph, X = Cl, n = 3, M = Mo (**1**) or W (**5**)
R = Ph, X = Cl, n = 2, M = Mo (**2**) or W (**6**)
R = Ph, X = Br, n = 2, M = Mo (**3**) or W (**7**)
R = Me, X = Cl, n = 2, M = Mo (**4**) or W (**8**)

Scheme 1.



M = Mo (**9**)
M = W (**10**)

Scheme 2.

replaced even with an excess of dianion (Scheme 1). No polymeric $\{[(Ph_2Sn)(CO)_3MC_5H_4C(O)CH_2]_2\}_n$ or cyclic $\{[(CO)_3MC_5H_4C(O)CH_2]_2SnPh_2\}$ products were obtained [16], indicating that the electron-withdrawing groups on cyclopentadienyl rings significantly decrease the nucleophilicity of cyclopentadienyl metal anions.

Reactions of complexes **1** and **5** with dry HCl in cool CH_2Cl_2 solution gave complexes **9** and **10** in good yields, respectively, which indicates that the metal–metal bonds in complexes **1** and **5** are stable (Scheme 2). All solid complexes are stable in air, and they are soluble in chlorinated solvents. There are six metal carbonyls and two ketone carbonyls in complexes **1**–**8**, but their IR spectra only show three typical metal carbonyl stretching bands in the range of 2020–1890 cm^{-1} and one absorption band of ketone carbonyl on the cyclopentadienyl ring between 1652 and 1692 cm^{-1}. These data show that the complexes may be symmetrical, which is consistent with the results of X-ray crystal structures of complexes **4** and **5**. A significant shift toward higher wave numbers for the metal carbonyls in complexes **9** and **10** is observed, compared with those in complexes **1** and **5**. This may be attributed to the electron-withdrawing effect of chlorine strengthening the d–d interactions of Sn–Mo and Sn–W, in turn weakening metal–carbonyl back bonding. The ^1H NMR spectra exhibit the expected proton signals and two equivalent cyclopentadienyl rings. The Cp ring resonances are observed as two triplets which are separated by ca. 0.4 ppm in all complexes. However, a downfield shift trend of cyclopentadienyl protons with an increased number of halide ligands is observed. This may be attributed to the influence of an electron-withdrawing effect of the halide through a π-bonding interaction [17].

3.2. Crystal structures of complexes 4 and 5

The C_2 molecular structure of **4** is presented in Fig. 1. Selected bond lengths and angles are shown in Table 2. There is one solvated CH_2Cl_2 molecule in the crystal. The molybdenum center adopts a 3:4 piano four-legged square pyramid structure, as calculated by Kubacek for $CpML_4$ complexes [18]. Two Sn–Mo units are linked by the $(\eta^5\text{-}C_5H_4COCH_2)_2$ ligand and are located in a mutually *trans* position. The Sn–Mo bond distance is 2.7755(3) Å, considerably shorter than the sum of covalent radii (1.39 + 1.61 Å), which indicates partial

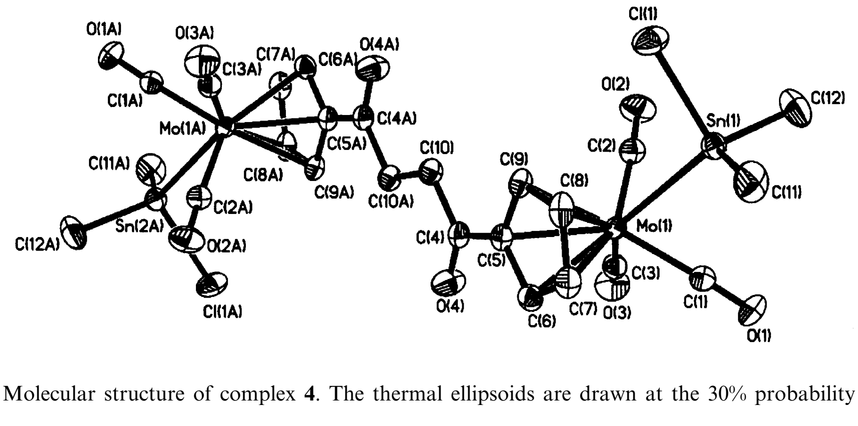


Fig. 1. Molecular structure of complex **4**. The thermal ellipsoids are drawn at the 30% probability level.

Table 2
Selected bond lengths (Å) and angles (°) for **4**

Mo(1)–C(2)	1.972(4)	C(1)–O(1)	1.145(4)
Mo(1)–C(1)	1.981(4)	C(2)–O(2)	1.139(4)
Mo(1)–C(3)	2.003(4)	C(3)–O(3)	1.125(4)
Mo(1)–C(5)	2.291(3)	C(4)–O(4)	1.205(4)
Mo(1)–C(6)	2.311(3)	C(4)–C(5)	1.481(5)
Mo(1)–C(9)	2.320(3)	C(4)–C(10)	1.491(5)
Mo(1)–C(7)	2.343(3)	Sn(1)–Cl(1)	2.399(1)
Mo(1)–C(8)	2.357(3)	Cl(2)–C(13)	1.743(5)
Mo(1)–Sn(1)	2.7755(4)	Sn(1)–C(11)	2.131(4)
Sn(1)–C(12)	2.115(4)		
C(2)–Mo(1)–C(1)	105.9(1)	C(12)–Sn(1)–C(11)	112.2(2)
C(2)–Mo(1)–C(3)	78.8(1)	C(12)–Sn(1)–Cl(1)	102.1(2)
C(1)–Mo(1)–C(3)	80.4(1)	C(11)–Sn(1)–Cl(1)	101.6(1)
C(2)–Mo(1)–Sn(1)	71.62(9)	C(12)–Sn(1)–Mo(1)	120.1(1)
C(1)–Mo(1)–Sn(1)	72.1(1)	C(11)–Sn(1)–Mo(1)	113.7(1)
C(3)–Mo(1)–Sn(1)	131.4(1)	Cl(1)–Sn(1)–Mo(1)	104.22(3)
C(5)–Mo(1)–Sn(1)	131.74(8)	O(1)–C(1)–Mo(1)	176.9(3)
O(4)–C(4)–C(10)	122.3(3)	O(2)–C(2)–Mo(1)	175.9(3)
C(5)–C(4)–C(10)	117.5(3)	O(3)–C(3)–Mo(1)	177.1(3)
C(9)–C(5)–C(4)	128.1(3)	O(4)–C(4)–C(5)	120.1(3)
C(6)–C(5)–C(4)	124.4(3)		

Table 3
Selected bond lengths (Å) and angles (°) for **5**

Sn(1)–C(11)	2.150(9)	W(1)–C(10)	2.349(8)
Sn(1)–C(23)	2.16(1)	W(1)–C(9)	2.373(9)
Sn(1)–C(17)	2.167(9)	O(1)–C(1)	1.16(1)
Sn(1)–W(1)	2.8154(7)	O(2)–C(2)	1.14(1)
W(1)–C(3)	1.964(9)	O(3)–C(3)	1.16(1)
W(1)–C(1)	1.97(1)	O(4)–C(5)	1.20(1)
W(1)–C(2)	1.99(1)	C(4)–C(5)	1.49(1)
W(1)–C(6)	2.298(8)	C(5)–C(6)	1.48(1)
W(1)–C(7)	2.313(8)	W(1)–C(8)	2.320(9)
C(11)–Sn(1)–C(23)	104.5(4)	O(4)–C(5)–C(6)	119.7(9)
C(11)–Sn(1)–C(17)	110.0(3)	O(4)–C(5)–C(4)	122.0(9)
C(23)–Sn(1)–C(17)	104.2(4)	C(6)–C(5)–C(4)	118.1(8)
C(11)–Sn(1)–W(1)	115.9(2)	C(10)–C(6)–C(5)	127.2(9)
C(23)–Sn(1)–W(1)	109.4(3)	C(7)–C(6)–C(5)	124.4(9)
C(17)–Sn(1)–W(1)	111.9(3)	C(16)–C(11)–Sn(1)	119.0(8)
C(3)–W(1)–C(1)	106.6(4)	C(12)–C(11)–Sn(1)	122.9(7)
C(3)–W(1)–C(2)	78.3(4)	C(3)–W(1)–Sn(1)	72.9(3)
C(1)–W(1)–C(2)	79.5(4)	C(1)–W(1)–Sn(1)	72.2(3)
C(24)–C(23)–Sn(1)	119.9(8)	C(2)–W(1)–Sn(1)	131.1(3)
O(1)–C(1)–W(1)	175.5(8)	C(18)–C(17)–Sn(1)	126.1(8)
O(2)–C(2)–W(1)	177.7(9)	C(22)–C(17)–Sn(1)	117.5(8)
O(3)–C(3)–W(1)	176.6(8)	C(28)–C(23)–Sn(1)	121.5(8)

multiple bond character in the Sn–Mo metal–metal bond (little π-bonding interactions between Sn and Mo) [19]. This bond distance is similar to that in the non-bridged acetylcyclopentadienyl complex $CH_3COC_5H_4$-$Mo(CO)_3SnPh_2Cl$ (2.7683(6) Å) [12], 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) [20]. The tin atom is a distorted tetrahedral geometry with Sn–C(11), Sn–C(12) and Sn–Cl(1) bond lengths of 2.131(4), 2.115(4) and 2.399(1) Å, respectively.

The molecular structure of **5** is shown in Fig. 2. Selected bond lengths and angles are shown in Table 3. There are three lattice water molecules in the crystal. The configuration of the tungsten atom is analogous to that of molybdenum atom in complex **4**. The Sn–W bond length is 2.8154(7) Å, which is slightly shorter than that in $CH_3C_5H_4W(CO)_3SnPh_3$ (2.8322(4) Å) [14], but longer than the Sn–Mo bond in complex **4**, for W and Mo have similar covalent radii. The configuration of the tin atom is analogous to that in complex **4**, namely a distorted tetrahedral geometry.

4. Supplementary material

Atomic coordinates, thermal parameters and bond lengths and angles for complexes **4** and **5** have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 146944 and 146945. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

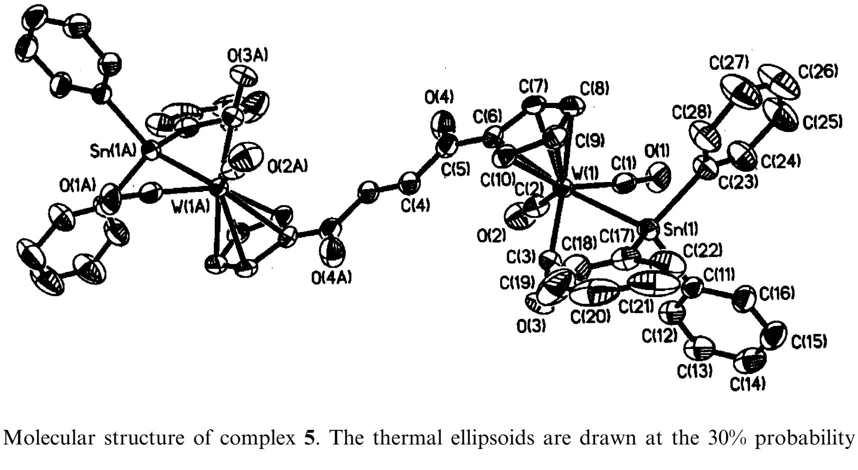


Fig. 2. Molecular structure of complex **5**. The thermal ellipsoids are drawn at the 30% probability level.

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