

Synthesis and crystal structures of cyclodiazastannoxides fused cyclopentadienyl M–Sn (M = Mo, W) bonded organometallic heterocycle

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Abstract

The condensation reaction of $\text{CH}_3\text{COC}_5\text{H}_4\text{M}(\text{CO})_3\text{SnCl}_3$ (M = Mo or W) with PyCONHNH_2 (Py = 2,3,4-pyridyl or 2-pyridylmethyl) in mild conditions yields cyclodiazastannoxides fused cyclopentadienyl M–Sn bonded organometallic heterocycle $\{\mu\text{-}[\text{C}_5\text{H}_4(\text{CH}_3)\text{C}=\text{N}-\text{N}=\text{C}(\text{O})\text{PyH}]\text{M}(\text{CO})_3\text{SnCl}_3\}$. The similar reaction of $\text{CH}_3\text{COC}_5\text{H}_4\text{M}(\text{CO})_3\text{SnCl}_3$ with ArCONHNH_2 (Ar = 2-furanyl) gives complexes $\mu\text{-}[\text{C}_5\text{H}_4(\text{CH}_3)\text{C}=\text{N}-\text{N}=\text{C}(\text{O})\text{Ar}]\text{M}(\text{CO})_3\text{SnCl}_2(\text{H}_2\text{O})$, in which the water molecule can be replaced by other N-donor ligands, such as pyridine or 4,4-bipyridine. Arene-bridged organometallic heterocyclic complexes $\mu\text{-}\{[\text{C}_5\text{H}_4(\text{CH}_3)\text{C}=\text{N}-\text{N}=\text{C}(\text{O})]_2\text{C}_6\text{H}_4\}\{\text{M}(\text{CO})_3\text{SnCl}_2(\text{Solvent})\}_2$ have also been prepared by the reaction of $\text{CH}_3\text{COC}_5\text{H}_4\text{M}(\text{CO})_3\text{SnCl}_3$ with terephthaloyl hydrazine. In these new organometallic heterocyclic complexes, it seems that the tin atom prefers to be six-coordinate through absorbing the chloridion or solvent molecules.

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Keywords: Cyclopentadienyl; Tin; Molybdenum; Tungsten; Heterocycle

1. Introduction

The synthesis and reactivity of heteronuclear transition metal complexes continues to be an active research area in organometallic chemistry because of their interesting structural and reactive features as well as their potential utility as polyfunctional catalysts, or precursors for preparing other polynuclear heterogenous catalysts [1–3]. 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 [4–17]. We recently became interested in studying the transition metal–tin bonded heterodimetallic complexes

owing to their unusual structural feature and reactivity [18–21]. Our recent investigation on this aspect displays that these transition metal–tin bonded heterodimetallic complexes can be used as the construction of novel heteronuclear organometallic macrocycles [22,23]. We also found that the reaction of functionalized acetylcyclopentadienyl M–Sn bonded heterodimetallic complexes with benzoylhydrazine gave a distorted dinuclear cyclodiazastannoxide [24], in which the tin atom prefers to be six-coordinate through absorbing the solvent molecules, instead of general five-coordinate in known bicyclodiazastannoxide analogues [25,26]. Our current interest is to investigate if the heteroatom in the aryl group of heteroarylhydrazine can substitute for the coordinate solvent molecule in such cyclodiazastannoxides to lead to some novel coordination modes. In this paper we present the results of this study. Reactions of $\text{CH}_3\text{COC}_5\text{H}_4\text{M}(\text{CO})_3\text{SnCl}_3$ (M = Mo and W) with heteroarylhydrazine give

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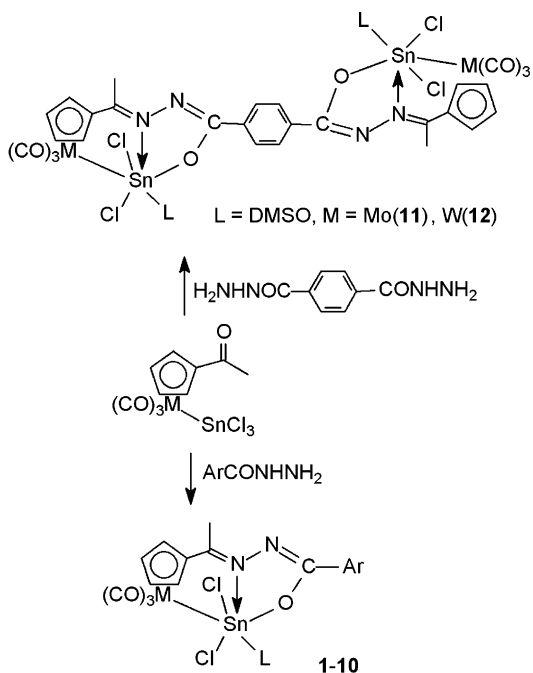
cyclodiazastannoxides fused cyclopentadienyl M–Sn bonded organometallic heterocycle.

2. Results and discussion

2.1. Syntheses and properties of complexes

The reaction of $\text{CH}_3\text{COC}_5\text{H}_4\text{M}(\text{CO})_3\text{SnCl}_3$ ($\text{M} = \text{Mo}$ or W) with PyCONHNH_2 ($\text{Py} = 2,3,4\text{-pyridyl}$ or 2-pyridylmethyl) at room temperature yields cyclodiazastannoxides **1–8** (Scheme 1). Compared with the analogous reaction of benzoylhydrazine [24], the reaction of PyCONHNH_2 is milder and faster possibly owing to the alkalescence of the pyridyl nitrogen atom accelerating to enolize the $-\text{NHCO}-$ to the $-\text{N}=\text{C}(\text{OH})-$ and deprotonize in sequence. Furthermore, the HCl molecule does not depart from the reaction system, which leads to the proton combining with the pyridyl nitrogen atom and the chloridion still bonding to the tin atom.

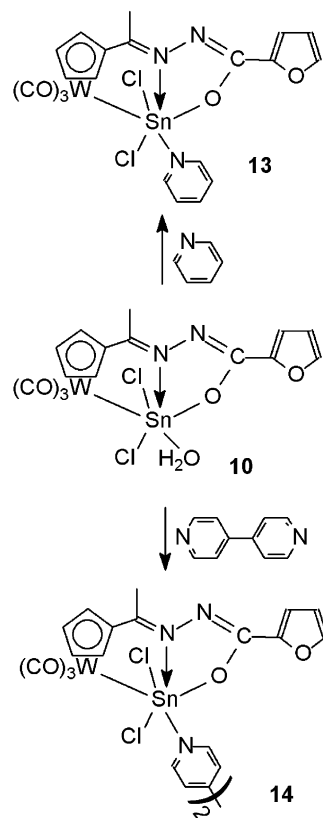
The reaction of $\text{CH}_3\text{COC}_5\text{H}_4\text{M}(\text{CO})_3\text{SnCl}_3$ ($\text{M} = \text{Mo}$ or W) with 2-furoic acid hydrazide or terephthaloyl hydrazine gives complexes **9–12** at higher temperature, compared with the reaction of PyCONHNH_2 . At the same time, the HCl molecule also escapes from the reaction system. In order to keep the six-coordinate tin atom in these complexes, solvent (**11** and **12**) or water (**9** and **10**) molecules coordinate to the tin atom. In addition, the interaction of the tin atom with water is weak, which



Scheme 1. Ar = 2-pyridyl, L = Cl, M = Mo(**1**), W(**2**); Ar = 3-pyridyl, L = Cl, M = Mo(**3**), W(**4**); Ar = 4-pyridyl, L = Cl, M = Mo(**5**), W(**6**); Ar = 2-pyridylmethyl, L = Cl, M = Mo(**7**), W(**8**); Ar = 2-furanyl, L = H_2O , M = Mo(**9**), W(**10**).

leads to the water molecule easily replaced by other N-donor ligands, such as pyridine or 4,4'-bipyridine. For example, the reaction of **9** with pyridine and 4,4'-bipyridine almost quantitatively yields complexes **13** and **14**, respectively (Scheme 2).

All complexes in solid are stable in air, and their solution can be handled in air without notable decomposition. These complexes, with the exception of **9** and **10** with moderate solubility in chlorinated solvents, have low solubility in common organic solvents, but soluble in strong polar solvents such as DMF or DMSO at room temperature. These complexes have also been characterized by element analyses, IR as well as ^1H NMR spectra. The characteristic ν_{NH} and $\nu_{\text{C}=\text{N}}$ peaks appear at ca. 3100 and 1630 cm^{-1} , respectively. Two or three typical metal carbonyl stretching bands have also been observed in the range of 2045–1934 cm^{-1} . Although there are six metal carbonyls and four $\text{C}=\text{N}$ bonds in complexes **11** and **12**, their IR spectra only show three typical metal carbonyl stretching bands with range of 2020–1890 cm^{-1} and one absorption band of $\text{C}=\text{N}$ bond at ca. 1620 cm^{-1} , indicating that these complexes should be symmetrical, which is consistent with the results of X-ray crystal structure of complex **12**. Their ^1H NMR spectra also exhibit the expected proton signals, such as two sets of Cp ring resonances, corresponding to the monosubstituted cyclopentadienyl group.



Scheme 2.

2.2. The description of crystal structures

The crystal structures of complexes **7**, **10** and **12** determined by single crystal X-ray diffraction are presented in Figs. 1–3, respectively. Selected distances and angles for complexes **7**, **10** and **12** are listed in Tables 1–3, respectively. In these complexes, the molybdenum or tungsten atom adopts a 3:4 piano four-legged square pyramid structure, and the tin atom is a distorted octahedral geometry. A new five-membered cyclodiazastannoxide made up of Sn–N–N–C–O is formed by imino nitrogen and enolic oxygen atoms combined to the tin atom, which fuses a pseudo five-membered metalloheterocycle made up of Sn–M–C–C–N to form a heterobicyclic system. It is interesting that the five-membered ring of Sn–N–N–C–O is almost planar, whose mean deviation from the plane is 0.0035 Å in **7**, 0.0067 Å in **10** and 0.0086 Å in **12**, respectively. In addition, the –C=N–N=C– moiety in these three complexes is also coplanar. The mean deviation from the plane is

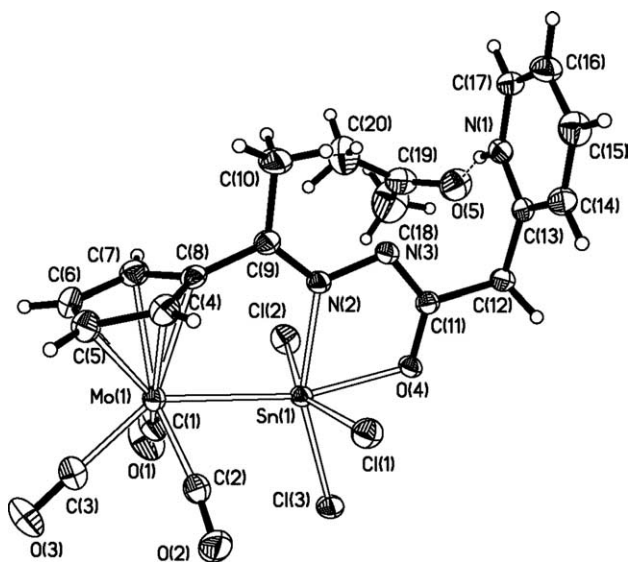


Fig. 1. The molecular structure of complex **7** · CH₃COCH₃. The thermal ellipsoids are drawn at the 30% probability level.

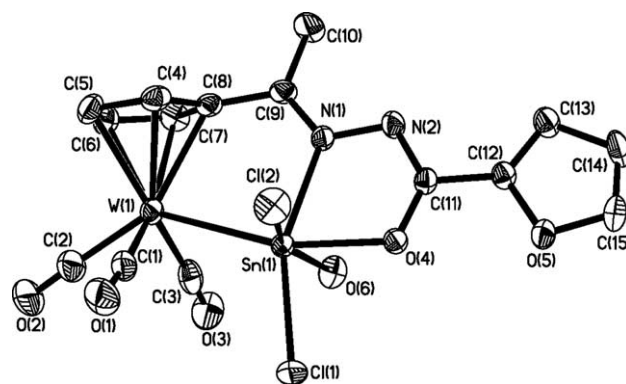


Fig. 2. The molecular structure of complex **10**. The thermal ellipsoids are drawn at the 30% probability level. The uncoordinated acetone molecules have been omitted for clarity.

only 0.0045 Å in **7**, 0.0039 Å in **10** and 0.0199 Å in **12**, respectively. The torsion angle of ∠C–N–N–C (–179.1(3)° in **7**, –179.2(7)° in **10** and 176.0(6)° in **12**, respectively) has also indicated that the –C=N–N=C– moiety has good coplanarity.

Although heteroatoms of the aryl groups in **7** and **10** do not coordinate to the tin atom of adjacent molecules, these heteroaryl groups markedly influence the structural parameters of complexes. The Mo–Sn bond distance in complex **7** is 2.8338(8) Å, significantly longer than that in acyclic 2,4-(NO₂)₂C₆H₃NHN=C(CH₃)C₅H₄Mo(CO)₃SnCl₃ (2.7040(7) Å) [24]. Furthermore, the average Sn–Cl bond distance (2.506(1) Å) in the former is also longer than that in the latter (2.342(2) Å). These may be the result of the six-coordinate tin in **7** weakening the bonding between the Sn–Cl. The W–Sn bond distance (2.8134(9) Å) in **10** is similar with that in **12** (2.8118(7) Å), but slightly longer than that in μ-[C₅H₄-(CH₃)C=N–N=C(O)C₆H₅]W(CO)₃SnCl₂(EtOH) (complex A, 2.7767(9) Å) [24]. The average Sn–Cl bond distance in **10** (2.432 Å) is comparable to those in **12** (2.455 Å) and complex A (2.4495 Å), and slightly shorter than that in **7** (2.506(1) Å). The Sn(1)–O(6) bond (2.322(5) Å) is significantly longer than the Sn(1)–O(4) bond (2.126(4) Å) in **10**, indicating that the interaction

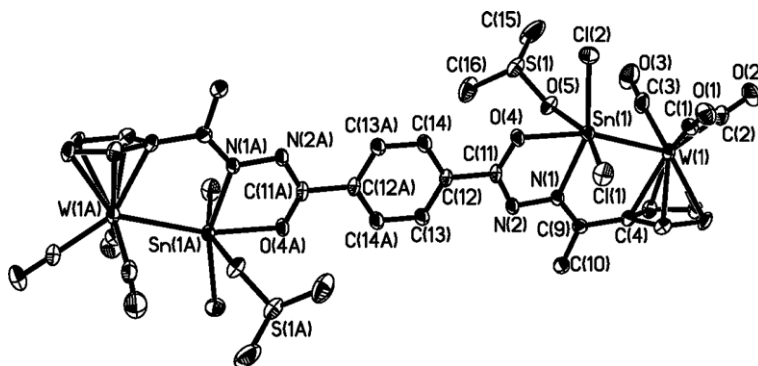


Fig. 3. The molecular structure of complex **12**. The thermal ellipsoids are drawn at the 30% probability level. The uncoordinated DMSO molecules have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **7**

<i>Bond lengths</i>	
Mo(1)–Sn(1)	2.8338(8)
Sn(1)–O(4)	2.166(2)
Sn(1)–N(2)	2.231(2)
Sn(1)–Cl(3)	2.442(1)
Sn(1)–Cl(2)	2.512(1)
Sn(1)–Cl(1)	2.563(1)
N(1)···O(5)	2.732
O(4)–C(11)	1.286(3)
N(2)–C(9)	1.275(4)
N(2)–N(3)	1.387(3)
C(8)–C(9)	1.479(4)
N(3)–C(11)	1.316(4)
C(11)–C(12)	1.515(4)
<i>Bond angles</i>	
O(4)–Sn(1)–N(2)	71.61(8)
O(4)–Sn(1)–Cl(3)	86.06(6)
N(2)–Sn(1)–Cl(3)	157.62(7)
O(4)–Sn(1)–Cl(2)	81.12(6)
Cl(3)–Sn(1)–Cl(2)	91.54(4)
O(4)–Sn(1)–Cl(1)	78.23(6)
N(2)–Sn(1)–Cl(1)	83.61(7)
Cl(3)–Sn(1)–Cl(1)	93.53(3)
Cl(2)–Sn(1)–Cl(1)	158.32(3)
O(4)–Sn(1)–Mo(1)	163.82(5)
N(1)–H···O(5)	165.2
N(2)–Sn(1)–Mo(1)	92.41(7)
Cl(3)–Sn(1)–Mo(1)	109.97(3)
Cl(1)–Sn(1)–Mo(1)	97.93(2)
C(11)–O(4)–Sn(1)	114.2(1)
C(9)–N(2)–N(3)	120.2(2)
C(9)–N(2)–Sn(1)	122.3(2)
N(3)–N(2)–Sn(1)	117.4(1)
N(2)–C(9)–C(8)	118.5(3)
C(11)–N(3)–N(2)	109.0(2)
O(4)–C(11)–N(3)	127.8(3)
<i>Torsion angles</i>	
C(9)–N(2)–N(3)–C(11)	–179.1(3)
C(4)–C(8)–C(9)–N(2)	93.4(4)
C(7)–C(8)–C(9)–N(2)	–99.3(4)
C(7)–C(8)–C(9)–C(10)	81.8(4)

of the tin atom with the water molecule is weak, which is consistent with the fact that the water molecule is easily replaced by other N-donor ligands.

It is also noteworthy that the Sn–N–N–C–O plane and the cyclopentadienyl plane in **7** are almost perpendicular to each other with a dihedral angle of 89.9°, which is larger than the corresponding dihedral angle of 75.3° in **10**, but smaller than that (109.2°) in **12**. The Sn–N–N–C–O plane with the furanyl plane in **10** as well as the Sn–N–N–C–O plane with the phenyl plane in **12** are closely parallel to each other with a dihedral angle of 4.9° in **10** and 4.6° in **12**, respectively. In addition, the C(11)N(2) double bond in **12** is nearly located coplanarly with the phenyl plane, which is only 0.0275 Å (C(11)) and –0.0491 Å (N(2)) from the phenyl plane. But, the C(11)N(2) double bond in **10** markedly deviates from the C(12)–O(5) furanyl plane (–0.1223 Å (N(2)) and –0.0633 Å (C(11)) from the plane).

Table 2
Selected bond lengths (Å) and angles (°) for **10**

<i>Bond lengths</i>	
W(1)–Sn(1)	2.8134(9)
Sn(1)–O(4)	2.126(4)
Sn(1)–N(1)	2.259(6)
Sn(1)–O(6)	2.322(5)
Sn(1)–Cl(1)	2.404(1)
Sn(1)–Cl(2)	2.459(2)
N(1)–N(2)	1.378(7)
N(1)–C(9)	1.290(8)
N(2)–C(11)	1.325(8)
O(4)–C(11)	1.307(8)
C(8)–C(9)	1.474(9)
C(11)–C(12)	1.460(9)
<i>Bond angles</i>	
O(4)–Sn(1)–N(1)	71.1(1)
O(4)–Sn(1)–O(6)	74.8(1)
N(1)–Sn(1)–O(6)	81.5(2)
O(4)–Sn(1)–Cl(1)	85.9(1)
N(1)–Sn(1)–Cl(1)	156.0(1)
O(6)–Sn(1)–Cl(1)	86.1(1)
O(4)–Sn(1)–Cl(2)	83.8(1)
O(6)–Sn(1)–Cl(2)	158.6(1)
Cl(1)–Sn(1)–Cl(2)	93.75(8)
O(4)–Sn(1)–W(1)	160.6(1)
N(1)–Sn(1)–W(1)	90.3(1)
C(11)–O(4)–Sn(1)	115.9(4)
C(4)–C(8)–C(9)	127.1(7)
N(1)–C(9)–C(8)	118.3(6)
O(4)–C(11)–N(2)	126.8(6)
N(2)–N(1)–Sn(1)	117.9(4)
C(11)–N(2)–N(1)	108.3(5)
C(9)–N(1)–N(2)	118.8(6)
C(9)–N(1)–Sn(1)	123.3(5)
O(6)–Sn(1)–W(1)	97.3(1)
Cl(1)–Sn(1)–W(1)	111.68(5)
Cl(2)–Sn(1)–W(1)	102.59(6)
<i>Torsion angles</i>	
C(9)–N(1)–N(2)–C(11)	–179.2(7)
C(7)–C(8)–C(9)–N(1)	–111.8(8)
C(4)–C(8)–C(9)–N(1)	77.2(9)
N(2)–C(11)–C(12)–O(5)	–177.2(6)

In conclusion, a series of cyclodiazastannoxides fused cyclopentadienyl M–Sn bonded organometallic heterocycle have been obtained by the condensation reaction of CH₃COC₃H₄M(CO)₃SnCl₃ (M = Mo or W) with heteroarylhydrazine or terephthaloyl hydrazine. The aryl heteroatoms in complexes do not coordinate to the tin atom, but these heteroaryl groups markedly influence the reactivity of acylhydrazine as well as the structural parameters of complexes. In these bicyclic heterobimetallic complexes, the tin atom prefers to be six-coordinate through absorbing the chloridion or solvent molecules.

3. Experimental

All reactions were carried out under an argon atmosphere using standard Schlenk and Cannula techniques.

Table 3
Selected bond lengths (Å) and angles (°) for **12**

Bond lengths	
W(1)–Sn(1)	2.8118(7)
Sn(1)–O(4)	2.144(5)
Sn(1)–O(5)	2.247(5)
Sn(1)–N(1)	2.263(6)
Sn(1)–Cl(2)	2.423(2)
Sn(1)–Cl(1)	2.487(2)
N(1)–C(9)	1.290(9)
N(1)–N(2)	1.390(7)
N(2)–C(11)	1.314(9)
O(4)–C(11)	1.298(9)
C(4)–C(9)	1.485(9)
C(9)–C(10)	1.48(1)
Bond angles	
O(4)–Sn(1)–O(5)	76.7(2)
O(4)–Sn(1)–N(1)	71.4(1)
O(5)–Sn(1)–N(1)	81.3(2)
O(4)–Sn(1)–Cl(2)	86.8(1)
O(5)–Sn(1)–Cl(2)	87.5(1)
N(1)–Sn(1)–Cl(2)	157.2(1)
O(4)–Sn(1)–Cl(1)	82.0(1)
O(5)–Sn(1)–Cl(1)	158.4(1)
N(1)–Sn(1)–Cl(1)	88.6(1)
Cl(2)–Sn(1)–Cl(1)	94.93(8)
O(4)–Sn(1)–W(1)	161.6(1)
Cl(1)–Sn(1)–W(1)	99.85(6)
C(9)–N(1)–N(2)	119.9(6)
C(9)–N(1)–Sn(1)	123.5(5)
N(2)–N(1)–Sn(1)	116.6(4)
C(11)–N(2)–N(1)	109.5(5)
C(11)–O(4)–Sn(1)	115.6(4)
N(1)–C(9)–C(4)	117.2(6)
O(4)–C(11)–N(2)	126.9(6)
N(1)–Sn(1)–W(1)	90.3(1)
Cl(2)–Sn(1)–W(1)	111.13(6)
O(5)–Sn(1)–W(1)	99.3(1)
Torsion angles	
C(9)–N(1)–N(2)–C(11)	176.0(6)
C(8)–C(4)–C(9)–N(1)	–116.4(8)
C(5)–C(4)–C(9)–N(1)	74.9(10)
N(2)–C(11)–C(12)–C(14)	–176.6(7)

Solvents were dried by the standard methods prior to use. The ^1H NMR spectra were obtained with a Mercury 300BB spectrometer, and the chemical shifts were reported in ppm with respect to the reference. IR spectra data were obtained from a Bio-Rad FTS 135 spectrometer using KBr discs. Element analyses were carried out on a Perkin–Elmer 2400C analyzer. $\text{CH}_3\text{COC}_5\text{H}_4\text{M}(\text{CO})_3\text{SnCl}_3$ (M = Mo or W) was prepared by the published method [24].

3.1. Preparation of complex 1

Pyridine-2-carboxylic hydrazide (70 mg, 0.5 mmol) was added to the solution of $\text{CH}_3\text{COC}_5\text{H}_4\text{Mo}(\text{CO})_3\text{SnCl}_3$ (0.26 g, 0.5 mmol) in 15 ml absolute ethanol. The reaction mixture was stirred continuously for 4 h at room temperature, during which a yellow precipitate

was formed gradually. The precipitate was filtered off, washed with anhydrous ether and recrystallized from hot acetone to yield yellow crystals of **1**· $\text{CH}_3\text{CO}\cdot\text{CH}_3\cdot\text{HCl}$ (0.30 g, 90%). ^1H NMR (CD_3COCD_3): δ 11.6 (s, 1H, NHCl), 8.69, 8.24, 8.13, 7.70 (d, d, t, m, 1H, 1H, 1H, 1H, protons in pyridyl), 6.57, 6.11 (s, s, 2H, 2H, C_5H_4), 2.37 (s, 3H, CH_3). IR: $\nu_{\text{NH}} = 3099.4$ (m), $\nu_{\text{CO}} = 2045.4$ (s), 2018.1 (vs), 1944.2 (vs); $\nu_{\text{C=O}}$ (in acetone) = 1703.6 (m), $\nu_{\text{C=N}} = 1624.8$ (w) cm^{-1} . Anal. Calc. for $\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{MoN}_3\text{O}_4\text{Sn}\cdot\text{CH}_3\text{COCH}_3\cdot\text{HCl}$: C, 33.07; H, 2.61; N, 6.09. Found (crystals from acetone): C, 33.39; H, 2.57; N, 5.93%. Anal. Calc. for $\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{MoN}_3\text{O}_4\text{Sn}\cdot\text{HCl}$: C, 30.40; H, 1.90; N, 6.65. Found (precipitate from the reaction mixture): C, 30.41; H, 2.19; N, 6.96%.

3.2. Preparation of complex 2

This complex was obtained similarly using pyridine-2-carboxylic hydrazide to react with $\text{CH}_3\text{COC}_5\text{H}_4\text{W}(\text{CO})_3\text{SnCl}_3$ as described above for **1**. After similar workup, yellow crystals of **2** were obtained. Yield: 92%. ^1H NMR (CD_3COCD_3): δ 10.62 (s, 1H, NHCl), 8.70, 8.23, 8.12, 7.71 (d, d, t, m, 1H, 1H, 1H, 1H, protons in pyridyl), 6.68, 6.24 (s, s, 2H, 2H, C_5H_4), 2.37 (s, 3H, CH_3). IR: $\nu_{\text{NH}} = 3121.4$ (m), $\nu_{\text{CO}} = 2031.1$ (sh), 2019.0 (vs), 1937.4 (vs); $\nu_{\text{C=O}}$ (in acetone) = 1694.0 (m), $\nu_{\text{C=N}} = 1645.0$ (w) cm^{-1} . Anal. Calc. for $\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{N}_3\text{O}_4\text{SnW}\cdot\text{CH}_3\text{COCH}_3\cdot\text{HCl}$: C, 29.32; H, 2.32; N, 5.40. Found (crystals from acetone): C, 29.39; H, 2.57; N, 5.28%.

3.3. Preparation of complex 3

This complex was obtained similarly using pyridine-3-carboxylic hydrazide to react with $\text{CH}_3\text{COC}_5\text{H}_4\text{Mo}(\text{CO})_3\text{SnCl}_3$ as described above for **1**. The yellow precipitate was filtered off, washed with anhydrous ether, and dried in vacuum. Yield: 89%. ^1H NMR (CD_3SOCD_3): δ 9.58, 9.26, 9.16, 8.32 (s, d, d, t, 1H, 1H, 1H, 1H, protons in pyridyl), 5.84, 5.78 (s, s, 2H, 2H, C_5H_4), 2.69 (s, 3H, CH_3). IR: $\nu_{\text{NH}} = 3092.3$ (w), $\nu_{\text{CO}} = 2019.9$ (vs), 1940.3 (br, vs); $\nu_{\text{C=N}} = 1630.5$ (w) cm^{-1} . Anal. Calc. for $\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{MoN}_3\text{O}_4\text{Sn}\cdot\text{HCl}$: C, 30.40; H, 1.90; N, 6.65. Found: C, 30.18; H, 2.19; N, 6.87%.

3.4. Preparation of complex 4

This complex was obtained similarly using pyridine-3-carboxylic hydrazide to react with $\text{CH}_3\text{COC}_5\text{H}_4\text{W}(\text{CO})_3\text{SnCl}_3$ as described above for **3**. After similar workup, yellow solids of **4** were obtained. Yield: 90%. ^1H NMR (CD_3SOCD_3): δ 9.48, 9.27, 9.14, 8.35 (s, d, d, t, 1H, 1H, 1H, 1H, protons in pyridyl), 5.89, 5.68 (s, s, 2H, 2H, C_5H_4), 2.64 (s, 3H, CH_3). IR: $\nu_{\text{NH}} = 3102.3$ (w), $\nu_{\text{CO}} = 2021.0$ (vs), 1932.9 (br, vs);

$\nu_{\text{C}=\text{N}} = 1629.4$ (w) cm^{-1} . Anal. Calc. for $\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{N}_3\text{O}_4\text{SnW} \cdot \text{HCl}$: C, 26.69; H, 1.67; N, 5.84. Found: C, 26.52; H, 1.78; N, 5.66%.

3.5. Preparation of complex 5

This complex was obtained similarly using pyridine-4-carboxylic hydrazide to react with $\text{CH}_3\text{COC}_5\text{H}_4\text{Mo}(\text{CO})_3\text{SnCl}_3$ as described above for **3**. After similar workup, yellow solids of **5** were obtained. Yield: 92%. ^1H NMR (CD_3COCD_3): δ 8.89, 8.32 (d, d, 2H, 2H, protons in pyridyl), 5.93, 5.75 (t, t, 2H, 2H, C_5H_4), 2.67 (s, 3H, CH_3). IR: $\nu_{\text{NH}} = 3085.6$ (w), $\nu_{\text{CO}} = 2017.8$ (vs), 1944.5 (br, vs); $\nu_{\text{C}=\text{N}} = 1629.3$ (w) cm^{-1} . Anal. Calc. for $\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{MoN}_3\text{O}_4\text{Sn} \cdot \text{HCl}$: C, 30.40; H, 1.90; N, 6.65. Found: C, 30.62; H, 2.27; N, 6.81%.

3.6. Preparation of complex 6

This complex was obtained similarly using pyridine-4-carboxylic hydrazide to react with $\text{CH}_3\text{COC}_5\text{H}_4\text{W}(\text{CO})_3\text{SnCl}_3$ as described above for **3**. After similar workup, yellow solids of **6** were obtained. Yield: 87%. ^1H NMR (CD_3COCD_3): δ 8.92, 8.46 (d, d, 2H, 2H, protons in pyridyl), 5.97, 5.77 (t, t, 2H, 2H, C_5H_4), 2.70 (s, 3H, CH_3). IR: $\nu_{\text{NH}} = 3083.4$ (w), $\nu_{\text{CO}} = 2019.9$ (vs), 1934.6 (br, vs); $\nu_{\text{C}=\text{N}} = 1629.6$ (w) cm^{-1} . Anal. Calc. for $\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{N}_3\text{O}_4\text{SnW} \cdot \text{HCl}$: C, 26.69; H, 1.67; N, 5.84. Found: C, 26.87; H, 1.54; N, 6.05%.

3.7. Preparation of complex 7

This complex was obtained similarly using 2-pyridylacetyl hydrazine to react with $\text{CH}_3\text{COC}_5\text{H}_4\text{Mo}(\text{CO})_3\text{SnCl}_3$ as described above for **1**. After similar workup, yellow crystals of **7** were obtained. Yield: 90%. ^1H NMR (CD_3COCD_3): δ 9.78 (s, 1H, NHCl), 8.65, 8.00, 7.64, 7.25 (d, d, t, m, 1H, 1H, 1H, 1H, protons in pyridyl), 6.56, 6.09 (s, s, 2H, 2H, C_5H_4), 4.23 (s, 2H, CH_2), 2.08 (s, 3H, CH_3). IR: $\nu_{\text{NH}} = 3096.2$ (w), $\nu_{\text{CO}} = 2046.5$ (s), 2025.4 (vs), 1944.6 (vs); $\nu_{\text{C}=\text{O}}$ (in acetone) = 1684.5 (m), $\nu_{\text{C}=\text{N}} = 1630.4$ (w) cm^{-1} . Anal. Calc. for $\text{C}_{17}\text{H}_{13}\text{Cl}_2\text{MoN}_3\text{O}_4\text{Sn} \cdot \text{CH}_3\text{COCH}_3 \cdot \text{HCl}$: C, 34.12; H, 2.84; N, 5.97. Found (crystals from acetone): C, 34.50; H, 2.88; N, 5.91%.

3.8. Preparation of complex 8

This complex was obtained similarly using 2-pyridylacetyl hydrazine to react with $\text{CH}_3\text{COC}_5\text{H}_4\text{W}(\text{CO})_3\text{SnCl}_3$ as described above for **1**. After similar workup, yellow crystals of **8** were obtained. Yield: 91%. ^1H NMR (CD_3COCD_3): δ 9.80 (s, 1H, NHCl), 8.51, 7.78, 7.63, 7.28 (d, d, t, m, 1H, 1H, 1H, 1H, protons in pyridyl), 6.65, 6.23 (s, s, 2H, 2H, C_5H_4), 4.22 (s, 2H, CH_2), 2.37 (s, 3H, CH_3). IR: $\nu_{\text{NH}} = 3098.7$ (w),

$\nu_{\text{CO}} = 2038.8$ (s), 2019.6 (vs), 1934.5 (vs); $\nu_{\text{C}=\text{O}}$ (in acetone) = 1686.4 (m), $\nu_{\text{C}=\text{N}} = 1625.6$ (w) cm^{-1} . Anal. Calc. for $\text{C}_{17}\text{H}_{13}\text{Cl}_2\text{N}_3\text{O}_4\text{SnW} \cdot \text{CH}_3\text{COCH}_3 \cdot \text{HCl}$: C, 30.32; H, 2.53; N, 5.31. Found (crystals from acetone): C, 30.54; H, 2.36; N, 5.45%.

3.9. Preparation of complex 9

2-Furoic acid hydrazide (63 mg, 0.5 mmol) was added to the solution of $\text{CH}_3\text{COC}_5\text{H}_4\text{Mo}(\text{CO})_3\text{SnCl}_3$ (0.26 g, 0.5 mmol) in 15 ml absolute ethanol. The reaction mixture was stirred and refluxed continuously for 4 h to obtain a yellow solution. The solvent was removed under a reduced pressure and the residual solid was recrystallized from CH_2Cl_2 /hexane to yield red crystals of **9** (0.30 g, 85%). ^1H NMR (CDCl_3): δ 7.49, 7.29, 6.52 (d, d, t, 1H, 1H, 1H, furyl protons), 6.19, 5.63 (s, s, 2H, 2H, C_5H_4), 2.12 (s, 3H, CH_3). IR: $\nu_{\text{H}_2\text{O}} = 3427.0$ (s); $\nu_{\text{CO}} = 2055.6$ (sh), 2026.7 (s), 1933.9 (vs); $\nu_{\text{C}=\text{N}} = 1618.8$ (m) cm^{-1} . Anal. Calc. for $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{MoN}_2\text{O}_5\text{Sn} \cdot \text{H}_2\text{O}$: C, 29.90; H, 1.99; N, 4.65. Found: C, 30.21; H, 1.67; N, 4.34%.

3.10. Preparation of complex 10

This complex was obtained similarly using 2-furoic acid hydrazide to react with $\text{CH}_3\text{COC}_5\text{H}_4\text{W}(\text{CO})_3\text{SnCl}_3$ as described above for **9**. After similar workup, red crystals of **10** were obtained. Yield: 80%. ^1H NMR (CDCl_3): δ 7.56, 7.36, 6.55 (d, d, t, 1H, 1H, 1H, furyl protons), 6.31, 5.73 (s, s, 2H, 2H, C_5H_4), 2.15 (s, 3H, CH_3). IR: $\nu_{\text{H}_2\text{O}} = 3427.6$ (s); $\nu_{\text{CO}} = 2030$ (vs), 1928.1 (br, vs); $\nu_{\text{C}=\text{N}} = 1625.4$ (m) cm^{-1} . Anal. Calc. for $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_5\text{SnW} \cdot \text{H}_2\text{O}$: C, 25.42; H, 1.69; N, 3.95. Found: C, 25.25; H, 1.68; N, 4.25%.

3.11. Preparation of complex 11

This complex was obtained similarly using terephthaloyl hydrazine (0.25 mmol) to react with $\text{CH}_3\text{COC}_5\text{H}_4\text{Mo}(\text{CO})_3\text{SnCl}_3$ (0.5 mmol) as described above for **9**. The reaction time was 12 h. After the reaction completed, the reaction mixture was cooled to 4 °C to yield yellow precipitate, which was filtered off, washed with anhydrous ether and recrystallized from hot DMSO to yield yellow crystals of **11**. Yield: 91%. ^1H NMR (CD_3SOCD_3): δ 8.26 (s, 4H, C_6H_4), 5.82, 5.75 (s, s, 2H, 2H, C_5H_4), 2.64 (s, 3H, CH_3). IR: $\nu_{\text{CO}} = 2039.3$ (vs), 1939.6 (br, vs); $\nu_{\text{C}=\text{N}} = 1621.7$ (w) cm^{-1} . Anal. Calc. for $\text{C}_{28}\text{H}_{18}\text{Cl}_4\text{Mo}_2\text{N}_4\text{O}_8\text{Sn}_2 \cdot 6\text{DMSO}$: C, 30.44; H, 3.45; N, 3.55. Found: C, 30.16; H, 3.47; N, 3.31%.

3.12. Preparation of complex 12

This complex was obtained similarly using terephthaloyl hydrazine (0.25 mmol) to react with

$\text{CH}_3\text{COC}_5\text{H}_4\text{W}(\text{CO})_3\text{SnCl}_3$ (0.5 mmol) as described above for **11**. After similar workup, yellow crystals of **12** were obtained. Yield: 90%. ^1H NMR (CD_3SOCD_3): δ 8.26 (s, 4H, C_6H_4), 6.00, 5.86 (s, s, 2H, 2H, C_5H_4), 2.68 (s, 3H, CH_3). IR: $\nu_{\text{CO}} = 2032.1$ (vs), 1931.2 (br, vs); $\nu_{\text{C=N}} = 1623.1$ (w) cm^{-1} . Anal. Calc. for $\text{C}_{28}\text{H}_{18}\text{Cl}_4\text{N}_4\text{O}_8\text{Sn}_2\text{W}_2 \cdot 6\text{DMSO}$: C, 27.39; H, 3.10; N, 3.19. Found: C, 27.35; H, 2.76; N, 3.45%.

3.13. Preparation of complex **13**

Pyridine (0.1 ml, 1.3 mmol) was added to a stirred solution of complex **10** (50 mg, 0.072 mmol) in 15 ml CH_2Cl_2 . The reaction mixture was continuously stirred overnight at room temperature, and then concentrated to ca. 5 ml to yield yellow solids of **13**. Yield: 92%. ^1H NMR (CD_3SOCD_3): δ 8.59, 7.82, 7.42 (d, t, t, 2H, 1H, 2H, pyridyl protons), 7.93, 7.20, 6.69 (d, d, t, 1H, 1H, 1H, furyl protons), 5.97, 5.85 (s, s, 2H, 2H, C_5H_4), 2.59 (s, 3H, CH_3). IR: $\nu_{\text{CO}} = 2018.2$ (vs), 1951.5 (s), 1917.6 (vs); $\nu_{\text{C=N}} = 1625.4$ (m) cm^{-1} . Anal. Calc. for $\text{C}_{20}\text{H}_{15}\text{Cl}_2\text{N}_3\text{O}_5\text{SnW}$: C, 31.99; H, 2.01; N, 5.60. Found: C, 32.45; H, 2.43; N, 5.65%.

3.14. Preparation of complex **14**

This complex was obtained similarly using 4,4'-bipyridine to react with complex **10** as described above for **13**. After similar workup, yellow solids of **14** were obtained. Yield: 93%. ^1H NMR (CD_3SOCD_3): δ 8.75, 7.86 (d, d, 4H, 4H, pyridyl protons), 7.93, 7.20, 6.69

(d, d, t, 2H, 2H, 2H, furyl protons), 5.96, 5.84 (s, s, 4H, 4H, C_5H_4), 2.59 (s, 3H, CH_3). IR: $\nu_{\text{CO}} = 2020.7$ (vs), 1922.6 (br, vs); $\nu_{\text{C=N}} = 1623.0$ (m) cm^{-1} . Anal. Calc. for $\text{C}_{40}\text{H}_{28}\text{Cl}_4\text{N}_6\text{O}_{10}\text{Sn}_2\text{W}_2$: C, 32.04; H, 1.88; N, 5.60. Found: C, 31.89; H, 2.19; N, 5.62%.

3.15. X-ray crystallography

Yellow crystals of **7** suitable for X-ray analysis were obtained from an acetone solution of **7** at -10°C , while yellow crystals of **10** were obtained by slow diffusion of hexane into the acetone solution of **10** at -10°C . Yellow crystals of **12** were obtained by slowly cooling a hot DMSO solution of **12**. An acetone molecule (C(22), C(23), C(24) and O(9)) in **10** was found to be disorder. Satisfactory results were obtained when C(22), C(23), C(24) and O(9) were given occupancy factor of 0.39 and C(22)', C(23)', C(24)' and O(9)' were given occupancy factor of 0.61. In addition, the uncoordinated DMSO molecules in **12** are also disorder. The occupancy factor was refined to 0.54 for S(2), C(17), C(18) and O(6) as well as 0.46 for 0.54 for S(2)', C(17)', C(18)' and O(6)'. The DMSO molecule (S(3), C(19), C(20) and O(7)) was found to be disorder in two positions. Satisfactory results were obtained when S(3), C(19), C(20) and O(7) were given occupancy factor of 0.60, S(3)', C(19)', C(20)' and O(7)' were given occupancy factor of 0.20, and S(3)'', C(19)'', C(20)'' and O(7)'' were given occupancy factor of 0.20, respectively. Intensity data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo $\text{K}\alpha$

Table 4
Crystal data and refinement parameters for compounds **7**, **10** and **12**

Compound	7 · CH_3COCH_3	10 · $3\text{CH}_3\text{COCH}_3$	12 · 4DMSO
Formula	$\text{C}_{20}\text{H}_{20}\text{Cl}_3\text{MoN}_3\text{O}_5\text{Sn}$	$\text{C}_{24}\text{H}_{30}\text{Cl}_2\text{N}_2\text{O}_9\text{SnW}$	$\text{C}_{40}\text{H}_{54}\text{Cl}_4\text{N}_4\text{O}_{14}\text{S}_6\text{Sn}_2\text{W}_2$
Formula weight	703.37	863.94	1754.11
Crystal size (mm)	$0.20 \times 0.18 \times 0.16$	$0.20 \times 0.18 \times 0.14$	$0.16 \times 0.12 \times 0.06$
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1$	$P\bar{1}$
Cell parameters			
a (Å)	9.163(3)	8.930(3)	9.405(2)
b (Å)	10.402(3)	17.281(6)	11.884(3)
c (Å)	13.861(5)	10.284(4)	14.787(4)
α (°)	86.428(5)	90.0	104.350(4)
β (°)	85.720(5)	90.687(6)	97.645(4)
γ (°)	83.348(5)	90.0	107.607(4)
V (Å ³)	1306.8(7)	1587.0(10)	1486.9(6)
Z	2	2	1
T (K)	293(2)	293(2)	293(2)
$d_{\text{calcd.}}$ (g cm^{-3})	1.788	1.808	1.959
2θ range (°)	2.96–52.84	4.56–52.72	2.92–56.26
$F(0\ 0\ 0)$	688	836	846
λ (Mo $\text{K}\alpha$) (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	1.777	4.624	5.135
Number of reflections measured	10869	9051	9643
Number of reflections observed (R_{int})	5323 (0.02471)	5872 (0.0251)	6914 (0.0275)
Number of parameters	301	393	437
Residuals R , R_w [$I > 2\sigma(I)$]	0.0260, 0.0490	0.0301, 0.0593	0.0442, 0.0869

radiation ($\lambda = 0.71073 \text{ \AA}$) using the $\omega/2\theta$ scan technique, and a semi-empirical absorption correction was applied for all three complexes. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 . The absolute structure parameter for **10** was $-0.010(6)$. All non-hydrogen atoms were refined anisotropically. A summary of the fundamental crystal data for **7**, **10** and **12** is listed in Table 4.

4. Supplementary information

Crystallographic data (CIF files) for the structures of compounds **7**, **10** and **12** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 267304 for **7**, CCDC No. 267305 for **10**, and CCDC No. 267306 for **12**. Copies of this information may be obtained free of charge from 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](http://www.ccdc.cam.ac.uk)).

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