New pentacoordinate bicyclodiazastannsulfide formed between the functionalized cyclopentadienyl ring and tin

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Abstract

New pentacoordinate bicyclodiazastannsulfide fused cyclopentadienyl M–Sn (M = Mo or W) bonded organometallic heterocycle {μ-[$C_5H_4(CH_3)C=N-N=C(S)Ar$]M(CO)$_3$SnCl$_2$} has been obtained by the condensation reaction of $CH_3COC_5H_4M(CO)_3SnCl_3$ with arylthiocarboxyhydrazide (ArCSNHNH$_2$, Ar = 2-furanyl, 2-thienyl, 2- or 4-hydroxyphenyl) in mild conditions. While the similar reaction of $CH_3COC_5H_4M(CO)_3SnCl_3$ with ArCONHNH$_2$ (Ar = 2- or 4-hydroxyphenyl) only gives non-cyclic compounds [$C_5H_4(CH_3)C=N-NHC(O)Ar$]M(CO)$_3$SnCl$_3$, in which the tin atom remains tetracoordinate. In bicyclodiazastannsulfide the tin atom prefers to adopt pentacoordinate geometry, while in the corresponding bicyclodiazastannoxide the tin atom is hexacoordinate. In addition, phenylhydrazine, 2- or 4-hydroxyphenylcarboxyhydrazide is used to react with $CH_3COC_5H_4M(CO)_3SnCl_3$, only tetracoordinate non-cyclic tin compound is obtained.
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1. Introduction

The synthesis and reactivity of heterodimetallic complexes with a directed polar metal–metal bond continues to be an active research area in organometallic chemistry due to their unusual structures, reactions and potential catalytic activities [1–12]. Among these complexes, M–Sn bonded complexes have drawn special attentions and been extensively investigated owing to their applications in many catalytic processes, which often display good selectivity compared to the mononuclear complexes possibly for the sake of the cooperation effect of two metals. Recently, many achievements have been gained in M—Sn bonded complexes, especially Mo–Sn or W–Sn bonded complexes [13–24].

Encouraged by the fascinating results we obtained on binuclear tin complexes before, we recently became interested in studying the transition metal–tin bonded heterodimetallic complexes owing to their unusual structural feature and reactivity [25–27]. The previous work of our group showed that the reaction of functionalized acetylcyclopentadienyl M–Sn bonded heterodimetallic complexes with phenylhydrazine formed a normal hydrazone, in which the tin atom is tetracoordinate, while their analogous reaction with aroylhydrazine yielded a novel bridging dinuclear bicyclodiazastannoxide [28,29], in which the tin atom, instead of assuming general pentacoordinate geometry in known bicyclodiazastannoxide analogues [30,31], prefers to be hexacoordinate through absorbing the chloridion or solvent molecules. It seems that it is difficult to obtain the pentacoordinate tin in these cyclopentadienyl M–Sn bonded heterocycles. Provided the knowledge that the sulfur atom has high affinity for many metals, we found it very intriguing to know if the sulfur atom substituting for the oxygen atom in aroylhydrazine can stabilize the
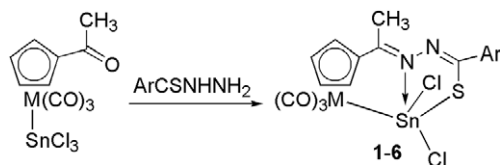
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pentacoordinate tin in these cyclopentadienyl M–Sn bonded heterocycles. In this paper we present the results of this study. As we predicted, the reaction of $CH_3COC_5H_4$-$M(CO)_3SnCl_3$ (M = Mo and W) with arylthiocarboxyhydrazide provides pentacoordinate bicyclodiazastannsulfide.

2. Results and discussion

2.1. Reaction of $CH_3COC_5H_4M(CO)_3SnCl_3$ with arylthiocarboxyhydrazide

The reaction of $CH_3COC_5H_4M(CO)_3SnCl_3$ (M = Mo or W) with arylthiocarboxyhydrazide at room temperature yields bicyclodiazastannsulfides **1–6** (Scheme 1). These complexes have low solubility in common organic solvents, moderate solubility in strongly polar solvents such as acetone, DMF and DMSO at room temperature. The complexes have been characterized by element analyses, IR as well as ^{1}H NMR spectra. No characteristic ν_{NH} peak is observed in their IR spectra. The peak due to O–H stretching has been found at 3352.8 cm^{-1} in **5** and 3326.9 cm^{-1} in **6**, respectively. The $\nu_{C=N}$ peaks appear around 1638–1604 cm^{-1}. The metal carbonyl stretching bands have also been observed in the region of 2037–1917 cm^{-1}. Their ^{1}H NMR spectra demonstrate the structures by exhibiting the expected proton signals, such as two sets of Cp ring resonances, corresponding to the monosubstituted cyclopentadienyl group. Owing to low solubility, only ^{13}C NMR spectra of complexes **4** and **5** can be observed in satisfactory quality, which indicate two sets of signals of the imino carbon atoms as well as three signals of metal carbonyl carbon atoms. In addition, the ^{119}Sn NMR signal of **4** in CD_3SOCD_3 occurs at −347.5 ppm.

The structures of **2**, **3** and **5** have been confirmed further by X-ray single crystal diffraction analyses. Their structures are presented in Figs. 1–3, respectively. Although heteroatoms of the aryl groups in these three complexes do not coordinate to the tin atom of adjacent molecules, unlike in analogous bicyclodiazastannoxide fused cyclopentadienyl M–Sn bonded heterocycle [28,29], the tin atom in complexes **2**, **3** and **5** is pentacoordinate, and has a distorted trigonal bipyramidal coordination with one chlorine atom and one nitrogen atom occupying the axial positions. The axial angle of ∠Cl–Sn–N is very analogous in these complexes (159.6(1)° for **2**, 160.6(1)° for **3** and 160.66(5)° for **5**, respectively). Other geometric features of complexes **2**, **3** and **5** are also markedly different from those of their bicyclodiazastannoxide analogues. For example, five-mem-
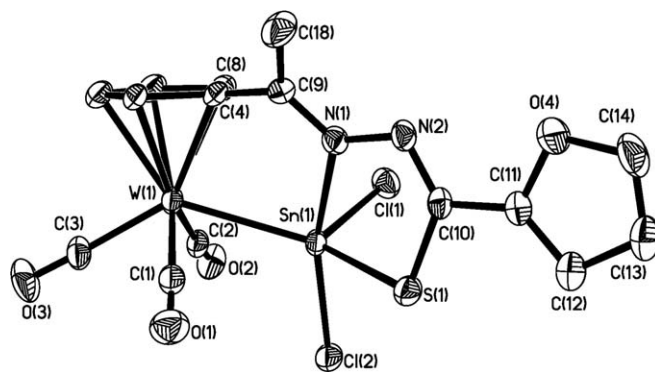

Fig. 1. The molecular structure of complex **2**. The thermal ellipsoids are drawn at the 30% probability level. The uncoordinated solvent acetone molecule has been omitted for clarity. Selected bond distances (Å) and angles (°): W(1)–Sn(1), 2.7419(5); Sn(1)–Cl(1) 2.361(1), Sn(1)–Cl(2), 2.455(1), Sn(1)–N(1) 2.417(4), Sn(1)–S(1) 2.443(1), N(1)–C(9) 1.281(6), N(2)–C(10) 1.298(6), N(1)–N(2) 1.397(5), S(1)–C(10) 1.752(5) Å; N(1)–Sn(1)–Cl(2) 159.64(10), Cl(1)–Sn(1)–N(1) 90.75(10), S(1)–Sn(1)–W(1) 136.97(4), C(9)–N(1)–N(2) 116.3(4), C(9)–N(1)–Sn(1), 122.3(3), N(2)–N(1)–Sn(1) 120.8(3), C(10)–N(2)–N(1) 111.8(4), N(2)–C(10)–S(1) 127.6(4), C(10)–S(1)–Sn(1) 101.20(16), N(1)–C(9)–C(18) 126.2(5), C(9)–N(1)–N(2)–C(10) 153.5(4), N(2)–C(10)–C(11)–O(4) −6.4(7), C(4)–C(8)–C(9)–N(1) −56.4(7)°.
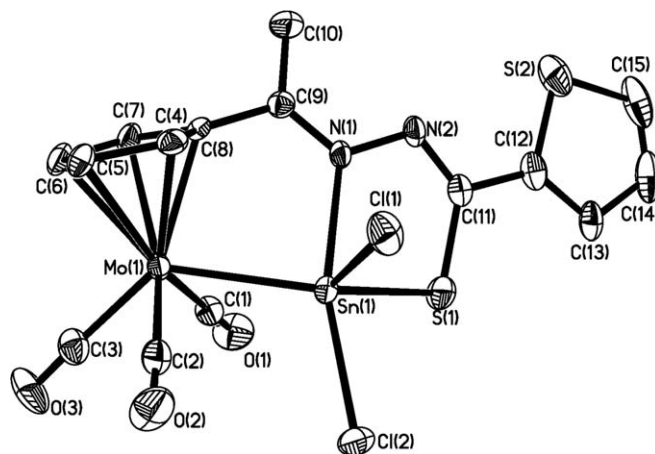

Fig. 2. The molecular structure of complex **3**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): Mo(1)–Sn(1) 2.7300(7), Sn(1)–Cl(1) 2.365(1), Sn(1)–Cl(2) 2.446(1), Sn(1)–N(1) 2.387(4), Sn(1)–S(1) 2.448(1), S(1)–C(11) 1.760(6), N(1)–C(9) 1.281(8), N(1)–N(2) 1.391(6), N(2)–C(11) 1.286(8) Å; N(1)–Sn(1)–Cl(2) 160.6(1), Cl(1)–Sn(1)–N(1) 87.1(1), S(1)–Sn(1)–Mo(1) 134.67(5), C(9)–N(1)–N(2) 118.0(4), C(9)–N(1)–Sn(1) 122.6(4), N(1)–C(9)–C(10) 125.1(5), C(11)–N(2)–N(1) 113.1(5), N(2)–C(11)–S(1) 127.4(5), C(4)–C(8)–C(9)–N(1) 65.9(7), C(9)–N(1)–N(2)–C(11) −159.5(5), N(2)–C(11)–C(12)–S(2) 1.4(8)°.

bered ring of Sn–N–N–C–S remarkably deviates from the coplanarity, with mean deviation from the plane of 0.1340 Å in **2**, 0.1422 Å in **3** and 0.1425 Å in **5**, respectively. In addition, the —C=N—N=C— moiety in these three complexes is also uncoplanar. The mean deviation from the plane is 0.1338 Å in **2**, 0.1023 Å in **3** and 0.1126 Å in **5**, respectively. The torsion angle of ∠C–N–N–C (153.5(4)° in **2**, −159.5(5)° in **3** and −157.6(2)° in **5**, respec-

Scheme 1. Ar = 2-furanyl, M = Mo (**1**), W (**2**); Ar = 2-thienyl, M = Mo (**3**), W (**4**); Ar = p-hydroxylphenyl, M = Mo (**5**), W (**6**).
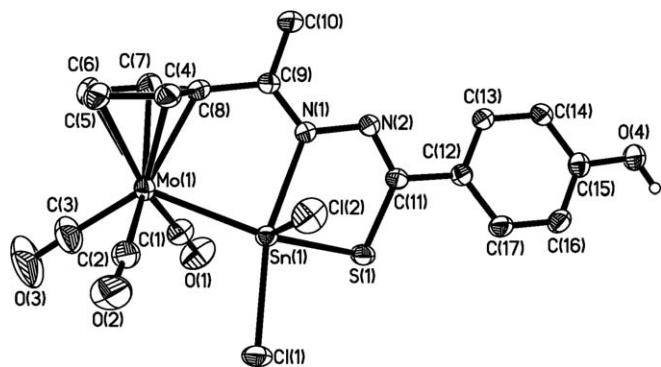
Fig. 3. The molecular structure of complex **5**. The thermal ellipsoids are drawn at the 30% probability level. The solvent uncoordinated acetone molecule has been omitted for clarity. Selected bond distances (Å) and angles (°): Mo(1)–Sn(1) 2.7365(3), Sn(1)–Cl(1) 2.4319(7), Sn(1)–Cl(2) 2.3797(8), Sn(1)–N(1) 2.390(2), Sn(1)–S(1) 2.4322(7), S(1)–C(11) 1.754(3), O(4)–C(15) 1.369(3), N(1)–C(9) 1.287(3), N(1)–N(2) 1.383(3), N(2)–C(11) 1.298(3) Å; Cl(2)–Sn(1)–Cl(1) 96.25(3), N(1)–Sn(1)–Cl(1) 160.66(5), S(1)–Sn(1)–Mo(1) 135.93(2), C(9)–N(1)–N(2) 117.4(2), C(9)–N(1)–Sn(1) 123.11(17), N(2)–N(1)–Sn(1) 119.52(15), C(11)–N(2)–N(1) 113.3(2), C(11)–S(1)–Sn(1) 100.69(9), N(2)–C(11)–S(1) 126.4(2), N(1)–C(9)–C(10) 124.8(2), C(9)–N(1)–N(2)–C(11) −157.6(2), N(2)–C(11)–C(12)–C(13) −17.7(4), C(4)–C(8)–C(9)–N(1) 68.8(4)°.

tively) has also indicated that the —C=N—N=C— moiety has poor coplanarity.

It is also noted that the coordination number of tin in complexes **2**, **3**, **5** and the corresponding bicyclodiazastann-oxides markedly affects their geometric parameters. Some key bond distances, such as M–Sn, Sn–N, Sn–O, Sn–S and Sn–Cl bond distances, are listed in Table 1. It can be seen that the W–Sn bond distance (2.7419(5) Å) in **2** is shorter than those in bicyclodiazastannoxide analogues,

such as in μ-[C_5H_4(CH$_3$)C=N—N=C(O)C_6H_5]W(CO)$_3$-SnCl$_2$(EtOH) (complex **A**, 2.7767(9) Å) [28], μ-[C_5H_4-(CH$_3$)C=N—N=C(O)C_4H_3O]W(CO)$_3$SnCl$_2$(H$_2$O) (complex **B**, 2.8134(9) Å) [29], and μ-{[C_5H_4(CH$_3$)C=N—N=C(O)]$_2C_6H_4${W(CO)$_3$SnCl$_2$(DMSO)}$_2$ (complex **C**, 2.8118(7) Å) [29]. Furthermore, the Mo–Sn bond distances in complexes **3** and **5** are 2.7300(7) Å and 2.7365(3) Å, respectively, also shorter than that in corresponding bicyclodiazastannoxide analogues, such as {μ-[C_5H_4(CH$_3$)C=N—N=C(O)PyH]M(CO)$_3$SnCl$_3$} (complex **D**, 2.8338(8) Å) [28]. On the other hand, the Sn–N bond distance in these three complexes (2.417(4) Å in **2**, 2.387(4) Å in **3** and 2.390(2) Å in **5**, respectively) is longer than that in the related bicyclodiazastannoxides, such as 2.259(6) Å in complex **B**, 2.231(2) Å in complex **D**.

2.2. Reaction of CH$_3$COC$_5$H$_4$M(CO)$_3$SnCl$_3$ with o- or p-hydroxyphenylcarboxyhydrazide

It is known that the hydroxyl group in phenol, a powerful electron-donating group, can coordinate to the tin atom in many mononuclear bicyclodiazastannoxides [30–33]. The observation that the phenolic oxygen atom in complex **5** does not coordinate to the tin atom and the knowledge that the tin atom in bicyclodiazastannoxide usually displays hexacoordinate through absorbing complexing solvent molecules encouraged us to explore whether the phenolic oxygen atom can coordinate to the tin atom in the dinuclear bicyclodiazastannoxides. At the same time, to further confirm the existence of pentacoordinate tin in bicyclodiazastannsulfide as well as the hexacoordinate tin in bicyclodiazastannoxide, the reaction of p-hydroxyphenyl

Table 1
Comparison of some key bond distances (Å) in bicyclodiazastannsulfides and bicyclodiazastannoxides

Compound	M–Sn	Sn–Cl	Sn–N	Sn–S	Sn–O	Reference
μ-[C_5H_4(CH$_3$)C=N–N=C(S)C_4H_3O]W(CO)$_3$SnCl$_2$ (**2**)	2.7419(5)	2.361(1) 2.455(1)	2.417(4)	2.443(1)		This work
μ-[C_5H_4(CH$_3$)C=N–N=C(S)C_4H_3S]Mo(CO)$_3$SnCl$_2$ (**3**)	2.7300(7)	2.365(1) 2.446(1)	2.387(4)	2.448(1)		This work
μ-[C_5H_4(CH$_3$)C=N—N=C(S)(C_6H_4OH-p)]Mo(CO)$_3$SnCl$_2$ (**5**)	2.7365(3)	2.4319(7) 2.3797(8)	2.390(2)	2.4322(7)		This work
μ-[C_5H_4(CH$_3$)C=N—N=C(O)C_6H_5]W(CO)$_3$SnCl$_2$(EtOH) (**A**)	2.7767(9)	2.445(3) 2.454(4)	2.237(9)		2.10(1)	[28]
μ-[C_5H_4(CH$_3$)C=N—N=C(O)C_4H_3O]W(CO)$_3$SnCl$_2$(H$_2$O) (**B**)	2.8134(9)	2.404(1) 2.459(2)	2.259(6)		2.126(4)	[29]
μ-{[C_5H_4(CH$_3$)C=N—N=C(O)]$_2C_6H_4${W(CO)$_3$SnCl$_2$(DMSO)}$_2$ (**C**)	2.8118(7)	2.487(2) 2.423(2)	2.263(6)		2.144(5)	[29]
μ-[C_5H_4(CH$_3$)C=N—N=C(O)PyH]Mo(CO)$_3$SnCl$_3$ (**D**)	2.8338(8)	2.563(1) 2.512(1) 2.442(1)	2.231(2)		2.166(2)	[29]
[C_5H_4(CH$_3$)C=N—NHC(O)(C_6H_4OH-p)]W(CO)$_3$SnCl$_3$ (**10**)	2.7138(9)	2.349(2) 2.346(3) 2.353(2)				This work
[C_5H_4(CH$_3$)C=N—NHC(O)(C_6H_3(NO$_2$)$_2$)]Mo(CO)$_3$SnCl$_3$ (**E**)	2.7040(7)	2.325(2) 2.348(2) 2.352(2)				[28]
[C_5H_5Fe(CO)$_2$]$_2$[(o-NH$_2$)C_6H_4C(O)=N—N=CHC_6H_4O]Sn	2.5421(8) 2.5242(7)		2.247(4)		2.149(5) 2.198(4)	[31]

carboxyhydrazide or salicylhydrazide with $CH_3COC_5H_4M$-$(CO)_3SnCl_3$ is carried out. However, upon treatment of these two reaction reagents under similar reaction conditions with $ArCSNHNH_2$ only yields nonbridged complexes **7–10** (Scheme 2), in which the benzoylhydrazone does not enolize the –NHCO– moiety to the $-N=C(OH)-$ moiety. Neither the imino nitrogen atom, nor carbonyl oxygen atom or the phenolic oxygen atom does not coordinate to the tin atom.

These complexes also have low solubility in common organic solvents, moderate solubility in strongly polar solvents such as acetone, DMF and DMSO at room temperature. Their IR spectra confirm the tetracoordinate tin complexes having a $-C=N-NHC=O-$ moiety. The characteristic v_{NH} peak is observed in the region 3186–3289 cm^{-1}. The $v_{C=N}$ peaks appear around 1605–1615 cm^{-1}, similar with those in complexes **1–6**. In addition, a $v_{C=O}$ absorption band between 1633–1648 cm^{-1} is observed in these four complexes. The ^{13}C NMR spectra of complexes **8** and **10** can be clearly observed, which display one signal of the carbonyl carbon atom (168.4 ppm in **8** and 166.9 ppm in **10**, respectively) as well as one signal of the imino carbon atom (159.5 ppm in **8** and 160.6 ppm in **10**, respectively).

The structure of complex **10** has also been confirmed by X-ray single crystal diffraction analyses. As seen in Fig. 4, the tin atom is tetracoordinate with a distorted tetrahedral geometry, similar with that in $[C_5H_4(CH_3)C=N-NHC-(O)(C_6H_3(NO_2)_2)]Mo(CO)_3SnCl_3$ (complex **E**) [28], and the SnCl$_3$ group is away from the aroylhydrazone moiety. The cooperation effects of several factors maybe result in the formation of the non-cyclic tetracoordinate tin complex rather than a bridging penta- or hexacoordinate tin complex. With such a weaker donor of the oxygen atom compared with the sulfur atom, the electron-donating hydroxyl group of phenol weakening the enolizability of the –NHCO– moiety to the $-N=C(OH)-$ moiety. In addition, the large strain maybe exists in the corresponding bicyclodiazastannoxide, if formed.

Compared with the pentacoordinate tin complex **2** and the hexacoordinate tin complexes **A**, **B** and **C**, the tetracoordinate tin complex **10** has shorter W–Sn bond distance (2.7138(9) Å) (see Table 1). The Sn–Cl bond distances in complex **10** are similar to those in the tetracoordinate tin complex **E**, but shorter than those in penta- and hexacoordinate tin complexes. These short bond distances obviously arise from the increment of the coordination number of the
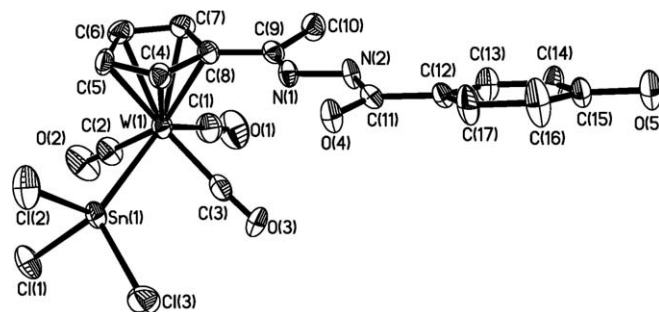

Fig. 4. The molecular structure of complex **10**. The thermal ellipsoids are drawn at the 30% probability level. The solvent uncoordinated acetone molecule has been omitted for clarity. Selected bond distances (Å) and angles (°): W(1)–Sn(1) 2.7138(9), Sn(1)–Cl(2) 2.346(3), Sn(1)–Cl(1) 2.349(2), Sn(1)–Cl(3) 2.353(2), N(1)–C(9) 1.275(9), N(1)–N(2) 1.377(7), N(2)–C(11) 1.385(9), O(4)–C(11) 1.221(8), O(5)–C(15) 1.364(8) Å; Cl(2)–Sn(1)–Cl(1) 98.76(10); Cl(1)–Sn(1)–Cl(3) 100.45(10), C(9)–N(1)–N(2) 117.4(6), N(1)–N(2)–C(11) 118.2(6), O(4)–C(11)–N(2) 120.6(6), C(9)–N(1)–N(2)–C(11) 177.8(6), N(1)–N(2)–C(11)–O(4) −1.3(10), O(4)–C(11)–C(12)–C(13) 169.4(8), C(4)–C(8)–C(9)–N(1) −3.3(11)°.

tin atom weakening the bonding between the Sn–Cl as well as the Sn–M.

Combined with previous work, it seems that the tin atom prefers to be pentacoordinate in these heterobimetallic bicyclodiazastannsulfides; while in corresponding bicyclodiazastannoxide analogues, it is usually hexacoordinate. However, when salicylhadrazide, *p*-hydroxyphenylcarboxyhydrazide and phenylhydrazine are used to react with $CH_3COC_5H_4M(CO)_3SnCl_3$, only non-cyclic tetracoordinate tin complexes are obtained. Furthermore, the structural feature of the tin center in these heterobimetallic complexes significantly depends on the coordination number of the tin atom.

3. Experimental

Solvents were dried by the standard methods prior to use. All reactions were carried out under an argon atmosphere using standard Schlenk and Cannula techniques. NMR spectra were obtained with a Mercury 300BB or Bruker AV300 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 2400 C analyzer. $CH_3COC_5H_4M(CO)_3SnCl_3$ (M = Mo or W) [28] and arylthiocarboxyhydrazide [34] were prepared by the published methods.

3.1. Preparation of complex **1**

2-Furanthiocarboxyhydrazide (21 mg, 0.15 mmol) was added to the solution of $CH_3COC_5H_4Mo(CO)_3SnCl_3$ (76.9 mg, 0.15 mmol) in 10 ml absolute ethanol. The reaction mixture was stirred continuously for 2 h at room temperature, during which a yellow precipitate was formed gradually. The solvent was concentrated to ca. 2 ml under a reduced pressure, and the precipitate was filtered off,
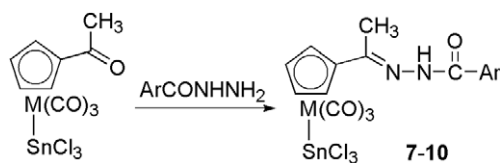
Scheme 2. Ar = *o*-hydroxylphenyl, M = Mo (**7**), W (**8**); Ar = *p*-hydroxylphenyl, M = Mo (**9**), W (**10**).

washed with cold absolute ethanol and recrystallized from acetone/hexane to yield yellow crystals of **1**. Yield: 81%. ^{1}H NMR (DMSO-d_6): δ 8.13, 7.49, 6.85 (s, d, m, 1H, 1H, 1H, C_4H_3O), 6.24, 6.05 (s, s, 2H, 2H, C_5H_4), 2.67 (s, 3H, CH_3). IR: ν_{CO} = 2031.6 (vs), 1981.3 (vs), 1935.3 (vs); $\nu_{C=N}$ = 1607.7 (m) cm^{-1}. Anal. Calc. for $C_{18}H_{16}Cl_2Mo$-N_2O_5SSn: C, 32.83; H, 2.43; N, 4.26. Found: C, 32.67; H, 2.92; N, 3.95%.

3.2. Preparation of complex 2

This complex was obtained similarly using 2-fur-anthiocarboxyhydrazide to react with $CH_3COC_5H_4W$-$(CO)_3SnCl_3$ as described above for **1**. After similar workup, red crystals of **2** were obtained. Yield: 85%. ^{1}H NMR (DMSO-d_6): δ 8.05, 7.42, 6.78 (s, d, m, 1H, 1H, 1H, C_4H_3O), 6.34, 6.07 (s, s, 2H, 2H, C_5H_4), 2.63 (s, 3H, CH_3). IR: ν_{CO} = 2024.8 (vs), 1967.6 (vs), 1923.3 (vs); $\nu_{C=N}$ = 1608.1 (m) cm^{-1}. Anal. Calc. for $C_{18}H_{16}$-$Cl_2N_2O_5SSnW$: C, 28.95; H, 2.14; N, 3.75. Found: C, 28.72; H, 2.45; N, 3.68%.

3.3. Preparation of complex 3

This complex was obtained similarly using 2-thio-phenethiocarboxyhydrazide to react with $CH_3COC_5H_4$-$Mo(CO)_3SnCl_3$ as described above for **1**. The reaction time was 3 h. After similar workup, yellow crystals of **3** were obtained. Yield: 84%. ^{1}H NMR (DMSO-d_6): δ 7.95, 7.25 (m, m, 2H, 1H, C_4H_3S), 6.16, 5.96 (s, s, 2H, 2H, C_5H_4), 2.61 (s, 3H, CH_3). IR: ν_{CO} = 2036.3 (vs), 1984.4 (vs), 1920.0 (vs); $\nu_{C=N}$ = 1637.9 (m) cm^{-1}. Anal. Calc. for $C_{15}H_{10}Cl_2MoN_2O_3S_2Sn$: C, 29.22; H, 1.62; N, 4.55. Found: C, 28.76; H, 2.01; N, 4.45%.

3.4. Preparation of complex 4

This complex was obtained similarly using 2-thio-phenethiocarboxyhydrazide to react with $CH_3COC_5H_4$-$W(CO)_3SnCl_3$ as described above for **1**. The reaction time was 3 h. After similar workup, red crystals of **4** were obtained. Yield: 82%. ^{1}H NMR (CD$_3$COCD$_3$): δ 7.86, 7.72, 7.14 (d, d, m, 1H, 1H, 1H, C_4H_3S), 6.35, 6.01 (t, t, 2H, 2H, C_5H_4), 2.53 (s, 3H, CH_3). ^{13}C NMR (CD$_3$COCD$_3$): δ 22.4 (CH_3), 88.5, 94.2, 94.9 (C_5H_4), 128.7, 131.9, 132.9, 140.4 (C_4H_3S), 162.5, 166.9 (C=N), 206.9, 216.9, 223.6 (CO). ^{119}Sn NMR (DMSO-d_6): δ − 347.5. IR: ν_{CO} = 2029.2 (vs), 1970.6 (vs), 1917.8 (vs); $\nu_{C=N}$ = 1609.7 (m) cm^{-1}. Anal. Calc. for $C_{15}H_{10}Cl_2$-$N_2O_3S_2SnW$: C, 25.57; H, 1.42; N, 3.98. Found: C, 25.80; H, 1.74; N, 3.78%.

3.5. Preparation of complex 5

This complex was obtained similarly using 4-hydroxy-benzothiocarboxyhydrazide to react with $CH_3COC_5H_4$-$Mo(CO)_3SnCl_3$ as described above for **1**. The reaction time

was 3 h. After similar workup, yellow crystals of **5** were obtained. Yield: 84%. ^{1}H NMR (DMSO-d_6): δ 10.4 (s, 1H, OH), 7.99, 6.89 (d, d, 2H, 2H, C_6H_4), 6.20, 5.98 (s, s, 2H, 2H, C_5H_4), 2.61 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 21.4 (CH_3), 89.2, 94.7, 99.3 (C_5H_4), 115.4, 122.0, 126.6, 129.9 (C_6H_4), 161.5, 162.5 (C=N), 206.6, 223.5, 227.8 (CO). IR: ν_{OH} = 3352.8 (br); ν_{CO} = 2029.2 (vs), 1936.7 (br, vs); $\nu_{C=N}$ = 1619.4 (m), 1616.5 (m) cm^{-1}. Anal. Calc. for $C_{20}H_{18}Cl_2MoN_2O_5SSn$: C, 35.09; H, 2.63; N, 4.09. Found: C, 35.65; H, 2.86; N, 3.59%.

3.6. Preparation of complex 6

This complex was obtained similarly using 4-hydroxy-benzothiocarboxyhydrazide to react with $CH_3COC_5H_4$ $W(CO)_3SnCl_3$ as described above for **1**. The reaction time was 3 h. After similar workup, red crystals of **6** were obtained. Yield: 79%. ^{1}H NMR (CD$_3$COCD$_3$): δ 8.09, 6.94 (d, d, 2H, 2H, C_6H_4), 6.46, 6.11 (t, t, 2H, 2H, C_5H_4), 2.68 (s, 3H, CH_3). IR: ν_{OH} = 3326.9 (br); ν_{CO} = 2024.0 (vs), 1927.0 (br, vs); $\nu_{C=N}$ = 1604.9 (m) cm^{-1}. Anal. Calc. for $C_{20}H_{18}Cl_2N_2O_5SSnW$: C, 31.09; H, 2.33; N, 3.63. Found: C, 31.28; H, 2.62; N, 3.70%.

3.7. Preparation of complex 7

Salicylhydrazide (22.8 mg, 0.15 mmol) was added to the solution of $CH_3COC_5H_4Mo(CO)_3SnCl_3$ (76.9 mg, 0.15 mmol) in 10 ml absolute ethanol. The reaction mixture was stirred and refluxed continuously for 3 h to obtain a yellow solution. The solvent was removed under a reduced pressure and the residual solid was recrystallized from acetone/hexane to yield yellow crystals of **7** (76.9 mg, 74%). ^{1}H NMR (DMSO-d_6): δ 12.07 (s, 1H, OH), 7.98, 7.50, 7.00 (d, m, m, 1H, 1H, 2H, C_6H_4), 5.86, 5.78 (s, s, 2H, 2H, C_5H_4), 2.57 (s, 3H, CH_3). IR: ν_{OH} = 3425.6 (br); ν_{NH} = 3286.5 (w), ν_{CO} = 2061.8 (vs), 1989.4 (s), 1943.4 (vs), 1930.1 (vs); $\nu_{C=O}$ = 1633.6 (m); $\nu_{C=N}$ = 1615.1 (m) cm^{-1}. Anal. Calc. for $C_{20}H_{19}Cl_3MoN_2O_6Sn$: C, 34.07; H, 2.70; N, 3.97. Found: C, 33.66; H, 2.71; N, 3.89%.

3.8. Preparation of complex 8

This complex was obtained similarly using salicylhyd-razide (22.8 mg, 0.15 mmol) to react with $CH_3COC_5H_4W$-$(CO)_3SnCl_3$ (90 mg, 0.15 mmol) as described above for **7**. After similar workup, yellow crystals of **8** were obtained. Yield: 79%. ^{1}H NMR (DMSO-d_6): δ 12.22 (br, 1H, OH), 8.05, 7.56, 7.06 (d, m, m, 1H, 1H, 2H, C_6H_4), 6.11, 5.96 (s, s, 2H, 2H, C_5H_4), 2.65 (s, 3H, CH_3). ^{13}C NMR (DMSO-d_6): δ 19.6 (CH_3), 85.0, 93.9, 94.0 (C_5H_4), 117.1, 119.1, 125.9, 129.3, 133.9, 134.4 (C_6H_4), 159.5 (C=N), 168.4 (C=O), 212.9 (CO). IR: ν_{OH} = 3423.8 (br); ν_{NH} = 3287.6 (m); ν_{CO} = 2049.7 (vs), 1981.7 (s), 1949.4 (sh), 1937.4 (vs); $\nu_{C=O}$ = 1647.2 (s); $\nu_{C=N}$ = 1610 (m) cm^{-1}. Anal. Calc. for $C_{20}H_{19}Cl_3N_2O_6SnW$: C, 30.28; H, 2.40; N, 3.53. Found: C, 30.51; H, 2.79; N, 3.97%.

Table 2
Crystal data and refinement parameters for complexes **2**, **3**, **5** and **10**

Compound	**2** · CH$_3$COCH$_3$	**3**	**5** · CH$_3$COCH$_3$	**10** · CH$_3$COCH$_3$
Formula	C$_{18}$H$_{16}$Cl$_2$N$_2$O$_5$SSnW	C$_{15}$H$_{10}$Cl$_2$MoN$_2$O$_3$S$_2$Sn	C$_{20}$H$_{18}$Cl$_2$MoN$_2$O$_5$SSn	C$_{20}$H$_{19}$Cl$_3$N$_2$O$_6$SnW
Formula weight	745.83	615.90	683.95	792.26
Crystal size(mm)	0.24 × 0.16 × 0.12	0.24 × 0.14 × 0.10	0.22 × 0.12 × 0.10	0.22 × 0.14 × 0.12
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$Pna2_1$	$P2_1/c$	$P2_1/n$
Cell parameters				
a (Å)	9.0838(14)	19.498(3)	10.2796(8)	12.941(4)
b (Å)	20.514(3)	10.6125(15)	16.7830(12)	15.431(5)
c (Å)	12.548(2)	9.8148(14)	14.3355(11)	14.067(5)
β (°)	96.881(2)	90.0	91.5510(10)	113.456(4)
V (Å)^3	2321.3(6)	2030.9(5)	2472.3(3)	2576.9(14)
Z	4	4	4	4
T (K)	293(2)	293(2)	293(2)	293(2)
Calcd. density (g cm^{-3})	2.134	2.014	1.838	1.803
2θ Range (°)	3.82–50.06	4.18–50.04	3.74–50.06	3.62–50.06
$F(000)$	1408	1184	1336	1356
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	6.379	2.333	1.851	1.803
No. of reflections measured	12 520	10 208	13 310	13 759
No. of reflections observed [R_{int}]	4099 [0.0306]	3447 [0.0291]	4364 [0.0191]	4546 [0.0390]
No. of parameters	274	236	293	301
Residuals R, Rw [$I > 2\sigma(I)$]	0.0261, 0.0538	0.0272, 0.0638	0.0207, 0.0485	0.0373, 0.0949
GOF	1.040	1.072	1.028	1.021

3.9. Preparation of complex 9

This complex was obtained similarly using 4-hydroxyl-phenylhydrazide to react with CH$_3$COC$_5$H$_4$Mo(CO)$_3$SnCl$_3$ as described above for **7**. After similar workup, yellow crystals of **9** were obtained. Yield: 78%. ^{1}H NMR (DMSO-d_6): δ 8.00, 6.88 (d, d, 2H, 2H, C$_6$H$_4$), 5.77, 5.72 (s, s, 2H, 2H, C$_5$H$_4$), 2.56 (s, 3H, CH$_3$). IR: v_{OH} = 3380.5 (br); v_{NH} = 3186.2 (w), v_{CO} = 2051.1 (vs), 1929.1 (s), 1962.7 (vs); $v_{C=O}$ = 1645.4 (m); $v_{C=N}$ = 1605.4 (m) cm^{-1}. Anal. Calc. for C$_{20}$H$_{19}$Cl$_3$MoN$_2$O$_6$Sn: C, 34.07; H, 2.70; N, 3.97. Found: C, 34.52; H, 2.35; N, 4.35%.

3.10. Preparation of complex 10

This complex was obtained similarly using 4-hydroxylphenylhydrazide to react with CH$_3$COC$_5$H$_4$W-(CO)$_3$SnCl$_3$ as described above for **7**. After similar workup, red crystals of **10** were obtained. Yield: 82%. ^{1}H NMR (DMSO-d_6): δ 8.07, 6.96 (d, d, 2H, 2H, C$_6$H$_4$), 6.03, 5.91 (s, s, 2H, 2H, C$_5$H$_4$), 2.57 (s, 3H, CH$_3$). ^{13}C NMR (DMSO-d_6): δ 19.2 (CH$_3$), 84.8, 93.7, 95.0 (C$_5$H$_4$), 115.1, 119.1, 123.5, 129.8 (C$_6$H$_4$), 160.6 (C=N), 166.9 (C=O), 213.0 (CO). IR: v_{OH} = 3426.3 (br); v_{NH} = 3288.5 (m); v_{CO} = 2044.7 (vs), 1979.0 (s), 1951.7 (vs); $v_{C=O}$ = 1645.5 (m); $v_{C=N}$ = 1605.6 (m) cm^{-1}. Anal. Calc. for C$_{20}$H$_{19}$Cl$_3$N$_2$O$_6$SnW: C, 30.28; H, 2.40; N, 3.53. Found: C, 30.46; H, 2.63; N, 3.95%.

3.11. X-ray crystallography

Crystals of complexes **2**, **3**, **5** and **10** suitable for X-ray analysis were obtained by slow diffusion of hexane into the acetone solution of these complexes at −18 °C. Crystals of complexes **2**, **5** and **10** crystallize with one molecular acetone, respectively. Intensity data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using the ω/2θ scan technique, and a semi-empirical absorption correction was applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. The absolute structure parameter for **3** was 0.00(3). All non-hydrogen atoms were refined anisotropically. A summary of the fundamental crystal data for **2**, **3**, **5** and **10** is listed in Table 2.

Appendix A. Supplementary information

Crystallographic data (CIF files) for the structures of complexes **2**, **3**, **5** and **10** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 600530 for **2**, CCDC no.600527 for **3**, 600528 for **5**, and CCDC no. 600529 for **10**. 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). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.010.

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