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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-[$C_5H_4(CH_3)C{=}N{-}N{=}C(S)Ar$]$M(CO)_3SnCl_2$} 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 [$C_5H_4(CH_3)C{=}N{-}NHC(O)Ar$]$M(CO)_3SnCl_3$, 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.

Keywords: Cyclopentadienyl; Tin; Group 6 carboxyl metal compound; Thicarboxydrazide; Heterocycle

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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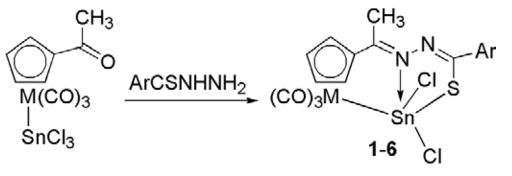
pentacoordinate tin in these cyclopentadienyl M–Sn bonded heterocycles. In this paper we present the results of this study. As we predicted, the reaction of $CH_3COC_5H_4$-$M(CO)_3SnCl_3$ (M = Mo and W) with arylthiocarboxyhydrazide provides pentacoordinate bicyclodiazastannsulfide.

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 $\nu_{\mathrm{C=N}}$ 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-membered 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**).

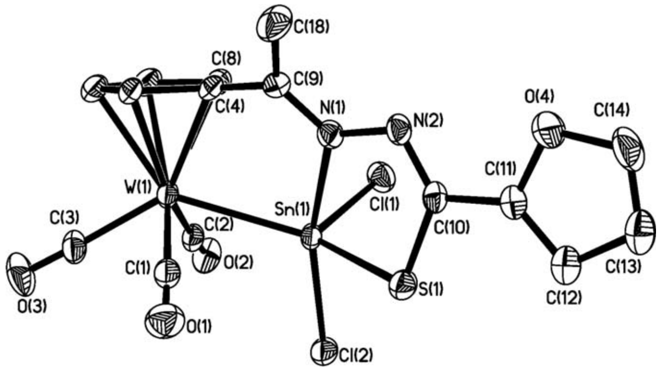


Fig. 1. The molecular structure of complex **2**. The thermal ellipsoids are drawn at the 30% probability level. The uncoordinated solvent acetone molecule has been omitted for clarity. Selected bond distances (Å) and angles (°): W(1)–Sn(1), 2.7419(5), Sn(1)–Cl(1) 2.361(1), Sn(1)–Cl(2), 2.455(1), Sn(1)–N(1) 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)°.

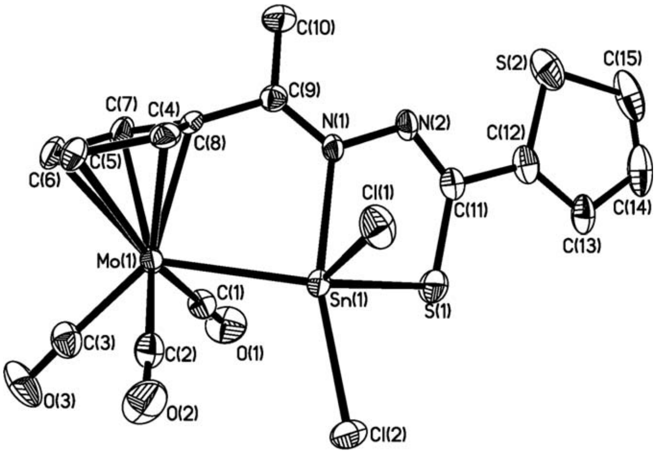


Fig. 2. The molecular structure of complex **3**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): Mo(1)–Sn(1) 2.7300(7), Sn(1)–Cl(1) 2.365(1), Sn(1)–Cl(2) 2.446(1), Sn(1)–N(1) 2.387(4), Sn(1)–S(1) 2.448(1), S(1)–C(11) 1.760(6), N(1)–C(9) 1.281(8), 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)°.