



# The modification of $\text{ArSCH}_2(3,5\text{-Me}_2\text{Pz})$ ( $\text{Ar} = \text{phenyl}$ or $2\text{-pyridyl}$ , $\text{Pz} = \text{pyrazol-1-yl}$ ) by organotin group and related reactions

Yun-Fu Xie, Guang-Tong Zeng, Hai-Bin Song, Liang-Fu Tang\*

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

## ARTICLE INFO

### Article history:

Received 7 May 2010

Received in revised form

1 June 2010

Accepted 3 June 2010

Available online 15 June 2010

### Keywords:

3,5-Dimethylpyrazole

Organotin

Group 6 metal carbonyl complex

S,N chelating ligand

Oxidative addition

## ABSTRACT

Reaction of 1-aryltiomethyl-3,5-dimethylpyrazole [ $\text{ArSCH}_2(3,5\text{-Me}_2\text{Pz})$ ,  $\text{Ar} = \text{phenyl}$  or  $2\text{-pyridyl}$ ,  $\text{Pz} = \text{pyrazol-1-yl}$ ] with  $\text{Mo}(\text{CO})_6$  produces complexes  $\text{ArSCH}_2(3,5\text{-Me}_2\text{Pz})\text{Mo}(\text{CO})_4$ , while similar reaction with  $\text{W}(\text{CO})_6$  yields analogous complexes  $\text{ArSCH}_2(3,5\text{-Me}_2\text{Pz})\text{W}(\text{CO})_4$  and concomitant desulfurized complex  $(3,5\text{-Me}_2\text{PzH})\text{W}(\text{CO})_5$  in the reaction of  $\text{PhSCH}_2(3,5\text{-Me}_2\text{Pz})$ . Succeedent treatment of complexes  $\text{PhSCH}_2(3,5\text{-Me}_2\text{Pz})\text{M}(\text{CO})_4$  with  $\text{SnCl}_4$  gives heterobimetallic complexes  $\text{PhSCH}_2(3,5\text{-Me}_2\text{Pz})\text{M}(\text{CO})_3(\text{Cl})$  ( $\text{SnCl}_3$ ) ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) in good yields.  $\text{ArSCH}_2(3,5\text{-Me}_2\text{Pz})$  act as S,N chelating bidentate ligands through the sulfur and the pyrazolyl nitrogen atoms in the aforementioned complexes. The modification of  $\text{ArSCH}_2(3,5\text{-Me}_2\text{Pz})$  by organotin group at the methylene group has been successfully carried out, which yields functionalized ligands  $\text{Ph}_3\text{SnCH}(\text{SAr})(3,5\text{-Me}_2\text{Pz})$ . Markedly different reactions are observed, upon treatment of  $\text{Ph}_3\text{SnCH}(\text{SPh})(3,5\text{-Me}_2\text{Pz})$  and  $\text{Ph}_3\text{SnCH}(\text{SPy})(3,5\text{-Me}_2\text{Pz})$  ( $\text{Py} = 2\text{-pyridyl}$ ) with  $\text{W}(\text{CO})_5\text{THF}$ . The former yields complex  $\text{Ph}_3\text{SnCH}(\text{SPh})(3,5\text{-Me}_2\text{Pz})\text{W}(\text{CO})_4$ , as well as  $\text{PhSCH}_2(3,5\text{-Me}_2\text{Pz})\text{W}(\text{CO})_4$  with a partial loss of the organotin moiety, while no reaction takes place in the latter. In addition, reaction of  $\text{Ph}_3\text{SnCH}(\text{SPy})(3,5\text{-Me}_2\text{Pz})$  with  $\text{Mo}(\text{CO})_6$  results in the oxidative addition reaction of the  $\text{Sn}-\text{C}_{\text{sp}^3}$  bond to the molybdenum(0) atom to yield novel heterometallacyclic complex  $\text{CH}(\text{SPy})(3,5\text{-Me}_2\text{Pz})\text{Mo}(\text{CO})_3\text{SnPh}_3$ , in which [(2-pyridyl)thiomethyl](3,5-dimethylpyrazol-1-yl)methide acts as a tridentate  $\kappa^3\text{-[N,C,N]}$  chelating ligand through the carbon atom, the pyrazolyl and the pyridyl nitrogen atoms, as the sulfur atom does not coordinate to the molybdenum atom anymore. Interestingly, treatment of this heterometallacyclic complex with  $\text{P}(\text{OR})_3$  ( $\text{R} = \text{Ph}$  or  $\text{Et}$ ) gives rise to the isomerization of the C–S bond to the C–N bond, generating the thione–S coordinated complex  $\text{CH}(\text{NC}_4\text{H}_4\text{C} = \text{S})(3,5\text{-Me}_2\text{Pz})\text{Mo}(\text{CO})_2(\text{P}(\text{OR})_3)\text{SnPh}_3$ , in which the ligand binds in a novel tridentate, monoanionic  $\kappa^3\text{-[N,C,S]}$  chelating mode to the molybdenum atom.

© 2010 Elsevier B.V. All rights reserved.

## 1. Introduction

Bis(pyrazol-1-yl)methanes modified by organic functional groups on the bridging carbon atom have drawn extensive attention in recent years, owing to their versatile coordination chemistry towards main group and transition metals [1–3]. Recently, we have developed the modification of bis(pyrazol-1-yl)methanes by organotin groups on the methine carbon atom and proved that the reactivity of these functionalized bis(pyrazol-1-yl)methanes markedly depends on the properties of substituents on the tin atom [4–6]. For example, the reaction of triarylstannylbis(3,5-dimethylpyrazol-1-yl)methane with  $\text{W}(\text{CO})_5\text{THF}$  results in the oxidative addition reaction of the  $\text{Sn}-\text{C}_{\text{sp}^3}$  bond to the tungsten(0) atom to yield novel four-membered metallacyclic complex

$\text{CH}(3,5\text{-Me}_2\text{Pz})_2(\text{CO})_3\text{WSnAr}_3$  [5], while the analogous reaction of bis(3,5-dimethylpyrazol-1-yl)methane functionalized by organotin halide leads to the oxidative addition of the relatively electrophilic  $\text{Sn}-\text{X}$  ( $\text{X}$  represents halogen) bond to the tungsten(0) atom [4]. Interestingly, treatments of  $\text{CH}(3,5\text{-Me}_2\text{Pz})_2(\text{CO})_3\text{WSnAr}_3$  with both nucleophilic [7] and electrophilic [8] reagents bring about unusual ring-expansion reactions. These results inspire us to explore the analogous reactivity of other ligands with similar structural features, and 1-phenylthiomethyl-3,5-dimethylpyrazole [9] provides an available case. The lithiation of this ligand at the methylene group has been successfully carried out [9], and the corresponding lithium compound can react with various electrophiles, which makes it as a useful synthetic intermediate. On the other hand, this ligand is anticipated to act as a hybrid S,N chelating ligand. In this paper, we investigate the modification of 1-phenylthiomethyl-3,5-dimethylpyrazole and its analog, namely 1-(2-pyridyl)thiomethyl-3,5-dimethylpyrazole, by organotin group at the methylene group and their related reactions with group 6 metal carbonyl complexes.

\* Corresponding author. Fax: +86 22 23502458.

E-mail address: lftang@nankai.edu.cn (L.-F. Tang).

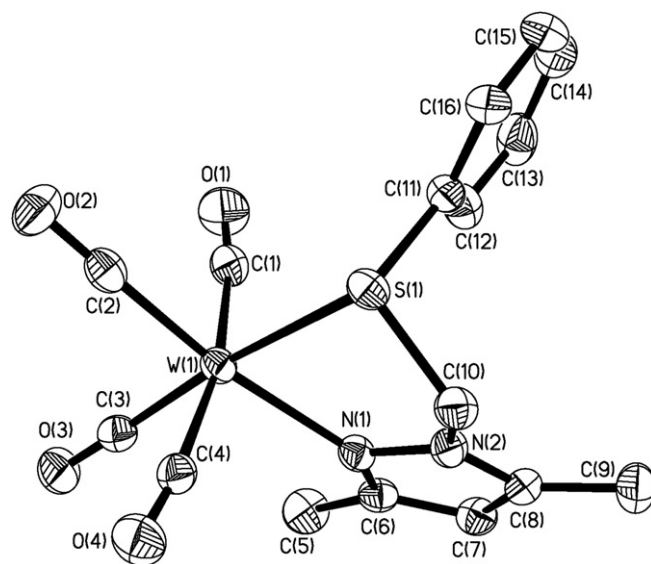
## 2. Results and discussion

### 2.1. Related reaction of 1-phenylthiomethyl-3,5-dimethylpyrazole

1-Phenylthiomethyl-3,5-dimethylpyrazole [PhSCH<sub>2</sub>(3,5-Me<sub>2</sub>Pz), Pz = pyrazol-1-yl] has been synthesized for about two decades [9], but its coordination chemistry has drawn little attention. To gain more convictive knowledge on its coordination ability to transition metals and comprehensive foundations for further research, we started our investigations with the reaction of this ligand with M(CO)<sub>6</sub> (M = Mo or W) (Scheme 1). Reaction of PhSCH<sub>2</sub>(3,5-Me<sub>2</sub>Pz) with Mo(CO)<sub>6</sub> produced PhSCH<sub>2</sub>(3,5-Me<sub>2</sub>Pz)Mo(CO)<sub>4</sub> (**1**), similar reaction with W(CO)<sub>6</sub> yielded analogous complex PhSCH<sub>2</sub>(3,5-Me<sub>2</sub>Pz)W(CO)<sub>4</sub> (**2**) and concomitant desulfurized complex (3,5-Me<sub>2</sub>PzH)W(CO)<sub>5</sub>. Succedent reaction of complexes PhSCH<sub>2</sub>(3,5-Me<sub>2</sub>Pz)M(CO)<sub>4</sub> with SnCl<sub>4</sub> gave heterobimetallic complexes PhSCH<sub>2</sub>(3,5-Me<sub>2</sub>Pz)M(CO)<sub>3</sub>(Cl)(SnCl<sub>3</sub>) (M = Mo (**3**) and W (**4**), respectively) in good yields.

Complexes **1–4** have been characterized by elemental analyses, IR and NMR spectroscopy. These spectroscopic data support the suggested structures. The IR spectra of complexes **1** and **2** show four bands in the carbonyl stretching region, implying a typical *cis*-tetracarbonyl arrangement [10]. While three carbonyl stretching bands are observed in the seven-coordinate complexes **3** and **4**. The structures of complexes **2** and **4** have been further confirmed by X-ray structural analyses.

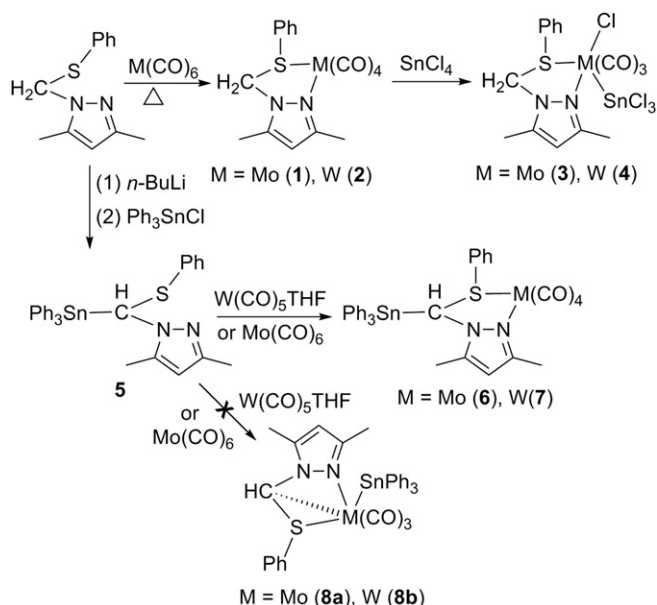
The crystal structures of complexes **2** and **4** are presented in Figs. 1 and 2, respectively. In these two complexes, 1-phenylthiomethyl-3,5-dimethylpyrazole acts as a hybrid S,N chelating ligand, as expected. The W–N bond distance in complex **2** is 2.264(4) Å, similar to those found in other octahedral tungsten(0) complexes with pyrazol-1-yl ligands, such as 2.292(6) Å in CH<sub>2</sub>(3-*p*-MeOph-5-MeSPz)<sub>2</sub>W(CO)<sub>4</sub> [11] and 2.268(4) Å as well as 2.270(4) Å in Me<sub>3</sub>SiCH(3,5-Me<sub>2</sub>Pz)<sub>2</sub>W(CO)<sub>4</sub> [12]. The W–S bond distance of 2.5398(12) Å is also comparable to those reported in tungsten(0) complexes with thioether ligands, such as 2.543(2) and 2.554(2) Å in W(CO)<sub>4</sub>L (L = 1,1,1-tetrakis(methylthiomethyl)methane) [13] as well as 2.585(2) and 2.565(2) Å in (Fc<sup>t</sup>BuSMe)W(CO)<sub>4</sub> (Fc = 1,1'-ferrocenyl) [14]. It is noteworthy that two *cis*-carbonyl groups in this complex considerably deviate from linearity with the W(1)–C



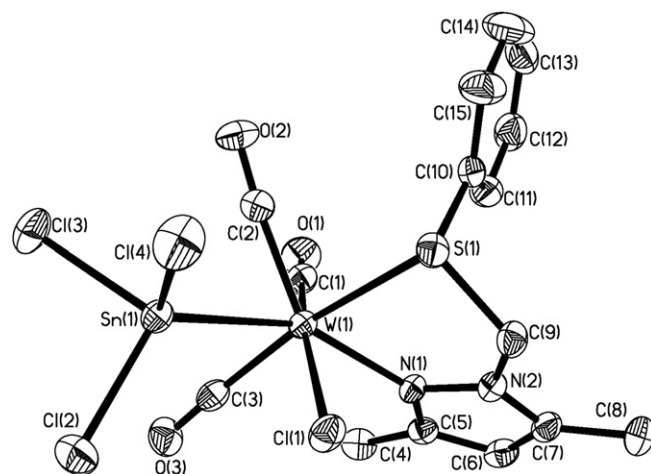
**Fig. 1.** The molecular structure of **2**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): W(1)–N(1) 2.264(4), W(1)–S(1) 2.5398(12), C(10)–S(1) 1.810(4), C(10)–N(2) 1.438(5) Å; W(1)–C(1)–O(1) 171.8(4), W(1)–C(2)–O(2) 178.5(4), W(1)–C(3)–O(3) 178.1(4), W(1)–C(4)–O(4) 172.8(4), C(1)–W(1)–C(4) 169.80(18), C(3)–W(1)–S(1) 173.61(14), C(3)–W(1)–N(1) 99.22(15), C(10)–S(1)–W(1) 96.46(13), N(1)–W(1)–S(1) 77.18(8), N(2)–C(10)–S(1) 111.3(3)°.

(1)–O(1) angle of 171.8(4)° and the W(1)–C(4)–O(4) angle of 172.8(4)°, indicating the presence of steric repulsion between the ligand and these carbonyls. The W–N bond distance of 2.219(4) Å in complex **4** is slightly shorter than that in complex **2**, while the W–S bond distance of 2.5702(15) Å in complex **4** is longer than the corresponding bond distance in complex **2**. These two complexes have similar bite angle N–W–S of 76.23(11)° in complex **4** and 77.18(8)° in complex **2**, respectively.

When PhSCH<sub>2</sub>(3,5-Me<sub>2</sub>Pz) was treated with butyllithium, the methylene group was deprotonated to afford LiCH(SPh)(3,5-Me<sub>2</sub>Pz) [9]. Treatment of this lithium compound with Ph<sub>3</sub>SnCl yielded Ph<sub>3</sub>SnCH(SPh)(3,5-Me<sub>2</sub>Pz) (**5**), which was confirmed by X-ray



**Scheme 1.** Related reaction of 1-phenylthiomethyl-3,5-dimethylpyrazole.



**Fig. 2.** The molecular structure of **4**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): W(1)–N(1) 2.219(4), W(1)–Cl(1) 2.5409(14), W(1)–S(1) 2.5702(15), W(1)–Sn(1) 2.7711(8), Sn(1)–Cl(4) 2.3483(18), Sn(1)–Cl(2) 2.3487(17), Sn(1)–Cl(3) 2.3897(17), C(9)–S(1) 1.823(6), C(9)–N(2) 1.461(6) Å; C(3)–W(1)–S(1) 170.80(15), N(1)–W(1)–Sn(1) 150.73(10), N(1)–W(1)–S(1) 76.23(11), Cl(2)–Sn(1)–Cl(3) 97.38(7), Cl(3)–Sn(1)–W(1) 120.56(5), C(9)–S(1)–W(1) 98.80(18), N(2)–C(9)–S(1) 111.7(3)°.

Download English Version:

<https://daneshyari.com/en/article/1324053>

Download Persian Version:

<https://daneshyari.com/article/1324053>

[Daneshyari.com](https://daneshyari.com)