



Functionalized bis(1-methylimidazol-2-yl)methane and 1-(1-methylimidazol-2-yl)methyl-3,5-dimethylpyrazole and their reactions

Hai-Jun Li, Xia-Li Liu, Ke Ding, Hai-Bin Song, Liang-Fu Tang*

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300071, People's Republic of China

ARTICLE INFO

Article history:

Received 20 November 2013

Received in revised form

9 January 2014

Accepted 17 January 2014

Keywords:

1-Methylimidazole

3,5-Dimethylpyrazole

Organotin

Carbonyl tungsten

Sulfur

ABSTRACT

Bis(1-methylimidazol-2-yl)methane and 1-(1-methylimidazol-2-yl)methyl-3,5-dimethylpyrazole [$\text{CH}_2(\text{min})(\text{pz})$] could be deprotonated with *n*-BuLi at the bridging carbon atom. The corresponding anions were inactive in the reaction with Ph_3SnCl but reacted with sulfur, followed by reaction with Ph_2SnCl_2 to give organotin derivatives $\text{Ph}_2\text{ClSnSCH}(\text{min})_2$ (**1**) and $\text{Ph}_2\text{ClSnSCH}(\text{min})(\text{pz})$ (**4**) (min = 1-methylimidazol-2-yl and pz = 3,5-dimethylpyrazol-1-yl, respectively). The structure of **1** determined by X-ray structural analyses indicated that bis(1-methylimidazol-2-yl)methylthiolate acted as a bidentate monoanionic κ^2 -[N,S] chelating ligand. Reaction of **1** with $\text{W}(\text{CO})_5\text{THF}$ yielded heterobimetallic complex $\text{Ph}_2\text{ClSnSCH}(\text{min})_2\text{W}(\text{CO})_5$ (**2**), while similar reaction of **4** with $\text{W}(\text{CO})_5\text{THF}$ resulted in the decomposition of **4** to give pyrazole derivative $\text{W}(\text{CO})_5(\text{pzH})$. The structure of **2** has been confirmed by X-ray structural analyses, showing that **1** coordinated to the tungsten atom through the free nitrogen atom. Reaction of $\text{CH}_2(\text{min})(\text{pz})$ with $\text{W}(\text{CO})_5\text{THF}$ yielded bidentate chelating complex $\text{CH}_2(\text{min})(\text{pz})\text{W}(\text{CO})_4$, which when treated with *n*-BuLi, followed by reaction with Ph_3SnCl , gave the final product $\text{CH}_2(\text{minSnPh}_3)(\text{pz})\text{W}(\text{CO})_4$.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The coordination behavior of bis(pyrazol-1-yl)methanes towards main group and transition metals has been extensively investigated in recent years [1], suggesting an encouraging advantage that their electronic and steric effects can be readily adjusted by changing the substituents on the pyrazolyl rings. The deprotonation of their methylene bridge to give bis(pyrazol-1-yl)methide anions has been reported [2,3] and the resulting anions can react with various electrophiles to yield versatile heteroscorpionate ligands [4–6], which widely broadens the application areas of bis(pyrazol-1-yl)methanes. Our recent investigations demonstrated that bis(pyrazol-1-yl)methanes functionalized with organic functional groups on the methine carbon atom displayed unusual reactivity [7–10]. For instance, the reaction of 2-hydroxyphenyl functionalized bis(pyrazol-1-yl)methanes with $\text{W}(\text{CO})_5\text{THF}$ resulted in the cleavage of a $\text{C}_{\text{sp}^3}\text{--N}$ bond to form novel pyrazole derivatives [7]. Another intriguing example is the reaction of bis(3,5-dimethylpyrazol-1-yl)methylthiolate with $\text{Fe}_3(\text{CO})_{12}$, followed by the treatment with RX, which gave rise to the

formation of unexpected (3,5-dimethylpyrazol-1-yl)dithioformate derivatives [8]. These results inspire us to explore the related reactivity of other ligands with similar structural features. As the isoelectronic and isosteric ligand of pyrazole, imidazole has been widely used in the coordination chemistry and bioinorganic chemistry [11,12] and the replacement of pyrazole by 1-methylimidazole to form bis(1-methylimidazol-2-yl)methane has been described in the literature [13]. This ligand acted as a good donor to various main group and transition metals because of the strong donating ability of imidazole [14–28]. The coordination behavior of bis(1-methylimidazol-2-yl)methane is very similar to that of bis(pyrazol-1-yl)methanes, such as acting as a chelating bidentate ligand upon coordinating to metals. The lithiation of bis(1-methylimidazol-2-yl)methane at the methylene group could be successfully carried out, and the corresponding anion could readily react with various electrophiles to form new polydentate ligands [13,29–36]. As an extension of our investigations on functionalized bis(pyrazol-1-yl)methanes, herein we report the modification of bis(1-methylimidazol-2-yl)methane and 1-(1-methylimidazol-2-yl)methyl-3,5-dimethylpyrazole at the methylene group as well as their related reactions. These functionalized ligands showed markedly different reaction patterns, compared to the analogs of bis(pyrazol-1-yl)methanes.

* Corresponding author. Fax: +86 22 23502458.

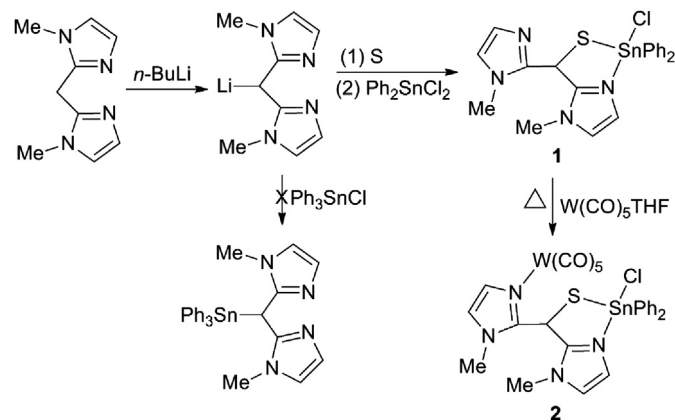
E-mail address: ltang@nankai.edu.cn (L.-F. Tang).

2. Results and discussion

2.1. Functionalized bis(1-methylimidazol-2-yl)methane and its reactions

Being different from bis(3,5-dimethylpyrazol-1-yl)methide anion [37], we herein found that bis(1-methylimidazol-2-yl)methide anion, prepared in situ by the lithiation of bis(1-methylimidazol-2-yl)methane at the methylene group using *n*-BuLi at low temperature, did not react with Ph₃SnCl. The expected derivative Ph₃SnCH(min)₂ (min = 1-methylimidazol-2-yl) could not be obtained (Scheme 1), with almost full recovering of starting materials after workup. The reason is not completely clear at present, which may be relative to the isomerism of carbanions originated from diheteroarylmethanes [38], leading to the replacement of pyrazole by 1-methylimidazole increasing the acidity of methylene protons, therefore decreasing the nucleophilicity of the corresponding anion towards Ph₃SnCl. However, bis(1-methylimidazol-2-yl)methylthiolate anion could be obtained by the reaction of lithiated bis(1-methylimidazol-2-yl)methane with sulfur, which was stable at room temperature, and readily reacted with Ph₂SnCl₂ to give complex **1**. This complex has been characterized by elemental analyses, as well as NMR spectra. The characteristic proton signal of CH group appeared at 6.16 ppm, markedly shifted to lower field than that of the methylene group in bis(1-methylimidazol-2-yl)methane (4.24 ppm) [13], mainly owing to the deshielding effect by the electronegative sulfur atom. It should be noted that although complex **1** possessed two different imidazolyl rings in solid (Fig. 1), only one set of ¹H NMR signals for the bis(1-methylimidazol-2-yl)methide group were observed in solution, which should be the result of the fast exchange in the coordination behavior of two imidazole ligands on the NMR time scale. Similar phenomenon has also been observed for organotin derivatives of bis(pyrazol-1-yl)methylthiolate [39]. In addition, the ¹¹⁹Sn NMR signal of complex **1** appeared at –230.4 ppm, similar to those of other five-coordinated organotin derivatives [39–41].

The molecular structure of **1** has been further confirmed by X-ray structural analyses, which consisted of two crystallographically independent molecules with similar structural parameters. One of them is presented in Fig. 1. As shown in the figure, bis(1-methylimidazol-2-yl)methylthiolate coordinates to the tin atom by only one nitrogen atom and the sulfur atom, acting as a bidentate monoanionic κ²-[N,S] chelating ligand. The tin atom adopts a five-coordinate distorted trigonal bipyramidal geometry with the N(3) and Cl(1) atoms occupying the axial positions. The Sn–N bond distance is 2.248(5) Å, shorter than that in five-coordinate



Scheme 1. The modification of bis(1-methylimidazol-2-yl)methane.

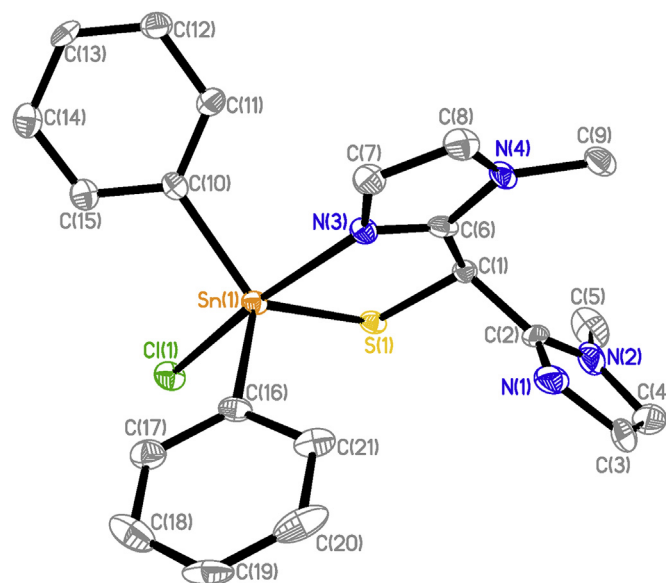


Fig. 1. The molecular structure of **1**. The thermal ellipsoids are drawn at the 30% probability level. The uncoordinated solvent was omitted for clarity. Selected bond distances (Å) and angles (°): Sn(1)–N(3) 2.248(5), Sn(1)–S(1) 2.419(2), Sn(1)–Cl(1) 2.501(2), C(1)–S(1) 1.839(6) Å; N(3)–Sn(1)–Cl(1) 167.0(1), C(16)–Sn(1)–C(10) 121.1(2), C(10)–Sn(1)–N(3) 90.9(2), C(10)–Sn(1)–N(3) 90.9(2), C(10)–Sn(1)–S(1) 123.1(2), N(3)–Sn(1)–S(1) 80.7(1), S(1)–Sn(1)–Cl(1) 86.48(5), C(1)–S(1)–Sn(1) 102.5(2), C(6)–C(1)–S(1) 112.4(4)°.

organotin derivative Ph₂ClSnSeCH(pz)₂ with a similar fundamental skeleton (2.373(4) Å, pz = 3,5-dimethylpyrazol-1-yl) [39], possibly owing to the stronger donor ability of the imidazolyl nitrogen, compared to the corresponding pyrazolyl nitrogen [28,32].

Compound **1** is anticipated to act as a good donor for transition metals owing to the high affinity of sulfur for many metals as well as the strong donating ability of the free imidazolyl nitrogen atom. At the same time, **1** is expected to be able to provide multiple coordination sites since the oxidative addition of the Sn–halogen [42] and Sn–S [43] bonds to low-oxidative transition metals is known. However, upon treatment of **1** with W(CO)₅THF at 45 °C, only complex **2** was obtained. When the reaction was carried out at a higher temperature, no isolable product was obtained. Complex **2** has been characterized by IR and NMR spectra. Its IR spectrum showed a pattern of ν_{CO} bands for the W(CO)₅ fragment. A ν_{CO} band was observed at 2069.6 cm^{–1}, which was assigned to the A_{1eq} mode for the pseudo C_{4v} metal center in a metal pentacarbonyl moiety [44]. Its NMR spectra also support the proposed structure. For example, two sets of ¹H and ¹³C signals corresponding to the imidazolyl moieties were observed in its ¹H and ¹³C NMR spectra, suggesting their location in different coordination environments. Furthermore, two signals of the carbonyl carbon atoms with ca. a 1:4 intensity ratio were observed in its ¹³C NMR spectrum. The ¹¹⁹Sn NMR signal occurred at –234.0 ppm, very similar to that of **1**, consistent with the fact of the reaction center away from the tin atom.

The molecular structure of **2** was confirmed by X-ray structural analyses, and is presented in Fig. 2, which manifests that **1** coordinates to the tungsten atom through the free nitrogen atom only. The fundamental framework of **1** is kept in **2**. The Sn–N and Sn–S bond distances are not significantly changed in these two complexes. But the axial angle N–Sn–Cl of 162.0(2)° in **2** is smaller than the corresponding angle (167.0(1)°) in **1**, implying possibly the bigger steric repulsion in **2**. The tungsten atom adopts a six-coordinate distorted octahedral geometry. The W–N bond

Download English Version:

<https://daneshyari.com/en/article/1322460>

Download Persian Version:

<https://daneshyari.com/article/1322460>

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