

Molybdenum complexes of poly[(methylthio)methyl]borates

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ARTICLE INFO

Article history:

Received 12 March 2018

Accepted 25 April 2018

Available online 4 May 2018

Keywords:

Molybdenum

Scorpionates

Poly[(methylthio)methyl]borates

NMR spectroscopy

X-ray diffraction

ABSTRACT

Organometallic molybdenum compounds bearing poly[(methylthio)methyl]borates, $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2(\kappa^3\text{-PhTt})]$ and $[\text{Bu}_4\text{N}]\{[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2\text{Cl}]_2(\kappa^2:\kappa^2\text{-RTt})\}$, where PhTt = phenyltris[(methylthio)methyl]borate and RTt = tetrakis[(methylthio)methyl]borate, have been obtained by ligand exchange reaction from $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2(\text{NCMe})_2\text{Cl}]$ and appropriate borate. The PhTt ligand provides tridentate face-capping coordination to the central metal while the RTt acts as a bridging ligand and connects two $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2\text{Cl}]$ monomeric units by unusual $\kappa^2:\kappa^2$ -coordination mode. Both compounds were fully characterized by spectroscopic methods and X-ray crystallography.

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1. Introduction

The discovery of poly(pyrazolyl)borates by Trofimenko et al. in 1966 initiated long-standing interest in coordination chemistry of tridentate face-capping ligands [1–6]. Due to the tripodal coordination mode to the metal atoms, the poly(pyrazolyl)borates and their congeners have become known as scorpionates [4]. The main advantage of scorpionate ligands lies in simple modification of the parent structure that enables a fine tuning of their electronic and steric properties, which is very useful for design of new catalysts [7–10], modeling of active site of metalloenzymes and drug design [11–15].

Scorpionate ligands with sulfur donor atoms [16–23] are of particular interest mainly due to structural analogy with sulfur-rich metalloenzymes (e.g. rubredoxins, deazaflavin reducing hydrogenase, $[\text{NiFe}_4\text{S}_4]$ -based CO-dehydrogenase or FeMo nitrogenase cofactor) [24–27]. The tetrakis[(methylthio)methyl]borate (RTt) ligand, as the first representative of the sulfur donor scorpionates, was described in 1994 and face-capping coordination mode was demonstrated on $[\text{Bu}_4\text{N}][\text{Mo}(\kappa^3\text{-RTt})(\text{CO})_3]$ complex [16]. Furthermore, the soft scorpionate in the coordination sphere allows molybdenum atom to be protonated using strong acid to afford hydride compound $[\text{Mo}(\kappa^3\text{-RTt})(\text{CO})_3\text{H}]$ [16]. Subsequently, chemistry of various poly[(alkylthio)methyl]borates have been demon-

strated on numerous of metal complexes [17–19,28–30]. For example, bridging coordination of phenyltris[(methylthio)methyl]borate (PhTt) was described for homoleptic copper(I) tetramer $[\text{Cu}(\text{PhTt})_4]$ [18]. The sterically demanding phenyltris[(*tert*-butylthio)methyl]borate (PhTt^{tbu}) allows to isolate tetrahedral complexes $[(\kappa^3\text{-PhTt}^{\text{tbu}})\text{NiCl}]$ [19]. Subsequent reaction with MeLi did not yield expected species with Ni–Me bond but unprecedented metallacycle $[(\kappa^2\text{-PhTt}^{\text{tbu}})\text{Ni}(\eta^2\text{-CH}_2\text{SBU}^t)]$ [31]. Although donor-acceptor interactions $S \rightarrow M$ is by far the most common bond between the borate ligand and metals atom, in several cases, an unspecified η^2 - or η^6 -bond between borate phenyl moiety and metal has been also described [19,32] (Scheme 1).

The aim of this work is to evaluate coordination properties of two sulfur-donating scorpionate ligands toward molybdenum(II) complex $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{NCMe})_2(\text{CO})_2\text{Cl}]$ (**1**). Such complex is well-known precursor of scorpionate complexes that enables, in particular cases, to isolate κ^2 -intermediates as previously demonstrated on reaction with tris(pyrazolyl)methane [33]. In our case, reactivity of typical scorpionate ligand PhTt will be compared with RTt in order to describe the effect of additional (methylthio)methyl function, which could form donor-acceptor interaction with another Lewis acid.

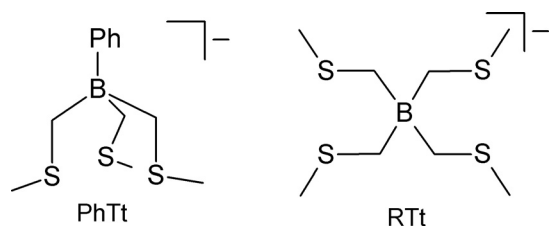
2. Results and discussion

The reaction of $[\text{Bu}_4\text{N}][\text{PhTt}]$ with molybdenum(II) complex $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2(\text{NCMe})_2\text{Cl}]$ (**1**) in THF solution gives complex $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2(\kappa^3\text{-PhTt})]$ (**2**), where PhTt acts as a typical tridentate tripodal ligand (Scheme 2). Thus, during the reaction, both

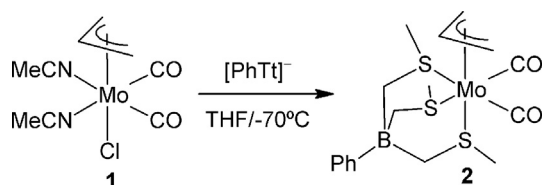
Abbreviations: PhTt[−], phenyltris[(methylthio)methyl] borate; RTt[−], tetrakis[(methylthio)methyl] borate.

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Scheme 1. Ligands used in this work.



Scheme 2. Syntheses of PhTt complex 2.

acetonitrile ligands as well as chloride are exchanged by three sulfur donor atoms of PhTt.

The complex **2** was characterized by multinuclear NMR spectroscopy. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2** reveal one set of signals corresponding with expected C_s symmetry. The low-field signals were assigned to the B–Ph phenyl protons. The allyl ligand gives well-distinguished signals at higher field. In the ^1H NMR spectrum, the central proton of the allyl ligand resonates at 4.02 ppm as a triplet of triplets while the doublets at 3.14 ppm ($J = 6.6$ Hz) and 1.51 ppm ($J = 9.9$ Hz) were assigned to *syn*- and *anti*-protons, respectively, based on observed coupling constant values [34]. In $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, allyl carbons resonate at 76.4 (1C) and 57.3 ppm (2C). The methyl and methylene groups of the PhTt ligand appear in ^1H NMR spectrum as five broad unresolved resonances with chemical shift in range of 3.0–1.2 ppm. The number of resonances suggests face-capping PhTt coordination mode while their broadness implies fluxional behavior in solution. Since the spectra were measured in non-coordinating solvent, the broadening is hardly caused by some dissociative/associative process. Therefore, it is attributed to a simple conformation change of the methylene and thiomethyl groups that is in line with literature data published for $[(\text{RTt})_2\text{Fe}]$ [17].

We note that anionic scorpionate ligands are often taken as more sterically demanding analogs of cyclopentadienyl (Cp) as they donate 6e in face-capping coordination mode. In our case, the formal replacement of Cp by PhTt results in considerably lowering of the carbonyl stretching frequencies (Table 1). It is attributed to diffuse vacant orbitals necessary for π -back bonding, located on thiomethyl functions, leading to limited competition with CO for electron density. The Cp ligand as well as the PhTt are negatively charged. In case of Cp ligand, the charge is equally distributed over the π -system and contributes to Cp–M bonding. On the contrary, the negative charge of PhTt is formally solely local-

Table 1
Infrared data for selected η^3 -allyl molybdenum complexes.^a

| | $\nu_a(\text{CO})$ | $\nu_s(\text{CO})$ |
|--|--------------------|--------------------|
| 1 | 1949 ^b | 1851 ^b |
| 2 | 1945 | 1860 |
| 3 | 1932 | 1846 |
| $[(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2]$ | 1963 ^c | 1889 ^c |

^a The wavenumber are given in cm^{-1} .

^b Data reported literature [35].

^c Data reported literature [36,37].

ized on the boron atom with no influence on sulfur–metal bonding situation as unambiguously confirmed by ^{11}B NMR spectroscopy. Hence, the ^{11}B NMR spectrum of **2** shows a sharp signal at -16.8 ppm nearing the value observed for free PhTt anion (-14.4 ppm) [38]. This result is in line with previous NMR data obtained for other [(alkylthio)methyl]borate complexes [16,17].

Solid-state structure of the compound **2** was determined by single crystal X-ray diffraction analysis (Fig. 1). Selected bond distances and bond angles are listed in Table 2. The molecule **2** shows pseudo-octahedral structure with one face capped by three sulfur donor atoms of PhTt ligand. Remaining three positions are occupied by two carbonyls and centroid of allyl ligand. When the $\text{Cg}(\eta^3\text{-allyl})\text{-Mo}$ bond is taken as a principal axis, sulfur atoms in *trans*-position to carbonyls are considered to lay in equatorial plane (denoted S_{eq}) while the remaining one in axial position (S_{ax}). The framework of the allyl ligand is eclipsed with the OC–Mo–CO moiety, representing the most common arrangement of the $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2]$ fragment [39–42]. Due to the *trans*-effect of carbonyl ligands, the bond distances $\text{Mo}-S_{\text{eq}}$ are considerably shorter than observed for $\text{Mo}-S_{\text{ax}}$ [$\Delta\text{Mo}-\text{S} = 0.0871(5)$ Å]. Similar effect was previously demonstrated on several molybdenum and tungsten complexes [32,42–46]. We note that the $\text{Mo}-S_{\text{eq}}$ bonds in **2** are longer than previously reported for molybdenum(0) compound $[\text{Bu}_4\text{N}][(\kappa^3\text{-RTt})\text{Mo}(\text{CO})_3]$ ($\text{Mo}-\text{S} = 2.571(3)$, $2.564(3)$, $2.577(3)$ Å) [16], which could be related with weaker π -back donation into antibonding σ^* -orbitals of the C–S bonds [47]. Due to steric effect of allyl ligand, the PhTt ligand does not reach typical C_3 -symmetrical coordination mode with equal orientation of the methyl groups. As a result, both methyl groups neighboring the allyl ligand are directed below the equatorial plane. This configuration spreads the S–Mo–S bond angle adjacent to thiomethyl groups oriented toward each other [$\text{S}2\text{-Mo}-\text{S}3 = 89.03(1)$ Å].

The reaction of **1** with $[\text{Bu}_4\text{N}][\text{RTt}]$ gives dimeric compound $[\text{Bu}_4\text{N}][\{(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2\text{Cl}\}_2(\kappa^2\text{-RTt})]$ (**3**) in mixture with previously described dimer $[\text{Bu}_4\text{N}][\{(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2\}_2(\mu_2\text{-Cl})_3]$ (**4**) [48,49] as evidenced by ^1H NMR spectroscopy and mass spectrometry (Scheme 3). Low solubility of **4** in hot hexane enables to isolate the RTt complex **3** in pure form. We note that the yield of **3** strongly depends on reaction conditions. In THF solution, **3** is formed as the main product and was isolated in 55% yield while the use of non-coordinating CH_2Cl_2 produces compound **4** as the only tractable product. We suggest that formation of **3** is in competition with previously described solvent-induced ionization of **1**, which affords $[(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{NCMe})_3][\{(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2\}_2(\mu_2\text{-Cl})_3]$ [50]. Due to presence of large ammonium cation, **4** is precipitated as a low soluble species. Analogously, precipitation of $[\{(\eta^3\text{-methylallyl})\text{Mo}(\text{CO})_2\}_2(\mu_2\text{-Cl})_3]^-$ anion using Bu_4N^+ has been described recently [23].

Dimeric nature of the compound **3** was elucidated from mass spectrometry. The base peak in positive mode ($m/z = 243$) confirms presence of Bu_4N^+ cation while the base peak in negative mode ($m/z = 713$), with a progression in the isotope pattern by $m/z = 1$, was assigned to monoanionic species consisting of two $(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2\text{Cl}$ moieties and one RTt ligand. Such observation is fully in agreement with ^1H NMR spectrum revealing presence of Bu_4N^+ and η^3 -coordinated allyl ligands in molar ratio 1:2. Allyl ligand of the compound **3** gives one triplet of triplets at 3.94 ppm (H^{meso}) and two doublets at 3.08 (H^{syn}) and 1.67 ppm (H^{anti}) in ^1H NMR spectrum and two signals at 74.4 and 57.2 ppm in $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum implying C_s symmetric coordination sphere of molybdenum. As the dimer **3** belongs to the point group C_2 , one may expect appearance of five chemically inequivalent allyl protons and three inequivalent carbons. Different patterns are probably caused by pure delocalization of electron density over the RTt ligand, which results in negligible effects of groups distant from molybdenum that ensures its C_s symmetric coordination sphere. This effect is,

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