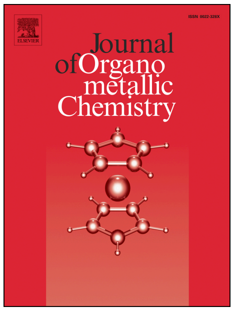

Two synthetic routes to bis(1-methyl-imidazole-2-thione)methane and bis(1-benzyl-imidazole-2-thione)methane complexes including sulfur atom insertion into copper −NHC bonds

Miriam Slivarichova, Rosenildo C. da Costa, Joshua Nunn, Ruua Ahmad, Mairi F. Haddow, Hazel A. Sparkes, Thomas Gray, Gareth R. Owen

PII: S0022-328X(17)30301-7

DOI: 10.1016/j.jorganchem.2017.05.015

Reference: JOM 19941

To appear in: *Journal of Organometallic Chemistry*

Received Date: 17 February 2017

Revised Date: 3 May 2017

Accepted Date: 4 May 2017

Please cite this article as: M. Slivarichova, R.C. da Costa, J. Nunn, R. Ahmad, M.F. Haddow, H.A. Sparkes, T. Gray, G.R. Owen, Two synthetic routes to bis(1-methyl-imidazole-2-thione)methane and bis(1-benzyl-imidazole-2-thione)methane complexes including sulfur atom insertion into copper−NHC bonds, *Journal of Organometallic Chemistry* (2017), doi: 10.1016/j.jorganchem.2017.05.015.

Two synthetic routes to bis(1-methyl-imidazole-2-thione)methane and bis(1-benzyl-imidazole-2-thione)methane complexes including sulfur atom insertion into copper−NHC bonds

Miriam Slivarichova,[b] Rosenildo C. da Costa,[a] Joshua Nunn, [b] Ruua Ahmad,[b] Mairi F. Haddow,[b] Hazel A. Sparkes,[b] Thomas Gray,[b] and Gareth R. Owen*[a,b]

Dedicated to Professor John A. Gladysz on the occasion of his 65th birthday.

Keywords: NHCs / Thiones / Copper / Sulfur atom insertion / Crystallography

[a] The School of Applied Science, Univeristy of South Wales, Treforest, UK, CF37 4AT
Tel: 01443 654527 E-mail: gareth.owen@southwales.ac.uk
[b] The School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK, BS8 1TS

The synthesis of novel bis-thione ligand, bis(1-benzyl-imidazole-2-thione)methane, **SS**$^{\mathbf{Bn}}$ is reported for the first time. This ligand along with the previously reported bis(1-methyl-imidazole-2-thione)methane, **SS**$^{\mathbf{Me}}$ has been utilised in the synthesis of a series of copper(I) halide complexes. The syntheses have been achieved by two methodologies. The first method involves the direct addition of the ligands to the copper halide salts, CuCl, CuBr and CuI. The second methodology involves an insertion of a sulfur atom into the copper–NHC bond of the preformed organometallic complexes, [CuBr(**CS**$^{\mathbf{Me}}$)]$_2$ and [CuI(**CS**$^{\mathbf{Me}}$)]$_2$ {where **CS**$^{\mathbf{Me}}$ = 1-(3-methyl-2H-imidazol-1-yl-2-thione)methyl-3-methyl-2H-imidazol-2-ylidene} and [CuBr(**CS**$^{\mathbf{Bn}}$)]$_2$ and [CuI(**CS**$^{\mathbf{Bn}}$)]$_2$ {where **CS**$^{\mathbf{Bn}}$ = 1-(3-benzyl-2H-imidazol-1-yl-2-thione)methyl-3-benzyl-2H-imidazol-2-ylidene}. These sulfur atom insertion reactions provide an indirect route to the first copper−halide complexes containing the **SS**$^{\mathbf{Me}}$ and **SS**$^{\mathbf{Bn}}$ ligands. All six complexes prepared have been fully characterized by spectroscopic and analytical methods as well as X-ray crystallography. Dinuclear structures were obtained for the complexes containing **SS**$^{\mathbf{Me}}$, mononuclear complexes were obtained for the copper–chloride and copper–bromide complexes containing **SS**$^{\mathbf{Bn}}$ and an extended network containing [Cu$_4$I$_4$] clusters bridged by the **SS**$^{\mathbf{Bn}}$ were formed for the corresponding copper–iodide complex for the latter ligand. The coordination and structural features of the two bis-thione ligands are discussed.

1. Introduction

There has been a significant and long standing interest in the 1-R-imidazole-2-thione heterocycle (**Hmt**$^{\mathbf{R}}$, where the R group is an alkyl or aryl group) and its incorporation within polydentate ligand motifs (Figure 1).[1] Much of this work has focused on anionic so-called "flexible soft scorpionate ligands" which contain a borohydride bridging unit between the heterocycles, for example [**Tm**]$^{-}$ and [**Bm**]$^{-}$ where R = Me in Figure 1.[2] Neutral bidentate and tridentate ligands bridged by CH$_2$ and CH units have also been extensively studied.[3,4]

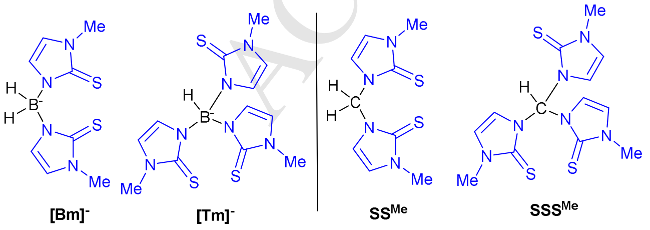

Figure 1 – Bidentate and tridentate ligands containing two or three of the methyl substituted 1-R-imidazole-2-thione units. The anionic ligands, bridged by borohydride are shown on the left and neutral ligands featuring CH$_2$ and CH units are shown on the right.

In a recent publication, we coordinated bis(1-methyl-imidazole-2-thione)methane (**SS**$^{\mathbf{Me}}$) to a series of zinc salts.[3n] This ditopic ligand has previously been utilised to prepare a wide range of complexes in which it exhibits a range of different coordination modes, some of which are highlighted in Figure 2. Examples of complexes containing **SS**$^{\mathbf{Me}}$ have been reported with d-block metals such as silver,[3f,o] gold,[3o] rhodium,[3g,k,l] iridium,[3l] nickel,[3j] iron,[3m] cobalt,[3j] zinc,[3n,q] and rhenium[3h] in addition to other metals such as tin,[3d] lead[3c,i], antimony[3a] and bismuth.[3a,r] The ligand has a number of interesting features. The number of atoms from one sulfur to the other is seven. This means that for a κ^2-*SS* coordination mode an eight-membered metallacycle is formed with the metal centre. This ring size is larger than normally found in most compounds containing chelating ligands. One of the consequences of this larger chelation size has been a positioning of the central methylene unit in close proximity to the metal centre (Figure 3). This is demonstrated in the complexes [Rh(COD)(κ^2-*SS*-**SS**$^{\mathbf{Me}}$)]X (where X = [PF$_6$]$^-$ and [BF$_4$]$^-$), published in 2006 by Hill.[3g] The ligand in this complex adopts a weak interaction between one of the hydrogen atoms on the central CH$_2$ unit of the ligand and the rhodium centre at lower temperatures in solution as well as in the solid state. While the C–H–Rh interaction is relatively long for the **SS**$^{\mathbf{Me}}$ ligand, the corresponding B–H–Rh interaction in the related complex [Rh(COD)(κ^2-*SS*-**Bm**)] was found to be significantly shorter.[5] The activation of the B–H bond in the borohydride based ligands is now well established leading to the formation of metal–borane (σ–acceptor) complexes.[2a,6] On the other hand, the activation of a C–H bond in the **SS**$^{\mathbf{Me}}$ ligand, is unknown although there are rare examples of related compounds