

# A strikingly fast route to methylmercury acetylides as a new opportunity for monomethylmercury detection

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## Abstract

Methylmercury  $\sigma$ -complexation to 1-alkynes is exploited in a new practical and sensitive quantitation of monomethylmercury in water and in biological tissues; indeed, methylmercury halides are detected at the nanomolar level by 10-(3-trimethylsilyl-2-propynyl)-9-(10*H*)-acridinone, in dichloromethane and in the presence of  $\text{Bu}_4\text{NF} \cdot 3\text{H}_2\text{O}$ .

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## 1. Introduction

Alkynyl ligands behave as good  $\sigma$ -donors and weak  $\pi$ -acceptors towards the group 11 and 12 metals [1], as discussed in a few reviews on the chemistry of metal-alkynyl complexes [2]. In particular, the interaction of acetylene with  $\text{HgCl}_2$  in the gas phase leading to  $\pi$ -complexes of  $\text{HgCl}_2$  with one or two molecules of acetylene, has a zero energy barrier [3].

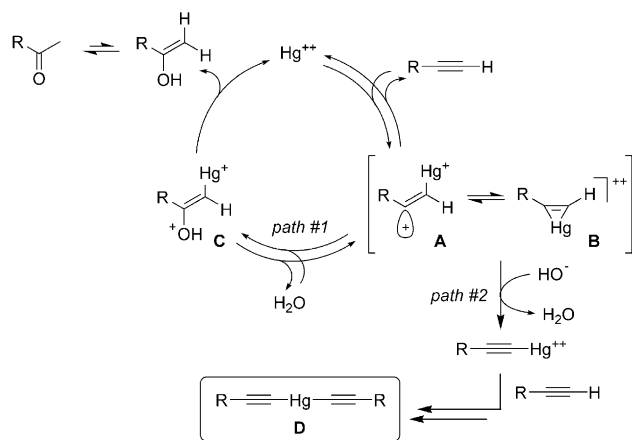
Scheme 1 summarizes the possible interactions of  $\text{Hg}^{++}$  with a terminal alkyne in aqueous media. Vinyl cation **A** or  $\pi$ -complex **B** present two possible reacting centers: (i) the positively charged carbon which reacts with nucleophiles, as happens with water under acidic conditions, affording **C** (path #1) which eventually leads to a carbonyl compound (*anti-Markovnikov* hydration of alkynes), (ii) the vinylic proton, whose acidity is magnified by the positive charge on the  $\beta$ -carbon, which reacts with bases, as happens with water under alkaline

conditions, to give mercury acetylides **D** (path #2) [4]. The latter process is closely related to the key step of the Sonogashira coupling reaction, where a 1-alkyne, treated with a Cu(I) salt and a tertiary amine, is converted into a Cu(I) acetylide [5].

Alkyne-mercury  $\pi$ -coordination is at the basis of the mercury-catalysed electrophilic additions to alkynes. Structures **A** and/or **B** are trapped by various nucleophiles to give vinyl halides, vinyl esters, ethers and so on. The mercury-catalysed hydration of acetylene to give acetaldehyde is an example of an old industrial process based on this chemistry, as demonstrated by a group of patents dating back to the beginning of the last century [6]. Nowadays, acetaldehyde manufacture is no more based on acetylene but on ethylene, a much cheaper raw material, through the Wacker process [7]. However, acetaldehyde plants using acetylene as the feedstock have operated throughout the world from the 1930s to the 1980s, and often left behind environmental injuries in terms of land or water bodies pollution by mercury. The most dramatic example was offered by the outbreak of methylmercury poisoning in Japan, known as the Minamata disease [8]; further heavy environmental

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Scheme 1.

impacts by former acetaldehyde manufacture have been recently reported in Italy [9], in China [10] and in Kazakhstan [11]. Thus, acetylene chemistry has been co-responsible of the overall anthropogenic contribution to the mercury budget of the biosphere.

Combining the fast biogeochemical cycling of mercury [12] in the environment and the toxicity associated to the neurotoxic bioaccumulative monomethylmercury (MMHg) derivatives [13], it is apparent why so powerful efforts have been directed to the study of the environmental chemistry of mercury in general, and in particular to the development of sensors [14] and labels [15], as testified by the number of papers on Hg(II) signaling that have recently appeared in the literature [16]. Conversely, no MMHg sensors have been developed so far at the best of our knowledge, thus a simple methodology for the recognition and detection MMHg derivatives of general formula  $\text{CH}_3\text{HgL}$ , where L is an inorganic or organic [17] ligand, is highly desirable [18].

We now show that alkyne–mercury coordination chemistry may be also exploited in an environmental profitable way for MMHg detection. To this purpose, the development of new analytical protocols for the fast and cheap control of priority pollutants represents a main goal of analytical green chemistry.

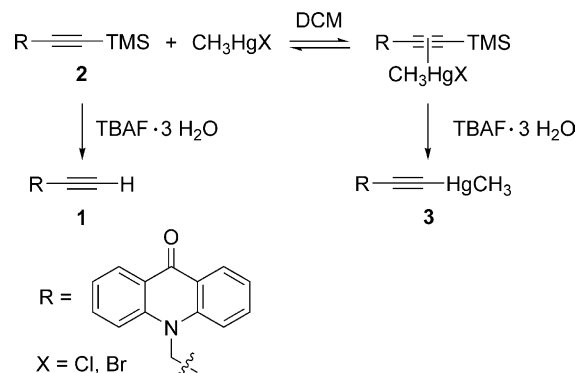
Here, we propose to exploit the alkyne–mercury  $\pi$ -coordination chemistry (Scheme 1, path #2), to detect MMHg at the nanomolar level, by exploiting a strikingly fast reaction of  $\text{CH}_3\text{HgBr}$  with 1-trimethylsilyl alkynes in the presence of tetrabutylammonium fluoride (TBAF) in dichloromethane (DCM). In particular, a fluorescent 1-trimethylsilyl alkyne was selected in order to profit from the high sensitivity of fluorimetric detection.

## 2. Results and discussion

The reaction of MMHg with 1-alkynes in alkaline aq. conditions is known to afford the corresponding

methylmercury acetylides [19], in analogy to the known chemistry of Hg(II) which affords diacetylides under the same reaction conditions [4]. In addition, we previously demonstrated that the reaction of Hg(II) and MMHg with phenylacetylene in water is not affected by the contemporary presence of Cu(II), Zn(II), Cd(II) and Pb(II) in concentrations  $10^4$  higher than mercury [19b]. On the way to develop a synthesis of methylmercury acetylides in organic solvents, and particularly in DCM, one of the best solvents for MMHg, we observed that no reaction occurs in this solvent between  $\text{CH}_3\text{HgBr}$  or  $\text{CH}_3\text{HgCl}$  and phenylacetylene in the presence either of inorganic heterogeneous bases (alkaline carbonates) or of tertiary amines. However, when phenylacetylene was replaced by trimethylsilyl phenylacetylene, a very fast reaction occurred in the presence of TBAF. Indeed, using a  $5 \times 10^{-6}$  M standard solution of  $\text{CH}_3\text{HgBr}$  in DCM, an excess of trimethylsilyl phenyl acetylene (50 equiv.) and TBAF (50 equiv.), after 20 min at 20 °C conversion of MMHg into methylmercury acetylide was virtually complete, as determined by HPLC/UV (Detection Limit = 500 pg as Hg injected). In a similar way, when an excess (50 equiv.) of fluorescent 10-(3-trimethylsilyl-2-propynyl)-9-(10*H*)-acridinone (**2**) was added to  $\text{CH}_3\text{HgBr}$  ( $1 \times 10^{-8}$  M in DCM) and TBAF (50 equiv.) in DCM, formation of 10-(3-methylmercury-2-propynyl)-9-(10*H*)-acridinone **3** was observed in >85% yield after 20 min at 20 °C; 40–50% of **2** was protodesilylated to **1** (Scheme 2).

To sum up these preliminary results, we have at disposal a MMHg receptor in the form of a silylated alkyne which interacts with the analyte in DCM in a fast and efficient way, and the opportunity to exploit the sensitivity of fluorimetric detection. The analytical protocol ensures MMHg recognition up to  $6 \times 10^{-9}$  M scale and with a Detection Limit of 5 pg, as Hg injected. Furthermore, 1-alkynes as Hg(II) and  $\text{CH}_3\text{Hg}^+$  receptors benefit for a substantial lack of interference from other ions; only Cu(I) [20a–c] and Ag(I) [21a–c] could in principle interfere in triple bond complexation, but they are not



Scheme 2.

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