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

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Abstract

Methylmercury σ-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 $Bu_4NF \cdot 3H_2O$.

Keywords: Monomethylmercury; Acetylides; Trimethylsilylalkynes; HPLC; Fluorimetric detection

1. Introduction

Alkynyl ligands behave as good σ-donors and weak π-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 $HgCl_2$ in the gas phase leading to π-complexes of $HgCl_2$ with one or two molecules of acetylene, has a zero energy barrier [3].

Scheme 1 summarizes the possible interactions of Hg^{++} with a terminal alkyne in aqueous media. Vinyl cation **A** or π-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 β-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 π-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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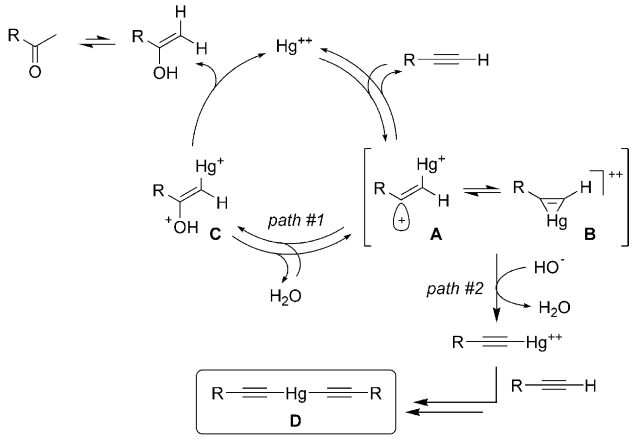


Scheme 1.

impacts by former acetaldehyde manufacture have been recently reported in Italy [9], in China [10] and in Kazakistan [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 CH_3HgL, where L is an inorganic or organic [17] ligand, is highly desirable [18].

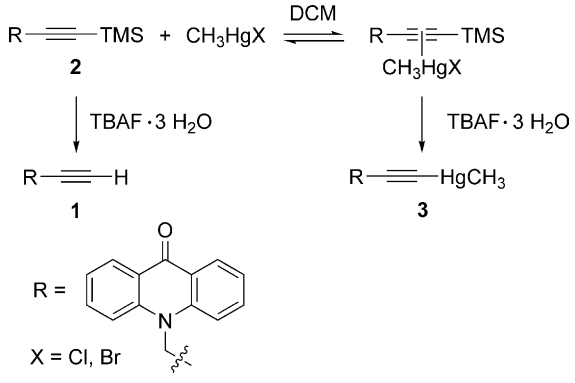
We now show that alkyne–mercury coordination chemistry may be also exploited in an environmental profitable way for MMHg detection. To this purpose, the development of new analytical protocols for the fast and cheap control of priority pollutants represents a main goal of analytical green chemistry.

Here, we propose to exploit the alkyne–mercury π-coordination chemistry (Scheme 1, path #2), to detect MMHg at the nanomolar level, by exploiting a strickingly fast reaction of CH_3HgBr 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 CH_3HgBr or CH_3HgCl 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 5×10^{-6} M standard solution of CH_3HgBr 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 CH_3HgBr (1×10^{-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 protodesylilated 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 6×10^{-9} M scale and with a Detection Limit of 5 pg, as Hg injected. Furthermore, 1-alkynes as Hg(II) and CH_3Hg^+ 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.

Table 1
Analysis of standard solutions of CH_3HgBr in DCM

Run	CH_3HgBr (μg/L)[a]	[**2**] and [TBAF] (equiv.)	*t* (min)	**3**[b] μg/L ± CL[c]	Yield (%)
1	40	50	20	33.2 ± 0.5	83
2	30	50	20	24.2 ± 0.4	81
3	20	50	20	16.5 ± 0.5	83
4	10	100	20	8.5 ± 0.7	85
5	7.5	110	35	6.7 ± 0.7	88
6	5	150	35	4.6 ± 0.8	92
7	1.2	800	35	1.15 ± 0.2	95

[a] Expressed as mercury.
[b] Determined by interpolation of chromatographic peak areas using a calibration curve.
[c] Confidence limits determined by 95% confidence bands of calibration curve.

extractable in DCM as MMHg is, unless suitable organic ligands are added, for example tertiary phosphates for Cu(I) [22] or dicyclohexano-18-crown-6 for Ag(I) [23].

To develop a complete analytical flow chart, we had first to develop an efficient sample treatment and, second, to ensure lack of interference by other matrix components. Thus, MMHg is extracted from an aqueous sample with DCM and the organic phase analysed according to a very simple analytical protocol (see Section 4). Table 1 collects a series of results obtained with standard solutions of CH_3HgBr in DCM.

DCM is also recognized as one of the best solvents for the extraction of MMHg from biological tissues after leaching the sample with an aq. solution of KBr/H_2SO_4/$CuSO_4$ [22].

To optimize the overall methodology for biological samples, a certified reference material (CRM 464-55) consisting of tuna fish muscle was tested in a series of analyses (see Section 4). After leaching the sample with a KBr/H_2SO_4/$CuSO_4$ aq. solution, MMHg was extracted as CH_3HgBr in DCM; derivatisation was carried out by means of an excess of 10-(3-trimethylsilyl-2-propynyl)-9-(10*H*)-acridinone **2** and TBAF in DCM. In five replicates carried out on CRM 464-55 (certified MMHg content = 5.12 μg/g, expressed as Hg), mean derivatization yield was 88 ± 5% with respect to MMHg extracted (see Table 2).

To confirm the performance of this analytical procedure, we compared the results of MMHg determinations via **2b** with MMHg analyses using GC-ECD [24d–e]. Two different specimens of tissues of a tuna fish were used (Table 3, runs 1,2), as well as a sample of clams (run 3) harvested in an intertidal lagoon in Northern Adriatic Sea, which was thoroughly examined by us in the last decade for the heavily mercury contamination of its sedimentary compartment [9].

In all the three specimens a good agreement between the two analytical procedures is apparent.

3. Conclusions

The organometallic chemistry of mercury and its coordination with alkynes is proposed here as a new tool to detect MMHg; in particular, the use of a fluorescent trimethylsilylalkyne joins the binding ability of 1-alkynes for MMHg to the advantages of fluorimetric analysis in terms of sensitivity and reduction of matrix interference. As the result, this new mercuration reaction seems promisingly exploitable in MMHg recognition and quantitation in biological samples, in a simple analytical protocol using common commercial instrumentation. This original route to MMHg determination competes in terms of efficiency with the routinely

Table 2
Analysis of MMHg in the certified material CRM 464-55 (tuna fish muscle, certified MMHg content = 5.12 μg/g, expressed as Hg)

Run	CRM 464-55		Extracted Hg[b] μg/g (%)	MMHg found[c] μg/g ± CL[d]	Yield (%)[e]
	Sample weight (g)	Total Hg (μg)[a]			
1	0.2200	1.13	4.95 (97)	4.2 ± 0.1	85
2	0.2176	1.11	4.40 (86)	4.0 ± 0.1	91
3	0.2065	1.06	4.50 (88)	4.2 ± 0.1	93
4	0.2003	1.03	4.61 (90)	3.8 ± 0.2	80
5	0.0637	0.326	4.71 (92)	4.1 ± 0.6	87

[a] THg, absolute total mercury content.
[b] Total mercury extracted per gram of sample, determined by standard CVAFS (SD ± 0.05).
[c] Expressed as Hg and determined by interpolation of chromatographic peak areas using calibration curve.
[d] Confidence limits determined by 95% confidence bands of calibration curve.
[e] Yield obtained, as percent recovery with respect to mercury extracted.

Table 3
Analysis of MMHg in tissues

Run	Sample	THg[a] (μg/g)	MMHg found μg/g ± SD[b] (this method)	MMHg found μg/g ± SD[c] (GC-ECD)
1	Tuna muscle	3.30	2.9 ± 0.1	3.0 ± 0.1
2	Tuna gill	2.25	2.0 ± 0.1	2.1 ± 0.1
3	Clam muscle	0.55	0.40 ± 0.04	0.44 ± 0.03

[a] Total mercury, determined by standard CVAFS.
[b] Expressed as mercury and determined by interpolation of chromatographic peak areas using calibration curve ($n = 10$).
[c] $n = 3$ [16].

used GC-ECD techniques, as apparent from Table 3, and in terms of practicality with the widely used ethylation-based protocols which require sample pretreatment with sodium tetraethyl borate under strictly controlled conditions, followed by GC-pyrolysis-CVAFS [25]. Finally, the combined use of an alkyne as the derivatising agent of MMHgBr joined to an extraction step from acidic aqueous solutions into DCM, makes this protocol practically unaffected by other potential interfering species such as Ag(I)Br and Cu(I)Br.

4. Experimental

4.1. 10-(2-Propynyl)-9(10H)-acridinone (*1*)

NaH (0.18g, 7.5 mmol) is added to a solution of 9(10*H*)-acridinone (0.98 g, 5 mmol) in 25 mL of dimethylformamide (DMF). The solution was stirred for 30 min at 50 °C and allowed to cool to room temperature. Propargyl bromide (0.65 mL, 80% solution in toluene, 6 mmol) was added and the solution was stirred at 50 °C for 6 h. The reaction mixture was quenched with water (80 mL) and the solid product was recrystallized from hot ethanol to obtain 0.69 g of pure **1** (2.95 mmol, 59%). m.p. = 212–215 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.43 (t, $J = 2.5$ Hz, 1H), 5.22 (d, $J = 2.5$ Hz, 2H), 7.33 (d, $J = 7.9$ Hz, 2H), 7.57 (d, $J = 8.5$ Hz, 2H), 7.77 (dt, $J = 1.7/8.0$ Hz, 2H), 8.55 (dd, $J = 1.7/8.0$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 36.8, 73.9, 77.2, 114.5, 121.8, 122.7, 127.9, 134.1, 141.7, 178.1; GC–MS (70 eV) *m/z* (%): 69 (13), 75 (16), 102 (14), 140 (58), 166 (81), 194 (82), 204 (65), 232 (43), 233 (100).

4.2. 10-(3-Trimethylsilyl-2-propynyl)-9(10H)-acridinone (*2*)

BuLi (0.72 mL, 2.5 M solution in hexanes, 1.8 mmol) is added at −78 °C to a solution of **1** (0.35 g, 1.5 mmol) in 15 mL of THF and the reaction mixture is stirred for 1 h at −78 °C. Trimethylsilylchloride (0.24 mL, 1.8 mmol) is added and the solution is stirred for 3 h at −78 °C. The reaction is quenched with phosphate buffer (pH 6.88), the aqueous layer is extracted with THF and the combined organic layers are dried (Na_2SO_4) and evaporated at reduced pressure. The desired silylated alkyne is obtained in 70% yield (0.32 g, 1.1 mmol) as an oil after purification by flash-chromatography on silica (cyclohexane:ethyl acetate 80:20). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.16 (s, 9H), 5.06 (s, 2H), 7.35 (dt, $J = 0.8/8.0$ Hz, 2H), 7.63 (d, $J = 8.5$ Hz, 2H), 7.79 (ddd, $J = 1.7/7.0/8.5$ Hz, 2H), 8.57 (dd, $J = 1.7/8.0$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 0.30, 37.9, 91.0, 98.5, 114.8, 121.5, 122.6, 127.6, 133.9, 141.7, 178.1; GC–MS (70 eV) *m/z* (%): 73 (12), 83 (38), 111 (12), 137 (17), 166 (32), 252 (16), 290 (24), 305 (98), 194 (100).

4.3. 10-(3-Methylmercury-2-propynyl)-9(10H)-acridinone (*3*)

CH_3HgCl (0.04 g, 0.164 mmol) is added to a solution of 10-(3-trimethylsilyl-2-propynyl)-9(10*H*)-acridinone **2** (0.05 g, 0.164 mmol) in 2 mL of CH_2Cl_2. The solution is stirred for 5 min at room temperature, tetrabutylammonium fluoride (0.052 g, 0.164 mmol) is added and the reaction mixture is stirred for additional 15 min at room temperature. The organic phase is evaporated to dryness and the product is purified by flash-chromatography on silica (cyclohexane:ethyl acetate 80:20). The solid obtained is recrystallized by hot ethanol to yield 0.028 g (0.062 mmol, 38%) of pure acetylide **3**. m.p. = dec. at 155–160 °C (ethanol); ^{1}H NMR (300 MHz, $CDCl_3$, $T = 50$ °C) δ: 0.63 (d, J relative to 199 Hg = 147.7 Hz, 3H), 0.63 (s, 3H), 5.0 (s, 2H), 7.27–7.38 (m, 2H), 7.64–7.83 (m, 4H), 8.57 (dd, $J = 1.6/8.0$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, $T = 50$ °C) δ: 6.7, 37.6, 77.2, 98.8, 114.8, 121.6, 122.9, 127.9, 133.9, 141.9, 178.2; GC–MS (70 eV) *m/z* (%): 140 (26), 166 (52), 194 (60), 204 (50), 217 (6), 232 (100), 255 (5), 449 ([M^+] relative to 202 Hg, 23).

4.4. Analytical tools and procedures

Analytical HPLC was performed on a Perkin–Elmer binary pump LC 250 instrument connected to a Perkin–Elmer LC 240 fluorescence detector using a reversed-phase column (Supelcosil LC-18, 25 cm × 4.6 mm, 5 μm film-thick). For the analysis of 10-(3-trimethylsilyl-

2-propynyl)-9(10*H*)-acridinone (t_R = 7.34 min, λ_{ex} = 251 nm, λ_{em} = 418 nm, ϕ_{em} = 0.50 in H_2O/ CH_3CN = 2/8 v/v) the elution program was: 10 min isocratic CH_3CN/ H_2O = 55/45 v/v, gradient ramp up to 100% CH_3CN in 10 min, 5 min isocratic 100% CH_3CN, flow = 1 mL/ min. Calibration curve for standard CH_3HgBr solutions is linear in the range examined (5–50 μg/L of CH_3HgBr expressed as Hg, r = 0.9994). Cold Vapor Atomic Fluorescence spectroscopy (CVAFS) was performed using a Tekran Mercury Detector 2500 instrument connected to a Hewlett Packard integrator HP 3395 and using argon as carrier gas. ^1H and ^{13}C NMR spectra were recorded using a Varian Inova 300 MHz spectrometer, using tetramethylsilane (TMS) as internal standard; chemical shifts are reported in ppm (δ) downfield from TMS. GC–MS analyses (70 eV) were performed with a Hewlett–Packard 5890 Series II instrument connected to a Hewlett–Packard 5971 quadrupole mass detector.

Stock solutions of CH_3HgBr in DCM (100 mg L^{-1} as Hg) are prepared by weighting 0.0295 g of CH_3HgBr and diluting to volume with DCM in a 200 mL volumetric flask and are stored at −20 °C. Diluted solutions are freshly prepared just before use. Stock solutions of silylated alkyne (122 mg L^{-1}, 4×10^{-4} M) are prepared by dissolving 12.2 mg in DCM in a 100 mL volumetric flask and diluting to volume with DCM. Stock solutions of TBAF (105 mg L^{-1}, 4×10^{-4} M) are prepared by dissolving 10.5 mg of TBAF in DCM in a 100-mL volumetric flask and diluting to volume with DCM.

4.5. Typical experimental procedure for CH_3HgBr analysis in standard solutions with Hg content higher than 10 μg/L (Table 1, Run 1)

A 4×10^{-4}-M solution of 10-(3-trimethylsilyl-2-propynyl)-9(10*H*)-acridinone **2** in DCM (0.125 mL, 5×10^{-5} mmol, 50 equiv.) is added to 5 mL of a 2×10^{-7} M solution of MMHg in DCM (40 μg/L as Hg, 1×10^{-6} mmol). The mixture is stirred for 5 min at 20 °C and 0.125 mL of a 4×10^{-4} M solution of TBAF in DCM (5×10^{-5} mmol, 50 equiv.) are added. After additional stirring for 15 min at 20 °C, the solvent is slowly evaporated (T = 35 °C, P = 28 mmHg), the residue is dissolved into the desired volume of CH_3CN and mercury acetylide **3** is directly analyzed by HPLC with fluorimetric detection.

4.6. Typical experimental procedure for CH_3HgBr analysis in standard solutions with Hg contents lower than 10 μg/L (Table 1, Run 5)

A 4×10^{-4} M solution of 10-(3-trimethylsilyl-2-propynyl)-9(10*H*)-acridinone **2** in DCM (0.205 mL, 8.25×10^{-5} mmol, 110 equiv.) is added to 20 mL of a 3.7×10^{-8} M solution of MMHg in DCM (7.5 μg/L as Hg, 7.5×10^{-7} mmol). The mixture is stirred for 5 min at 20 °C and 0.205 mL of a 4×10^{-4} M solution of TBAF in DCM (8.25×10^{-5} mmol, 110 equiv.) are added. After additional stirring for 15 min at 20 °C, the solvent is slowly evaporated to a volume of about 5 mL. The mixture is stirred again for 15 min at 20 °C, the solvent is slowly evaporated (T = 35 °C, P = 28 mmHg), the residue is dissolved into the desired volume of CH_3CN and mercury acetylide **3** is directly analyzed by HPLC with fluorimetric detection.

4.7. Typical experimental procedure for MMHg analysis in tissues (Table 2, Run 1)

The lyophilized and homogenized sample (0.1–0.2 g) is poured into a centrifuge teflon tube and washed with acetone (2 × 3 mL) and toluene (1 × 3 mL). The sample is then centrifuged at 3000 rpm for 5 min, the organic layer is removed and the sample is dried using a gentle nitrogen flow. A mixture consisting of KBr (1.5 M in 5% H_2SO_4, 5 mL), $CuSO_4$ (1 M in H_2O, 1 mL) and DCM (5 mL) is added to the residue, the tube is tightly closed and the resulting mixture is vigorously shaken for 20 min, then centrifuged at 3000 rpm for 20 min. The organic layer is removed and the extraction is repeated with a second aliquot of DCM (5 mL). A first 0.5 mL aliquot of the combined organic layers is analyzed by CVAFS in order to check the extraction efficiency and to evaluate the total mercury content; a second 2 mL aliquot is further on purified from co-extracted polar organic components by silica gel (5 g) chromatography with DCM (25 mL). Mercury recovery in the chromatographic step was confirmed to be quantitative by CVAFS. A solution of 10-(3-trimethylsilyl-2-propynyl)-9(10*H*)-acridinone **2** in DCM (4×10^{-4} M, 0.5 mL) is added to the DCM solution of MMHg, the mixture is stirred for 5 min at 20 °C, then a solution of TBAF in DCM (4×10^{-4} M, 0.5 mL) is added. After additional stirring for 15 min at 20 °C, the solvent is slowly evaporated (T = 35 °C, P = 28 mmHg), the residue is dissolved into the desired volume of CH_3CN and mercury acetylide **3** is directly analyzed by HPLC with fluorimetric detection.

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