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Convenient Room-Temperature, Mercury-Assisted Synthesis of Tetrazoles by 1,3-Dipolar Cycloaddition

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Dedicated to Professor Rolf Huisgen on the occasion of his 90th birthday

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The intermolecular 1,3-dipolar cycloaddition of organomercury(II) azides R^1HgN_3 (R^1 = Me, Ph) to organonitriles R^2CN (R^2 = Me, Ph, C_6F_5) forms organomercury(II) tetrazoles $R^1Hg(N_4C)R^2$ [R^1 = Me, R^2 = Me (**1**); R^1 = Me, R^2 = Ph (**2**); R^1 = Ph, R^2 = Me (**3**); R^1 = Ph, R^2 = Ph (**4**); R^1 = Ph, R^2 = C_6F_5 (**5**)]. The reaction is a direct and regioselective formation of the tetrazole moiety, which is easily performed at room temperature or slightly elevated temperature without a catalyst and furnishes quantitatively the pure product. In addition to characterization by multinuclear NMR spectroscopy, IR and Raman spectroscopy, as well as mass spectrometry, the mercury content was determined. Furthermore, X-ray diffraction studies were performed, and the crystal structures for **1**–**3** and **5** are reported.

Introduction

Cycloaddition reactions with azides and cyanides/nitriles for the synthesis of tetrazoles are known for almost 110 years. In 1901, a method for the synthesis of tetrazoles by the reaction of hydrazoic acid (HN_3) with cyanamide, yielding 5-aminotetrazole, was first reported.[1] In 1932 followed the first reaction with heptanenitrile, benzonitrile, *p*-tolunitrile, and benzylcyanide as representatives of organic cyanides.[2] Although numerous individual examples of cycloaddition to tetrazoles were known, the development of the general synthetic principle has been achieved by Rolf Huisgen in 1957–58.[3] He first recognized the possibility of varying the 1,3-dipole and dipolarophile and its high value for the synthesis of five-membered heterocycles. His study of the mechanism of addition of diazoalkanes to angularly strained double bonds led to the concept of 1,3-dipolar cycloaddition.[4] This 1,3-dipolar cycloaddition, which is also known as Huisgen cycloaddition or Huisgen reaction, is an organic chemical reaction belonging to the larger class of [2+3] cycloadditions. Sharpless et al. introduced the term "click chemistry" in 2002 as a chemical philosophy that describes chemistry tailored to generate compounds by joining small units together in a practical, quick, and reliable way.[5] The authors reported a very easy transformation of *p*-toluenesulfonyl cyanide and acyl cyanides with various aromatic and aliphatic azides under solvent-free conditions to yield exclusively the 1,5-disubstituted 5-acyl and 5-sulfonyltetrazoles, which was the first example of a direct synthesis of a 1,5-substituted tetrazole by an intermolecular [2+3] cycloaddition.[5c,6] Comprehensive reviews on 1,3-dipolar cycloaddition chemistry were published in 1984 and 2002.[7] In addition, the role of protic and dipolar aprotic solvents in the synthesis of heterocyclic compounds by 1,3-dipolar cycloaddition was investigated and is summarized in a review.[8] Further work on the formation of tetrazoles by the intermolecular condensation of organic azides with nitriles was performed.[9] Dialkylaluminum azide was also used as 1,3-dipole, which gave good yields at low reaction temperature and with a simple work-up procedure.[10] To the best of our knowledge, this work describes the first examples of organomercury(II) tetrazoles prepared by Huisgen 1,3-dipolar cycloaddition. In this context, mercury was only recently used as a catalyst for the synthesis of mercury(II) tetrazolate coordination polymers by an in situ hydrothermal [2+3] cycloaddition.[11] Few compounds with a mercury atom bonded to a tetrazole[12] and the crystal structure of a mercury 5-nitraminotetrazolate were described.[13] Furthermore, mercury was used for the preparation of mercury(II) tetrazolate coordination polymers, but mercury(II) chloride had to be employed to obtain the framework with mercury atoms.[11]

In this contribution, a detailed study of the synthesis and characterization of organomercury(II) tetrazoles with methyl/methyl (**1**), methyl/phenyl (**2**), phenyl/methyl (**3**), phenyl/phenyl (**4**), and phenyl/pentafluorophenyl (**5**) substituents is presented.

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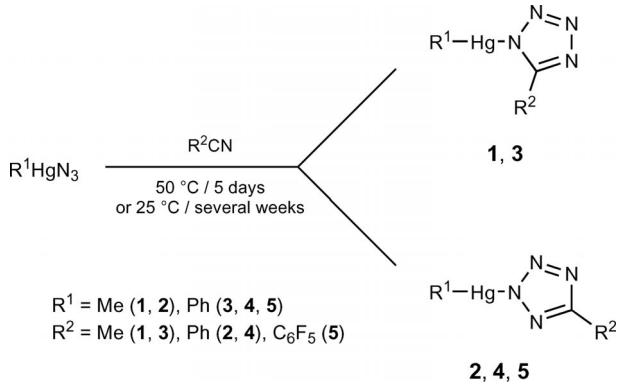
Results and Discussion

The synthesis route for the preparation of the organomercury(II) tetrazoles **1**–**5** is the intermolecular 1,3-dipolar cycloaddition of organomercury(II) azides with various nitriles to obtain the corresponding organomercury(II) tetrazoles $R^1Hg(N_4C)R^2$ [R^1 = Me, R^2 = Me (**1**); R^1 = Me, R^2 = Ph (**2**); R^1 = Ph, R^2 = Me (**3**); R^1 = Ph, R^2 = Ph (**4**); R^1 = Ph, R^2 = C_6F_5 (**5**)] (Scheme 1).



Scheme 1. Dissolution of $RHgN_3$ in nitriles to form organomercury(II) tetrazoles **1**–**5**.

The synthesis of **1**–**5** is performed in a facile fashion by dissolving the corresponding organomercury(II) azides in selected organonitriles at room temperature and slightly warming the reaction mixture. The organonitriles serve in this synthesis as the solvent as well as the reagent, thus a large excess is obvious. After removing the solvent, no other byproducts are observed, and the reaction furnishes the pure products quantitatively, without the need for further purification or isolation. In addition, the reactants are not sensitive to air or water; therefore, no extra precautions need to be taken. The synthesis works at ambient pressure without using a catalyst. The reaction of phenylmercury(II) azide with trimethylsilyl cyanide furnished only crystals of phenylmercury(II) cyanide, which can be explained by the ability of trimethylsilyl cyanide to act as a cyanide transfer agent. It was previously found that the cycloaddition can only be achieved without a catalyst if the nitrile is sufficiently activated by strong electron-withdrawing groups.[3b,5b,5c,8,9b,9c,14] Electron-withdrawing groups tend to lower the LUMO of the nitriles and thus increase the interaction with the HOMO of the azide.[14,15] It is reported that the reaction of various organic azides with various nitriles failed with nitriles that were not activated, even with the use of various catalysts.[9b] Despite the fact that electron-donating acetonitrile was used for the preparation of **1** and **3**, the reaction gave the desired compounds in quantitative yields. The solubilities of nonhygroscopic compounds **1**–**5** are very low in common solvents, whereas the compounds are more soluble in polar solvents than in nonpolar solvents. None of the compounds are soluble in water. In particular, aryl-substituted compounds **2**–**5** are rather insoluble, and compounds **4** and **5** are most insoluble because they contain two aryl groups.

The 1,3-dipolar cycloaddition of **1**–**5** only gave one of the two possible isomeric tetrazole products. For **1** and **3**, the 1,5-disubstituted tetrazole products, whereas for **2**, **4**, and **5**, the 2,5-disubstituted tetrazole products were obtained. This preferred orientation in the cycloaddition seems to be a general phenomenon of 1,3-dipolar cycloaddition,[4,9b,16] which is also verified by computational calculations,[15] and was observed in the cycloaddition of organic azides and nitrile groups bound to a sulfur atom, as well.[5c] Huisgen described that dipolarophiles with multiple bonds including a heteroatom usually add to the dipole in only one of the two possible directions and explained this observation by the smaller σ-bond energy of one of the two possible directions as well as by steric effects.[4] Thus, the interaction of electronic and steric effects is responsible for the orientation of the cyanide moiety inside the tetrazole ring. The electron-donating methyl group (+I effect) leads to the formation of 1,5-disubstituted tetrazoles, whereas the slightly electron-withdrawing phenyl group and the stronger electron-withdrawing pentafluorophenyl group (–I effect) lead to 2,5-disubstituted tetrazoles. Furthermore, even more important for the regioselectivity of the addition are steric effects.[4] The steric demands of benzonitrile and pentafluorobenzonitrile are larger than that of acetonitrile, which results in the different orientation of the dipolarophile in **1** and **3** relative to that in **2**, **4**, and **5**.

Furthermore, it is possible to obtain tetrazoles **1**–**5** at ambient temperature. After several weeks in a saturated solution of methylmercury(II) azide or phenylmercury(II) azide in acetonitrile, benzonitrile, or pentafluorobenzonitrile, crystals of **1**–**5** are formed. The formation of the tetrazole compounds even at room temperature without any catalyst is due to the strongly polarized and activated azide bond in phenylmercury(II) azide and especially in methylmercury(II) azide.[17] This reactivity even at room temperature is quite unusual, because 1,3-dipolar cycloadditions usually require a catalyst or heating to reflux for a reaction to occur or reach completion.[3b,5b,9d,9f,10,11] Similar reactivity at ambient temperature was found with dialkylaluminum compounds, in which the aluminum center acts as a Lewis acid and thereby activates the nitrile.[10] Furthermore, even the electron-donating acetonitrile reacts at ambient temperature to yield **1** and **3**, which is quite uncommon for 1,3-dipolar cycloadditions.[3b,5b–5d,6,8,9,9g,10,14,16] Even the use of mercury(II) chloride as catalyst for the hydrothermal cycloaddition of pyrazinecarbonitriles with sodium azide needs elevated temperatures (>110 °C) and a Teflon-lined reactor.[11] In contrast to the results described by Sharpless et al.,[6] the reaction of a fluorinated aromatic nitrile (pentafluorobenzonitrile) with an azide [phenylmercury(II) azide] furnished the corresponding tetrazole compound **5**, primarily even without heating.

All compounds were thoroughly characterized by ^1H, ^{13}C and ^{199}Hg NMR spectroscopy. In the ^1H NMR spectra of **1** and **2**, the $^2J_{H–^{199}Hg}$ couplings were determined to be 217 Hz for **1** and 220 Hz for **2**, values which are slightly higher than that for the corresponding methylmercury(II) azide.[17] The ^1H NMR spectra of **2**–**5** show the expected

AA′BB′C spin system of monosubstituted phenyl rings, whereas the resonances of the phenyl hydrogen atoms attached to the tetrazole ring are shifted to higher frequency relative to those of the phenyl hydrogen atoms directly attached to the mercury atom. In the ^{13}C NMR spectra, the shifts of the carbon atom in the tetrazole ring (carbon C1) are 159.0/159.4 ppm for **1/3** and 163.3/163.5 ppm for **2/4**. It is well established that, for 2,5-disubstituted tetrazoles such as **2** and **4**, the C1 resonances are shifted to higher frequency relative to those in 1,5-disubstituted tetrazoles **1** and **3**.[12] For the other resonances in the ^{13}C NMR spectra of **1**–**4**, ^{199}Hg satellites could also be observed, which verify clearly the attachment of the corresponding methyl or phenyl group to the mercury atom. The ^{13}C NMR spectra of **1** and **2** show the resonances for the methyl group attached to the mercury atom at –2.0 ppm for **1** and –2.6 ppm for **2** with coupling constants $^1J_{C–199Hg}$ of 1633 Hz for **1** and 1638 Hz for **2**. Both coupling constants are higher than that of the starting material, methylmercury(II) azide (1491 Hz). For **3**, all possible $^{13}C–^{199}Hg$ couplings of the phenyl carbon atoms could be observed. The coupling constant of 2561 Hz for the $^1J_{C–199Hg}$ coupling is very large because of the sp^2 hybridization and therefore the higher s character of the C–Hg hybrid orbital. The $^2J_{ortho\text{-}C}$, $^3J_{meta\text{-}C}$, and $^4J_{para\text{-}C}$ coupling constants were determined to be 117, 204, and 35 Hz, respectively. Because of the low solubility of **4**, only the $^2J_{ortho\text{-}C}$ and $^3J_{meta\text{-}C}$ couplings could be detected, with coupling constants of 119 ($^2J_{C–199Hg}$) and 207 Hz ($^3J_{C–199Hg}$), which matches quite well the values for **3**. These coupling constants are in agreement with the values for other phenylmercury(II) compounds.[18] The assignment of the phenyl carbon atoms attached to the mercury atom in the ^{13}C NMR spectra was performed as described for phenylmercury(II) azide and phenylmercury(II) chloride.[17,18b] This leads to a smaller coupling constant for the ^2J in comparison to the $^3J_{C–199Hg}$ coupling. Because of the low solubility of **5** and the fluorine substituents on one of the two phenyl rings, only the *ortho*-, *meta*-, and *para*-carbon atoms of the phenyl ring attached to the mercury atom could be observed, without any ^{199}Hg satellites. The ^{199}Hg NMR shifts correspond to the electron density of the substituents, thus a higher electron density leads to a shift to lower frequency. Therefore, the signal for **3** at –1324 ppm is shifted to lower frequency relative to those for **1** (–980 ppm) and **2** (–1007 ppm). Since there are methyl groups attached at Hg in both **1** and **2**, the ^{199}Hg NMR shifts are very close for these compounds. Furthermore, the resonances for tetrazole compounds **1**–**3** are slightly shifted to lower frequency relative to those for the corresponding azide compounds,[17] which were used as starting material. All ^{199}Hg NMR spectra were recorded in the same solvent, because the chemical shift of the ^{199}Hg nucleus significantly depends on the polarity of the solvent.[19] Because of the very low solubility of the doubly aryl-substituted compounds **4** and **5**, no signal could be observed in the ^{199}Hg NMR spectra, even with extended scan rates. The sufficient solubility of **1** permitted the recording of a ^{15}N NMR spectrum. The ^{15}N NMR spectrum of **1** shows two resonances at –2.5 and –80.4 ppm instead of the four expected signals of the tetrazole ring (Figure 1).

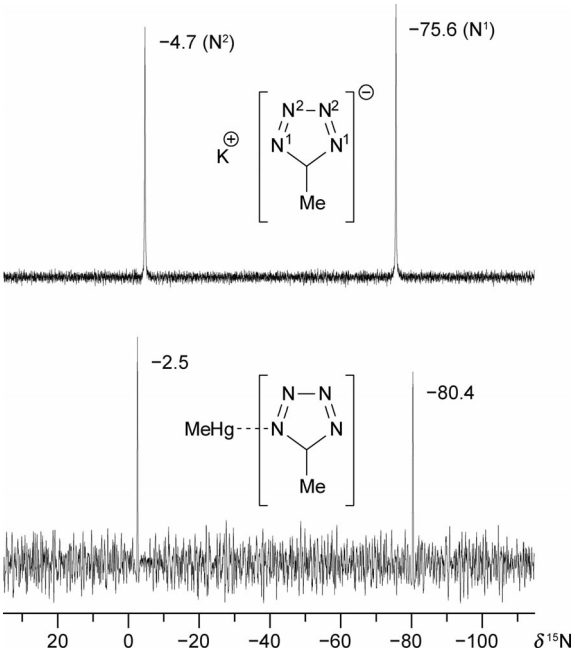


Figure 1. ^{15}N NMR spectrum of $CH_3Hg(N_4C)CH_3$ (**1**) (bottom) and $K[(N_4C)CH_3]$ (top) in CD_3OD at 25 °C (δ in ppm).

This phenomenon can be explained by the anionic nature of the tetrazole moiety when dissolved in polar solvents, due to the high stability of $MeHg^+$, which results in an anionic and symmetrical 5-methyltetrazolate (Figure 1). Comparison with an authentic sample of potassium 5-methyltetrazolate (CD_3OD: ^{15}N δ = –4.7, –75.6 ppm), synthesized according to a procedure in the literature,[20] confirms the ^{15}N NMR resonances and the assumption of the more ionic nature of **1** in polar solvents. A similar behavior of the $MeHg^+$ group was also observed for methylmercury(II) azide, where this also appears only in polar solvents.[17] Further investigations on the polarity dependence on the solvent were not possible because of the low solubility of **1** in other solvents, especially in nonpolar solvents. Furthermore, the solubilities of **2**–**5** in general are even worse; therefore, no resonances in the ^{15}N NMR spectra, independent of the solvent, were observed.

The Raman spectra of **1**–**5** show the Hg–C stretching vibrations for **1** and **2** at 555 and 565 cm^{-1}, respectively. The corresponding Hg–C stretching vibrations for **3**–**5** are found at smaller wavenumber (all at 240 cm^{-1}) because of the rigidness of the phenyl ring and the more polar Hg–C bond. All Hg–C stretching vibrations are in very good agreement with the stretching vibrations found in similar methyl- and phenylmercury(II) moieties.[17,21]

Single crystals suitable for X-ray diffraction measurements were obtained by slow evaporation of the solvent at ambient temperatures in acetonitrile (for **1**, **3**), benzonitrile (for **2**), or pentafluorobenzonitrile (for **5**). A full list of the crystallographic refinement parameters and structure data

for **1**–**3** and **5** is shown in Table 2. Compound **1** crystallizes in the monoclinic space group *C*2/*c* with eight formula units per unit cell. The molecular structure is shown in Figure 2.

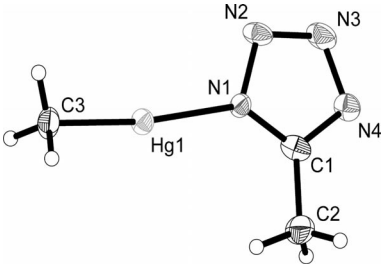


Figure 2. Molecular structure of **1**. Selected distances [Å] and angles [°]: Hg1–N1 2.113(7), Hg1–C3 2.062(9), N1–N2 1.368(9), N2–N3 1.294(10), N3–N4 1.354(10), N1–C1 1.327(11), N4–C1 1.317(11), C1–C2 1.481(11), C3–Hg1–N1 172.2(3), Hg1–N1–N2 117.7(5), Hg1–N1–C1 135.4(5).

The Hg–C and Hg–N bond lengths are 2.062(9) and 2.113(7) Å, respectively, and are comparable to those in similar organomercury(II) compounds.[11,13,17,22] In agreement with the bond lengths of the corresponding methylmercury(II) azide,[17] the Hg–C bond of **1** is shorter than the Hg–N bond. The mercury atom is, as expected, doubly coordinated in an almost linear fashion, with an C3–Hg–N1 angle of 172.2(3)°. A comparison of selected bond lengths and angles for **1**–**3** and **5** is summarized in Table 1. Each mercuy atom is surrounded by three further molecules with weak Hg···N contacts of 2.876(8), 2.922(9), and 3.138(9) Å (with a van der Waals radius, r_{vdW}, of 3.1 Å).[23] Compound **2** crystallizes in the monoclinic space group *C*2/*c* with eight formula units per unit cell (Figure 3).

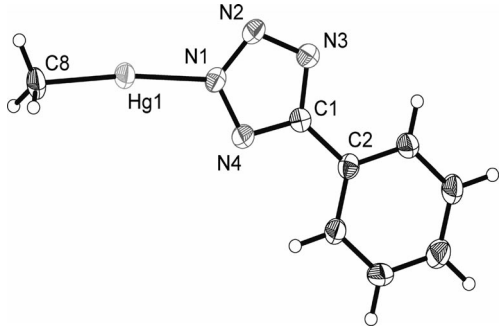


Figure 3. Molecular structure of **2**. Selected distances [Å] and angles [°]: Hg1–N1 2.094(3), Hg1–C8 2.042(4), N1–N2 1.317(5), N2–N3 1.323(4), N3–C1 1.350(5), C1–N4 1.330(5), N1–N4 1.334(5), C1–C2 1.473(5), C8–Hg1–N1 173.1(2), Hg1–N1–N2 127.0(3), Hg1–N1–N4 120.6(2).

Compared to **1**, the Hg–C bond length [2.042(4) Å] and the Hg–N bond length [2.094(3) Å] are shorter, whereas the C8–Hg–N1 angle of 173.1(2)° also shows a slightly nonlinear arrangement (Table 1). Each mercury atom in **2** is surrounded by two molecules with intermolecular Hg···N distances of 2.743(4) and 3.097(4) Å (r_{vdW} = 3.1 Å)[23] Compound **3** crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell (Figure 4).

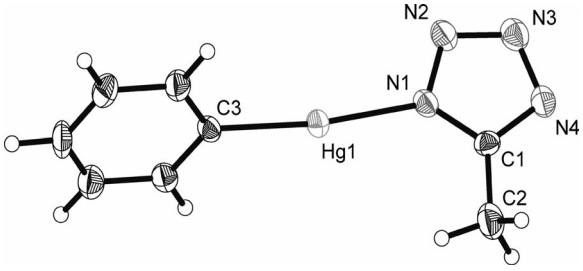


Figure 4. Molecular structure of **3**. Selected distances [Å] and angles [°]: Hg1–N1 2.090(4), Hg1–C3 2.046(5), N1–N2 1.343(7), N2–N3 1.305(6), N3–N4 1.355(7), N1–C1 1.339(7), N4–C1 1.327(7), C1–C2 1.463(9), C3–Hg1–N1 172.3(2), Hg1–N1–N2 119.4(4), Hg1–N1–C1 132.6(4).

The Hg–C [2.046(5) Å] and Hg–N [2.090(4) Å] bond lengths in **3** are shorter than those in **1** but are very close to those in **2**. The C3–Hg–N1 angle of 172.3(2)° has the same size as the structures described above (Table 1). The values for the Hg1–N1–N2 and the Hg1–N1–C1 angles are quite the same as those for **1**. Each mercury atom in **3** is surrounded by two molecules with intermolecular Hg···N distances of 2.815(6) and 2.906(6) Å (r_{vdW} = 3.1 Å).[23] In contrast to **1**–**3**, compound **5** crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. The molecular structure is shown in Figure 5.

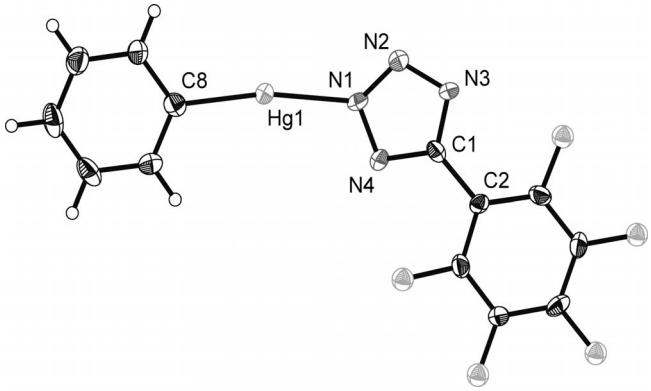


Figure 5. Molecular structure of **5**. Selected distances [Å] and angles [°]: Hg1–N1 2.115(5), Hg1–C8 2.049(6), N1–N2 1.313(7), N2–N3 1.309(7), N3–C1 1.338(8), C1–N4 1.324(8), N1–N4 1.331(7), C1–C2 1.478(8), C8–Hg1–N1 168.5(2), Hg1–N1–N2 129.0(4), Hg1–N1–N4 116.3(4).

Table 1. Selected bond lengths [Å] and angles [°] for $CH_3Hg(N_4C)CH_3$ (**1**), $CH_3Hg(N_4C)C_6H_5$ (**2**), $C_6H_5Hg(N_4C)CH_3$ (**3**), and $C_6H_5Hg(N_4C)C_6F_5$ (**5**).

	$CH_3Hg(N_4C)CH_3$ (**1**)	$CH_3Hg(N_4C)C_6H_5$ (**2**)	$C_6H_5Hg(N_4C)CH_3$ (**3**)	$C_6H_5Hg(N_4C)C_6F_5$ (**5**)
Hg1–C3/C8	2.062(9)	2.042(4)	2.046(5)	2.049(6)
Hg1–N1	2.113(7)	2.094(3)	2.090(4)	2.115(5)
C3/C8–Hg1–N1	172.2(3)	173.1(2)	172.3(2)	168.5(2)
Hg1–N1–N2	117.7(5)	127.0(3)	119.4(4)	129.0(4)
Hg1–N1–C1/N4	135.4(5)	120.6(2)	132.6(4)	116.3(4)

The Hg–N bond of 2.115(5) Å is the longest found in this work, whereas the Hg–C bond length of 2.049(6) Å is between the corresponding bond lengths for **1** and **3**. Also the C8–Hg–N1 angle of 168.5(2)° is more bent relative to the other reported crystal structures. In contrast to those in **1** and **3**, the Hg1–N1–N2 angle is about 10° larger and the Hg1–N1–N4 angle is, in agreement with this, more than 15° smaller (Table 1). This leads to a general rotation of the tetrazole moiety related to the mercury atom. This bigger bend is also found in **2** and is due to the 2,5-disubstitution of the tetrazole ring. Each mercury atom in **5** is surrounded by two molecules with Hg···N contacts of 2.716(5) Å, which are the shortest ones found in this work, and 2.957(6) Å (r_{vdW} = 3.1 Å).[23] Furthermore, it was also possible to obtain and analyze crystals of compound **4**, but these crystals led only to a poor data set. However, it was possible to find a basic refinement, which clearly shows a 2,5-disubstituted tetrazole and verifies the ^{13}C NMR spectroscopic data described above.

Conclusions

In summary, the covalent organomercury(II) tetrazoles $R^1Hg(N_4C)R^2$ [R^1 = Me, R^2 = Me (**1**); R^1 = Me, R^2 = Ph (**2**); R^1 = Ph, R^2 = Me (**3**); R^1 = Ph, R^2 = Ph (**4**); R^1 = Ph, R^2 = C_6F_5 (**5**)] were prepared by reaction of the corresponding organomercury(II) azides with organonitriles. Thereby, the direct and regioselective formation of tetrazole rings by 1,3-dipolar cycloaddition of organomercury(II) azides with organonitriles was observed. This intermolecular [2+3]-cycloaddition involved simple stirring of the organomercury(II) azides in neat organonitriles at moderate temperatures (starting at 25 °C) without the need of using a catalyst. The reaction gave the product in quantitative yields, and no further purification was necessary. The reactions presented in this study are therefore a perfect example of the ideal "click chemistry".

Experimental Section

The solvents acetonitrile and benzonitrile were dried by standard methods and freshly distilled prior to use. Pentafluorobenzonitrile (Acros Organics) was used as received. Methylmercury(II) azide and phenylmercury(II) azide were prepared according to the literature procedure.[17]

Raman spectra were recorded with a Bruker MultiRAM FT-Raman instrument fitted with a liquid-nitrogen-cooled germanium detector and a Nd:YAG laser (λ = 1064 nm), infrared spectra were measured with a Perkin–Elmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSamplIR II ATR device. All spectra were recorded at ambient temperature; the samples were neat solids. NMR spectra were recorded with a JEOL Eclipse 400 ECX instrument, and chemical shifts were determined with respect to external Me_4Si (^1H: 399.8 MHz; ^{13}C: 100.5 MHz), $MeNO_2$ (^{14}N: 28.9 MHz; ^{15}N: 40.6 MHz), and Me_2Hg (^{199}Hg: 71.7 MHz). $HgCl_2$ (0.5 M in THF) was used as external standard for ^{199}Hg NMR spectroscopy, and the shift (δ = –1517 ppm) was referenced to that of Me_2Hg (δ = 0 ppm). Because of the significant temperature dependence of the ^{199}Hg NMR resonances, all samples were measured at 25 °C. Mass spectrometric data were obtained with a JEOL MStation JMS 700 spectrometer (DCI+). Hg-containing fragments are referred to the isotope with the highest natural abundance, ^{202}Hg. Determinations of the mercury content were performed with a Varian Vista RL CCD Simultaneous ICP-AES spectrometer with a mercury ICP standard [CertiPUR®, $Hg(NO_3)_2$ in HNO_3 (10%), Merck]. C/H/N analysis was not performed because of potential

Table 2. Crystal and structure data for $CH_3Hg(N_4C)CH_3$ (**1**), $CH_3Hg(N_4C)C_6H_5$ (**2**), $C_6H_5Hg(N_4C)CH_3$ (**3**), and $C_6H_5Hg(N_4C)C_6F_5$ (**5**).

	$CH_3Hg(N_4C)CH_3$ (**1**)	$CH_3Hg(N_4C)C_6H_5$ (**2**)	$C_6H_5Hg(N_4C)CH_3$ (**3**)	$C_6H_5Hg(N_4C)C_6F_5$ (**5**)
Refined formula	$C_3H_6HgN_4$	$C_8H_8HgN_4$	$C_8H_8HgN_4$	$C_{13}H_5F_5HgN_4$
Formula weight	298.69	360.76	360.76	512.78
Crystal dimensions /mm]	0.24 × 0.13 × 0.04	0.42 × 0.04 × 0.02	0.20 × 0.10 × 0.05	0.45 × 0.40 × 0.20
Crystal description	Colorless platelets	Colorless platelets	Colorless platelets	Colorless blocks
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*C*2/*c*	*C*2/*c*	$P2_1/c$	$P\bar{1}$
a [Å]	13.0734(6)	23.5388(11)	10.6192(9)	6.4318(4)
b [Å]	8.2417(4)	4.3982(2)	8.8615(4)	8.5654(4)
c [Å]	11.4459(5)	19.2321(10)	10.5311(9)	13.0661(7)
α [°]	90.0	90.0	90.0	82.186(4)
β [°]	101.638(5)	111.678(8)	112.681(10)	84.896(5)
γ [°]	90.0	90.0	90.0	69.442(5)
V [Å]^3	1207.91(10)	1850.25(19)	914.36(14)	667.07(7)
Z	8	8	4	2
$\rho_{calcd.}$ [g cm^{-3}]	3.2850(5)	2.5902(2)	2.6207(3)	2.5530(2)
μ /mm^{-1}	25.377	16.593	16.788	11.600
Temperature [K]	100(3)	173(2)	200(3)	200(3)
θ range [°]	4.32–25.99	4.24–25.99	3.90–26.00	4.28–25.99
Reflections measured	2689	8682	7903	5360
Reflections independent	1185	1815	1786	2607
Reflections unique	841 (R_{int} = 0.0436)	1495 (R_{int} = 0.0529)	1377 (R_{int} = 0.0506)	2306 (R_{int} = 0.0531)
*R*1, *wR*2 (2σ data)	0.0287, 0.0624	0.0178, 0.0373	0.0239, 0.0423	0.0312, 0.0694
*R*1, *wR*2 (all data)	0.0418, 0.0643	0.0233, 0.0379	0.0425, 0.0442	0.0356, 0.0703
Data/restraints/parameters	1185/0/74	1815/0/119	1786/0/118	2607/0/208
GOF on F^2	0.908	0.926	0.942	1.007
Residual electron density	–2.036/1.148	–0.590/0.874	–0.795/0.963	–2.080/1.293

mercury contamination of the analyzer. Melting points were determined in capillaries with a Büchi Melting Point B-540 instrument. For all compounds, an Oxford Xcalibur3 diffractometer with a CCD area detector was employed for data collection using Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SIR97,[24] SHELXS-97[25]) and refined by full-matrix least-squares on F^2 (SHELXL).[25] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in a difference Fourier map and placed with a C–H distance of 0.98 Å for CH_3 groups and 0.95 Å for aromatic CH groups (see Table 2). ORTEP plots are shown with thermal ellipsoids at the 50% probability level.

CCDC-793779, -793780, -793781, and -793782 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

CAUTION! *Mercury and most mercury-containing compounds are very toxic. Avoiding contact with these compounds is mandatory, especially avoid inhalation of the volatile organomercury compounds.*

General Procedure for the Preparation of $R^1Hg(N_4C)R^2$ [R^1 = Me, R^2 = Me (1); R^1 = Me, R^2 = Ph (2); R^1 = Ph, R^2 = Me (3); R^1 = Ph, R^2 = Ph (4); R^1 = Ph, R^2 = C_6F_5 (5)]: R^1HgN_3 [0.39 mmol (**1**, **2**), 0.31 mmol (**3**–**5**)] was dissolved in R^2CN [5 mL (**1**–**4**), 15 mL (**5**)] at ambient temperature and stirred for 5 d at 50 °C. The solvent was removed in vacuo and yielded colorless solids.

Methyl (5-Methyl-1*H*-tetrazol-1-yl)mercury (1): M.p. 189 °C. Raman: $\tilde{\nu}$ = 3015 (10), 2930 (48), 2861 (3), 2811 (2), 2812 (2), 2736 (1), 1495 (18), 1450 (4), 1421 (4), 1401 (2), 1390 (2), 1375 (4), 1241 (25), 1198 (40), 1131 (6), 1108 (9), 1085 (3), 1041 (1), 1011 (7), 805 (1), 697 (32), 555 (100, νHgC_{Methyl}), 394 (11), 296 (6), 233 (15), 220 (20), 202 (22) cm^{-1}. IR: $\tilde{\nu}$ = 2997 (w), 2927 (m), 2806 (w), 1494 (s), 1425 (m), 1371 (vs), 1261 (w), 1238 (m), 1192 (m), 1129 (w), 1106 (s), 1081 (s), 1042 (w), 1010 (m), 990 (w), 804 (m), 791 (s), 724 (w), 694 (m) cm^{-1}. ^{1}H NMR (CD_3OD): δ = 2.55 (s, 3 H, CH_3-C_{Tetr}), 1.04 (s, $^2J_{H–199Hg}$ = 217 Hz, 3 H, CH_3Hg) ppm. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 159.0 (s, C_{Tetr}), 9.8 (s, CH_3-C_{Tetr}), –2.0 (s, $^1J_{C–199Hg}$ = 1633 Hz, CHg) ppm. ^{15}N NMR (CD_3OD): δ = –2.5 (s), –80.4 (s) ppm. $^{199}Hg\{^1H\}$ NMR (CD_3OD) δ = –980 ppm. MS (DCI+): *m*/*z* (%) = 301 (100) [M^+], 273 (7) [$M^+ – CCH_3$], 259 (4) [$M^+ – CH_3CN$], 217 (7) [CH_3Hg]. $C_3H_6HgN_4$ (298.69): calcd. Hg 67.2; found Hg 66.6.

Methyl (5-Phenyl-2*H*-tetrazol-2-yl)mercury (2): M.p. 161 °C. Raman: $\tilde{\nu}$ = 3064 (20), 3044 (11), 3007 (2), 2961 (2), 2923 (28), 1693 (2), 1609 (100), 1585 (4), 1525 (53), 1492 (3), 1444 (49), 1357 (4), 1243 (3), 1200 (14), 1172 (17), 1154 (11), 1139 (3), 1114 (5), 1043 (9), 1026 (3), 1014 (9), 1007 (13), 998 (68), 789 (7), 695 (5), 618 (6), 565 (59, νHgC_{Methyl}), 509 (3), 466 (3), 381 (5) 325 (14), 234 (16) cm^{-1}. IR: $\tilde{\nu}$ = 3071 (w), 3061 (w), 3042 (w), 3006 (w), 2921 (m), 2805 (w), 1584 (w), 1524 (w), 1456 (m), 1443 (vs), 1428 (m), 1384 (w), 1356 (m), 1279 (w), 1262 (w), 1240 (m), 1200 (w), 1170 (m), 1139 (s), 1113 (w), 1099 (w), 1071 (m), 1045 (m), 1027 (m), 1006 (m), 997 (w), 918 (w), 842 (w), 807 (m), 786 (m), 727 (vs), 709 (m), 694 (s), 686 (s) cm^{-1}. ^{1}H NMR (CD_3OD): δ = 8.02/7.51 (2 H/3 H, PhC_{Tetr}), 1.06 (s, $^2J_{H–199Hg}$ = 220 Hz, 3 H, CH_3Hg) ppm. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 163.3 (s, C_{Tetr}), 131.3 (s, *p*-*C*), 130.2 (s, *m*-*C*), 129.1 (s, *C*-C_{Tetr}), 128.3 (s, *o*-*C*), –2.6 (s, *C*Hg, $^1J_{C–199Hg}$ = 1638 Hz) ppm. $^{199}Hg\{^1H\}$ NMR (CD_3OD): δ = –1007 ppm. MS (DCI+): *m*/*z* (%) = 363 (59) [M^+], 273 (16) [$M^+ – CC_6H_5$], 259 (8) [$M^+ – C_6H_5CN$], 217 (10) [CH_3Hg]. $C_8H_8HgN_4$ (360.76): calcd. Hg 55.6; found Hg 54.7.

(5-Methyl-1*H*-tetrazol-1-yl)phenylmercury (3): M.p. 166 °C. Raman: $\tilde{\nu}$ = 3142 (5), 3061 (31), 3049 (40), 2983 (6), 2941 (16), 2895 (6), 2874 (5), 2861 (5), 1602 (4), 1573 (20), 1499 (10), 1482 (10), 1459 (5), 1448 (5), 1434 (5), 1370 (5), 1331 (6), 1264 (4), 1245 (16), 1195 (8), 1185 (5), 1165 (8), 1153 (5), 1133 (5), 1105 (5), 1083 (6), 1043 (4), 1022 (19), 998 (100), 987 (6), 702 (10), 694 (10), 664 (30), 617 (7), 397 (7), 315 (14), 296 (7), 264 (9), 240 (57, νHgC_{Phenyl}), 225 (27) cm^{-1}. IR: $\tilde{\nu}$ = 3068 (m), 3047 (w), 3030 (w), 3017 (w), 2958 (m), 2929 (m), 2872 (m), 2858 (m), 1726 (s), 1599 (w), 1576 (m), 1498 (s), 1479 (m), 1459 (w), 1431 (vs), 1388 (m), 1379 (s), 1369 (vs), 1329 (w), 1287 (m), 1273 (m), 1244 (s), 1130 (m), 1121 (m), 1103 (s), 1084 (m), 1073 (s), 1041 (w), 1022 (m), 1018 (m), 1003 (w), 998 (m), 907 (w), 852 (w), 733 (vs), 727 (s), 723 (s), 700 (s), 696 (vs), 692 (vs), 664 (w) cm^{-1}. ^{1}H NMR (CD_3OD): δ = 7.48/7.37/7.29 (2 H/2 H/1 H, $PhHg$), 2.63 (s, 3 H, CH_3Tetr) ppm. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 159.4 (s, C_{Tetr}), 145.8 (s, $^1J_{C–199Hg}$ = 2561 Hz, *C*Hg), 138.4 (s, $^2J_{C–199Hg}$ = 117 Hz, *o*-*C*), 129.9 (s, $^4J_{C–199Hg}$ = 35 Hz, *p*-*C*), 129.7 (s, $^3J_{C–199Hg}$ = 204 Hz, *m*-*C*), 9.9 (s, CH_3-C_{Tetr}) ppm. $^{199}Hg\{^1H\}$ NMR (CD_3OD): δ = –1324 ppm. MS (DCI+): *m*/*z* (%) = 363 (60) [M^+], 335 (36) [$M^+ – CCH_3$], 321 (48) [$M^+ – CH_3CN$], 279 (68) [C_6H_5Hg]. $C_8H_8HgN_4$ (360.76): calcd. Hg 55.6; found Hg 55.3.

Phenyl (5-Phenyl-2*H*-tetrazol-2-yl)mercury (4): M.p. 194 °C. Raman: $\tilde{\nu}$ = 3140 (3), 3063 (28), 3050 (31), 1608 (76), 1571 (16), 1524 (39), 1480 (3), 1444 (28), 1359 (5), 1307 (4), 1237 (3), 1195 (2), 1182 (5), 1173 (12), 1157 (7), 1131 (2), 1110 (6), 1077 (3), 1067 (2), 1042 (13), 1022 (14), 998 (100), 789 (4), 694 (5), 664 (20), 618 (8), 379 (3), 317 (11), 258 (6), 240 (25, νHgC_{Phenyl}), 212 (16) cm^{-1}. IR: $\tilde{\nu}$ = 3047 (w), 1571 (m), 1523 (w), 1477 (m), 1458 (m), 1443 (s), 1431 (m), 1427 (m), 1396 (w), 1377 (w), 1357 (m), 1329 (w), 1305 (w), 1278 (m), 1262 (w), 1236 (m), 1171 (m), 1157 (w), 1130 (m), 1108 (m), 1071 (m), 1064 (m), 1041 (m), 1029 (m), 1021 (m), 1006 (m), 997 (m), 929 (w), 866 (w), 788 (m), 745 (m), 731 (vs), 723 (m), 711 (w), 695 (vs), 692 (vs), 663 (w) cm^{-1}. ^{1}H NMR (CD_3OD): δ = 8.08/7.53 (2 H/3 H, PhC_{Tetr}), 7.42/7.35/7.27 (2 H/2 H/1 H, $PhHg$) ppm. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 163.5 (s, C_{Tetr}), 146.6 (s, *C*Hg), 138.2 [s, $^2J_{C–199Hg}$ = 119 Hz, $(o\text{-}C)_{Ph(Hg)}$], 131.3 [s, $(p\text{-}C)_{Ph(Tetr)}$], 130.3 [s, $(m\text{-}C)_{Ph(Tetr)}$], 129.9 [s, $(p\text{-}C)_{Ph(Hg)}$], 129.8 [s, $^3J_{C–199Hg}$ = 207 Hz, $(m\text{-}C)_{Ph(Hg)}$], 129.2 (s, *C*-C_{Tetr}), 128.3 [s, $(o\text{-}C)_{Ph(Tetr)}$] ppm. $^{199}Hg\{^1H\}$ NMR (CD_3OD): not detected. MS (DCI+): *m*/*z* (%) = 425 (92) [M^+], 335 (25) [$M^+ – CC_6H_5$], 321 (29) [$M^+ – C_6H_5CN$], 279 (60) [C_6H_5Hg]. $C_{13}H_{10}HgN_4$ (422.83): calcd. Hg 47.4; found Hg 48.1.

(5-Pentafluorophenyl-2*H*-tetrazol-2-yl)phenylmercury (5): M.p. 173 °C. Raman: $\tilde{\nu}$ = 3146 (6), 3060 (49), 3051 (31), 3021 (5), 2996 (5), 2982 (5), 2967 (5), 2954 (5), 1674 (20), 1660 (37), 1632 (18), 1574 (27), 1535 (71), 1486 (100), 1435 (8), 1389 (12), 1341 (6), 1334 (8), 1285 (9), 1265 (8), 1232 (7), 1194 (12), 1185 (17), 1165 (11), 1115 (22), 1098 (11), 1079 (10), 1053 (11), 1041 (8), 1030 (39), 1000 (79), 988 (12), 913 (5), 838 (25), 769 (12), 715 (6), 693 (5), 665 (41), 616 (12), 585 (32), 505 (29), 446 (23), 432 (30), 389 (18), 377 (12), 364 (10), 315 (18), 287 (10), 278 (9), 255 (27), 240 (75, νHgC_{Phenyl}), 223 (19), 202 (29) cm^{-1}. IR: $\tilde{\nu}$ = 3076 (w), 3058 (w), 2963 (m), 1674 (w), 1650 (m), 1633 (m), 1576 (w), 1535 (s), 1511 (vs), 1481 (vs), 1433 (m), 1388 (m), 1374 (m), 1359 (m), 1341 (m), 1262 (m), 1230 (m), 1183 (m), 1143 (w), 1098 (s), 1064 (m), 1052 (m), 1030 (m), 996 (vs), 910 (w), 873 (w), 835 (s), 802 (m), 768 (m), 727 (s), 690 (m), 664 (w), 616 (w), 584 (w) cm^{-1}. ^{1}H NMR (CD_3OD): δ = 7.43/7.35/7.28 (2 H/2 H/1 H, $PhHg$) ppm. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 138.2 [s, $(o\text{-}C)_{Ph(Hg)}$], 129.9 [s, $(p\text{-}C)_{Ph(Hg)}$], 129.8 [s, $(m\text{-}C)_{Ph(Hg)}$] ppm; other carbon atoms not detected due to low solubility. ^{19}F NMR (CD_3OD): δ = –141.4 (m, *o*-*F*), –155.1 (m, *p*-*F*), –164.8 (m, *m*-*F*) ppm. $^{199}Hg\{^1H\}$ NMR (CD_3OD): not detected. MS (DCI+): *m*/*z* (%) = 515 (100) [M^+], 335 (6) [$M^+ – CC_6F_5$], 321 (8)

$[M^+ - C_6F_5CN]$, 279 (27) $[C_6H_5Hg]$. $C_{13}H_5F_5HgN_4$ (512.78): calcd. Hg 39.1; Hg 37.8.

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