

An Unusual Case of Bis-methoxymercuration of Diphenylethyne. Molecular Structure of $\text{PhC(HgCl)}_2\text{C(OMe)}_2\text{Ph}$

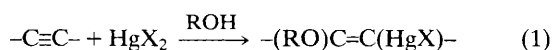
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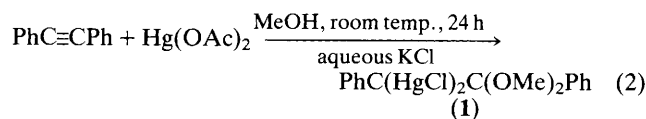
Addition of aqueous KCl to the reaction of diphenylethyne and mercury(II) acetate in methanol induces an unprecedented geminal double mercuration of the triple bond; the X-ray crystal structure of the product shows an unusually short Hg(1)–Hg(2) interatomic distance.

The mercuration of alkynes has long been a reaction of importance because of its industrial and laboratory applications and it is now the subject of both synthetic and mechanistic investigations.¹ The reaction can be tuned to obtain either demercurated organic products or, under milder conditions, mercury containing adducts. For instance, reactions carried out in acetic acid with a variety of substrates and in methanol, in some favourable cases, yield the corresponding solvomercurated alkenes (equation 1).²



We wish to report on the double methoxymercuration of diphenylethyne, on the unusual conditions of product formation, and on the structure of the *gem*-dimercury(II) compound obtained.

The reaction of diphenylethyne (1 g, 5.6 mmol) with mercury(II) acetate (3.65 g, 11.4 mmol) in 100 ml of MeOH, for 24 h at room temperature, was quenched by addition of aqueous KCl (20%, 50 ml), and 1,1-bis(chloromercurio)-2,2-dimethoxy-1,2-diphenylethane [(1) 2.04 g, yield 51% based on alkyne] precipitated as a white solid (equation 2).[†]



[†] Spectroscopic data for (1): ¹H NMR (300 MHz, CDCl₃) δ 7.4–7.0 (m, 10H, Ph), 3.47 (s, 6H, OMe); ¹³C{¹H} NMR (75.43 MHz, CDCl₃) δ 140.98, 139.77, 128.65, 128.48, 127.82, 127.53, 127.44, 107.79 (s, Ph), 133.33 [t, *J*_{Hg-C} 87.9 Hz, C(HgCl)₂], 96.87 [s, C(OMe)₂]. Compound (1) decomposes without melting above 280 °C.

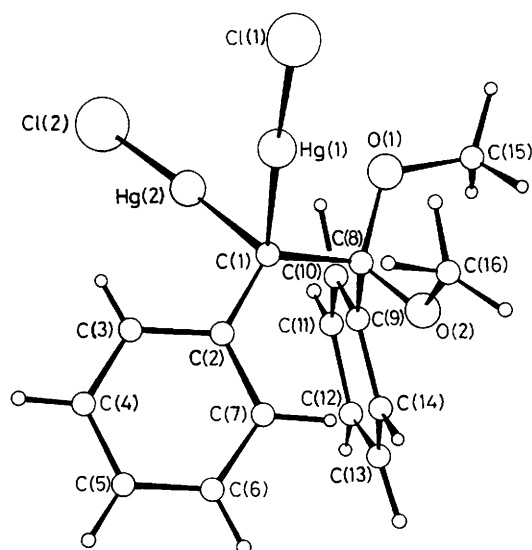


Figure 1. Molecular structure of (1). Selected bond distances (Å): Hg(1)–C(1) 2.121(14), Hg(1)–Cl(1) 2.320(5), Hg(2)–C(1) 2.110(10), Hg(2)–Cl(2) 2.313(4), C(1)–C(8) 1.578(13), O(1)–C(8) 1.415(13), O(2)–C(8) 1.408(12), C(1)–C(2) 1.469(13), C(8)–C(9) 1.565(19). Selected bond angles (°): Hg(1)–C(1)–Hg(2) 98.9(5), Cl(1)–Hg(1)–C(1) 176.5(3), Cl(2)–Hg(2)–C(1) 176.2(3), C(2)–C(1)–C(8) 120.5(9), C(1)–C(8)–C(9) 110.5(7), O(1)–C(8)–O(2) 114.3(8). Selected torsion angles (°): Hg(1)–C(1)–C(8)–O(1) –44.8(9), Hg(2)–C(1)–C(8)–O(1) 59.8(8), C(2)–C(1)–C(8)–C(9) 66.4(12), Hg(2)–C(1)–C(8)–C(9) –59.7(9).

This is in striking contrast to the fact that the reaction in the absence of added KCl yielded quantitatively 1-acetoxymercurio-2-methoxy-1,2-diphenylethene as a mixture of the *Z* and *E* isomers (**2a,b**) in a 3 : 1 ratio, even in the presence of excess mercury acetate.^{2c} Moreover, it is in contrast with the expected and simple ligand displacement reaction commonly used to change alkenyl-, alkyl-, phenyl-, and ferrocenyl-mercury acetates into the corresponding, often crystalline, mercury chloride derivatives.³ For instance, the reactions of alkynes with mercury(II) acetate in acetic acid gave 1-chloromercurio-2-acetoxy-vinyl adducts after treatment with aqueous KCl.^{2b,c}

Formation of (1) was highly reproducible and (1) was also obtained in the presence of excess alkyne or excess mercury(II) acetate, every time that the reaction mixture was treated with aqueous KCl. Under all circumstances, the expected chloromercury vinyl adduct, *i.e.*, the product of monomercuriation, was not observed in the crude product by either ¹H or ¹³C NMR.

In related experiments, diphenylethyne was recovered quantitatively when reacted with HgCl₂ in MeOH for 48 h, after either removal of the solvent or precipitation by addition of water or aqueous KCl. Furthermore, treatment of solid (**2a**) and (**2b**), dissolved in methanol, with aqueous KCl gave the corresponding mixture of 1-chloromercurio-2-methoxy-1,2-diphenylethene.

Polymercurated products have been reported to form by treatment of acetylene with aqueous mercury(II) salts.⁴ Earlier work on the mercuriation of acetylenic fatty acids and esters indicated the formation of RC(O)C(HgOAc)₂R structures,⁵ although the exact nature of such organomercurials has yet to be determined.⁶ Compounds having Hg₃C and Hg₂C moieties

have also been isolated under various conditions,⁷ and crystal structures have been reported as well.⁸

White and air stable needle-shaped crystals of (1), suitable for X-ray analysis, were obtained on cooling of a hot methanol solution of the crude product. Figure 1 shows a projection of the molecule with arbitrary numbering scheme.† The molecule contains an acetal type carbon and the C(HgCl)₂ moiety.

The Hg(1)–Hg(2) interatomic distance is 3.213(7) Å. Assuming that the observed distance is truly non-bonding, the value corresponds to an intramolecular atomic radius of 1.606 Å. This represents the shortest value observed for adjacent mercury atoms.¹¹ For instance, the Hg–Hg distance reported for 3,3-bis(chloromercurio)pentane-2,4-dione is 3.412 Å;^{8a} in the case of tetrakis(cyanomercurio)methane hydrate, C(HgCN)₄·H₂O, the shortest Hg–Hg tetrahedron edge is 3.280 Å long.^{8b} It is possible that the short value observed in (1) is due to the hindrance of the large phenyl and –C(OMe)₂Ph groups.§

The Hg(1)–O(1) intramolecular distance is 2.86(9) Å. This value, when compared to the sum of the van der Waals radii of mercury and oxygen (2.90 Å),¹² is indicative of a possible weak intramolecular bonding interaction. Bond angles at C(1) and C(8) are all quite distorted from the tetrahedral, but the Hg(1)–C(1)–Hg(2) angle is particularly small (98.9°). The C(2)–C(1)–C(8) angle, on the carbon bearing the mercury atoms, is 10° larger than the C(1)–C(8)–C(9) angle, on the acetal carbon. The two phenyl rings, which are in a *gauche* position, are planar and form a dihedral angle of 87.0(4)°. The r.m.s. maximum displacements from mean planes are 0.021(14) and 0.024(13) Å for the C(2) ··· C(7) and C(9) ··· C(14) rings, respectively. The two Hg–C bonds are in agreement with those in the 2.127–2.153 Å range reported for the mercuriation products of dimethyl and diethyl malonate¹³ and for other mercurated aliphatic compounds. As expected for an organomercurial, the Cl–Hg–C bond angles are both close to 180°. The remaining geometrical parameters of the molecule are as expected. The molecules are joined together in the crystal by van der Waals contacts only.

† Crystal data for (1): C₁₆H₁₆O₂Hg₂Cl₂, *M* = 712.39, triclinic, space group *P*1̄, *a* = 14.836(2), *b* = 9.239(3), *c* = 7.232(2) Å, α = 110.41(3), β = 102.03(2), γ = 73.47(2)°, *U* = 884.06 Å³, *Z* = 2, *D_x* = 2.68 g cm⁻³, λ(Mo–Kα) = 0.71069 Å, μ = 176.53 cm⁻¹. A prismatic specimen of about 0.3 × 0.4 × 0.6 mm was employed to collect the diffraction data at room temperature on a Siemens AED single crystal diffractometer. The intensities were collected in the 3–27° θ range with a modified version of the Lehmann and Larsen method.⁹ Unit cell parameters were determined by least-squares of setting angles of 29 reflections (11 < θ < 19°). A total of 3880 reflections were collected and 2484 of them, having *I* > 2σ(*I*), were considered observed and corrected for a decay in intensity (30% every 50 counts) and for absorption.¹⁰ The structure was solved by direct methods with SHELX76 and refined by block-matrix least squares using anisotropic thermal parameters for all the non-H atoms and with variable isotropic thermal parameters for H atoms, to the final agreement values of *R* = 0.034 and *R_w* = 0.033 with *w* = 0.4202 (σ²*F* + 0.00147 *F*²). The largest peak in the final difference Fourier map is close to the Hg(2) atom position with density 1.6 × 10⁻³ e Å⁻³. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ As suggested by a referee, other factors cannot be excluded, especially the possibility of a weak intramolecular bonding between the two adjacent d¹⁰ mercury centres.

Work is in progress in order to elucidate the mechanistic features of this process.

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