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Stereoselective Synthesis of *meso*-α,α′-Bis(Chloromercurio)-α,α′-bis(trimethylsilyl)-*m*-xylene

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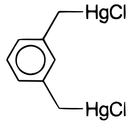
*Summary: The reaction of the dilithio compound 1,3-[{Li(tmeda)}$_2${C$_6$H$_4$(CHSiMe$_3$)$_2$}] (**2**) with Hg(OAc)$_2$ followed by treatment with aqueous HCl is highly stereoselective and yields quantitatively meso-1,3-[C$_6$H$_4$-(CHSiMe$_3$HgCl)$_2$] (**3**). In the solid state, molecules of **3** are connected through the formation of intermolecular head-to-tail Hg$_2$Cl$_2$ bridges. The resulting polymer has a ladder-type structure.*

Introduction

Polyfunctional organomercurials[1a−f] such as tetramercuriomethanes,[1a] trimercuriobenzenes,[1b] and α,*ω*-dimercurioalkanes[1c,d] constitute a well-developed class of compounds. Owing to the discovery of their unique ability to complex anions[2] and also to serve as precursors to a variety of other polymetalated species,[3,4] their chemistry has recently attracted renewed interest. As part of our ongoing efforts in this area,[4,5] we have initiated a systematic search for new bifunctional organomercurials.

We recently reported the synthesis of α,α′-*m*-xylenediylbis(mercurychloride)[5] (**1**) and decided to focus our attention on the preparation of some of its analogues.



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α,α′-Bis(trimethylsilyl)-*m*-xylene can be easily lithiated at the benzylic postions to yield α,α′-dilithio-α,α′-bis(trimethylsilyl)-*m*-xylene (**2**) as a tetramethylethylenediamine (tmeda) adduct.[6] In principle, the dimercuration of **2** could yield a racemic mixture of the optically active enantiomers (*rac* form), the *meso* isomer, or a mixture of the *rac* and *meso* isomers. In this paper we report that the mercuration of α,α′-dilithio-α,α′-bis(trimethylsilyl)-*m*-xylene is highly stereoselective and yields solely *meso*-α,α′-bis(chloromercurio)-α,α′-bis(trimethylsilyl)-*m*-xylene.

Results and Discussion

Compound **2** is readily available by reaction of α,α′-bis(trimethylsilyl)-*m*-xylene and *n*-BuLi in the presence of tmeda.[6] Dropwise addition of a THF solution of **2** to a THF solution containing an excess of Hg(OAc)$_2$, followed by treatment with a dilute aqueous HCl solution, results in the formation of the corresponding mercury derivative 1,3-[C$_6$H$_4$(CHSiMe$_3$HgCl)$_2$] (**3**), which was isolated in almost quantitative yield (Scheme 1). In contrast to **1** which was found to dissolve only in polar solvents such as DMF or DMSO,[5] compound **3** dissolves in CH$_2$Cl$_2$ and THF. It can be recrystallized by addition of toluene to a THF solution.

The two methyne carbon centers of **3** are chiral. Compound **3** could therefore exist in the *rac* form, in the *meso* form, or as a mixture of isomers. However, the ^{1}H NMR spectrum of **3** exhibits a single methyne resonance, a single methyl resonance, and three distinct aromatic proton signals. Accordingly, the ^{199}Hg NMR spectrum of **3** exhibits a single resonance at −1127 ppm (DMSO-*d*$_6$), which can be compared to that of Ph(CH$_2$)-HgCl (−1184 ppm in DMSO-*d*$_6$).[7] These NMR spectroscopic data suggest as a whole that **3** exists either in the *rac* or in the *meso* form. The results of the X-ray single-crystal analysis revealed that **3** is the *meso* isomer.

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Scheme 1

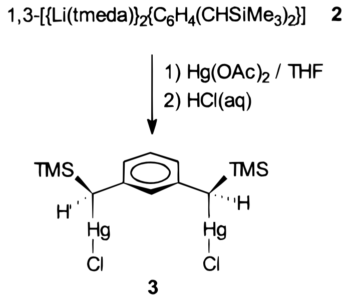

Table 1. Crystal Data and Data Collection and Structure Refinement Details for 3

Crystal Data	
formula	$C_{14}H_{24}Cl_2Hg_2Si_2$
M_r	720.59
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	9.351(1)
b (Å)	10.178(1)
c (Å)	11.769(2)
α (deg)	90.26(1)
β (deg)	101.28(1)
γ (deg)	109.51(1)
V (Å^3)	1032.4(2)
ρ_{calc} (g cm^{-3})	2.318
Z	2
F(000) (e)	660
μ(Mo Kα) (cm^{-1})	152.17
Data Collection	
T (°C)	−74
scan mode	ω/θ
hkl range	0−11, −12 to +11, −14 to +14
[(sin θ)/λ]$_{max}$ (Å^{-1})	0.64
no. of measd rflns	3776
no. of unique rflns (R_{int})	3773 (0.0000)
no. of rflns used for refinement	3768
abs corr	ψ scans
T_{min}/T_{max}	0.33/0.99
Refinement	
no. of refined params	181
final R values ($I > 2\sigma(I)$)	
R1 (%)	0.0412
wR2 (%)	0.1087
max/min peak and hole in diff map (e Å^{-3})	+2.949/−3.533 (located at Hg atoms)

Crystals of **3** belong to the triclinic space group $P\bar{1}$ with two molecules in the unit cell (Table 1). As shown in Figure 1, the two trimethylsilyl groups are positioned on the same side of the aromatic ring and the two Hg−Cl moieties are almost parallel to each other (dihedral angles C(2)−C(1)−C(7)−Hg(1) = 43.4° and C(2)−C(3)−C(8)−Hg(2) = 40.5°). As a result, molecules of **2** approach an approximate C_s symmetry with a mirror plane perpendicular to the aromatic ring passing through the C(2) and C(5) carbon atoms. There are no other unusual features in the structure of **2** which merit comments, with the exception of the C(7)−Hg(1)−Cl(1) and C(8)−Hg(2)−Cl(2) angles (176.4(3) and 174.8(3)°, respectively), which slightly deviate from the ideal linear coordination usually encountered at divalent mercury centers.

In the solid state, molecules of **3** are associated through intermolecular sub-van der Waals Hg···Cl contacts (r_{vdw}(Hg) = 1.7−2.0 Å,[8] r_{vdw}(Cl) = 1.8 Å)[9] (Table 2). The formation of dimeric units can first be recognized (Figure 2). These dimers are formed by reciprocal chelation of a Hg−Cl moiety of one molecule by its bidentate counterpart, a phenomenon also observed in the structure of {[2,4,6-$(CH_3)_3C_6H_2$]N[$(CH_2)_2HgCl]_2$}.[10] Additional head-to-tail Hg_2Cl_2 bridges (Table 2) connect the dimers to form parallel ladder-type polymeric chains (Figure 2), which are reminiscent of those encountered in the solid state of organomercury halides such as Ph(CH_2)HgCl.[11] In that respect, the supramolecular structure of **3** differs from that of **1**, which forms a very intricate three-dimensional network.[5]

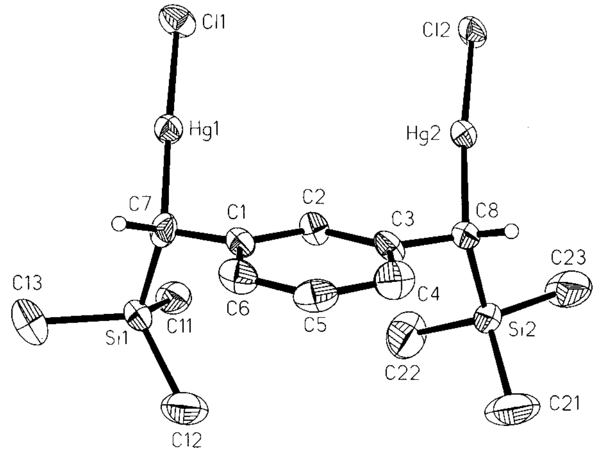

Figure 1. Structure of **3** in the crystal: ORTEP drawing with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Hg(1)−C(7), 2.078(9); Hg(2)−C(8), 2.101(9); Hg(1)−Cl(1), 2.329(2); Hg(2)−Cl(2), 2.345(2); C(1)−C(7), 1.502(12); C(3)−C(8), 1.513(12); C(7)−Hg(1)−Cl(1), 176.4(3); C(8)−Hg(2)−Cl(2), 174.8(3).

Table 2. Intermolecular Hg···Cl Distances (Å) in the Supramolecular Structure of 3[a]

Hg(1a)···Cl(1)^{i}	3.566	Hg(2a)···(1)^{i}	3.311
Hg(1a)···Cl(2)^{i}	3.400	Hg(2a)···Cl(2b)^{ii}	3.303

[a] Symmetry position of the chlorine atom with respect of the position of the mercury atom: (i) $-x, -y, -z + 2$; (ii) $-x - 1, -y - 1, -z + 2$.

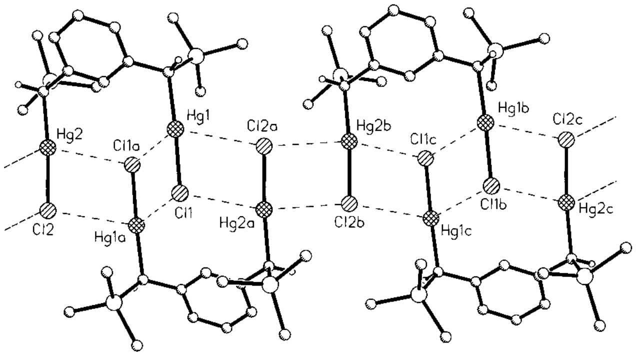

Figure 2. View of a portion of a polymeric chain of **3**. The reciprocal chelation of a Hg−Cl moiety of one molecule by its counterpart is evident from this view.

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Conclusion

The high stereoselectivity observed in the reaction leading to the formation of **3** constitutes the main finding of the present work. There is no apparent reason which allows an easy rationalization of this phenomenon. Examination of the literature indicates that anion template effects occur in mercury chemistry.[2a] It is thus possible that such effects are at play in the formation of **3**.

Experimental Section

General Considerations. Nuclear magnetic resonance spectra were obtained on a JEOL-GX 400 instrument (400 MHz for ^{1}H, 100.5 MHz for ^{13}C, 71.56 MHz for ^{199}Hg). Neat $HgMe_2$ was used as an external standard for the ^{199}Hg NMR spectra. The proton and carbon signals of the deuterated solvent were used as internal standards for the ^{1}H and ^{13}C NMR spectra, respectively. All NMR measurements were carried out at 25 °C. The Laboratory for Microanalysis at Technische Universität München performed the elemental analyses. All experiments were carried out under a dry inert atmosphere of N_2 using standard Schlenk techniques or a glovebox (Labmaster 130, Fa. M. Braun). All melting points were measured on samples in sealed capillaries and are uncorrected. THF was dried over Na/K and distilled prior to use. All other solvents were used without further purification. All commercially available starting materials were purchased from Aldrich Chemicals and used as provided. Compound **2** was synthesized according to the literature procedure.[6]

***meso*-α,α′-Bis(chloromercurio)-α,α′-bis(trimethylsilyl)-*m*-xylene (3).** A solution of 1,3-[$\{Li(tmeda)\}_2\{C_6H_4(CHSiMe_3)_2\}$] (0.41 g, 0.82 mmol) in THF (4 mL) was added dropwise to a THF (10 mL) solution of $Hg(OAc)_2$ (2.0 g, 6.60 mmol) at 0 °C. The resulting mixture was warmed to room temperature and was stirred overnight. After evaporation of the solvent, the residue was washed with 2 M aqueous HCl (2 × 25 mL) and hexane (3 × 15 mL) to afford after drying a 96% yield (0.57 g) of analytically pure **3**; mp 147 °C. Anal. Calcd. for $C_{14}H_{24}Cl_2Hg_2Si_2$: C, 23.32; H; 3.33. Found C, 22.88; H, 3.01. NMR data for **3** in DMSO-d_6: ^{1}H NMR δ 0.00 (s, 18 H, Si(CH_3)$_3$), 2.95 (s, 2 H, CH), 6.72 (d, $^3J = 7.3$ Hz, 2 H, H-4/6), 6.96 (s, 1 H, H-2), 6.96 (t, $^3J = 7.3$ Hz, 1 H, H-5); $^{13}C\{^1H\}$ NMR δ 0.2 Si(CH$_3$)$_3$, 46.5 (CH), 124.4 (C-4/6), 127.9 (C-2), 129.1 (C-5), 142.7 (C-1/3); ^{199}Hg NMR δ −1127 (DMSO-d_6), −1142 (THF-d_8), −1145 (DMF-d_7).

Crystal Structure Determination of 3. A single crystal of suitable quality and size was mounted in a glass capillary and used for measurements of precise cell constants and intensity data collection on an Enraf-Nonius CAD4 diffractometer (Mo Kα radiation, λ(Mo Kα) = 0.710 73 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. *Lp* correction was applied, and intensity data were corrected for absorption effects. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[12] The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso}(fix) = 1.5U_{eq}$ of the attached C atom). Further information on crystal data, data collection, and structure refinement are summarized in Table 1. Important bond lengths and angles have been gathered in the caption of Figure 1 and in Table 2.

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Supporting Information Available: Tables of atomic coordinates and isotropic thermal parameters, all bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, and thermal parameters for **3** (4 pages). Ordering information is given on any current masthead page.

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