Preliminary communication

Difunctionalization of primary aromatic amines with ethylene; synthesis of μ-arylnitrilobis(ethane-2,1-diyl)dimercury(II) complexes. Crystal structure of $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{N-}(\text{CH}_2\text{CH}_2\text{HgCl})_2$

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Abstract

Reaction of primary aromatic amines, mercuric acetate, and ethylene in tetrahydrofuran under pressure (ca. 40 atm) yields the organomercurials $\text{ArN}(\text{CH}_2\text{CH}_2\text{HgOAc})_2$ (Ar = Ph, $2\text{-ClC}_6\text{H}_4$, $3\text{-ClC}_6\text{H}_4$, or $4\text{-ClC}_6\text{H}_4$) or, after treatment of the crude products with sodium halide, $\text{ArN}(\text{CH}_2\text{CH}_2\text{HgX})_2$ (Ar = $4\text{-MeC}_6\text{H}_4$, $4\text{-MeOC}_6\text{H}_4$, or $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, X = Cl; Ar = $2,4\text{-Cl}_2\text{C}_6\text{H}_3$, $2,6\text{-Cl}_2\text{C}_6\text{H}_3$, or $2,4,6\text{-Br}_3\text{C}_6\text{H}_2$, X = Br). The X-ray diffraction study of $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{HgCl})_2$ shows the molecules to have near linear C–Hg–Cl stereochemistry, and to be arranged in centrosymmetric dimers with weak $\text{Hg} \cdots \text{Cl}$ intermolecular bonding.

Aminomercuration of 1,4- and 1,5-, and 1,6-dienes with a mercuric salt and a primary aromatic amine leads to functionalization of both NH bonds and formation of nitrogen-containing heterocycles [1,2]. However, analogous aminomercurations of simple olefins (RCH=CH_2, R = H, Me, Ph, etc.) generally result in monofunctionalization giving 2-(arylamino)alkylmercurials, $\text{ArNH}(\text{CHRCH}_2\text{HgX})$ [2,3]. Difunctionalization of ArNH_2 has been observed only in two such reactions, both for R = H [4,5]. There was minimal characterization of the products, only analysis for $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{Hg}\overline{\text{N-2-C(O)}}\text{C}_6\text{H}_4\overline{\text{CO}})_2$ [4] and an unspecified acidolysis for $\text{PhN}(\text{CH}_2\text{CH}_2\text{HgOAc})_2$ [5]. In each case, the monofunctionalised species $\text{ArNH}(\text{CH}_2\text{CH}_2\text{HgX})$ (**1**) was still the major product, and the two products were not separated for Ar = Ph, X = OAc [5]. We have now prepared a range of $\text{ArN}(\text{CH}_2\text{CH}_2\text{HgX})_2$ compounds (**2**) without significant formation of **1**, and have determined the crystal structure of a representative example.

μ-Arylnitrilobis(ethane-2,1,-diyl)bis(acetatomercury(II)) complexes were prepared by reaction of mercuric acetate, the appropriate aniline (mole ratio 2/1, except 1/1

for Ar = 2,4,6-Me$_3$C$_6$H$_2$), and an excess of ethylene in tetrahydrofuran (thf) in a sealed Carius tube (pressure ca. 35–40 atm) at room temperature.

$$ArNH_2 + 2\ Hg(OAc)_2 + 2\ C_2H_4 \rightarrow ArN(CH_2CH_2HgOAc)_2 + 2\ AcOH$$
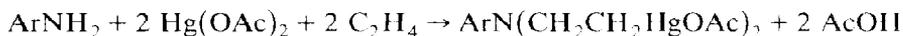
After release of the excess of ethylene, either the crude acetatomercury(II) complex was filtered off (2a–2d, Table 1), or a saturated aqueous or aqueous ethanolic solution of sodium chloride or bromide was added to a filtered solution of the acetato complex in thf, leading to precipitation of the corresponding ArN(CH$_2$CH$_2$HgX)$_2$ (X = Cl or Br) derivative (2e–2j).

Analytically pure compounds (yields, Table 1) were obtained following recrystallization from thf (2a–2f), thf/CHCl$_3$ (2g–2i) or CHCl$_3$ (2j). No ν(NH) absorptions were observed in the infrared spectra, ruling out formation of monofunctionalized species (1). Principal identification was by ^{1}H NMR spectroscopy, the most important features being two methylene triplets with characteristic ^{199}Hg^{1}H coupling constants (Table 1). Their magnitudes, especially values for 2a, 2b in CDCl$_3$, are similar to those for 2-methoxyethylmercurials [6]. The ^{199}Hg NMR spectrum of each compound showed a single resonance (overlapping triplet of triplets for 2a–2f, pseudo pentets for 2g–2j, for which ^2J(HgH) and ^3J(HgH) have similar values), indicating equivalent mercury atoms, at δ ca. -1240 (X = OAc), ca. -985 (X = Cl), and ca. -1105 ppm (X = Br) from external Me$_2$Hg.

An X-ray crystallographic study established details of the structure of 2j *.

The molecules have a novel "running man" appearance with near linear C–Hg–Cl stereochemistry, and are arranged in centrosymmetric dimers with weak intermolecular Hg $\cdots$ Cl bonds (Fig. 1). The distances are within the sum (3.53 Å) of the Van der Waals radii of chlorine [9] and mercury [10]. Mercury–chlorine and mercury–carbon distances are similar to those for other organomercuric chlorides [11], and in particular to those for the only other crystallographically characterized aminomercuration product, Et$_2$NCH$_2$CH$_2$HgCl (3) [12]. The intermolecular Hg...Cl bond distances are similar to those (3.184–3.442 Å) recently observed in tetrameric 2-(2'-pyridyl)phenylmercuric chloride [13]. Although the bond angles of

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* *Crystal data*: C$_{13}$H$_{19}$Cl$_2$Hg$_2$N, (2j), $M = 661.25$, triclinic, a 11.168(7), b 10.284(7), c 8.533(4) Å, α 70.46(5), β 68.36(2), γ 67.18(6)°, $U = 818.36$ Å^3, D_m (insufficient crystals), D_c 2.68(3) g cm^{-3} for $Z = 2$, $F(000)$ 595.8, $\mu = 190.3$ cm^{-1} for Mo-K_α (0.7107 Å). Space group $P\bar{1}$ confirmed by refinement. 4753 unique data from a crystal $0.13 \times 0.10 \times 0.06$ mm, Philips PW1100 diffractometer, ω-scan, scan range $\pm(1.3 + 0.3\tan\theta)$ in 2θ from calculated Bragg angle at 0.1° s^{-1}. Corrections for decomposition, absorption and Lorentz and polarization effects were applied. Maximum and minimum transmission factors were 0.4031 and 0.1206 respectively. Scattering factors for neutral atoms [7] were corrected for anomalous dispersion. Calculations were carried out on Dec Vax 11/780 computers; the major program used was that of Sheldrick [8].

The structure was solved by conventional heavy atom methods; non-hydrogen atoms located and refined, hydrogen atoms in geometrically idealized positions (a riding model used in refinement). The mercury and chlorine atoms were refined anisotropically in the final refinement cycles in which 79 variables were refined using 1286 data ($I \geqslant 3\sigma(I)$). The hydrogen atoms were all given the same isotropic thermal parameter, which was refined. The C(1)–C(6) ring was refined as a rigid group with C–C fixed at 1.40 Å. The model converged at $R = 0.073$ and $R_w = 0.064$.

A table of atomic coordinates and a complete list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

Table 1

Preparations and properties of $ArN(CH_2CH_2HgX)_2$ complexes **2a–2j**

Ar	Compound X =	Number	Reaction[a] time (d)	Yield[b] (%)	m.p. (dec) (°C)	$\delta(CH_2Hg)$[c] ($^2J(HgH)$) ppm (Hz)	$\delta(CH_2N)$[c] ($^3J(HgH)$) ppm (Hz)
Ph	OAc	**2a**	7	75	192	1.78(227)[d]	3.54(133)[d]
2-ClC$_6$H$_4$	OAc	**2b**	2	66	114[e]	1.74(228)[f]	3.31(190)[f]
3-ClC$_6$H$_4$	OAc	**2c**	21	75	174–5	1.75(233)	3.54(125)
4-ClC$_6$H$_4$	OAc	**2d**	21	52	139–140	1.76(227)	3.53(139)
4-MeC$_6$H$_4$	Cl	**2e**	2	62	145	1.80(225)	3.55(152)
4-MeOC$_6$H$_4$	Cl	**2f**	2	61	132	1.79(225)	3.51(157)
2,6-Cl$_2$C$_6$H$_3$	Br	**2g**	1	40	>150[g]	1.84(214)	3.50(215)
2,4-Cl$_2$C$_6$H$_3$	Br	**2h**	1	74	155	1.80(222)	3.40(209)
2,4,6-Br$_3$C$_6$H$_2$	Br	**2i**	1	59	171	1.84(215)	3.50(216)
2,4,6-Me$_3$C$_6$H$_2$	Cl	**2j**	3	45	126	2.08(217)[h]	3.42(193)[h]

[a] At room temperature. [b] Recrystallized analytically pure products. [c] In $(CD_3)_2SO$. [d] In $CDCl_3$, 2.14(223); 3.59(242). [e] Dec. at 150°C. [f] In $CDCl_3$, 2.11(208); 3.31(276). [g] Dec. without melting. [h] In C_5D_5N.

2j around nitrogen approach triangular, this does not arise from conjugation of the nitrogen lone pair with the phenyl ring since C(1)–N is a normal single bond. Furthermore, the interplanar angle between the aryl ring and the C(1')NC(1'') plane
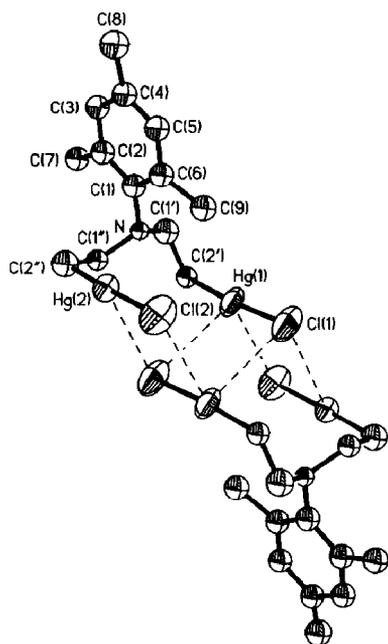
Fig. 1. The structure of $2,4,6-Me_3C_6H_2N(CH_2CH_2HgCl)_2$ (**2j**. Selected bond distances and angles: Hg(1)–Cl(1) 2.34(2), Hg(2)–Cl(2) 2.35(1), Hg(1)–C(2') 2.10(4), Hg(2)–C(2'') 2.04(4), C(2')–C(1') 1.55(4), C(2'')–C(1'') 1.55(4), N–C(1') 1.43(4), N–C(1'') 1.47(5), N–C(1) 1.46(3) Å; C(2')–Hg(1)–Cl(1) 175(1), C(2'')–Hg(2)–Cl(2) 178(1), Hg(1)–C(2')–C(1') 109(3), Hg(2)–C(2'')–C(1'') 110(2), C(2')–C(1')–N 116(2), C(2'')–C(1'')–N 117(3), C(1')–N–C(1'') 114(3), C(1)–N–C(1') 118(2), C(1)–N–C(1'') 116(2)°. Significant intermolecular contacts: Hg(1)···Cl(2)[a] 3.20(1), Hg(1)···Cl(1)[a] 3.38(1), Hg(2)···Cl(1)[a] 3.23(1) ([a] $2-x$, $\bar{y}$, $\bar{z}$).

is 84.3°, probably owing to steric repulsion between the *ortho*-methyl groups and the substituted ethyl groups, precluding conjugation.

The complexes **2** are obtained under the present conditions regardless of the $ArNH_2/Hg(OAc)_2$ ratio, e.g., for Ar = Ph, **2a** was obtained with 1/2, 1/1, 2/1, and 7/1 mole ratios. Examination of representative crude products showed no evidence for $ArNH(CH_2CH_2HgX)$ species **1**, though a small amount of the mercuration product, $4-NH_2C_6H_4HgOAc$ was obtained from one reaction with aniline. Thus, conversion of **1** into **2** is evidently faster than formation of **1** or indeed mercuration of the aromatic amines in the present systems. In view of the importance of aminomercuration–demercuration in organic synthesis [e.g. 1–3], the complexes **2**, essentially a new class of aminomercuration products, are of great synthetic potential and interest.

References

1 J. Barluenga, C. Najera, and M. Yus, J. Heterocyclic Chem., 18 (1981) 1297; 17 (1980) 917; Synthesis, (1979) 896.
2 R.C. Larock, Solvomercuration/Demercuration Reactions in Organic Synthesis, Springer-Verlag, Berlin, 1986, p. 443–504.
3 A.J. Bloodworth, The Organic Compounds of Mercury, Ch. 3 in C.A. McAuliffe (Ed.), The Chemistry of Mercury, Macmillan, London, 1977.
4 G. Sachs, J. Chem. Soc., (1949) 733.
5 A. Lattes and J.J. Perie, C.R. Acad. Sci. Paris, Sér. C, 262 (1966) 1591.
6 S. Brownstein, Disc. Farad. Soc., 34 (1962) 25; M.M. Kreevoy and J.F. Schaefer, J. Organomet. Chem., 6 (1966) 589.
7 International Tables for X-ray crystallography, 1974, Vol. IV, Birmingham, Kynoch Press (Present distributor, D. Reidel, Dordrecht).
8 G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, Cambridge, England, 1976.
9 L. Pauling, The Nature of the Chemical Bond, Cornell Univ. Press, Ithaca, NY, 3rd edit., 1960.
10 A.J. Canty and G.B. Deacon, Inorg. Chim. Acta, 45 (1980) L225.
11 J.L. Wardell, Mercury, Ch. 17 in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 2, Pergamon, Oxford, 1982.
12 K. Toman and G.G. Hess, J. Organomet. Chem., 49 (1973) 133.
13 E.C. Constable, T.A. Leese, and D.A. Tocher, J. Chem. Soc., Chem. Commun., (1989) 570.