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Preliminary communication

The crystal structure of (phenylazophenyl-*C*,*N*′)mercury(II) chloride: a dimeric *trans*-metallation reagent

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Abstract

An X-ray diffraction study of (phenylazophenyl-*C*,*N*′)mercury(II) chloride has shown it to be dimeric via long Hg–Cl bridging interactions of 3.367 Å.

The use of simple organomercury compounds as *trans*-metallation reagents in organometallic chemistry in general, and in organotellurium chemistry in particular [1], is long established. Some years ago we introduced (phenylazophenyl-*C*,*N*′)mercury(II) chloride as a convenient intermediate in the formation of cyclotellurated azobenzenes [2], but a more recent reinvestigation of that reaction suggested that a product containing both tellurium and mercury "contaminated" the major product [3]. The reaction of mercurated 2-phenylpyridine with *p*-ethoxyphenyltellurium(IV) trichloride affords well defined ionic compounds containing both mercury and tellurium [4]. With selenium tetrabromide, the same reagent gives a material which ^{1}H and ^{13}C NMR spectroscopy show to contain mercurated and selenated 2-phenylpyridine in 1/1 ratio [5].

Constable [6] has demonstrated the tetrameric nature of 2-(2-pyridyl)phenylmercury(II) chloride, and so it is not unreasonable that hetero-bimetallic intermediates may be isolated from *trans*-metallation reactions. The observation in the mass spectrum of (phenylazophenyl-*C*,*N*′)mercury(II) chloride of a significant fragment of $m/e = 799$ (100%) having the correct isotopic distribution for $[(C_{12}H_9N_2)HgClHg(C_{12}H_9N_2)]^+$ suggested that this material was not monomeric, and that, in this case also, heterobimetallic intermediates in *trans*-metallation reactions might, under favourable circumstances, be isolable.

The cell parameters and reflection intensities were measured with graphite monochromated Mo-K_α radiation for a bright red crystal, 0.6 0.06 0.05 mm of the

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title compound using an Enraf–Nonius CAD-4 diffractometer, operating in the ω–2θ scan mode. Three standard reflections were monitored at regular intervals to check the stability of the system. 2929 reflections ($\theta \leqslant 25°$) were scanned, of which 2055 were unique, and 1306 with $F > 5\sigma(F)$ were used in the structure analysis.

Crystal data. $C_{12}H_9N_2ClHg$, $M = 417.3$, monoclinic, space group $P2_1/c$, a 10.648(3), b 4.582(4), c 23.900(7) Å, β 94.05(2)°, V 1163 Å^3, $Z = 4$, D 2.38 g cm^3, $F(000) = 768$, μ 13.70 mm^{-1}.

The atomic coordinates for mercury were found by Patterson methods. The lighter atoms were located by a Fourier difference synthesis. As not all the hydrogen atoms could be located from difference maps, the hydrogens were placed in calculated positions (C–H 1.08 Å) and allowed to "ride" on their respective carbon atoms in the subsequent least squares refinements. Non-hydrogen atoms were allowed to vibrate anisotropically. Unit weights were used and the refinements converged to give $R = 0.0471$, when all the shifts were $< 0.02\sigma$. An empirical absorption correction was applied using DIFABS [7].

Computations were carried out on the Birmingham University Honeywell Computer and at the University of Manchester Regional Computer Centre with SHELXS-86 [8] and SHELX-76 [9]. Plots of the structure were drawn using PLUTO [10] *.

The structure of the complex, together with the atom numbering, is shown in Fig. 1. The complex exists as a dimer, $[(C_{12}H_9N_2)_2Hg_2Cl_2]$; the mercury atom is bonded to a carbon atom and a chlorine atom, Hg–C(1) 2.01(2) Å, Hg–Cl 2.309(6) Å, with secondary interactions to N(2) and two symmetry related chlorine atoms. The bridging chlorine, Cl′ (located at $-x$, $1-y$, $1-z$) is 3.367(6) Å from the mercury atom, and there is another weaker interaction with with the chlorine at (x, $1+y$, z), Hg...Cl″ 3.632(5) Å. The Hg–C and Hg–Cl primary bond distances lie within the ranges 1.922–2.228 and 2.239–3.289 Å, respectively, found for Hg–C and Hg–Cl bond lengths in searches of the Cambridge Crystallographic Database (for comparison, the sum of the Pauling single-bond covalent radii are 2.01 and 2.43 Å). The Hg...N(2) distance is 2.70(2) Å, indicative of a rather weak interaction as previously implied from a ^{13}C NMR study [11].

These distances may be compared to those found [5] in the related 2-(2-pyridyl)phenylmercury(II) chloride, where Hg–C, Hg–Cl(primary), and Hg–Cl(secondary) have mean bond lengths 2.07, 2.32 and 3.43 Å, respectively. In this structure also a Hg...Cl contact of intermediate length (3.184 Å) is observed; as in the title compound, the Hg...N contacts are weak, the distances being 2.627 and 2.673 Å for the two independent molecules.

The conformation of the organic ligand can be described in terms of the angles which the phenyl rings make with the central group of coplanar atoms, C(6)–N(1)–N(2)–C(7); these angles are virtually identical at 9.7 and 8.0° and the Hg...N interaction thus has no effect on the orientation of the C(1)–C(6) phenyl ring. Taken as a whole, the non-hydrogen atoms of the ligand are coplanar to within

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* The atomic coordinates and a complete list of bond lengths and angles are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (U.K.). Any request should be accompanied by the full literature citation for this communication.

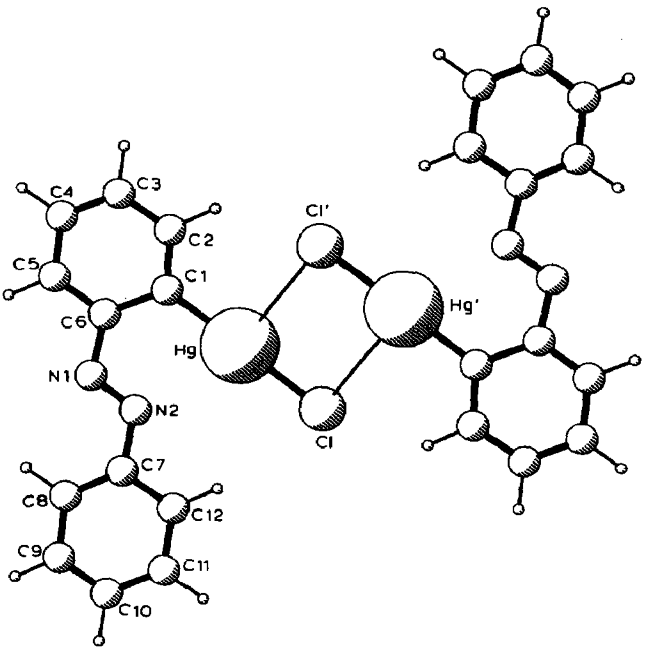

Fig. 1. Structure of the $[(C_{12}H_9N_2)_2Hg_2Cl_2]$ complex with atom-numbering scheme.

+/− 0.22 Å, the mercury and chlorine atoms being displaced by 0.45 and 0.84 Å from the ligand mean plane.

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