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Preliminary communication

X-RAY STUDY OF THE MOLECULAR STRUCTURE OF α-MERCURY AND α-PLATINUMMERCURY DERIVATIVES OF L-MENTHYL PHENYLACETATE

G.Z. SULEIMANOV, V.V. BASHILOV, A.A. MUSAEV, V.I. SOKOLOV* and O.A. REUTOV
Institute of Organo-Element Compounds, Vavilova St. 28, Moscow 117312 (U.S.S.R.)

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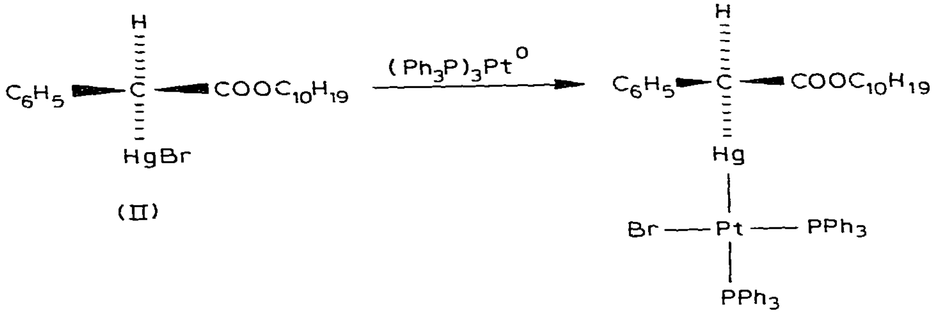
Summary

The molecular structures of the L-menthyl ester of *S*-α-bromomercuriphenylacetic acid, diastereomer II, $[\alpha]_D^{20}$ −18°, and of the related L-menthyl ester of α-bromobis(triphenylphosphine)platinummeruriphenylacetic acid, VI, have been investigated by the X-ray method. Insertion of L_2Pt carbenoid appears to occur into the Hg—Br bond in II and two phosphine ligands in the product VI occupy *cis* positions in a planar square around the platinum atom. The Hg—Pt distance is 2.50 Å; there is intermolecular Hg—Br coordination in II, the distance being 3.23 Å.

Recently, we reported [1] the preparation of both diastereomers of $C_6H_5CH(HgBr)COOC_{10}H_{19}$: I, $[\alpha]_D^{20}$ −132°, *R*-configuration of the asymmetric carbon atom, and II, $[\alpha]_D^{20}$ −18°, *S*-configuration of the same centre, which served as models for the study of the insertion of Pt^0 complexes into the



(VI)

mercury—element bond [2]. Here we describe the structure of more soluble diastereomer II and that of the bimetallic derivative VI prepared as shown below.

The diastereomeric composition of the organomercurial, $[\alpha]_D$ −18°, according to PMR spectra [3], was 94% of I and 6% of II. Colourless crystals of II were grown from hexane on cooling, yellow-green crystals of VI were obtained directly from the reaction carried out in benzene at ambient temperature. The X-ray experiment was performed using a Syntex $P2_1$ automatic diffractometer (Institute of Physics, Baku) with Mo-K_α rays at room temperature. Calculations were performed on a NOVA-1200 computer using XT-Syntex programmes.

The structure of the organomercuryplatinum compound is shown on Fig. 1.

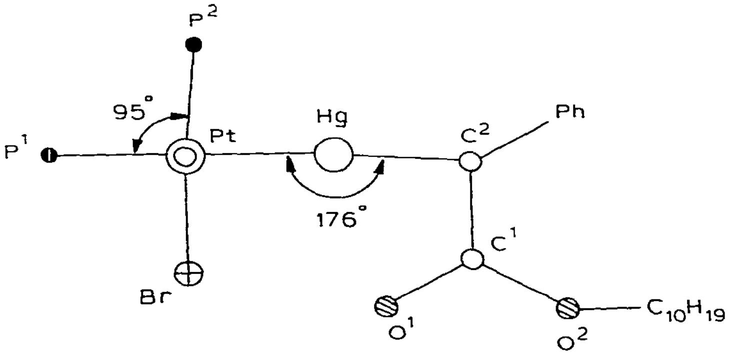


Fig. 1. The structure of the essential part of molecule VI.

TABLE 1

SOME IMPORTANT INTERATOMIC DISTANCES IN THE MOLECULES OF α-MERCURY AND α-PLATINUMMERCURY DERIVATIVES OF L-MENTHYL PHENYLACETATE

$PhCH(HgBr)COOC_{10}H_{19}$	l (Å)	$PhCH[HgPt(Ph_3P)_2Br]COOC_{10}H_{19}$	l (Å)
C—Hg	2.05	C—Hg	1.96
Hg—Br	2.46	Hg—Pt	2.499
		Pt—Br	2.36
		Pt—P^1	2.30
		Pt—P^2	2.31

Some significant values of valence angles and bond lengths are collected in Table 1, full data will be published elsewhere.

The most important feature of the structure of VI is the *cis* arrangement of phosphine ligands around platinum in a planar square. Similar *cis* geometry in organomercuryplatinums was previously disclosed by Struchkov et al. [4,5] for two molecules derived from the R_2Hg organomercurials. In this communication we for the first time establish the same geometry for the L_2Pt insertion product into the Hg—Hal bond in an organomercurial halide. The formation of *cis* isomers in all cases studied so far should be considered as a characteristic feature of this reaction [6], and suggests a planar transition state as has been previously discussed [4]*.

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*As a corollary may be considered the similar result concerning related insertion of zerovalent platinum into a Sn—C bond to also give a *cis* configuration [7].

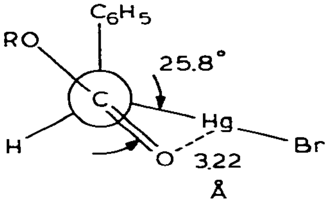

Fig. 2. Newman projection of molecule II viewed along the bond $C^1—C^2$.

An important detail of the structure is the Pt—Hg bond, 2.499(2) Å in VI which is shorter compared to 2.569 Å [4] and 2.617 Å [5] in other bimetallic molecules. This shortening can be connected with the presence of the alkyl moiety instead of strongly electron-withdrawing perfluorinated groups in former models.

Comparison of the structures of II and VI shows that there is practically no significant difference in bond lengths and valence angles in the organic moiety. The C—Hg bond is 1.96 Å in VI and 2.05 Å in II. Intermolecular distances Hg· · ·Br in the organomercurial bromide II are 3.23 Å, which indicates the coordination common for organomercurial halides [8]. As a consequence, molecules of II are packed pairwise as dimers in the crystal. Noteworthy is the dihedral angle 25.8° between planes $O^1C^1O^2C^2$ and C^1C^2Hg and the related short distance $Hg—O^2$, 3.22 Å. This particular conformation is likely to be favoured by the intramolecular coordination, at least in crystal.

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