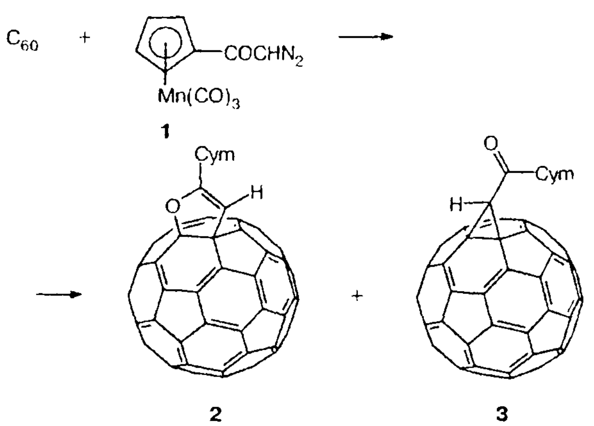
Scheme 1



Mn(CO)$_3$ group in both products: 1950 and 2028 cm^{-1} (2), 1955, 1965, and 2035 cm^{-1} (3). In addition, the IR spectrum of adduct **3** exhibits a peak of the ketone CO group at 1690 cm^{-1}, which is absent in the spectrum of **2**. ^{1}H NMR spectra (CS$_2$) each contain two triplets characteristic of the α- and β-protons of monosubstituted cymanthrene: δ 5.44 and 4.98 for **2** and δ 5.90 and 5.03 for **3**. In addition, the ^{1}H NMR spectrum of compound **2** contains a singlet at δ 6.26, while that of compound **3** contains a singlet at δ 5.00. The mass spectra of **2** and **3** show peaks with *m/z* 880 [M$^+$ − 3 CO], which is characteristic of cymanthrene fragmentation. The electronic absorption spectra of products **2** and **3** exhibit absorption maxima at 430 and 699 nm, which correspond to a 6,6-monoadduct. Hence, the structures of methanofullerene and isomeric dihydrofuranofullerene may be assigned to adducts **3** and **2**, respectively. In our case, no fulleroid product (5,6-adducts) was detected. Dihydrofuran derivatives, along with methanofullerenes, are also formed in reactions of C_{60} with diazo ketones containing no organometallic substituent.[3]

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(Benzamidomethyl)dimethylsilanol hydrochloride. Oxonium structure and intra- and intermolecular coordination interactions

S. A. Pogozhikh,[a] *O. A. Zamyshlyaeva,*[b] *E. P. Kramarova,*[b]
M. Yu. Antipin,[a] *Yu. E. Ovchinnikov,*[a]* *and Yu. I. Baukov*[b]*

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: yuo@xray.ineos.ac.ru
[b]*Russian State Medical University,*
1 ul. Ostrovityanova, 117869 Moscow, Russian Federation.
Fax: +7 (095) 434 4787. E-mail: vvnmeduni@glasnet.ru

Recently,[1,2] we published some preliminary data on the synthesis and structure of the first representatives of monosubstituted amides of the general formula RC(O)NHCH$_2$SiMe$_2$X (R = Alk, Ar; X = Hal) in which not only the amide oxygen atom but also the NH hydrogen atom can be involved in coordination. Such compounds are promising as model subjects for studying competitive intra- and intermolecular coordination. The formation of an O→Si intramolecular coordination bond is typical of *N*-silylmethyl derivatives of amides and related compounds containing, at least, one sufficiently electronegative Si-substituent.[3] Ordinary monosubstituted amides usually form intermolecular coordination bonds.[4]

In a continuation of these investigations, we studied the structure of a crystalline specimen of benzamidomethylsilanol hydrochloride by X-ray diffraction analysis. The starting compound for the preparation of the latter was disiloxane (**1**),[2] whose reaction with thionyl

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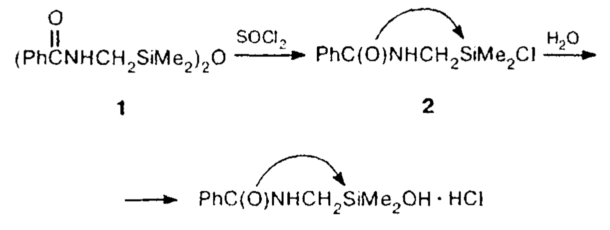
chloride in benzene gave *N*-(chlorodimethylsilylmethyl)benzamide (**2**)[2] (yield 72%, m.p. 93—95 °C (from benzene)). Compound **2** was kept for a long period of time under conditions not excluding contact with atmospheric moisture. After about a year, the specimen melted at a higher temperature (124—127 °C) and corresponded in elemental composition to (benzamidomethyl)dimethylsilanol hydrochloride (**3** · HCl). Found (%): C, 48.59; H, 6.33; N, 5.36. $C_{10}H_{16}ClNO_2Si$. Calculated (%): C, 48.87; H, 6.56; N, 5.70. A single crystal for X-ray diffraction analysis was obtained by recrystallization from acetonitrile.



1 **2**

3 · HCl

An X-ray diffraction analysis showed that hydrochloride **3** · HCl is a cation-anionic H-associate where the five-coordinate Si atom has a trigonal-bipyramidal environment with O atoms in axial positions. One of them is included in a five-membered chelate ring and forms an O→Si intramolecular coordination bond, while the other is part of the oxonium group. The CO—Si and Si—O(H_2) bond lengths are equal to 1.904 and 1.981 Å, respectively; the central atom deviates from the equatorial plane (Δ_{Si}) by −0.024 Å (the minus sign indicates that the deviation occurs towards the carbonyl O atom). The $-\overset{+}{O}<$ group is a rather good leaving Si-substituent in S_N-Si-reactions and occupies an intermediate position between OC_6F_5 and OTf groups as regards their influence on the parameters of hypervalent bonding in the O—Si—O hypervalent fragment among compounds bearing an $OSiC_3O$ coordination element.[5] In particular, the CO—Si and Si—O bond lengths and Δ_{Si} are equal to 2.078, 1.787, and 0.16 Å in $L^{(7)}SiMe_2OC_6F_5$ and to 1.753, 2.786, and −0.30 Å in $L^{(6)}SiMe_2OTf$, respectively ($L^{(n)}$ is the *n*-membered bidentate lactamomethyl ligand).

Additional (N)H...Cl...$(HO)_2$ intramolecular interactions were detected in the crystal of the hydrochloride (Fig. 1). Each Cl atom is three-coordinate and involved in H-bonding with one NH and two OH hydrogen atoms. The N...Cl distances are equal to 3.16 Å, while the Cl...O distances are equal to 3.03 and 3.07 Å, the sum of the van der Waals radii[6] of the N and Cl atoms being equal to 3.30 Å and that of the O and Cl atoms being equal to 3.27 Å. In all cases, the Cl...H...X angles (X = O, N) are close to 180°. The hydrogen bonds cross-link the molecules in the crystal, thus forming a three-dimensional network.

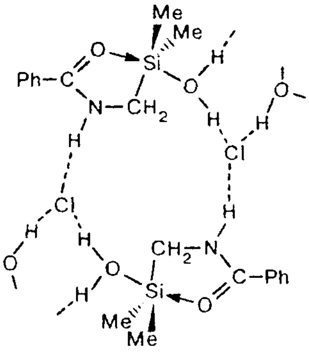


Fig. 1. Intermolecular H-bonds in the cation-anionic associate **3** · HCl.

In conclusion, note that the $\mathrm{O{-}Si{-}\overset{+}{O}}$ hypervalent fragment of the hydrochloride **3** · HCl can serve as a model of the transition state of acid-catalyzed S_N-Si-reactions of compounds having an Si—O bond (silanols, siloxanes, and alkoxysilanes), where the first stage is a transformation of the "poor leaving" oxygen-containing group into a "good leaving" oxonium group.

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