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SYNTHESIS AND CHARACTERIZATION OF CATIONIC DIAMINOCYCLOPROPENYLIDENE MERCURY COMPLEX

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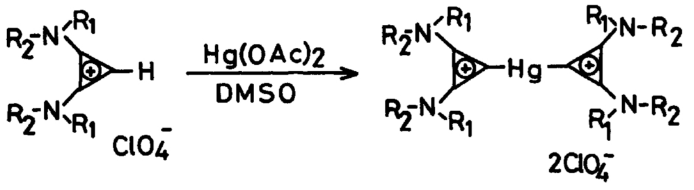
Cationic diaminocyclopropenylidene mercury complexes (1) were synthesized by the reaction of diaminocyclopropenium perchlorate with mercury acetate. Coordination of two diaminocyclopropenylidenes to divalent mercury was confirmed on the basis of microanalyses and spectral measurements. The value of $^{13}C-^{199}Hg$ coupling constant in 1 indicates a diagnostic of sp hybridization of the C-Hg bond.

Cyclopropenylidene has attracted much attention because of its nucleophilicity, aromaticity and highly strained structure.2) A few neutral metal complexes of diphenylcyclopropenylidene have been isolated and their interesting physico-chemical properties have been reported.3) We have found that introduction of amino groups to cyclopropenium ion,4) cyclopropenone5) and related electron system6) gives marked effect on the electronic structure of those three-membered ring due to strong interaction with the peripheral amino groups. It is expected that enhancement of nucleophilicity at the 3-carbon atom of 1,2-bisdialkylaminocyclopropenium ion enables us to prepare a new type of organometallic compounds involving cyclopropenium ion. We wish to report the synthesis of stable cationic mercury complexes of diaminocyclopropenylidene and their reaction behavior towards electrophiles.

A solution of bisdiisopropylaminocyclopropenium perchlorate (2a) and an equimolar amount of mercury acetate in dimethylsulfoxide was heated at 120° for 30 min. After cooling, addition of ether containing small amounts of methanol led to white precipitates. Crystallization of the crude product from dichloromethane-ether afforded the cationic mercury complex (1a) as colorless crystals, mp 280° (dec.), in 75% yield. In a similar manner the reaction of (2b) with $Hg(OAc)_2$ gave (1b) in

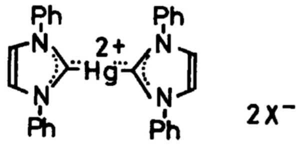


(2) (1)

	R_1	R_2
a.	i-Pr	i-Pr
b.	t-Bu	Me

60% yield, mp 160° (dec.). The structures of 1a and 1b were determined on the basis of elemental analysis[7] and spectral data. In the infrared spectrum 1a shows two characteristic absorptions for diaminocyclopropenium ion[8] at 1861 and 1536 cm^{-1} and a strong absorption at 1095 cm^{-1} due to perchlorate ion. The pmr spectrum (DMSO-d_6) of 1a shows two kinds of signals of isopropyl groups; a pair of doublet at δ 1.38, 1.50 and a pair of septuplet at 4.12, 4.18. The restricted rotation about the C-N bond causes two isopropyl groups in different magnetic circumstance. The cmr spectra of the metal complexes show some interesting features.[9] The ring carbons bonded to amino group in 1a were observed at 142.7 ppm, which was down field shift of 8.9 ppm from that in 2a. The ring carbon bonded to mercury resonates at 137.3 ppm with ^{199}Hg satellites. The ^{13}C-^{199}Hg coupling constant in 1a (2508 Hz) and 1b (2500 Hz) is comparable to that of diphenylethynylmercury (2584 Hz).[10] This very large coupling constant indicates that the carbon atom in the C-Hg bond has sp hybridized orbital. Thus these spectral characterics can be interpreted in terms of metallo-cyclopropenium ion. The rotational barrier about the C-N bond was examined by means of the cmr measurement at varying temperature. The free energy of activation ($\Delta G_c^{\neq}$) in 1a has been found to be 17.1 kcal/mol. This value is approximately similar to those of 2a (17.8 kcal/mol) and 1,2-bisdiisopropylamino-3-methylcyclopropenium perchlorate (16.2 kcal/mol). It is, therefore, concluded that σ-inductive effect is operative in the mercury-carbon bond of this system.

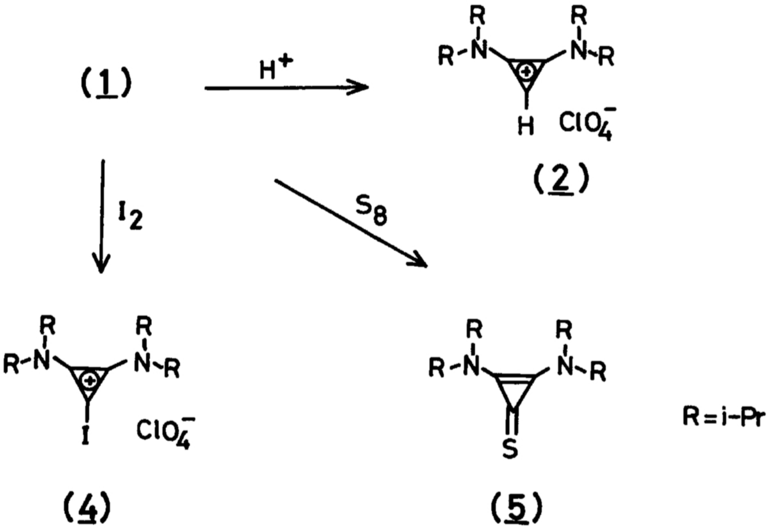
Schönberr and Wanzlick reported[11] a cationic mercury complex (3) obtained by treatment of 1,3-diphenylimidazolium ion with mercury(II) salts. In the complex 3 divalent mercury atom is bonded with two ligands through the sp^2 orbital of the 2-carbon atom. Although there is essential difference between 1 and 3 in nature of the metal-carbon bonding, replacement of the sp^2 carbon atom of 3 with cyclopropenium core C_3^+ leads to a new cationic mercury complex 1.



(3)

Reaction behaviour of the mercury complex 1a towards electrophiles has been examined. Divalent mercury atom was replaced with electrophilic reagents. Three cases are briefly described below.

To a stirred solution of 1a in dichloromethane was added twice molar amounts of iodine in dichloromethane. After stirring for 1 hr, the solution was washed with dil. perchloric acid, and dried over anhydrous magnesium sulfate. Removal of the solvent followed by recrystallization from acetone-ether gave white crystals of 1,2-bisdiisopropylamino-3-iodocyclopropenium perchlorate (4a) in 55% yield. A mixture of 3a and 1.2 times molar amount of sulfur in pyridine was refluxed for 20 hr with stirring. The solvent was removed under reduced pressure. The residual material was chromatographed on silica gel with ethylacetate-benzene. Recrystallization from dichloromethane-ether gave bisdiisopropylaminocyclopropenethione (5a)[5] in 35% yield. A solution of 3a in ethanol and 70% perchloric acid (3:1) was refluxed for 10 hr. The solution was poured into water and extracted with dichloromethane. The organic layer was dried and evaporated to give diaminocyclopropenium perchlorate 2a in quantitative yield. These products were identified by comparison of infrared and pmr spectra with those of authentic compounds.



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9) FT-cmr spectra were measured at 15.04 MHz. ^{13}C chemical shifts are in ppm from external tetramethylsilane, and the coupling constants are accurate within 2 Hz.

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