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X-ray diffraction studies of three 1-phenylethynylgermatranes with two phenyl groups in atrane skeleton

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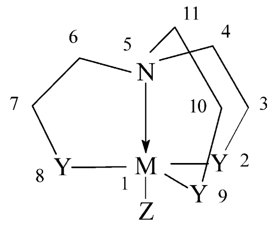
Abstract

Single crystal structures of *treo*-$N(CH_2CH_2O)_2(CHPhCHPhO)GeC{\equiv}CPh$ (**1**), *erythro*-$N(CH_2CH_2O)_2(CHPhCHPhO)GeC{\equiv}CPh$ (**2**) and $N(CH_2CH_2O)_2(CH_2CPh_2O)GeC{\equiv}CPh$ (**3**) were determined by X-ray diffraction studies. These compounds show transannular N→Ge interactions; the strength of this interaction depends on the Ph groups position in atrane skeleton (**1**, $d(N\rightarrow Ge)=2.210(4)$ Å; **2**, $d(N\rightarrow Ge)=2.166(4)$ Å; **3**, $d(N\rightarrow Ge)=2.138(3)$ Å). The structures of these compounds are discussed along with performed DFT calculations data. General trends for molecular structures of the group 14 elements (Si, Ge) metallatranes containing carbon substituents in atrane framework are reviewed.

Keywords: Metallatranes; Germatranes; Hypervalent interactions; X-ray diffraction studies; DFT calculations

1. Introduction

The chemistry of metal derivatives of aminoalcohols such as triethanolamine—metallatranes (A)—has attracted considerable attention [1]. The particular interest has been shown in silatranes and germatranes due to a broad spectrum of their biological activity, which fosters the importance of these species for applications in medical science and pharmacology [4,5]. On the other side, these compounds are important from the theoretical point of view, the nature of intramolecular N→M interaction being the subject of interest [1–3]. Up to date several relationships between the nature of substituent at metal atom [both axial (Z) and three equatorial (Y=O, N–R, S, CH_2)] and the strength of N→M bond have been found for metallatranes (A). In general, stronger electron withdrawing substituent resulted in contraction of N→M distance in these compounds [6–8].



A

It should be noted that the structural chemistry of metallatranes with various substituents attached to carbon atoms of atrane cage has been studied to a very limited extent; accordingly, the influence of these substituents with different electronic and steric properties on the transannular bond strength is still unclear. Among atrane cage substituted metallatranes 3,7,10-trimethyl-substituted compounds [2–4,9] and so-called ‘tribenzometallatranes’ [derivatives of tris(2-hydroxyphenyl)amine (or 2,2′,2″-nitrilotriphenol)] [10–13] are the most known to date. There are only few reports concerning metallatranes

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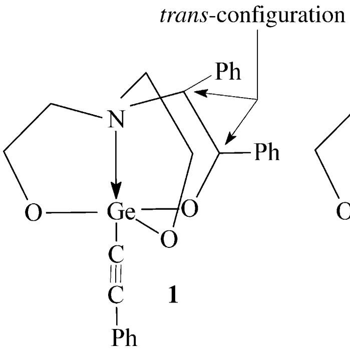
bearing other groups attached to carbon atoms of atrane fragment. The work of Herrmann and co-workers dealing with silatranes, which contain terpene moieties in one arm of triethanolamine ligand should be particularly mentioned [14]. Very recently we have reported on molecular structure of four germatranes contained phenyl group in position 3 or 4 of atrane cage [15]. Although, one phenyl group does not influence significantly N→Ge distance in three studied compounds, however, in the case of 1-trimethylsiloxy-3-phenylgermatrane the elongation of N→Ge distance in comparison with that in unsubstituted analogue was found. Here and after the terms 'substituted' and 'unsubstituted' mean metallatranes with or without any substituents at carbon atoms of atrane cage (positions 3, 4, 6, 7, 10, 11), respectively. At the same time, one could expect that the presence of two phenyl groups at 3- or 4-position of atrane skeleton may considerably influence the nature of N→Ge bond and affect the structure and properties of these molecules. To the best of our knowledge, no diphenylsubstituted main group atranes had been reported in literature when we began this study. However, it is worth to note, that Kim and Do very recently reported the preparation of (R,R,R)–$Cp^*Ti(OCHPhCH_2)_3N$, they also found the distinction in catalytic behavior (styrene polymerization) of this compound in comparison with that for monomethyl-, dimethyl-, and trimethylsubstituted cyclopentadienyltitanatranes [16]. Nugent et al. also prepared the number of transition metals atranes with (R,R,R)–$N(CH_2CHPhOH)_3$ as a ligand, but no X-ray structures were reported [17–19].

Here we describe the molecular structures of three diphenylsubstituted 1-phenylacetylenyl germatranes (**1**, **2**, **3**) as well as their synthesis and spectral characterization. These complexes were synthesized as a part of our research program dedicated to the investigation of main group elements derivatives of alkanolamines (metallatranes and metallocanes) and triethylenetetramines (azametallatranes) [9,15,20–27].



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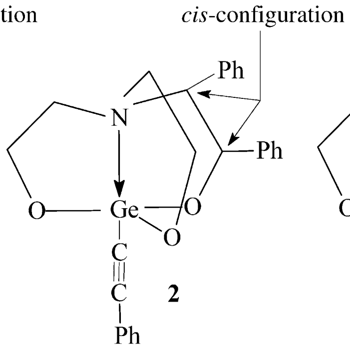

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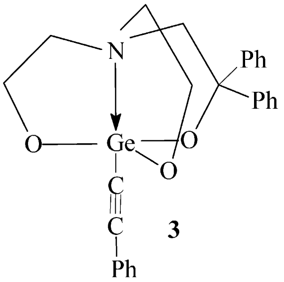

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Our motivation was: (1) to study the possible influence of two phenyl groups in different positions of atrane framework on structure of germatranes in solid state; (2) to compare our data with those previously found for other substituted group 14 elements atranes (X-ray data) and with DFT calculation results. The comparison of presented data with those for four recently studied germatranes **4–6**: **4**, $N(CH_2CH_2O)_3GeC{\equiv}CPh$ [22]; **4**·$CHCl_3$, $N(CH_2CH_2O)_3GeC{\equiv}CPh\cdot CHCl_3$ [28]; **5**, $N(CH_2CHMeO)_3GeC{\equiv}CPh$ [9]; **6** $N(CH_2CH_2O)_2(CH_2CHPhO)GeC{\equiv}CPh$ [15] was particularly important.

2. Experimental

2.1. Materials and procedures

All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. Starting materials $PhC{\equiv}CGe(OEt)_3$ [29] and trialkanolamines [30] were prepared according to the literature. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR 400 spectrometer (in $CDCl_3$); chemical shifts (in the ^1H and ^{13}C NMR spectra) are given in ppm relative to internal Me_4Si. The IR spectra were recorded on Zeiss UR-20. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University.

2.1.1. Preparation of *treo*-$N(CH_2CH_2O)_2(CHPhCHPhO)GeC{\equiv}CPh$ (**1**), *erythro*-$N(CH_2CH_2O)_2(CHPhCHPhO)GeC{\equiv}CPh$ (**2**) and $N(CH_2CH_2O)_2(CH_2CPh_2O)GeC{\equiv}CPh$ (**3**)

The germatranes were synthesized by stirring of equivalent amounts of $PhC{\equiv}CGe(OEt)_3$ and the appropriate trialkanolamine using benzene as the solvent. After 24 h the reaction mixture was filtered to give the product as a white solid, which was then washed with *n*-hexane and dried in vacuo. Crystals suitable for structural analysis were obtained by slow evaporation of the *n*-hexane/chloroform solution.

treo-$N(CH_2CH_2O)_2(CHPhCHPhO)GeC{\equiv}CPh$ (**1**). Anal. Calcd for $C_{26}H_{25}GeNO_3$: C 66.16, H 5.34, N 2.97. Found C 66.11, H 5.22, N 3.02. ^1H NMR δ 7.52–7.50, 7.32–7.10 (2m, 15H, Ph-rings protons), 5.21 (d, 1H, OCHPh), 3.73 (d, 1H, NCHPh), 4.13–4.02, 3.84–3.78, 3.36–3.29, 3.00–2.96,