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1,1′-Diphenyl-bis-germatrane with persistent radical cation

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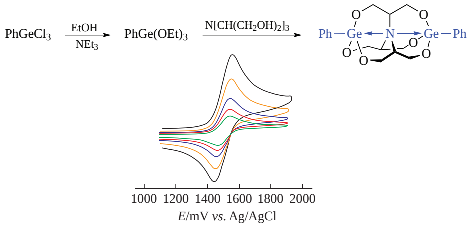
Bis-phenyl derivative of a novel family of bis-metallatranes, 1,1′-diphenyl-bis-germatrane, was synthesized and characterized. One-electron oxidation of this compound is electrochemically and chemically reversible providing a persistent radical cation.

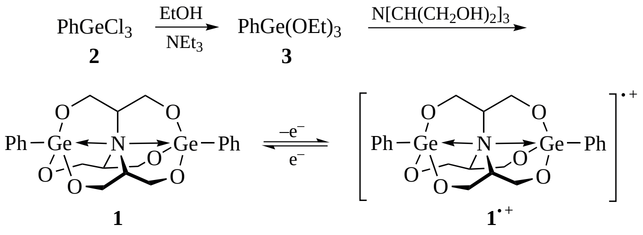


Keywords: organogermanium compounds, metallatranes, redox properties, radical cations, cyclic voltammetry, actuator systems.

Germatranes, cage compounds with trigonal bipyramid coordination of Ge and an intramolecular 3c–4e bonding, are known for half a century.[1] Redox reactions of metallatranes and the products of their one-electron oxidation, radical cations, attract attention for surface modification, spin writing and as possible actuator systems.[2,3] With this, redox-related experimental and theoretical properties of germatranes are contradictory,[3] so correct description of the type and localization of HOMO in such systems requires a special attention.[4,5] In view of development of hyperbonded systems beyond 3c–4e and the perspectives of their applications, germatranes and recently prepared bis-germatranes[5] are of an acute interest from both theoretical and experimental points of view; stabilizing their radical cations being another special issue. In this preliminary report, we present synthesis of 1,1′-diphenyl-bis-germatrane and generation of its persistent radical cation.

The title compound was synthesized by ethoxylation of (trichloro)phenylgermane **1** followed by reaction of thus formed (triethoxy)phenylgermane with tris(1,3-dihydroxyprop-2-yl)amine (Scheme 1, for the preparation of the polyol amine see ref. 6).†

The obtained 1,1′-diphenyl-bis-germatrane **1** was characterized by several instrumental techniques (for details, see Online Supplementary Materials). In particular, Figure 1 shows the polyisotopic HRMS (ESI-MS) spectrum with a specific isotope cluster for compounds containing two germanium atoms.



Scheme 1

Redox properties of bis-germatrane **1** were assessed using cyclic voltammetry at a glassy carbon (GC) disc electrode in a 0.1 M Bu_4NPF_6/MeCN solution. The voltammograms recorded at the scan rates from 0.05 to 1 V s^{-1} (Figure 2) demonstrated a reversible one-electron oxidation leading to formation of radical

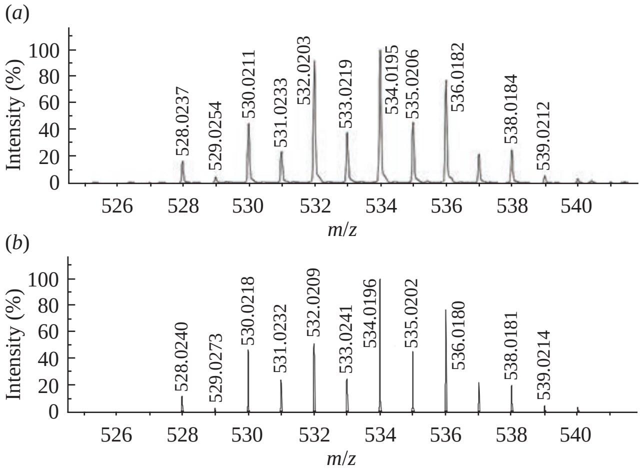


Figure 1 HRMS (ESI-MS) spectrum of 1,1′-diphenyl-bis-germatrane **1** (the molecular ion formation upon H^+-ionization): (*a*) experimental and (*b*) calculated.

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† Triethylamine (0.43 g, 4.3 mmol) and EtOH (0.14 g, 4.3 mmol) were added to a solution of $PhGeCl_3$ (0.30 g, 1.16 mmol) in light petroleum (10 ml) at 0 °C. The mixture was stirred at 0 °C for 30 min, and then at 40–45 °C for 2 h. After cooling to room temperature, $Et_3N\cdot HCl$ was filtered off and washed with light petroleum. Tris(1,3-dihydroxyprop-2-yl)amine (0.14 g, 0.58 mmol) in MeOH (5 ml) was added to the combined filtrate at 0 °C; the mixture was stirred for 30 min and then at room temperature for 8 h. The solvent was evaporated to a half, the solution was cooled to 0 °C, and the precipitated 1,1′-diphenyl-bis-germatrane **1** was filtered off as amorphous white solid (yield, 0.14 g, 45%).

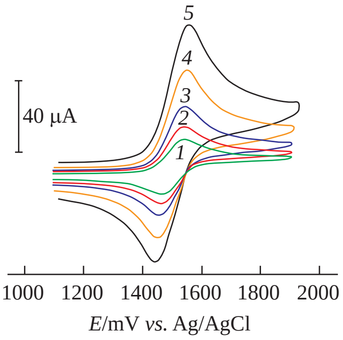

Figure 2 Cyclic voltammograms of 3×10^{-3} M 1,1′-diphenyl-bis-germatrane **1** at a GC disc electrode (1.7 mm) in 0.1 M Bu_4NPF_6/MeCN at scan rates of (*1*) 0.05, (*2*) 0.1, (*3*) 0.2, (*4*) 0.5 and (*5*) 1.0 V s^{-1}. Temperature 298 K.

cation $\mathbf{1}^{\bullet+}$ (see Scheme 1). Within the given scan rate range, the behaviour of this reversible one-electron system is comparable to that of a standard ferrocene solution under the same conditions, showing similar forward and reverse peak currents with the 1 : 1 ratio. Extrapolating E_p's to zero peak currents allows one to estimate the formal potential of this bis-germatrane **1** as $E^{0'}$ = 1.506 V. The separation of anodic and cathodic peak potentials is ΔE_p = 0.063 V, which is very close to 0.059 V, a theoretical value for electrochemically reversible reactions.[‡,7–9] The data on electrooxidation of phenylgermanium derivatives are quite scarce, but from few electrochemical studies on phenyl mono-germane derivatives, their *chemically irreversible* oxidation occurs at 1.16–1.24 V *vs*. Fc^+/Fc[10] (*ca* 1.4 V *vs*. Ag/AgCl). On the other hand, *chemically reversible* oxidation at $E_{1/2}$ = 0.88 V[§] *vs*. Ag/AgCl[6] was reported for the precursor of bis-germatrane, tris(1,3-dihydroxyisopropyl)amine. Reversibility of oxidation of the bis-germatrane can then be considered as an argument that the center of electron withdrawal (HOMO) in this molecule does not locate on the Ph substituent but is rather bis-atrane nitrogen-located. Consequently, the resulting radical cation center is sterically protected inside the bis-atrane cage providing the remarkable stability to the whole system.

The involvement of (N)p_z electrons into the 3c–4e system in germatranes increases their oxidation potentials by 400–500 mV compared to E_p of triethanolamine.[3,11] The same shift observed for bis-germatrane **1** might reflect similar intramolecular interactions, supposedly corresponding to a 5c–6e system, though a more detailed analysis is complicated by the absence of E_p of phenyl germatrane so far. Nevertheless, some estimation can be done using the E_p^{ox} of phenyl silatrane, which is reported to be the same as that of 3-thienyl silatrane and approximately 100 mV more positive than E_p of methyl silatrane.[9] By analogy, from E_p of 3-thienyl and methyl germatranes (1.65 and 1.5 V, respectively), the E_p of phenyl germatrane is expected to be about 1.6–1.65 V. The E_p's of other aryl germatranes also conform this value.[3] In this rough estimation, E_p of the new bis-germatrane **1** is slightly lower than expected. Furthermore, E_p of 2-(3-bromothienyl)-bis-germatrane (1.975 V *vs*. SCE, ref. 5) is also slightly lower (applying –0.31 V reference electrode conversion) than that of its germatrane analogue (1.705 *vs*. $Ag/AgNO_3$, ref. 3). With a substituent-located HOMO in these compounds, the formal electron-donor effect of bis-atrane cage appears stronger than that of a simple atrane, albeit an opposite trend would be expected supposing the participation of N lone pair in two N→Ge dative interactions in bis-germatranes. Further work on structural characterization and electronic properties of this new class of carcass systems and of their radical cations is forthcoming.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.09.004.

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[‡] It is worth noting that the increase in the value of ΔE_p with potential sweep rate fully correlates with uncompensated resistance that was evaluated from the cyclic voltammograms recorded for a ferrocene solution under similar conditions in the same range of potential sweep rates. Peak potential *vs*. peak current plots are linear for both **1** and ferrocene solution, their slopes are identical and correspond to uncompensated resistance in Ohm (thus, this indicates high chemical and electrochemical reversibility of oxidation of **1**). Extrapolation of the linear plot to zero current makes it possible to obtain potential values independent of uncompensated resistance. This approach allows one to get the values of $E^{0'}$ and ΔE_p with good reproducibility (~1 mV).

[§] Apparently, there is confusion between $E_{1/2}$ and $E_{p/2}$ in ref. 6; allowing 57 mV for $E_p - E_{p/2}$ separation (ref. 7), one comes up with 0.94 V *vs*. Ag/AgCl.