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# Novel aromatic species containing group 14 atoms\*

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*Abstract*: The dianions of tetraphenylsilole and tetraphenylgermole behave as aromatic species, as shown by the equalization of C–C bond lengths in these rings and by nucleus-independent chemical shift (NICS) calculations. Similarly, the dianions of 9-silafluorene and 9-germafluorene are aromatic. In the latter species, the heteroatom five-membered rings are more aromatic than the attached benzene rings.

Also to be recognized as aromatically stabilized compounds are the stable unsaturated diiminocarbenes, diiminosilylenes, and diiminogermylenes. Evidence for the aromatic delocalization in these molecules comes from NMR, NICS calculations, Raman spectroscopy, isodesmic molecular orbital (MO) calculations, and calculated isomerization stabilization energies. From the presently available evidence, the aromaticity appears to alternate, with C > Ge > Si, going down group 14.

Keywords: aromaticity; siloles; germoles; silylenes; germylenes.

## INTRODUCTION

An extensive science of aromatic compounds of the group 14 elements, Si, Ge, and, Sn has developed entirely within the past 15 years. Especially noteworthy are the comprehensive studies by Tokitoh, Okazaki, and their coworkers, on the synthesis of group 14 heteroaromatics, including heterobenzenes, naphthalenes, phenanthrenes, and anthracenes [1], as well as the remarkable syntheses by Sekiguchi and his coworkers [2] of Si and Ge analogs of cyclopropenium ions, cyclobutadiene dianions, hetero-cyclopentadiene anions, and a disilabenzene.

In this paper, we consider first the aromaticity of dianions of siloles and germoles, stannoles, silafluorenes, and germafluorenes. In a later section, we take up the question of aromatic delocalization in stable diiminosilylenes and germylenes, compared with the corresponding stable carbenes.

### SILOLE, GERMOLE, AND STANNOLE DIANIONS

The best-studied examples of siloles and germoles are the tetraphenyl-substituted compounds. These can be synthesized from diphenylacetylene, as shown in Scheme 1.

Reduction of diphenylacetylene with lithium metal in diethyl ether leads to an anion-radical which couples to form dilithiotetraphenylbutadiene. Reaction with  $SiCl_4$  or  $GeCl_4$  yields the corresponding dihalometalloles, **1** and **2**, which can be converted to the dianions by reaction with lithium metal in tetrahydrofuran (THF) (Scheme 1).

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Scheme 1 Synthesis of metallole dianions.

The disodium salt of tetraphenylsilole was first synthesized by Joo and coworkers in 1990 [3]. The dilithium derivative 1 was reported by Boudjouk in 1993; the NMR spectrum of 1 was interpreted in terms of a delocalized structure [4]. Firm evidence for electron delocalization and aromaticity in 1 and 2 is provided by the X-ray crystal structures of these salts [5,6]. The significant bond lengths for these dianions and for a nonaromatic reference compound are given in Scheme 2.



Scheme 2 Bond lengths (pm) in silole and germole dianions.

Looking first at the nonaromatic silole molecule (PhC)<sub>4</sub>Si(Cl)CH<sub>3</sub>, we note that it has double and single bonds, as expected. The bond lengths  $C_1-C_2$  (and  $C_3-C_4$ ) are short, and the  $C_2-C_3$  distance is long, consistent with the silacyclopentadiene structure. The situation for the dianions, as their dilithium salts, is entirely different. The dilithiosilole **1** crystallizes in a  $\eta_1-\eta_5$  structure, while the Ge analog **2** exists in two different crystalline forms, with structures  $\eta_1-\eta_5$  and  $\eta_5-\eta_5$ . In all three structures, the  $C_1-C_2$ ,  $C_2-C_3$ , and  $C_3-C_4$  bond distances are nearly equal. This indicates an effective  $\pi$ -electron delocalization around the ring, and hence aromaticity.

Recently, Saito and coworkers have synthesized the Sn analog of these compounds, 1,1-dilithio-2,3,4,5-tetraphenylstannole, **3** [7]. In this dianion also, the C–C bond lengths become nearly equalized:  $C_1-C_2 = 142.2$ ,  $C_2-C_3 = 144.2$ , and  $C_3-C_4 = 144.6$  pm. Thus, dilithiostannole **3** should be added to the list of aromatic metallole dianions. Nucleus-independent chemical shift (NICS) calculations also support the conclusion that **1**, **2**, and **3** have substantial diamagnetic ring currents and so are aromatic.

One other metallole dianion has been studied structurally, the dilithium salt of 2,3,4,5-tetraethyl-1-germole [8]. Nearly equal bond lengths in the five-membered ring were found, indicating that this dianion is also delocalized and aromatic. A 1,1-dilithiotetramethylsilole dianion has also been reported. The NMR properties of this dianion, particularly the downfield <sup>29</sup>Si chemical shift, are consistent with cyclic delocalization in this molecule as well [9].

#### METALLAFLUORENE DIANIONS

Next we will consider the dibenzo analogs of metalloles, the metallafluorenes. These may be synthesized from *o*-dibromobenzene and the metal tetrahalides, as illustrated for Si in Scheme 3. Reduction of the dichlorofluorenes requires much more vigorous conditions than for the dichlorosiloles. Conversion to the dianion required heating with molten potassium metal in refluxing THF.



Scheme 3 Synthesis of dipotassiosilafluorene, 4.

The structures for the dianions of 9-silafluorene (4) and 9-germafluorene (5) are revealing. These are shown in Scheme 4, along with the structures of the corresponding dichlorofluorenes as reference compounds. In the latter, bond lengths in the five-membered rings are quite different, consistent with the cyclopentadiene-like structure of the central ring; bond lengths in the fused benzene rings are the same, as expected. In metallafluorene dianions 4 and 5, the bond distances in the five-membered ring become nearly equal, just as in the silole dianions 1 and 2. The bond lengths in the fused benzene rings become *different*, alternating around the ring: long, short, long, short, long. Thus, bonds in the benzene rings become partially localized in these dianions. The conclusion to be drawn is that *the five-membered, metallole rings are more aromatic than the benzene rings*, and take aromaticity away from the benzene rings [10,11].



Scheme 4 Structures of dianions of silafluorene 4 and germafluorene 5, compared with the corresponding dichlorides. Bond lengths in pm.

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NICS calculations for these metallafluorene dianions, and for the corresponding—but unknown—carbon dianion, support the above conclusion. Data are shown in Scheme 5. The NICS values for the five-ring decrease from C to Si to Ge, but in all three dianions the NICS values are larger for the five-membered ring than for the benzene rings [11].



Scheme 5 NICS values for heterofluorene dianions (NICS 2.0).

Very similar bond localization in fused benzene rings was reported by Boudjouk and coworkers, for the dianions of both a 1-silaindene (6) and a 1-germaindene (7) [12,13]. A stannaindene dianion [14] and a stannafluorene dianion [15] have also been reported recently. The structures have not yet been published, but the NMR properties of these dianions suggest that they too are delocalized and aromatic.

## **DIIMINOSILYLENES AND GERMYLENES**

The chemistry of stable carbenes, silylenes, and germylenes has developed markedly since the discovery of these species in the 1990s [16–18]. The best-known examples of silylenes and germylenes are five-membered rings with two nitrogen atoms in the ring, such as **8–11**. In these molecules, there is clearly stabilization by electron donation from nitrogen into the vacant p-orbital of the divalent atom. In addition, in the unsaturated silylene and germylene **8** and **10**, additional stability may be conferred by electron delocalization in the 6  $\pi$ -electron rings (Scheme 6).

Especially for the stable silylenes, M = Si, a number of tests of aromatic delocalization have been described in recent reviews [17]. The photoelectron spectra of the prototypical silylene **8** was interpreted in terms of aromatic delocalization, but can also be rationalized without such delocalization. The Raman spectra of **8** and **10** shows enormous enhancement of the C=C stretching mode compared with tetravalent analogs, **8**-Cl<sub>2</sub> and **10**-Cl<sub>2</sub>. This is a strong indication of extensive conjugation in the silylene and germylene [19].





**Scheme 6** Structures possibly contributing to stabilization of stable carbenes and carbene analogs (M = C, Si, Ge, Sn).

Schleyer and Puhlhofer have suggested the isomerization stabilization energy (ISE) as a measure of aromatic delocalization [20]. In this approach, the total energy difference is calculated between the molecule of interest, containing a methyl group, and an isomer with an exocyclic methylene fragment. Applied to the unsaturated silylene, for example, the calculation compares the molecules shown below:



Calculated ISE values are -14.2 for the silylene, -17.2 for the germylene, and -16.6 for the corresponding carbene, in kcal mol<sup>-1</sup> [21]. These numbers do not provide a measure of the relative stabilization in these three molecules, since they ignore differences in ring strain, etc. However, they are consistent with significant delocalization and aromaticity in all three substances. For comparison, the ISE for benzene is -33.2 kcal mol<sup>-1</sup>.

Perhaps the best comparison of aromatic stabilization in these molecules is obtained from isodesmic molecular orbital (MO) calculations. One such set of calculations has been done for reactions shown in the equation below [22].



 $\Delta H$  values for this process for C, Si, and Ge are given in Table 1, along with the results from NICS 1.0 calculations. Both calculations are consistent in showing the greatest stabilization for the carbene, followed by the germylene and then the silylene. Thus, it seems that the stabilization and aromaticity of the carbenoid species alternates going down group 14: C > Ge > Si and probably Si > Sn.

for carbenoid molecules, and electronegativity for group 14 atoms.				
ţBu	Е	NICS(1)	$\Delta E_{stab}$	Х
 N	С	-10.2	30.9	2.50
E:	Si	-7.6	16.6	1.74
N 	Ge	-8.4	20.5	2.02
ťBu	Sn	-6.5		1.72

 Table 1 NICS calculations and isodesmic stabilization enthalpies

 for carbenoid molecules, and electronegativity for group 14 atoms

This alternation is unexpected, and further detailed studies will be necessary to confirm these results. However, it is interesting to note that the electronegativities of the group 14 atoms also alternate down group 14, with C > Ge > Si > Sn.

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