^{13}C NMR-Study of 1,1-Dipotassio-2,3,4,5-Tetraphenyl-1-Silacyclopentadienide Dianion [SiC$_4$Ph$_4$]$^{2-}$•2[K$^+$] and 1,1-Dipotassio-2,3,4,5-Tetraphenyl-1-Germacyclopentadienide Dianion [GeC$_4$Ph$_4$]$^{2-}$•2[K$^+$]

Jang-Hwan Hong[†]

Abstract

The chemical shifts in the ^{13}C NMR spectra of 2,3,4,5-tetraphenyl-1-silacyclopentdienide dianion [SiC$_4$Ph$_4$]$^{2-}$•2[K$^+$] (**3**) and 2,3,4,5-tetraphenyl-1-germacyclopentdienide dianion [GeC$_4$Ph$_4$]$^{2-}$•2[K$^+$] (**4**) were compared to those of [SiC$_4$Ph$_4$]$^{2-}$•2[Li$^+$] (**5**), [SiC$_4$Ph$_4$]$^{2-}$•2[Na$^+$] (**6**), and [GeC$_4$Ph$_4$]$^{2-}$•2[Li$^+$] (**7**). The average polarizations in two phenyl groups of two potassium salts are decreased over 15% to 20% comparing to those of the lithium salts and sodium salt {[EC$_4$Ph$_4$]$^{2-}$•2[M$^+$] (E=Si, Ge, M=Li, Na) due to the effect of the counter potassium cation.

Keywords: Silole, Germole, Dianion, Aromaticity, Potassium

1. Introduction

The last decades have witnessed tremendous progresses in the field of group 14 metallole dianions and the related metallole anions[1-6] since the first silole dianion had been reported[7]. In particular the syntheses and characterizations of the silole anion [1-*tert*-butyl-SiC$_4$Ph$_4$]$^{1-}$, the silole dianion [SiC$_4$Ph$_4$]$^{2-}$, the bissilole dianion [Ph$_4$C$_4$Si-SiC$_4$Ph$_4$]$^{2-}$, and the germole dianion [GeC$_4$Ph$_4$]$^{2-}$ as aromatic compounds[8-10], previously considered merely as intangible intermediates, had been the starting points for the exploring synthetic, theoretical, and materials chemistry of group 14 metalloles and their anions[11-27].

Metallole dianions [C$_4$H$_4$E]$^{2-}$ had been predicted to be highly aromatic and the diamagnetic susceptibility exaltations for the alkali-metal salts [C$_4$H$_4$E]$^{2-}$•2[M$^+$] (E=Si, Ge, Sn, Pb, M=Li, Na, K) evaluated were extraordinarily negative providing large aromatic ring current theoretically with increasing ASE (Aromatic Stabilization Energy) of the η^5-lithium salts [C$_4$H$_4$E]$^{2-}$•2[Li$^+$][16, 17].

Nowadays all of group 14 metallole dianions from silole dianion to stannoles dianion are considered highly

aromatic[5, 6] (Scheme 1).

In these points it is very interesting to find out any effect of counter-cation to the aromaticity of 2,3,4,5-tetraphenyl substituted silole dianion or germole dianion. Meanwhile there is no report for the effect of the counter-cation in group 14 metallole dianions as long as we know honestly until now. In addition the correct assignments of 10 signals in ^{13}C NMR spectra of 2,3,4,5-tetraphenyl substituted silole, germole, and their dianions have been a controversial subject with the chemical shift-aromaticity relationship theoretically and experimentally[16, 27-31].

Here we report ^{13}C NMR study of two potassium salts, [SiC$_4$Ph$_4$]$^{2-}$•2[K$^+$] (**3**) and [GeC$_4$Ph$_4$]$^{2-}$•2[K$^+$] (**4**) (Scheme 2).

2. Results and Discussion

Sonication of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**1**) or 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopentadiene (**2**) with more than four equivalents of potassium in THF-d_8 produces a dark red solution. The ^{13}C NMR study of the respective solution shows the only one species, to which the respective structure of [SiC$_4$Ph$_4$]$^{2-}$•2[K$^+$] (**3**) and [GeC$_4$Ph$_4$]$^{2-}$•2[K$^+$] (**4**) is assigned. Each ^{13}C-NMR spectrum of **3** and **4** presents ten peaks, consistent with C_2 symmetry, and the ^{29}Si spectrum of **3** shows only one resonance (Table 1).

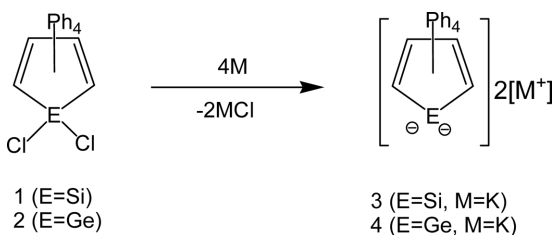Department of Nanopolymer Material Engineering, Pai Chai University, Daejon 302-735, Korea

†Corresponding author : jhong@pcu.ac.kr
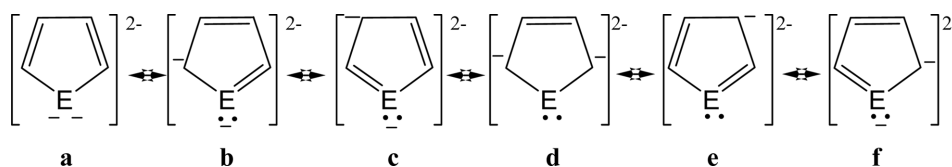
Scheme 1. Mesomeric structures of group 14 metalloles dianions.

Scheme 2. Syntheses of the dipotassium salts {[SiC$_4$Ph$_4$]$^{2-}$ •2[K]$^+$ (3) and [GeC$_4$Ph$_4$]$^{2-}$•2[K]$^+$ (4)}.

The chemical shift of C$_\alpha$ in (3) at 150.48 ppm is close to the chemical shift of C$_\alpha$ at 151.22 ppm in the lithium salt [SiC$_4$Ph$_4$]$^{2-}$•2[Li]$^+$ (5) and the chemical shift of C$_\alpha$ at 153.74 ppm in the sodium salt [SiC$_4$Ph$_4$]$^{2-}$•2[Na]$^+$ (6). However, the chemical shifts of C$_\beta$ at 136.63 ppm in [SiC$_4$Ph$_4$]$^{2-}$•2[K$^+$] (3) is quite different from the chemical shift of C$_\beta$ at 129.71 ppm in the lithium salt (5) and the chemical shift of C$_\beta$ at 130.92 ppm in the sodium salt (6).

The chemical shifts of two phenyl groups in the potassium salt (3) are similar to those in the lithium salt (5) and the sodium salt (6) except for the chemical shifts of C$_i$ at 147.41 ppm in (3), at 151.67 ppm in (5), and at 151.29 ppm in (6). The chemical shifts of two C$_i$ in the potassium salt (3) are close to each other (ΔC$_i$ = 2.17 ppm, at 147.41 ppm and 145.24 ppm), but the chemical shifts of two C$_i$ in (5) and (6) are quite separated: in the lithium salt (5) (ΔC$_i$ = 5.84 ppm, at 151.67 ppm and 146.71 ppm) and in the sodium salt (6) (ΔC$_i$ = 4.58 ppm, at 151.29 ppm and at 145.83 ppm). The average polarization of two phenyl groups in the potassium salt (3) is observed as 23.68 ppm {Sum(C$_i$ − C$_p$)/2 }, which is much smaller than 28.10 ppm in the lithium salt (5) and 29.17 ppm in the sodium salt (6) even though both polarizations in (5) and (6) are very similar to each other (Table 2).

The chemical shifts of C$_\alpha$ and C$_\beta$ in the germole dianion [GeC$_4$Ph$_4$]$^{2-}$•2[K$^+$] (4) are observed at 174.6 ppm and 141.1 ppm, those are much more deshielded than

the chemical shifts of C$_\alpha$ and C$_\beta$ at 165.57 ppm and 129.92 ppm in the lithium salt [GeC$_4$Ph$_4$]$^{2-}$•2[Li$^+$] (7) (ΔC$_\alpha$ = 9.03 ppm and ΔC$_\beta$ = 11.18 ppm). The average polarization of two phenyl groups in the potassium salt (4) is observed as 24.7 ppm {Sum(C$_i$ − C$_p$)/2 }, which is about 4 ppm smaller than 28.64 ppm in the lithium salt (7). Incidentally the polarization of 24.7 ppm in the potassium salt (4) is almost the same as that of 23.68 ppm in the potassium salt [SiC$_4$Ph$_4$]$^{2-}$•2[K$^+$] (3) (Δ = 1.0 ppm) even if silicon atom is of the 4th periodic element and germanium atom is of the 3rd periodic element. Furthermore the chemical shifts of two *para*-carbon atoms in both potassium salts are very similar to each other {at 121.6 ppm and 123.7 ppm in (4) and 121.54 ppm and 123.76 ppm in (3)} (Table 1).

The effect of the substituent on silicon atom and germanium atom on the phenyl groups was reported as inductive effect rather than mesomeric effect being transferred through covalent bonds to result in the direct through-space polarization of multiple bonds (field effect), the increasing of the substituent's inductive effect decreases with the decreasing in the shielding of *ipso*-carbon in the phenyl group[28,31]. It was reported that the commonly accepted charge transfer-chemical shift relationship is strongly influenced by not only the substituents but the counter cation while THF complexation of the Li counter cation has a small influence on the NMR shift of silolide anions theoretically[32]. However, the polarizations of the phenyl groups in metallole dianions [EC$_4$Ph$_4$]$^{2-}$•2[M$^+$] (E=Si, Ge, M=Li, Na, K) are considered to be related with the effect of different central metal and different counter cation since there is no substituent on the central metals to induce an inductive effect.

The average polarizations of two phenyl groups are observed as less than 10 ppm for the neutral metalloles of [Cl$_2$SiC$_4$Ph$_4$] (1) (8.79 ppm), [Cl$_2$GeC$_4$Ph$_4$] (2) (8.05 ppm), and other group 14 metalloles, they are observed as more than 40 ppm for 3-silolenes with 2,5-carbodianions of {[Ph$_4$C$_4$SiMe$_2$]$^{-2}$•2[Li$^+$], [Ph$_4$C$_4$SiMeH]$^{-2}$

•2[Li$^+$], [Ph$_4$C$_4$Si(n-Bu)$_2$]$^{-2}$•2[Li$^+$], and [Ph$_4$C$_4$Si(t-Bu)$_2$]$^{-2}$ •2[Li$^+$][33-35]. The polarization in each potassium salts (**3**) and (**4**) is observed as 23.68 ppm and 24.7 ppm respectively. Those polarizations are smaller than 28.10 ppm in (**5**), 29.17 ppm in (**6**), and 28.64 ppm in (**7**), they are rather close to the polarizations of 21.9 ppm and 22.3 ppm in [2,2'-(Me$_3$Si)$_2$-3,3'-Ph$_2$C$_4$Si]$^{-2}$•2[M$^+$] (M=Na, K)[36] (Table 2). The system of the analogue had been calculated as higher aromatic system due to the substituents of two trimethylsily groups on alpha-carbons while the naked counter lithium cation was investigated to have a strong interaction with five-atoms of the dianion ring showing a small covalent character and the lithium cation in THF solvent had weaker interaction with the dianion ring due to the stronger coordination by THF[32]. However, the potassium cation had been anticipated to have only electrostatic interaction with the dianion rings in even THF solvent since the potassium cation and ammonium ion have the same cation-π interaction energies due to the similar ionic radii with the same hydration energies[37]. The trend for binding energies in gas phase is Li$^+$>Na$^+$>K$^+$>Rb$^+$: as the ion gets larger the charge is dispersed over a larger sphere, binding interaction of a classical electrostatic effect is weaken[37]. However the sequence is reversed in aqueous solution due to the strong binding of lithium with water. In this point lithium cation is most strongly solvated by THF, but the naked potassium cation in THF induces the cation π-interaction with the dianion ring, which makes a small cancelation of the negative charge in the dianion ring. In soilid state the inversed sandwich crystal structures of the potassium salts are known for [EC$_4$Me$_4$]$^{2-}$•2[K$^+$] (E=Si, Ge)[12,15]. It seems to be the reason why the polarizations in two potassium salts of (**3**) and (**4**) are much smaller than those in the lithium and sodium salts of (**5**), (**6**), and (**7**). The reduced polarizations are also seemed to be related to the deshielded chemical shifts of the *para*-carbon atoms in two potassium salts of (**3**) and (**4**), the chemical shifts in which are almost the same as each other {121.54 ppm and 123.76 ppm in (**3**), 121.6 ppm and 123.7 ppm in (**4**)}. These chemical shifts are more deshielded than the chemical shifts of the *para*-carbon atoms in the lithium salts and the sodium salt {119.48 and 121.83 ppm for [SiC$_4$Ph$_4$]$^{2-}$•2[Li$^+$] (**5**), 118.25 and 121.42 ppm for [SiC$_4$Ph$_4$]$^{2-}$•2[Na$^+$] (**6**), and 119.29 and 121.91 ppm for [GeC$_4$Ph$_4$]$^{2-}$•2[Li$^+$] (**7**)}. These polarizations in the metallole dianions [EC$_4$Me$_4$]$^{2-}$•2[M$^+$] are coincided with the information from the study of mono substituted benzene derivatives, the calculated charges for the σ- and π-populations of *para*-carbon atom are correlated well with its chemical shift[38].

In the potassium salt [GeC$_4$Ph$_4$]$^{2-}$•2[K$^+$] (**4**) the most characteristic thing is the most deshielded chemical shifts of C$_\alpha$ at 174.6 ppm comparing to the chemical shifts of C$_\alpha$ at 150.48 ppm in (**3**), at 151.22 ppm in (**5**), at 153.74 ppm in (**6**), and 165.57 ppm in (**4**). The

Table 1. ^{13}C-NMR chemical shifts of silole, germole, and their dianions

	[Cl$_2$SiC$_4$Ph$_4$] (**1**)[a]	[Cl$_2$GeC$_4$Ph$_4$] (**2**)[a]	[Ph$_4$C$_4$Si]$^{-2}$•2[K$^+$] (**3**)[a]	[Ph$_4$C$_4$Ge]$^{-2}$•2[K$^+$] (**4**)[a]
C$_\alpha$, C$_\beta$	132.28, 154.74	132.76, 149.99	150.48, 136.63	174.6, 141.1
	Ph	Ph	Ph	Ph
C$_i$	135.37, 136.67	134.69, 136.59	147.41, 145.24	149.1, 145.5
C$_o$	129.27, 129.48	129.59, 129.51	132.96, 130.10	129.9, 132.9
C$_m$	128.24, 127.84	128.37, 128.08	127.65, 127.14	127.5, 127.2
C$_p$	127.10, 127.37	127.71, 127.47	121.54, 123.76	121.6, 123.7
(C$_i$ − C$_p$)	8.27, 9.30	6.98, 9.12	25.87, 21.48	27.6, 21.8
Sum(C$_i$ − C$_p$)/2	8.79	8.05	23.68	24.7
[29]Si-Ring	6.90	-	-9.49	-
Solvent	CDCl$_3$	CDCl$_3$	THF-d_8	THF-d_8
Reference	9	10	This work	This work

[a] The assignment of ^{13}C NMR signals are based on the suggestion of the published reports theoretically and experimentally[16,31-34].

Table 2. $^{13}C/^{29}Si$-NMR chemical shifts of silole dianions and germole dianions

	$[Ph_4C_4Si]^{-2} \cdot 2[Li^+]$ (5) [a]	$[Ph_4C_4Si]^{-2} \cdot 2[Na^+]$ (6) [a]	$[Ph_4C_4Ge]^{-2} \cdot 2[Li^+]$ (7) [a]	$[2,2'\text{-}(Me_3Si)_2\text{-}3,3'\text{-}Ph_2C_4Si]^{-2} \cdot 2[Na^+]$	$[2,2'\text{-}(Me_3Si)_2\text{-}3,3'\text{-}Ph_2C_4Si]^{-2} \cdot 2[K^+]$
C_α, C_β	151.22, 129.71	153.74, 130.92	165.57, 129.92	140.2 , 149.2	141.3, 149.7
Substituent	Ph	Ph	Ph	β-Ph	β-Ph
C_i	151.67, 145.83	151.29, 146.71	152.17, 146.30	143.1	145.0
C_o	129.97, 133.43	129.48, 133.16	129.92, 133.49	131.0	132.0
C_m	126.38, 126.38	126.72, 126.55	126.38, 126.38	125.4	126.7
C_p	119.48, 121.83	118.25, 121.42	119.29, 121.91	121.2	122.7
$(C_i - C_p)$	32.19, 24.00	33.04, 25.29	32.88, 24.39	21.9	22.3
$Sum(C_i - C_p)/2$	28.10	29.17	28.64	-	-
^{29}Si-Ring	68.54	92.79	-	44.9	49.3
Solvent	THF-d_8	THF-d_8	THF-d_8	C_6D_6/THF	C_6D_6/THF
Reference	9	7	10	36	36

[a] The assignment of ^{13}C NMR signals are based on the suggestion of the published reports theoretically and experimentally[16,28-31].

chemical shift of C_α at 174.6 ppm in (4) is comparable to the chemical shift of C_α at 187.68 ppm in the stannole dianion $[SnC_4Ph_4]^{2-} \cdot 2[Li^+]$, the strong high-frequency resonance of which has been explained by the paramagnetic contribution of a tin-carbon bond[44]. The chemical shift of the ^{29}Si NMR in $[SiC_4Ph_4]^{2-} \cdot 2[K^+]$ (3) is observed at -9.49 ppm, the shielding of which is extraordinary from the chemical shifts at 68.54 ppm in (5), at 92.79 ppm in (6), and those in the other group 14 metalloles dianions[1-6]. The effect of planarization at the ring silicon atom and aromaticity of the silolide anion had been calculated less than 30 ppm in downfield ^{29}Si NMR shift while the direct effect of the substituent was calculated in changes of the chemical shifts being between +100 and -100 ppm for the different substituents[32]. The aromaticity had been further weakened in $[Si_4(SiH_3)_4]^{2-} \cdot 2Na^+$ and $[Si_4(SiH_3)_4]^{2-} \cdot 2K^+$ by replacing lithium with the sodium and potassium cations[40,41]. From these results it is suggested that non-covalent attractive force between potassium cation and pi-electrons of $[SiC_4Ph_4]^{2-} \cdot 2[K]^+$ (3) and $[GeC_4Ph_4]^{2-} \cdot 2[K]^+$ (4) affects the chemical shifts changes in ^{13}C NMR and ^{29}Si NMR spectra.

3. Experimental

All reactions were performed under an inert nitrogen atmosphere using standard Schlenk techniques. Air sen-sitive reagents were transferred in a nitrogen-filled glovebox. THF and ether were distilled from sodium benzophenone ketyl under nitrogen. Hexane and pen-tane were stirred over concentrated H_2SO_4 and distilled from CaH_2. NMR spectra were recorded on JEOL GSX270 and GSX400 spectrometers.

$[SiC_4Ph_4]^{2-} \cdot 2[K^+]$ (3) and $[GeC_4Ph_4]^{2-} \cdot 2[K^+]$ (4); The respective $[Cl_2SiC_4Ph_4]$ (1) (0.11 g, 0.23 mmol) and $[Cl_2GeC_4Ph_4]$ (2) (0.10 g, 0.20 mmol) was transferred into 5 mm NMR tube, they were sonicated with an excess of potassium in THF-d_8 for 2 h to give a red-purple solution. Then ^{13}C- and ^{29}Si-NMR spectroscopic study was performed. Then the respective reaction of 3 and 4 with an excess of methyl iodide and trimethylsilyl chloride gave a yellow solution in a minute, the formations of 1,1-dimethyl and 1,1-bi(trimethylsilyl) substituted silole and germole were confirmed by the characteristic signals in ^1H and ^{13}C NMR spectra of them[9,10].

4. Conclusions

In the potassium salts of $[SiC_4Ph_4]^{2-} \cdot 2[K^+]$ (3) and $[GeC_4Ph_4]^{2-} \cdot 2[K^+]$ (4) there is no substituent on silicon atom and germanium atom, the ^{13}C NMR study of them shows that they are aromatic system. There is no solvation effect between potassium cation and THF, non-covalent

attractive force between potassium cation and pi-electrons of $[SiC_4Ph_4]^{2-} \cdot 2[K]^+$ (**3**) and $[GeC_4Ph_4]^{2-} \cdot 2[K]^+$ (**4**) affects the chemical shifts changes in ^{13}C NMR and ^{29}Si NMR spectra of them.

Acknowledgments

References

[1] V. Y. Lee, A. Sekiguchi, M. Ichinohe, and N. Fukaya, "Stable aromatic compounds containing heavier group 14 elements", J. Organomet. Chem., Vol. 611, pp. 228-235, 2000.

[2] M. Hissler, P. W. Dyer, and R. Reau, "Linear organic π-conjugated systems featuring the heavy group 14 and 15 elements", Coord. Chem. Rev., Vol. 244, pp. 1-44, 2003.

[3] H. Grützmacher, "Five-membered aromatic and antianromatic rings with gallium, germanium, and bismuth centers: A short march through the periodic table", Angew. Chem. Int. Ed. Engl., Vo. 34, pp. 295-298, 2005.

[4] V. Y. Lee and A. Sekiguchi, "Aromaticity of group 14 organometallics: Experimental aspects", Angew. Chem. Int. Ed. Engl., Vol. 46, pp. 6596–6620, 2007.

[5] M. Saito and M. Yoshioka, "The anions and dianions of group 14 metalloles", Coord. Chem. Rev., Vol. 249, pp. 765-780, 2005.

[6] M. Saito, "Challenge to expand the concept of aromaticity to tin- and lead-containing carbocyclic compounds: Synthesis, structures and reactions of dilithiostannoles and dilithioplumbole", Coord. Chem. Rev., Vol. 256, pp. 627-636, 2012.

[7] W.-C. Joo, J.-H. Hong, S.-B. Choi, H.-E. Son, and C. H. Kim, "Synthesis and reactivity of 1,1,-disodio-2,3,4,5- tetraphenyl-1-silacyclopentadiene", J. Organomet. Chem., Vol. 391, pp. 27-36, 1990.

[8] J.-H. Hong and P. Boudjouk, "A stable aromatic species containing silicon. Synthesis and characterization of 1-t-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide anion", J. Am. Chem. Soc., Vol. 115, 5883-5884, 1993.

[9] J.-H. Hong, P. Boudjouk, and S. Castellino, "Synthesis and characterization of two aromatic silicon-containing dianions: The 2,3,4,5-tetraphenylsilole dianion and the 1,1'-disila-2,2',3,3',4,4', 5,5'- octaphenylfulvalene dianion", Organometallics, Vol. 13, pp. 3387-3389, 1994.

[10] J.-H. Hong and P. Boudjouk, "Synthesis and characterization of a delocalized germanium-containing dianion: dilithio-2,3,4,5-tetraphenyl-germole", Bull. Soc. Chim. Fr., Vol. 132, pp. 495-498, 1995.

[11] R. West, H. Sohn, U. Bankwitz, J. Calabrese, T. Apeloig, and T. Mueller, "Dilithium derivative of tetraphenylsilole: An η1-η5 dilithium", J. Am. Chem. Soc., Vol. 117, pp. 11608-11609, 1995.

[12] W. P. Freeman, T. D. Tilley, G. P. A. Yap, and A. L. Rheingold, "Siloyl anions and silole dianions: Structure of [K([18]crown-6)+]2[C4Me4Si2-]", Angew. Chem. Int. Ed. Engl., Vol. 35, pp. 882-884, 1996.

[13] R. West, H. Sohn, D. R. Powell, T. Müller, and Y. Apeloig, "Dianion of tetraphenylgermole is aromatic", Angew. Chem., Int. Ed. Engl, Vol. 35, pp. 1002-1004, 1996.

[14] S.-B. Choi, P. Boudjouk, and J.-H. Hong, "Unique Bis-$η^5/η^1$ bonding in a dianionic germole. Synthesis and structural characterization of the dilithium salt of the 2,3,4,5-tetramethyl germole dianion", Organometallics, Vol. 18, pp. 2919-2921, 1999.

[15] W. P. Freeeman, T. D. Tilley, L. M. Liable-Sands, and A. L. Rheingold, "Synthesis and study of cyclic π-Systems containing silicon and germanium. The question of aromaticity in cyclopentadienyl analogues", J. Am. Chem. Soc., Vol. 118, pp. 10457-10468, 1996.

[16] B. Goldfuss, P. V. R. Schleyer, and F. Hampel, "Aromaticity in silole dianions: Structural, energetic, and magnetic aspects", Organometallics, Vol. 15, pp. 1755-1757, 1996.

[17] B. Goldfuss and P. V. R. Schleyer, "Aromaticity in group 14 metalloles: Structural, energetic, and magnetic criteria", Organometallics, Vol. 16, pp. 1543-1552, 1997.

[18] L. Aubouy, N. Huby, L. Hirsch, A. V. D. Lee, and P. Gerbier, Molecular engineering to improve the charge carrier balance in single-layer silole-based OLEDs, New J. Chem., Vol. 33, pp. 1290-1300, 2009.

[19] U. Bankwitz, H. Sohn, D. R. Powell, and R. West, "Synthesis, solid-state structure, and reduction of 1,1-dichloro-2,3,4,5-tetramethylsilole", J. Organomet. Chem., Vol. 499, pp. C7-C9, 1995.

[20] J.-H. Hong, Y. Pan, and P. Boudjouk, "A novel lithocenophane derivative of a trisgermole dianion: [Li(thf)(tmeda)][2,3,4,5-Et$_4$-Ge,Ge-{Li(2,3,4,5-Et$_4$C$_4$Ge)$_2$}

C4Ge]", Angew. Chem. Int. Ed. Engl., Vol. 35, pp. 186-188, 1996.

[21] H. Sohn, D. R. Powel, R. West, J.-H. Hong, and W.-C. Joo, "Dimerization of the Silole Anion [C4Ph4-SiMe]⁻ to a Tricyclic Diallylic Dianion", Organometallics, Vol. 16, pp. 2770-2772, 1997.

[22] Y. Pan Y, J.-H. Hong, S.-B. Choi, and P. Boudjouk, Surprising reaction of non-nucleophilic bases with 1-hydrosiloles: Addition and not deprotonation, Organometallics, Vol. 16, pp. 1445-1451, 1997.

[23] J.-H. Hong and P. Boudjouk, Synthesis and characterization of a novel pentavalent silane: 1-Methyl-1,1-dihydrido-2,3,4,5-tetraphenyl-1-silacyclopentadiene silicate, [Ph4C4SiMeH2-]·[K +], Organometallics, Vol. 14, pp. 574-576, 1995.

[24] J.-H. Hong, "Synthesis and NMR-study of the 2,3,4,5-tetraethylsilole dianion [SiC4Et4]²⁻•2[Li]⁺", Molecules, Vol. 16, pp. 8033–8040, 2011.

[25] J.-H. Hong, Dissociation of the disilatricyclic diallylic dianion [(C4Ph4SiMe)2]⁻² to the silole anion [MeSiC4Ph4]⁻ by halide ion coordination or halide ion nucleophilic substitution at the silicon atom, Molecules, Vol. 16, pp. 8451-8462, 2011.

[26] X. Zhan, C. Risko, F. Amy, C. Chan, W. Zhao, S. Barlow, A. Kahn, J.-L. Bredas, and S. R. Marder, Electron affinities of 1, 1-diaryl-2, 3, 4, 5-tetraphenylsiloles: direct measurements and comparison with experimental and theoretical estimates, J. Am. Chem. Soc., Vol. 127, pp. 9021-9029, 2005.

[27] S. N. Tandura, S. P. Kolesnikov, K. S. Nosov, V. Y. Lee, M. P. Egorov, and O. M. Nefedov, Electron density distributions in substituted 2, 3, 4, 5-tetraphenyl-1-germacyclopenta-2, 4-dienes studied by NMR spectroscopy, Russian Chemical Bulletin, Vol. 46, pp. 1859-1861, 1997.

[28] S. N. Tandura, S. P. Kolesnikov, M. P. Egorov, K. S. Nosov, and O. M. Nefedov, Correlation NMR spectroscopy of 1,1-dichloro-2,3,4,5-tetraphenyl-1-germacyclopenta-2,4-diene, Russian Chemical Bulletin, Vol. 46, pp. 602-604, 1997.

[29] S. N. Tandura, S. P. Kolesnikov, K. S. Nosov, M. P. Egorov, and O. M. Nefedov, Charge localization in the dianion of tetraphenylgermole according to ¹³C NMR data", Main Group Metal Chemistry, Vol. 22, pp. 9-14, 1999.

[30] S. N. Tandura, N. A. Troitskii, S. P. Kolesnikov, K. S. Nosov, and M. P. Egorov, ¹³C NMR study of 2,3,4,5-tetraphenylsilole dilithium salt, Russian Chemical Bulletin, Vol. 48, pp. 214-217, 1999.

[31] N. A. Troitski, S. N. Tandura, S. P. Kolesnikov, S.-.B. Choi, and P. Boudjouk, NMR study of 1-hydro-2,3,4,5-tetraphenylsilole derivatives, Main Group Metal Chemistry, Vol. 24, pp. 1-4, 2001.

[32] C. Fekete, H. Kovács, L. Könczöl, Z. Benk, and L. Nylászi, "Substituent effect on the aromaticity of the silolide anion, Struct. Chem., Vol. 25, pp. 377-387, 2014.

[33] D. H. O'Brien and D. L. Breeden, "Tetraanion of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene", J. Am. Chem. Soc., Vol. 103, pp. 3237-3239, 1981.

[34] T. Wakahara and W. Ando, "Reaction of hydrosilanes with lithium. formation of silole anions from 1-methylsilole via carbodianion", Chem. Lett., Vol. 26, pp. 1179-1180, 1997.

[35] J.-H. Hong, Synthesis and NMR-study of 1-trimethylsilyl substituted silole anion [Ph4C4Si(SiMe3)]⁻•[Li]⁺ and 3-silolenide 2,5-carbodianions {[Ph4C4Si(n-Bu)2]⁻²•2[Li]⁺, [Ph4C4Si(t-Bu)2]⁻²•2[Li]⁺} via silole dianion [Ph4C4Si]⁻²•2[Li]⁺, Molecules, Vol. 18, pp. 10568-10579, 2013.

[36] C. Fekete, L. Nyulászi, and I. Kovács, "Synthesis and NMR characterization of 2,5-bis(Trimethylsilyl)-3,4-diphenyl-1-silacyclopentadienyl dianion", Phosphorus, Sulfur Silicon Relat. Elem., Vol. 189, pp. 1076-1083, 2014.

[37] D. A. Dougherty, "The Cation-π Interaction", Acc. Chem. Res., Vol. 46, pp. 885–893, 2013.

[38] W. J. Hehre, R. W. Taft, and R. D. Topsom, "Ab initio calculations of charge distributions in monosubstituted benzenes and in meta-and para-substituted fluorobenzenes. comparison with ¹H, ¹³C, and ¹⁹F NMR substituent shifts", Progress in Physical Organic Chemistry, Vol. 12, pp. 159-187, 1976.

[39] M. Saito, R. Haga, M. Yoshioka, K. Ishimura, and S. Nagase, "The aromaticity of the stannole dianion", Angew. Chem. Int. Ed. Engl., Vol. 44, pp. 6553-6556, 2005.

[40] S. Kim, S. Wang, and H. F. Schaefer III, Structures, energetics, and aromaticities of the tetrasilacyclobutadiene dianion and related compounds: (Si4H4)²⁻, (Si4H4)²⁻·2Li⁺, [Si4(SiH3)4]²⁻·2Li⁺, [Si4(SiH3)4]²⁻·2Na⁺, and [Si4(SiH3)4]²⁻·2K⁺, J. Phys. Chem. A, Vol. 115, pp. 5478-5487, 2011.

[41] V. Y. Lee, R. Takanashi, R. Kato, T. Matsuno, M. Ichinohe, and A. Sekiguchi, "Heavy analogues of the 6p-electron anionic ring systems: Cyclopentadienide ion and cyclobutadiene dianion", J. Organomet. Chem., Vol. 692, pp. 2800-2810, 2007.