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# A phenyl-substituted germole dianion and its reaction with hafnocene dichloride

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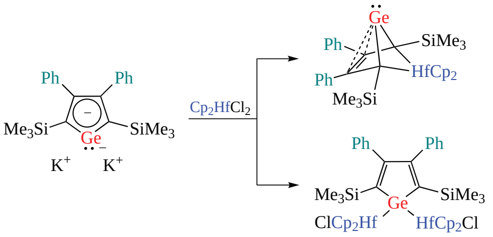
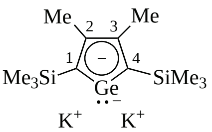
**The reaction of phenyl-substituted dipotassium germacyclopentadienediide with one equivalent of hafnocene dichloride at low temperature provides a bicyclic germylene. With two equivalents of hafnocene dichloride, a dinuclear hafnium complex with a μ-coordinating germolyl dianion ligand is formed.**



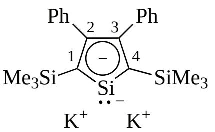
*Keywords*: germanium, germoles, organogermanium compounds, hafnium complexes, anions, aromaticity.

The interest in heterocyclopentadienes of group 14 elements (tetroles) is driven by their favourable photophysical properties such as small HOMO/LUMO gaps, high electron affinity and the occurrence of the aggregation induced emission (AIE) effect.[1] In the past, the question of aromaticity and their use as ligands in organometallic chemistry fueled investigations on the synthesis of tetrole mono- and dianions and their properties.[2] Recently, Saito's and our group demonstrated that alkali metal salts of silyl-substituted tetrole dianions are suitable precursors for a series of low coordinated compounds of group 14 elements.[2(*d*),3] For example, the reaction of dipotassium cyclopentadienediides **1** and **2** with hafnocene dichloride provides access to bicyclic germylenes **3** and silylenes **4** that are stabilized by homoconjugation with the remote $C^2{=}C^3$ double bond.[4] Tetrylenes **3** and **4** are examples of a new class of heavy carbenes based on the bicyclo[2.1.1]hexene framework, the so-called BCH tetrylenes.[3(*b*),5] In particular, the follow-up chemistry of BCH germylene **3** proved to be very intriguing, calling for variations in the substitution pattern of the germole ring.[6] We report here the results of our investigations on the synthesis of dipotassium germacyclopentadienediide **6** and its surprisingly different reactivity *versus* hafnocene dichloride when compared with compound **1**.

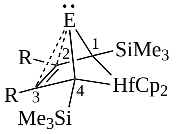
The synthesis of the precursor germole dibromide **5** was achieved following the Fagan–Nugent route *via* a zirconacyclopentadiene (Scheme 1).[7] We note here that the zirconium/germanium exchange reaction proceeds in sufficiently high yields (65%) only when we used $GeBr_4$ as the electrophile. The use of $GeCl_4$ in hexanes is not recommended as the isolated yield of the corresponding dichloride drops to 6%. In general, it is noteworthy that the germole ring could not be formed *via* a reductive cyclization of the corresponding geminal dialkinylarylgermane, which is a very efficient procedure for the synthesis of the corresponding 2,3-diaryl-substituted siloles (the Tamao–Yamaguchi route).[1(*f*),8] Germole **5** was fully characterized by NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction[†] (see also Online Supplementary Materials). Reduction of germole dibromide **5** with excess of potassium



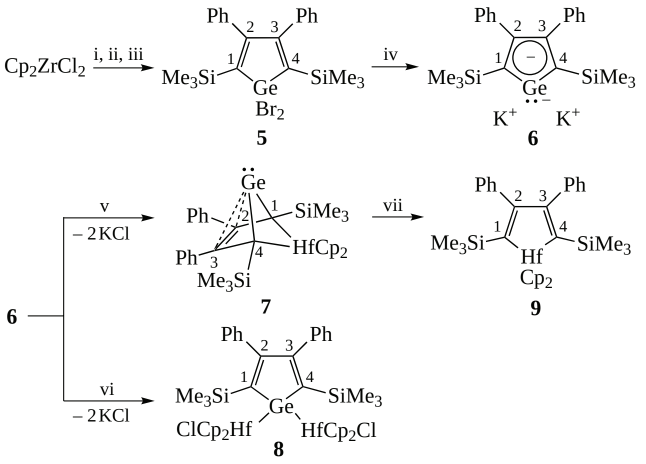
**1**



**2**



**3** E = Ge, R = Me
**4** E = Si, R = Ph



**Scheme 1** *Reagents and conditions*: i, BuLi (2 equiv.), *n*-hexane, –90 °C, 1 h; ii, PhC≡$CSiMe_3$ (2 equiv.), *n*-hexane, –90 → 20 °C, 12 h; iii, $GeBr_4$ (1 equiv.), *n*-hexane, –40 → 20 °C, 12 h; iv, K metal (10 equiv.), THF, 20 °C, 18 h; v, $Cp_2HfCl_2$ (1 equiv.), THF, –80 → 20 °C, 16 h; vi, $Cp_2HfCl_2$ (2 equiv.), THF, 0 °C, 2 h; vii, $O_2$.

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[†] Colorless crystals of germole **5** were grown from hexanes at –30 °C.

*Crystal data for* **5**. $C_{22}H_{28}Br_2GeSi_2$, $M = 581.03$, monoclinic, space group $C2/c$, 100 K, $a = 20.4104(7)$, $b = 10.4473(3)$ and $c = 11.4731(4)$ Å, $\beta = 97.5853(16)°$, $V = 2425.04(14)$ Å$^3$, $Z = 4$, $d_{calc} = 1.591$ g cm$^{-3}$, $F(000) = 1160$. A crystal with dimensions $0.350\times0.350\times0.250$ mm$^3$ was selected, and intensities of 95517 reflections were measured using a Bruker Apex II CCD diffractometer, $\lambda[\mathrm{MoK}\alpha] = 0.71073$ Å, $2.013° \leqslant \theta \leqslant 40.249°$. Independent reflections 7624 ($R_{int} = 0.0254$). Final $R$ indices $[I > 2\sigma(I)]$, $R_1 = 0.0177$, $wR_2 = 0.0421$, $R$ indices (all data), $R_1 = 0.0247$, $wR_2 = 0.0439$, GOF = 1.057.

metal in THF at ambient temperature yields the potassium salt of germole dianion **6** in almost quantitative yield. This species **6** was characterized by NMR spectroscopy and by XRD analysis of a suitable single crystal. The $^{13}$C NMR resonances of the C(1)/C(4) and C(2)/C(3) carbon atoms of the heterole ring were assigned by 2D $^{1}$H/$^{13}$C NMR spectroscopy and they were significantly different from those of the starting dibromo germole **5** (Table 1), which mirrors the specific electronic situation in the dianion of salt **6**. Greenish yellow crystals of the THF solvate of dipotassium germacyclopentadienediide **6**·2THF were obtained from a THF solution at ambient temperature. The XRD analysis reveals a crystal structure[†] which is very similar to that of the corresponding silicon compound **2**·2THF.[4(c)] In the solid state, the germole rings form a one-dimensional polymeric zigzag chain (Figure 1). They are linked by potassium ions that are coordinated in a η$^5$-fashion to one germole ring and *via* the germanium atom of the next ring in a η$^1$-manner. Coordination to one THF molecule completes the coordination sphere of the potassium ions. In the polymeric chain, each germole ring adopts a bis-η$^5$, bis-η$^1$-coordination mode. All germanium/potassium distances are very similar (341.5–343.7 pm), and their magnitudes indicate a mostly ionic interaction between isolated potassium cations and germole dianions. The germole ring in species **6** is planar (sum of the inner cyclic bond angles: 540°).

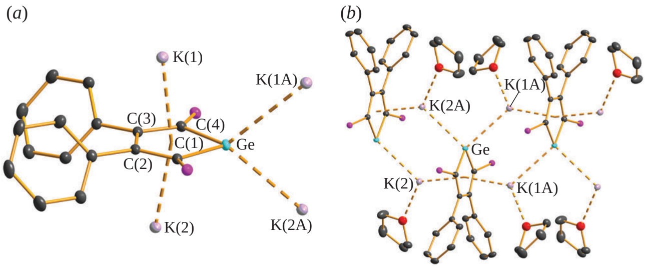

**Figure 1** (*a*) Molecular structure of polymeric **6**·2THF in the crystal. (*b*) Repeating units of **6**·2THF in the crystal. Selected bond lengths (pm) and angles (°): C(1)−C(2) 143.39(20), C(2)−C(3) 143.14(24), C(3)−C(4) 142.73(17), Ge−C(1) 194.61(14), Ge−C(4) 194.69(16), Ge−K(1) 341.47(4), Ge−K(2) 343.70.9(4), Ge−K(1A) 343.11(5), Ge−K(2A) 341.56(4), K(1)−germole centroid 279.62(4), K(2)−germole centroid 280.23(4), Σα (germole ring) 540.0 (thermal ellipsoids at 50% probability, all hydrogen atoms and methyl groups of Me$_3$Si are omitted for clarity).

**Table 1** Pertinent $^{13}$C NMR and structural parameters of germole and silole derivatives.

| Compound | $\delta_C$/ppm | Distance/pm | | |
|---|---|---|---|---|
| | C(1)/C(4) and C(2)/C(3) | C(1)–C(2) and C(3)–C(4) | C(2)–C(3) | Ge–C(1) and Ge–C(4) |
| **5** | 138.6<br>162.8 | 135.4<br>135.4 | 152.7 | 193.8 |
| **6** | 163.0<br>141.2 | 143.4<br>142.7 | 143.1 | 194.6<br>194.7 |
| **8** | 173.1<br>166.6 | 136.4<br>136.4 | 148.1 | 200.5 |
| **3**[a] | 156.2<br>130.8 | 141.5<br>142.0 | 139.5 | 194.9<br>194.2 |
| **4**[a] | 145.8<br>140.5 | 143.8<br>143.8 | 142.3 | 186.0<br>186.1 |

[a] From ref. 4(*c*).

The short λ$^2$-Ge−C(1)/C(4) bonds (194.61 and 194.69 pm *vs.* 201–208 pm reported for stable germylenes)[9] and the nearly equidistant innercyclic C−C bonds (142.7−143.4 pm) indicate the delocalization of the 6π-electrons of the germole dianion (Figure 1). These molecular structural parameters of the germole dianion of salt **6** are very similar to those previously reported for other tetrole dianions including those of the potassium salts **1** and **2** and suggest a comparable bonding situation including cyclic conjugation of the π-electron system.[4(c)]

The reactivity of potassium germacyclopentadienediide **6** *versus* hafnocene dichloride was tested to allow a comparison with the previously studied analogue **1**. The reaction of **1** with hafnocene dichloride in THF at –80 °C provides access to the BCH germylene **3** in high yields.[4(a)] The same reaction with **6** under similar conditions gives the phenyl-substituted BCH germylene **7** in 72% yield (Scheme 1). Germylene **7** is highly reactive against oxygen and it forms on contact with air quantitatively hafnacyclopentadiene **9**.[4(a)] Both compounds, **7** and **9**, were characterized by NMR spectroscopy (Online Supplementary Materials).[4(a),6(a)] We noted for the reaction of potassium germacyclopentadienediide **6** with hafnocene dichloride at higher reaction temperatures the increasing formation of the disubstitution product **8**. Optimization of the reaction conditions and adjustment of the stoichiometry allowed the selective formation and isolation of the bis-hafnocene chloride-substituted germole **8** (Scheme 1). A similar disubstitution product has been reported previously by the group of Saito for a related stannole dianion.[10] $^{1}$H and $^{13}$C NMR spectroscopy showed two broad singlets for the cyclopentadienyl hydrogen and carbon atoms, which indicates hindered rotation around the Ge–Hf single bond due to the steric bulk of the two HfCp$_2$Cl groups. The $^{13}$C NMR chemical shifts of the germole ring carbon atoms differ significantly from those of the germole dibromide **5** and from the germole dianion of salt **6** (Table 1, Figure 2). Noteworthy is the large low field shift of the resonance of C(1)/C(4) by almost $\Delta\delta^{13}$C = 35 compared to dibromide **5**.

Red crystals of germole **8** suitable for XRD analysis were grown from pentane/THF solution at –30 °C.[†] The molecular structure of germole **8** in the crystal is of $C_2$ symmetry (Figure 2), and the C–C bond lengths in the germole ring are similar to those of dibromide **5** revealing its 1,3-diene character with localized single and double bonds (Table 1). The Ge–C(1)/(4) distance of 200 pm is significantly longer compared to the dibromide **5** and the germole dianion of salt **6** and longer than the sum of the covalent radii (196 pm).[11] The large Ge–Hf atomic distance in germole **8** (286 pm) is noteworthy as it exceeds the sum of the covalent radii of both atoms (273 pm) and also the Ge–Hf single

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[†] Yellow crystals of potassium germacyclopentadienediide **6** were grown from THF at 20 °C.

*Crystal data for* **6**. $C_{30}H_{44}GeK_2O_2Si_2$, $M = 643.62$, triclinic, space group $P\bar{1}$, 100 K, $a = 10.4092(8)$, $b = 11.8887(10)$ and $c = 15.1092(13)$ Å, $\alpha = 69.1808(19)°$, $\beta = 70.9322(18)°$, $\gamma = 79.8943(19)°$, $V = 1648.1(2)$ Å$^3$, $Z = 2$, $d_{calc} = 1.297$ g cm$^{-3}$, $F(000) = 676$. A crystal with dimensions $0.400 \times 0.080 \times 0.050$ mm$^3$ was selected, and intensities of 82581 reflections were measured using a Bruker Apex II CCD diffractometer, $\lambda$[MoKα] = 0.71073 Å, $1.505° \leqslant \theta \leqslant 33.728°$. Independent reflections 13191 ($R_{int} = 0.0697$). Final $R$ indices [$I > 2\sigma(I)$], $R_1 = 0.0355$, $wR_2 = 0.00697$, $R$ indices (all data), $R_1 = 0.0632$, $wR_2 = 0.0781$, GOF = 1.020.

Red crystals of complex **8** were grown from pentane/THF (4 : 1) at –30 °C.

*Crystal data for* **8**. $C_{42}H_{48}Cl_2GeHf_2Si_2$, $M = 1109.45$, trigonal, space group $P3_221$, 100 K, $a = 11.7949(2)$, $b = 11.7949$ and $c = 25.3318(7)$ Å, $V = 3052.03(14)$ Å$^3$, $Z = 3$, $d_{calc} = 1.811$ g cm$^{-3}$, $F(000) = 1614$. A crystal with dimensions $0.250 \times 0.200 \times 0.150$ mm$^3$ was selected, and intensities of 101559 reflections were measured using a Bruker Apex II CCD diffractometer, $\lambda$[MoKα] = 0.71073 Å, $1.994° \leqslant \theta \leqslant 30.033°$. Independent reflections 5679 ($R_{int} = 0.0631$). Final $R$ indices [$I > 2\sigma(I)$], $R_1 = 0.0269$, $wR_2 = 0.0583$, $R$ indices (all data), $R_1 = 0.0305$, $wR_2 = 0.0596$, GOF = 1.123.

The structures were solved by direct methods and refined by full-matrix techniques against $F^2$ in anisotropic approximation (for further details, see Online Supplementary Materials).

CCDC 2106879–2106881 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.cdc.cam.ac.uk.

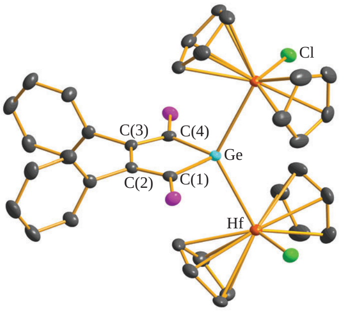
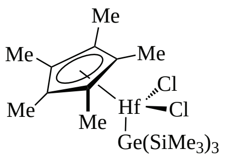
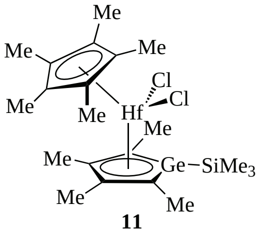


**Figure 2** Molecular structure of germole **8** in the crystal. Selected bond lengths (pm) and angles (°): C(1)−C(2)/C(3)−C(4) 136.41(70), C(2)−C(3) 148.10(98), Ge−C(1)/Ge−C(4) 200.47(57), Ge−Hf 285.85(6), Hf–Cl 240.16(21), $\Sigma\alpha$(germole ring) 539.9 (thermal ellipsoids at 50% probability, all hydrogen atoms and methyl groups of $Me_3Si$ are omitted for clarity).

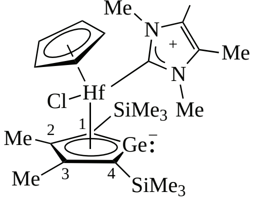
bond in complex **10** (274 pm).[11,12] It reaches the Ge–Hf separations in $\eta^5$-complexes of hafnium and germole anions **11** and dianions **12** (280–292 pm).[6(a),13] The long Ge–Hf distances in germole **8** indicates the steric strain imposed by the large size of the two $HfCp_2Cl$ substituents. An alternative description of germole **8** is that of a dinuclear hafnium complex with a μ-coordinating germole dianion ligand. Tetrolyl ligands in previously reported mono- or dianion complexes of hafnium (*e.g.*, **11** or **12**) are $\eta^5$-coordinated to the metal centre.[2(d),6(a),13,14] Informative is the comparison with the hafnium complex **12**.[6(a)] The C–C ring bond lengths of the germole ligand in complex **12** are almost equal and in the range of C–C bonds in delocalized molecular systems [C(1)–C(2) 144.5 pm, C(2)–C(3) 140.7 pm, C(3)–C(4) 143.4 pm] indicating π-conjugation through the heterocycle. In contrast, complex **8** has a μ-$\eta^1$,$\eta^1$-coordinating localized germole dianion ligand. Thus, the germole dianion ligand shows a flexible coordination behavior and accommodates very different electronic situations at the hafnium center. The situation is similar to that of the stannole dianion $[Sn(C(SiBu^tMe_2)CPh)_2]^{2-}$ which forms $\eta^5$-complexes with Cp*Ru[14] and serves as a μ-$\eta^1$,$\eta^1$-bonded ligand with $Cp_2HfCl$.[10]



**10**
(Hf–Ge 274 pm)



**11**
(Hf–Ge 280 pm)



**12**
(Hf–Ge 292 pm)

To conclude, the potassium salt of germole dianion **6** was obtained in preparative amounts. Similar to its methyl analogue **1**, the reaction of salt **6** with hafnocene dichloride at low temperature provides the BCH germylene **7** in good yields. On the other hand, variation of reaction conditions and stoichiometry provided access to a bimetallic complex **8** with a bridging μ-$\eta^1$,$\eta^1$-dianionic germole ligand. This contrasts the behavior of its methyl analogue **1** for which a similar bimetallic complex could not be isolated as a pure compound.

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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.2022.01.014.

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