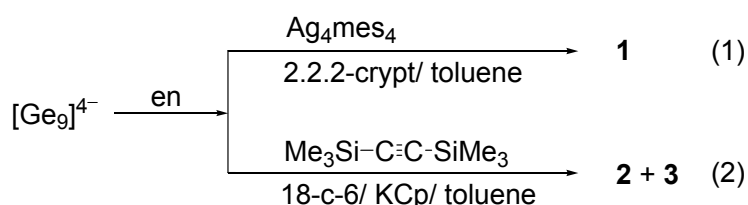


Syntheses, Crystal Structures and ^1H NMR Spectra of the mono substituted Zintl anions $[\text{Ge}_9\text{-R}]^{3-}$ with R = mesityl and vinyl

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Reaction of $[\text{Ge}_9]^{4-}$ with Ag_4mes_4 yielded the first structural characterized Ge_9 cluster $[\text{Ge}_9\text{-mes}]^{3-}$, **1a** with one *exo*-bonded aryl ligand in the compound $[\text{K}(\text{2.2.2-crypt})_3[\text{Ge}_9\text{-mes}]$, **1** (Scheme 1). [1, 2]



Scheme 1: Scheme of the syntheses of **1**, **2** and **3**.

The first mono- and a further bis-vinylated Ge_9 cluster $[\text{Ge}_9\text{-(CHCH}_2\text{)}]^{3-}$, **2a** and $[\text{Ge}_9\text{-(CHCH}_2\text{)}_2]^{2-}$, **3a** in the compounds $[\text{K}(\text{18-c-6})_4[\text{Ge}_9\text{-(CHCH}_2\text{)}](\text{C}_5\text{H}_5)$, **2** and $[\text{K}(\text{18-c-6})_3[\text{Ge}_9\text{-(CHCH}_2\text{)}_2](\text{C}_5\text{H}_5)$, **3**, respectively were achieved by adapting a synthesis procedure described before. [3, 4]

From a series of ^1H NMR spectra recorded directly from reaction solutions, we assume a coexistence of mono-, two- and probably three-fold vinylated Ge_9 clusters.

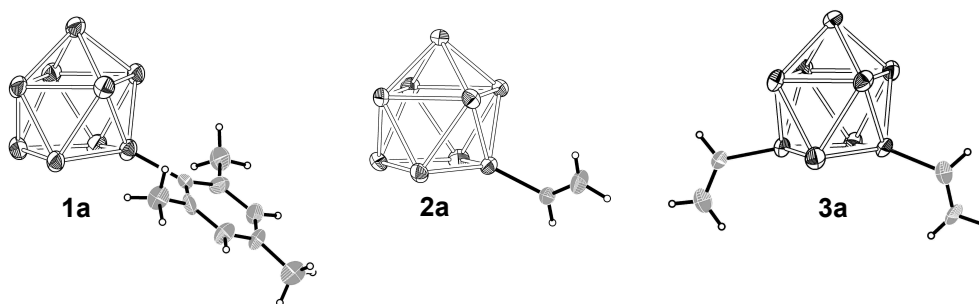


Figure 1: Mono- and disubstituted Ge_9 clusters **1a**, **2a** and **3a**.

Literature and Notes:

[1] mes: mesityl. [2] 2.2.2-crypt: 4,7,13,16,21,24-hexaoxa-1,10-diazobicyclo-[8.8.8]-hexacosane. [3] 18-c-6: 1,4,7,10,13,16-hexaoxacyclooctadiene. [4] Hull, M. W; Sevov, S. C. *Inorg. Chem.* **2007**, *46*, 10953.