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Organo-Zintl Clusters Soluble in Conventional Organic Solvents: Setting the Stage for Organo-Zintl Cluster Chemistry

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Organo-Zintl cluster ions were synthesized by reactions of alkynes with Ge_9^{4-} clusters in ethylenediamine. The triple bonds are hydrogenated to double bonds during the process. The resulting dialkenylated species $[RHC{=}CHGe_9CH{=}CHR]^{2-}$ have lower charge, their alkali-metal cations can be exchanged for tetralkylammonium cations, and the resulting compounds are soluble in nonpolar solvents. This was demostrated with $[H_2C{=}CHGe_9CH{=}CH_2]^{2-}$, which was structurally characterized with $[K\text{-}(18\text{-crown-}6)]^+$, $[Me_4N]^+$, and $[Pr_4N]^+$ as countercations. The solubility of its salt with $[Oc_4N]^+$ in various conventional organic solvents was studied.

Despite a recent resurgence in interest in deltahedral Zintl ions of group 14, their chemistry has been confined almost exclusively to very polar amine-based solvents (mostly ethylenediamine and liquid ammonia with a couple of examples in *N*,*N*-dimethylformamide, DMF),[1,2] which are not typical for the majority of chemical reactions. This solvent limitation greatly narrows the ability to expand the chemistry of these remarkable cluster anions. Previous attempts to bring the clusters into other solvents have failed mainly because either (a) the anions react with the solvents, (b) their alkali-metal salts do not dissolve in nonpolar solvents despite the frequent use of crypts and crown ethers as sequestering agents for the cations, or (c) they react with the organic cations when attempts are made to replace the alkali-metal countercations with “greasy” cations in order to improve their solubility in nonpolar solvents. The latter problem is caused by the highly reducing nature of the E_9^{4-} (E = Si, Ge, Sn, Pb) clusters, which are known to readily produce free (solvated) electrons in ethylenediamine and liquid ammonia.[1,3] These reaction conditions are analogous to solutions of elemental alkali metals, which are known to easily reduce organic cations, typically quaternary ammonium cations producing an amine and an organic radical.[4] All of these considerations indicate that in order to pair Zintl cluster anions with organic cations and to subsequently bring them into conventional solvents one needs to (a) lower the negative charge of the anions and/or (b) prevent the release of free electrons from them. We have recently shown that nine-atom germanium clusters can be readily functionalized with organic substituents to produce species with a charge of 2−, i.e., $[RGe_9R]^{2-}$.[5,6] These organo-Zintl derivatives are significantly less reducing than the naked clusters and do not generate solvated electrons in solution. Here we report that the alkali-metal countercations of such organo-Zintl anions can undergo facile exchange for tetraalkylammonium cations. The resulting compounds are soluble and stable in many conventional solvents such as benzene, toluene, tetrahydrofuran (THF), ethers, dioxane, diglyme, acetone, etc.

In a previous publication, we reported that Ge_9 clusters can be alkenylated by reactions with alkynes in ethylenediamine and presented the structure of $[FcCH{=}CHGe_9CH{=}CHFc]^{2-}$ (**1**) made by a reaction with $FcC{\equiv}CH$ (Fc = ferrocenyl) as well as the mass spectra of analogous compounds from reactions with $PhC{\equiv}CH$, $^tBuC{\equiv}CH$, $PhC{\equiv}CPh$, and $MeOC_6H_4C{\equiv}CH$.[6] During the reaction, the triple bond is hydrogenated to a double bond by the combination of solvated electrons from the clusters and protons from the ethylenediamine. Initially, a reaction with the simplest alkyne, acetylene, was not carried out because of synthetic complications with the handling of gaseous reagents. The same reaction, however, can be carried out with its liquid derivative, $Me_3SiC{\equiv}CSiMe_3$, instead. This reaction results in the divinyl-substituted cluster $[CH_2{=}CHGe_9CH{=}CH_2]^{2-}$ (**2**), which was structurally characterized in a compound with $[K\text{-}(18\text{-crown-}6)]^+$ countercations (Figure 1a).[7,8] The anion was also confirmed in solution by ^1H NMR and electrospray mass spectrometry (ESMS; in the Supporting Information).

In addition to the structurally characterized divinyl-Zintl ion, we confirmed by ESMS the formation of analogous

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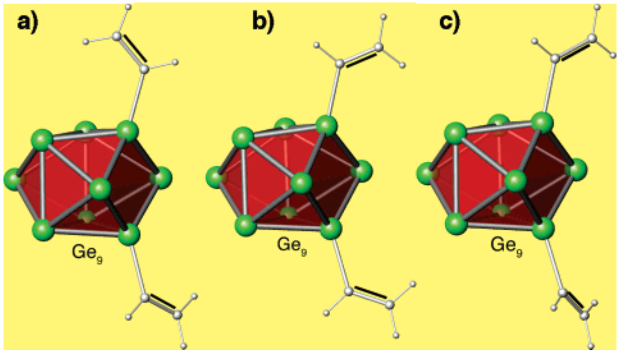

Figure 1. Structure of **2** in (a) [K-(18-crown-6)]$_2$[**2**]·en, (b) [$(CH_3)_4N$]$_2$[**2**]·0.5en, and (c) [$(CH_3CH_2CH_2)_4N$]$_2$[**2**]. The only difference between the anions in the three compounds is the orientation of the two vinyl groups with respect to the cluster, and this suggests rotational flexibility around the Ge−C bonds in solutions.

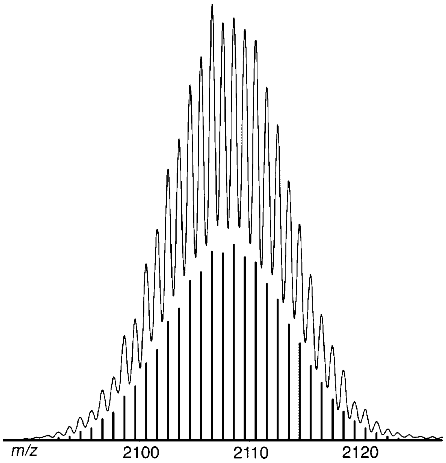

Figure 2. The only high-mass peak in the positive-ion ESMS of [Oc_4N]$_2$ in THF corresponds to {[Oc_4N]$_3$[CH_2═$CHGe_9CH$═CH_2]}$^+$. The theoretical isotope distribution is shown under the peak.

compounds with a series of alkynes having various secondary functional groups including (3-$H_2NC_6H_4$)C≡CH, HC≡C(CH_2)$_4$C≡CH, HC≡C(CH_2)$_3$C≡N, (EtO)$_2$CHC≡CH, PhC≡CMe, HC≡CC_6H_4C≡CH, and (2-C_5H_4N)C≡CH (in the Supporting Information). Thus, in addition to the C═C double bonds, many of the resulting compounds have additional functionalities such as amines, pyridines, nitriles, phenyl rings, ethers, triple bonds, etc. All of these functional groups are potential starting points for further organic transformations and reactions of the organo-Zintl ions such as coordination to transition metals, polymerization, various coupling reactions, grafting onto surfaces, etc. Nonetheless, as mentioned before, the insolubility of the alkali-metal salts made these anions inaccessible in solvents appropriate for such reactions. This problem has now been resolved by cation exchange with tetraalkylammonium cations.

The cation-exchange procedure is quite simple and involves the following general steps.[7] First, the Ge_9-cluster precursor K_4Ge_9 is dissolved in ethylenediamine without the use of sequestering agents. Next, it is difunctionalized in a reaction with an alkyne; we used Me_3SiC≡$CSiMe_3$ for demonstration purposes. Tetraalkylammonium halide is added either directly to the ethylenediamine solution or as a solution in a less polar solvent such as toluene or THF. The solvents are then pumped out, and the quaternary ammonium organo-Zintl salt is extracted by the solvent of interest. This leaves potassium halide as an insoluble precipitate. Our ion-exchange reactions were carried out with tetramethyl-, tetrapropyl-, and tetraoctylammonium halides, [Me_4N]Cl, [Pr_4N]Br, and [Oc_4N]Br (Oc = octyl), respectively. The first two compounds, [Me_4N]$_2$[**2**]·0.5en and [Pr_4N]$_2$[**2**], were structurally characterized by single-crystal X-ray diffraction[8] (Figure 1), while the octyl derivative was evidenced by ESMS in THF (Figure 2) and ^{1}H NMR in benzene-d_6 (in the Supporting Information). The MS experiment showed the organo-Zintl anion paired with three tetraoctylammonium cations, i.e., {[Oc_4N]$_3$[CH_2═$CHGe_9CH$═CH_2]}$^+$, as the only high-mass peak (the full spectrum is available as Supporting Information). The NMR spectrum is similar to that of the K-crown derivative carried out in pyridine-d_5 and showed the three resonances of the vinyl protons at 6.88, 6.21, and 5.99 ppm, each split to a doublet of a doublet (identical

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(7) Details for the general methods and characterization techniques are available in the Supporting Information. **Synthesis of [K-(18-crown-6)]$_2$2·en.** K_4Ge_9 (91 mg, 0.112 mmol) was dissolved in 2 mL of ethylenediamine (red solution) in a test tube inside a glovebox. $Me_3SiCCSiMe_3$ (55 mg, 0.322 mmol) was added dropwise, and the reaction mixture was stirred for 2 h. The resulting red-orange solution was filtered and layered with a solution of 18-crown-6 (355 mg, 1.343 mmol) dissolved in 8 mL of toluene. It yielded well-formed orange needlelike crystals of the compound after 3 days (ca. 77% crystalline yield). ^{1}H NMR (pyridine-d_5): δ 7.32 (A, dd, J(A,B) = 12 Hz, J(A,C) = 19 Hz, $Ge_9C\mathit{H}$═CH_2), 6.41 (C, dd, J(A,C) = 19 Hz, J(B,C) = 4 Hz, Ge_9CH═$CH_B\mathit{H}_C$), 5.93 (B, dd, J(A,B) = 12 Hz, J(B,C) = 4 Hz, Ge_9CH═$C\mathit{H}_BH_C$), 3.52 (s, 18-crown-6), 2.75 (s, −CH_2−, en), 1.47 (b, −NH_2, en). **Synthesis of [$(CH_3)_4N$]$_2$[2]·0.5en.** K_4Ge_9 (81 mg, 0.100 mmol) was dissolved in 2 mL of ethylenediamine (red solution) in a test tube inside a glovebox. $Me_3SiCCSiMe_3$ (93 mg, 0.550 mmol) was added dropwise, and the reaction mixture was stirred for 2 h. The resulting red-orange solution was centrifuged and filtered. Me_4NCl (63 mg, 0.575 mmol) was added, and the mixture was sonicated for 0.5 h. The solution was set aside, and nicely shaped orange needlelike crystals grew within a few hours. **Synthesis of [$(CH_3CH_2CH_2)_4N$]$_2$[2].** K_4Ge_9 (87 mg, 0.107 mmol) was dissolved in 2 mL of ethylenediamine (red solution) in a test tube inside a glovebox. $Me_3SiCCSiMe_3$ (73 mg, 0.429 mmol) was added, and the reaction mixture was stirred for 2 h. The resulting red-orange solution was centrifuged, filtered, and layered with a solution of Pr_4NBr (100 mg, .376 mmol) dissolved in 8 mL of toluene. It yielded blocklike crystals of the compound after about 1 week. **Synthesis of [$(CH_3(CH_2)_6CH_2)_4N$]$_2$[2].** K_4Ge_9 (80 mg, 0.099 mmol) was dissolved in 2 mL of ethylenediamine (red solution) in a test tube inside a glovebox. $Me_3SiCCSiMe_3$ (87 mg, 0.511 mmol) was added, and the reaction mixture was stirred for 2 h. The resulting red-orange solution was centrifuged and filtered. Oc_4NBr (253 mg, 0.463 mmol) dissolved in 1 mL of toluene was added. The solution was centrifuged and filtered again, and the supernate was pumped down to remove the solvent. [Oct_4N]$_2$[**2**] was extracted from the resulting matrix with the solvent of choice (e.g., THF). ^{1}H NMR (benzene-d_6): δ 6.88 (A, dd, J(A,B) = 12 Hz, J(A,C) = 19 Hz, $Ge_9C\mathit{H}$═CH_2), 6.21 (C, dd, J(A,C) = 19 Hz, J(B,C) = 4 Hz, Ge_9CH═$CH_B\mathit{H}_C$), 5.99 (B, dd, J(A,B) = 12 Hz, J(B,C) = 4 Hz, Ge_9CH═$C\mathit{H}_BH_C$).

(8) Single-crystal X-ray diffraction data of [K-(18-crown-6)]$_2$[**2**]·en, [$(CH_3)_4N$]$_2$[**2**]·0.5en, and [$(CH_3CH_2CH_2)_4N$]$_2$[**2**] were collected on a Bruker X8 APEX II diffractometer equipped with a CCD area detector at 100 K using graphite-monochromated Mo Kα radiation. Crystal data for [K-(18-crown-6)]$_2$[**2**]·en: triclinic, $P\bar{1}$, a = 10.947 Å, b = 14.386 Å, and c = 16.227 Å, α = 85.946°, β = 71.136°, and γ = 89.264°, V = 2412.2 Å^3, Z = 2, R1/wR2 = 2.36/5.40 and 3.54/5.91 for observed data ($I \geq 2\sigma_I$) and all data, respectively. Crystal data for [$(CH_3)_4N$]$_2$[**2**]·0.5en: monoclinic, $C2/c$, a = 30.277 Å, b = 13.322 Å, and c = 15.423 Å, β = 118.552°, V = 5464.2 Å^3, Z = 2, R1/wR2 = 2.96/7.29 and 4.62/7.29 for observed data ($I \geq 2\sigma_I$) and all data, respectively. Crystal data for [$(CH_3CH_2CH_2)_4N$]$_2$[**2**]: monoclinic, $P2_1/c$, a = 10.923 Å, b = 16.846 Å, and c = 22.427 Å, β = 92.006°, V = 4124.7 Å^3, Z = 2, R1/wR2 = 4.26/11.64 and 6.11/12.70 for observed data ($I \geq 2\sigma_I$) and all data, respectively.

coupling constants with the K-crown derivative), which unambiguously identifies the protons. For comparison, the vinyl protons in vinyl cyanide are found at 6.20, 6.08, and 5.70 ppm and have very similar coupling constants.

The shape and metrics of the Ge_9 cores and the positioning of the Ge−C exo bonds with respect to the cores in the methyl and propyl derivatives are virtually identical with those in the alkali-metal salt (Figure 1). The only difference in the three structures is the position of the double bonds with respect to the Ge−C exo bonds and, subsequently, to the cluster itself. This indicates dynamic rotation in solution and is consistent with the observation of only three proton resonances for the two vinyl arms in the ^{1}H NMR spectra.

The solubility tests were carried out with the tetraoctylammonium salt. The results showed excellent solubility in diethyl ether, THF, dimethyl sulfoxide (DMSO), dioxane, and DMF, moderate solubility in benzene (^{1}H NMR in the Supporting Information), toluene, diglyme, and acetone, and poor solubility in hexanes. In contrast, the potassium salts of Zintl ions, either with 2,2,2-crypt or 18-crown-6 sequestering agents, are not soluble at all in THF, benzene, toluene, and acetone and have very poor solubility in DMSO. The reason for the different solubilities is most likely the degree of screening of the charge-carrying atom from the solvent. Space-filling models of tetraalkylammonium cations clearly show that the charge carrier (the nitrogen atom) is screened completely by the hydrophobic, nonpolar alkyl groups (in the Supporting Information). Sequestering agents such as 2,2,2-crypt and 18-crown-6, on the other hand, cannot fully cover the alkali-metal cations, and they are exposed to solvents through large openings (in the Supporting Information). Such cations are not well solvated by the nonpolar solvent molecules and, subsequently, do not dissolve in these solvents. The tetraalkylammonium cations, on the other hand, are superior phase-transfer catalysts and can interact readily with nonpolar solvent molecules via their alkyl chains. Their solvation by the nonpolar solvent induces the transfer of the charge-balancing organo-Zintl anions into the solvent (shuttling mechanism) and results in good overall solubility.

The results presented here firmly establish a synthetic route (the alkyne route) to accessing organo-Zintl clusters and demonstrate that a wide range of organic functional groups are compatible with Zintl clusters. Additionally, these organo-Zintl ions are soluble in conventional solvents after cation exchange. This sets the stage for subsequent organic transformations in the realm of organo-Zintl chemistry.

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Supporting Information Available: X-ray crystallographic files in CIF format, ORTEP drawings of **2**, space-filling drawings of cations, mass spectra of reactions of Ge_9 clusters with various alkynes, ^{1}H NMR spectra of $[K\text{-}(18\text{-crown-}6)]_2[\mathbf{2}]\cdot$en in pyridine-$d_5$ and of $[Oc_4N]_2[\mathbf{2}]$ in benzene-d_6, and details of the experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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