Synthesis and Characterization of Na$_2${Ge(C$_6$H$_3$-2,6-Trip$_2$)}$_2$ and K$_2${Sn(C$_6$H$_3$-2,6-Trip$_2$)}$_2$ (Trip = -C$_6$H$_2$-2,4,6-*i*-Pr$_3$): A New Class of Multiply Bonded Main Group Compounds

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It has long been recognized that multiple bonding in the heavier main group 14 elements[1] differs fundamentally[2] from that observed for carbon compounds. For example, the structures of Si, Ge, Sn, or Pb species corresponding to alkenes display an increasing tendency to adopt nonplanar, trans-bent structures with progressively weaker element−element bonding as the group is decended.[2] About thirty structures of compounds of formula R$_2$MMR$_2$ (M = Si, Ge, Sn, or Pb, R = organo group) are known, and their spectroscopic and chemical properties have been studied in detail.[1] In contrast, experimental data from the heavier group 14 species which correspond to alkynes (RMMR) are almost nonexistent.[3] The singly reduced species [K(THF)$_6$][{Sn(C$_6$H$_3$-2,6-Trip$_2$)}$_2$] (**1**)[4] represents the closest such approach, but its structure strongly suggests that the singly bonded isomeric form of the neutral (and as yet unisolated) distannylene {Sn(C$_6$H$_3$-2,6-Trip$_2$)}$_2$ is preferred over the triple bonded "distannyne" valence isomer.[5] Thus, the ion, [{Sn(C$_6$H$_3$-2,6-Trip$_2$)}$_2$]$^-$, has a Sn−Sn distance of 2.8123(9) Å and a planar, but nonlinear, C(*ipso*)-SnSnC(*ipso*) array featuring an Sn−Sn−C angle of 95.2(13)°. This suggests that there is a lone pair of electrons located at each tin which occupy orbitals high in s character with p orbitals employed in Sn−Sn and Sn−C σ-bonding. The remaining p orbital at each tin may then overlap to form a π orbital which in **1** is occupied by one electron. The tins can thus be considered to be connected by a two-electron σ bond and a π bond of order 0.5 to afford an overall, Sn−Sn bond order of 1.5 (cf. Sn−Sn single bond of 2.80 Å in gray tin).[6] To further investigate the bonding in such compounds, we are engaged in a program to synthesize the related doubly reduced [RMMR]$^{2-}$ and neutral RMMR (M = Sn, Ge, Sn, or Pb, R = organo group) species. Here, the isolation and characterization of the doubly reduced compounds Na$_2${Ge(C$_6$H$_3$-2,6-Trip$_2$)}$_2$ (**2**) and K$_2${Sn(C$_6$H$_3$-2,6-Trip$_2$)}$_2$ (**3**) (Trip = C$_6$H$_2$-2,4,6-*i*-Pr$_3$) are described.

The synthesis[7] of **2** and **3** was accomplished by the reduction of the halides M(Cl)C$_6$H$_3$-2,6-Trip$_2$ (M = Ge or Sn)[4,8] with excess alkali metal in benzene solution over a longer period than for **1**. Both **2** and **3** were obtained as dark-red air-sensitive crystalline solids. They have very similar structures (Figures 1 and 2), but the crystals are not isomorphous.[9] The structure of **2** is characterized by an inversion center at the midpoint of the Ge−Ge bond, whereas **3** has a 2-fold axis of symmetry along the K(1)- -K(2) vector. Important structural data for **2** and **3** are provided in Table 1.

The structures of both **2** and **3** have a trans configuration (Ge−Ge−C = 102.37(8)° and Sn−Sn−C = 107.50(14)°) featuring a planar M$_2${C(ipso)}$_2$ (M = Ge or Sn) array. The symmetry restriction on each molecule also requires that the Ge$_2$Na$_2$ and Sn$_2$K$_2$ arrays are planar. The alkali metal countercations are associated with each dianion by coordination in a π sandwich fashion to *ortho*-Trip groups. The Ge−Ge distance in **2**, 2.3943(13) Å, may be compared with the 2.44 Å of a single Ge−Ge bond[5] and the 2.213(2)−2.443(2) Å range for dimeric compounds of formula (GeR$_2$)$_2$.[1k,l] The Ge−C distance, 2.065(3) Å, is at the upper end of the Ge−C scale[10] for three- and four-coordinate Ge compounds and may be contrasted with the 1.989(5) Å Ge−C bond length in Ge(Cl)C$_6$H$_3$-2,6-Trip$_2$.[8] The Na- -C distances are slightly shorter than in alkali−metal complexes with similar ligands[11] whereas the Na- -Ge contacts, ca. 3.1 Å, are longer than the single bond distance of 2.86 Å (predicted from the sum of

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(5) The two valence isomers of heavier group 14 RMMR compounds may be represented by R−M≡M−R (dimetallyne) and R−$\ddot{\mathrm{M}}$−$\ddot{\mathrm{M}}$−R (dimetylene) which contain triple and single M−M bonds, respectively. The triple-bonded form becomes less stable (and the single bonded form more stable) as the group is descended. For discussion see refs 1(l) and 3.

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(7) All manipulations were carried out under anaerobic and anhydrous conditions. The synthesis of Ge(Cl)C$_6$H$_3$-2,6-Trip$_2$ was carried out in a manner similar to that reported for Sn(Cl)C$_6$H$_3$-2,6-Trip$_2$.[4] For **2**: Ge(Cl)C$_6$H$_3$-2,6-Trip$_2$ (1.29 g, 2.19 mmol) in benzene (20 mL) was added to finely divided sodium (0.30 g, 13.05 mmol) in benzene (10 mL) at room temperature with stirring. The reaction mixture was stirred for an additional 16 h at room temperature and the resulting deep-red solution was filtered. The filtrate was reduced to incipient crystallization (ca. 12 mL). The solution was stored in a ca. 6 °C refrigerator to yield red crystals (0.38 g, 23.3%), mp 234−236 °C. ^{1}H NMR (C$_6$D$_6$): δ 1.11 (d, 24H, *p*-CH(C*H*$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz, 1.29 (d, 48H, *o*-CH(C*H*$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz), 2.92 (sept, 4H, *p*-C*H*(CH$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz), 3.60 (sept, 8H, *o*-C*H*(CH$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz), 6.93 (m, 6H, *p*-C$_6$H$_3$, overlap), 7.04 (s, 8H, *m*-Trip). ^{13}C NMR (C$_6$D$_6$): δ 23.67 (*o*-CH(*C*H$_3$)$_2$), 24.17 (*p*-CH(*C*H$_3$)$_2$), 25.56 (*o*-CH(*C*H$_3$)$_2$), 30.810 (*o*-*C*H(CH$_3$)$_2$), 34.15 (*p*-*C*H(CH$_3$)$_2$), 120.58 (*m*-Trip), 121.50 (*m*-C$_6$H$_3$), 128.52 (*o*-C$_6$H$_3$), 142.09 (*i*-Trip), 145.38 (*p*-C$_6$H$_3$), 147.27 (*p*-Trip), 148.32 (*o*-Trip), 176.16 (*i*-C$_6$H$_3$). UV−vis (λ_{max}, ϵ), in hexane: 549, 1700; 425, 2800. For **3**: Sn(Cl)C$_6$H$_3$-2,6-Trip$_2$ (1.2 g, 1.9 mmol) in benzene (20 mL) was added to finely divided potassium (0.45 g, 11.4 mmol) in benzene (10 mL) at room temperature with stirring. The reaction mixture was stirred for an additional 6 h at room temperature and evaporated to dryness. The residue was extracted with toluene (40 mL) and the deep-red (nearly black) solution was filtered. The filtrate was reduced to incipient crystallization (ca. 15 mL). The solution was stored in a ca. 6 °C refrigerator to yield the produce **3** as red crystals (0.43 g, 30%), mp 228−230 °C (dec). ^{1}H NMR (C$_7$D$_8$) 60 °C. 1.02 (d, 12H, *p*-CH(C*H*$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz), 1.11 (d, 12H, *p*-CH(C*H*$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz), 1.16 (d, 12H, *p*-CH(C*H*$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz), 1.19 (d, 12H, *o*-CH(C*H*$_3$)$_2$) $^3J_{HH}$ = 6.6 Hz), 1.30 (d, 12H, *o*-CH(C*H*$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz), 1.41 (d, 12H, *o*-CH(C*H*$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz), 2.76 (sept, 2H, *o*-C*H*(CH$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz), 2.89 (sept, 2H, *o*-C*H*(CH$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz), 2.92 (sept, 4H, *p*-C*H*(C*H*$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz), 3.06 (sept, 2H, *o*-C*H*(CH$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz), 3.24 (sept, 2H, *o*-C*H*(CH$_3$)$_2$) $^3J_{HH}$ = 6.9 Hz), 6.51 (t, 2H, *p*-C$_6$H$_3$, $^3J_{HH}$ = 7.2 Hz), 6.81 (d, 4H, *m*-C$_6$H$_3$, $^3J_{HH}$ = 6.9 Hz), 6.83 (s, 8H, *m*-Trip). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 23.83 (*o*-CH(*C*H$_3$)$_2$), 24.43 (*p*-CH(*C*H$_3$)$_2$), 24.57 (*o*-CH(*C*H$_3$)$_2$), 25.75 (*p*-CH(*C*H$_3$)$_2$), 30.63 (*o*-CH(*C*H$_3$)$_2$), 34.24 (*p*-*C*H(CH$_3$)$_2$), 34.98 (*o*-*C*H(CH$_3$)$_2$), 120.49 (*m*-Trip), 130.42; 132.22 (*m*-C$_6$H$_3$), 141.45; 141.51 (*o*-C$_6$H$_3$), 146.62; 146.98 (*i*-Trip), 147.07; 147.22 (*p*-C$_6$H$_3$), 148.35; 148.44 (*o*-Trip), 150.18 (*p*-C$_6$H$_3$), 169.80 (*i*-C$_6$H$_3$). UV−vis (λ_{max}, ϵ) in toluene: 552, 3200; 412, 4200. Both compounds gave satisfactory C, H combustion analyses.

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(9) Crystal data at 130 K with Mo Kα (λ = 0.71073 Å) radiation. For **2**: a = 13.316(7) Å, b = 13.476(7) Å, c = 14.410(9) Å, α = 72.99(5)°, β = 76.91(5)°, γ = 61.23(4)°, triclinic, space group $P\bar{1}$, Z = 1, wR2 R1 = 0.048 for 7345 ($I > 2\sigma(I)$) data. For **3**: a = 17.021(3) Å, c = 29.173(5) Å tetragonal, space group $P4_12_12$, Z = 4, wR$_2$ R1 = 0.048 for 4050 ($I > 2\sigma(I)$) data.

10.1021/ja982717g CCC: $15.00

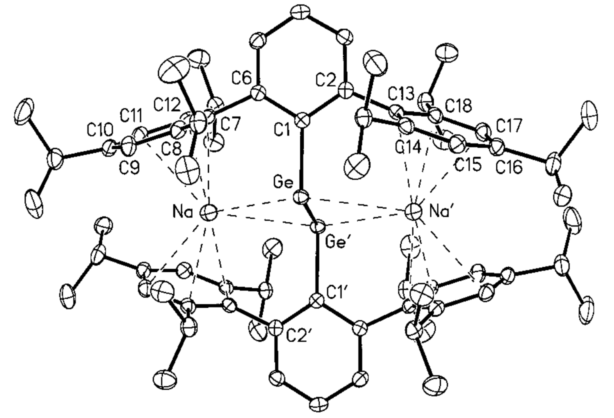

Figure 1. Thermal ellipsoid plot (30%) of **2**. H atoms are omitted for clarity.

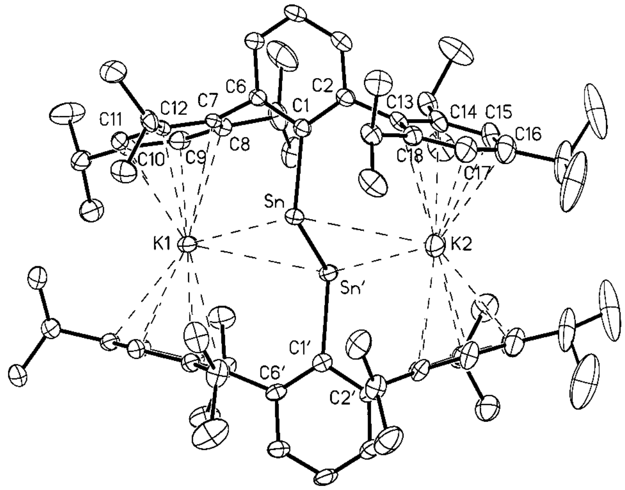

Figure 2. Thermal ellipsoid plot (30%) of **3**. H atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **2** and **3**

2		**3**	
Ge–Ge′	2.3943(13)	Sn–Sn′	2.7763(9)
Ge–C(1)	2.065(3)	Sn–C(1)	2.274(6)
Ge–Na	3.121(3)	Sn–K	3.579(2)
	3.074(3)		3.591(2)
Na- -C(18)′	2.647(3)	K- -C(12)	3.138(6)
Na- -C(17)′	2.831(3)	K- -C(11)	3.076(7)
Na- -C(13)′	2.813(3)	K- -C(10)	3.101(7)
Na- -C(7)	2.799(3)	K- -C(9)	3.126(6)
Na- -C(12)	2.650(3)	K- -C(8)	3.193(7)
Na- -C(11)	2.893(3)	K- -C(7)	3.196(6)
Ge–Ge′–C(1)	102.37(8)	Sn–Sn′–C(1)	107.50(14)

the covalent radii of Na[12] and Ge[6]) or the 2.975(3) Å Na–Ge distance in [Na(15-crown-5)][C_4Me_4GeMes].[13] Within the -C_6H_3-2,6-$Trip_2$ ligand the Trip rings subtend an angle of ca. 76° to the central C(1) ring plane. However, as is apparent from Figure 1, the Trip ring planes deviate from the extended lines of the C(6)–C(7) and C(2)–C(13) vectors by 7.5 and 4.2°, thereby giving the appearance of being 'bent back' from the Na^+ ions. In addition, the Ge–C(*ipso*) vector deviates by 6.6° from the plane of the central ring. In the tin species **3** the Sn–Sn distance, 2.7663(9) Å, may be compared to the 2.8123(9) Å found in the monoreduced **1**[4] and 2.768(1)–3.639(1) Å range in compounds of formula $(SnR_2)_2$.[11,2] The Sn–C bond length, 2.274(6) Å, like the Ge–C bond in **2**, is rather long. The K–Sn interactions, 3.579(2) and 3.591(2) Å, are longer than the sum of the covalent radii (3.36 Å)[6,12] and longer than the K–Sn distance, 3.548(3) Å, in $(\eta^6\text{-PhMe})_3KSn\{CH_2(t\text{-Bu})\}_3$.[14] Within the -$C_6H_3$-2,6-$Trip_2$ ligand there are angles of 80.0 and 88.5° between the planes of the C(7) and C(13) rings and that of the central, C(1), ring. There is also a bent-back angle of 8.7° at the C(7) and C(13) rings and the angle between the Sn–C(1) vector and the C(1) ring plane is 7.2°.

The simplest view of the bonding of **2** and **3** is identical to that described for the radical anion $[Sn\{C_6H_3\text{-}2,6\text{-}Trip_2\}_2]^-$ of **1**,[4] except that the π orbital is now doubly occupied. This bonding picture is in agreement with that of the neutral As[15] and Sb[16] dipnictenes with which **2** and **3** are isoelectronic.[17] However, the Ge–Ge and Sn–Sn bond lengths in **2** and **3** are ca. 0.1 Å longer than the As–As and Sb–Sb double bond distances[15,16,18] although the covalent radii of the pairs Ge/As and Sn/Sb are very similar.[6,12] The relatively longer and weaker bonds in **2** and **3** may be due to Coulombic repulsions between adjacent negative charges. Support for this view comes from the fact that the Sn–Sn single bond distance in the dianionic compound $[Li(NH_3)_4]_2$-$[Sn_2Ph_4]$[19] is 2.905(3) Å which is ca. 0.1 Å longer than a normal single bond. In addition, the Sn–Sn distance in **3** is just slightly shorter than that in **1**. Apparently, the increased bond-order and bond strengths just overcome the increased repulsion resulting from the addition of the second electron. An unexpected feature of the structural data for **2** and **3** is that the M–M–C angle is wider for Sn than it is for Ge. This could be due to a number of factors among which are cation–anion interactions or packing effects. Oddly, the angle at antimony in $\{Sb(C_6H_3\text{-}2,6\text{-}Trip_2)\}_2$ is also wider (by ca. 2°) than it is in the corresponding arsenic species.[18]

Data on a singly reduced analogue of **2**, the solvent-separated ion pairs of **2** and **3**, as well as neutral compounds related to **2** and **3** will be necessary to better understand their bonding. Efforts to synthesize such compounds and the exploration of their chemistry are in hand.

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Supporting Information Available: Tables of data collection parameters, atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (25 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[17] In addition to being isoelectronic to the dipnictenes, **2** and **3** feature two absorption bands in their UV–vis spectra which may be due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

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