Organometallics **2004,** *23,* 2841−2844

Characterization of Ge_5R_4 (R = $CH(SiMe_3)_2$, C_6H_3-2,6-Mes_2): Germanium Clusters of a New Structural Type with Singlet Biradical Character

Anne F. Richards, Marcin Brynda, Marilyn M. Olmstead, and Philip P. Power*

Department of Chemistry, University of California, Davis, One Shields Avenue,
Davis, California 95616

Received January 30, 2004

*Summary: Reduction of the bulky organogermanium(II) halides Ge(Cl){CH(SiMe$_3$)$_2$} and Ge(Cl)C$_6$H$_3$-2,6-Mes$_2$ (the former in the presence of GeCl$_2$·(dioxane)) afforded the clusters Ge$_5$R$_4$ (R = CH(SiMe$_3$)$_2$ (**1**), C$_6$H$_3$-2,6-Mes$_2$ (**2**)), which have an unsubstituted germanium atom capping a butterfly Ge$_4$R$_4$ array. The bonding involves six two-center−two-electron Ge−Ge bonds and a lone pair at the unsubstituted germanium as well as nonbonded electron density at two of the substituted germaniums that indicates possible biradical character.*

Recent work involving the reduction of various terphenyl-substituted group 14 element (tetrel) halides, ArMX (Ar = terphenyl; M = Ge, Sn, Pb; X = Cl, Br), has resulted in the isolation of several new classes of compounds. These include the alkyne analogues ArMMAr,[1,2] their singly and doubly reduced congeners $[ArMMAr]^{-/2-}$,[3,4] the neutral radical c-Ge_3Ar_3 and its allyl anion analogue $[Ge_3Ar_3]^-$,[5] and the cluster Sn_8Ar_4.[6] In addition, the inclusion of the unsubstituted low-valent metal halides in these reduction mixtures permitted the ready isolation of unusual clusters with unsubstituted tetrels and/or two different tetrels, as in $Ge_6(C_6H_3$-2,6-$Trip_2)_2$ (Trip = C_6H_2-2,4,6-Pr^i_3) and $Sn_4(GeC_6H_3$-2,6-$Trip_2)_2$.[7] Such "element rich"[8] species represented a departure from the conventional neutral clusters of the group 14 elements, which usually feature a 1:1 tetrel:substituent stoichiometry.[9] Except for the Zintl anions and their derivatives, only a few element-rich heavier tetrel clusters have been characterized. They include $Sn_8\{Si(SiMe_3)_3\}_6$,[10] $Sn_8\{C_6H_3$-2,6-$Mes_2\}_4$,[6] $Ge_8\{N(SiMe_3)_2\}_6$,[11] and the cationic $[Ge_{10}(SiBu^t_3)_6I]^+$.[12] We now report the synthesis and characterization of two new, element-rich clusters of the formula Ge_5R_4 (R = $CH(SiMe_3)_2$ (**1**), C_6H_3-2,6-Mes_2 (**2**); Mes = C_6H_2-2,4,6-Me_3)). In addition, we report DFT calculations on Ge_5R_4 (R = Me, Ph) model species which reproduce the major features of the experimental structures and facilitate interpretation of the bonding within these species.

The $Ge_5\{CH(SiMe_3)_2\}_4$ cluster, **1**, was synthesized[13] (eq 1) by the reduction of a mixture of $Ge(Cl)\{CH(SiMe_3)_2\}$ and 0.5 equiv of $GeCl_2$·(dioxane) with magnesium powder in THF, followed by workup in hexane, which afforded the product **1** as orange crystals. Single-crystal X-ray diffraction[14] revealed the structure shown in Figure 1. It consists of an array of four $Ge\{CH(SiMe_3)_2\}$ units capped by a germanium that carries no

$$Ge(Cl)CH(SiMe_3)_2 + 0.5GeCl_2\cdot(dioxane) \xrightarrow[\text{THF}]{\text{Mg (powder)}} \underset{\mathbf{1}}{Ge_5\{CH(SiMe_3)_2\}_4} + MgCl_2 + dioxane \quad (1)$$

---

* To whom correspondence should be addressed. E-mail: pppower@ucdavis.edu.

(1) Stender, M.; Phillips, A. D.; Wright, R. J.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1785.

(2) Phillips, A. D.; Wright, R. J.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 5930.

(3) Olmstead, M. M.; Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 11705.

(4) Pu, L.; Senge, M. O.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1998**, *120*, 12682.

(5) Olmstead, M. M.; Pu, L.; Simons, R. S.; Power, P. P. *J. Chem. Soc., Chem. Commun.* **1997**, 1595.

(6) Eichler, B. E.; Power, P. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 796.

(7) Richards, A. F.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed.* **2003**, *42*, 4071.

(8) Three biradicaloid neutral tin clusters, Sn_5Ar_6, Sn_7Ar_8 (Ar = C_6H_3-2,6-$Et_2)_2$, and $Sn_5(C_6H_3$-2,6-$(OPr^i)_2)_6$, which have two unsubstituted tin atoms, are known. They are not strictly metal rich in the sense that the number of organic substituents exceeds that of the metal atoms. For an account of this and related work, see: (a) Sita, L. R. *Adv. Organomet. Chem.* **1995**, *38*, 187. (b) Drost, C.; Hildebrand, M.; Lonnecke, P. *Main Group Met. Chem.* **2002**, *25*, 93.

(9) Sekiguchi, A.; Sakurai, H. *Adv. Organomet. Chem.* **1995**, *37*, 1.

(10) Wiberg, N.; Lerner, H.-W.; Wagner, S.; Nöth, H.; Seifert, T. *Z. Naturforsch., B* **1999**, *54*, 877.

(11) Schnepf, A.; Köppe, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 911.

(12) Sekiguchi, A.; Ishida, Y.; Kabe, Y.; Inchinohe, M. *J. Am. Chem. Soc.* **2002**, *124*, 8776.

(13) All manipulations were carried out under anaerobic and anhydrous conditions. (a) A 1:1 mixture of $Ge(Cl)CH(SiMe_3)_2$ (2 mmol, 0.472 g) and $GeCl_2$·(dioxane) (1.0 mmol, 0.232 g) in THF (20 mL) was added dropwise to a suspension of magnesium powder in the THF (20 mL) at −78 °C. The temperature of the reaction was maintained below 0 °C for 8 h, after which time the THF was removed and the orange solution extracted into hexane. This was stored for approximately 6 weeks at ca. −30 °C, during which time orange crystals of **1** formed. Yield: 12% (0.11 g). Mp: 134−136 °C. ^1H NMR (C_6D_6, 399.7 MHz, 25 °C): δ (ppm) 0.849, 0.926 (s, 18H, $SiMe_3$), 1.278, 1.296 (s, 1H, CH), $^{13}C\{^1H\}$ NMR (C_6D_6, 100.59 MHz, 25 °C): δ (ppm) 3.46, 3.56, 27.70, 29.42, IR (Nujol, IR, KBr plates): ν (cm^{-1}) 1710 (m), 1520 (s), 1380 (s), 740 (s), 620 (s), 500 (s), 390 (s). (b) A THF solution of $Ge(Cl)C_6H_3$-2,6-Mes_2 (0.424 g, 1 mmol) was added quickly to a THF suspension of KC_8 (0.128 g, 0.95 mmol) at −78 °C. The reaction mixture was allowed to reach ambient temperature, and stirring was maintained for 20 h. Under vacuum the THF was removed and the dark solid extracted into toluene. Storage at ca. −30 °C overnight afforded almost black crystals of **2**. Yield: 20% (0.065 g). Mp: 207−208 °C. ^1H NMR (C_6D_6, 400 MHz, 25 °C): δ (ppm) 2.00 (s, 12H, *o*-CH_3), 2.16 (s, 6H, *p*-CH_3), 6.80 (s, 4H, *m*-Mes), 6.93 (d, 2H, $^3J_{H-H}$ = 7.6 Hz, *m*-C_6H_3), 7.19 (t, ^{1}H, $^3J_{H-H}$ = 7.6 Hz, *p*-C_6H_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ (ppm) 20.82 (*p*-CH_3), 20.99 (*o*-CH_3), 128.31 (*o*-Mes), 128.68 (*m*-Mes), 130.54 (*o*-C_6H_3), 135.58 (*m*-C_6H_3), 136.23 (*p*-C_6H_3), 139.21 (*p*-Mes), 141.78 (*i*-Mes).

(14) (a) Crystal data were collected at 90 K with Mo Kα (λ = 0.710 73 Å) radiation. **1**: triclinic, $P\bar{1}$, $Z = 2$, $a = 9.7224(17)$ Å, $b = 12.734(2)$ Å, $c = 20.337(4)$ Å, $\alpha = 83.645(3)°$, $\beta = 81.830(4)°$, $\gamma = 79.433(3)°$, R1 = 0.0506 for 6301 ($I > 2\sigma(I)$) data and wR2 = 0.128 for all 8829 data. **2**: orthorhombic, *Pccn*, $Z = 4$, $a = 14.6845(16)$ Å, $b = 23.524(3)$ Å, $c = 27.959(3)$ Å, R1 = 0.075 for 5513 ($I > 2\sigma(I)$) data and wR2 = 0.217 for all 8590 data.

10.1021/om049921z CCC: \$27.50

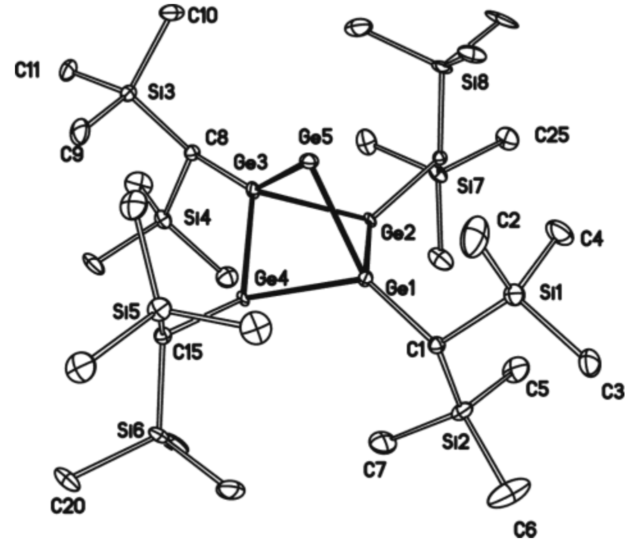


Figure 1. Thermal ellipsoid plot (30%) of $Ge_5\{CH(SiMe_3)_2\}_4$. H atoms are not shown. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2) = 2.422(1), Ge(1)−Ge(4) = 2.4013(9), Ge(2)−Ge(3) = 2.4320(9), Ge(3)−Ge(4) = 2.4163(9), Ge(1)−Ge(5) = 2.464(1), Ge(3)−Ge(5) = 2.458(1), Ge(1)−C(1) = 1.960(5), Ge(3)−C(8) = 1.962(6), Ge(2)−C(22) = 2.004(6), Ge(4)−C(15) = 2.006(6); C(1)−Ge(1)−Ge(5) = 137.7(2), Ge(4)−Ge(1)−Ge(5) = 76.69(3), Ge(2)−Ge(1)−Ge(5) = 77.18(3), Ge(4)−Ge(1)−Ge(2) = 87.29(3), Ge(1)−Ge(2)−Ge(3) = 83.52(3), Ge(2)−Ge(3)−Ge(4) = 86.73(3), Ge(1)−Ge(4)−Ge(3) = 84.30(3).

alkyl group. There is a disorder in the structure in which the Ge(2), Ge(4), and Ge(5) atoms are displaced to positions Ge(2A) and Ge(4A) and Ge(5A) so that there is an approximate pseudo mirror plane incorporating atoms Ge(1) and Ge(3), the midpoints of the Ge(2)−Ge(2A), Ge(4)−Ge(4A), and Ge(5)−Ge(5A) vectors, and the α-carbons of the ligands. However, the occupancy of the 2A, 4A, and 5A positions is only 11%. Thus, only the major-occupancy positions (89%) are illustrated. In the $(GeR)_4$ (R = $CH(SiMe_3)_2$) moiety the Ge−Ge distances are in the narrow range 2.4011(9)−2.432(1) Å and have the average value 2.418(9) Å, which is close to the 2.44 Å in elemental germanium.[15] The Ge(1)−C(1) and Ge(3)−C(8) bond lengths average 1.96(2) Å, whereas the higher coordinate Ge(2)−C(22) and Ge(4)−C(14) bonds are near 2.00(2) Å. Both distances lie close to the sum of the covalent radii of germanium and carbon (1.99 Å). The $(GeR)_4$ array has a butterfly structure with a fold angle of 134.3° along the Ge(2)- - -Ge(4) vector. The transannular Ge(1)- - -Ge(3) and Ge(2)- - -Ge(4) separations are 3.233(1) and 3.329(1) Å. The alkyl-free germanium Ge(5) is connected to the $(GeR)_4$ moiety through bonding to Ge(1) (2.464(1) Å) and Ge(3) (2.458(1) Å). The Ge(5)−Ge(2) and Ge(5)−Ge(4) distances are much longer at 3.049(1) and 3.019(1) Å, respectively, and indicate no bonding interaction. The four alkyl groups lie close to equatorial positions with respect to the Ge(1)−Ge(4) ring, and the four α-carbons show maximum deviations of only 0.025 Å from their averaged plane.

The related cluster **2** was synthesized as dark green, almost black crystals by the reduction of $Ge(Cl)C_6H_3$-2,6-Mes_2 with KC_8 (eq 2). The synthesis of **2** resembles

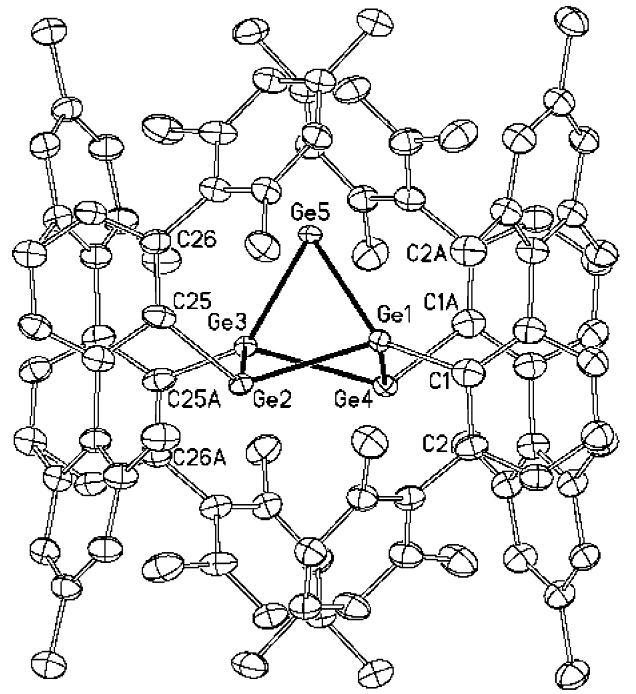


Figure 2. Thermal ellipsoid plot (30%) of the non-hydrogen atoms of $Ge_5(C_6H_3$-2,6-$Mes_2)_4$. H atoms are not shown. Selected bond distances (Å) and angles (deg): Ge(1)−Ge(2) = 2.718(3), Ge(1)−Ge(4) = 2.711(2), Ge(2)−Ge(3) = 2.735(2), Ge(3)−Ge(4) = 2.707(3), Ge(1)−Ge(5) = 2.693(3), Ge(3)−Ge(5) = 2.699(2), Ge(1)−C(1) = 2.052(8), Ge(2)−C(25) = 2.185(8); C(1)−Ge(1)−Ge(5) = 148.0(2), C(1)−Ge(1)−Ge(4) = 111.5(2), C(1)−Ge(1)−Ge(2) = 131.1(2), Ge(4)−Ge(1)−Ge(5) = 77.87(8), Ge(4)−Ge(1)−Ge(2) = 89.7(1), Ge(1)−Ge(2)−Ge(3) = 80.99(9), Ge(2)−Ge(3)−Ge(4) = 89.4(1), Ge(1)−Ge(4)−Ge(3) = 81.6(1).

$$\mathrm{Ge(Cl)C_6H_3\text{-}2,6\text{-}Mes_2} \xrightarrow[\mathrm{THF}]{\mathrm{KC_8}} \underset{\mathbf{2}}{\mathrm{Ge_5(C_6H_3\text{-}2,6\text{-}Mes_2)_4}} + \mathrm{KCl} + \mathrm{C} + \text{other products} \quad (2)$$

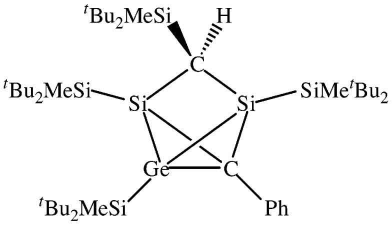
that of c-$Ge_3(C_6H_3$-2,6-$Mes_2)_3$ and $KGe_3(C_6H_3$-2,6-$Mes_2)_3$,[5] except that care was taken not to exceed a stoichiometric ratio of reductant and workup was performed using toluene rather than hexane; otherwise, the trigermanium clusters[5] are obtained. Presumably, the greater solubility of the larger cluster **2** in toluene permits its extraction into this solvent and smaller clusters, if they exist in these solutions, are not as readily crystallized. Ligand stripping occurs during the synthesis to afford the unsubstituted Ge(5). Such an occurrence is a common feature of the reduction of heavier group 14 species, as exemplified by the synthesis of $Sn_8(C_6H_3$-2,6-$Mes_2)_4$.[6] The X-ray crystal data for **2** reveal a structure very similar to that of **1** (Figure 2). Disorder of the germanium positions of the core is also apparent, but it differs from that in **1**, because there is a crystallographically required 2-fold symmetry axis parallel to the *c* axis midway between Ge(2)−Ge(3) and Ge(1)−Ge(4). All germaniums occupy two sites at 50% occupancy. The Ge−Ge distances in the $\{GeC_6H_3$-2,6-$Mes_2\}_4$ array average 2.72(1) Å and are significantly longer than those in **1**. The lengthening is most probably due to the great steric congestion imposed by the four C_6H_3-2,6-Mes_2 groups (note that the C_6H_3-2,6-Mes_2 substituent also

---

(15) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, U.K., 1984; p 1279.

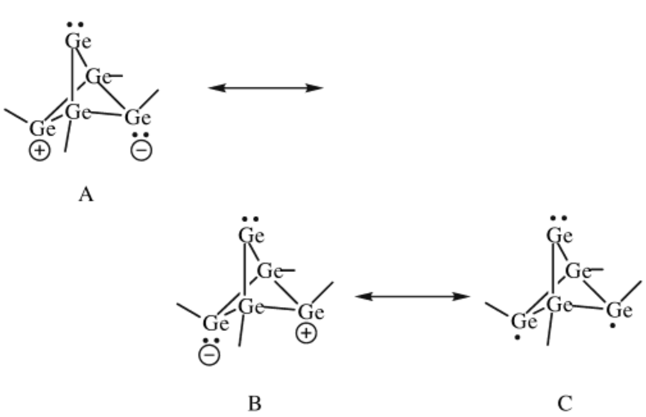
stabilizes trigermanium clusters[5]). The increased crowding is also reflected in the greater pyramidality at the three-coordinate germaniums Ge(2) and Ge(4), $\sum$°(Ge) = 308.99° (Ge(2)), 313.02° (Ge(4)) (cf. $\sum$°(Ge) = 336.0° (Ge(2)), and 340.7° (Ge(4)) in **1**), and the more axial orientation of the C_6H_2-2,6-Mes_2 substituents. The Ge−C distances involving the three- and four coordinate germaniums also differ considerably, having average values near 2.054(8) and 2.185(8) Å.

The observation of similar structures for **1** and **2** shows that the unusual Ge_5R_4 structural motif is reproducible within the limits imposed by the steric requirements of the ligands. The structures can be viewed as related to bicyclo[1.1.1]pentanes as well as the biradicaloids Sn_5Ar_6 (Ar = C_6H_3-2,6-Et_2[8a] or C_6H_2-2,6-$(OPr^i)_2$[8b]) of Sita and Drost. In **1** and **2** Ge(1) and Ge(3) can be viewed as the bridgehead atoms, but this description does little to facilitate understanding of the cluster bonding which can be viewed in several other ways. Very crudely, the four GeR moieties can supply three electrons each and the unsubstituted Ge atom (which carries a lone pair) two electrons, for cluster bonding, to afford a 14-electron total for a 5-vertex cluster.[16] According to Wade's rules a nido cluster is predicted, and indeed, it is possible to argue that the Ge_5 array resembles a nido shape with Ge(5) at an apex, if the fact that two of the four Ge(5)−Ge interactions are significantly longer than the other two is overlooked. In reality, Ge(5) interacts with only two of the germaniums (Ge(1) and Ge(3)) in the $(GeR)_4$ unit. The remaining two germaniums, Ge(2) and Ge(4), have pyramidal three-coordination, which suggests the existence of nonbonded electron density at these centers. The closest structure available for comparison is the recently described 2,4-disila-1-germatricyclo[2.1.0.0^{2,5}]pentane,[17] which has a structure resembling **1** and **2**, as shown by



In this compound the capping group is the carbenoid C(H)SiMeBu^t_2, which, like the unsubstituted germanium, also provides two electrons to the cage. Otherwise, the remaining four groups are group 14 element ER species, as in **1** and **2**. The main difference is that there is a transannular Ge−C bond, whereas the analogous Ge−Ge bond is absent in **1** and **2**, where it is manifested by electron density at the two corresponding germaniums (Ge(2) and Ge(4)).

To throw further light on the bonding, calculations[18] were carried out on the model species Ge_5R_4 (R = Me, Ph). An optimized structure similar to that experimentally obtained for **1** was calculated in both cases, with Ge−Ge distances in the $(GeR)_4$ unit near 2.4 Å and a fold angle near 138°. Inspection of the orbital pictures shows that for the HOMO there is non bonded electron density at Ge(2) and Ge(4) with some correlation to weak Ge(5)−Ge(2) and Ge(5)−Ge(4) interactions. HOMO-1 is strongly correlated with Ge(5)−Ge(1),Ge(3) bonding, and HOMO-2 is exclusively related to Ge−Ge σ-bonding within the $(GeR)_4$ unit. HOMO-3 correlates with the lone-pair character at Ge(5) with some transannular Ge−Ge bonding involving Ge(2)−Ge(5) and Ge(4)−Ge(5) and nonbonded electron density at Ge(1) and Ge(3). HOMOs −4 to −7 mainly concern Ge−Ge and Ge−C bonding. Overall, the calculations support the existence of a lone pair at Ge(5) and electron density at Ge(2) and Ge(4) and suggest that the two-center−two-electron Ge−Ge bonding description of the six Ge−Ge bonds inthe cluster is a reasonable approximation. In valence bond terms the resonance forms indicated by A and B may be the simplest picture of the bonding



---

[16] A similar bonding scheme is obtainable from the interaction of three orbitals of the unsubstituted germanium and the planar c-Ge_4R_4 array, which affords three bonding, three antibonding, and one nonbonding MO. However, this does not take into account the fact that the apical Ge is connected to the Ge_4R_4 moiety only through two Ge−Ge bonds.

[17] Lee, V. Y.; Inchinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2002**, *124*, 9962.

[18] Alternatively, in a gedanken experiment, the cluster may be ionized to Ge^{2+} and the formally aromatic dianion $[c\text{-}Ge_4R_4]^{2-}$. However, the covalency of the Ge−Ge bonds make such a scheme unlikely. The geometry optimizations were performed in the gaseous phase using DFT theory with a hybrid B3LYP functional. The molecular structures were first preoptimized with the Los Alamos LanL2DZ basis set using an effective core potential (ECP) approximation; a subsequent full optimization of the geometry to the real minima was performed with the 6−31g* basis set. All of the calculations were performed with the Gaussian03 package,[18a] and the representations of the molecular structures and molecular orbitals were generated with the MOLEKEL program.[18b] The optimized geometrical parameters do not differ significantly between the two model structures containing methyl and phenyl substituents. In the Ge_5Ph_4 model the calculated bond distances are significantly shorter than those obtained from the crystal structure. This is most likely related to the steric constraints present in the crystal cell due to the interaction between bulky C_6H_3-2,6-Mes_2 groups. The optimized Ge−Ge bond angles (deg) and distances (Å) in Ge_5Ph_4 are as follows: Ge(1)−Ge(2) = 2.426, Ge(1)−Ge(4) = 2.427, Ge(2)−Ge(3) = 2.423, Ge(3)−Ge(4) = 2.426, Ge(1)−Ge(5) = 2.394, Ge(3)−Ge(5) = 2.394; Ge(4)−Ge(1)−Ge(5) = 77.4, Ge(2)−Ge(1)−Ge(5) = 77.0, Ge(4)−Ge(1)−Ge(2) = 87.5, Ge(1)−Ge(2)−Ge(3) = 82.6, Ge(2)−Ge(3)−Ge(4) = 87.5, Ge(1)−Ge(4)−Ge(3) = 82.4, Ge(1)−Ge(2)−Ge(3)−Ge(4) = 32.9. (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomeli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ciolowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Koramomi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Reploge, E. S.; Pople, J. A. *Gaussian 03*, Revision A.1; Gaussian, Inc., Pittsburgh, PA, 2003. (b) Flukiger, P.; Luthi, H. P.; Portmann, S.; Weber, J. *MOLEKEL 4.3*; Swiss Center for Scientific Computing, Manno, Switzerland, 2000−2002.

in these clusters. However, the bonding can also be represented by the singlet biradicaloid form C. Stable singlet biradicaloid compounds represent a growing class of main-group compounds whose importance is only beginning to be recognized.[8,19,20]

Acknowledgment. We are grateful to the National Science Foundation for financial support through the CRC program and the donors of the Petroleum Research Fund administered by the American Chemical Society. M.B. thanks the Swiss National Science Foundation for support through Grant No. 8220-067593.

Supporting Information Available: Crystallographic data, as CIF files, for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049921Z

---

(19) Grützmacher, H.; Breher, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 4006.

(20) Scheschkewitz, D.; Amii, H.; Gornitzka, H.; Schoeller, W. W.; Bourissou, D.; Bertrand, G. *Science* **2002**, *295*, 1344.