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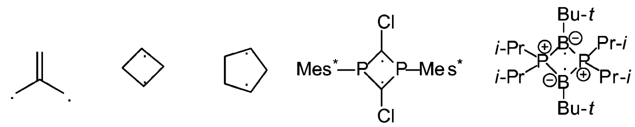
Synthesis and Characterization of the Non-Kekulé, Singlet Biradicaloid $Ar'Ge(\mu\text{-}NSiMe_3)_2GeAr'$ ($Ar' = 2,6\text{-}Dipp_2C_6H_3$, $Dipp = 2,6\text{-}i\text{-}Pr_2C_6H_3$)

Chunming Cui, Marcin Brynda, Marilyn M. Olmstead, and Philip P. Power*

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

Received February 12, 2004; E-mail: pppower@ucdavis.edu

Biradicals are thought to play a crucial role in bond breaking and formation.[1] Typical organic biradicals such as trimethylenemethyl (**I**), cyclobutane-1,3-diyl (**II**), and cyclopetane-1,3-diyl (**III**) are short-lived species. Upon modification of the substituents at the central atoms, a few biradicals can be observed spectropically.[2] However, in 1995 Niecke and co-workers reported the 1,3-diphosphacyclobutane-2,4-diyl Mes*P(μ-CCl)$_2$PMes* (Mes* = 2,4,6-t-$Bu_3C_6H_2$) (**IV**), which is a stable compound with carbon-centered singlet biradical character.[3] Following this finding, several further biradicals with C_2P_2 framework were also reported.[4] More recently, Bertrand and co-workers have described a different class of boron-centered singlet biradicaloids, for example i-$Pr_2P(\mu$-BBu-$t)_2PiPr_2$ (**V**), and have examined some of their reactions.[5]



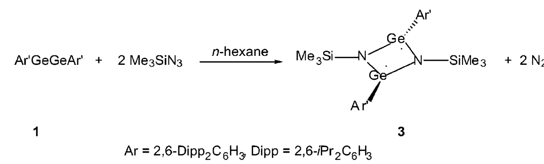
I II III IV V

For heavier Group 14 elements, Sita and Kinoshita have reported the pentastanna[1.1.1]propellane $Sn_5(C_6H_3\text{-}2,6\text{-}Et_2)_6$ and related derivatives, which possess singlet biradical character.[6] In addition, the germanium moiety in the Zintl phase Ba_3Ge_4 has biradical characteristics.[7] We have recently reported the synthesis and structures of the germanium and tin alkyne analogues Ar′MMAr′ (M = Ge, **1**; M = Sn, **2**)[8] and are currently investigating their reaction chemistry with a variety of unsaturated small molecules including CO, H_2, alkynes, isonitriles, nitriles, and azides and so on. We now report that the reaction of **1** with the azide Me_3SiN_3 leads to the formation of the new singlet biradicaloid, the germanium-centered Ar′Ge(μ-$NSiMe_3)_2$GeAr′ (Ar′ = 2,6-$Dipp_2C_6H_3$, Dipp = 2,6-i-$Pr_2C_6H_3$).

The reaction of **1** with an excess of Me_3SiN_3 in n-hexane at ca. 25 °C yielded, after workup, dark violet, almost black crystals of Ar′Ge(μ-$NSiMe_3)_2$GeAr′ (**3**, Scheme 1).[9] Compound **3** is extremely air and moisture sensitive and rapidly changes to a white powder once exposed to the atmosphere. The dark violet color disappears when it is heated to 145 °C in a sealed capillary tube. Crystals of **3** could be stored under an inert atmosphere, but its solutions in benzene, toluene, and cyclohexane become pale yellow after 2 days. The isolation of products of these reactions are currently under investigation. Compound **3** has been characterized by ^{1}H and ^{13}C NMR, IR, UV spectroscopy, and single-crystal X-ray analysis.

The structure of **3** has a crystallographically required center of symmetry with a perfectly planar Ge_2N_2 core (Figure 1).[10] The geometry at nitrogen is trigonal-planar (sum of interligand angles = 359.97(8)°) and that of germanium is pyramidal (sum of interligand angles = 322.10(7)°). The two Ar′ rings are arranged in a trans fashion across the four-membered Ge_2N_2 ring. The Ge−N bond lengths (1.8626(16) and 1.8741(16) Å) are within the range found in other dimeric germanium imide species (1.70−1.88 Å).[11] The Ge−Ge separation (2.755 Å) is about 0.3 Å longer than a normal Ge−Ge single bond (average 2.44 Å),[12] but it is comparable to those found in the cyclic dimers $(R'_2GeNR'')_2$ (R′ = 2,4,6-$Me_3C_6H_2$, R″ = $NCC_{12}H_8$; R'_2 = $MeNCH_2CH_2NMe$, R″ = NSi-(t-$Bu)_3$) and $(GeNR)_2$ (R = Mes*, 2,4,6-$(CF_3)_3C_6H_2$) (2.66−2.86 Å) in which there is no Ge−Ge bonding.[11] The long Ge−Ge separation is consistent with the biradical character of **3**. Nonetheless, **3** displays no EPR signal at 77−300 K. It has normal ^{1}H and ^{13}C NMR signals which also indicate that it has a singlet ground state.

Scheme 1



DFT calculations performed on the model compound MeGe(μ-$NSiH_3)_2$GeMe, where the ligand Ar′ was replaced with a smaller methyl group and $SiMe_3$ with SiH_3, predict geometrical features that are similar to those found in the X-ray structure of **3**.[13] Inspection of the frontier Kohn−Sham orbitals (Figure 2) shows that the HOMO corresponds mainly to a nonbonding combination centered on germanium atoms with a minor component at the nitrogen centers. This HOMO orbital also has a weak Ge−C component. The HOMO-1 and HOMO-2 orbitals correspond to out of phase and in phase combinations of nitrogen p orbitals with minor ligand components. The calculated energy differences between the orbitals are HOMO−LUMO, $\Delta E = 57.97$; HOMO−HOMO-1, $\Delta E = 30.44$; HOMO-1-HOMO-2 $\Delta E = 16.53$ kcal/mol. The energy difference between the optimized singlet and triplet state of MeGe-(μ-$NSiH_3)_2$GeMe with use of the spin-corrected energy gap method proposed by Yamaguchi and co-workers[14] is 17.51 kcal/mol, which is very similar to the 17.2 kcal/mol calculated for **V**.[5a]

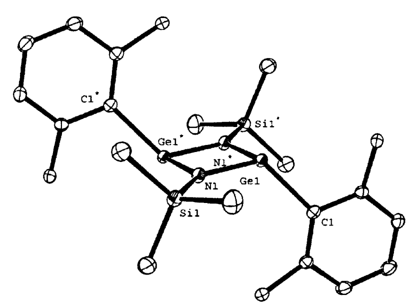


Figure 1. Thermal ellipsoid of **3** with 30% probability. Hydrogen atoms and Dipp rings (except *ipso* carbon atoms) are not shown. Selected bond distances (Å) and angles (deg) for **3**: Ge1−N1 1.8626(16), Ge1−N1* 1.8741(16), Ge1−C1 2.0413(18), Ge1−Ge1* 2.7550(4); N1−Ge1−N1* 85.00(7), Ge1−N1−Ge1* 95.00(7), N1−Ge1−C1 123.28(7), N1*-Ge1−C1 113.82(7), Si1−N1−Ge1 135.35(9), Si1−N1−Ge1* 129.62(9).

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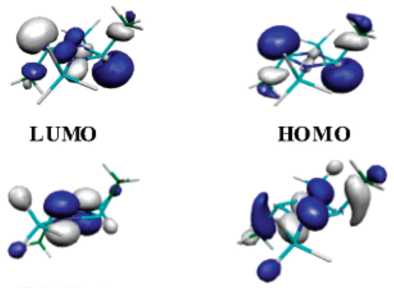

Figure 2. Representations of the frontier Kohn−Sham orbitals of the MeGe(μ-NSiH$_3$)$_2$GeMe from DFT calculations.[13]

The UV−vis spectrum of **3** in *n*-hexane shows a strong absorption maximum at $\lambda = 521$ nm ($\epsilon = 5600$), which is red-shifted compared to those of **IV** (478 nm)[3] and **V** (446 nm).[5a] This corresponds to an energy difference of 54.88 kcal/mol, which is close to the calculated HOMO−LUMO gap (57.97 kcal/mol) for MeGe(μ-NSiH$_3$)$_2$GeMe.

In summary, the reaction of **1** with the azide Me$_3$SiN$_3$ afforded a new non-Kekulé molecule, **3**. Compound **3** has Ge-centered biradical character as indicated by the intense color, the Ge−Ge separation, and its high reactivity toward solvents.[15] The DFT calculations support no bonding interaction between the two germanium atoms as well as a singlet ground state. The extent of the biradical character of **3**, as judged by occupancy numbers for bonding and nonbonding orbitals associated with the two radical sites, is not currently available, but the similarities of the calculated singlet−triplet energies for **V** and **3** suggest their similar occupancy.[16]

Acknowledgment. We thank the National Science Foundation for support of this work. The work of M. Brynda in Davis was supported by Swiss National Science Foundation Grant 8220-067593. We are also grateful to Professor G. Bertrand and M. F. Lappert[17] for useful discussions.

Supporting Information Available: The X-ray data (cif) for **3**. This material is available free of charge via Internet at http://pubs.acs.org.

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(9) All manipulations were carried out under anaerobic and anhydrous conditions. **3**: to a solution of **1** (0.100 g, 0.106 mmol) in *n*-hexane (3 mL) was added an excess of Me$_3$SiN$_3$ (0.073 g, 0.64 mmol). After the reaction mixture was stirred at room temperature for 48 h, it was stored at 5 °C for 2 days to afford dark violet crystals of **3** (0.104 g, 88%). Mp: 145 °C (dec). ^{1}H NMR (d_8-toluene, 399.77 MHz): δ −0.30 (s, 18H, Si*Me*$_3$), 0.91 (d, 24H, CH*Me*$_2$), 1.18 (d, 24H, CH*Me*$_2$), 2.75 (sept, 8H, C*H*Me$_2$), 6.91 (m, 6H, Ar-*H*), 7.10 (m, 12H, Ar-*H*). ^{13}C NMR (d_8-toluene, 100.52 MHz): δ 5.15 (Si*Me*$_3$), 23.92 (CH*Me*$_2$), 26.34 (CH*Me*$_2$), 31.82 (*C*HMe$_2$), 123.2, 125.9, 129.0, 131.2, 137.2, 139.1, 154.6, 174.4 (Ar−C). IR (KBr, Nujol): 1928 (w), 1586 (w), 1571 (m), 1552 (w), 1421 (w), 1340 (w), 1318 (w), 1245 (s), 1226 (w), 1178 (w), 1160 (m), 1125 (w), 1070 (w), 1055 (m), 955 (m), 915 (s), 834 (s), 816 (m), 790 (m), 755 (s), 741 (s). UV−vis (*n*-hexane): $\lambda_{max} = 521$ nm ($\epsilon = 5600$).

(10) Crystal data for **3** at 91(2) K with Mo Kα ($\lambda = 0.710\,73$ Å): monoclinic, space group *C*2/*c*, $a = 23.9746(16)$, $b = 11.6981(7)$, and $c = 25.186(2)$ Å, $\beta = 107.243(4)°$, R1 = 0.0385 for 7873 observed reflections ($I > 2\sigma(I)$), wR2 = 0.1056 (all data).

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(13) The geometry optimizations were performed in gaseous phase using DFT theory with hybrid B3LYP functional. The molecular structure of MeGe-(μ-NSiH$_3$)$_2$GeMe was first optimized with Los Alamos LanL2DZ basis set using an effective core potential (ECP) approximation; a subsequent optimization of the geometry was performed with 6-31g* basis set using unrestricted calculations with broken symmetry (BS) technique. All the calculations were performed with the Gaussian 03 package[13b] and the representations of the molecular structures and molecular orbitals were generated with the MOLEKEL program.[13b] The optimized geometrical parameters (bond distances (Å) and angles (deg), geometry optimized for a singlet state) are almost identical with those found in the crystal structure of **3**: Ge1−N1 1.866, Ge1−N1* 1.868, Ge1−C1 1.980, Ge1−Ge1* 2.735; N1−Ge1−N1* 85.8, Ge1−N1−Ge1* 94.2, N1−Ge1−C1 108.6, Si1−N1−Ge1 133.0, Si1−N1−Ge1* 132.8. The only exceptions are the angles between the N−Ge and Ge−C bonds, which are slightly less opened in the optimized model structure ($\Delta = 14.7°$). This is most probably related to the more important sterical constraints imposed by the bulky Dipp ligand. (a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr. T.; Kudin, K. N. Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyata, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene. M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Ciolowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; 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.

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(15) Compound **3** also reacts directly with H$_2$ in solution at room temperature and pressure to give a product that has been identified tentatively as Ar′(H)Ge(μ-NSiMe$_3$)$_2$Ge(H)Ar′. Details of the reactivity of **3** will be reported subsequently.

(16) The calculated occupancy for **V** is ca. 0.17, see: Jung, Y.; Head-Gordon, M. *ChemPhysChem* **2003**, *4*, 522.

(17) Professor M. F. Lappert has informed us that he and co-workers have synthesized a biradicaloid Sn$_2$N$_2$ species with different substtuents and via a route different than that in Scheme 1.

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