Characterization and Bonding of the Cation $[\mathrm{Ge}\{\mathrm{N}(\mathrm{C}_6\mathrm{H}_3\text{-}2,6\text{-}i\text{-}\mathrm{Pr}_2)\mathrm{CMe}\}_2\mathrm{CH}]^+$: Comparison with the Isoelectronic $\mathrm{Ga}\{\mathrm{N}(\mathrm{C}_6\mathrm{H}_3\text{-}2,6\text{-}i\text{-}\mathrm{Pr}_2)\mathrm{CMe}\}_2\mathrm{CH}$

Matthias Stender, Andrew D. Phillips, and Philip P. Power*

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

Received June 25, 2001

The recently reported, two-coordinate, low-valent metal complexes M(Dipp$_2$nacnac) (M = Al[1] or Ga;[2] Dipp$_2$nacnac = $\{\mathrm{N}(\mathrm{C}_6\mathrm{H}_3\text{-}2,6\text{-}i\text{-}\mathrm{Pr}_2)\mathrm{C}(\mathrm{Me})\}_2\mathrm{CH}$), M′(Cl)(Dipp$_2$nacnac) (M′ = Ge and Sn),[3] and M′(X)(Mes$_2$nacnac) (X = Cl or N_3)[4] have shown that large β-diketiminate ligands[5] are particularly useful for stabilizing unusual, low oxidation state main group element derivatives. In particular, the two-coordinate, low-valent Al and Ga compounds have a rich chemistry which is currently under intensive exploration.[6,7] Computational data show that the HOMO involves the Al or Ga lone pair which may act as the donor orbital and is the source of its Lewis base behavior.[8] Surprisingly, the LUMO is not based on the Al 3p or Ga 4p orbital. Instead, it is a N−C π*-orbital located on the $\mathrm{N}_2\mathrm{C}_3$ skeleton of the β-diketiminate ring. We wished to examine the effects of varying the metal atom on the ordering of the molecular energy levels. Specifically, the replacement of the Al or Ga by a cationic center is of importance owing to the current interest in electrophilic catalysts stabilized by bidentate nitrogen ligands.[9−11] We now report the synthesis of the cationic [Ge(Dipp$_2$nacnac)]$^+$ (isoelectronic to Ga(Dipp$_2$nacnac)[2]) as [Ge(Dipp$_2$nacnac)][HO$\{\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_3\}_2$] and show that the energies and ordering of the orbitals differ considerably from those of its Al and Ga analogues.

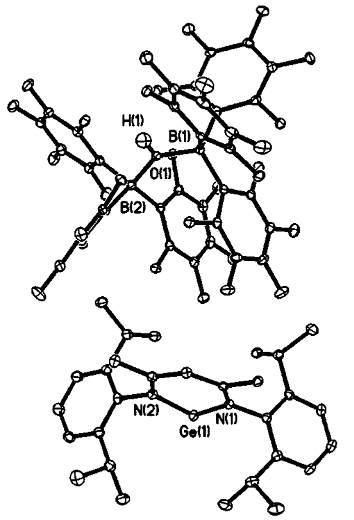

Figure 1. Thermal ellipsoid (30%) plot of **1**. H atoms (except OH) are not shown.

The title compound [Ge(Dipp$_2$nacnac)][HO$\{\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_3\}_2$] (**1**) was synthesized[12] as colorless crystals by adding $\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_3$ to Ge(Cl)(Dipp$_2$nacnac) in the presence of water. It was characterized by ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR and IR spectroscopy, as well as X-ray crystallography.[13] The structure (Figure 1) consists of separate cations and anions. The closest approach of the anion to Ge in **1** involves a fluorine at 3.01 Å. This distance is much longer than the 1.79 or 1.91 Å (quasi terminal) and 2.09 Å (bridging) Ge−F distances in the structure of GeF_2.[14] The structural parameters of the borate anion are similar to those reported in the salt [Ir(η^5-$\mathrm{C}_5\mathrm{H}_5$)($\mathrm{C}_8\mathrm{H}_{12}$)H][HO$\{\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_3\}_2$].[15] The cation structure consists of an essentially planar $\mathrm{GeN}_2\mathrm{C}_3$ array with two-coordinate Ge, a Ge−N distance of 1.894(2) Å, and a N−Ge−N angle of 93.0(1)°. The β-diketiminate N−C and C−C ring distances have average values of 1.348(4) and 1.392(3) Å and indicate delocalization of the π-electrons. The Dipp groups are oriented almost perpendicular to the $\mathrm{GeN}_2\mathrm{C}_3$ plane. These data can be compared to the slightly longer Ge−N distances (1.901(5) and 1.917(5) Å), and the acute N−Ge−N angle (81.7(2)°) in the aminotropoiminate (ATI) salt [$\{(i\text{-Pr})_2\mathrm{ATI}\}$Ge][($\eta^5$-$\mathrm{C}_5\mathrm{H}_5$)(Cl)$_2$Zr($\mu$-Cl)$_3$Zr(Cl)$_2$($\eta^5$-$\mathrm{C}_5\mathrm{H}_5$)] which has an essentially two-coordi-

---

(1) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4274.

(2) Hardman, N. J.; Eichler, B. E.; Power, P. P. *Chem. Commun.* **2000**, 1991.

(3) Ding, Y.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Power, P. P. *Organometallics* **2001**, *20*, 1190.

(4) Ayers, A. E.; Klapotke, T. M.; Dias, H. V. R. *Inorg. Chem.* **2001**, *40*, 1000.

(5) Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514.

(6) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 453.

(7) (a) Hardman, N. J.; Power, P. P. *Inorg. Chem.* **2001**, *40*, 2474. (b) Hardman, N. J.; Cui, C.; Roesky, H. W.; Fink, W. H.; Power, P. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2172.

(8) Hardman, N. J.; Phillips, A. D.; Power, P. P. *Adv. Chem. Ser.*, in press.

(9) Lee, L. W. M.; Piers, W. E.; Elsegood, M. R. J.; Clegg, W.; Parvez, M. *Organometallics* **1999**, *18*, 2947.

(10) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673.

(11) Cosledan, F.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1999**, 705.

(12) All manipulations were carried out under anaerobic conditions. A solution of 0.56 g (1.07 mmol) Ge(Cl)(Dipp$_2$nacnac)^3 in toluene (10 mL) was added at room temperature to a solution of 0.55 g (1.08 mmol) $\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_3$ in toluene (10 mL) which had been treated with 20 μL of degassed $\mathrm{H}_2\mathrm{O}$ (Ge(Cl)Dipp$_2$nacnac) did not display a reaction with $\mathrm{H}_2\mathrm{O}$ after stirring for several days at room temperature). The yellow solution was stirred for 12 h. The solvent was removed under reduced pressure, and the remaining white solid was extracted with hexanes (40 mL). After filtration through Celite the volume of the solution was reduced to incipient crystallization (ca. 25 mL). Storage for 12 h at ca. 25 °C yielded colorless crystals of [Ge(Dipp$_2$nacnac)][(μ-HO)(B$\{\mathrm{C}_6\mathrm{F}_5\}_3$)$_2$] suitable for X-ray crystallography. Yield: 0.33 g, 0.22 mmol, 21%, mp 93−95 °C (turns yellow above 85 °C; forms a yellow oily solid above the melting point). Calcd for $\mathrm{C}_{65}\mathrm{H}_{42}\mathrm{N}_2\mathrm{OB}_2\mathrm{F}_{30}\mathrm{Ge}$: C, 50.98; H, 2.77. Found: C, 50.34; H, 2.91. ^{1}H NMR ($\mathrm{C}_6\mathrm{D}_6$): δ (ppm) = 9.45 (m, broad, 1H, O*H*), 7.2−7.1 (m, 6H, Ph), 4.23 (s, 1H, γ-CH), 3.41 (sept, 4H, ^3J = 6.8 Hz, C*H*Me$_2$), 1.59 (s, 6H, Me), 0.94 (d, 12H, ^3J = 6.8 Hz, CH*Me*$_2$), 0.68 (d, 12H, ^3J = 6.8 Hz, CH*Me*$_2$). ^{13}C NMR ($\mathrm{C}_6\mathrm{D}_6$): δ (ppm) = 173.1 (CN), 145.9, 145.1, 124.5 (Ph), 92.4 (γ-C), 28.5 (*C*HMe$_2$), 24.2 (CH*Me*$_2$), 23.6 (CH*Me*$_2$), 22.7 (Me), 137.9 (d, $J_{\mathrm{C-F}}$ = 246 Hz), 139.5 (d, $J_{\mathrm{C-F}}$ = 250 Hz), 149.3 (d, $J_{\mathrm{C-F}}$ = 244 Hz). ^{11}B NMR ($\mathrm{C}_6\mathrm{D}_6$): δ (ppm) = −3.52. ^{19}F NMR ($\mathrm{C}_6\mathrm{D}_6$): δ (ppm) = −136.5 (m, $^3J_{\mathrm{F-F}}$ = 20 Hz, *m*-F), −160.7 (m, $^3J_{\mathrm{F-F}}$ = 20 Hz, *p*-F), −165.7 (m, $^3J_{\mathrm{F-F}}$ = 20 Hz, *o*-F). IR (Nujol): ν (cm^{-1}) = 3540 (w, sharp, ν {(O−H)} 750(w).

(13) Crystal data at 90 K with Mo Kα (λ = 0.71073 Å) radiation: $\mathrm{C}_{65}\mathrm{H}_{42}\mathrm{N}_2\mathrm{OB}_2\mathrm{F}_{30}\mathrm{Ge}$, fw 1531.22, colorless block, a = 20.2586(7) Å, b = 17.5332(6) Å, c = 18.5394(6) Å, β = 109.736(1)°, monoclinic, space group $P2_1/c$, V = 6198.3(4) Å^3, Z = 4, ρ_{calcd} = 1.641 g cm^{-3}, μ = 0.631 mm^{-1}, R1 = 0.0561 for 10167 ($I > 2\sigma(I)$) reflections.

(14) Trotter, J.; Akhtar, M.; Bartlett, N. *J. Chem. Soc. A* **1966**, 30.

(15) Danopoulos, A. A.; Galsworthy, J. R.; Green, M. L. H.; Cafferhey, S.; Doerrer, L. H.; Hursthouse, M. B. *Chem. Commun.* **1998**, 2529.

10.1021/ic0155582 CCC: $20.00

Table 1. Selected Experimental and Computational Structural Parameters for Gallium and Germanium β-Diketiminates

	Ga(Dipp$_2$-nacnac)[a]	[Ge(Dipp$_2$-nacnac)]$^+$ [b]	[Ge{N(H)C(H)}$_2$CH]$^+$ [b]
M−N(Å)	2.054(2)	1.894(2)	1.910
C−N	1.338(2)	1.348(4)	1.357
C−C	1.400(2)	1.392(3)	1.401
N−M−N	87.53(5)	93.0(1)	93.0

[a] Reference 2. [b] This work.

nate cationic Ge with weak interactions of ca. 3.12 Å to two chlorides from counteranions (cf. 2.368(2) Å for the Ge−Cl single bond in {(i-Pr)$_2$ATI}GeCl).[16] A further comparison is possible with the structure of [HB(3,5-Me$_2$pz)$_3$Ge][I] (pz = pyrazolyl) in which Ge(II) is pyramidally coordinated by three nitrogens (av Ge−N = 2.03(2) Å).[17] The 0.14 Å increase in the Ge−N distance in comparison to **1** is probably due to the higher Ge coordination number.

The structure of **1** may also be compared to the isoelectronic species Ga(Dipp$_2$nacnac).[2] Data for both structures and computational results[18] for [Ge{N(H)C(H)}$_2$CH]$^+$ are given in Table 1. The Ge−N and Ga−N distances differ by ca. 0.16 Å. This is partly due to the smaller radius of Ge; cf. 1.22 Å for Ge vs 1.25 Å for Ga.[19] However, most of the difference is probably a result of the $\delta+$ at Ge which strengthens the attraction between Ge and N. In spite of this, the Ge−N bonds are longer than single bonds between two-coordinate Ge and three-coordinate N in neutral rings, e.g., Ge−N, av 1.859(2) Å in {Ge(NC$_6$H$_3$-2,6-i-Pr$_2$)}$_3$[20] or 1.85(4) Å in {Ge(NC$_6$H$_2$-2,4,6-t-Bu$_3$)}$_2$.[21] This can be attributed to the partial dative character of the Ge−N bonding to the β-diketiminate ligand.

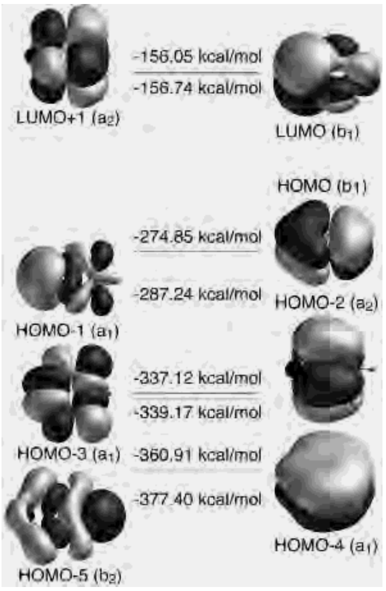

Figure 2. Calculated[18] valence electron density surfaces and energies of the frontier molecular orbitals in [Ge{N(H)CH}$_2$CH]$^+$.

Further insight into the bonding in [Ge(Dipp$_2$nacnac)]$^+$ is provided by the electron density surfaces and orbital energies shown in Figure 2.[18] Unlike Ga(Dipp$_2$nacnac), the lone pair corresponds to the HOMO−1 rather than the HOMO. The LUMO, which is associated with the Ge 4p orbital, is just slightly lower than the C−N π^* orbital (LUMO+1) which corresponds to the LUMO in the case of Ga(Dipp$_2$nacnac). Replacing Ga by Ge$^+$ has resulted in lowering the energy of the lone pair and 4p levels, and this is in accordance with the higher electronegativity and charge at the Ge. The orbitals most strongly associated with Ge−N bonding are the HOMO (which is π-bonding with respect to Ge−N and C−C and antibonding with respect to C−N) and the HOMO−3 level (which has Ge−N σ-bonding among other σ-bonding components). There is also a Ge−N bonding component in HOMO−4 which is a π-bond that encompasses the whole ring. The Ge−N bond may also be strengthened by the N−H− lone pair interaction as part of HOMO−5. However, it can be seen that the lone pair HOMO−1 is antibonding with respect to the Ge−N bond. Although the Ge−N bonds have multiple character, it is probable that the overall bond order is less than unity. It will be interesting to see if the HOMO−1 shows Lewis base behavior despite the formal positive charge at Ge.

Acknowledgment. We are grateful to the National Science Foundation for financial support and Albemarle Corporation for a generous gift of B(C$_6$F$_5$)$_3$. This work was partially supported by the National Computational Science Alliance under Grant No. 10047 using the SGI Origin 2000.

Supporting Information Available: An X-ray file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0155582

---

(16) Dias, H. V. R.; Wang, Z. *J. Am. Chem. Soc.* **1997**, *119*, 4650.
(17) Reger, D. L.; Coan, P. S. *Inorg. Chem.* **1996**, *35*, 258.
(18) Calculations by a hybrid method[18a] of Hartree−Fock and density functional theories (DFT) with Becke's exchange functional (B3)[18b] and the Lee−Yang−Parr nonlocal correlation function (LYP).[18c] A basis set of 6-31G was employed for all atoms. Calculations were done using the Gaussian 98 suite of programs.[18d] The molecule represents an energy minimum and was optimized as having C_{2v} symmetry. (a) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. (b) Becke, A. D. *Chem. Phys.* **1993**, *98*, 5648. (c) Lee C.; Wang, Y.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785. (d) 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.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Monokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Hallacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Conzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
(19) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon: Oxford, 1984; pp 1274, 1280.
(20) Bartlett, R. A.; Power, P. P. *J. Am. Chem. Soc.* **1990**, *112*, 3660.
(21) Hitchcock, P. B.; Lappert, M. F.; Thorne, A. J. *Chem. Commun.* **1990**, 1587.