ORGANOMETALLICS
Communication
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Synthesis, Characterization, and Thermolysis of Dibenzo-7-dimethylgermanorbornadiene

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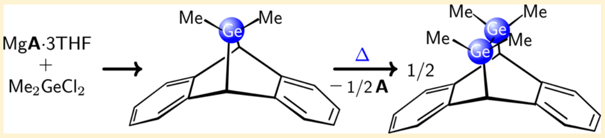
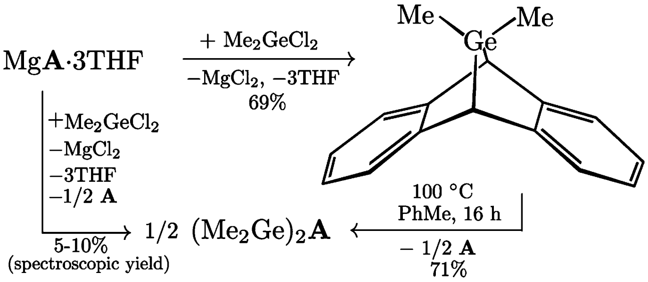
Supporting Information

ABSTRACT: The dibenzo-7-dimethylgermanorbornadiene Me_2GeA (**A** = $C_{14}H_{10}$) has been synthesized in one step by treatment of Mg**A**·3THF with Me_2GeCl_2 in tetrahydrofuran (−35 °C) and isolated in 69% yield. The thermolysis of Me_2GeA in toluene leads to the effective expansion of the bicyclic framework to the dibenzo-7,8-tetramethyldigermabicyclo[2.2.2]octadiene $(Me_2Ge)_2A$, isolated in 71% yield (based on germanium). The bicyclic compounds Me_2GeA and $(Me_2Ge)_2A$ have been characterized by single-crystal X-ray diffraction studies and their structures discussed.



Interesting primarily as sources of germylenes (R_2Ge), 7-germanorbornadienes are traditionally prepared in a cumbersome multistep synthesis culminating with the [4 + 2] Diels−Alder reaction of a germole with a benzyne.[1] Herein we show that dibenzo-7-dimethylgermanorbornadiene Me_2GeA (**A** = $C_{14}H_{10}$) can be assembled directly in good yield in a one-step synthesis from Mg**A**·3THF and Me_2GeCl_2 (see Scheme 1).

Scheme 1. Synthesis of Me_2GeA (Isolated in 69% Yield) by Treatment of MgA·3THF with Me_2GeCl_2 at −35 °C and Formation of $(Me_2Ge)_2A$ (Isolated in 71% Yield)



Assembling 7-heteroatom-norbornadiene architectures via the salt metathesis reaction of an anthracenide salt and a main-group halide reaction partner is precedented for silicon,[2,3] tin,[4,5] and more recently phosphorus,[6] yet Me_2GeA has not been previously reported in the literature. In 1980 Neumann was first to report the synthesis of a 7-germanorbornadiene and established that such species are thermal precursors to germylene (Me_2Ge), the heavier analogue of a carbene. Proposing this process occurs in two steps through the intermediacy of a biradical,[1] he showed that Me_2Ge inserts into the Ge−C bond of a 7-germanorbornadiene, giving rise to 7,8-digermabicyclo[2.2.2]octadienes.[7] Exploring the behavior of the latter species upon thermolysis, the tetramethyldigermene $Me_2Ge{=}GeMe_2$ was generated for the first time;[8] similar to the case for other heavy alkenes,[9] tetramethyldigermene could be trapped by anthracene, giving rise to $(Me_2Ge)_2A$ in a [4+2] Diels−Alder cycloaddition process.[7,8]

Our recent synthesis and isolation of unprotected 7-phosphanorbornadienes obtained directly from the reaction of select dichlorophosphines with Mg**A**·3THF[6] made us wonder if 7-germanorbornadienes could be accessed similarly. Addition of solid Mg**A**·3THF (1 equiv) to a chilled (−35 °C) tetrahydrofuran (THF) solution of Me_2GeCl_2 (1 equiv) effected an immediate color change to pale yellow. ^1H NMR spectroscopic analysis of the crude reaction mixture, after removal in vacuo of all volatile materials, revealed the formation of one major product, Me_2GeA, as well as the presence of small amounts of $(Me_2Ge)_2A$ and anthracene. Isolated pure in 69% yield by selective crystallization from a chilled saturated Et_2O solution, Me_2GeA is an air-stable, crystalline, colorless compound.

We wondered if under similar reaction conditions other germanium dichlorides could be used to form the 7-germanorbornadiene architecture; treatment of diphenylgermanium dichloride (Ph_2GeCl_2), germanium tetrachloride ($GeCl_4$), or the germanium(II) dichloride (dioxane)$GeCl_2$ with Mg**A**·3THF in thawing THF, however, only led to the formation of anthracene, magnesium chloride, and insoluble reduced germanium species, likely $(Ph_2Ge)_n$ and Ge(0).[11] These results mirror our previous observation that $PhPCl_2$ and PCl_3 do not give rise to the corresponding 7-phosphanorbornadiene derivatives on treatment with Mg**A**·3THF.[6,12]

Probing the thermal stability and chemical behavior toward retro Diels−Alder chemistry, a solution of Me_2GeA in toluene was heated for ca. 16 h at 100 °C, to ensure complete consumption of the starting material. ^1H NMR analysis of the

Special Issue: Gregory Hillhouse Issue

Received: June 22, 2015

DOI: 10.1021/acs.organomet.5b00529
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crude mixture indicated the formation of anthracene and (Me$_2$Ge)$_2$**A**, which after removal of anthracene using a charcoal plug was isolated as a pure substance in 71% yield (based on germanium). Obtained previously from Li$_2$**A** and [Me$_2$Ge(Cl)]$_2$ in 59% yield,[7] (Me$_2$Ge)$_2$**A** is an air-stable, colorless compound that crystallizes readily from Et$_2$O. When the thermolysis of Me$_2$Ge**A** was performed in the presence of excess diphenylacetylene (6 equiv), a competent trap for dimethylgermylene,[1] the only observed products were anthracene and (Me$_2$Ge)$_2$**A**. This suggests that, at the high temperature necessary for the thermolysis, Me$_2$Ge**A** is a better trap for dimethylgermylene than the alkyne. It is likely that the process of (Me$_2$Ge)$_2$**A** formation in the thermolysis of Me$_2$Ge**A** involves the insertion of dimethylgermylene into the Ge−C bond of Me$_2$Ge**A**, although dimerization of free Me$_2$Ge followed by reaction of Me$_2$Ge=GeMe$_2$ with anthracene cannot be excluded. Using DFT methods,[13] we estimated the change in free energy (ΔG) associated with the thermal conversion of Me$_2$Ge**A** to (Me$_2$Ge)$_2$**A** in the transformation 2 Me$_2$Ge**A** → (Me$_2$Ge)$_2$**A** + **A** to be ca. −37 kcal/mol of (Me$_2$Ge)$_2$**A** (see DFT Calculations in the Supporting Information).

The higher thermal stability of Me$_2$Ge**A** in comparison to that of benzo-7-dimethylgermanorbornadiene, with a half-life $t_{1/2}$ = 40 min in CCl$_4$ solution at 70 °C,[1] suggests a stabilizing effect of the second benzo group on the 7-heteronorbornadiene architecture, also observed in the case of phosphorus and nitrogen.[6,14]

X-ray-quality crystals of Me$_2$Ge**A** and (Me$_2$Ge)$_2$**A** were grown from saturated solutions in diethyl ether (see Figures 1 and 2 and X-ray Diffraction Studies in the Supporting Information). Of approximate C_{2v} symmetry, the two structures feature a strained architecture at the germanium centers, with a C13−Ge−C14 angle of 77.72(5)° in Me$_2$Ge**A** and a C13−Ge2−Ge1 angle of 95.53(3)° in (Me$_2$Ge)$_2$**A**, respectively. The strain imposed by the bicyclic architectures is also visible in the Ge−C bond lengths, which average 1.943 Å for Ge−C$_{\text{methyl}}$, typical for single, covalent Ge−C bonds,[15] but are significantly lengthened for those connecting the germanium atoms to the bridgehead (C$_{\text{bh}}$) carbon atoms of the anthracene framework to 2.016 Å (av) in (Me$_2$Ge)$_2$**A** and to 2.030 Å (av) in the more strained Me$_2$Ge**A**. These values compare well with those reported for 1,4-dihydro-9,9-dimethyl-1,2,3,4-tetraphenyl-1,4-germanaphthalene, the only other reported solid-state structure of a 7-germanorbornadiene, with Ge−C$_{\text{bh}}$ bond distances averaging 2.02 Å and C$_{\text{bh}}$−Ge−C$_{\text{bh}}$ angle approximating 78.5°.[16] A CCDC search reveals the X-ray structure of (Me$_2$Ge)$_2$**A** to be the first reported for a 7,8-digermabicyclo[2.2.2]octadiene.[17]

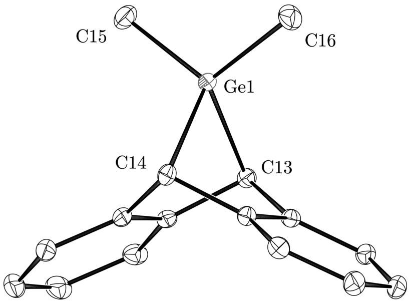

Figure 1. Solid-state molecular structure of Me$_2$Ge**A** with ellipsoids at the 50% probability level, rendered using PLATON.[10] Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ge(1)−C(13) 2.030(1), Ge(1)−C(14) 2.029(1), Ge(1)−C(15) 1.940(2), Ge(1)−C(16) 1.947(2); C(13)−Ge(1)−C(14) 77.72(5).

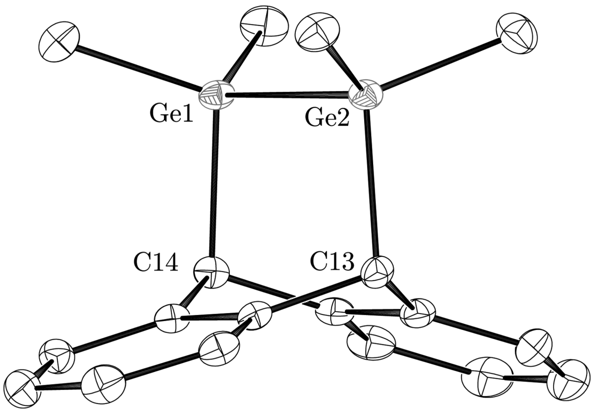

Figure 2. Solid-state molecular structure of (Me$_2$Ge)$_2$**A** with ellipsoids at the 50% probability level, rendered using PLATON.[10] Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): C(13)−Ge(2) 2.015(1), C(14)−Ge(1) 2.017(1), Ge(1)−Ge(2) 2.4128(2); C(13)−Ge(2)−Ge(1) 95.53(3).

The preparation of (Me$_2$Ge)$_2$**A** from Me$_2$Ge**A**, in turn prepared in one step from Mg**A**·3THF and Me$_2$GeCl$_2$, is significantly better than that originally reported[7] and may enable an expansion of the chemistry of Ge$_2$Me$_4$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00529.

Crystallographic data for Me$_2$Ge**A** (CIF)
Crystallographic data for (Me$_2$Ge)$_2$**A** (CIF)
Further characterization data of the compounds, details of DFT studies, and crystallographic details (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based upon work supported by the National Science Foundation under CHE-1362118. The authors declare no competing financial interests.

■ DEDICATION

This work is dedicated in fond remembrance of Professor Gregory L. Hillhouse.

■ REFERENCES

(1) Neumann, W. P.; Schriewer, M. *Tetrahedron Lett.* **1980**, *21*, 3273−6.

(2) Smith, C. L.; Pounds, J. *J. Chem. Soc., Chem. Commun.* **1975**, 910−911.

(3) Appler, H.; Gross, L. W.; Mayer, B.; Neumann, W. P. *J. Organomet. Chem.* **1985**, *291*, 9−23.

(4) Ramsden, H. E. Magnesium and Tin Derivatives of Fused-ring Hydrocarbons and the Preparation Thereof. US Patent US3354190, 1967.
(5) Bogdanović, B. *Acc. Chem. Res.* **1988**, *21*, 261−267.
(6) Velian, A.; Cummins, C. C. *J. Am. Chem. Soc.* **2012**, *134*, 13978−13981.
(7) Bleckmann, P.; Minkwitz, R.; Neumann, W. P.; Schriewer, M.; Thibud, M.; Watta, B. *Tetrahedron Lett.* **1984**, *25*, 2467−2470.
(8) Sakurai, H.; Nakadaira, Y.; Tobita, H. *Chem. Lett.* **1982**, *11*, 1855−8.
(9) (a) Ziche, W.; Auner, N.; Behm, J. *Organometallics* **1992**, *11*, 2494−2499;(b) Kyushin, S.; Ikarugi, M.; Takatsuna, K.; Goto, M.; Matsumoto, H. *J. Organomet. Chem.* **1996**, *510*, 121−133;(c) Wiberg, N.; Wagner, S.; Vasisht, S.-K.; Polborn, K. *Can. J. Chem.* **2000**, *78*, 1412−1420;(d) Kyushin, S.; Meguro, A.; Unno, M.; Matsumoto, H. *Chem. Lett.* **2000**, *29*, 494−495;(e) Fischer, R.; Baumgartner, J.; Kickelbick, G.; Marschner, C. *J. Am. Chem. Soc.* **2003**, *125*, 3414−3415.
(10) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.
(11) Neumann, W. P.; Kühlein, K. *Tetrahedron Lett.* **1963**, *4*, 1541−1545.
(12) Velian, A.; Nava, M.; Temprado, M.; Zhou, Y.; Field, R. W.; Cummins, C. C. *J. Am. Chem. Soc.* **2014**, *136*, 13586−13589.
(13) Neese, F. *ORCA-an ab initio, density functional and semiempirical program package, Version 3.0.2*; University of Bonn, Bonn, Germany, 2014.
(14) Carpino, L. A.; Padykula, R. E.; Barr, D. E.; Hall, F. H.; Krause, J. G.; Dufresne, R. F.; Thoman, C. J. *J. Org. Chem.* **1988**, *53*, 2565−2572.
(15) Pyykkö, P.; Atsumi, M. *Chem. - Eur. J.* **2009**, *15*, 12770−12779.
(16) Egorov, M. P.; Ezhova, M. B.; Antipin, M. Y.; Struchkov, Y. T. *Main Group Metal Chemistry* **1991**, *14*, 19−25.
(17) These data can be obtained free of charge from The Cambridge Crystallographic Data Centre; http://www.ccdc.cam.ac.uk/data_request/cif.

DOI: 10.1021/acs.organomet.5b00529
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