Octakis(2,6-diethylphenyl)octastannacubane

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pound may be considered a weakly bonded dimer of ferrocenyldimethylgallane, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)Ga(CH_3)_2$. The Ga(1)–C(1)–Ga(1a) bond angle is 80.7 (3)° while the C(1)–Ga(1a)–C(1a) bond angle is 99.3 (3)°. The Ga···Ga contact of 2.999 (1) Å across the Ga_2C_2 ring does not indicate significant metal–metal interaction.

The Ga–C bond distances in $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)Ga(CH_3)_2]_2$ warrant closer examination. The Ga(1)–C(1) bond distance of 1.992 (5) Å in the Ga_2C_2 four-membered ring is comparable to Ga–C distances within trimethylgallium adducts.[5] While the Ga(1)–C(7) bond distance of 1.964 (5) Å in the dimethylgallium fragment compares well with the Ga–C distance of 1.968 (4) Å reported for trimesitylgallium,[6] a more informative comparison would concern Ga–C distances in compounds containing dimethylgallium fragments. The recently reported organogallium–aza crown ether complex $[Ga(CH_3)_2][C_{12}H_{25}N_2O_4][Ga(CH_3)_3]_2$[7] is a convenient example. The Ga–C bond distances of 1.95 (2) and 1.97 (2) Å in the $Ga(CH_3)_2$ fragment of the organogallium–aza crown complex are comparable to Ga–C distances found in the title compound for the dimethylgallium fragment. At a distance of 2.587 (5) Å, the remaining Ga(1)–C(1a) bond distance in the Ga_2C_2 fragment is among the longest gallium–carbon bonds reported.

It is interesting to view the Ga–C bonding within the Ga_2C_2 fragment of the title compound as a balance of electronic and steric effects. The fact that the shorter Ga–C bonds in the Ga_2C_2 fragment (Ga(1)–C(1) and Ga(1a)–C(1a)) involve the Ga–C bond cis to the remainder of each ferrocenyl group while the longer Ga–C bonds (Ga(1)–C(1a) and Ga(1a)–C(1)) involve the Ga–C bond trans to the remainder of the ferrocenyl group is noteworthy. If it is assumed that each carbon atom of the Ga_2C_2 fragment contributes one sp^2 hybrid orbital and one electron while each gallium atom contributes two sp^3 hybrid orbitals and one electron, the steric effects imposed by the ferrocenyl groups and the dimethylgallium units would manifest themselves most prominently in steric repulsion between these groups. Thus, steric repulsion between these groups would ultimately force a rotation of these two groups away from each other. This would result in the Ga–C orbital overlap being greater (i.e., a shorter Ga–C bond) in the Ga–C bond cis to the unsubstituted cyclopentadienyl group. Moreover, the short Ga–C bond is roughly in the plane of the σ-bonded cyclopentadienyl ring and benefits from a greater orbital overlap whereas the longer Ga–C bond is tilted further out of the cyclopentadienyl plane, thus resulting in a less effective overlap and weaker (longer) bond.

The literature reveals only three other ferrocenyl–group 13 metal alkyl derivatives that have been structurally characterized: a series of ferrocenylalanes.[8] Interestingly, the $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_4)Al_2R_4Cl]$ (R = CH_3, C_2H_5) ferrocenylalanes were prepared by an analogous reaction which resulted in the ferrocenylgallane described herein (eq 1). As this area of main-group chemistry is largely unexplored, fundamental issues of structure, bonding, and reactivity abound. Future contributions will address these issues.

Acknowledgment. We are grateful to the National Science Foundation for support of this work to G.H.R. (RII-8520554).

Supplementary Material Available: A summary of data collection and refinement, plots of molecules, and tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (9 pages); a listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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[5] (5) For representative Ga–C bond distances, see, for example: Zaworotko, M. J.; Rogers, R. D.; Atwood, J. L. *Organometallics* **1982**, *1*, 1179 and references cited therein.

[6] (6) Beachley, O. T., Jr.; Churchill, M. R.; Pazik, J. C.; Ziller, J. W. *Organometallics* **1986**, *5*, 1814.

[7] (7) Lee, B.; Pennington, W. T.; Robinson, G. H. *Organometallics* **1990**, *9*, 1709.

[8] (8) (a) Atwood, J. L.; Bailey, B. L.; Kindberg, B. L.; Cook, W. J. *Aust. J. Chem.* **1973**, *26*, 2297. (b) Atwood, J. L.; Shoemaker, A. L. *J. Chem. Soc., Chem. Commun.* **1976**, 536. (c) Rogers, R. D.; Cook, W. J.; Atwood, J. L. *Inorg. Chem.* **1979**, *18*, 279. (d) Robinson, G. H.; Bott, S. G.; Atwood, J. L. *J. Coord. Chem.* **1987**, *16*, 219.

Octakis(2,6-diethylphenyl)octastannacubane

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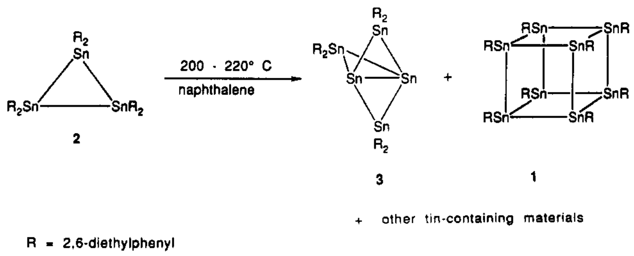
Summary: Thermolysis of hexakis(2,6-diethylphenyl)cyclotristannane (**2**) in naphthalene provides red octakis(2,6-diethylphenyl)octastannacubane (**1**), which has been fully characterized, including crystallographic analysis. Compound **1** represents the first example of the organostannane cluster series $(RSn)_n$.

Recently, several theoretical investigations have centered on predicting the stability of the class of group IVA polycyclic structures M_nH_n (M = Si, Ge, Sn, and Pb), where n = 4 (tetrahedrane), n = 6 (prismane), and n = 8 (cubane).[1] An interesting result of these investigations is the prediction that the cubane[2] structures possess lower degrees of strain energy as one descends the group IVA with octaplumbacubane, Pb_8H_8, being the most stable structure.[3] The conclusion, therefore, is that the heavier atom

Scheme I



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[1] (1) (a) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, *60*. (b) Nagase, S.; Nakano, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1081. (c) Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 329.

[2] (2) Pentacyclo$[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]$octane by IUPAC nomenclature convention.

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cubane analogues should be viable synthetic targets. In keeping with this idea, the first octasilacubane derivative, Si_8R_8 (R = *tert*-butyldimethylsilyl), was recently prepared; however, no structural information regarding this compound has appeared.[4] Herein, we report the preparation and molecular structure of an octastannacubane derivative, Sn_8R_8 (R = 2,6-diethylphenyl; 1), which provides the first opportunity to correlate theory with experiment for the heavier atom analogues of this unique structural class (Scheme I).

We have previously reported that thermolysis of hexakis(2,6-diethylphenyl)cyclotristannane (2) at 200–220 °C provides the blue-violet pentastanna[1.1.1]propellane derivative 3, which can be isolated in pure form by flash chromatography on silica gel with a 5:1 hexane/toluene eluant (Scheme I).[5] After removal of 3, other highly colored tin-containing compounds remain on the column, and these can be separately isolated by slowly increasing the percentage of toluene in the eluant. At a 1:1 ratio, a red fraction was collected that upon removal of the solvent provided the deep red microcrystalline octastannacubane 1, and analytically pure material could be obtained by recrystallization from pentane at −40 °C. While this production of 1 from 2 has not yet been optimized, it is reproducible, and at the present time, it provides approximately 50 mg of product from 10 g of the cyclotristannane (0.76% yield).

The spectroscopic data of 1 are supportive of the Sn_8R_8 formulation. Thus, a ^1H NMR (300 MHz, toluene-d_8) spectrum shows that, at 20 °C, all of the organic ligands are equivalent on the NMR time scale with resonances appearing at δ (ppm) 0.91 (t, 6 H), 2.73 (q, 4 H), 6.97 (d, 2 H), and 7.14 (s, 1 H). Furthermore, in contrast with all other known polycyclic polystannanes,[5,6] there appears to be only a small barrier to rotation about the tin–carbon bonds in 1, which implies less steric congestion among the neighboring organic groups.[7] A ^{119}Sn NMR (112 MHz, toluene-d_8, δ referenced to external Me_4Sn) spectrum revealed a single resonance at +44.3 ppm that had two pairs of observable coupling satellites, which are assigned to $^1J(^{119}Sn-^{117}Sn)$ = 1576 Hz and $^2J(^{119}Sn-^{117}Sn)$ = 1345 Hz, respectively.[8] The inability to observe the expected $^3J(^{119}Sn-^{117}Sn)$ coupling constant for 1 is attributed to an insufficient sample size and poor signal-to-noise ratios that prevent resolution of these satellites, which are predicted to be of smaller intensity than the others. In the presence of air, toluene solutions of 1 decolorize within a few minutes and a FAB mass spectrum of this solution showed no molecular ion for 1 but, rather, a strong isotope cluster pattern for $M^{\bullet +}$ at *m/z* 2196–2220, which corresponds to the molecular formula for $C_{80}H_{104}Sn_8O_{12}$.[9] Apparently, it is possible for oxygen to rapidly insert into each of the 12 tin–tin bonds of 1, and therefore, the 2,6-diethylphenyl ligands probably provide minimal kinetic stabilization of this structure. Finally, red crystals of 1 are thermochromic in the solid state, becoming pale yellow at −196 °C; however, no absorption maxima for solutions of 1 in hexane appear in the region 360–900 nm (λ_{max} 275 nm (ϵ_{max} 112000), 320 nm (sh) (ϵ 32000), 450 nm (sh) (ϵ 2000)).

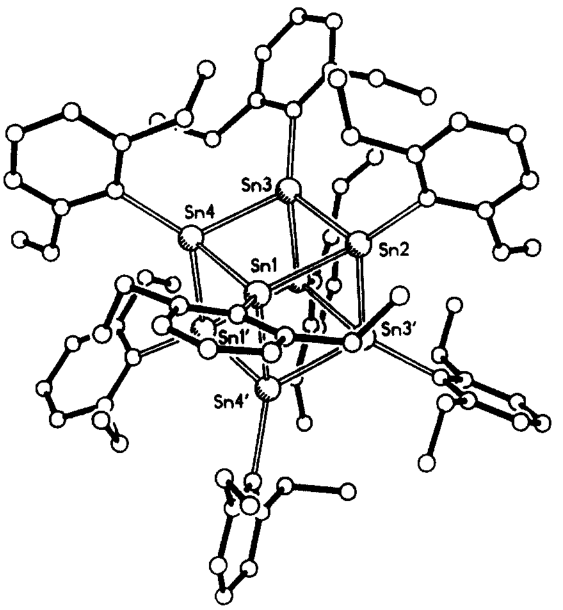

Figure 1. Molecular structure of 1 with all non-hydrogen atoms represented by spheres of varying sizes. Atoms labeled with a prime (′) are related to nonprimed atoms by the crystallographic C_2 axis at 0, *y*, $^1/_4$ in the unit cell. Hydrogen atoms have been omitted for purposes of clarity. Bond lengths (Å): Sn_1-Sn_2 = 2.857 (2), Sn_1-Sn_4 = 2.864 (2), $Sn_1-Sn_{4'}$ = 2.858 (2), Sn_2-Sn_3 = 2.853 (2), $Sn_2-Sn_{3'}$ = 2.855 (2), Sn_3-Sn_4 = 2.839 (2), Sn–C = 2.17 (2)–2.22 (2). Bond angles (deg): $Sn_2Sn_1Sn_4$ = 90.6 (1), $Sn_2Sn_1Sn_{4'}$ = 89.8 (1), $Sn_4Sn_1Sn_{4'}$ = 89.9 (1), $Sn_1Sn_2Sn_3$ = 89.1 (1), $Sn_1Sn_2Sn_{3'}$ = 89.8 (1), $Sn_3Sn_2Sn_{3'}$ = 90.2 (1), $Sn_2Sn_3Sn_4$ = 91.1 (1), $Sn_2Sn_3Sn_{2'}$ = 89.9 (1), $Sn_4Sn_3Sn_{2'}$ = 90.3 (1), $Sn_1Sn_4Sn_3$ = 89.2 (1), $Sn_1Sn_4Sn_{1'}$ = 90.1, $Sn_3Sn_4Sn_{1'}$ = 90.1 (1).

In order to conclusively prove the structure of 1, a crystallographic analysis was performed.[10] As shown in Figure 1, the eight tin atoms of 1 compose a cubic arrangement with the tin–tin bond lengths falling within the range 2.839 (2)–2.864 (2) Å and all of the Sn–Sn–Sn bond angles being nearly 90°. In addition, all of the Sn–Sn–C bond angles of 1 are greater than the value of 109°28′ expected if the tin atoms have idealized tetrahedral ge-

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[3] Calculated HF/6-31G* strain energy values (kcal mol^{-1}) for M_8H_8 are as follows: 158.6 (M = C); 99.1 (M = Si); 86.0 (M = Ge); 70.1 (M = Sn); 59.6 (M = Pb).[1c]

[4] Matsumoto, H.; Higuchi, K.; Hoshino, Y.; Koike, H.; Naoi, Y.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1083.

[5] Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 6454.

[6] (a) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 3769. (b) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.*, in press.

[7] Variable-temperature ^1H NMR spectra revealed a coalescence temperature of −40 °C.

[8] Since the relative intensities of each of these satellites to the main signal are predicted to be equal, unequivocal assignment of these coupling constants is not yet possible.

[9] The compound $[RSnO_{1.5}]_8$ (R = 2,6-diethylphenyl) represents the first example of an organosesquistannoxane that we believe to possess bicoordinate oxygen atoms, at least in the gas phase, in a manner similarly found for the closely related sulfur compound $[RSnS_{1.5}]_4$ (R = 2,4,6-trimethylphenyl) (see: Berwe, H.; Haas, A. *Chem. Ber.* **1987**, *120*, 1175) and the structurally analogous organosesquisiloxanes $[RSiO_{1.5}]_8$ (for R = Ph, see: Hossain, M. A.; Hursthouse, M. B.; Malik, K. M. A. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2258).

[10] Crystal data for 1: single crystals of $C_{80}H_{104}Sn_8$ are, at 20 °C, monoclinic, space group *C*2/*c* (No. 15), with *a* = 27.257 (4) Å, *b* = 13.084 (3) Å, *c* = 25.225 (5) Å, β = 116.36 (1)°, *V* = 8060 (3) $Å^3$, and *Z* = 4 (d_{calcd} = 1.661 g cm^{-3}; μ_a(Mo $K\bar{\alpha}$) = 2.49 mm^{-1}). A total of 5556 independent reflections having 2θ(Mo $K\bar{\alpha}$) < 45.8° (the equivalent of 0.6 limiting Cu $K\alpha$ spheres) were collected on a computer-controlled $P\bar{1}$ Nicolet autodiffractometer using full (0.90° wide) ω scans and graphite-monochromate Mo $K\bar{\alpha}$ radiation. The structure was solved with use of "direct methods" techniques with the Siemens SHELXTL-PLUS software package as modified at Crystalytics Co. The resulting structural parameters have been refined to convergence (R_1 (unweighted, based on *F*) = 0.035 for 2221 independent reflections having 2θ(Mo $K\bar{\alpha}$) < 45.8° and $I > 3\sigma(I)$) with use of counterweighted full-matrix least-squares techniques and a structural model that incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all included hydrogen atoms. Since four of the eight terminal methyl groups did not give chemically reasonable C–C–H angles when refined as rigid rotors, all methyl hydrogens were omitted from the structure factor calculations. The remaining hydrogen atoms were inlcuded in the structure factor calculations as idealized atoms (assuming sp^2 or sp^3 hybridization of the carbon atoms and a C–H bond length of 0.96 Å) "riding" on their respective carbon atoms.

ometries, with these bond angles being in the range 117.3 (4)–133.0 (5)°. Interestingly, these structural data are in close agreement with the tin–tin bond lengths of 2.887 Å and the 90° bond angles predicted for the parent Sn_8H_8 octastannacubane derivative.[1c]

At the present time, the mechanism by which the octastannacubane 1 is formed from the cyclotristannane 2 is a matter of speculation. It is reasonable to assume, however, that a highly reactive transient intermediate, such as "RSn", might be generated under thermal conditions via the disproportionation $2R_2Sn \rightarrow RSn + R_3Sn^{\bullet}$[11] and that this species then undergoes rapid oligomerization to produce a family of $(RSn)_n$ compounds, of which the cubane structure ($n = 8$) is either the most thermodynamically stable or the most kinetically stabilized member. Similar mechanisms for the formation of cyclopolystannanes, $(R_2Sn)_n$, from the oligomerization of transient stannylenes, R_2Sn, are well-known.[12] Given the documented stability of 1, we are currently exploring alternate, and potentially higher yielding, routes to 1 and other members of the $(RSn)_n$ series.

Acknowledgment. We thank Dr. Cynthia Day of Crystalytics Co. for the structural analysis of 1 and the National Science Foundation (Grant CHE-9001462) for support of this work. High-resolution mass spectra were provided by Dr. Catherine Costello of the facility supported by the National Institutes of Health (Grant R-R-00317; principal investigator Professor K. Biemann), from the Division of Research Resources.

Supplementary Material Available: Detailed information regarding the crystallographic analysis of 1, including listings of atomic coordinates, temperature factors, bond lengths, and bond angles and an ORTEP representation of 1 (11 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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[11] A similar disproportionation of R_2Sn [R = bis(trimethylsilyl)-methyl] has been observed under photolytic conditions; see: Hudson, A.; Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Dalton Trans.* **1976**, 2369.

[12] (a) Watta, B.; Neumann, W. P.; Sauer, J. *Organometallics* **1985**, *4*, 1954. (b) Masamune, S.; Sita, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 6390.

Imino Carbene Complexes of Tungsten and Chromium as Synthons for Nitrile Ylides in Reactions with Alkynes, Alkenes, Nitriles, and Aldehydes

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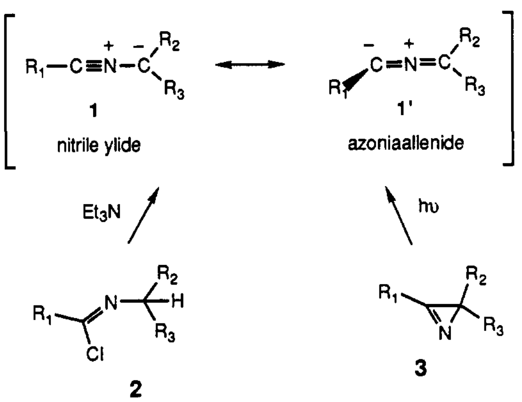
Summary: The stable and isolable imino carbene complexes of chromium and especially tungsten are found to be synthons for nitrile ylides and have the advantage that the range of 1,3-dipolarophiles is not limited to electron acceptors but is broad enough to include electronically neutral as well as electron-rich systems.

Nitrile ylides were first reported by Huisgen in 1961,[1] and since that time a variety of methods have been reported for their generation.[2] Two of the more popular methods are Huisgen's original method, consisting of elimination of hydrogen chloride from chloroimidates of the type 2 (Scheme I), and the photoinduced ring opening of 1-aziridines that was first reported by Schmid and Padwa.[3] The [3 + 2] dipolar cycloadditions of these species have been investigated in detail with a variety of π-bonded functional groups.[2,4] These cycloadditions are generally limited to dipolarophiles that are electron acceptors, and the regiochemistry observed is most consistent with the azoniaallenide structure 1′ for these intermediates.[2,5] Calculations[6] and experiment[2,4] reveal that the largest coefficient in the HOMO of these dipoles is nor-

Scheme I



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[1] (a) Huisgen, R. *Naturwiss. Rundsch.* **1961**, *14*, 43. (b) Huisgen, R. *Proc. Chem. Soc., London* **1961**, 357.

[2] For a comprehensive review up to 1983, see: Hansen, H. J.; Heimgartner, H. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; Vol. 1, pp 177–290.

[3] (a) Padwa, A.; Smolanoff, J. *J. Am. Chem. Soc.* **1971**, *93*, 548. (b) Giezendanner, H.; Märky, M.; Jackson, B.; Hansen, H. J.; Schmid, H. *Helv. Chim. Acta* **1972**, *55*, 745.

[4] For more recent citations, see: (a) De Meijere, A.; Teichmann, S.; Yu, D.; Kopf, J.; Oly, M.; Von Thienen, N. *Tetrahedron* **1989**, *45*, 2957. (b) Bozhkova, N.; Heimgartner, H. *Helv. Chim. Acta* **1989**, *72*, 825. (c) Ried, W.; Maria, F. *Helv. Chim. Acta* **1988**, *71*, 1681. (d) Wipf, P.; Prewo, R.; Bieri, J. H.; Germain, G.; Heimgartner, H. *Helv. Chim. Acta* **1988**, *71*, 1177. (e) Maerkl, G.; Troetsch-Schaller, I.; Hoelzl, W. *Tetrahedron Lett.* **1988**, *29*, 785. (f) Bossio, R.; Marcaccini, S.; Pepino, R. *Tetrahedron Lett.* **1986**, *27*, 4643. (g) Hoffman, R. W.; Barth, W. *Chem. Ber.* **1985**, *118*, 634. (h) Wipf, P.; Heimgartner, H. *Chimia* **1984**, *38*, 357.

[5] For more recent citations on the spectroscopy of nitrile ylides, see: (a) Orton, E.; Collins, S. T.; Pimentel, G. C. *J. Phys. Chem.* **1986**, *90*, 6139. (b) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928. (c) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Am. Chem. Soc.* **1985**, *107*, 7204. (d) Wentrup, C.; Fischer, S.; Berstermann, H. M.; Kuzaj, M.; Luerssen, H.; Burger, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 85. (e) Turro, N. J.; Cha, Y.; Gould, I. R.; Padwa, A.; Gasdaska, J. R.; Tomas, M. *J. Org. Chem.* **1985**, *50*, 4415.

[6] (a) Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 6397. (b) Caramella, P.; Gandour, R. W.; Hall, J. A.; Deville, C. G.; Houk, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 385.

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