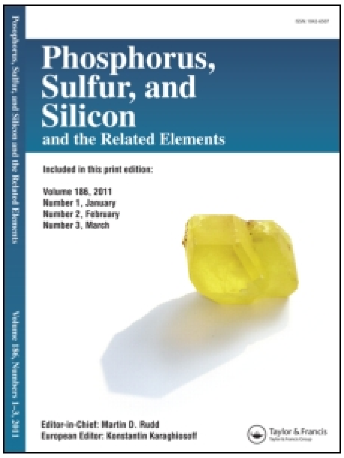

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

MEDIUM-SIZED GERMANIUM HETEROCYCLES: FIRST SYNTHESIS AND CONFORMATIONAL ANALYSIS OF A STERICALLY HINDERED EIGHT MEMBERED 12*H*-DIBENZO[*d,g*] [1,3,2]DIOXAGERMOCIN

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To cite this Article Pastor, Stephen D. , Smith, Andrea R. and Rims, Grety(1996) 'MEDIUM-SIZED GERMANIUM HETEROCYCLES: FIRST SYNTHESIS AND CONFORMATIONAL ANALYSIS OF A STERICALLY HINDERED EIGHT MEMBERED 12*H*-DIBENZO[*d,g*] [1,3,2]DIOXAGERMOCIN', Phosphorus, Sulfur, and Silicon and the Related Elements, 115: 1, 169 — 177

To link to this Article: DOI: 10.1080/10426509608037964

URL: http://dx.doi.org/10.1080/10426509608037964

Phosphorus, Sulfur, and Silicon, 1996, Vol. 115, pp. 169–177
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MEDIUM-SIZED GERMANIUM HETEROCYCLES: FIRST SYNTHESIS AND CONFORMATIONAL ANALYSIS OF A STERICALLY HINDERED EIGHT-MEMBERED 12*H*-DIBENZO[*d,g*][1,3,2]DIOXAGERMOCIN[1]

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Dedicated to Prof. John G. Verkade on the occasion of his 60th birthday

(Received February 29, 1996; in final form March 5, 1996)

The first reported synthesis, characterization, and conformational analysis of the eight-membered germocin 2,2′-(4,6-di-^{t}BuC$_6$H$_2$O)$_2$GeMe$_2$ (3) is described. The VT ^{1}H NMR, ^{13}C{^{1}H} NMR, and crystallographic data of **3** is consistent with a boat-chair conformation for the ring in both solution and the solid state. The free energy of activation ($\Delta G^{\ddagger}_{299}$) for ring inversion is 55.6 kJ · mole^{-1} (13.3 cal · mole^{-1}).

Key words: 12*H*-Dibenzo[*d,g*][1,3,2]dioxagermocin, conformational analysis, ring inversion, free energy of activation.

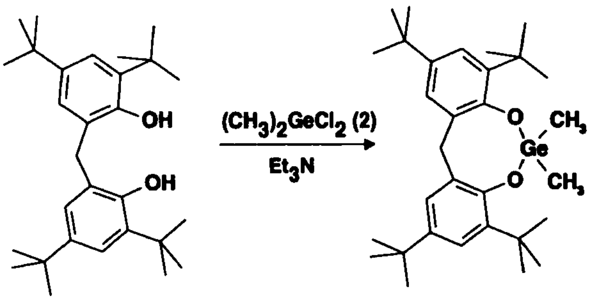
Although the conformational analysis of both carbocyclic and small-membered heterocyclic compounds has been extensively developed, the conformational analysis of medium-sized heterocycles has not until very recently received much attention.[2] Investigations directed towards developing an understanding of the conformational preferences exhibited by dioxametallocins containing phosphorus has been stimulated in part by recent studies. In particular, 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin derivatives have been shown to provide unique coordination geometries when employed as ligands for transition-metal-catalyzed hydroformylation reactions.[3–5] The equatorial axial aptitude of 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocins incorporated in pentaoxyphosphoranes has important ramifications on literature proposals describing activated states for cyclic adenosine monophosphites where trigonal bipyramidal geometries about phosphorus are invoked.[6] Certain sterically congested molecules incorporating medium-sized organophosphorus heterocycles exhibit unique spectral properties.[7,8] Several reviews on the conformational analysis of 12*H*-dibenzo[*d,g*]-[1,3,2]dioxaphosphocins have appeared.[9,10] Studies on the conformation of the corresponding 12*H*-dibenzo[*d,g*][1,3,2]dioxasilocin ring system have been reported,[11] including a very recent crystallographic study.[12,13]

Nothing is known about the corresponding ring system with germanium. The synthesis, characterization, and crystallographic analysis of a substituted 12*H*-dibenzo-[*d,g*][1,3,2]dioxagermocin ring system is reported herein.

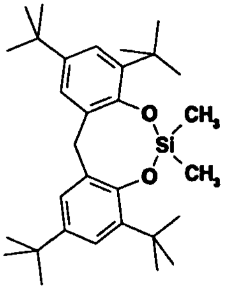
RESULTS AND DISCUSSION

Synthesis

The seven-membered dibenzo[*d,f*][1,3,2]dioxagermepin ring system was synthesized by Zuckerman and co-workers[14] by the reaction of the corresponding dibenzo[*d,f*]-[1,3,2]dioxasilepin with germanium(IV) chloride. Spirocyclic germanium(IV) complexes were prepared by Holmes *et al.* by the reaction of catechol with germanium(IV) chloride using triethylamine as an hydrogen chloride acceptor.[15] The 6,6-dimethyl-substituted 12*H*-dibenzo[*d,g*][1,3,2]dioxagermocin **3** was prepared as a white crystalline solid by the reaction of the bisphenol **1** with one equivalent of dimethylgermanium(IV) chloride (**2**) using triethylamine as an acid acceptor (66% recrystallized) (Figure 1).



1 **3**



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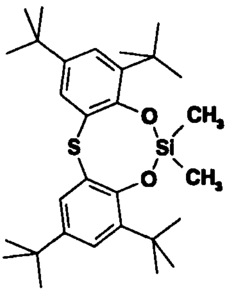

5

Variable Temperature ^1H NMR

In the ^1H NMR spectrum of **3** at 60°C, a broad singlet is observed at δ 0.30, which was assigned to the protons of the two methyl groups bonded to germanium. At 120°C in toluene-d_8, a sharp singlet is observed for the methyl group protons bonded to germanium. Similar behavior was observed for the C(12) bridging methylene protons in **3**, which at 120°C are observed as a sharp singlet at δ 4.10 (Figure 2).[16]

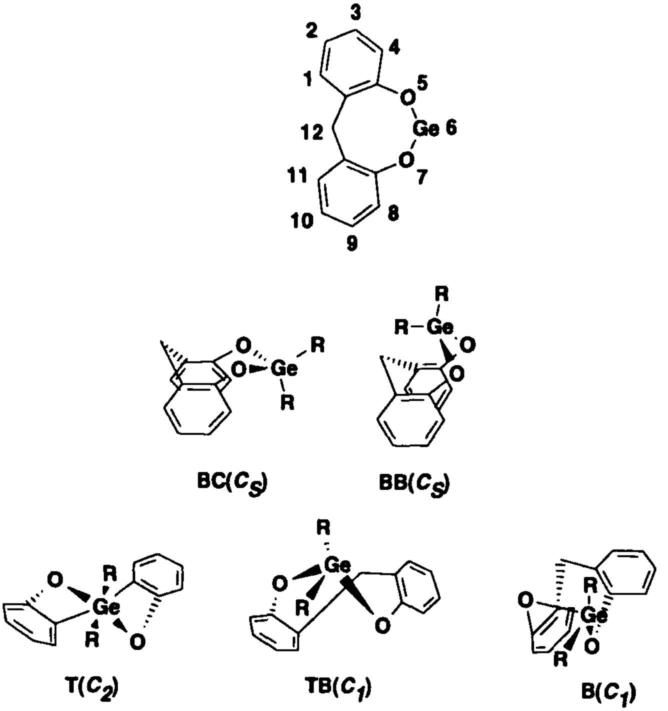

FIGURE 1 The *Chem. Abstr.* numbering system and conformations of the 12*H*-dibenzo[*d,g*][1,3,2]dioxagermocin ring system. The TB structure illustrated represents only one member of a family of flexible TB forms.

In the ^1H NMR spectrum (CD_2Cl_2) of **3** at −90°C, two singlets were observed at δ −0.03 and δ 1.01 that integrated to 3 protons each, which were assigned to two nonequivalent methyl groups bonded to germanium. At −90°C two doublets are observed at δ 3.36 and δ 4.28, which are assigned to two nonequivalent protons bonded to the C(12) carbon atom with two bond *J*-coupling of −13.2 Hz.[17] In the ^1H NMR spectrum of **3** at −90°C, two singlets are observed at δ 1.24 and δ 1.29 that integrated to eighteen protons each, which were assigned to the protons of two equivalent pairs of *tert*-butyl groups. At −90°C, two doublets are observed at δ 7.08 and δ 7.30 that integrated to two protons each, which were assigned to two equivalent pairs of aromatic protons with $^3J_{HCCH} = 2.2$ Hz. The process that renders the methyl groups bonded to germanium as well as the protons bonded to the C(12) carbon atom equivalent can be reasonably assigned to inversion of the 12*H*-dibenzo[*d,g*]-[1,3,2]dioxagermocin ring with the free energy of activation $\Delta G^{\ddagger}_{299} = 55.6$ kJ·mole^{-1} (13.3 kcal·mole^{-1}). This value is slightly less than that measured for the related 12*H*-dibenzo-[*d,g*][1,3,2]dioxasilocin **4** (58.2 kJ·mole^{-1})[11a] and 12*H*-dibenzo[*d,g*]-[1,3,6,2]-dioxathiasilocin **5** (58.2 kJ·mole^{-1}).[11b]

Solution and Solid-State Conformation

The commonly accepted nomenclature to describe the conformation of eight-membered rings is used herein; namely the boat-chair (C_s symmetry), boat-boat (C_s sym-

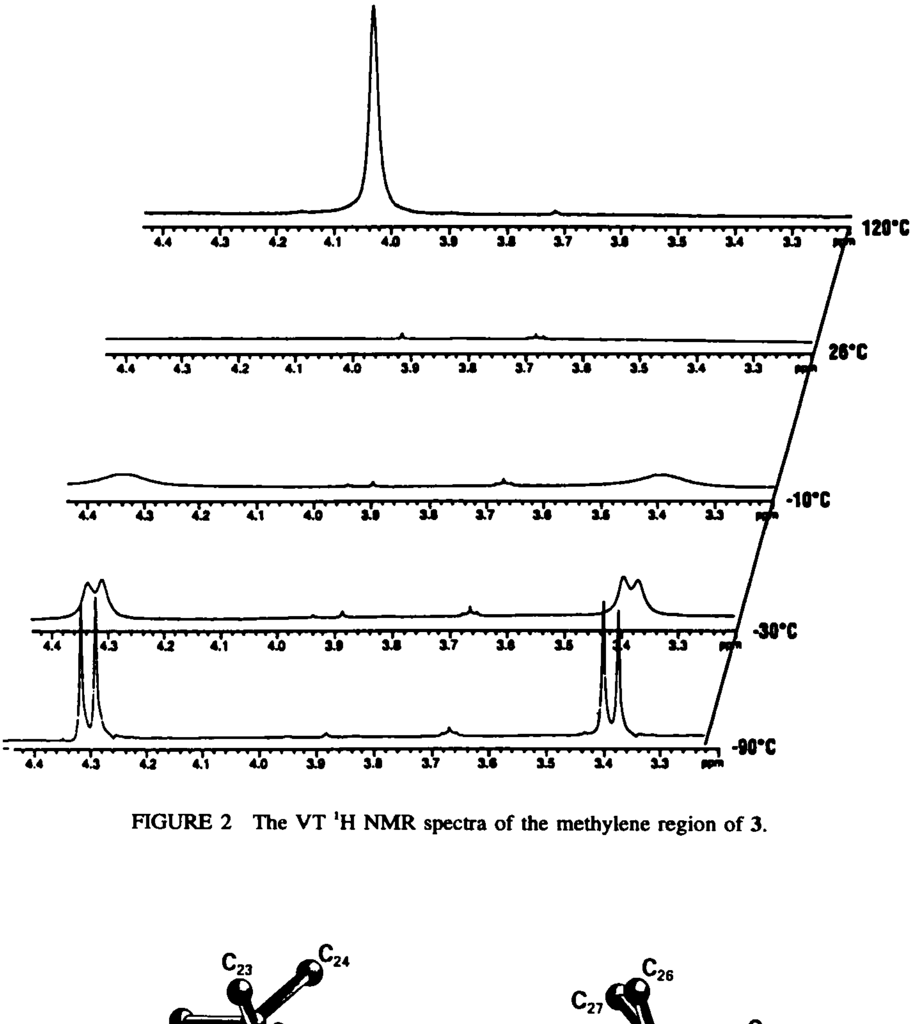

FIGURE 2 The VT ^{1}H NMR spectra of the methylene region of 3.

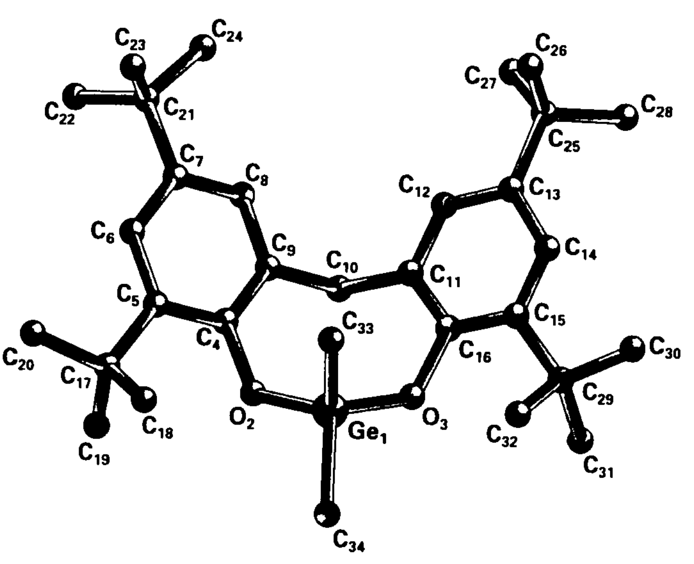

FIGURE 3 A ball-and-stick view of 3 showing the crystallographic numbering scheme (arbitrary).

TABLE I

Selected bond lengths and torsion angles in 3

Bond Lengths Å		Torsion Angles (°)	
Ge(1)-C(33)	1.920	O(2)-Ge(1)-O(3)-C(16)	90.7
Ge(1)-C(34)	1.918	Ge(1)-O(3)-C(16)-C(11)	-70.7
Ge(1)-O(2)	1.793	O(3)-C(16)-C(11)-C(10)	-3.7
Ge(1)-O(3)	1.794	C(16)-C(11)-C(10)-C(9)	98.2
O(2)-C(4)	1.390	C(11)-C(10)-C(9)-C(4)	-99.7
O(3)-C(16)	1.402	C(10)-C(9)-C(4)-O(2)	5.7
C(4)-C(9)	1.410	C(9)-C(4)-O(2)-Ge(1)	69.0
C(9)-C(10)	1.507	C(4)-O(2)-Ge(1)-O(3)	-89.8
C(10)-C(11)	1.510	C(33)-Ge(1)-O(2)-C(4)	28.5
C(11)-C(16)	1.409	C(34)-Ge(1)-O(2)-C(4)	160.2

metry), twist-boat (C_1 symmetry), and Twist (C_2 symmetry), which are abbreviated BC, BB, TB, and T, respectively.[18–20] Arshinova has noted that the boat conformer (C_1 symmetry; abbreviated B) should also be considered as it is commonly found in the solid state (Figure 1).[9] The B conformation represents a highly distorted TB geometry about halfway between the symmetric C_2 T and BB geometry.[18] The B conformation is characterized by a $C_{aromatic}$-O—P—O torsion angle of 0°.[9a]

The originally observed dependence of the magnitude of the C(12)-germinal protons in substituted 5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctenes upon ring conformation,[19,21–23] was extended to probe the conformation of 12*H*-dibenzo[*d*,*g*]-[1,3,2]dioxametallocins in solution.[9–11] The observation of a geminal coupling constant of -12 to -13 Hz in 12*H*-dibenzo[*d*,*g*][1,3,2]dioxametallocins is consistent with a BC conformation.[9]

The magnitude of the observed coupling constant (-13.2 Hz) for nonequivalent C(12) methylene protons below 26°C, the coalescence temperature, is consistent with a BC conformation in solution. The VT ^{1}H NMR spectral data of 3 requires that below the coalescence temperature that the ring conformer possess a σ plane of symmetry passing through the germanium and C(12)-carbon atom. This must be the case inorder to explain both the observation of anisochronous methyl groups bonded to germanium and anisochronous protons bonded to the C(12) carbon atom along with the observation of both two equivalent pairs of *tert*-butyl groups and two equivalent pairs of aromatic protons. The presence of twisted conformations that rapidly

TABLE II

Atomic coordinates (Cartesian) of 3

Ge1	-1.4765	-2.0591	2.7808	C18	2.0643	-2.9987	2.0352
O2	-0.0874	-0.9283	2.8612	C19	2.8755	-0.9820	3.3345
O3	-2.9893	-1.1212	3.0028	C20	3.9569	-1.6561	1.2079
C4	0.3696	-0.3242	1.6961	C21	1.6875	1.5406	-1.9916
C5	1.6226	-0.6351	1.1886	C22	2.9836	2.2934	-1.7242
C6	1.9948	-0.0245	-0.0158	C23	1.9342	0.4482	-3.0221
C7	1.1734	0.9081	-0.6816	C24	0.6618	2.5356	-2.5580
C8	-0.0230	1.2270	-0.1061	C25	-5.5893	1.1618	-1.5809
C9	-0.4641	0.6358	1.0864	C26	-5.2380	2.5346	-1.8041
C10	-1.7462	1.0979	1.7288	C27	-5.4310	0.3487	-2.6804
C11	-3.0219	0.4728	1.2160	C28	-7.0407	1.2231	-1.3923
C12	-3.6793	1.0189	0.1008	C29	-5.6586	-2.1457	2.3028
C13	-4.8866	0.5502	-0.3528	C30	-6.9953	-2.5217	1.6592
C14	-5.4871	-0.4970	0.3559	C31	-5.9450	-1.5487	3.6928
C15	-4.8938	-1.0886	1.4890	C32	-4.8621	-3.4590	2.4423
C16	-3.6482	-0.6007	1.8797	C33	-1.5142	-2.8887	1.0493
C17	2.6142	-1.5595	1.9263	C34	-1.3237	-3.0772	4.3985

pass through the required symmetry plane cannot be rigorously excluded, although the observed magnitude of the geminal coupling constant suggests this is not the case.

Although the magnitude of the observed geminal coupling constant of **3** is also consistent with a BB conformation, calculations on the corresponding 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocins[23] and 12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocins[24] indicate that the BB conformation is considerably higher in energy. Similar conclusions have been reached for the corresponding carbocycle.[25,26] The BB conformation is observed in the 6,6-dimethyl-substituted 12*H*-dibenzo[*d*,*g*][1,3,2]dioxasilocin **4** in the solid state.[27] Caution must be observed, however, in comparing solid-state and solution conformations. Lattice energy and the resultant crystal-packing effects in the solid state can render the solid-state geometry of flexible conformations different from that in solution.[25]

Crystals of **3** suitable for X-Ray crystallography were obtained by crystallization from acetonitrile. The BC conformation is found for the eight-membered ring in **3** (see Figure 3). The Ge—O bond lengths (1.79 Å) are somewhat shorter than found in pentacoordinated species (1.83–1.84 Å),[28] but within the observed range for other reported tetracoordinate species (1.78–1.79 Å).[29] The O—Ge—O bond angle is 108.2°. Both the Ge—O(2)—C(4) and Ge—O(3)—C(16) bond angles are 119.4°. The BB conformation previously found for **4** in the solid state was suggested to be due to the relief of steric interactions of the methyl groups bonded to silicon with the adjacent *tert*-butyl substituents.[30] The observation of a BC conformation for **3** is consistent with the longer Ge—O bonds (1.79 Å) compared to the shorter Si—O bonds in **4** (1.62 Å), which is expected to reduce the steric interactions of the methyl groups bonded to germanium with the adjacent *tert*-butyl substituents. The pseudoaxial (1.920 Å) and pseudoequatorial (1.918 Å) Ge—C bond lengths are essentially equal, and in the range previously reported for a Ge—C bond (1.94 Å).[31]

The crystallographic and NMR spectral data are in accord with the 12*H*-dibenzo[*d,g*][1,3,2]dioxagermocin ring in **3** adopting a BC conformation in both the solid-state and solution. The differences observed in solid-state and solution conformation between the 12*H*-dibenzo[*d,g*][1,3,2]dioxagermocin **3** and the 12*H*-dibenzo[*d,g*][1,3,2]dioxasilocin **4** ring systems is suggested to be largely due to steric effects.[32]

EXPERIMENTAL

All melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR (499.84 and 300.08 MHz) spectra were taken on a Varian Model Gemini-300 or Unity-500 spectrometers. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. Significant ^{1}H NMR data are tabulated in the following order: multiplicity (m, multiplet; s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dq, doublet of quartets; dt, doublet of triplets; ddq, doublet of doublets of quartets), atom assignments, coupling constant in Hertz, and number of protons. Merck silica gel 60 (200–400 mesh) was used for column chromatography. Merck precoated (0.25 mm) silica gel F-254 plates were used for TLC. Reagents were purchased from commercial laboratory supply houses. Solvents were dried prior to use when necessary with appropriate drying agents. Reactions were carried out in flame-dried apparatus under a dry inert atmosphere of either nitrogen or argon. Elemental analyses were performed by the Analytical Research Department, Ciba-Geigy Corporation.

6,6-Dimethyl-2,4,8,10-tetrakis(1,1-dimethylethyl)-12H-dibenzo[d,g][1,3,2]dioxagermocin (**1**): To a solution of 1.00 g (5.6 mmol) of dimethylgermanium dichloride and 3.0 mL (21.5 mmol) of triethylamine in 50 mL of toluene was added dropwise over a 15 min period a solution of 2.45 g (5.76 mmol) of 2,2′-methylenebis[4,6-bis(1,1-dimethylethyl)phenol] in 75 mL of toluene. The reaction mixture was heated at 90°C for 6 h and then the resultant mixture was stirred at ambient temperature overnight. The precipitate of triethylamine hydrochloride was removed by filtration and the volatiles were removed *in vacuo*. The residue was recrystallized twice from acetonitrile to give 1.99 g (66%) of a white crystalline solid, mp 212–215°C; ^{1}H NMR (benzene-d_6)(300.08 MHz)(60°C) δ 0.30 (br s, CH_3, 6 H), 1.30 (s, 18 H), 1.40 (s, 18), 4.10 (br s, C(12)—H, 2 H), 7.35 (d, 2 H), 7.50 (d, 2 H); ^{1}H NMR (toluene-d_8)(499.87 MHz)(120°C) δ 0.34 (s, CH_3, 6 H), 1.31 (s, 18 H), 1.41 (s, 18), 4.03 (s, C(12)—H, 2 H), 7.28 (d, 2 H), 7.45 (d, 2H); ^{1}H NMR (CD_2Cl_2)(499.87 MHz)(−90°C) δ −0.03 (s, CH_3, 3 H), 1.01 (s, CH_3, 3 H), 1.24 (s, 18 H), 1.29 (s, 18), 3.36 (d, C(12)—H, $^2J_{HCH}$ = 13.2 Hz, 1 H), 4.28 (d, C(12)—H, $^2J_{HCH}$ = 13.2 Hz, 1 H), 7.08 (d, $^3J_{HCCH}$ = 2.2 Hz, 2 H), 7.30 (d, $^3J_{HCCH}$ = 2.2 Hz, 2 H); $^{13}C\{^1H\}$ NMR (toluene-d_8)(125.70 MHz)(100°C) δ 0.18, 31.12, 31.92, 34.00, 34.60, 35.68, 122.31, 126.00, 134.12, 139.76, 144.02, 153.14; MS m/z 522 ($^{Ge70}M^+$), 524 ($^{Ge72}M^+$), 526 ($^{Ge74}M^+$). Anal. Calcd. for $C_{31}H_{48}O_2Ge$: C, 70.8; H, 9.1. Found: C, 71.0; H, 9.5.

Crystals suitable for crystallographic analysis (colorless plates) were prepared by recrystallization from acetonitrile. Crystal data: $GeO_2C_{31}H_{48}$; formula weight ($g \cdot mol^{-1}$) = 525.31; crystal size (mm) 0.31 × 0.43 × 0.10; space group = P1; cell parameters: a = 10.505 (1) Å, b = 10.864 (1) Å, c = 13.700 (2)

Å, $\alpha = 81.65°$ (1), $\beta = 75.20°$ (1), $\lambda = 84.63°$ (1), V = 1439 (1) $Å^3$, Z = 2; d_{calcd} 1.168 $g \cdot cm^{-3}$; F_{000} = 2368 (electrons); μ (MoKα) 0.997 cm^{-1}; Enraf-Nonius automatic diffractometer; Graphite monochromator Cu Kα radiation (1.5418 Å); Temperature (K) = 193; 3–75° θ range from data collection; number of observed reflections ($I > 3\sigma$) 5221; variables 307; R = 0.052; R_w = 0.055; μ = 1.69 mm^{-1}; weighting scheme $w = 1/\sigma^2(|F_o|)$.

ACKNOWLEDGEMENT

The authors wish to thank Ciba-Geigy for support and permission to publish this work, and Ms. S. Loggins (Ciba Additives Scientific Documentation Dept.) for on-line computer literature searches.

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