

Synthesis, X-ray, and DFT Study of the Double-Bond Pyramidalization in 1,7,8,9-Tetraphenyl-4,10,10-trimethyl-4-aza-10-silatricyclo[5.2.1.0.^{2,6}]deca-8-ene-3,5-dione and Its Germanium Analogue

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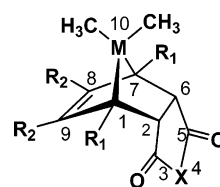
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Diels–Alder adducts of 1-sila-2,3,4,5-tetraphenyl-1,1-dimethyl-2,4-cyclopentadiene and 1-germa-2,3,4,5-tetraphenyl-1,1-dimethyl-2,4-cyclopentadiene with *N*-methylmaleimide and maleic anhydride were prepared by high-pressure reactions. Their X-ray structures were determined and compared to literature data. In addition, the B3LYP/6-31G* method was used to study their molecular and electronic structure. X-ray analysis revealed that the extent of pyramidalization of the double bond in all studied compounds is small (molecules **1** and **2**) or negligible (**3**). B3LYP/6-31G* calculations were found to overestimate pyramidalization by 5.3–9.4°, presumably due to crystal-packing forces. The effect of phenyl groups on the geometry of the double bond is discussed.

Introduction

The effect of heteroatoms on pyramidalization of the double bond in the norbornene moiety, either alone or fused to another strained ring, has attracted considerable interest from experimental as well as theoretical points of view.¹ Particularly interesting in this context are molecules in which the carbon atom of the methano-bridge is replaced by a group 14 element. Contrary to the parent hydrocarbon, all such molecules studied experimentally so far exhibit only small or negligible deviation of the double bond from planarity.^{2,3}

In this study we report on the preparation and X-ray structures of novel cycloadducts **1** and **2** (Figure 1). In addition, X-ray structure analysis of the known compound **3** was undertaken for the sake of completeness. We also intended to measure the X-ray structure of the silicon analogue of **3**, synthesis of which has been previously reported in the literature,⁴ but we were not able to grow X-ray quality crystals. In the second part of the paper, the geometries of **1–3** will be compared with the geometries of previously published structurally related silicon and germanium compounds, with particular emphasis on pyramidalization of the double bond. Finally, the effect of phenyl groups on the extent of the double-bond folding will be explored. For this purpose we shall use density functional theory (DFT) using the B3LYP/6-31G* method, which has been successfully used in studying geometries of organosilicon compounds.⁵ It was also proven to provide a reliable description of the geometry



- 1** M=Si; X=NMe; R₁=R₂=Ph
1a M=Si; X=NMe; R₁=H, R₂=Ph
1b M=Si; X=NMe; R₁=R₂=H
2 M=Ge; X=NMe; R₁=R₂=Ph
2a M=Ge; X=NMe; R₁=H, R₂=Ph
2b M=Ge; X=NMe; R₁=R₂=H
3 M=Ge; X=O; R₁=R₂=Ph
3a M=Ge; X=O; R₁=H, R₂=Ph
3b M=Ge; X=O; R₁=R₂=H

Figure 1. 7-Metallonbornenes investigated in this study

of the double bonds incorporated into strained polycyclic molecules by us^{6–9} and by other research groups.¹⁰ Recently, however, its reliability for calculating geometries with the second-row elements was questioned by Schaefer and Allinger.¹¹ Therefore, we thought it would be of interest to check whether the latter holds also for molecule **1**, as well as for the closely related germyl adducts considered in the present work. We were particularly interested in possible consequences of such an inaccuracy, if any, on pyramidalization of the double bond.

Results and Discussion

Compounds **1–3** were prepared by high-pressure-assisted Diels–Alder reactions¹² of 1-sila-2,3,4,5-tetraphenyl-1,1-di-

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(1) For a recent review article see: Vázquez, S.; Camps, P. *Tetrahedron* **2005**, *61*, 5147–5208, and references therein.

(2) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Am. Chem. Soc.* **1990**, *112*, 1710–1722.

(3) Paddon-Row, M. N.; Wong, S. S.; Jordan, K. D. *J. Chem. Soc., Perkin Trans. 2* **1990**, 417–423.

(4) Henry, G. K.; Shinimoto, R.; Zhou, Q.; Weber, W. P. *J. Organomet. Chem.* **1988**, *350*, 3–8.

(5) For a recent review article see: Karni, M.; Apeloig, Y.; Kapp, J.; Schleyer, P. v. R. In *The chemistry of organic silicon compounds*, Vol. 3; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, 2001; pp 1–188, and references therein.

(6) Williams, R. V.; Colvin, M. E.; Tran, N.; Warrenner, R. N.; Margetić, D. *J. Org. Chem.* **2000**, *65*, 562–567.

(7) Antol, I.; Eckert-Maksić, M.; Margetić, D.; Maksić, Z. B.; Kowski, K.; Rademacher, P. *Eur. J. Org. Chem.* **1998**, 1403–1408.

(8) Margetić, D.; Warrenner, R. N.; Butler, D. N. Paper 39, *Sixth electronic computational chemistry conference*; 1999; Homeier, H., Ed., <http://www.chemie.uni-regensburg.de/ECCC6/>.

(9) Eckert-Maksić, M.; Margetić, D.; Kirin, S.; Milić, D.; Matković-Čalোগović, D. *Eur. J. Org. Chem.* **2005**, 4612–4620.

(10) Saracoglu, N.; Talaz, O.; Azizoglu, A.; Watson, W. H.; Balci, M. *J. Org. Chem.* **2005**, *70*, 5403–5408.

(11) Ma, B.; Lii, J.-H.; Schaefer, H. F., III; Allinger, N. L. *J. Phys. Chem.* **1996**, *100*, 8763–8769.

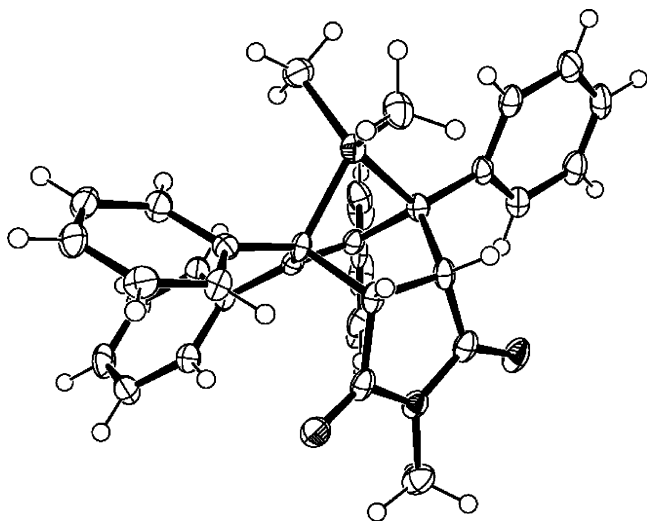


Figure 2. ORTEP plot of molecule **1**. Atoms are presented as thermal ellipsoids at 30% probability. The atom-numbering scheme is given in Figure 1.

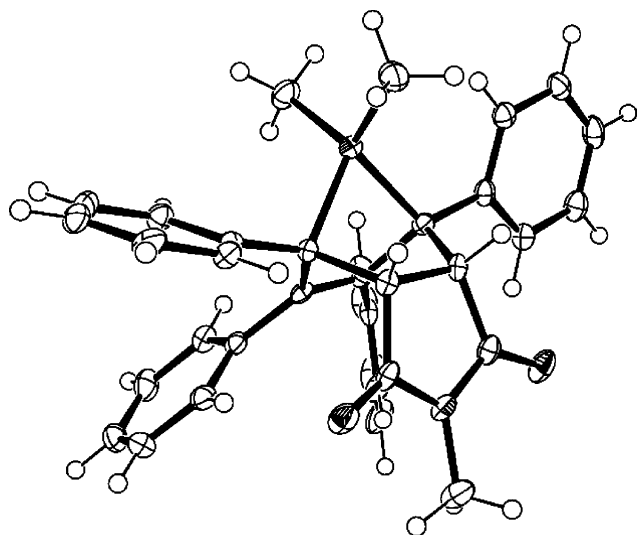


Figure 3. ORTEP plot of molecule **2**. Atoms are presented as thermal ellipsoids at 30% probability. The atom-numbering scheme is given in Figure 1.

methyl-2,4-cyclopentadiene and 1-germa-2,3,4,5-tetraphenyl-1,1-dimethyl-2,4-cyclopentadiene as reactive dienes.^{13,14} Under reaction conditions employed (8 kbar, 70 °C in dichloromethane), these organometallic dienes readily underwent $[4\pi+2\pi]$ cycloadditions with electron-poor dienophiles (maleic anhydride and *N*-methylmaleimide) to give the desired cycloadducts **1–3** as the single products.

The molecular structure and stereochemistry of the so-obtained cycloadducts were determined by NMR spectroscopic analysis and NOE experiments (see Experimental Section) and by means of X-ray diffraction analysis. The X-ray structures are displayed in Figures 2–5. Both approaches revealed that all three adducts have an *endo*-configuration, in accordance with expected stereochemical outcome.¹⁵ The measured ¹H and ¹³C

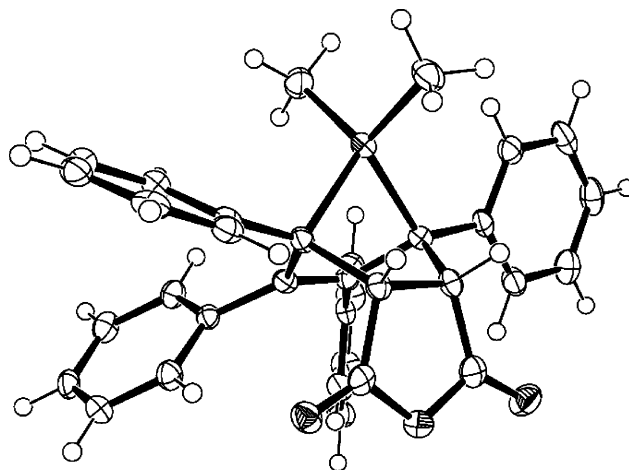


Figure 4. ORTEP plot of molecule **3**. Atoms are presented as thermal ellipsoids at 30% probability. The atom-numbering scheme is given in Figure 1.

NMR chemical shifts of the studied molecules are in accord with those observed earlier in structurally related cycloadducts.¹³ The same holds for the ²⁹Si chemical shift of **1**, which reflects a typical ²⁹Si nuclear deshielding^{16,17} when compared with unstrained organosilicon compounds.¹⁸ It is also worth noting that in the crystal structure they do not possess a plane of symmetry (see Experimental Section), in sharp contrast to the situation encountered in solution.

Crystal Molecular Structure of 1–3. In addition to confirming stereochemistry, the X-ray data reveal several interesting features of the molecular structure of the considered adducts **1–3** (Table 1). We shall commence discussion by considering the structure of molecule **1**. Perhaps, the most prominent feature of its molecular structure concerns orientation of the phenyl groups with respect to the basic plane of the 7-silanorbornene ring defined by the C(2), C(6), C(8), and C(9) atoms. The deviation angles have values of 18.7°, 79.9°, 90.2°, and 55.2° for the phenyl rings attached to the C(1), C(7), C(8), and C(9) atoms, respectively. It is interesting to note that one of the phenyl rings at the bridgehead positions (Ph(C7)) is almost perpendicular to the C(2)–C(6)–C(8)–C(9) plane, while the Ph(C1) ring deviates from coplanarity with the C(2)–C(6)–C(8)–C(9) plane by only 18.7°. Similarly, one of the aromatic rings attached to the olefinic carbon atoms is rotated by 90.2° (Ph(C8)) and the other by 55.2° (Ph(C9)) relative to the same plane. It is noteworthy that the orientation of the phenyl groups encountered in the crystal of **1** strongly resembles those in the crystal structure of structurally related 11,11-dimethyl-9,10-epoxy-1,4-sila-1,2,3,4-tetraphenyl-1,4,4a,9,9a,10-hexahydroanthracene **4** (where Ph(C1), Ph(C7), Ph(C8), and Ph(C9) angles are 27.2°, 85.3°, 80.2°, and 42.5°, respectively).¹⁹ On the other hand, in tetraphenyl silabenzenorbornadiene molecule **6** (Chart 1), all phenyl rings are perpendicular to the C(2)–C(6)–C(8)–C(9) plane. Another characteristic feature common to all silanorbornene derivatives studied so far concerns elongation of the endocyclic C–Si interatomic distances within the 7-silanorbornene ring relative to their exocyclic counterparts, the latter

(12) Matsumoto, K.; Acheson, R. M., Eds. *Organic Synthesis at High Pressures*; Wiley: New York, 1990.

(13) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215–263.

(14) Hota, N. K.; Willis, C. J. *J. Organomet. Chem.* **1968**, *15*, 89–96.

(15) Dubac, J.; Guérin, C.; Meunier, P. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; pp 1961–2036.

(16) Sakurai, H.; Sakabo, H.; Nakadaira, Y. *J. Am. Chem. Soc.* **1982**, *104*, 6156–6158.

(17) Marinetti-Mignani, A.; West, R. *Organometallics* **1987**, *6*, 141–144.

(18) Marsmann, H. In *NMR—Basic Principles and Progress*; Diehl, P., Fluck, E., Koesfeld, R., Eds.; Springer: Berlin, 1981; Vol. 17.

(19) Kirin, S. I.; Vikić-Topić, D.; Meštrović, E.; Kaitner, B.; Eckert-Maksić, M. *J. Organomet. Chem.* **1998**, *566*, 85–91.

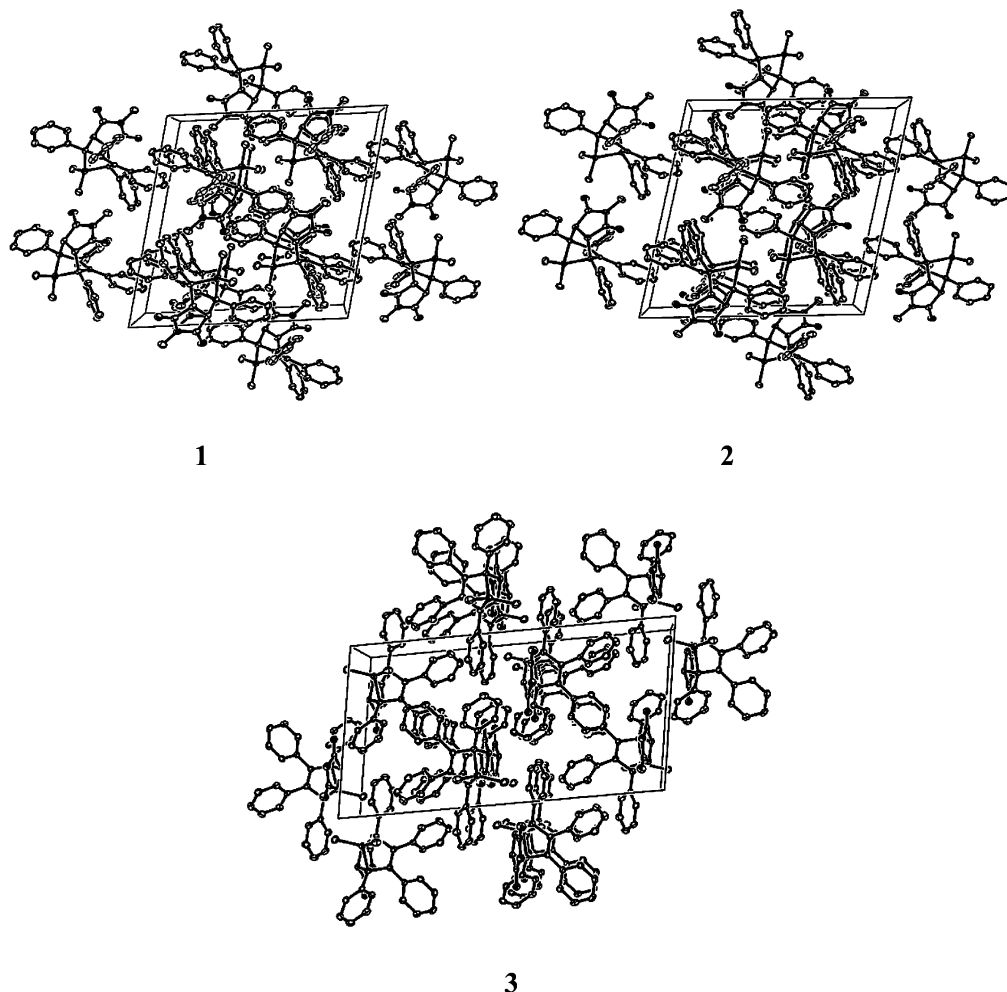


Figure 5. Crystal packing of molecules 1–3.

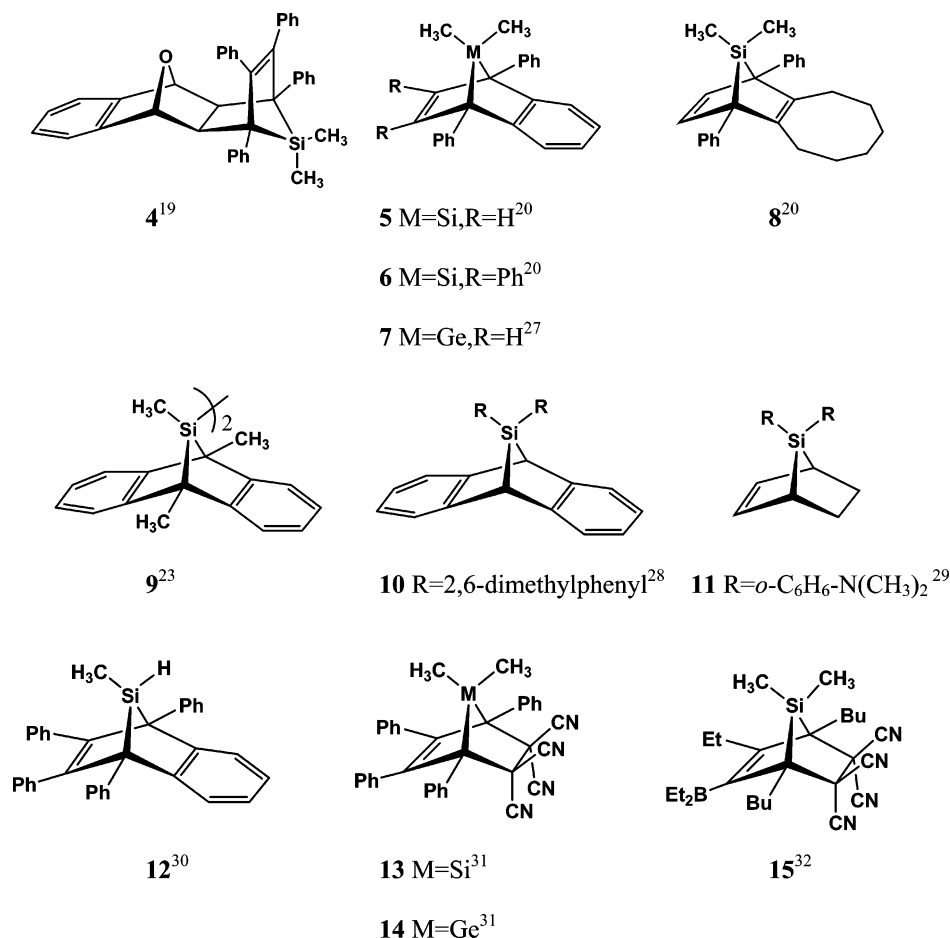
Table 1. Selected X-ray and B3LYP/6-31G* Geometrical Parameters of Molecules 1–3^a

	1 X-ray	1 calc	2 X-ray	2 calc	3 X-ray	3 calc
			<i>d</i> (Å)			
C(1)–C(2)	1.584(4)	1.584	1.580(3)	1.577	1.575(3)	1.574
C(6)–C(7)	1.568(4)	1.577	1.561(3)	1.569	1.564(3)	1.570
C(2)–C(3)	1.509(4)	1.537	1.519(3)	1.537	1.517(3)	1.530
C(5)–C(6)	1.504(4)	1.525	1.517(3)	1.524	1.509(3)	1.519
C(3)–X(4)	1.394(3)	1.393	1.377(3)	1.394	1.391(3)	1.390
C(5)–X(4)	1.378(4)	1.389	1.377(3)	1.388	1.386(3)	1.386
C(2)–C(6)	1.548(4)	1.561	1.553(3)	1.562	1.545(3)	1.553
C(1)–C(9)	1.547(4)	1.548	1.533(3)	1.541	1.534(3)	1.542
C(7)–C(8)	1.531(4)	1.543	1.526(3)	1.536	1.534(3)	1.536
C(8)–C(9)	1.356(4)	1.368	1.355(3)	1.369	1.354(3)	1.370
C(1)–M(10)	1.915(3)	1.938	2.004(2)	2.000	2.017(2)	2.000
C(4)–M(10)	1.910(3)	1.933	2.000(2)	1.995	2.009(2)	1.997
M(10)–C(11 _{syn} -) ^b	1.856(3)	1.888	1.937(2)	1.946	1.931(3)	1.944
M(10)–C(11 _{anti} -)	1.864(3)	1.891	1.941(2)	1.947	1.948(2)	1.947
			θ (deg)			
C(1)–C(9)–C(8)	112.9(3)	112.9	113.6(19)	113.5	113.8(16)	113.4
C(7)–C(8)–C(9)	112.3(2)	112.5	112.9(19)	113.1	113.2(18)	113.2
C(1)–M(10)–C(7)	83.1(12)	82.8	79.6(9)	80.7	79.5(9)	80.7
C(2)–C(1)–C(9)	104.9(2)	105.2	105.5(18)	106.0	107.4(18)	106.1
C(6)–C(7)–C(8)	107.1(2)	107.6	107.5(18)	108.5	107.7(17)	108.2
			ψ /deg			
C(7)–C(8)–C(9)–C(Ph9)	2.2(2)	9.6	3.2(2)	8.6	1.0(19)	10.4
C(1)–C(9)–C(8)–C(Ph8)	0.8(2)	0.4	1.6(2)	2.6	0.1(2)	1.1
			E_{tot}			
		–1847.126175		–3632.643784		–3613.185052

^a Butterfly bendings (ψ) and bond angles (θ). ^b *syn(anti)* orientation of methyl groups is defined with respect to the double bond.

being of the same order of magnitude as in unstrained silanes.^{20–22} This trend is customarily explained by electron

density delocalization from the endocyclic C–Si σ bonds into π^* system of the double bond.²³

Chart 1. Literature Examples of 7-Silanorborn(adi)ene and 7-Germanorborn(adi)ene Derivatives Investigated by X-ray Crystallography

The measured values of bond angles (Table 1) are also in the range of the bond angles found in the structurally related compounds.^{14,15} We shall single out only the C(1)–Si(10)–C(7) angle, which was found to be 83.1°, indicating that molecule **1** has a markedly strained structure. Finally, we note that the double bond in the 7-silanorbornene ring is practically planar, again in accordance with the situation found earlier in structurally related molecules (Chart 1). Specifically, the pyramidalization angles at C(8) and C(9) of 2.1° and 0.8° were found. This result is in accord with the expected decrease of π -electron density of the double bond due to π -electron transfer from the double bond into low-lying unoccupied σ -molecular orbital of the silicon (germanium) bridge.²⁴ On the other hand, it is in contrast to the related norbornenes and 7-oxanorbornenes, where experimental nonplanarity of the double bond lies within a range of 5–16°.^{25,26}

The molecular structures of **2** and **3** closely resemble that of **1**. This holds in particular for the orientations of the phenyl

groups relative to the basic molecular plane defined by the C(2), C(6), C(8), and C(9) atoms. Furthermore, in analogy with the adduct **1**, the endocyclic C(1)–Ge(10) bonds (2.000–2.017 Å) in **2** and **3** are found to be longer than the exocyclic ones (1.931–1.948 Å). The latter values are similar to the typical literature value for the carbon–germanium single-bond distance of 1.950 Å. Furthermore, the C(1)–Ge(10)–C(7) angles in **2** and **3** were found to be 79.9° and 79.5°, which are slightly smaller than the corresponding values found in the literature (Chart 1).

It is also noteworthy that, likewise in compound **1**, the aromatic rings attached to the olefinic bond are only slightly displaced from the plane defined by the C(1), C(9), C(8), and C(7) atoms. Specifically, germanium adduct **2** exhibits $\psi = 3.2^\circ$ at C(9) and 1.6° at C(8), while in adduct **3** deviation of the double bond from planarity is even less pronounced ($\psi = 1.0^\circ$ at C(9) and 0.1° at C(8)).

Comparison with X-ray Structures of Related Molecules.

It is interesting to put the results considered so far into perspective by comparison with available results of X-ray analysis of related 7-silanorborn(adi)ene and 7-germanorborn(adi)ene derivatives. They are collected in Chart 1.

In carrying out this analysis we were particularly interested in the geometry of the double bond. Unfortunately, it appeared that in most of the older studies pyramidalization of the double bond was not considered.^{33,34} Therefore we extracted pyrami-

(20) Baxter, S.; Mislow, K.; Blount, J. *Tetrahedron* **1980**, *36*, 605–616.

(21) Shafiee, F.; Damewood, J. R., Jr.; Haller, K. J.; West, R. *J. Am. Chem. Soc.* **1985**, *107*, 6950–6956.

(22) Carrell, H.; Donohue, J. *Acta Crystallogr. Sect. B* **1972**, *28*, 1566–1571.

(23) Sekiguchi, A.; Ziegler, S. S.; Haller, K. J.; West, R. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 197–202.

(24) See for example: Bock, H.; Solouki, B. In *Photoelectron spectra of silicon compounds*; Patay, S., Rappaport, Z., Eds.; *The Chemistry of Organic Silicon Compounds*, Vol. 1; Wiley: Chichester, 1989; pp 555–651.

(25) Carrupt, P.-A.; Vogel, P. *J. Mol. Struct. (THEOCHEM)* **1985**, *124*, 9–23.

(26) Eckert-Maksić, M.; Novak-Doumbouya, N.; Kiralj, R.; Kojić-Prodić, B. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1483–1487.

(27) Maslennikova, O. S.; Nosov, K. S.; Faustov, V. I.; Egorov, M. P.; Nefedov, O. M.; Aleksandrov, G. G.; Eremenko, I. L.; Nefedov, S. E. *Russ. Chem. Bull. (Translation of Izv. Akad. Nauk, Ser. Khim.)* **2000**, *49*, 1275–1282.

dalization angles from the coordinates deposited with the CCDC where possible.³⁵ This analysis revealed that most of the 7-silanorbornene and 7-germanorbornene derivatives reported so far exhibit a negligible to small degree of olefinic bond pyramidalization, in accordance with the results obtained for molecules **1–3**. It is also interesting to note that examples of the *endo*- as well as the *exo*-deviations of the substituents attached to the olefinic carbon atoms from planarity were found. The crystal structure of *syn*-benzo-1,2,3,4,11-pentaphenyl-11-silanorbornadiene (**12**) reported by Müller and co-workers is particularly interesting in this context.³⁰ The unit cell of this compound consists of two independent molecules having slightly different geometries. Similarly to **1–3**, both molecules exhibit the asymmetric out-of-plane bending of the double bond. In one of the molecules one of the olefinic carbon atoms is essentially planar ($\psi = 0.1^\circ$), while the pyramidalization at the second olefinic carbon is as large as 13.9° . In the second molecule of the unit cell phenyl groups bonded to the olefinic carbon atoms are displaced toward the *endo*-face of the bicyclic ring by 9.8° and 2.5° , respectively.

On the other hand, the X-ray structures of **13** and **14** published by Mochida and co-workers³¹ exhibit *exo*-folding of the double bond with pyramidalization angles at the olefinic carbon atoms of 6.1° and 4.5° , respectively. Furthermore in the crystal structure of **15**,³² one of the phenyl groups at the olefinic carbon atoms is displaced out by 3.7° in the *exo*- and the other one by 2.5° in the *endo*-direction (relative to the 7-silanorbornadiene ring). On the basis of these facts we conclude that the extent of the folding of the double bond in the considered molecules is a result of a fine balance of (a) the nature of the substituents and their substitution pattern at the 7-metallonorbornene ring and (b) intermolecular forces and crystal-packing effects.^{36,37}

It should be underlined in this context that similar trends were also found in crystal structures of several tetraphenylated norbornene derivatives.^{38,39} Characteristic examples are provided by the crystal structures of Diels–Alder adducts of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one, such as **16**³⁸ and **17**³⁹ (Chart 2). These structures are asymmetric in the crystal, and the phenyl rings attached to the olefinic C(8)–C(9) bond are displaced from the plane defined by C(1), C(9), C(8), and C(7) by $\psi = 11.9^\circ$ (C8) and 1.1° (C9) in molecule **16** and by 14.7° (C8) and 3.8° (C9) in adduct **17**.

In contrast to the trends observed in the crystal structures of the studied compounds, analysis of the available ¹³C NMR

(28) Kako, M.; Mori, M.; Hatakenaka, K.; Kakuma, S.; Nakadaira, Y.; Yasui, M.; Iwasaki, F. *Tetrahedron* **1997**, *53*, 1265–1274.

(29) Belzner, J.; Ihmels, H.; Kniesel, B. O.; Gould, R. O.; Herbst-Irmer, R. *Organometallics* **1995**, *14*, 305–311.

(30) Schuppan, J.; Herrschaft, B.; Müller, T. *Organometallics* **2001**, *20*, 4584–4592.

(31) Mochida, K.; Shimizu, H.; Kugita, T.; Nanjo, M. *J. Organomet. Chem.* **2003**, *673*, 84–94.

(32) Wrackmeyer, B.; Milius, W.; Bhatti, M. H.; Ali, S. *J. Organomet. Chem.* **2003**, *665*, 196–204.

(33) Nefedov, M.; Egorov, M. P. Structure and reactivity of 7-sila- and 7-germanorbornadienes as precursors of silylenes and germlylenes. In *Frontiers of Organosilicon Chemistry*; Bassindale, A. R., Gaspar, P. P. Eds.; The Royal Society of Chemistry: Cambridge, 1991; pp 145–158.

(34) Egorov, M. P.; Ezhova, M. B.; Antipin, M. Yu.; Struchkov, Y. T. *Main Group Metal Chem.* **1991**, *14*, 19–23.

(35) All crystallographic data presented here were retrieved from the Cambridge Crystallographic Data Centre (CCDC), www.ccdc.cam.ac.uk.

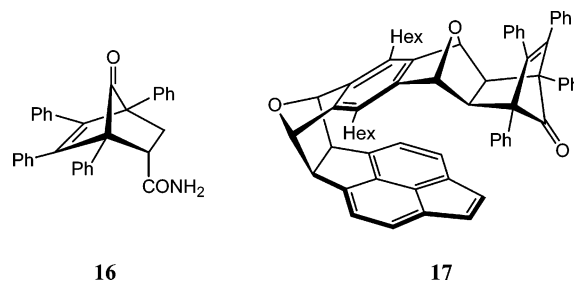
(36) Tiekink, E. R. T.; Hall, V. J.; Buntine, M. A.; Hook, J. *Z. Kristallogr.* **2000**, *215*, 23–33.

(37) Martin, A.; Orpen, A. G. *J. Am. Chem. Soc.* **1996**, *118*, 1464–1470.

(38) Neudorff, W. D.; Lentz, D.; Anibarro, M.; Schlueter, A. D. *Chem.-Eur. J.* **2003**, *9*, 2745–2757.

(39) Yoshitake, Y.; Misaka, J.; Abe, M.; Yamasaki, M.; Eto, M.; Harano, K. *Org. Biomol. Chem.* **2003**, *1*, 1240–1249.

Chart 2. 1,7,8,9-Tetraphenylnorbornene Derivatives **16** and **17**



spectroscopic data of the considered compounds does not allow any conclusion about the extent of pyramidalization at the olefinic carbon atoms. This is not surprising given that even in *syn*- and *anti*-sesquinorbornenes, which are paradigmatic examples of the pyramidalized and planar strained olefins, respectively, the ¹³C chemical shifts of the olefinic carbon atoms differ by only ca. 2.0 ppm (151.6 vs 153.9 ppm).⁴⁰

Computational Analysis. Having the experimental values at our disposal we are now in a position to check the validity of the B3LYP/6-31G* method for calculating geometries and, in particular, its reliability for calculating pyramidalization angles at the olefinic carbon atoms in sila (germa) norbornenes. The relevant calculated structural parameters of **1–3**, along with their total energies, are summarized in Table 1. Comparison of the calculated geometries with the X-ray data reveals that there is a good agreement between two sets of data, particularly if experimental errors are taken into account. The largest discrepancy is observed for the C(1)–Si(10) bond (0.023 and 0.032 Å for the endocyclic and exocyclic bond, respectively), in accordance with previously published finding.¹¹ On the other hand, the C(1)–Ge(10) bond distances appear to be slightly underestimated (Table 1).

As to the pyramidalization angles, we observe that the B3LYP method overestimates the extent of pyramidalization of the double bond in all three adducts (Table 1) by $\psi = 5.3$ – 9.4° . This result is somewhat surprising, since in most of the systems reported so far the B3LYP method was found to underestimate double-bond folding.^{6,8,41} To check whether this discrepancy is due to inaccuracy of the calculated C–Si bond lengths, the structure of **1** was reoptimized with the C(1)–Si(10) and C(7)–Si(10) bond lengths constrained to the experimental value of 1.910 Å. This calculation resulted in a change of pyramidalization angles of as small as 0.1° , implying that the observed overestimation of the endocyclic carbon–silicon bonds has a negligible effect on the calculated pyramidalization angles in **1**.

We shall close this discussion by considering the effect of the phenyl groups on the pyramidalization angles in some of the studied molecules. For this purpose, we relay on the results of the B3LYP/6-31G* calculations. The calculated angles for molecules **1–3b** are summarized in Table 3.

Starting with molecules **1–3**, we observe that replacement of the phenyl groups at the bridgehead position with the hydrogen atoms leads to an increase in pyramidalization at the C(8), while the pyramidalization angle at C(9) decreases. It is also worth noting that replacement of the phenyl groups at the olefinic positions has the same effect (Table 3). A similar trend is observed for the other sets of studied molecules. For instance, the B3LYP/6-31G*-optimized structure of the adduct **13** (Chart

(40) Paquette, L. A.; Künzer, H.; Green, K. E.; De Lucchi, O.; Licini, G.; Pasquato, L.; Valle, G. *J. Am. Chem. Soc.* **1986**, *108*, 3453–3460.

(41) Margetić, D.; Williams, R. V. *J. Org. Chem.* **2004**, *69*, 7134–7142.

Table 2. Crystallographic Details Collected at 100 K

	1	2	3
empirical formula and weight	C ₃₅ H ₃₁ NO ₂ Si, 525.21	C ₃₅ H ₃₁ GeNO ₂ , 571.16	C ₃₄ H ₂₈ GeO ₃ , 558.12
wavelength	0.71073 Å	0.71073 Å	0.71073 Å
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>P2(1)/c</i>	<i>P2(1)/c</i>	<i>P2(1)/c</i>
unit cell dimens	<i>a</i> = 15.7865(19) Å <i>α</i> = 90° <i>b</i> = 11.9788(14) Å <i>β</i> = 103.035(2)° <i>c</i> = 15.5336(19) Å <i>γ</i> = 90°	<i>a</i> = 15.8304(17) Å <i>α</i> = 90° <i>b</i> = 11.9315(13) Å <i>β</i> = 103.268(2)° <i>c</i> = 15.6080(17) Å <i>γ</i> = 90°	<i>a</i> = 11.8390(12) Å <i>α</i> = 90° <i>b</i> = 10.2678(11) Å <i>β</i> = 98.830(2)° <i>c</i> = 22.278(2) Å <i>γ</i> = 90°
volume	2861.8(6) Å ³	2869.4(5) Å ³	2676.0(5) Å ³
Z	4	4	4
density (calcd)	1.220 Mg/m ³	1.320 Mg/m ³	1.383 Mg/m ³
absorp coeff	0.114 mm ⁻¹	1.099 mm ⁻¹	1.179 mm ⁻¹
<i>F</i> (000)	1112	1184	1152
cryst size	0.12 × 0.12 × 0.04 mm ³	0.33 × 0.24 × 0.10 mm ³	0.22 × 0.20 × 0.14 mm ³
<i>θ</i> range for data collect	1.32 to 26.00°	1.32 to 26.00°	1.74 to 25.99°
index ranges	-11 ≤ <i>h</i> ≤ 19, -14 ≤ <i>k</i> ≤ 14, -19 ≤ <i>l</i> ≤ 18	-18 ≤ <i>h</i> ≤ 19, -13 ≤ <i>k</i> ≤ 14, -19 ≤ <i>l</i> ≤ 15	-14 ≤ <i>h</i> ≤ 12, -11 ≤ <i>k</i> ≤ 12, -25 ≤ <i>l</i> ≤ 27
no. of reflns collected	15 896	15 859	14 830
no. of indep reflns	5605 [<i>R</i> (int) = 0.0624]	5637 [<i>R</i> (int) = 0.0314]	5260 [<i>R</i> (int) = 0.0294]
completeness to <i>θ</i> = 26.00°	99.5%	99.7%	99.8%
absorp corr	empirical (SADABS)	empirical (SADABS)	empirical (SADABS)
max. and min transmn	0.9954 and 0.9864	0.8980 and 0.7130	0.8524 and 0.7815
refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
no. of data/restraints/params	5605/0/355	5637/0/355	5260/0/345
goodness-of-fit on <i>F</i> ²	1.005	1.003	1.003
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0466, <i>wR</i> ₂ = 0.0845	<i>R</i> ₁ = 0.0310, <i>wR</i> ₂ = 0.0702	<i>R</i> ₁ = 0.0333, <i>wR</i> ₂ = 0.0671
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0965, <i>wR</i> ₂ = 0.1175	<i>R</i> ₁ = 0.0458, <i>wR</i> ₂ = 0.0848	<i>R</i> ₁ = 0.0466, <i>wR</i> ₂ = 0.0694
largest diff peak and hole	0.309 and -0.296 e Å ⁻³	0.618 and -0.311 e Å ⁻³	0.629 and -0.390 e Å ⁻³

Table 3. Comparison of Experimental and Calculated Interplanar Angles between the Phenyl Groups and the C2–C6–C8–C9 Plane (deg) in 1–3 and the Effect of Phenyl Groups on the Pyramidalization Angles

	X-ray		B3LYP		X-ray		B3LYP		X-ray		B3LYP	
	1	1	1a	1b	2	2	2a	2b	3	3	3a	3b
	Interplanar Angles											
Ph(C1)	18.7	20.4			25.3	46.8			22.5	19.1		
Ph(C7)	79.9	83.6			74.0	80.0			82.9	52.6		
Ph(C8)	90.2	81.8	78.3		71.9	90.3	64.8		85.8	93.9	75.5	
Ph(C9)	55.2	35.6	27.4		33.6	24.5	33.6		42.5	32.8	40.6	
	Pyramidalization Angles											
Ψ(C8)	0.8	0.4	4.7	1.4	1.6	2.6	2.7	2.5	0.1	1.1	2.9	2.5
Ψ(C9)	2.1	9.7	7.0	1.4	3.2	8.6	7.2	2.5	1.0	10.5	7.4	2.5

1) exhibits asymmetric deformation of the double bond by 2.5° at C(8) and 4.8° at C(9) in the *exo*-direction. This should be compared with the experimentally determined folding of 6.1° in the *exo*-direction. Replacement of the phenyl groups at the bridgehead positions with the hydrogen atoms leading to **13a** results in a pyramidalization angle of 4.3° in the *endo*-direction and 8.4° in the *exo*-direction at C(8) and C(9) atoms, respectively. Finally, in the unsubstituted adduct **13b** a pyramidalization angle of 1.6° at both olefinic atoms toward the *endo*-face of the molecule was found. As a last example we shall consider the effect of gradual replacement of the phenyl groups on the geometry of the double bond in the adduct **14**. For this molecule B3LYP calculations predict a symmetrical structure with 7.3° *exo*-bending, which is in fair agreement with the measured angle of 4.5° in the crystal structure (X-ray geometry was used as the initial guess in optimization).³¹ When the phenyl groups of **14** at the bridgehead positions C(7) and C(8) were replaced by the hydrogen atoms leading to **14a**, the double bond was found to be asymmetrically bent with *ψ* = 8.3° in the *endo*-direction and *ψ* = 2.1° in the *exo*-direction at the C(8) and C(9) atoms, respectively. Finally, replacement of all four phenyl groups with

hydrogen atoms resulted in a symmetrical structure, **14b**, exhibiting only minute *endo*-pyramidalization (1.6°).

Conclusion

The synthesis and X-ray structures of 7-silanorbornene and 7-germanorbornene derivatives **1–3** are presented. The compounds were prepared by high-pressure-assisted cycloaddition reactions of 1-sila-2,3,4,5-tetraphenyl-1,1-dimethyl-2,4-cyclopentadiene and 1-germa-2,3,4,5-tetraphenyl-1,1-dimethyl-2,4-cyclopentadiene with *N*-methylmaleimide in high yields. The reactions gave *endo*-adducts as the single products with olefinic bonds exhibiting negligible (**3**) to very small (**1** and **2**) pyramidalization in the *endo*-direction. Pyramidalization of the double bond in the adducts **1–3** was also compared with available X-ray data for a number of 7-silanorborn(adi)ene and 7-germanorborn(adi)ene derivatives. On the basis of analysis of these results it was concluded that the extent of pyramidalization in the studied molecules strongly depends on the nature and substitution pattern, as well as on the saddle effects of the crystal-packing forces. Finally, it is shown that the B3LYP/6-31G* method considerably overestimates the extent of the double bond bending in **1–3**.

Experimental Section

Computational Methods. All geometry optimizations were carried out with the Gaussian 98 suite of programs⁴² employing the density functional theory (DFT) hybrid B3LYP method using the 6-31G* basis set.^{43,44} Harmonic vibration frequencies were calculated for all localized stationary structures to verify whether they are minima. Pyramidalization angles at the olefinic carbon atoms are reported in terms of the butterfly bending angle (ψ) as defined in refs 41 and 45. Calculations were carried out on the dual Athlon MP and Pentium III personal computers under the Linux Redhat 8.0 operating system.

Experimental Details. Silole and germole were prepared by known methods.^{46,47} The ¹H, ¹³C, and ²⁹Si NMR spectra were recorded in CDCl₃ solutions containing tetramethylsilane as internal standard on Bruker AMX300 or 600 MHz instruments. Melting points were determined using a Gallenkamp digital melting point apparatus and are uncorrected. The high-resolution mass spectra were recorded on a Micromass Platform II single quadrupole AutoSpec instrument. Centrifugal radial chromatography was carried out with a chromatotron, Model No. 79245T, using 1 mm plates with silica gel 60F₂₅₄ as the stationary phase with ethyl acetate–petroleum ether (40–60 °C) mixture as eluent. High-pressure reactions were performed using a high-pressure piston-cylinder apparatus, in Teflon cells, and pentane as piezotransmitter liquid. The single-crystal X-ray data were collected on a Bruker SMART APEX diffractometer equipped with a CCD area detector at 100 K. All structures were solved by direct methods and refined using full-matrix least-squares with the SHELX-97 software package.⁴⁸

1,7,8,9-Tetraphenyl-4,10,10-trimethyl-4-aza-10-sila-1 α ,2 α ,6 α ,7 α -tricyclo [5.2.1.0.2⁶]deca-8-ene-3,5-dione (1). A solution of 1-sila-2,3,4,5-tetraphenyl-1,1-dimethyl-2,4-cyclopentadiene (50 mg, 0.121 mmol) and *N*-methylmaleimide (13 mg, 0.121 mmol) in dichloromethane (1 mL) was pressurized at 8 kbar at 70 °C for 3 days. Solvent was then removed in vacuo to afford a yellow solid, which was recrystallized from ethyl acetate to afford **1** as a yellow solid (48 mg, 76%, mp 252–254 °C). ¹H NMR (CDCl₃) δ (ppm): 0.28 (3H, s, SiCH₃), 0.65 (3H, s, SiCH₃), 3.07 (3H, s, NCH₃), 4.30 (2H, s, *Hexo*), 6.58–7.29 (20H, m, HAR). ¹³C NMR (CDCl₃) δ (ppm): –6.4 (SiCH₃), –3.5 (SiCH₃), 25.0 (C₂,C₆), 49.5 (NCH₃), 53.7

(C₁,C₇), 125.3 (CAr), 126.0 (CAr), 127.1 (CAr), 127.4 (CAr), 129.6 (CAr), 130.2 (CAr), 136.4 (C=C), 137.7 (CAr), 141.1 (CAr), 177.1 (C=O). ²⁹Si NMR (CDCl₃) δ (ppm): 46.6. HRMS calcd for C₃₅H₃₁NO₂Si: *m/z* 525.2124, found 525.2129. Anal. Calcd for C₃₅H₃₁NO₂Si: C, 79.96; H, 5.94; N, 2.66. Found: C, 80.39; H, 5.54; N, 3.02.

1,7,8,9-Tetraphenyl-4,10,10-trimethyl-4-aza-10-germa-1 α ,2 α ,6 α ,7 α -tricyclo [5.2.1.0.2⁶]deca-8-ene-3,5-dione (2). A solution of 1-germa-2,3,4,5-tetraphenyl-1,1-dimethyl-2,4-cyclopentadiene (50 mg, 0.109 mmol) and *N*-methylmaleimide (12 mg, 0.109 mmol) in dichloromethane (1 mL) was pressurized at 8 kbar at 70 °C for 3 days. Solvent was then removed in vacuo to afford a yellow solid, which was subjected to radial chromatography (petroleum ether–ethyl acetate, 20:1, then the solvent polarity was gradually increased to pure ethyl acetate) to afford **2** as a yellow solid (50 mg, 85%, mp 249–251 °C). An X-ray sample was obtained by crystallization from ethyl acetate. ¹H NMR (CDCl₃) δ (ppm): 0.47 (3H, s, GeCH₃), 0.79 (3H, s, GeCH₃), 3.05 (3H, s, NCH₃), 4.35 (2H, s, *Hexo*), 6.59 (2H, d, *J* = 8.1 Hz, HAR), 6.89–6.90 (6H, m, HAR), 7.06–7.08 (2H, m, HAR), 7.12–7.16 (4H, m, HAR), 7.21–7.23 (4H, d, *J* = 7.7 Hz, HAR). ¹³C NMR (CDCl₃) δ (ppm): –5.3 (GeCH₃), –0.7 (Ge CH₃), 25.1 (C₂,C₆), 50.6 (NCH₃), 56.8 (C₁,C₇), 125.3 (CAr), 126.0 (CAr), 127.3 (CAr), 127.5 (CAr), 129.5 (CAr), 130.4 (CAr), 136.9 (C=C), 138.8 (CAr), 144.1 (CAr), 174.3 (C=O). HRMS calcd for C₃₅H₃₁NO₂Ge: *m/z* 571.1567, found 571.1581. Anal. Calcd for C₃₅H₃₁NO₂Ge: C, 73.72; H, 5.48; N, 2.46. Found: C, 73.42; H, 5.23; N, 2.76.

1,7,8,9-Tetraphenyl-10,10-dimethyl-4-oxa-10-germa-1 α ,2 α ,6 α ,7 α -tricyclo [5.2.1.0.2⁶]deca-8-ene-3,5-dione (3).¹⁴ A solution of 1-germa-2,3,4,5-tetraphenyl-1,1-dimethyl-2,4-cyclopentadiene (25 mg, 0.0545 mmol) and maleic anhydride (9 mg, 0.0545 mmol) in dichloromethane (1 mL) was pressurized at 8 kbar at 70 °C for 3 days. Solvent was then removed and residue recrystallized from ethyl acetate to afford **3** as a colorless solid (12 mg, 40%, mp 222–224 °C). An X-ray sample was obtained by crystallization from dichloromethane–petroleum ether. ¹H NMR (CDCl₃) δ (ppm): 0.53 (3H, s, GeCH₃), 0.86 (3H, s, GeCH₃), 4.62 (2H, s, *Hexo*), 6.66–7.23 (20H, m, HAR). ¹³C NMR (CDCl₃) δ (ppm): –5.1 (GeCH₃), –0.3 (GeCH₃), 25.4 (C₂,C₆), 51.7 (NCH₃), 57.1 (C₁,C₇), 125.9 (CAr), 126.4 (CAr), 127.4 (CAr), 127.5 (CAr), 129.3 (CAr), 130.5 (CAr), 136.2 (C=C), 137.7 (CAr), 142.7 (CAr), 172.1 (C=O). HRMS calcd for C₃₄H₂₈O₃Ge: *m/z* 558.1250, found 558.1259. Anal. Calcd for C₃₄H₂₈O₃Ge: C, 73.29; H, 5.07. Found: C, 73.56; H, 4.72.

Full crystallographic data for compounds **1**, **2**, and **3** have been deposited with the Cambridge Crystallographic Data Centre, deposition numbers CCDC 271104, CCDC 271105, and CCDC 271106. Copies may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Cartesian coordinates for all calculated structures are available free of charge via the Internet at <http://pubs.acs.org>.

OM050671B

(42) 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.; Morokuma, 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. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(43) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372–1377.

(44) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

(45) Margetić, D.; Williams, R. V.; Warrenner, R. N. *J. Org. Chem.* **2003**, *68*, 9186–9190.

(46) Kirin, S. I.; Klärner, F.-G.; Eckert-Maksić, M. *Synlett* **1999**, 351–353.

(47) Eckert-Maksić, M.; Kazazić, S.; Kazazić, S.; Kirin, S. I.; Klasinc, L.; Srzić, D.; Žigon, D. *Rapid Commun. Mass. Spectrom.* **2001**, *15*, 462–465.

(48) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.