Organometallics **2008,** *27,* 4847–4853

Articles

Bis-alkene Complexes of Stannylium and Germylium Ions

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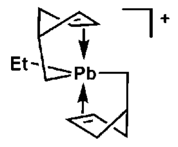
Received May 12, 2008

Bis-alkene complexes of triorgano-substituted cations of stannylium and germylium ions were synthesized by alkyl fragmentation reactions and were characterized by NMR spectroscopy and for the tin compound also by X-ray structure analysis of the corresponding perfluorinated tetraarylborate. According to experimental results and quantum mechanical computations, the central group 14 element adopts in these pentacoordinated cations a distorted trigonal-bipyramidal coordination geometry with the two C═C double bonds occupying the apical positions. This geometrical arrangement places seven carbon atoms at a distance less than the sum of the van der Waals radii around the central atom. Quantum mechanical computations at the MP2/6-311G(d,p) (C,H) SDD (Sn, Ge, Si) level reveal substantial interaction energies between the group 14 element and the C═C double bond and electron density distributions that are typical for noncovalent π-donor interactions.

Introduction

Triorgano-substituted cations of the heavier group 14 elements have recently received considerable attention.[1] Many examples with the central element stabilized by intramolecular interaction with remote donor substituents having lone pairs are known, and this interaction leads to tetra- or pentacoordination for the formally positively charged element atom.[2] Previously, it was shown that the stabilization by a π-donor ligand as it is provided in the norbornyl framework[3] or by remote aryl groups[4,5] is sufficient to generate and characterize organo-substituted cations of the group 14 elements. Well-characterized examples of alkene complexes which are ubiquitous in transition metal chemistry are however still very rare in main group chemistry.[6] Recently we reported on a bisalkene complex of a triorganolead cation, **1**, in which two cyclopent-3-enylmethyl substituents coordinate via their C═C double bonds to the electron-deficient lead center.[7] In extension of this study, we report here on the synthesis and characterization of the homologous tin and germanium compounds and about our attempts toward the synthesis of the corresponding silicon compound.



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Results and Discussion

The synthesis of stannyl and germyl cations **2a**,**b** exploits remote attack of a strong electrophile, such as trityl cation, on tetraalkyl stannane or germane, which yields the cationic species and alkenes.[7,8] The reaction is thought to proceed via stannyl- or germyl-substituted carbocations, which in a second step eliminates the alkene.[8] The intended synthesis of the silyl cation **2c** followed established synthetic protocols such as the hydride transfer reaction.[1,9,10] The reaction of silylhydride **3c** with trityl cation under varying conditions (Scheme 1), however, did not lead to the clean formation of cation **2c** but to complicated mixtures of unidentified products. In contrast, cations **2a**,**b** are

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(1) For recent review, see:(a) Müller, T. *Adv. Organomet. Chem.* **2005**, *53*, 155. (b) Zharov, I.; Michl, J. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*, Vol 2; Rappoport, Z., Ed.; Wiley: Chichester, 2002; p 633.

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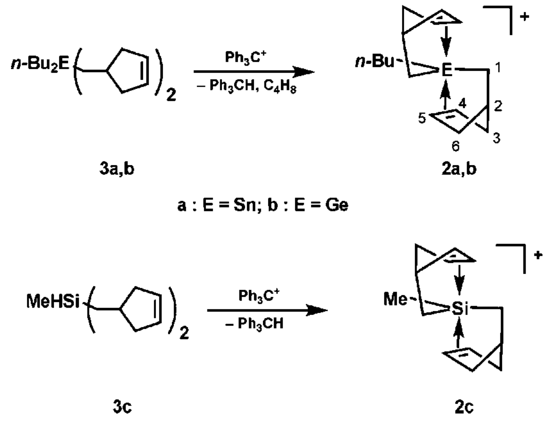
10.1021/om800432x CCC: $40.75

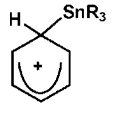
Scheme 1. Formation of Organometallic Cations 2a,b and Attempted Synthesis of Silyl Cation 2c



cleanly formed from bis(cyclopentenemethyl)-substituted precursors **3a**,**b** after hydride abstraction by trityl cation and butene elimination (Scheme 1). The obtained solutions of the salts **2a**,**b**$\cdot$[B(C_6F_5)$_4$] in aromatic solvents or in methylene chloride proved to be stable at room temperature at least for several weeks.

The formation of cations **2a**,**b** is confirmed by ^{1}H, ^{13}C, and, for **2a**, ^{119}Sn NMR spectroscopy. The ^{119}Sn NMR signal for **2a** is strongly downfield shifted compared to the precursor stannane **3a** ($\delta(^{119}\text{Sn}) = 207.6$ in toluene-d_6, $\Delta\delta$ (^{119}Sn(**2a**/**3a**) = 183)), indicating positive charge accumulation at the tin atom.[11] It is however significantly less deshielded than the tin atoms in triaryl-substituted stannylium ions ($\delta(^{119}\text{Sn})$ = 700–800).[1,10a,c,d] The ^{119}Sn NMR chemical shift of stannyl cation **2a** remains nearly unchanged when the NMR solvent is changed from toluene-d_8 to methylene chloride-d_2 ($\delta(^{119}\text{Sn})$ = 210.2) This observation rules out the possibility for a significant interaction between solvent molecules and cation **2a**, such as the formation of trialkylstannyl toluenium ions in toluene.[1,12] In addition, the appreciable difference in the ^{119}Sn NMR chemical shift between the spiro cation **2a** and the stannanorbornyl cation **5a**[3a] (($\delta(^{119}\text{Sn}) = 334$, $\Delta\delta(^{119}\text{Sn}(\mathbf{5a}/\mathbf{2a}) = 126.4)$) discards a conceivable fast equilibrium of norbornyl cations **6a** (Scheme 2), for which a ^{119}Sn NMR chemical shift near that of **5a** is to be expected.

The presence of only eight ^{13}C NMR signals for each of the cations **2a** and **2b** suggests that both cyclopentenylmethyl substituents are equivalent in solution and indicates a symmetric structure for cations **2a**,**b**. The ^{13}C NMR chemical shifts of the saturated carbon atoms C^1–C^3 and C^6 are similar to those found for the norbornyl cations **5a**,**b**[3a] and to the lead analogue **1**[7]



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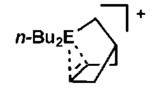

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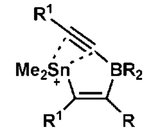
a : E = Sn; b : E = Ge



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R = Et, *i*-pr; R^1 = alkyl, aryl

Scheme 2. Degenerate Equilibrium between Stannanorbornyl Cations 6a

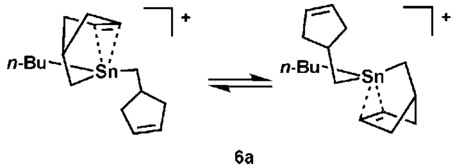

Table 1. Selected NMR Parameter of Bis(cyclopentenylmethyl) Cations of Group 14 Elements (NMR data for norbornyl cations 5a,b and lead cation 1 are given for comparison; NMR chemical shifts in ppm, $^1J_{CH}$ coupling constants in parentheses in Hz)

compd	E	δ(E)	$\delta(C^1)$	$\delta(C^2)$	$\delta(C^3,C^6)$	$\delta(C^4,C^5)$	$\Delta\delta(C^4,C^5)$
2a[a]	Sn	207.6	25.7	36.3	41.5	139.6 (169)	10.9
5a[b,c]	Sn	334.0	25.0	35.3	40.4	141.5 (170)	11.1
2b[a]	Ge		19.4	37.2	41.3	145.2 (173)	15.0
5b[b,c]	Ge		18.2	36.5	40.5	144.8 (173.2)	14.6
1[d]	Pb	806.7	48.4	35.6	39.3	136.1	5.9

[a] At 298 K in toluene-d_8. [b] At 298 K in benzene-d_6. [c] From ref 3a. [d] From ref 7.

(see Table 1). The ^{13}C NMR data of the vinylic carbon atoms C^4 and C^5 is indicative of the cage structure of cations **2a**,**b**. The significant low-field shift of the ^{13}C NMR signal compared to the neutral precursor compounds ($\Delta\delta(C^4,C^5)$ = 10.9 (**2a**) and 15.0 (**2b**)) is in agreement with intramolecular coordination of the positively charged element atom to the remote C^4=C^5 double bond. In the case of the tin compound the direct bonding between the tin atom and the vinylic carbon atoms $C^{4,5c}$ is demonstrated by a significant scalar coupling constant (^1J(SnC) = 17.6 Hz) since the alternative coupling path along four bonds cannot lead to substantial scalar coupling.[13a] The detected ^1J(SnC) is an order of magnitude smaller than regular couplings along a C–Sn single bond ($^1J(\text{SnC}) \approx 300$ Hz),[13] a fact that can be rationalized by the particular bonding situation in cation **2a**. Similar strongly reduced ^1J(SnC) coupling constants were reported for zwitterionic compounds of the type **7** (^1J(SnC) = 40–80 Hz)[13b] and for the norbornyl cation **5a** (^1J(SnC) = 26 Hz).[3a]

Crystals of **2a**$\cdot$[B(C_6F_5)$_4$] suitable for X-ray structure analysis were grown by slow diffusion from hexane into toluene solution. The salt **2a**$\cdot$[B(C_6F_5)$_4$] crystallizes with 0.5 equiv of toluene and reveals two independent cations in the asymmetric unit. These two molecules differ from each other only in the conformation of the butyl group (see Supporting Information for details). The structure of the salt reveals well-separated cations and anions (Figure 1a). No fluorine atom of the borate anion approaches the tin atom at a distance smaller than 400 pm. The tin atom in cation **2a** adopts a distorted trigonal-bipyramidal coordination geometry (Figure 1b,c). The planarity of the trigonal base is indicated by the summation of the three C–Sn–C angles α (117.2°, 122.0°, 120.8°) to 360°. The coordination sphere of tin is completed by the C=C double bonds of the two cyclopentenylmethyl substituents, which take up the apical positions. The steric requirements of this

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(11) NMR chemical shifts are not clear indicators of charge at a nucleus. Increased positive charge accumulation at a nucleus leads however to smaller energy differences between occupied and virtual orbitals. According to qualitative NMR chemical shift theory, this results in a larger paramagnetic (i.e., deshielding) contribution to the NMR chemical shielding constant. In consequence, very often the formation of cations by lowering the coordination number, i.e., from R_4Sn to R_3Sn^+, is accompanied by a significant low-field shift of the Sn resonance. For the basic theory, see: Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699.

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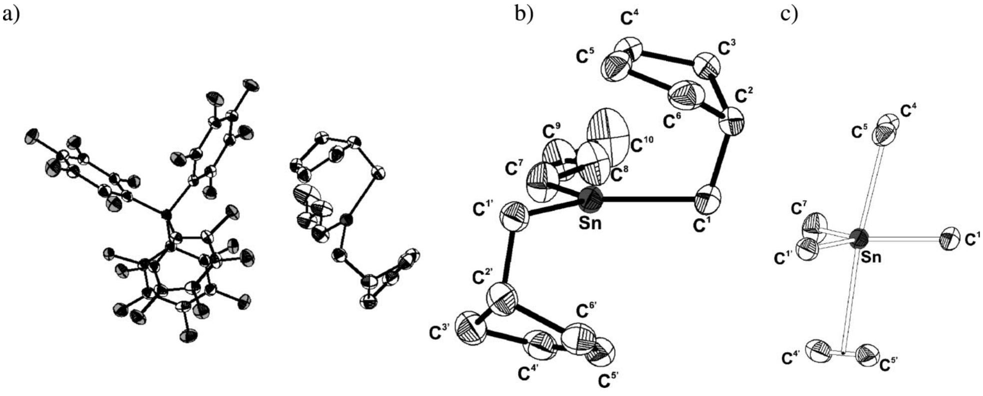

Figure 1. (a) Arrangement of one ion pair of **2a**·[B(C_6F_5)$_4$] in the crystal. (b) Molecular structure of cation **2a** in the crystal. (c) Coordination sphere of the tin atom in cation **2a**. Selected interatomic distances in pm: Sn−C^4 277.11(108), Sn−C^5 278.02(086), Sn(centerC^4C^5) 269.49(7) Sn−$C^{4'}$ 278.98(100), Sn−$C^{5'}$ 280.83(102), Sn(center$C^{4'}C^{5'}$) 271.53(7), Sn−C^1 213.84(81), Sn−$C^{1'}$ 215.28(75), Sn−C^7 215.68(87), C^4C^5 132.95(116), $C^{4'}C^{5'}$ 135.93(150). (Color code: B black, C white, Sn dark gray, F light gray, thermal ellipsoids at 30% probability level).

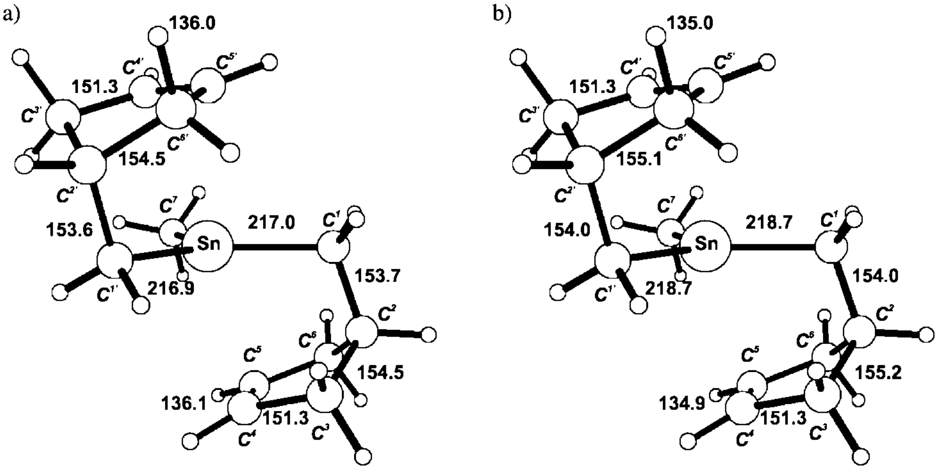

Figure 2. Molecular structure of cation **8a**. (a) As obtained at the MP2/6-311+G(d,p) (C,H), Sn (SDD) level of theory. Selected interatomic distances in pm: Sn−C^4 282.3, Sn−C^5 284.3, Sn(centerC^4C^5) 276.8, Sn−$C^{4'}$ 284.1, Sn−$C^{5'}$ 286.1, Sn(center$C^{4'}C^{5'}$) 275.0. (b) As obtained at the B3LYP/6-311+G(d,p) (C,H), Sn (SDD) level of theory. Selected interatomic distances in pm: Sn−C^4 295.3, Sn−C^5 296.0, Sn(centerC^4C^5) 287.9, Sn−$C^{4'}$ 295.4, Sn−$C^{5'}$ 296.0, Sn(center$C^{4'}C^{5'}$) 284.5.

intramolecular interaction enforce deviations from the ideal trigonal-bipyramidal coordination (see Figure 1c). In particular the axis along the midpoints of the two C═C double bonds is tilted by $\gamma = 11.9°$ toward the C_3Sn plane, and the midpoints form with the tin atom an angle β, which differs significantly from 180° ($\beta = 164.7°$). The two C_2Sn planes (C^4C^5Sn and $C^{4'}C^{5'}Sn$) are twisted and enclose a dihedral angle δ of 59.2°. This spatial arrangement places seven carbon atoms at distances less than 290 pm.

Therefore, the molecular structure of the tin cation **2a** closely resembles that of the related plumbyl cation **1**.[7] In addition, there is a close concurrence between the experimental structure of cation **2a** and the molecular structure computed[14] for the methyl-substituted model cation **8a** (at MP2/A, see Technical Section for details). That is, all computed bond lengths for stannyl cation **8a** do not differ from experimental values obtained for **2a** by more than 3 pm (see Figure 2a). In particular, the coordination geometry predicted for **8a** closely resembles in all details that of **2a** (see Table 2). Furthermore, the MP2-based method is superior compared to the B3LYP hybrid density functional method in describing the coordination sphere of the tin atom, as found in the crystal (see Figure 2 and Table 2). The convincing agreement justified a thorough theoretical analysis of the bonding in bis-alkene complexes of group 14 organometallic cations on the basis of stannyl cation **8a** and its congeners **8b** and **2c** at the MP2 level of theory. The optimized structures of all three group 14 cations **8a**,**b** and **2c** are very similar to each other, major differences arising only for structural parameters that are related to the different size of the central atom (see Table 2). For example, in all investigated cases the coordination sphere of the element atom E and its three closest substituents is trigonal planar, which is indicated by the sum of the CEC bond angles α of $\sum\alpha = 360°$. The predicted C═C double bond lengths in cations **8a**,**b** and **2c** fall in a close range of 135.9−136.2 pm, which is only slightly elongated compared to the C═C double bond lengths in tricoordinated cations **9a**−**c** (r(C═C) = 134.5 pm at MP2/A). The elongation of the C═C double bonds is most pronounced for the silicon cation **2c**, while for the tin and the germanium cations **8a**,**b** nearly identical C═C bond lengths are predicted.

In all three cases the C═C double bonds complete a distorted trigonal-bipyramidal coordination sphere for the element atom, and the distances between the central element atom and the carbon atoms of the C═C bond increase with the size of the

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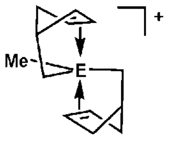
[14] All computations were done using: Frisch, M. J.; et al. *Gaussian 03*, Revision C.02; Gaussian Inc.: Pittsburgh, PA, 2003.

Table 2. Selected Experimental (italic) and Computed Structural Parameter of Bis(cyclopentenemethyl) Cations of Group 14 Elements (bond lengths in pm and bond angles and dihedral angles in deg)

compd	E	method	Ctr.−E[a]	=C−E	C^4=C^5 $C^{4'}$=$C^{5'}$	Σ α(CEC)	β(Ctr.ECtr.′)[a]	δ(C^4C^5E/C^4C^5E)	γ(Ctr.Ctr./base)[a,b]
2[a]	Sn	X-ray	*269.49*	277.11	132.95	360.0	164.7	59.2	11.9
			271.53	278.02	135.93				
				280.08					
				279.00					
8a		MP2/A	276.84	282.3	135.99	360.0	164.7	58.7	13.1
				284.3					
			275.03	286.0	136.07				
				284.1					
8a		B3LYP/A	284.46	292.46	134.98	360.0	164.5	55.2	14.6
			287.90	292.39	134.87				
				295.36					
				296.02					
8[b]	Ge	MP2/A	268.32	270.4	135.88	360.0	167.5	56.9	10.1
				272.5					
			262.76	276.9	136.09				
				276.6					
2c	Si	MP2/A	257.40	273.9	136.20	359.9	168.9	56.3	9.0
				273.0					
			264.89	267.9	135.92				
				265.1					

[a] Ctr. = center of the C^4=C^5 double bond. [b] Base = plane spanned by the element atom and the carbon atoms C^1, $C^{1'}$, and C^7.

element atom. Noteworthy, this distance is for all three cations significantly smaller than the sum of the van der Waals radii of the contributing atoms (see Table 2, sum of the van der Waals radii:[15] vdW(CSi) = 380 pm; vdW(CGe) = 385 pm; vdW(CSn) = 387 pm). These structural parameters, the small increase in the C=C bond length comparing cations **9** with cations **8a**,**b** and **2c**, and the close proximity of the element atoms to the C=C double bonds suggest bonding interactions between the C=C double bonds and the element atom in cations **7a**,**b** and **1c**.



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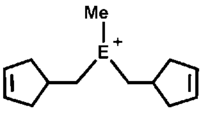
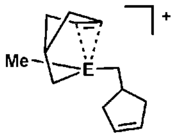
a: E = Sn; b: E=Ge



9

a: E = Sn; b: E=Ge; c: E=Si



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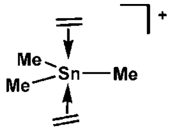
a: E = Sn; b: E=Ge; c: E=Si

The bonding energy (I_E) of the specific interaction of the positively charged group 14 element atom and the two remote C=C double bonds is computed by comparing the absolute energies of cations **9** with that of cations **8a**,**b** and **2c** (see Table 3). The interaction energy I_E is in all three cases substantial and of similar size (I_E(**8a**) = 133.2 kJ mol^{-1}, I_E(**8b**) = 126.5 kJ mol^{-1}, I_E(**8c**) = 128.7 kJ mol^{-1}). Interestingly, the energy for the interaction with two C=C bonds in **8a**,**b** and **2c** is less than twice the stabilization energy predicted for the interaction of the positively charged element atom and the C=C bond for the norbornyl cations **10** (see Table 3). In all three cases I_E for the norbornyl cations **10a**−**c** is approximately two-thirds of the I_E predicted for the bis-alkene complexes **8a**,**b** and **2c**. The smaller calculated binding energy for the second alkene is however not a result of the distorted and therefore unfavorable coordination geometry around the central element in the spiro bicyclic cations **8a**,**b** and **2c**. In contrast, even for the stepwise formation of the strain-free bis-ethene complex **11a** of trimethyl stannylium **11c**, the first complexation step, which yields the ethene complex **11b**, is energetically more favored than coordination of the second ethene molecule. Also in this case the interaction energy I_E computed for **11b** (I_E = 87.7 kJ mol^{-1}) is ca. 66% of the I_E predicted for **11a** (I_E = 132.1 kJ mol^{-1}, see Table 3). This result suggests that the interaction between the empty p-orbital at the element atom and the π-orbital of one individual alkene is more efficient in the tetracoordinated monoalkene complexes **10a**−**c** and **11b**, as it is in the case of the pentacoordinated dialkene complexes **8a**,**b**, **2c**, and **11a**. This might be the result of the competition between the two donor π-orbitals of the alkenes for the acceptor p-orbital of the central element atom.

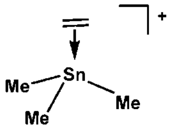
Table 3. Characteristic Bonding Parameter of Cyclopentenylmethyl Cations of Group 14 Elements 2c and 8−10 and Related Cations[a]

compd	E	I_E	occ(π(C=C))	occ(p(E))	charges (E)
8a	Sn	133.2	1.79	0.25	2.08
10a	Sn	83.7			
9a	Sn	0	1.88	0.12	2.16
8b	Ge	126.5	1.75	0.32	1.77
10b	Ge	82.7			
9b	Ge	0	1.88	0.19	1.89
2c	Si	128.7	1.76	0.32	1.97
10c	Si	88.9			
9c	Si	0	1.88	0.19	2.02
11a	Sn	132.1			
11b + C_2H_4	Sn	87.7			
11c + 2 C_2H_4	Sn	0			

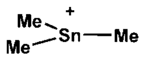
[a] Interaction energies I_E (kJ mol^{-1}) calculated at MP2/A and orbital occupations occ (au) and computed charges according to NBO theory.



11a



11b



11c

An NBO analysis[16] of the MP2/A wave function suggests a significant charge transfer from the C=C double bonds to the positively charged element atom for all three cations **8a**,**b** and

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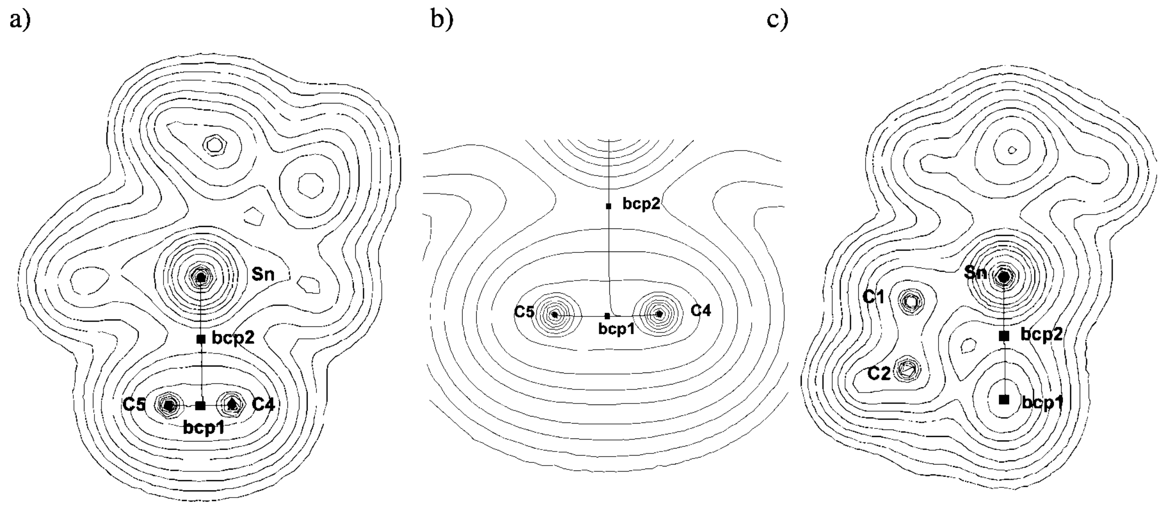

Figure 3. (a) Computed electron density map of the Sn/C^4=C^5 plane in cation **7a**. (b) Enlarged portion of **3a** showing the deviation of the electron density from the ideal T-shape. (c) Computed electron density map of the plane along the Sn bcp1 axis and perpendicular to the C^4C^5 vector in cation **7a**, which shows the bond path from the Sn atom via bcp2 leading to the close vicinity of bcp1. Note also the elliptical electron distribution around bcp1.

Table 4. Properties of the Charge Density ρ at Selected Bond Critical Points in Cyclopentenylmethyl-Substituted Group 14 Cations[a]

		Si		Ge		Sn	
		2c	**9c**	**8b**	**9b**	**8a**	**9a**
bcp1′ /bcp1	ρ	0.33740/0.33594	0.34410/0.34393	0.33753/0.33642	0.34376/0.34366	0.33702/0.33658	0.34409/0.34415
	n	1.91/1.89	2.01/2.01	1.91/1.90	2.00/2.00	1.90/1.90	2.01/2.01
	$\nabla^2\rho$	−0.26159/−0.26008	−0.26758/−0.26741	−0.26139/−0.26008	−0.26693/−0.26682	−0.26105/−0.26042	−0.26756/−0.26766
	ε	0.36861/0.35555	0.45003/0.44883	0.37214/0.36385	0.44755/0.44701	0.36385/0.36228	0.44913/0.44953
bcp2′ /bcp2	ρ	0.02808/0.03205		0.02824/0.03130		0.02838/0.02924	
	$\nabla^2\rho$	0.00290/0.00149		0.00850/0.00878		0.01111/0.01177	
	ε	0.15633/0.12685		0.51433/0.55864		0.60204/0.61557	

[a] Computed at the HF/6-311G(d,p) (E) tzvpp level of theory [ρ (e bohr^{-3}), $\nabla^2\rho$ (e bohr^{-5})].

2c. This electron transfer leads to a considerable occupation of the formally empty n(p)-orbital at the central element atom (0.25−0.32 e in **8a**,**b** and **2c** compared to 0.12−0.19 e in the tricoordinated cations **9a**−**c**) and somewhat depleted π-orbitals of the C=C double bonds (1.75−1.79 e in **8a**,**b** and **2c** versus 1.88 e in **9a**−**c**). This interaction reduces slightly the electron deficiency at the central element atom in **8a**,**b** and **2c** compared that in the tricoordinated cations **9** by 0.05−0.12 e (see Table 3).

The topological analysis[17,18] of the charge density for the optimized structures of cations **8a**,**b** and **2c** reveals only two bond critical points[19] with their corresponding bond paths on each C=C/E plane (see Figure 3a for an example). The first bond path connects two carbon atoms (C^4/C^5 or $C^{4'}$/$C^{5'}$) and has the bond critical point bcp1. The large value of the charge density ρ at bcp1, the large negative value of the Laplacian of the charge density ρ, $\nabla^2\rho$, and the nonzero ellipticity ϵ at bcp1 are near those of typical C=C double such as in open cations **9** (see Table 4 and Figure 3c).[18,20] The charge densities at bcp1 and the derived covalent bond orders n[21] in each of the bis-alkene complexes **8a**,**b** and **2c** are however smaller compared to those densities predicted for the bond critical points at the C=C double bonds in cations **9**. On the other hand they are significantly larger than those predicted for benzene at the same level of theory (ρ = 0.31534 e bohr^{-3}; n = 1.5). The second bond path connects the element atom with the carbon atom C^4 ($C^{4'}$) and has the bond critical point bcp2 (bcp2′). This second bond path is however strongly curved. In fact, it closely approaches bcp1 (bcp1′) before it merges with the first bond path reaching the carbon atom C^4 ($C^{4'}$) (see Figure 3b). As a result, the topology of the computed electron density ρ for the cations **8a**,**b** and **2c** is only slightly distorted from an ideal T-structure (see Figure 3). This small variation from the ideal

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(17) For a monograph on the methodology, see: Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, 1990.

(18) The topological analysis of the charge density was done with the AIM 2000 program: (a) Biegler-König, F.; Schönbohm, J.; Bayles, D. *J. Comput. Chem.* **2001**, *22*, 545. For a monograph on the methodology, see: (b) Biegler-König, F.; Schönbohm, J. *J. Comput. Chem.* **2002**, *23*, 1489.

(19) Chemical bonds between a pair of atoms can be identified by (3,−1) critical points (the so-called bond critical points, bcp) of the charge density. At such bcp's the gradient vector of $\rho(r)$ vanishes and the Hessian matrix of $\rho(r)$ at bcp has three nonvanishing eigenvalues, two of which are negative. The positive eigenvalue is associated with the bond path itself along which the charge density $\rho(r)$ reaches a minimum at the bcp.

(20) For further comparison the properties of the bond critical points of the CC bonds in ethane, ethene, benzene, and ethyne are given. Ethane: ρ = 0.25062 e bohr^{-3}; $\nabla^2\rho$ =−0.166626 e bohr^{-5}; ϵ = 0. Benzene: ρ = 0.31534 e bohr^{-3}; $\nabla^2\rho$ =−0.243182 e bohr^{-5}; ϵ = 0.23491. Ethene: ρ = 0.34518 e bohr^{-3}; $\nabla^2\rho$ =−0.274364 e bohr^{-5}; ϵ = 0.41863. Ethyne: ρ = 0.39543 e bohr^{-3}; $\nabla^2\rho$ =−0.285338 e bohr^{-5}; ϵ = 0.

T-shape of the electron density in the C═C/E plane is however not a result of a fundamentally different bonding situation but merely a consequence of the lower symmetry of the compounds. T-shaped electron densities are reminiscent of the parent norbornyl cation.[22] In addition, they are typical for π-complexes between Lewis acids and CC multiple bonds with relatively large interatomic distances and are associated with a weak interaction.[23] Accordingly, ρ at bcp2 is rather small and its Laplacian is positive, indicating a noncovalent interaction between the element atom and the C═C double bond.

Conclusion

The stannyl and germyl cations **2a**,**b** are synthesized in aromatic solvents by electrophilic attack of a trityl cation on the corresponding butylstannane and -germanes **3a**,**b** in the presence of a weakly coordinating anion. All attempts to prepare the corresponding silyl cation using varying conditions failed however. The most prominent feature of the molecular structure of the tin cation **2a** as revealed by an X-ray analysis of single crystals of the salt **2a**·[TPFPB] is the distorted trigonal-bipyramidal coordination polyhedron with the two C═C double bonds of the cyclopentenylmethyl substituents at the apical positions. Quantum mechanical calculations at the MP2/6-311+G(d,p) (E) SDD level predict for methyl-substituted cations **8a** and its homologues **8b** and **2c** very similar structures. In the case of cation **8a** it closely resembles that found experimentally for cation **2a**. As the result of a sizable electron transfer from the remote C═C double bonds to the positively charged element atom, for all three cations **8a**,**b** and **2c**, similar substantial binding energies I_E are predicted. The topological analysis of the electron density revealed nearly T-shaped electron distributions in the planes, which are spanned by the C═C double bonds and the element atom for each cation. This particular distribution of the electron density and its properties at the bond critical points suggests a pure π-donor type interaction between the central element atom and the C═C double bond, reminiscent of the norbornyl cation.[22] Finally, the results of the computations do not reveal any serious differences between the silyl cation **2c** and its higher homologues **8a**,**b**, therefore suggesting that the nonavailability of the silyl cation **2c** is not of thermodynamic origin.

Technical Section

Computational Details. All molecular structure optimizations and the NBO analysis were done using the Gaussian03 Rev. C.02 package of programs.[14] The molecular structures of the cations **2c** and **8**−**11** were optimized using the nonlocal DFT level of theory and Becke's three-parameter hybrid functional and the LYP correlation (B3LYP)[24] along with the standard Pople 6-311+G(d,p) basis set for H and C and the Stuttgart/Dresden SDD pseudopotentials for the elements Si, Ge, and Sn.[25] This basis set (6-311+G(d,p) (C,H) SDD (Si, Ge, Sn)) is denoted as basis set A. Subsequent frequency calculations at the B3LYP/A level of theory verified these structures as minima (zero imaginary frequencies) on the potential energy surface (PES). Calculations, which used for silicon and germanium also a 6-311+G(d,p) basis set, revealed very similar structures. For consistency only the results obtained with pseudopotentials for the central group 14 element are quoted. Finally, the molecular structures of cations **2c** and **8**−**11** were optimized at the MP2/A level.[26] The structures obtained at the MP2/A level are the basis of the discussion. The NBO analysis[16] was performed using the MP2/A wave functions. The atoms-in-molecules analysis[18] was done with the AIM2000 program applying wave functions obtained from single-point calculations at the HF/6-311G(d,p) (C,H) tzvpp (Si, Ge, Sn) level of theory at the MP2/A optimized structures.

Experimental Details

General Procedures. Diethyl ether and hexane were distilled from sodium/benzophenone. Toluene, toluene-d_8, and pentane were distilled from sodium. All reactions were carried out under inert conditions. Elemental analyses were carried out on a Foss-Heraeus CHN-O-RAPID. NMR spectra were recorded on a Bruker DPX-250 or DPX-400 spectrometer at $T = 303$ K. ^{1}H and ^{13}C NMR spectra were calibrated using residual solvent signals δ^1H(CHCl$_3$) = 7.24, δ^{13}C(CDCl$_3$) = 77.0, δ^1H(CHDCl$_2$) = 5.34, δ^{13}C(CD$_2$Cl$_2$) = 53.5, δ^1H(C$_6$D$_5$CD$_2$H) = 2.03, and δ^{13}C(C$_6$D$_5$CD$_3$) = 20.4. ^{119}Sn NMR spectra were calibrated using external Et$_4$Sn (δ^{119}Sn = 1.4 vs Me$_4$Sn). The assignment was made using literature data,[3,7] DEPT-NMR, and homo- and heteronuclear 2D NMR spectra. Chloromethyl-3-cyclopentene[27,28] and trityl tetrakis(pentafluorphenyl) borate[28,29] were prepared according to literature procedures.

[Bu$_2$Sn(CH$_2$C$_5$H$_7$)$_2$], 3a. The Grignard reagent which was prepared from 2.33 g (19.62 mmol) of cyclopent-3-enylmethyl chloride and 486 mg (20 mmol) of magnesium in diethyl ether was added dropwise to a solution of 2.981 g (9.81 mmol) of dibutyldichlorostannane at room temperature. Immediately a white precipitate was formed. The mixture was stirred overnight, and the solvent was removed under reduced pressure. The resulting slurry was extracted with three 30 mL portions of pentane. The organic extracts were collected, and the solvent was removed under reduced pressure. The title compound was obtained as a colorless oil (2.98 g, 7.54 mmol, 77% yield). ^{1}H NMR (250.131 MHz, C$_6$D$_6$): δ 5.77 (s, 4H, H$^{4/5}$), 2.68−2.59, 2.10−2.00 (2m, 6H, 4H, H$^{3/6}$ and H^2), 1.72−1.53 (m, 4H, H^9), 1.53−1.39 (m, 4H, H^8), 1.19 (d, 4H, $^3J_{HH}$ = 7.3 Hz, H^1), 1.07−0.79 (m, 10H, H^7 and H^{10}). ^{13}C{^{1}H} NMR (62.902 MHz, C$_6$D$_6$): δ 128.9 (C$^{4/5}$), 42.2 ($^3J_{CSn}$= 37.4 Hz, C$^{3/6}$), 35.6 ($^2J_{CSn}$= 20.4 Hz, C^2), 28.4 ($^2J_{CSn}$= 18.8 Hz, C^8), 26.6 ($^3J_{CSn}$= 56.2 Hz, C^9), 17.2 ($^1J_{C117Sn}$= 296.0 Hz, $^1J_{C119Sn}$= 309.6 Hz, C^1), 12.6 (C^{10}), 8.7 ($^1J_{C117Sn}$= 297.6 Hz, $^1J_{C119Sn}$= 311.2 Hz, C^7). ^{119}Sn NMR (93.28 MHz, C$_6$D$_6$): δ 24.6.

[Bu$_2$Ge(CH$_2$C$_5$H$_7$)$_2$], 3b. Compound **3b** was obtained similar to the procedure described for the tin compound **3a** from 2.16 g (18.5 mmol) of cyclopent-3-enylmethylchloride, 486 mg (20 mmol) of magnesium in diethyl ether, and 2.38 g (9.25 mmol) of dibutyldichlorogermane at room temperature. Germane **3b** was obtained as a colorless oil (2.20 g, 6.29 mmol, 77% yield). ^{1}H NMR

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(21) According to ref 18 the covalent bond order n can be related to the charge density at the bond critical point $\rho(r_b)$ via the two-parameter fit $\ln(n) = \{A(\rho(r_b) - B)\}$. Using HF/6-311G(d,p)//MP2/6-311G(d,p) wave functions for ethane, ethene, benzene, and ethyne, a least-squares fit to bond orders of 1, 2, 1.5, and 3 yields $A = 7.56716$ and $B = 1.90631$ for C−C bonds.

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(250.131 MHz, $CDCl_3$): δ 5.66 (s, 4H, $H^{4/5}$), 2.56−2.47 (m, 4H, $H^{3/6}$), 2.43−2.28 (m, 2H, H^2), 1.97−1.89 (m, 4 H, $H^{3/6}$), 1.37−1.31 (m, 8H, H^9 and H^8), 0.97 (d, 4H, $^3J_{HH} = 6.8$ Hz, H^1), 0.89 (6H, $^3J_{HH} = 7.9$ Hz, H^{10}), 0.74 (4H, $^3J_{HH} = 8.4$ Hz, H^7). $^{13}C\{^1H\}$ NMR (62.902 MHz, C_6D_6): δ 130.2 ($C^{4/5}$), 42.4 ($C^{3/6}$), 35.4 (C^2), 27.5, 26.8 (C^8, C^9), 21.1 (C^1), 13.8 (C^{10}), 13.6 (C^7).

[MeSi(H)($CH_2C_5H_7$)$_2$], 3c. Compound **3c** was obtained similar to the procedure described for the tin compound from 2.390 g (20.5 mmol) of cyclopent-3-enylmethyl chloride, 548 mg (33.6 mmol) of diethyl ether, and 1.159 g (10.07 mmol) of methyldichlorosilane at room temperature. Silane **3c** was obtained after purification by bulb-to-bulb distillation in a yield of 76.4% (1.59 g, 7.70 mmol). ^1H NMR (250.131 MHz, $CDCl_3$): δ 5.65 (s, 4H, $H^{4/5}$), 3.84 (octet, 1H $^3J_{HH} = 3.6$ Hz, $^1J_{SiH} = 179.8$ Hz, SiH), 2.56−2.46, m 4H, $H^{3/6}$), 2.34 (sept, 2H, $^3J_{HH} = 7.4$ Hz, H^2), 2.00−1.89 (m, 4H, $H^{3/6}$), 0.9−0.7 (m, 4H, H^1), 0.08 (d, 3H, $^3J_{HH} = 3.6$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (62.902 MHz, $CDCl_3$): δ 130.1 ($C^{4/5}$), 42.0 ($C^{3/6}$), 34.5 (C^2), 21.0 (C^1), −5.3 (Me). ^{29}Si NMR (79.46 MHz, C_6D_6): δ −14.0 ($^1J_{SiH} = 179.8$ Hz).

Cation Synthesis, General Procedure. The neat precursor was added slowly to a vigorously stirred solution of an equimolar amount of trityl tetrakispentafluorophenyl borate in 2.5 mL of toluene-d_8. The mixture was stirred continuously for another 0.5 h and then allowed to separate into two phases, a light yellow upper phase and a dark orange lower phase. The phases were separated and both were monitored by NMR spectroscopy. The upper phase contained only the byproduct triphenylmethane. The solvent of the lower phase was evaporated under reduced pressure, and the oily residue was washed three times with 3 mL portions of pentane.

[BuSn($CH_2C_5H_7$)$_2$]$^+$[B(C_6F_5)$_4$]$^-$, 2a·[B(C_6F_5)$_4$]$^-$. Reaction of 0.281 g (0.71 mmol) of di-3-cyclopentenylmethyldibutylstannane, **3a**, with 0.655 g (0.71 mmol) of trityl tetrakispentafluorophenyl borate gave a brown oily product. Crystals suitable for X-ray diffraction were obtained by diffusion from hexane into a toluene solution at room temperature (0.387 g, 0.36 mmol, 51% yield of $[BuSn(CH_2C_5H_7)_2]^+[B(C_6F_5)_4]^- \cdot 0.5C_6H_5CH_3$).

[BuSn($CH_2C_5H_7$)$_2$]$^+$[B(C_6F_5)$_4$]$^-$·0.5$C_6H_5CH_3$. ^1H NMR (250.131 MHz, CD_2Cl_2): δ 7.32−7.10 (m, 2.5H, C_6H_5-CH_3), 6.19 (s, 4H, $^1J_{HC} = 169.1$ Hz, $H^{4/5}$), 3.43 (m, 2H, $^3J_{HSn} = 202.8$ Hz, H^2), 2.69 (dd, 4H, $^2J_{HH} = 15.2$ Hz, $^3J_{HH} = 5.7$ Hz, $H^{3/6}$), 2.30 (s, 1.5 H, C_6H_5−CH_3), 2.01 (d, 4H, $^2J_{HH} = 15.2$ Hz, $H^{3/6}$), 1.75−1.64 (m, 4H, H^8 and H^7), 1.57 (d, 4H, $J_{HH} = 3$ Hz, H^1), 0.99 (t, 3H, $^3J_{HH} = 7$ Hz, H^{10}), 0.90 (qd, 2H, $^3J_{HH} = 7$ Hz, H^9). $^{13}C\{^1H\}$ NMR (62.902 MHz, CD_2Cl_2): δ 148.4 (d, $^1J_{CF} = 242.8$ Hz, $C^{meta}F$), 139.0 ($^1J_{CSn} = 17.6$ Hz $C^{4/5}$), 138.4 (d, $^1J_{CF} = 242.8$ Hz, $C^{para}F$), 137.2 (C^{ipso}, toluene), 136.5 (d, $^1J_{CF} = 244.7$ Hz, $C^{ortho}F$), 129.1 (C^{ortho}, toluene), 128.3 (C^{meta}, toluene), 125.4 (C^{para}, toluene), 41.0 ($^3J_{CSn} = 27.6$ Hz, $C^{3/6}$), 35.4 ($^2J_{CSn} = 31.0$ Hz, C^2), 29.7 ($^2J_{CSn} = 31.1$ Hz C^8), 27.0 (C^9), 25.5 ($^1J_{C119Sn} = 311.2$ Hz, $^1J_{C117Sn} = 298.5$ Hz C^1), 21.2 (CH_3, toluene), 20.0 ($^1J_{C119Sn} = 305.2$ Hz, $^1J_{C117Sn} = 294.0$ Hz C^7), 13.2 (C^{10}). ^{119}Sn NMR (129.211 MHz, CD_2Cl_2): δ 210.2.

[BuSn($CH_2C_5H_7$)$_2$]$^+$[B(C_6F_5)$_4$]$^-$. $^{13}C\{^1H\}$ NMR (62.902 MHz, C_7D_8): δ 150.9 (d, $^1J_{CF} = 244.5$ Hz, $C^{meta}F$), 139.9 (d, $^1J_{CF} = 244.7$ Hz, $C^{para}F$), 139.6 ($^1J_{CSn} = 17.4$ Hz, $C^{4/5}$), 138.0 (d, $^1J_{CF} = 241.9$ Hz, $C^{ortho}F$), 41.5 ($^3J_{CSn} = 27.7$ Hz, $C^{3/6}$), 36.3 ($^2J_{CSn} = 30.3$ Hz, C^2), 30.4 ($^2J_{CSn} = 30.5$ Hz, C^8), 27.7 (C^9), 25.7 ($^1J_{C119Sn} = 311.3$ Hz, $^1J_{C117Sn} = 299.6$ Hz, C^1), 20.3 ($^1J_{C119Sn} = 305.4$ Hz, $^1J_{C117Sn} = 290.7$ Hz, C^7), 14.3 (C^{10}). ^{119}Sn NMR (93.284 MHz, C_7D_8): δ 207.6. MS (positive ion): *m/z* 339 ($C_{16}H_{27}Sn^+$). MS (negative ion): *m/z* 677. Anal. Calcd for $C_{40}H_{27}BF_{20}Sn$: C, 47.23; H, 2.68. Found: C, 47.29; H, 2.77.

[BuGe($CH_2C_5H_7$)$_2$]$^+$[B(C_6F_5)$_4$]$^-$, 2b·[B(C_6F_5)$_4$]$^-$. Reaction of 0.237 g (0.68 mmol) of di-3-cyclopentenylmethyldibutylgermane with 0.627 g (0.68 mmol) of trityl tetrakispentafluorophenyl borate gave a brownish-white glassy powder (0.350 g, 0.36 mmol, 53% yield of $[BuGe(CH_2C_5H_7)_2]^+[B(C_6F_5)_4]^-$). ^1H NMR (250.131 MHz, C_7D_8): δ 5.81 (s, 4H, $H^{4/5}$), 2.38 (bs 2H, H^2), 1.71, 1.65 (2m, 8H, $H^{3/6}$), 1.24−0.94 (3 bm, 10H, H^8, H^9, H^7, H^1), 0.73 (t, 3H, $^3J_{HH} = 6.5$ Hz, H^{10}). $^{13}C\{^1H\}$ NMR (62.902 MHz, C_7D_8)): δ 149.2 (d, $^1J_{CF} = 242.1$ Hz, $C^{meta}F$), 145.2 ($^1J_{CH} = 173$ Hz $C^{4/5}$), 139.0 (d, $^1J_{CF} = 244$ Hz, $C^{para}F$), 137.2 (d, $^1J_{CF} = 246.7$ Hz, $C^{ortho}F$), 41.3 (t, $^1J_{CH} = 133$ Hz, $C^{3/6}$), 37.2 (d, $^1J_{CH} = 149.0$ Hz, C^2), 26.7 (t, $^1J_{CH} = 128$ Hz C^9), 25.8 (t, $^1J_{CH} = 125$ Hz, C^8), 19.4 (t, $^1J_{CH} = 133$ Hz, C^1), 18.9 (t, $^1J_{CH} = 137$ Hz, C^7), 13.2 (q, $^1J_{CH} = 125$ Hz, C^{10}).

X-ray Crystallographic Analysis for 2a·[B(C_6F_5)$_4$]$^-$·0.5C_6H_5-CH_3. X-ray crystal structure analysis was performed on a STOE IPDS (Mo Kα radiation, $\lambda = 71.073$ pm, graphite monochromator at 173(2) K). $C_{43.50}H_{31}BF_{20}Sn$, MW = 1063.18, crystal size 0.30 × 0.24 × 0.13 mm^3; triclinic, space group $P\bar{1}$, $a = 1271.73(8)$ pm, $b = 1582.92(11)$ pm, $c = 2195.94(15)$ pm, $\alpha = 91.004(6)°$, $\beta = 101.361(5)°$, $\gamma = 107.137(5)°$; volume = $4.1280(5) \times 10^9$ pm^3; $Z = 4$, $D_{calc} = 1.711$ Mg/m^3; $F(000) = 2108$; theta range for data collection 2.70−25.20°; index ranges $-15 \le h \le 15$, $-18 \le k \le 18$, $-26 \le l \le 26$; 50 399 reflections collected, of which 14 683 [R(int) = 0.0563] were independent. Final R indices [$I > 2\sigma(I)$]: R1 = 0.0726, wR2 = 0.1832. Goodness-of-fit on F^2: 1.195. Cambridge database file: CCDC 676617

Acknowledgment. The Cluster for Scientific Computation (CSC) at the Carl von Ossietzky University Oldenburg is thanked for providing computational resources. R.P. thanks the Fonds der Chemischen Industrie for a scholarship.

Supporting Information Available: Table of absolute energies of cations **2c** and **8**−**11** and Cartesian coordinates of compounds **8a**,**b** and **2c**. NMR spectra of compounds **2a**·[B(C_6F_5)$_4$], **2b**·[B(C_6F_5)$_4$], and **3a**−**c**. CIF file for **2a**·[B(C_6F_5)$_4$]·0.5$C_6H_5CH_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800432X