## Aromatic Group 14 Compounds

## **Dismutational and Global-Minimum Isomers of Heavier** 1,4-Dimetallatetrasilabenzenes of Group 14\*\*

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Dedicated to Prof. Robert West on occasion of his 85th birthday

Abstract: Aromatic species with heavier Group 14 elements show remarkable differences in terms of stability, structure, and reactivity. Herein we report our experimental and theoretical investigations regarding isomers of germanium- and tincontaining benzene analogues  $E_2Si_4R_6$  (E = Ge, Sn). The germanium-substituted dismutational isomer with a tricyclic six-membered scaffold is isolable, but unlike the homonuclear Si<sub>6</sub> analogue slowly rearranges even at room temperature to give the propellane-type global minimum isomer. In case of E = Sn the dismutational isomer may be an intermediate on the pathway to the propellane-type species obtained, but cannot be detected even at low temperature. Unprecedentedly large chemical shift anisotropies in the <sup>29</sup>Si NMR spectra that increase from the  $Si_6$  species through  $Ge_2Si_4$  to  $Sn_2Si_4$  are rationalized by progressively larger paramagnetic-term contributions to the chemical shift tensor as a result of diminishing HOMO-LUMO gaps, which are also reflected in the absorption spectra, as well as by appearance and symmetry of these frontier orbitals.

As the archetypical example of aromaticity, benzene is ubiquitous in the chemical sciences and beyond.<sup>[1]</sup> With regard to the design of extended conjugated systems,<sup>[2]</sup> benzene analogues involving heavier Group 14 elements and their isomers are of theoretical<sup>[3]</sup> and experimental<sup>[4]</sup> interest. As recently calculated by Boldyrev and Ivanov, Hückel-aromatic isomers are possible in the incorporation of

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up to three silicon atoms in a six-atom carbon scaffold.<sup>[5]</sup> Experimentally, benzene or naphthalene analogues containing up to two heavier elements are known, for example, silabenzene  $\mathbf{1}$ ,<sup>[6]</sup> 1,2-disilabenzene,<sup>[6]</sup> 1,4-disilabenzene,<sup>[7]</sup> germabenzene  $\mathbf{2}$ ,<sup>[8]</sup> and 2-stannanaphthalene  $\mathbf{3}$ <sup>[9]</sup> (Scheme 1).



**Scheme 1.** Stable heavier Hückel aromatics (Tbt=2,4,6-(CH-(SiMe\_3)\_2)\_3C\_6H\_2) and dismutational (4) and global minimum (5) isomer of Si<sub>6</sub>R<sub>6</sub> (R=Tip=2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>).

The dismutational aromatic isomer of a hexasilabenzene (4)<sup>[10]</sup> and its rearrangement to the alleged global minimum isomer  $\mathbf{5}^{[11]}$  shed light on the particularities of silicon in this context. In addition, Kyushin et al. very recently reported a polycyclic hexasilabenzvalene derivative.<sup>[12]</sup> We therefore became interested in the partial substitution of the silicon atoms in isomers of hexasilabenzene by germanium and tin. To date, there is only one example of a six-membered Hückel aromatic with two germanium atoms, which has been obtained by Power et al. from the reaction of digermyne with a nitrile.<sup>[13]</sup> The only stable, potentially aromatic ring motif based exclusively on silicon and germanium/tin is a 1,2disila-3,4-digermacyclobutadiene dianion,<sup>[14]</sup> despite the fact that various methods for the synthesis of compounds with Si-Ge/Sn  $\pi$ -bonds have been known for some time.<sup>[15]</sup> Herein, we focus on the formal replacement of the two unsubstituted silicon atoms of 4 and 5 by germanium and tin. The resulting Si<sub>4</sub>Ge<sub>2</sub> and Si<sub>4</sub>Sn<sub>2</sub> derivatives, 8, 9, and 11 show an increasing electronic anisotropy resulting in unprecedented deshielding of the NMR resonance signals at saturated silicon atoms of the scaffolds.

For the synthesis of Si<sub>4</sub>Ge<sub>2</sub> derivative **8** we chose disilenide  $6^{[16]}$  and GeCl<sub>2</sub>·dioxane<sup>[17a]</sup> as a source of silicon and germanium, respectively. As any attempt to isolate the plausible intermediate, disilenyl-substituted chlorogermylene **7**, or even the detection by NMR spectroscopy at low temperature failed, we decided to investigate its in situ generation and direct subsequent reduction to **8**. Indeed, the 1:1 reaction of disilenide and GeCl<sub>2</sub>·dioxane at -78 °C in toluene (in THF tetrasilabutadiene Si<sub>4</sub>Tip<sub>6</sub> is formed),<sup>[16a]</sup> and subsequent addition of one equivalent of lithium/naphthalene (Li/C<sub>10</sub>H<sub>8</sub>) in THF afforded **8**, which was isolated as dark green crystals (m.p. > 225 °C) in 42 % yield from *n*-hexane



**Scheme 2.** Synthesis of dismutational isomer of 1,4-digermatetrasilabenzene 8 (Tip =  $2,4,6-iPr_3C_6H_2$ ).

(Scheme 2).<sup>[18]</sup> The green color of **8** is due to the longest wavelength absorption in the UV/Vis spectrum at  $\lambda_{max} = 669$  nm ( $\varepsilon = 340 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ), which is considerably redshifted compared to the hexasila congener (**4**:  $\lambda_{max} = 623$  nm; dark green crystals; Table 1). Additional absorptions in the UV/Vis spectrum appear at  $\lambda_{max} = 557$  ( $\varepsilon = 320 \text{ Lmol}^{-1} \text{ cm}^{-1}$ )

Table 1: <sup>29</sup>Si NMR and UV/Vis spectroscopy data of 4, 5, 8, 9, and 11.

Parameter	4	5	8	9	11
$\delta^{29}$ SiTip <sub>2</sub>	-84.8	174.6	-88.6	236.0	284.4
$\delta^{29} { m SiTip_2}^{[a]}$	-	14.8	-	14.5	52.7
$\delta^{ m 29}$ SiTip	124.6	-7.5	185.8	29.8	23.8
$\lambda_{max}$ [nm]	623	473	669	518	679
	(629) <sup>[b]</sup>	(475) <sup>[b]</sup>	(679) <sup>[c]</sup>	(486) <sup>[c]</sup>	

[a] SiTip<sub>2</sub> unit tethering two "propeller blades". [b] Calculated value with Dip instead of Tip group. [c] Calculated value with Ph instead of Tip. (Tip = 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, Dip = 2,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>3</sub>, Ph = C<sub>6</sub>H<sub>5</sub>).

and 439 nm ( $\varepsilon = 3690 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ). A coupled clusters calculation on **8Ph** (Ph instead of Tip substituents)<sup>[19-22]</sup> shows that the HOMO–LUMO pair contribution dominates the lowest vertical electronic transition ( $S_1 \leftarrow S_0$ ). The calculated absorption band at 679 nm is in very good agreement with experiment. The surprisingly stable **8** can be exposed to air for days as a solid or for hours in solution without detectable changes.

The solid-state structure of **8** (Figure 1)<sup>[18]</sup> as determined by X-ray diffraction analysis confirms that the centrosym-

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*Figure 1.* Molecular structure of **8** in the solid state (thermal ellipsoids at 30%; hydrogen atoms are omitted for clarity). Selected interatomic distances [Å]: Si1-Si2 2.3402(12), Si1-Ge1 2.4297(10), Si2-Ge1 2.3878(9), Si2-Ge1' 2.3601(9), Ge1…Ge1' 2.8624(7).

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metric structure is of tricyclic connectivity similar to that of the Si<sub>6</sub> analogue **4**.<sup>[10]</sup> In the central four-membered ring, the Si2–Ge1 (2.3878(9) Å) bond is only slightly longer than Si2– Ge1' (2.3601(9) Å) and both are shorter than that of Si–Ge single bonds in 1-disilagermirene (2.415(1) Å).<sup>[15a]</sup> As expected the diagonal Ge1···Ge1' (2.8624(7) Å) distance is substantially longer than a typical Ge–Ge single bond (2.498(2) Å)<sup>[23]</sup> suggesting the absence of a direct troughspace bonding interaction. In case of the corresponding Si<sub>6</sub>Tip<sub>6</sub> congener **4** (and **5** as well) an experimental chargedensity analysis confirmed the absence of direct bonding between the bridgehead atoms.<sup>[24]</sup>

The <sup>29</sup>Si NMR spectrum of **8** in [D<sub>6</sub>]benzene shows two resonance signals at  $\delta = 185.8$  and -88.6 ppm in a 1:1 ratio (Table 1). On the basis of the data of the Si<sub>6</sub> analogue **4**, the upfield signal at  $\delta = -88.6$  ppm is assigned to the two Tip<sub>2</sub>Si units ( $\delta = -84.8$  ppm), which was confirmed by a 2D <sup>29</sup>Si/<sup>1</sup>H correlation. The <sup>29</sup>SiTip resonance signal at  $\delta = 185.8$  ppm is observed further downfield than in **4** ( $\delta = 124.6$  ppm).

In contrast to **4**, in solution the digerma-substituted **8** slowly rearranges to the alleged global minimum isomer **9** even at room temperature. Complete conversion is achieved (either in THF, hexane, or benzene) after 12 h at 65 °C. The silicon-bridged digerma propellane **9** was isolated as orange crystals in 88 % yield from THF (Scheme 3).<sup>[18]</sup> Unlike in the



**Scheme 3.** Rearrangement of **8** to **9** (Tip = 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>).

case of **5**, no side products were detected during the rearrangement.<sup>[25]</sup>

Structure analysis by X-ray diffraction on single crystals confirms **9** as a  $Ge_2Si_4$  propellane-type structure with two of the "propeller blades" tethered by an additional SiTip<sub>2</sub> unit (Figure 2).<sup>[18]</sup> The distance between the unsubstituted

**Figure 2.** Molecular structure of  $9.2 C_6 H_6$  in the solid state (thermal ellipsoids at 30%; hydrogen atoms and  $C_6 H_6$  molecules are omitted for clarity). Selected interatomic distances [Å]: Ge1-..Ge2 2.7820(2), Ge1-Si3 2.4566(4), Ge1-Si2 2.4161(4), Ge1-Si1 2.4506(4), Si1-Si4 2.3722(5).



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bridgehead germanium atoms Ge1–Ge2 (2.7820(2) Å) is inbetween the corresponding distances in homo- and heteronuclear propellanes (Ge<sub>5</sub>Mes<sub>6</sub> 2.869(2) Å,<sup>[26a,e]</sup> Ge<sub>2</sub>Si<sub>3</sub>Mes<sub>6</sub> 2.767(1) Å;<sup>[26b,e]</sup> Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>). The redshift of the UV/Vis absorption at  $\lambda_{max} = 518$  nm ( $\varepsilon = 690$  Lmol<sup>-1</sup>cm<sup>-1</sup>) compared to that of Ge<sub>2</sub>Si<sub>3</sub>Mes<sub>6</sub> (415 nm) is attributed to the lifted degeneracy of the HOMO resulting from the reduction in idealized symmetry ( $C_2$  for **9** vs.  $D_{3h}$  for Ge<sub>2</sub>Si<sub>3</sub>Mes<sub>6</sub>).<sup>[26b]</sup> In addition a more intense absorption at  $\lambda_{max} = 381$  nm is observed ( $\varepsilon = 12040$  Lmol<sup>-1</sup>cm<sup>-1</sup>). The calculated value of the lowest vertical transition S<sub>1</sub>  $\leftarrow$  S<sub>0</sub> for **9Ph** (Ph instead of Tip)<sup>[19]</sup> is 486 nm in satisfactory agreement with the experimental value of 518 nm for **9**.

The <sup>29</sup>Si NMR spectrum of **9** in [D<sub>6</sub>]benzene shows three signals at  $\delta = 236.1$ , 29.8, and 14.6 ppm in a 1:2:1 ratio in accordance with the  $C_2$  symmetry (Table 1). The downfield resonance is assigned to one of the SiTip<sub>2</sub> units by 2D <sup>29</sup>Si/<sup>1</sup>H and thus to a tetracoordinate silicon atom. By analogy with the Si<sub>6</sub> analogue **5**,<sup>[11]</sup> we concluded that this most deshielded silicon atom should originate from the untethered "propeller blade" (Si3). Very recently, a cluster with two *spiro*-connected SiGe<sub>5</sub> motifs of similar geometry was reported that showed <sup>29</sup>Si NMR shift of  $\delta = 91.6$  ppm for the SiR<sub>2</sub> bridge.<sup>[27]</sup>

To experimentally address the 1,4-distannatetrasilabenzene isomers, we employed  $SnCl_2$ ·dioxane<sup>[17b]</sup> as a tin source under analogous reaction conditions as during the synthesis of **8**. The 1:1 in situ Li/C<sub>10</sub>H<sub>8</sub> reduction of the reaction mixture generated from **6** and SnCl<sub>2</sub>·dioxane in toluene directly affords the global minimum isomer of 1,4-distannatetrasilabenzene, **11**, in 22% isolated yield as dark-brown crystals (Scheme 4).<sup>[18]</sup> The anticipated intermediate **10** could not be detected even at -80 °C suggesting a much lower stability of the dismutational isomer for the Sn<sub>2</sub>Si<sub>4</sub> scaffold and confirming the trend observed for Ge<sub>2</sub>Si<sub>4</sub>.



**Scheme 4.** Synthesis of global minimum isomer of 1,4-distannate trasilabenzene **11** (Tip = 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>).

The <sup>29</sup>Si NMR spectrum acquired in solution for **11** shows an even more downfield-shifted resonance signal at  $\delta$  = 284.46 ppm that corresponds to the tin-bridging SiTip<sub>2</sub> unit (Table 1). To our knowledge, the <sup>29</sup>Si NMR chemical shifts assignable to the untethered "propeller blades" of **9** and **11** represent the by far most deshielded <sup>29</sup>Si NMR signals of tetracoordinate silicon atoms in a molecular environment of a diamagnetic compound to date. In fact, such extreme deshieldings are not even found in cationic three-coordinate silylium ions (e.g. Mes<sub>3</sub>Si<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> in [D<sub>6</sub>]benzene:  $\delta$  = 225.5 ppm).<sup>[28]</sup> The <sup>119</sup>Sn NMR resonance signal of **11** at  $\delta$  = -1260.19 ppm is downfield-shifted compared with that of the unbridged homonuclear propellanes Sn<sub>5</sub>(2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>6</sub> ( $\delta$  = -1751 ppm),<sup>[26c,e]</sup> Sn<sub>5</sub>{(2,6-*i*PrO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}<sub>6</sub> ( $\delta$  =

-1893 ppm),<sup>[26d,e]</sup> and similar to Breher's Sn<sub>2</sub>Si<sub>3</sub>Mes<sub>6</sub> heteropropellane  $(\delta = -1348 \text{ ppm};)$ nuclear Mes = 2,4,6- $Me_3C_6H_2$ ).<sup>[26b]</sup> The two <sup>117</sup>Sn satellites with a coupling constant of  $J(^{119}\text{Sn}-^{117}\text{Sn}) = 3910 \text{ Hz}$  are comparable to that observed for  $Sn_2Si_3Mes_6$ .<sup>[26b]</sup> This is in qualitative agreement with the computational value (for details see below) obtained for the parent compound (**11H**, R = H,  $J(^{119}Sn1 - ^{117}Sn2) = 5879$  Hz). An additional pair of <sup>29</sup>Si satellites in the <sup>119</sup>Sn spectrum of **11**  $(^{1}J = 326 \text{ Hz})$  presumably originates from unresolved coupling to the different <sup>29</sup>Si nuclei. According to the calculations, the  ${}^{1}J(Sn-Si)$  coupling constants of **11H** are indeed predicted to be of similar magnitude  $[{}^{1}J({}^{119}\text{Sn}-{}^{29}\text{Si}1) = {}^{1}J({}^{119}\text{Sn}-{}^{29}\text{Si}2) =$ -434 Hz,  ${}^{1}J({}^{129}\text{Sn}{-}^{29}\text{Si4}) = -467$  Hz]. The  ${}^{2}J(\text{Sn}{-}\text{Si})$  value is apparently too small to be resolved experimentally [11H:  $^{2}J(^{119}\text{Sn}-^{29}\text{Si3}) = 45 \text{ Hz}].$ 

An X-ray diffraction study on single crystals confirms the constitution of the  $Sn_2Si_4$  propellane-type structure **11** (Figure 3).<sup>[18]</sup> The distance between the tin atoms Sn1–Sn2



*Figure 3.* Molecular structure of **11** in the solid state (thermal ellipsoids at 30%; hydrogen atoms and co-crystallized solvent are omitted for clarity).Selected interatomic distances [Å]: Sn1...Sn2 3.1099(3), Sn1-Si1 2.6382(8), Sn1-Si2 2.6017(8), Sn1-Si4 2.6565(8), Si1-Si3 2.3856(10).

(3.1099(3) Å) is slightly longer than the corresponding distance in Breher's heteronuclear propellane Sn<sub>2</sub>Si<sub>3</sub>Mes<sub>6</sub> (3.097(1) Å).<sup>[26b]</sup> The UV/Vis absorption of **11** at  $\lambda_{max} = 679 \text{ nm} (\varepsilon = 770 \text{ Lmol}^{-1} \text{ cm}^{-1})$  is again red-shifted compared to that of Sn<sub>2</sub>Si<sub>3</sub>Mes<sub>6</sub> ( $\lambda_{max} = 550 \text{ nm}$ ) due to the loss of degeneracy of the HOMO resulting from lower symmetry ( $C_2$  for **11** vs.  $D_{3h}$  for Sn<sub>2</sub>Si<sub>3</sub>Mes<sub>6</sub>).<sup>[26b]</sup> Additional absorptions appear at  $\lambda_{max} = 555$  ( $\varepsilon = 1250 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ) and 456 nm ( $\varepsilon = 11630 \text{ Lmol}^{-1} \text{ cm}^{-1}$ ).

Compounds **5**, **9**, and **11** show exceedingly deshielded <sup>29</sup>Si NMR resonance signals for the tetracoordinate SiTip<sub>2</sub> atoms of the untethered propeller blades (see Table 1). The deshielding effect is enhanced with increasing atomic number of the unsubstituted bridgehead atoms E (**5**, E = Si:  $\delta = 174.6$ ; **9**, E = Ge:  $\delta = 236.0$ ; **11**, E = Sn:  $\delta = 284.5$  ppm) and much more pronounced than in the closely related untethered propellane species Si<sub>2</sub>Si<sub>3</sub>Mes<sub>6</sub>,<sup>[26b]</sup> Ge<sub>2</sub>Si<sub>3</sub>Mes<sub>6</sub>,<sup>[26b]</sup> (E = Si:  $\delta = 25.5$ ; E = Ge:  $\delta = 66$ ; E = Sn:  $\delta = 98$  ppm). This differing behavior is even more remarkable in view of the fact that the tethering SiTip<sub>2</sub> moiety and thus the symmetry-breaking motif is located at the opposite end (with respect to the untethered SiTip<sub>2</sub> bridge) of the molecular structures of **5**, **9**, and **11**.

To clarify the reasons for this, we have analyzed the physical origins of the chemical shieldings using first-principles methods with the program ReSpect.<sup>[30,31]</sup> We extended the series of bridged and unbridged propellanes beyond the experimentally accessible (5, 9 and 11) to include the leadsubstituted species as well. The calculations revealed that the diamagnetic terms are virtually constant within each of the two homologous series of species (for details see Supporting Information). This implies that shielding effects caused by magnetically induced diatropic currents are also almost identical as confirmed by the calculated, very similar induced current strengths and topologies in each series. Moreover, the integrated currents in both series are also virtually equal (ca. 10 nAT<sup>-1</sup> diatropic molecular current). According to our findings regarding the current topology<sup>[10b,11]</sup> these currents are mainly caused by the cluster-like electron pair at the bridgehead atoms resulting in a two-electron-3D aromatic cluster bonding.

A comparison between non-relativistic and fully relativistic levels of computation reveals that for the Si, Ge, and Sn substituted species the relativistic corrections are negligible. In case of the experimentally inaccessible lead-substituted species, relativity enhances the downfield shift even more (by almost  $\delta = 100$  ppm). A closer look at the paramagnetic electronic P<sub>1e</sub> term<sup>[31b,c]</sup> shows that in all cases the HOMO– LUMO excitation pair provides the dominating contribution greater than 90 % (Figure 4). In both compound series, the virtual as well as the occupied orbital are characterized by the presence of three main nodal planes,<sup>[32]</sup> which are related by a rotation about 90° with respect to the *y*-axis (left–right direction in the Figure). This geometrical relationship



**Figure 4.** Molecular orbitals and MO energy differences (in Hartree) of untethered propellane model species a)  $Si_2Si_3H_6$ , b)  $Ge_2Si_3H_6$ , c)  $Sn_2Si_3H_6$ , d)  $Pb_2Si_3H_6$ , and bridged propellane model species e)  $Si_2Si_4H_6$ , f)  $Ge_2Si_4H_6$ , g)  $Sn_2Si_4H_6$ , h)  $Pb_2Si_4H_6$ . HOMO(b1) denotes the highest occupied orbital of  $b_1$  symmetry and HOMO(e') the highest occupied orbital of e' symmetry.

between virtual and occupied MO of the important virtual excitation is required for a contribution to the  $P_{1e}$  terms of the chemical shielding tensors. Since the MO energy differences appear in the denominator of the corresponding expression for the paramagnetic part of shielding tensor the contribution decreases with increasing energy difference. The HOMO–LUMO gaps of the bridged propellane species are significantly lower than those of the untethered propellanes. This fact as well as the localization of the orbitals at the silicon atom of the untethered "propeller blade" leads to the larger paramagnetic terms in this case. Substitution of the Si atoms by Ge, Sn, and Pb narrows the MO energy differences in both series of compounds and the <sup>29</sup>Si resonances are therefore progressively shifted downfield.

The decreasing electronegativity going from Si to Pb results in a stabilization of MOs with antibonding contributions, in particular the LUMO. Experimentally, this energetic lowering of the LUMO with the increasing atomic number of the hetero atoms is also reflected in a red-shift of the longest wavelength absorption in the UV/Vis spectra (see Table 1). It is noteworthy that virtual transitions of rotational symmetry are also responsible for magnetically induced paratropic molecular ring/cluster currents. In heavy atoms, however, the contributions from diatropic currents are orders of magnitude smaller than those from the paratropic terms. Nevertheless, both mechanisms occur inherently parallel.

In conclusion, we have prepared digerma- and distannasubstituted heteronuclear derivatives of two recently reported hexasilabenzene isomers. Very notably, the dismutationally aromatic digermanium-derivative 8 is stable towards air and moisture even in solution. Upon mild heating, however, 8 readily rearranges into the thermodynamically more stable, but kinetically more labile propellane-type isomer 9. This trend is reflected in the fact that the bridged distannapropellane 11 is accessible by the same methodology, while the corresponding dismutational isomer cannot even be observed at low temperature. Clear-cut trends in the anisotropic NMR spectroscopic properties from silicon- to tinsubstituted derivatives confirm the extremely unusual electronic situation present in the entire class of compounds. To our knowledge, the <sup>29</sup>Si NMR chemical shifts assignable to the untethered "propeller blades" of 9 and 11 represent the by far most deshielded <sup>29</sup>Si NMR resonance signals of tetracoordinate silicon atoms in a molecular environment to date. The enhanced reactivity of the hetero-substituted propellanes 9 and 11 raises interesting prospects for their application in the construction of extended staffane-type materials,<sup>[33]</sup> a possibility which is currently being investigated in our laboratories.

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- [18] Experimental details are supplied in the Supporting Information. CCDC 939615 (8), 939616 (9), 948751 (11) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.
- [19] All calculations have been performed with the TURBOMOLE program package<sup>[20]</sup> version 6.3. The aryl groups were modeled as Ph groups. The structure optimization of 8 and 9 was carried out using RI-DFT with the BP86 density functional and def2-SV(P) basis sets on all elements. The excitation energies were

calculated with TURBOMOLE's ricc2 routine<sup>[20]</sup> using the def2-TZVPP basis sets on all elements and the RI approximation. CC2 is an approximation to the coupled clusters singles doubles (CCSD) level of theory.<sup>[21]</sup> D<sub>1</sub> diagnostics values of 0.088 for **8** and 0.050 for **9** from the CC2 calculation underline the fundamental single reference character of the electronic ground state wave function and confirm the picture of essentially non-radical closed-shell molecules.

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- [30] The Tip-substituents were modeled as hydrogen atoms. Structure optimization was carried out using DFT with the PBE density functional and cc-pVDZ basis sets on all elements except Sn for which the SVP all-electron basis set was used. Further non-standard settings were \$denconv 1.0D-8 and \$scfconv 7, and \$grid m4. The NMR signals were modeled with the ReSpect program package<sup>[31]</sup> employing the PBE density functional (PBEPBE, GGA) and uncontracted cc-pVDZ basis sets on light elements along with Dyall's VDZ basis on hetero atoms.
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