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Metallapropellanes

Pentagerma[1.1.1]propellane: A Combined Experimental and Quantum Chemical Study on the Nature of the Interactions between the Bridgehead Atoms**

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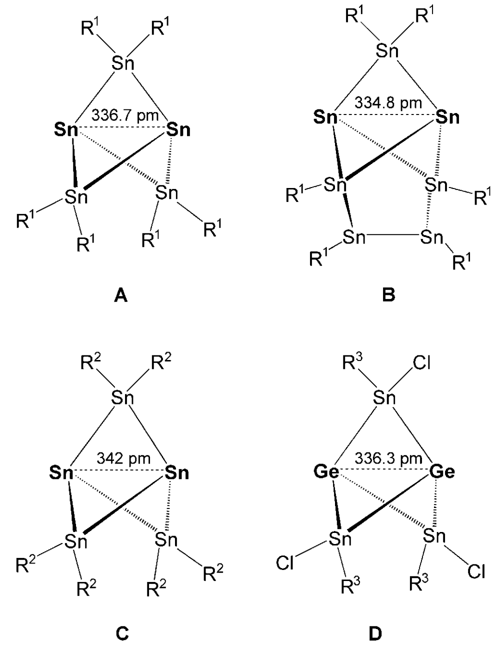
The question about the interactions between the bridgehead atoms of metallapropellanes has been extensively discussed in the literature.[1] Efforts mainly aim to clarify fundamental aspects of the nature of the interaction between the "inverted" bridgehead atoms. Even the "simplest" [1.1.1]propellane of Group 14, the all-carbon propellane [C_5R_6],[2] has attracted renewed interest. Recent experimental and quantum chemical investigations performed by Luger and coworkers revealed the existence of a bonding path between the two bridgehead carbon atoms.[3] By applying modern valence-bond theory, Wu, Shaik, Hiberty et al. described this two-electron σ bond as a charge-shift bond—neither classically covalent nor classically ionic.[4] For the heavier congeners of carbon, that is, for metalla[1.1.1]propellanes [E_5R_6] (E = Si, Ge, Sn), the situation is even more complicated.[1,5] Quantum chemical calculations concerning the pentasila[1.1.1]propellane [Si_5H_6] performed by Schleyer and Janoschek suggested substantial singlet biradical character[6] and that "*it would be misleading to represent the structure by drawing a line between the bridgehead atoms*".[7] Schoeller et al. have also predicted a long $Si_b\cdots Si_b$ separation[8] in the pentasila compound.[9] Nagase and Kudo have presented evidence that the overall biradical character of [Sn_5H_6] is very small and is comparable to that of the carbon homologue.[10] On the other hand, Gordon et al.[11] cast doubt on the existence of an "inverted" metal–metal bridgehead bond for metallapropellanes of the general formula [E_5H_6].[12] They suggested to assign a small biradical character to the ground state of the latter, consisting of a maximum of 14% within the Group 14 element series for the silicon derivative, which is in accordance with the assumption of Schleyer and Janoschek.[7] Nevertheless, the inherent singlet ground state of these species points towards noticeable $E_b\cdots E_b$ interactions,[13] and the energy splittings between their lowest-energy singlet and triplet state (ΔE_{S-T}) were calculated to be quite high (around 50 kcal mol^{-1}). Since "true" singlet biradicals usually show small ΔE_{S-T} values,[6] metallapropellanes unquestionably have less biradical and more closed-shell characteristics,[14] which makes their designation as "biradicaloids" more appropriate.[1,5,15]

Although numerous quantum chemical calculations have been performed for metalla[1.1.1]propellanes as well as hetero[1.1.1]propellanes,[16] synthetically accessible and structurally characterized species are very rare (Scheme 1).[17] Seminal work was performed by Sita and Kinoshita in the early 1990s; they succeeded in isolating the pentastanna[1.1.1]propellane [Sn_5R_6] (**A**) and the derivative [Sn_7R_8] (**B**, R = 2,6-$Et_2C_6H_3$).[18] The experimentally determined $Sn_b\cdots Sn_b$ separations of 336.7 and 334.8 pm are 20% longer than a regular Sn−Sn single bond. Structurally characterized compounds such as [Sn_5R_6] (**C**, R = 2,6-(iPrO)$_2C_6H_3$) and [$Ge_2\{Sn(Cl)R\}_3$] (**D**, R = 2,6-$Mes_2C_6H_3$) were reported later by the groups of Drost[19] and Power,[20] respectively. To date,



Scheme 1. Synthetically accessible metalla[1.1.1]propellanes of heavier Group 14 elements. R^1 = 2,6-$Et_2C_6H_3$, R^2 = 2,6-(iPrO)$_2C_6H_3$, R^3 = 2,6-$Mes_2C_6H_3$; Mes = 2,4,6-$Me_3C_6H_2$.

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however, metallapropellanes solely composed of silicon[21] or germanium[22] atoms are unknown, and experimental studies on the reactivity of metallapropellanes are still in their infancy. To shed more light on the accessibility and stability of metallapropellanes of this type and to investigate fundamental aspects of their bonding, we have specifically synthesized the first pentagerma[1.1.1]propellane $[\mathrm{Ge_5Mes_6}]$ (**1**)—one of the missing members within the Group 14 element series closing the gap to the theoretical predictions and discussions.

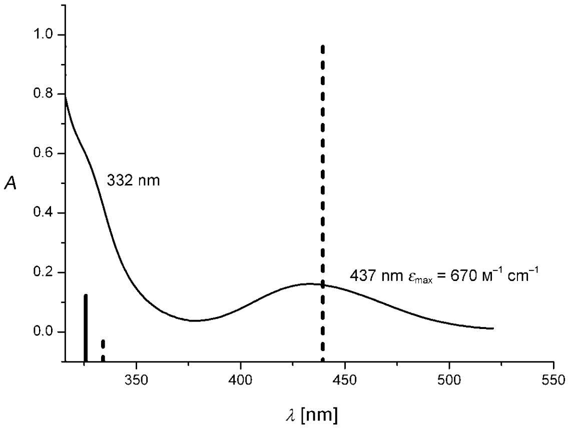
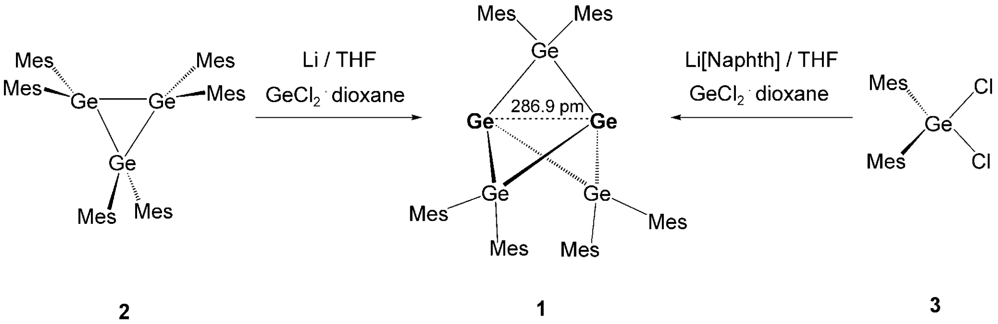


Figure 1. Experimental UV/Vis spectrum of **1** in THF and TD-DFT calculated UV/Vis transitions of A_2 (——) and E symmetry (– – –). The calculated transitions are hypsochromically shifted by about 10 nm and calibrated to the experimental spectrum.



Scheme 2. Synthesis of **1**.

The title compound $[\mathrm{Ge_5Mes_6}]$ (**1**) was initially prepared in very low yield from $[\mathrm{Ge_3Mes_6}]$ (**2**) with 6.0 equivalents lithium powder and 3.0 equivalents $\mathrm{GeCl_2{\cdot}dioxane}$ as oxidizing agent ($E^0_{1/2} = -0.76$ V vs. ferrocene/ferrocenium ($\mathrm{Fc/Fc^+}$); Scheme 2)[23a] in THF and purified by repeated crystallization from toluene/hexane at −30 °C. During our attempts to optimize the yield, we noticed that **1** can directly be prepared from $\mathrm{Mes_2GeCl_2}$ (**3**) using 3.3 equivalents freshly prepared lithium naphthalenide ($\mathrm{Li^+[Naphth]^{\bullet-}}$; 1.0 M in THF) in the presence of $\mathrm{GeCl_2{\cdot}dioxane}$ in THF. Note that $\mathrm{GeCl_2{\cdot}dioxane}$ as an additional germanium source and/or oxidizing agent is crucial for the successful synthesis of **1**.[23b,c] ^{1}H NMR spectroscopic monitoring of the crude reaction product showed that the target compound (**1**) is formed in about 10 % yield. After a non-optimized workup procedure, **1** was isolated in analytically pure form in low but reproducible yield of approximately 4 % as orange crystalline material. Compound **1** is sensitive to air but thermally very stable under argon (m.p. > 300 °C) and stable towards degassed water. The elemental analysis was consistent with the composition $[\mathrm{Ge_5Mes_6}]$. The EI mass spectra showed no peaks above the molecular ion envelope centered at m/z 1078, which corresponds to the expected value and isotope distribution for $[\mathrm{Ge_5Mes_6}]$ (see the Supporting Information). The lowest energy absorbance $\lambda_{\max}$ was observed in the UV/Vis spectrum of **1** in THF at 437 nm ($\varepsilon = 670\ \mathrm{M^{-1}\,cm^{-1}}$), alongside a characteristic shoulder at $\lambda = 332$ nm (Figure 1; see below for the assignment of the absorption bands). Compound **1** is EPR-silent at room temperature and 100 K. ^{1}H NMR spectroscopic investigations of $\mathrm{C_6D_6}$ solutions of **1** revealed two aryl-ring resonances at $\delta = 6.61$ and 6.26 ppm, whereas three further singlets at $\delta = 2.53$, 2.26, and 2.07 ppm were detected, which belong to the methyl substituents of the mesityl ligand. These data strongly suggested both the formation of a symmetric cluster compound and a hindered rotation of the Ge–$\mathrm{C_{ipso}}$ bond (non-equivalent *ortho*-methyl protons).

The molecular structure of **1** is shown in Figure 2 and confirms the formation of the first pentagerma[1.1.1]propellane featuring two ligand-free bridgehead germanium atoms ($\mathrm{Ge_b}$; Ge1 and Ge2 in Figure 2). The latter are bonded to three bridging germanium atoms ($\mathrm{Ge_{br}}$) at distances between 245.3(1) and 250.1(1) pm. Of particular interest is the separation of 286.9(2) pm between the two bridgehead atoms,[24] which is approximately

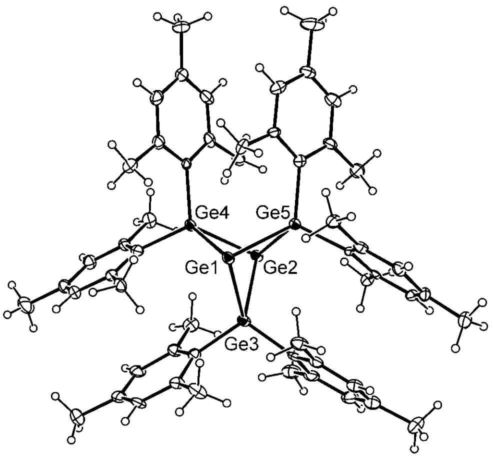


Figure 2. Molecular structure of $[\mathrm{Ge_5Mes_6}]$ (**1**). Displacement ellipsoids are drawn at the 30 % probability level. Selected bond lengths [pm]: Ge1⋯Ge2 286.9(2), Ge1–Ge3 248.9(2), Ge1–Ge4 247.6(1), Ge1–Ge5 245.3(1), Ge2–Ge3 246.6(1), Ge2–Ge4 248.5(2), Ge2–Ge5 250.1(1).

45 pm longer than usually observed for a regular Ge–Ge single bond. The quotient $q\{Ge_b\cdots Ge_b/av(Ge_b{-}Ge_{br})\} = 1.19$ is equal to that of the analogous tin propellane **A** reported by Sita et al. ($q = 1.18$).[18] In accordance with the ^{1}H NMR spectra, the mesityl ligands are symmetrically arranged around the cluster core. Owing to the propeller-like arrangement of the mesityl substituents, **1** adopts an almost ideal D_3-symmetric structure.

To gain further insight into the amount of interaction between the bridgehead germanium atoms in **1**, and to compare with the silicon (**4**) and tin (**5**) homologues, we carried out a series of DFT calculations (see the Supporting Information for details). In each case we found the following ordering of the frontier molecular orbitals: a) HOMO−1: $E_b\cdots E_b$ bonding orbital of a_1 symmetry; b) HOMO: degenerate set of $E_b{-}E_{br}$ cluster bonding orbitals of e symmetry; c) LUMO: $E_b\cdots E_b$ antibonding orbital of a_2 symmetry. Table 1 lists relevant interatomic distances of the DFT computed geometries of the singlet ground state (**QX**, a model for the (real) compounds **X** = **1**, **4**, and **5** obtained by omitting the 4-methyl group from the mesityl ligand; D_3 symmetry) as well as for the excited singlet (**SQX***) and triplet states (**TQX***) of these model compounds that involve a single excitation from the highest occupied a_1 orbital (HOMO−1) into the lowest unoccupied molecular orbital (LUMO, a_2 symmetry).

Table 1: Geometry parameters (in pm) of **Q1** and its silicon (**Q4**) and tin (**Q5**) homologues in their ground ($^1A_1$) as well as excited singlet and triplet A_2 states, obtained at the B3LYP/def2-TZVP level in D_3 symmetry.

E (**X**)	**QX** ($^1A_1$)		**SQX*** ($^1A_2$)		**TQX*** ($^3A_2$)	
	$E_b\cdots E_b$	$E_b{-}E_{br}$	$E_b\cdots E_b$	$E_b{-}E_{br}$	$E_b\cdots E_b$	$E_b{-}E_{br}$
Si (**4**)	265.4	239.3	307.4	241.9	283.4	242.2
Ge (**1**)	291.1	254.4	331.2	259.0	305.8	256.8
Sn (**5**)	344.1	292.0	389.1	296.5	362.5	294.4

Table 2 displays the wavelengths of the corresponding vertical and adiabatic excitation energies obtained from time-dependent density functional theory (TD-DFT) at the B3LYP/def2TZVP level (the optimization of the equilibrium geometries of the $^1A_2$ and $^3A_2$ states was performed in D_3 symmetry).

Table 2: Vertical and adiabatic excitation energies to the singlet and triplet A_2 states (wavelengths in nm) of **Q1** and its silicon (**Q4**) and tin (**Q5**) homologues, obtained at the B3LYP/def2-TZVP level in D_3 symmetry.

	SQX* ($^1A_2$)		**TQX*** ($^3A_2$)	
E (**X**)	vertical	adiabatic	vertical	adiabatic
Si (**4**)	325.7	337.0	546.8	576.6
Ge (**1**)	341.1	366.1	490.2	504.5
Sn (**5**)	398.4	420.2	522.1	538.4

The agreement between the computed ground state (**Q1**, $E_b\cdots E_b = 291.1$ pm) and the experimentally observed geometry of **1** ($E_b\cdots E_b = 286.9(2)$ pm) is very good. The excited singlet and triplet states of these clusters are particularly interesting from a bonding perspective. They feature much longer $E_b\cdots E_b$ separations (331.2 pm for **SQ1*** and 305.8 pm for **TQ1***) than the ground state. These findings suggest considerable $E_b\cdots E_b$ interactions in the latter. The calculated vertical singlet excitation energy of 341.1 nm ($^1A_2$) for **SQ1*** directly corresponds to the experimentally observed shoulder in the UV/Vis spectrum of **1** at $\lambda = 332$ nm, whereas the lowest energy absorbance at $\lambda_{max} = 437$ nm belongs to electronic transitions between the cluster bonding HOMO of e symmetry and the LUMO of a_2 symmetry. Furthermore, our DFT calculations predicted an almost linear decrease of the singlet excitation energy upon descending the group (see entries for **SQX*** in Table 2).

While comparing the singlet and triplet excitation energies within the homologous series, we noticed that the linear decrease is not reproduced for the corresponding triplet excitations. We essentially found a maximum for the germanium model system. The excited triplet state **TQ1*** ($^3A_2$) was revealed to be $\Delta E = 56.7$ kcal mol^{-1} higher in energy than the ground state, whereas only $\Delta E = 49.6$ kcal mol^{-1} was found for the silicon analogue **TQ4***. On the basis of these DFT findings within the homologous series, and in terms of ΔE_{S-T} energies alone, we would assign (if at all) the highest amount of biradical(oid) character to the silicon derivative and the smallest to the title compound **1**.

To address the bonding properties of **1** a little further, we performed electrochemical studies using cyclic voltammetry (see the Supporting Information). The known tin cluster $[Sn_5R_6]$ (**A**, R = 2,6-$Et_2C_6H_3$) is readily reduced in two separated, quasireversible one-electron reduction waves centered at $E^0_{1/2} = -1.96$ and -2.48 V vs. Fc/Fc$^+$.[18c] These electrochemical findings support the inherent electron deficiency of the bridgehead tin atoms in **A**. Overall, it is the change from a "through-cage" interaction via a partially lifted $E_b\cdots E_b$ interaction to separated, eight-valence-electron $(ER_2)_3E^-$ entities that appears to influence the redox potentials ΔE for cluster compounds of this type. At room temperature, **1** is quasireversibly reduced to the radical anion $[Ge_5Mes_6]^{\bullet -}$ (**6**) at a potential of $E^0_{1/2} = -2.18$ V vs. Fc/Fc$^+$. A second quasireversible reduction wave is observed for the process $[Ge_5Mes_6]^{\bullet -}$ (**6**) + $e^- \rightleftarrows [Ge_5Mes_6]^{2-}$ (**7**) at $E^0_{1/2} = -2.61$ V. Compared to **A**, both half-wave potentials of **1** are slightly more negative ($\Delta E(1) = -0.22$ V, $\Delta E(2) = -0.13$ V). Thus, in terms of electrochemical potentials alone, the inherent electron deficiency of the bridgehead atoms—although of comparable extent in the two compounds—should be slightly more pronounced for the tin case.

It was of further interest to support the electrochemical findings by EPR spectroscopy. The disproportionation constant K_{disp} for the reaction $2\,[Ge_5Mes_6]^{\bullet -}$ (**6**) $\rightleftarrows [Ge_5Mes_6]$ (**1**) + $[Ge_5Mes_6]^{2-}$ (**7**) was calculated to be 4.0×10^{-8}. This observation indicates the thermodynamic stability of the radical anion **6**. Indeed, freshly prepared samples of **6** (1 equiv sodium powder in THF) show strong signals in a frozen solution upon cooling to 100 K. Figure S2 in the Supporting Information summarizes the continuous-wave EPR spectra of **6** in THF recorded at the X band, along with the corresponding simulations for a system with an electron spin of $S = 1/2$. As expected, an axial g tensor with g values close to the free-electron value and with hyperfine couplings on all components was observed. The spin Hamiltonian parameters used for the simulations are $g_{\perp} = 1.980$ and $g_{\parallel} = 1.999$,[25] with hyperfine couplings to two equivalent germanium atoms ($I(^{73}\mathrm{Ge}) = 9/2$, 7.73 % n.a.) of $A_{\perp} \leq 20$ MHz and $A_{\parallel} = 41$ MHz. This result is in accordance with DFT calculations, which predicted the spin density to reside mainly on the bridgehead germanium atoms. Since the SOMO is $\mathrm{Ge_b\cdots Ge_b}$ antibonding in nature, the $\mathrm{Ge_b\cdots Ge_b}$ separations are considerably longer in the reduced form ($d = 290.6$ pm (**Q1**)→328.9 pm (**Q6**); BP86/def2-TZVP level), meaning that the "through cage" interaction is gradually lifted upon one-electron reduction (see the Supporting Information).

To address the central question of the amount of biradicaloid character in a more sophisticated way, we have performed additional quantum chemical calculations using the complete active space self-consistent field (CASSCF) method for the model compounds $[\mathrm{E_5Me_6}]$ (**qX**; see the Supporting Information). A (6,4) active space was used, obtained by distributing six electrons among four orbitals: the highest occupied a_1 level, the highest occupied (two-fold degenerate) e level, and the LUMO of a_2 symmetry. Table 3 reports the natural orbital occupation numbers of the frontier orbitals, obtained from (6,4)CASSCF calculations in the def2-TZVP basis at the B3LYP/def2-TZVP optimized geometries. The natural orbitals for the pentagerma[1.1.1]propellane **q1** are depicted in Figure 3. Furthermore, Wiberg bond indices (WBI) and results from population analyses based on occupation numbers (PABOON) are given in Table 3. Both methods reveal a much weaker interaction (39–76 %) between the bridgehead atoms ($\mathrm{E_b\cdots E_b}$) than between the bridgehead and bridging atoms ($\mathrm{E_b{-}E_{br}}$) of the cluster. The smallest quotients ζ were found for the all-tin propellane **q5**. This finding is in line with results from NBO analyses, which revealed more delocalized $\mathrm{E_b\cdots E_b}$ interactions upon descending the group. This qualitative description is further supported by the shape of the bonding (6,4)CASSCF natural orbital for **q1** (Figure 3, left), providing evidence for "delocalized tails" within the cluster core.

Table 3: Natural orbital occupation numbers of **q1** and its silicon (**q4**) and tin (**q5**) homologues, obtained at the (6,4)CASSCF/def2-TZVP//B3LYP/def2-TZVP level. Calculations of Wiberg bond indices (WBI) and population analyses based on occupation numbers (PABOON) were performed at the B3LYP/def2-TZVP level (see the Supporting Information).

E (**qX**)	Occupation number		WBI			PABOON		
			$\mathrm{E_b\cdots E_b}$	$\mathrm{E_b{-}E_{br}}$	ζ[a]	$\mathrm{E_b\cdots E_b}$	$\mathrm{E_b{-}E_{br}}$	ζ[a]
Si (**q4**)	1.900	0.102	0.67	0.88	0.76	0.82	1.28	0.64
Ge (**q1**)	1.902	0.101	0.55	0.81	0.68	0.60	1.11	0.54
Sn (**q5**)	1.907	0.097	0.39	0.82	0.48	0.44	1.14	0.39

[a] $\zeta = (\mathrm{E_b\cdots E_b})/(\mathrm{E_b{-}E_{br}})$.

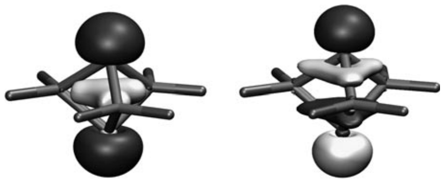
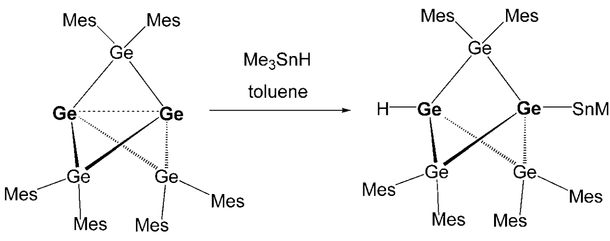


Figure 3. (6,4)CASSCF natural orbitals of **q1** with occupation numbers 1.902 (left) and 0.101 (right). Only the C atoms of the Me ligands are shown for clarity.

The CASSCF results show that occupation numbers of about 1.9 and 0.1 are found for all three systems. They are effectively independent of the Group 14 element within this series. To put these occupation numbers into perspective, we note that similar ones are obtained in (2,2)CASSCF calculations (with two electrons in the active space of the $1\sigma_g$ and $1\sigma_u$ orbitals) of the H_2 molecule at an internuclear separation of $5/3\,r_e$, where r_e is the equilibrium bond length. This is roughly the distance beyond which a restricted Hartree–Fock calculation shows a triplet instability for H_2. Clearly, in view of the computed excitation energies, the singlet ground-state wave function for **1** is stable, but it appears that the $\mathrm{E_b\cdots E_b}$ interactions in metallapropellanes of this type are perturbed to such an extent ("stretched bonds") that highly correlated quantum chemical methods provide evidence for some biradicaloid characteristics. This finding nicely illustrates the continuous nature of the conversion of an ordinary closed-shell molecule into a biradicaloid and eventually into a perfect biradical by the introduction of a suitable perturbation.[14] On the basis of our findings, approximately 10 % biradicaloid character could be assigned to these systems. This value is in accord with earlier studies, although our results did not show a distinct maximum for the silicon propellane.[7,11]

Our CASSCF findings prompted us to investigate the biradicaloid behavior of **1** in more detail.[26] As far as we are aware, no such biradicaloid reactivity has yet been reported for any metallapropellane known to date, and we speculated that typical reagents for radical-type reactivity would provide a suitable entry point. On reaction of **1** with an excess of $\mathrm{Me_3SnH}$ in toluene at room temperature, a spontaneous and clean reaction was observed within 15 minutes. The color of the solution changed from orange to colorless. The ^{1}H NMR spectrum of the crude product showed the characteristic signals for the addition product bicyclo[1.1.1]pentagermane $[\mathrm{H{-}Ge(GeMes_2)_3Ge{-}SnMe_3}]$ (**8**, Scheme 3). Along with the singlet for the $\mathrm{SnMe_3}$ group, overall six methyl and four aryl resonances were found for the mesityl substituents of the unsymmetrically substituted cluster. The Ge–H moiety was



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Scheme 3. Reaction of **1** with $\mathrm{Me_3SnH}$.

detected as singlet at $\delta = 6.85$ ppm ($J_{^{117}\text{Sn,H}} = 294$ Hz, $J_{^{119}\text{Sn,H}} = 307$ Hz). We are currently not able to comment on any mechanistic details, but work to clarify these points, as well as general reactivity studies, is currently in progress.[27] Overall, the predictions from the (6,4)CASSCF calculations on the biradicaloid character of **1** are consistent with the experimental observations on its behavior, and this result suggests that the pentagerma[1.1.1]propellane **1** features some radical-type reactivity.[28]

Experimental Section

Details concerning general synthetic techniques, NMR spectroscopic investigations, and X-ray crystal structure determinations, as well as computational details, are compiled in the Supporting Information.

Preparation of $[\text{Ge}_5\text{Mes}_6]$ (**1**): A freshly prepared lithium naphthalenide solution (1 M in THF, 10 mL, 10 mmol) was added dropwise at −78 °C to a stirred solution of $\text{Mes}_2\text{GeCl}_2$ (1.146 g, 3.0 mmol) and $\text{GeCl}_2\cdot$dioxane (0.463 g, 2.0 mmol) in THF (10 mL). The dark red solution was stirred for 1 h at this temperature and overnight at room temperature. After the solvent and naphthalene were removed in vacuo (60 °C), the residue was washed with *n*-hexane (2 × 10 mL) and acetonitrile (2 × 10 mL) and extracted with toluene (10 mL). The solution was partially evaporated, layered with acetonitrile (10 mL), and stored at −40 °C to afford orange crystals of **1**. To remove small amounts of by-products incorporated by the adhesion of the mother liquor, the crystals were washed with acetone. By repeated recrystallization of the mother liquor and flash chromatography (thoroughly dried silica gel, pentane/toluene 9:1) of the *n*-hexane/acetonitrile solution, another crop of **1** could be isolated in analytical pure form. Yield: 40 mg (37 µmol, 4 %); m.p. > 300 °C; EI-MS (70 eV) *m*/*z* (%): 1078 (25); elemental analysis (%) calcd for $\text{C}_{54}\text{H}_{66}\text{Ge}_5$: C 60.15, H 6.17; found C 61.08, H 6.14; ^{1}H NMR (400.1 MHz, C_6D_6): $\delta = 2.07$ (s, 18 H, *p*-CH_3), 2.26 (s, 18 H, *o*-$\text{C}H_3$), 2.53 (s, 18 H, *o*-$\text{C}H_3$), 6.26 and 6.61 ppm (s, 12 H, Mes-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6): $\delta = 21.7$, 26.8, 28.1 (*o*- and *p*-CH_3), 129.2, 129.4, 137.8, 142.4, 142.5, 143.4 ppm ($C_6\text{H}_2\text{Me}_3$); IR (ATR): $\tilde{\nu} =$ 464(vw), 497(vw), 548(vs), 585(w), 707(vw), 728(vw), 848(vs), 880(vw), 888(vw), 926(vw), 1022(m), 1241(vw), 1262(vw), 1296(w), 1367(m), 1413(w), 1438(s), 1556(vw), 1602(w), 2724(vw), 2855(vw), 2914(w), 2939(w), 2968(w), 3019 cm^{-1} (vw); UV/Vis: $\lambda_{\max} = 437$ ($\varepsilon = 670\ \text{M}^{-1}\,\text{cm}^{-1}$), 332 nm (shoulder).

Reaction of **1** with Me_3SnH: A solution of **1** (5 mg, 4.6 µmol) and Me_3SnH (excess) in toluene (3 mL) was stirred for 1 h at room temperature. The colorless solution was evaporated to dryness, and the excess Me_3SnH was removed in vacuo. The residue was redissolved in C_6D_6 and analyzed by ^{1}H NMR spectroscopy. ^{1}H NMR (400.1 MHz, C_6D_6): $\delta = 0.59$ (s, $^2J_{^{117}\text{Sn,H}} = 47$ Hz, $^2J_{^{119}\text{Sn,H}} = 49$ Hz, 9 H, SnMe_3), 2.09, 2.10, 2.31, 2.45, 2.48, and 2.51 (s, each 9 H, CH_3), 6.26, 6.28, 6.61, and 6.64 (s, each 3 H, Mes-H), 6.85 ppm (s, $J_{^{117}\text{Sn,H}} = 294$ Hz, $J_{^{119}\text{Sn,H}} = 307$ Hz, 1 H, Ge-H).

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Keywords: biradicaloid species · cluster compounds · density functional calculations · germanium · metallapropellanes

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[25] Only some minor features of the experimental spectrum could not be reproduced by the simulation. The value for $A_\perp$ can only be given as an approximation owing to signal overlap and a relatively large line width.

[26] It is important to note that the quantity of *radical character* is fundamentally different from the theory of *radical behavior*. Radical character serves as theoretical measure, whereas radical behavior is experimentally observed for such species. See reference [14] for more details.

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