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Poly(pyrazolyl)germanium(II) and -tin(II) Derivatives—Tuneable Monoanionic Ligands and Dinuclear Cationic Cages

Alexander Steiner and Dietmar Stalke*

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4,
D-37077 Göttingen, Germany

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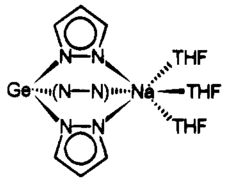
The barium complex $Ba[(Pz^*)_3Ge]_2\cdot{}^1/_2$dioxane **4**, and the separated ion pairs $[Ge_2(Pz^*)_3][GeCl_3]\cdot{}^1/_2$dioxane **5** and $[Sn_2(Pz^*)_3][SnCl_3]$, **6** (Pz* = 3,5-dimethyl pyrazol-1-yl), were obtained in the reaction of $Ba(Pz^*)_2$, **3**, with $GeCl_2\cdot$dioxane and $SnCl_2$, respectively, in THF. A molar ratio of 3:2 (**3**:$GeCl_2\cdot$dioxane) leads to the homoleptic complex **4**. Two monoanionic $[(Pz^*)_3Ge]$ ligands shield the central barium cation. X-ray structure determination proves two Pz* substituents of either germanate ligand donate to the central barium metal N(σ) (average Ba−N 280.3 pm) while the third is *side-on* coordinated. Both nitrogen atoms of either *side-on* ring coordinate to the barium center (average Ba−N 294.7 pm). If the molar ratio in the reaction is changed to 1:2 (**3**:$GeCl_2\cdot$dioxane, $SnCl_2$ respectively), **5** and **6** are formed. The solid state structures are of salt like ionic composition, determined by X-ray structure analysis. The $[E_2(Pz^*)_3]^+$ cations consist of two E(II) atoms (E = Ge, Sn), which are symmetrically *exo*-bidentate bridged by three pyrazolyl substituents, while $[ECl_3]^-$ is the counterion. In contrast to **5**, there are weak intermolecular interactions in **6**, involving two cations and two anions. In addition the unit cells of **4** and **5** contain an uncoordinated dioxane molecule as lattice solvent.

Introduction

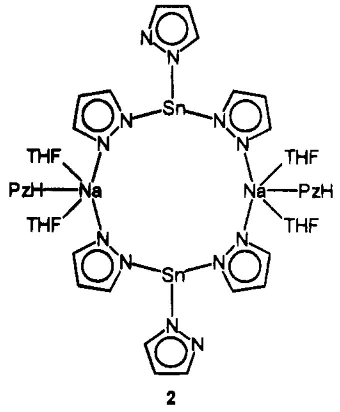
Aromatic nitrogen heterocycles play an important role in coordination chemistry. Neutral donor ligands, e.g. pyridine, 2,2′-bipyridyl, or polydentate macrocycles, stabilize a vast variety of transition metal complexes.[1] Monoanionic bidentate ligands such as pyrazolyl or imidazolyl are able to bridge two transition metal centers, resulting in multinuclear complexes.[2] The challenge was to design complexes in which heavy p-block elements are bridged *via* nitrogen heterocycles.

The bis(2-pyridyl)methyl anion is a monoanionic bidentate ligand with a highly delocalized charge.[3] We replaced the central CH unit of bis(2-pyridyl)methyl with a phosphorus or arsenic atom to give bis(2-pyridyl)phosphide and bis(2-pyridyl)arsenide. In the monomeric complexes $Me_2Al(\mu\text{-}Py)_2P$, $Me_2Al(\mu\text{-}Py)_2As$, and $Me_2Ga(\mu\text{-}Py)_2As$ the two pyridyl rings bridge group 15 and 13 centers, while leaving the phosphorus and arsenic atoms two coordinated.[4]

The sterically demanding monoanionic poly(pyrazol-1-yl)borate ligand is widely used to shield one side of a metal center.[5] Recently we described the formal replacement of the central BH unit in the tris(pyrazol-1-yl)borate $[(Pz)_3BH]^-$ (Pz = pyrazol-1-yl) by a Ge(II) or Sn(II) atom. Germanium(II) and tin(II) compounds are known for their amphoteric property.[6] The metal centers can interact with electrophiles because of their lone pair and also with nucleophiles to saturate their coordination sphere. The reaction of NaPz with $GeCl_2\cdot$dioxane and $SnCl_2$, respectively, in the molar ratio of 3:1 results in the complexes $(thf)_3Na[(\mu\text{-}Pz)_3Ge]$, **1**, and $[(thf)_2(PzH)Na\{(\mu\text{-}Pz)_2Sn(Pz)\}]_2$, **2**, by sodium chloride elimination.[7] While the $[(Pz)_3Ge]$ germanate unit in **1** acts as a tridentate ligand at the same sodium atom (**a**), the heteroarene rings in the $[(Pz)_3Sn]$ stannate unit of **2** turn around the Sn−N bond to coordinate only in a monodentate fashion two different sodium atoms in a dimer (**b**). The resulting product containes a central twelve-membered ring system. Nevertheless, in both complexes the pyrazolyl rings exclusively donate N(σ) to the metal center.



1



2

From our investigations of the phosphine,[8] sulfinaminato,[9] and (diphenylpyridyl)methyl[10] alkali metal compounds, we learned that often the heavy metals prefer π-interaction with a phenyl substituent rather than coordination of additional donor solvent. Thus, the N(σ) donating capacity should be combined with a potential π-interaction by using the pyrazol-1-yl ligand (**c**). With the type of bonding found in **1** and **2**, it seems quite easy to rotate the substituent about the E−N bond (E = Ge,

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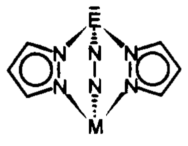
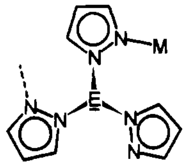
Sn) to vary the grip of the ligand. In ligands like $[(Bu^tO)_3E]^-$ (E = Ge, Sn and Pb)[6b,d] and $[\{Ph(Bu^t)C{=}N\}_3E]^-$ (E = Sn, Pb),[11] the rotation about the E–O or E–N bond would not vary that grip.



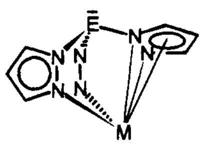
E = Ge; M = Na

a



E = Sn; M = Na

b



E = Ge; M = Ba

c

To verify the aforementioned coordination mode of the ligands, especially toward more polarizable heavy s-block metals, we used HPz* (Pz* = 3,5-dimethylpyrazol-1-yl) as starting material to synthezise the germanates and stannates, rather than the unsubstituted pyrazolyl ligand as in **1** and **2**, because the first provides higher steric demand, which should lead to better metal shielding and higher solubility of the products.

Furthermore, an excess of ECl_2 rather than the required 1:3 (ECl_2:HPz*) ratio should give access to multinuclear complexes in which the E(II) centers are bridged by the *exo*-bidentate Pz*-substituents. This work presents the synthesis and structures of $Ba[(Pz^*)_3Ge]_2\cdot{}^1/_2$dioxane, **4**, $[Ge_2(Pz^*)_3][GeCl_3]\cdot{}^1/_2$dioxane, **5**, and $[Sn_2(Pz^*)_3][SnCl_3]$, **6**, which are obtained in the reaction of $Ba(Pz^*)_2$, **3**, with ECl_2 in molar ratios of 3:2 or 1:2, respectively.

Results and Discussion

Preparation of 3–6. $Ba(Pz^*)_2$, **3**, is synthezised by refluxing a mixture of barium metal and 3,5-dimethylpyrazol in the molar ratio of 1:2 in THF and precipitates as a white powder. Elemental analysis proves the compound not to contain any solvent molecules after being washed with THF and dried in vacuum.

$$Ba + 2Pz^*H \rightarrow \underset{\mathbf{3}}{Ba(Pz^*)_2} + H_2$$

$Ba[(Pz^*)_3Ge)]_2\cdot{}^1/_2$dioxane **4** is obtained in the reaction of **3** with $GeCl_2\cdot$dioxane[12] in the molar ratio of 3:2 in THF.

$$\underset{\mathbf{3}}{3Ba(Pz^*)_2} + 2GeCl_2\cdot\text{dioxane} \rightarrow \underset{\mathbf{4}}{Ba[(Pz^*)_3Ge]_2\cdot{}^1/_2\text{dioxane}} + 2BaCl_2$$

However, the reaction of **3** with $GeCl_2\cdot$dioxane or $SnCl_2$, respectively, in the molar ratio 1:2 yields $[Ge_2(Pz^*)_3][GeCl_3]\cdot{}^1/_2$dioxane **5** and $[Sn_2(Pz^*)_3][SnCl_3]$, **6**.

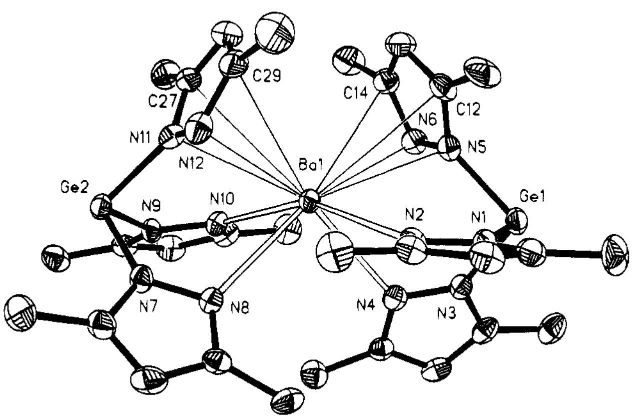


Figure 1. Crystal structure of **4**, depicting 50% anisotropic displacement parameters.

$$\underset{\mathbf{3}}{3Ba(Pz^*)_2} + 6GeCl_2\cdot\text{dioxane} \rightarrow \underset{\mathbf{5}}{2[Ge_2(Pz^*)_3][GeCl_3]\cdot{}^1/_2\text{dioxane}} + 3BaCl_2$$

$$\underset{\mathbf{3}}{3Ba(Pz^*)_2} + 6SnCl_2 \rightarrow \underset{\mathbf{6}}{2[Sn_2(Pz^*)_3][SnCl_3]} + 3BaCl_2$$

Colorless crystals of **4**, **5**, and **6** are grown from the decanted reaction solutions within 1d at room temperature. **4** melts at 220 °C. The ^1H NMR spectrum of **4** shows even at room temperature two signals for the methyl groups in the ratio 1:1 at δ 2.08 and 2.19. The six ring hydrogen atoms, however, give rise to a single line at δ 5.89. On the other hand in the ^1H NMR spectrum of **1** and **2** a resonance pattern of a triplet and a doublet in a 2:1 ratio for the Pz-ring hydrogen atoms in the $[(Pz)_3E]^-$ was detected. The mass spectrum of **4** reveals a peak at *m/z* 854 for $Ba[(Pz^*)_3Ge]_2$, suggesting that the compound remains partially intact in the gas phase.

Crystals of **5** and **6** melt at 276 and at 220 °C, respectively. The ^1H NMR spectra of **5** and **6** show only a single line for the methyl groups (δ 2.42 for **5** and 2.51 for **6**) and one signal for the ring hydrogen atoms at δ 6.02 (5.93), so that a symmetrically bridging Pz* substituent can be anticipated. However, two signals at δ −337 and −498 in the ^{119}Sn NMR spectrum of **6** indicate two different environments for the tin atoms in solution. Mass spectra of both compounds show lines at *m/z* 406 (**5**) and 498 (**6**), suggesting the existence of dimeric $[Pz^*ECl]_2$ molecules in the gas phase.

Crystal Structure of 4. The molecule is monomeric in the solid state (Figure 1). Half of a noncoordinating dioxane molecule is also present in the asymmetric unit. It is disordered around a crystallographic center of inversion. Two monoanionic $[(Pz^*)_3Ge]$-ligands envelope the central barium ion to give a homoleptic complex. Four of the six Pz*-substituents donate N(σ) toward the barium atom (average Ba1–N 280.3 pm), while two are coordinated *side-on* via their electron rich π-systems. The Ba–N *side-on* distances are slightly longer than the Ba–N(σ) bonds (average Ba1–N5/N11 296.7, average Ba1–N6/N12 292.7 pm). The Ba–C contacts are weaker than the Ba–N interactions as a consequence of the distorted electron distribution in the aromatic pyrazol ring system (average Ba1–C12/C27 339.3, average Ba1–C14/C29 327.5 pm). The electron density is mostly located at the ring nitrogen atoms; hence, the ring carbon atoms are less attractive to the electropositive barium atom. However, to our knowledge, **4** is the first example of a *side-on* coordination by a pyrazolyl ligand toward an alkaline earth metal. In the isovalent electronic poly(pyrazolyl)borate complex $Ba[(Pz^*)_3BH]_2$, all six nitrogen atoms coordinate the

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metal center exclusively N(σ). The whole complex adopts S_6-symmetry.[13] The Ba−N distances (276.0 pm) in this complex and also in the diphosphatriazene derivative $Ba[N\{P(NMe_2)_2N SiMe_3\}_2]_2$, in which barium is also coordinated by six nitrogen atoms,[14] are comparable with the Ba−N(σ) interactions in **4**. Considerably shorter Ba−N distances are observed in the low-coordinated barium bis[bis(trimethylsilyl)amides].[15]

The Ge−N bond distances to the *side-on* coordinating substituents (average Ge−N 197.6 pm) are slightly longer than those to the (N)σ-donating rings (average Ge−N 195.1 pm). In comparison the Ge−N bond lengths in **1** are 196.5 pm. In both complexes the monoanionic $[(Pz)_3Ge]^-$ germanate units can formally be regarded as Lewis acid−base pair adducts of an electron deficient germylene $(Pz)_2Ge$ and an electron rich Pz^--component. Nevertheless, the resulting species have three almost identical Ge−N bond lengths. The Ge−N bond order in both complexes is $^2/_3$. The anticipated C_{3v} symmetry of the $[(Pz)_3Ge]^-$ ligand was only found in **1**. Compared to the Ge−N distance in **4**, Ge−N single bonds in germylenes like $[(Me_3Si)_2N]_2Ge$[16] or $[Ge(\mu\text{-}NMes^*)]_2$[17] are about 10 pm shorter. The N−Ge−N bond angles in **1** (96.2°) and **4** (average 93.7°) indicate mainly s-character of the lone pair at the germanium atom. This effect is even more pronounced at the higher homologue tin atom in **2** (average 87.3°). Consequently, the N−E−N angle in **2** (E = Sn), which is much more acute than in **1** and in **4** (E = Ge) should result in stronger repulsion between the lone pairs of the nitrogen atoms. This may then cause the pyrazolyl rings of **2** to twist in order to reduce repulsion. So the $[(Pz)_3Sn]^-$ unit is forced into a conformation in which it can no longer efficiently envelope a single metal center but has to bridge two of them instead.

4 proves that in the $[Ge(Pz^*)_3]$ ligand the size of the concave side of the ligand is tunable to different sized metals and hence provides high coordinational flexibility. The Pz* substituent can also coordinate *side-on* via its π-system to soft Lewis acids. As their bonding to a π-system is almost exclusively ionic,[18] the arrangement of a metal cation in relation to a π-delocalized ring system can often be predicted by simple electrostatic point charge models.[19]

The Ba−C distances in the barocene π-complex $Ba(Cp^*)_2$[20] (Cp* = pentamethylcyclopentadienyl) are about 30 pm shorter than in **4**. The electronegative ring nitrogen atoms in the Pz* substituents of **4** accumulate most of the negative charge. Therefore the coordination toward the metal center is less symmetrical than in $Ba(Cp^*)_2$ (η^2 rather than η^5).[21] It is worthy to note, that both η^2-coordinated heteroarene rings in **4** are located *cis* relative to the metal center, rather than *trans*, as one might expect to minimize steric hinderence. The N_2(center)−Ba−N_2(center) angle of 129.5° in the $Ba(Pz^*)_2$ fragment, where N_2(center) is the center of the N5−N6 and N11−N12 bonds, is 17.5° more acute than the ring centroid−Ba−ring centroid angle of 147° in $BaCp_2$ from large scale MP2 *ab initio* calculations.[22] While the latter molecule is regarded to be quasilinear due to its small linearization energy, in **4** this bent arrangement of the two *side-on* Pz* rings is clearly caused by the shape of the $[(Pz^*)_3Ge]$ ligand. However, the question why both rings are located at the same side of the metal remains open.

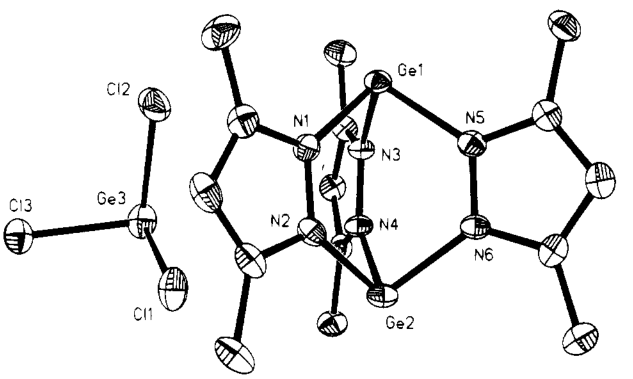

Figure 2. Crystal structure of **5**, depicting 50% anisotropic displacement parameters.

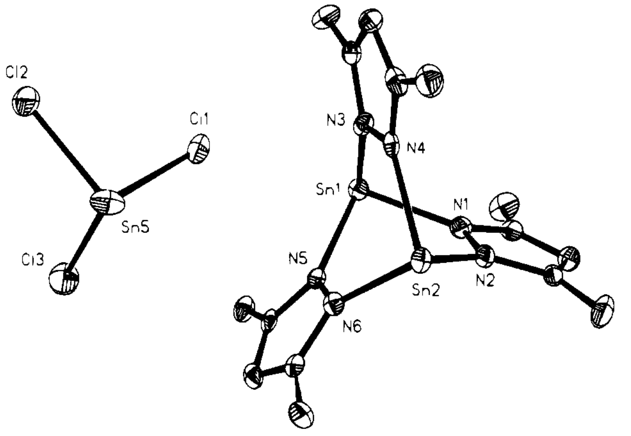

Figure 3. Crystal structure of **6**, depicting 50% anisotropic displacement parameters.

The wider N−B−N angle in $Ba[(Pz^*)_3BH]_2$ (111.2°) provides a wider grip of the $[(Pz^*)_3BH]$ ligand leaving the central barium atom exclusively N(σ)-coordinated. This coordination pattern seems to be unfavorable in **4** so one ring turns around to generate a bigger cavity on the concave side. The Ge••Na distance in **1** is 391 pm and the Ge••Ba distance in **4** is only 407.6 pm, although the difference in covalent radii between Na and Ba is 44 pm. It was only very recently that a similar coordination to **4** was described for a poly(pyrazolyl)borate system. The uranium compound $U[HB(Pz^*)_3]_2$ is the first example for a *side-on* coordinated pyrazolyl substituent in a poly(pyrazolyl)borate complex.[23]

Crystal Structures of 5 and 6. The molecular structures of $[E_2(Pz^*)_3][ECl_3]$, E = Ge(**5**) and Sn(**6**), (Figures 2 and 3) are very similar although not isostructural. The $[E_2(Pz^*)_3]$ unit forms a singly charged cage cation, while the anion is an $[E^{II}Cl_3]$ unit (Figure 2). In addition half a noncoordinated dioxane molecule is present in the asymmetric unit of **5**. The other half is generated by a center of inversion. The asymmetric unit of **6** contains two crystallographically independent ion pairs. The structure of the $[E_2(Pz^*)_3]^+$ cations in **5** and **6** can be

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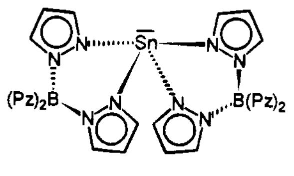
described as a "paddle-wheel" with an Ge(II) or Sn(II) shaft, because the two E(II) centers are bridged *exo*-bidentate by three Pz* substituents. The coordination polyhedron of the core consists of two E and six N atoms and can be rationalized as a dicapped trigonal prism. The six nitrogen atoms occupy the corners of the prism, while the E atoms are located above either triangular face of the prism. The $[ECl_3]^-$ counterions display the expected trigonal pyramidal structure.

The Ge−N bond distances in **5** range from 195.9 to 198.3 pm and are comparable to the related distances in **1** and **4**. The N−Ge−N angles vary from 89.4 to 91.3°. On average they are about 6° more acute than in **4**. The intramolecular distance between both germanium centers in the cationic cage is 363 pm. The Sn−N bond lengths in **6** range from 217.6 to 222.1 pm and the N−Sn−N angles from 85.1 to 92.0°. Similar Sn−N distances were observed in **2** and in the tetranuclear complex $[Sn(NBu^t)]_4$ where four Sn and four N atoms occupy the corners of a heterocubane core.[24] The intramolecular distances between the tin atoms in the cations of **6** are 399 and 401 pm. The structure of $[Me_2Si(Bu^tN)_2Sn_2Cl][SnCl_3]$[6d] is closely related to **6**. Because of three μ_2 bridging ligands (two nitrogen atoms and one chlorine atom), the two tin atoms in the cation are forced into a close contact of 329 pm.



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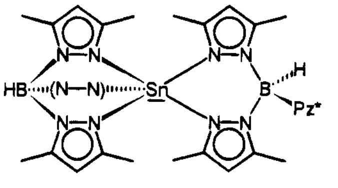

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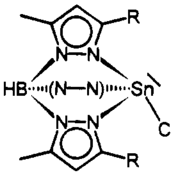
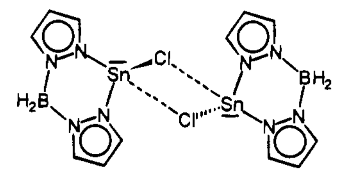


R = Me *t*-Bu

III **IV**



V

Two homoleptic tin(II)bis(poly(pyrazolyl))borate complexes are structurally described. The central tin(II) atom in $Sn[(\mu\text{-}Pz)_2B(Pz)_2]_2$,[25] **I**, is four-coordinate and in $HB(\mu\text{-}Pz^*)_3Sn(\mu\text{-}Pz^*)_2BH(Pz^*)$,[26] **II**, is five-coordinate. Because of the lone pair at the tin atom the coordination geometry at the central Sn(II) atom in both complexes is highly distorted. Also structurally characterized are the two monomeric chloro tin(II)(poly(pyrazolyl))borates $HB(\mu\text{-}Pz^*)_3SnCl$, **III**, and $HB(\mu\text{-}3\text{-}Bu^t\text{-}5\text{-}MePz)_3SnCl$,[27] **IV**, and the via weak intermolecular interactions maintained dimer $[H_2B(\mu\text{-}Pz)_2SnCl]_2$, **V**. The coordination polyhedra of the tin(II) atoms in **III** and **IV** is close to a trigonal bipyramid. The Cl and one N atom of the ring are in axial, while the equatorial positions are occupied by the remaining two N atoms and the lone pair. The chlorine atoms in **V** bridge both Sn centers by two short (248.5 pm) and two long (339.0 pm) Sn-Cl distances. The Sn−N distances in the highly crowded complexes **I** and **II** are significantly longer than in **6**. They vary from 224.8 to 262.5 pm in **I** and from 236.1 to 251.0 pm in **II**. Two short and one long Sn−N distance are observed in the chloro complexes **III** (221.4, 221.5 *vs* 249.1 pm) and **IV** (227.2, 229.0 *vs* 260.1 pm). The axial Sn−N bond is considerably elongated because the chlorine atom occupies the *trans*-position. In all complexes **I**−**V**[28] the N−Sn−N angles are 5 to 15° more acute than in **6**.

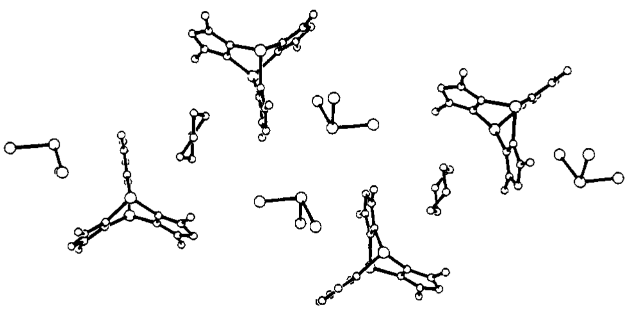


Figure 4. Packing diagram of **5**.

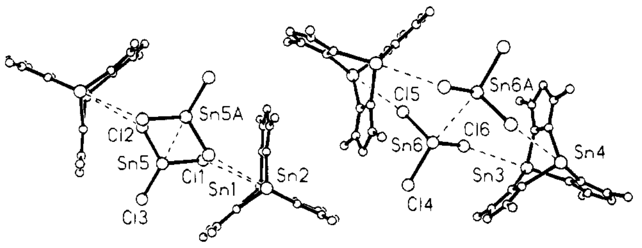


Figure 5. Packing diagram of **6**, depicting both crystallographically independent $[E_2(\mu\text{-}Pz^*)_3][ECl_3]$ units and their symmetry equivalents.

Although the cations of **5** and **6** show nearly local D_{3h} and the anions C_{3v} symmetry, both ions do not display crystallographic 3-fold symmetry. Figure 4 illustrates the arrangement of **5** in the crystal lattice. The centers of inversion are located at the centers of the dioxane molecules and in the middle of the 408 pm long Ge3··· Ge3 vectors between two anions. This and all other short intermolecular distances are about 160 pm longer than the sum of the related covalent radii[29] and can therefore be regarded as nonbonding distances.

The crystal packing of **6** is presented in Figure 5. The two crystallographically independent cations and anions are arranged near a center of inversion. Close intermolecular Sn···Cl contacts are found between both tin atoms of the cation and two chlorine atoms of the anion (Sn1···Cl1 330, Sn2···Cl2A 328, Sn3···Cl6 328 and Sn4···Cl5A 336 pm). They are comparable to those in **V**. The Sn···Sn distances between two anions are different (Sn5···Sn5A 360 pm, Sn6···Sn6A 380 pm). In $[Co(dpe)_2Cl][SnCl_3]$ (dpe = $Ph_2PCH_2CH_2PPh_2$) the intermolecular Sn···Sn distance in the $[Cl_3Sn\cdots SnCl_3]^{2-}$ unit is 360 pm.[30] The shortest intermolecular distances in **6** are about 100 pm longer than the sum of the related covalent radii. Nevertheless, in contrast to **5** intermolecular interactions between the counterions in **6** can be verified. This effect can even be detected in the structural parameters of the ions themselves. The Sn−N bond of the Pz*-ligands in *trans* position to the Sn(cation)···Cl (anion) contact is about 4 pm longer than the other two. The chlorine atoms, which are involved in long range Sn···Cl interactions, display

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(28) It is remarkable that the $[Sn(\mu\text{-}Pz^*)_3BH]^+$ fragments are detectable in the EI-mass spectra of **I** and **III** because they are isovalence electronic to the cations in **5** and **6**. Also the EI-mass spectrum of **IV** exhibits the fragment $[Sn(\mu\text{-}3\text{-}t\text{-}Bu\text{-}5\text{-}MePz)_3BH]^+$. However, the $[E_2(\mu\text{-}Pz^*)_3]^+$ cations were not detectable in the EI-mass spectra of **5** and **6**.

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Table 1. Selected Bond Lengths (pm) and Angles (deg) for **4–6**

	4 (M = Ge, M′ = Ba)	**5** (M = Ge)	**6** (M = Sn)	
			molecule 1	molecule 2
M–N	195.5(3) (N1)	196.4(3) (N1)	222.4(5) (N1)	222.1(5) (N7)
	195.1(3) (N3)	195.9(3) (N3)	218.2(5) (N3)	217.9(5) (N9)
	197.5(4) (N5)	197.3(4) (N5)	217.6(4) (N5)	217.8(5) (N11)
	194.6(3) (N7)	197.7(3) (N2)	221.6(5) (N2)	221.9(4) (N8)
	195.3(3) (N9)	197.1(4) (N4)	218.2(5) (N4)	217.7(5) (N10)
	197.6(3) (N11)	198.3(3) (N6)	218.7(4) (N6)	219.2(5) (N12)
M′–N	283.5(4) (N2)			
	277.9(4) (N4)			
	279.8(4) (N8)			
	279.9(4) (N10)			
	296.7(4) (N5)			
	292.6(4) (N6)			
	296.6(4) (N11)			
	292.8(4) (N12)			
M–Cl		229.2(1) (Cl1)	248.0(2) (Cl1)	243.0(2) (Cl4)
		232.9(2) (Cl2)	248.0(2) (Cl2)	247.4(2) (Cl5)
		231.2(1) (Cl3)	244.6(2) (Cl3)	249.5(2) (Cl6)
M···M′	408.4 (Ge1)			
	406.8 (Ge2)			
M···M		363.2 (cation)	399.4 (cation)	400.9 (cation)
		407.7 (anions)	359.5 (anions)	379.6 (anions)
N–M–N	96.9(1) (N1/3)	91.2(1) (N1/3)	85.6(2) (N1/3)	86.4(2) (N7/9)
	89.8(1) (N1/5)	90.2(1) (N1/5)	86.8(2) (N1/5)	85.6(2) (N7/11)
	94.7(1) (N3/5)	90.7(1) (N3/5)	91.8(2) (N3/5)	91.1(2) (N9/11)
	96.4(1) (N7/9)	91.4(1) (N2/4)	85.1(2) (N2/4)	85.4(2) (N8/N10)
	93.2(1) (N7/11)	89.4(1) (N2/6)	86.0(2) (N2/6)	86.2(2) (N8/12)
	91.3(1) (N9/11)	90.4(1) (N4/6)	92.0(2) (N4/6)	90.8(2) (N10/12)
Cl–M–Cl		97.90(6) (Cl1/2)	89.94(6) (Cl1/2)	96.92(7) (Cl4/5)
		94.66(5) (Cl1/3)	95.70(6) (Cl1/3)	95.02(7) (Cl4/6)
		98.39(5) (Cl2/3)	95.75(6) (Cl2/3)	89.48(6) (Cl5/6)

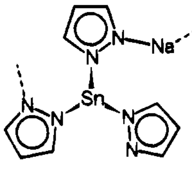
Table 2. Crystallographic Data for **4–6** at T = 153 K

	4	**5**	**6**
formula	$C_{32}H_{46}N_{12}OGe_2Ba$	$C_{17}H_{25}N_6OCl_3Ge_3$	$C_{15}H_{21}N_6Cl_3Sn_3$
fw	897.33	653.55	747.80
crystal size (mm)	0.4 × 0.4 × 0.3	0.7 × 0.6 × 0.4	0.5 × 0.4 × 0.2
space group	*C*2/*c*	$P2_1/n$	$P\bar{1}$
a (pm)	2488(2)	1329.6(4)	1167.7(3)
b (pm)	1267.3(8)	1352.4(4)	1216.8(3)
c (pm)	2412(2)	1386.4(3)	1695.3(5)
α (deg)	90	90	109.12(2)
β (deg)	96.53(8)	100.22(2)	94.22(2)
γ (deg)	90	90	93.30(2)
V (nm^{3})	7.556(10)	2.453(1)	2.261(1)
Z	8	4	4
ϱ_c (Mgm^{-3})	1.578	1.769	2.197
μ (mm^{-1})	2.655	4.000	3.656
F(000)	3600	1296	1416
2θ range (deg)	8–50	8–60	8–45
no. of measd reflns	9353	6695	8977
no. of unique reflns	6675	5264	5948
R1 ($I > 2\sigma(I)$)	0.035	0.044	0.035
wR2[a] (all data)	0.095	0.136	0.096
g_1/g_2[b]	0.0585/19.7917	0.0748/5.4262	0.0577/9.5457
ref params/ restraints	437/30	277/0	487/0
max diff peak/ hole(e nm^{-3})	1135/–1277	618/–1117	870/–1750

[a] $wR2 = \{[\sum w(F_c^2 - F_o^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$. [b] $w^{-1} = \sigma^2(F_o^2) + (g_1P)^2 + g_2P$; $P = [F_o^2 + 2F_c^2]/3$.

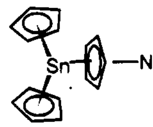
4 pm longer Sn-Cl bonds to the anionic tin centers than the terminal ones. This is the reason why the D_{3h} symmetry is prevented. The planes of the two Pz* substituents facing the anions intersect at an angle of 135 and 139°, respectively, and hence are opened significantly compared to the expected angle of 120°. There is no such effect observed in **5**. The Pz* ligand planes intersect at an angle close to 120° (from 116 to 122°)

The structure of the $[GeCl_3]$ unit in **5** is in good agreement with other examples for isolated $[GeCl_3]^-$-anions.[31] The arrangement of both crystallographically independent $[Cl_3Sn\cdots SnCl_3]^{2-}$ units in **6** is illustrated in Figure 6. Two Sn–Cl bonds are almost colinear with the Sn···Sn vector. The Cl3–Sn5···Sn5A angle is 166°, while the related Cl4–Sn6···Sn6A angle (154°) is more acute. Because the Sn5···Sn5A distance is 20 pm shorter than the Sn6···Sn6A distance, the Cl3-Sn5···Sn5A angle is wider because of the stronger lone pair-lone pair repulsion between the tin atoms.



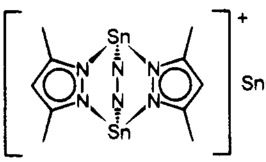
[Na(Pz*)$_3$Sn]$_2$

2



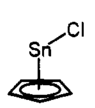
NaCp$_3$Sn

VI



[Pz*SnCl]$_2$

6



CpSnCl

VII

Structural Comparison with Cyclopentadienyl Analogues. Cyclopentadienyl complexes of most p-block metals are known.[32]

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Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{pm}^2 \times 10^{-1}$) for **4**[a]

	x	*y*	*z*	*U*(eq)
Ba1	1553(1)	4326(1)	1140(1)	20(1)
Ge1	699(1)	1630(1)	730(1)	26(1)
Ge2	2314(1)	7158(1)	1373(1)	24(1)
N1	271(1)	2755(2)	1020(1)	25(1)
N2	458(1)	3744(2)	1184(1)	24(1)
N3	931(1)	2425(2)	107(1)	24(1)
N4	1125(1)	3433(3)	133(1)	25(1)
N5	1326(1)	2044(2)	1263(1)	24(1)
N6	1841(1)	2091(3)	1099(1)	27(1)
N7	1556(1)	7200(2)	1070(1)	24(1)
N8	1271(1)	6383(2)	801(1)	24(1)
N9	2561(1)	6296(2)	780(1)	22(1)
N10	2419(1)	5261(3)	679(1)	23(1)
N11	2216(1)	5892(3)	1829(1)	24(1)
N12	1753(1)	5770(3)	2089(1)	30(1)
C1	−540(2)	1620(4)	1070(2)	44(1)
C2	−233(2)	2615(3)	1177(2)	31(1)
C3	−371(2)	3520(3)	1437(2)	32(1)
C4	67(2)	4203(3)	1431(2)	27(1)
C5	132(2)	5297(4)	1652(2)	40(1)
C6	694(2)	994(4)	−598(2)	39(1)
C7	868(2)	2082(3)	−432(2)	29(1)
C8	1018(2)	2886(3)	−758(2)	29(1)
C9	1178(1)	3713(3)	−393(2)	24(1)
C10	1382(2)	4779(3)	−520(2)	33(1)
C11	871(2)	1941(4)	2143(2)	41(1)
C12	1356(2)	2053(3)	1830(2)	29(1)
C13	1896(2)	2148(3)	2033(2)	34(1)
C14	2179(2)	2159(3)	1570(2)	29(1)
C15	2774(2)	2209(4)	1545(2)	40(1)
C16	1452(2)	9108(4)	1294(2)	50(1)
C17	1260(2)	8096(3)	1025(2)	30(1)
C18	773(2)	7848(4)	714(2)	35(1)
C19	795(2)	6787(3)	592(2)	26(1)
C20	382(2)	6109(4)	264(2)	32(1)
C21	3184(2)	7661(3)	468(2)	35(1)
C22	2957(1)	6576(3)	464(2)	27(1)
C23	3074(2)	5714(3)	158(2)	31(1)
C24	2731(1)	4912(3)	302(2)	26(1)
C25	2691(2)	3801(4)	107(2)	36(1)
C26	3158(2)	5177(4)	1870(2)	40(1)
C27	2603(2)	5200(3)	2046(2)	30(1)
C28	2380(2)	4620(4)	2442(2)	42(1)
C29	1859(2)	4995(4)	2453(2)	35(1)
C30	1439(2)	4638(5)	2812(2)	58(2)
O1D	551(11)	7930(23)	2316(14)	187(6)
C1D	348(12)	8989(21)	2204(14)	187(6)
C2D	−202(12)	9166(21)	2180(12)	187(6)
O2D	−485(9)	8270(24)	2356(13)	187(6)
C3D	−132(12)	8058(26)	2923(10)	187(6)
C4D	326(11)	7468(22)	2771(12)	187(6)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{pm}^2 \times 10^{-1}$) for **5**[a]

	x	*y*	*z*	*U*(eq)
Ge1	8996(1)	8017(1)	1653(1)	21(1)
Ge2	7753(1)	8260(1)	−889(1)	23(1)
Ge3	6523(1)	4692(1)	183(1)	33(1)
Cl1	7324(1)	5489(1)	−928(1)	42(1)
Cl2	7802(1)	4882(1)	1554(1)	49(1)
Cl3	6948(1)	3124(1)	−275(1)	36(1)
N1	9407(2)	7306(3)	545(2)	23(1)
N2	8983(2)	7453(3)	−425(2)	23(1)
N3	7552(2)	7734(3)	1156(2)	21(1)
N4	7093(2)	7774(3)	186(2)	21(1)
N5	8898(2)	9259(3)	896(2)	23(1)
N6	8379(2)	9367(3)	−52(2)	22(1)
C1	10772(4)	6316(4)	1540(3)	40(1)
C2	10162(3)	6635(3)	600(3)	28(1)
C3	10228(3)	6356(3)	−355(3)	31(1)
C4	9488(3)	6859(3)	−965(3)	26(1)
C5	9213(4)	6797(4)	−2055(3)	37(1)
C6	7131(4)	7213(4)	2750(3)	32(1)
C7	6864(3)	7379(3)	1675(3)	24(1)
C8	5957(3)	7194(3)	1038(3)	25(1)
C9	6133(3)	7452(3)	114(3)	23(1)
C10	5427(3)	7376(4)	−845(3)	28(1)
C11	9852(3)	10286(4)	2234(3)	32(1)
C12	9270(3)	10152(3)	1217(3)	24(1)
C13	9000(3)	10833(3)	482(3)	28(1)
C14	8441(3)	10332(3)	−303(3)	25(1)
C15	7915(4)	10722(4)	−1271(3)	34(1)
O1	5813(4)	9739(3)	−507(3)	60(1)
C16	5961(5)	10111(5)	458(5)	56(2)
C17	4899(6)	10133(5)	−975(5)	64(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

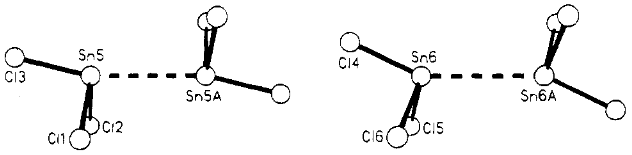

Figure 6. Crystallographically independent $[\text{Cl}_3\text{Sn}\cdot\cdot\text{SnCl}_3]^{2-}$ units in **6**.

Although cyclopentadienyl and pyrazol-1-yl are isoelectronic their coordination pattern varies due to different electron density distribution in the ring systems. While the Cp ligand favors η^5-coordination as a 6π-electron donor, the Pz-ligand prefers the *exo*-bidentate N(σ)-donation without loosing its resonance stability. Thus it seems to be worthy to compare the structural features of the discussed Pz-derivatives with related Cp-compounds. Two tris(cyclopentadienyl)stannate complexes of s-block metals are described.[33] $[\text{Mg(THF)}_6][(\eta^3\text{-Cp})_3\text{Sn}]_2$ is a solvent separated ion pair in which the anions exhibit a 3-fold symmetry.[34] In $[(\text{PMDETA})\text{Na}(\mu_2\text{-}\eta^5\text{-Cp})\text{Sn}(\eta^5\text{-Cp})_2$, **VI** [PMDETA = $\{(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\}_2\text{NCH}_3$], one of the three Cp ligands μ_2-η^5-bridges a tin and a sodium center and two are terminally η^5-bonded to the tin atom.[35] **VI** can be regarded as the Cp counterpart of the sodium tris(pyrazol-1-yl)stannate **2**. The N(σ)-donation of the Pz substituents leads to a completely different coordination pattern, yielding a cyclic dimer. Two Pz substituents bridge *exo*-bidentate tin and sodium centers, while one is bonded terminally to the tin atom. CpSnCl,[36] **VII**, is of similar composition to **5**, regarding it as trimeric Pz*SnCl. However, **VII** is monomeric in the solid state. The tin atom is η^5-coordinated to the Cp ligand. The structure is bent because of the lone pair at the tin(II) atom. In the related Pz* complex **6** an ionic structural pattern is favored due to the *exo*-bidentate bonding mode of the pyrazolyl units. As in **6** there are also weak intermolecular Sn··Cl interactions in the solid state of **VII**. It would be very interesting to investigate the structure of the conceivable binary SnPz_2 complex which is isoelectronic to stannocene.[37]

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Table 5. Atomic coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **6**[a]

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
Sn1	2072(1)	9365(1)	889(1)	18(1)	N6	2920(4)	7208(4)	−524(3)	17(1)
Sn2	4299(1)	6917(1)	312(1)	17(1)	C11	627(5)	8819(5)	−1067(4)	24(1)
Sn3	11813(1)	14318(1)	5755(1)	19(1)	C12	1521(5)	7994(5)	−1043(3)	17(1)
Sn4	14286(1)	12112(1)	5517(1)	19(1)	C13	1845(5)	7077(5)	−1693(3)	21(1)
Sn5	−820(1)	5746(1)	−574(1)	30(1)	C14	2725(5)	6613(5)	−1343(3)	18(1)
Sn6	9034(1)	10629(1)	4336(1)	45(1)	C15	3408(5)	5620(5)	−1755(4)	25(1)
Cl1	−388(1)	7721(2)	484(1)	38(1)	N7	13703(4)	14791(4)	5964(3)	20(1)
Cl2	−2585(2)	5468(1)	92(1)	37(1)	N8	14554(4)	14034(4)	5837(3)	18(1)
Cl3	−1787(2)	6402(2)	−1648(1)	40(1)	C16	13547(6)	16935(5)	6385(4)	32(2)
Cl4	8410(2)	10982(1)	3048(1)	35(1)	C17	14215(5)	15887(5)	6184(3)	23(1)
Cl5	7105(2)	10528(2)	4833(1)	55(1)	C18	15387(5)	15836(5)	6204(3)	23(1)
Cl6	9335(2)	12736(2)	5210(1)	56(1)	C19	15575(5)	14670(5)	5984(3)	19(1)
N1	3980(4)	9666(4)	972(3)	20(1)	C20	16710(5)	14140(5)	5911(4)	27(1)
N2	4742(4)	8829(4)	726(3)	19(1)	N9	12118(4)	13157(4)	6477(3)	20(1)
C1	4044(6)	11833(5)	1563(4)	35(2)	N10	13038(4)	12487(4)	6443(3)	20(1)
C2	4591(5)	10713(5)	1248(3)	21(1)	C21	10573(6)	13855(6)	7401(4)	34(2)
C3	5735(5)	10549(5)	1190(4)	26(1)	C22	11571(5)	13159(5)	7151(3)	22(1)
C4	5805(5)	9367(5)	865(3)	20(1)	C23	12119(5)	12474(5)	7543(4)	24(1)
C5	6866(5)	8730(6)	682(4)	29(1)	C24	13033(5)	12070(5)	7080(3)	23(1)
N3	2390(4)	8093(4)	1518(3)	18(1)	C25	13929(5)	11309(5)	7244(4)	29(1)
N4	3233(4)	7317(4)	1359(3)	17(1)	N11	12181(4)	12980(4)	4608(3)	20(1)
C6	995(5)	8812(5)	2579(4)	28(1)	N12	12971(4)	12161(4)	4541(3)	18(1)
C7	1916(5)	8051(5)	2205(3)	21(1)	C26	10758(5)	13546(6)	3679(4)	29(1)
C8	2447(5)	7253(5)	2496(3)	22(1)	C27	11658(5)	12807(5)	3841(3)	22(1)
C9	3269(5)	6808(5)	1943(3)	21(1)	C28	12126(5)	11887(5)	3273(4)	24(1)
C10	4102(5)	5929(5)	1967(4)	28(1)	C29	12940(5)	11512(5)	3735(3)	22(1)
N5	2180(4)	8073(4)	−338(3)	17(1)	C30	13714(6)	10551(5)	3441(4)	30(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Conclusion

Because of the long (and presumably weak) E(II)−N bond (E = Ge, Sn) in the tris(pyrazolyl)germanates and -stannates discussed here, this ligand is flexible enough to accommodate metals of various sizes like Na^+ and Ba^{2+}. It is possible to rotate a pyrazolyl substituent about the E−N bond, which is on average 10 pm longer than the mean E−N single bond. This feature allows the size of the basket provided by the ligand to be adjusted to the radius of the coordinated metal. While the ligands in **1** and **2** are exclusively N(σ)-donating toward sodium, the central barium ion in **4** is additionally *side-on* coordinated. The sodium and barium atoms can also be replaced by $E(II)^+$ units. An excess of ECl_2 leads to the salt like complexes **5** and **6**. The cage cations consist of two E-atoms which are bridged in an *exo*-bidentate manner *via* three Pz* ring systems, while $[ECl_3]^-$ represents the counterion. It would be interesting to see what coordination properties the mixed metal complexes **1**, **2** and **4** have toward soft acid d-block metal centers. They might provide a route to hard−soft bimetallic reagents due to coordination site selective behavior.

Experimental Section

All manipulations were performed under a dry N_2 inert gas atmosphere with Schlenk techniques or in an argon glove box. All solvents were dried over Na/K alloy and distilled prior to use. NMR spectra were obtained in THF-d_8 as solvent with $SiMe_4$ or $SnMe_4$ as external reference on a Bruker AM 250. IR spectra were recorded on a Bio-Rad FTS or a Perkin-Elmer 180, 325, or 735 B spectrometer as Nujol mulls between KBr plates and mass spectra on a Finnigan Mat 8230 or Varian Mat CH5 spectrometer. Elemental analyses were performed by the Analytisches Laboratorium des Instituts für Anorganische Chemie der Universität Göttingen.

Ba(Pz*)$_2$ (3). A mixture of 6.0 g (45 mmol) freshly cut barium metal and 8.6 g (90 mmol) 3,5-dimethylpyrazol is refluxed for 2 d in 100 mL THF. After the solution is cooled to room temperature, the colorless precipitate is washed twice with 50 mL of THF and dried in vacuum at 60 °C. Yield: 14.0 g (95%). IR (KBr/Nujol): υ [cm^{-1}] 1510 s, 1406 s, 1315 m, 1040 m, 1007 s, 787 s, 750 m, 730 m, 416 m. Anal. Calcd (found): C, 36.66 (36.42); H, 4.31 (4.35); N 17.11 (16.90).

[Ba{(Pz*)$_3$Ge}$_2$] (4). A 3 g sample of freshly prepared Ba(Pz*)$_2$ (9 mmol) is mixed with 0.7 g (3 mmol) of $GeCl_2$·dioxane and dissolved at 0 °C in THF. After overnight stirring, the mixture is refluxed for 2 h to complete the reaction. From the decanted reaction solution, colorless crystals, suitable for X-ray structure analysis, are obtained after 1 d at room temperature; yield 1.61 g (63%). Mp: 220 °C. NMR: ^1H (THF-d_8) δ 2.08 (s, 18H, CH_3), 2.19 (s, 18H, CH_3), 5.89 (s, 6H, CH). IR (KBr/Nujol): υ [cm^{-1}] 1543 m, 1510 m, 1404 m, 1304 m, 1261 m, 1109 s, 1076 w, 1024 s, 1017 s, 970 w, 872 w, 799 s, 751 w, 732 w. MS (70 eV) *m/z*: 96 (100%, Pz*), 854 (1%, M$^+$). Anal. Calcd (found): C, 42.23 (41.98); H, 4.96 (4.91); N 19.70 (19.88).

[Ge$_2$(Pz*)$_3$][GeCl$_3$]·$^1/_2$dioxane (5). A 0.70 g sample of freshly prepared Ba(Pz*)$_2$ is mixed with 1.39 g (6.0 mmol) $GeCl_2$·dioxane and dissolved in 30 mL THF at 0 °C. Overnight stirring is followed by 2 h refluxing to complete the reaction. After the precipitate has settled, the reaction solution is decanted. From that solution, colorless crystals, suitable for X-ray analysis, are obtained after 2 d at room temperature; yield 680 mg (56%). Mp: 276 °C. NMR: ^1H (THF-d_8) δ 2.42 (s, 18H, CH_3), 6.02 (s, 6H, CH); IR (KBr/Nujol): υ [cm^{-1}] 1568 m, 1634 m, 1420 w, 1402 w, 1342 w, 1262 m, 1187 w, 1184 m, 1104 w, 1047 s, 1023 m, 869 w, 805 s, 645 w, 598 w, 565 m, 490 w. MS (70eV) *m/z*: 169 (100%, Pz*Ge), 406 (12%, Pz*$_2$Ge$_2$Cl$_2$). Anal. Calcd (found): C, 31.24 (31.38); H, 3.86 (3.89); N 12.86 (12.64).

[Sn$_2$(Pz*)$_3$][SnCl$_3$] (6). A 1.00 g (3.00 mmol) sample of freshly prepared Ba(Pz*)$_2$ is mixed with 1.14 g (6.0 mmol) of $SnCl_2$ and dissolved in 30 mL of THF at 0 °C. Overnight stirring is followed by 2 h of refluxing to complete the reaction. After the precipitate has settled, the reaction solution is decanted. From that solution, colorless crystals, suitable for X-ray analysis, are obtained after 2 d at room temperature; yield 100 mg (7%). Mp: 220 °C. NMR: ^1H (THF-d_8) δ 251 (s, 18H, CH_3), 5.93 (s, 6H, CH); ^{119}Sn (Me_4Sn) δ −337.0 and −497.8. IR (KBr/Nujol): υ [cm^{-1}] 1567 m, 1528 m, 1330 w, 1307 w, 1284 w, 1262 w, 1147 w, 1121 m, 1078 w, 1037 s, 968 w, 789 m, 756 m, 665 w; MS (70eV) m/z: 215 (100%, Pz*Sn), 498(12%, Pz*$_2$-Sn$_2$Cl$_2$). Anal. Calcd (found): C, 24.09 (23.23); H, 2.83 (2.88); N 11.24 (11.14).

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X-ray Measurements of 4–6. The intensities for all structures were collected on a Stoe-Siemens-AED with graphite-monochromated Mo Kα radiation (λ = 71.073 pm). Data were collected from oil-coated rapidly cooled crystals,[38] at low temperatures with a profile-fitted method.[39] The structures were solved by direct or Patterson methods with SHELXS-90.[40] All structures were refined by full-matrix least-squares procedures on F^2, using SHELXL-93.[41] The hydrogen atoms were geometrically idealized and refined, using a riding model. The data for **4–6** were corrected for absorption by the semiempirical ψ-scan method.[42] The uncoordinated dioxane molecule in the structure of **3** was refined, using similarity restraints for 1–3 distances and for the ADP's. Selected bond lengths and angles of **4–6** can be found in Table 1, relevant crystallographic data for **4–6** in Table 2 and fractional coordinates are presented in Tables 3–5.

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Supporting Information Available: Tables of crystal data, fractional coordinates, bond lengths and angles, anisotropic displacement parameters and hydrogen atom coordinates of the structures of **4–6** (15 pages). Ordering information is given on any current masthead page.

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