The Formation of Heteroleptic Carbene Homologues by Ligand Exchange—Synthesis of the First Plumbanediyl Dimer**

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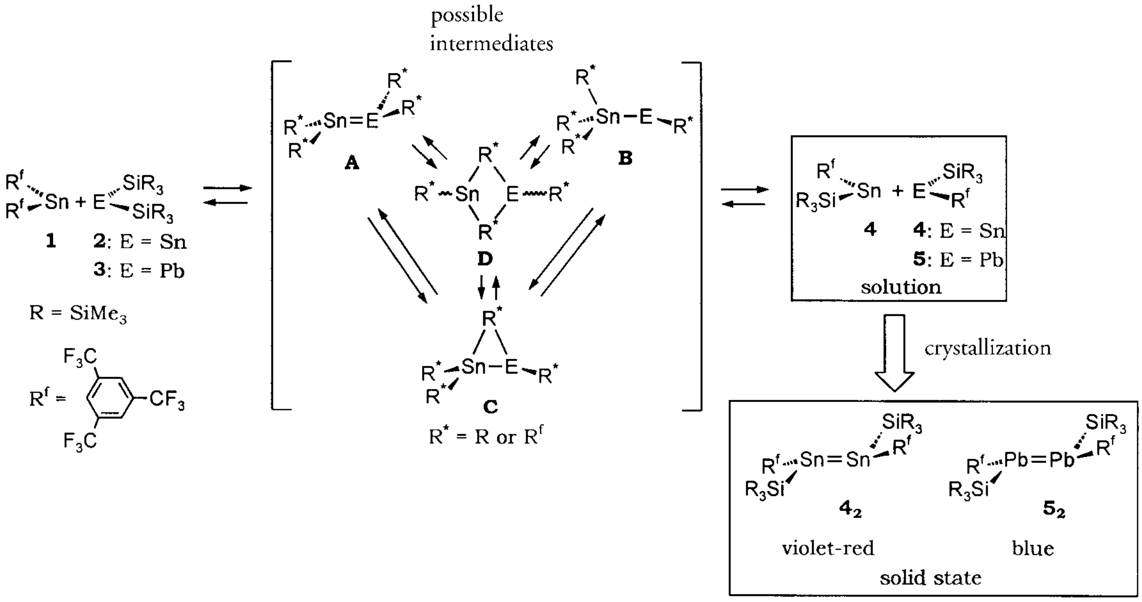
Dedicated to Professor Manfred Weidenbruch
on the occasion of his 60th birthday

Compounds of the heavier homologues of carbon containing double bonds ($R_2E{=}ER_2$, E = Si, Ge, Sn) differ strikingly from the corresponding alkenes, not only in their molecular structures but also in their chemical behavior. The type of bonding present in these molecules remains a very controversial subject.[1] The heaviest homologues, diplumbenes $R_2Pb{=}PbR_2$, were hitherto unknown. Plumbanediyls PbR_2 (also called plumbylenes), the constituent fragments homologous to carbenes, have, however, been isolated. They are monomeric even in the solid state, whereas the stannanediyls SnR_2 are known to dimerize in many cases, leading to the formation of distannenes $R_2Sn{=}SnR_2$.[2]



Scheme 1.

What happens if two carbene homologues, with differing dimerization tendencies, are mixed? Are mixed distannenes $R_2Sn{=}SnR'_2$ or even stannaplumbethenes $R_2Sn{=}PbR'_2$ accessible under such conditions? For our investigations we have chosen the stable monomeric stannanediyl $[2,4,6\text{-}(CF_3)_3\text{-}C_6H_2]_2Sn$ (**1**),[3] the distannene $[(Me_3Si)_3Si]_2Sn{=}Sn[Si(SiMe_3)_3]_2$ (**2**$_2$), and the plumbanediyl $[(Me_3Si)_3Si]_2Pb$ (**3**).[4] In hydrocarbon solvents diyls **1**, **2**, and **3** exist as monomeric R_2E carbene analogues (E = Sn, Pb) in a singlet ground state. When equimolar solutions of **1** and **2** or **1** and **3** are mixed, the heteroleptic compounds **4** and **5**, respectively, are obtained (Scheme 1).

Fractional crystallization of the reaction mixtures in solution at −60 °C led to thermochromic, needle-shaped crystals of the distannene **4**$_2$, which are violet-red at room temperature and brick-red at −180 °C, and blue prismatic crystals of the plumbanediyl dimer **5**$_2$. In both reactions a remarkable exchange of ligands has occurred with the result that each metal center E bears one $2,4,6\text{-}(CF_3)_3C_6H_2$ and one $(Me_3Si)_3Si$ substituent. To our knowledge, a comparable rearrangement has been never observed in carbene or olefin chemistry but has been reported as a mechanism for the isomerization of disilenes, digermenes, and distannenes.[1] Although we have no spectroscopic evidence,[6] it is likely that the intermediates **A**–**D** play a crucial role in course of this rearrangement. Calculations showed that for R* = H and E = Sn or Pb, all E_2H_4 isomers correspond to local minima on the energy hypersurface following the order **A** < **B** < **C** < **D** of increasing stability within a narrow energy range.[6] In solution the dimers **4**$_2$ and **5**$_2$ dissociate into the monomers **4** and **5**. Note that no mixed Sn=Pb dimer was obtained from solutions containing **4** and **5** in accordance with calculated dimerization energies (Table 1) which show that the dismutation reaction as shown in Equation (a) is slightly exothermic.

$$2\,H_2Sn{=}PbH_2 \rightarrow H_2Sn{=}SnH_2 + H_2Pb{=}PbH_2 \qquad (a)$$

$$\Delta(\Delta E_{\text{dim}}) = -10\ \text{kJ mol}^{-1}$$

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Table 1. Theoretical[a] and experimental data for various compounds of the type $R_2E{=}ER_2$ (E = C, Si, Ge, Sn, Pb).

	Theor. $d_{(E-E)}$ [pm]	Exp. $d_{(E-E)}$ [pm]	Theor. θ [°]	Exp. θ [°]	ΔE_{dim} [kJ mol^{-1}]	α [°]
C=C	135	134–137	0	0	739[c]	0
Si=Si	216	214–225	29.0	0–18	250[c]	9
Ge=Ge	234	221–235	43.7	12–36	180[c]	40
Sn=Sn	268	277–363	48.0	41.0, 41.5[b]	96	41
Pb=Pb	295	354	54.6	40.8	24	43
Sn=Pb	279	–	54.5(Sn) 49.3 (Pb)	–	55	–

[a] Calculation on Coupled-Cluster-Level.[9] [b] Data from very distorted distannenes were excluded.[1g] [c] Published data.[8]

Single-crystal X-ray diffraction experiments[7] performed at – 100 °C revealed that both compounds **4** and **5** crystallize as centrosymmetric *trans*-bent dimers $\mathbf{4}_2$ and $\mathbf{5}_2$ with idealized C_i symmetry (Figure 1). The experimentally determined tilt angles θ are 41.5° (E = Sn) and 40.8° (E = Pb). The Sn–Sn bond length in $\mathbf{4}_2$ [283.3(1) pm] is similar to the one in the distannene $\mathbf{2}_2$ [282 pm]. It is considerably longer, however, than the bond length in the distannene $R_2Sn{=}SnR_2$ [277 pm, R = $(Me_3Si)_2CH$, C_i symmetry][1f] and much shorter than the Sn–Sn distance in the stannanediyl dimer $R^f_2Sn{=}SnR^f_2$ [363 pm, $R^f = 2,4,6\text{-}(CF_3)_3C_6H_2$, C_i symmetry].[2b] The Pb–Pb bond length in $\mathbf{5}_2$ (353.7(1) pm) is long and exceeds the calculated bond length in the parent compound $H_2Pb{=}PbH_2$ (295 pm) by about 50 pm. However, the potential curves for the tilt angles θ and the E–E distances in particular are very shallow.[8] In this case, the longer bonds and smaller tilt angles θ are a consequence of the steric demands of the substituents. The relatively short Pb–F contacts (276.7, 278.2 pm) in $\mathbf{5}_2$ also contribute to Pb–Pb bond elongation, an effect which is also present in $\mathbf{4}_2$ (Sn–F: 294.9, 295.6 pm) but to a lesser extent.[2b] The question arises whether the very long Pb–Pb distance is still consistent with the presence of a double bond.

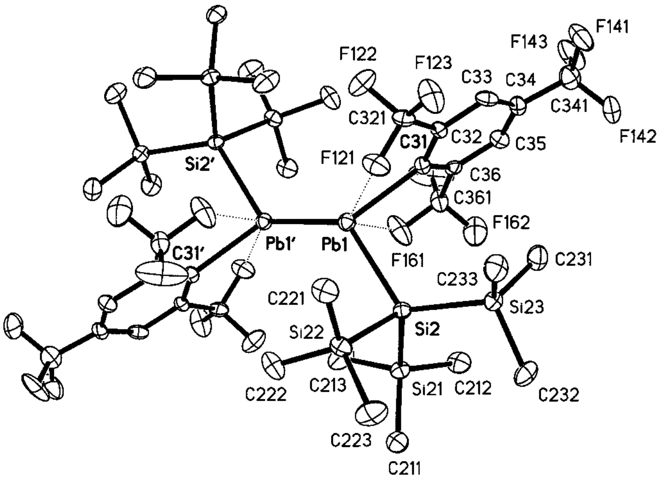

Figure 1. The structures of $\mathbf{4}_2$ and $\mathbf{5}_2$ in the crystal are very similar and only $\mathbf{5}_2$ is shown. Selected bond lengths [pm] and angles [°]: $\mathbf{4}_2$: Sn1–Sn1′ 283.3(1), Sn1–Si2 262.4(1), Sn1–C31 225.5(3); Si2-Sn1-Sn1′ 126.3(1), C31-Sn1-Sn1′ 107.8(1), Si2-Sn1-C31 103.8(1). $\mathbf{5}_2$: Pb1–Pb1′ 353.7(1), Pb1–Si2 270.5(2), Pb1–C31 236.9(7); Si2-Pb1-C31 96.7(2), Si2-Pb1-Pb1′ 124.82(5), C31-Pb1-Pb1′ 115.3(2).

In Table 1, theoretical[9] and experimental bonding parameters of the complete homologous series of unsaturated compounds of the type $R_2E{=}ER_2$ (E = C to Pb) are compared. While there is no acyclic olefin in which the carbon atoms deviate from planarity, and steric demands causes only slight bond elongation, the heavier homologues show increasing variations in bonds lengths and tilt angles θ with increasing main quantum number.

Frequently used indicators of the presence of double bonds such as *short bond lengths*, *planarity of the systems*, and *high dissociation energies* can be used to characterize "hard double bonds" like C=C bonds. According to these criteria no double bond is present in the plumbanediyl dimer $\mathbf{5}_2$. Several experimental results and extensive theoretical investigations in recent years,[1c] however, have shown that the application of these indicators to the (presumably) doubly-bonded dimers of the heavier carbene homologues is questionable. The presence of a double bond in compounds such as $\mathbf{5}_2$ cannot be confirmed with certainty until a more comprehensive and precise definition of a double bond than that given by the classical criteria becomes available.[10]

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[4] Selected physical data: **4**: m.p. (decomp.) 150 °C; ^1H NMR (250.133 MHz, C_6D_6, 300 K): $\delta = 0.15$ (CH_3), 7.88 (H_{arom}); ^{29}Si NMR (39.761 MHz, C_6D_6, 300 K): $\delta = -5.5$ [*Si*$(SiMe_3)_3$], -69.6 [Me_3*Si*$)_3Si$]; ^{19}F NMR (235.36 MHz, C_6D_6, 300 K): $\delta = -60.5$ [*ortho*-CF_3, $J(^{109/107}Sn,^{19}F) = 102$ Hz, $^1J(^{19}F,^{13}C) = 275.8$ Hz]; -63.0 [*para*-CF_3, $^1J(^{19}F,^{13}C) = 273.3$ Hz]; $^{119}Sn\{^1H\}$ NMR (74.631 MHz, C_6D_6, 300 K):

$\delta = 168$ ($W_{1/2} = 800$ Hz); UV/Vis (*n*-pentane): λ_{max} 540 nm. **5**: m.p. (decomp) approximately 90°C; ^{1}H NMR (250.133 MHz, C_6D_6, 300 K): $\delta = 0.25$ (CH_3), 8.04 (H_{arom}); ^{19}F NMR (235.36 MHz, C_6D_6, 300 K): $\delta = -66.6$ [*ortho*-CF_3, $J(^{207}Pb,^{19}F) = 374$ Hz, $^1J(^{19}F,^{13}C) = 275.4$ Hz]; -62.8 [*para*-CF_3, $^1J(^{19}F,^{13}C) = 272.5$ Hz]; UV/Vis (*n*-pentane): λ 586 nm; 1025 nm. Both compounds gave correct elemental analyses.

[5] Temperature-dependent ^{119}Sn NMR measurements, which would give valuable information about rearrangement processes or about the presence of a monomer/dimer equilibrium, could not be performed up to now for several reasons, such as very long aquisition times, the thermal lability of $\mathbf{4}_2$ at temperatures above room temperature, and the low solubility in inert solvents at low temperatures.

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[7] X-ray crystal structure analyses: P4 (Siemens), $\lambda(Mo_{K\alpha}) = 0.71073$ Å, ω scan mode, Lorenz and polarization correction, absorption correction (ψ scan, min/max. transmission: 0.73/0.99) for $\mathbf{5}_2$, solution by direct methods (SHELXS-86), refinement by a full-matrix least-squares procedure based on F_o^2 (SHELXL-93). $\mathbf{4}_2 \cdot C_5H_5$: monoclinic, space group $C2/c$ (no. 15), $a = 2213.3(4)$, $b = 1530.9(3)$, $c = 2057.1(4)$ pm, $\beta = 117.99(3)°$, $V = 6155(2)$ Å^3, $Z = 4$ (dimers), $\rho_{calcd} = 1.473$ Mgm^{-3}, $T = -100$ °C, $\mu = 1.049$ mm^{-1}, $3.4° < 2\theta < 55°$, 7264 measured reflections, 7080 independent, 332 parameters, 22 restraints, $R1$ [$F_o > 4\sigma(F_o)$] = 0.039, wR_2 [F_o^2; all data] = 0.110; $\mathbf{5}_2$: monoclinic, space group $I2/a$ (no. 15), $a = 2164.8(4)$, $b = 945.3(2)$, $c = 2864.2(6)$ pm, $\beta = 104.87(3)°$, $V = 5665(2)$ pm, $Z = 4$ (dimers), $\rho_{calcd} = 1.726$ Mgm^{-3}, $T = -100$ °C, $\mu = 6.190$ mm^{-1}, $3.9° < 2\theta < 48°$, 8675 measured reflections, 4419 independent, 289 parameters, $R1$ [$F_o > 4\sigma(F_o)$] = 0.038, wR_2 [F_o^2; all data] = 0.072. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-100326. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code + (44)1223336033; e-mail: deposit@ccdc.cam.ac.uk).

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[9] Calculations: Equilibrium structures of E_2H_4 were determined by CCD (Sn) and CCSD (Pb) calculations (Gaussian 94) with Stuttgart quasi-relativistic pseudopotentials [W. Kuechle, M. Dolg, H. Stoll, H. Preuss, *J. Chem. Phys.* **1991**, *74*, 1245] and extended basis sets for Sn and Pb: (4s4p2d)/[5s5p2d]; basis sets for H: (3s2p)/[4s2p] [T. H. Dunning, *J. Chem. Phys.* **1970**, *19*, 553]. The dimerization energies were calculated at the CCSD level and have been corrected with respect to basis set superposition errors (full Counterpoise method) and zero-point vibrations. The identification of local minima on the hypersurface was verified by frequency calculations [NIMAG = 0].

[10] The definition of a double bond by means of quantum mechanics is based on the presence of two electron pairs shared by two nuclei. It is independent of the topology or the inherent bond energy. Thus—within the framework of LCAO-MO approximation (LCAO = *L*inear *C*ombination of *A*tomic *O*rbitals)—methods such as NBO (NBO = *N*atural *B*ond *O*rbitals) or NLMO analyses (NLMO = *N*aturally *L*ocalized *M*olecular *O*rbitals) can be used [J. E. Carpenter, F. Weinhold, *J. Mol. Struct. Theochem* **1988**, *169*, 41]. A further valuable method outside this framework is the Electron Localization Function (ELF), which is a function of the kinetic energy of the electrons [B. Silvi, A. Savin, *Nature* **1994**, *371*, 683]. We will present a detailed quantum chemical analysis of the bonding in compounds such as $\mathbf{5}_2$ using these methods elsewhere.

Dynamic Error Correction in Autocatalytic Peptide Networks[**]

Kay Severin, David H. Lee, Jose A. Martinez, Michael Vieth, and M. Reza Ghadiri*

Life operates precariously in between two extremes: evolution requires new information to be generated through mistakes during the self-reproduction step, but at the same time living systems need to preserve their information against excessive accumulation of errors.[1] Here we describe autocatalytic peptide networks that stabilize themselves against errors by subjugating the mutant population for the synthesis of the wild-type peptide. The systems are based on three or four peptide fragments that undergo competitive condensation reactions in neutral aqueous solutions to produce the native sequence of a peptide replicator along with its mutant products. The peptide self-replication process is shown to respond to the spontaneous formation of errors—experimentally simulated by the background coupling reactions that yield the mutant peptides—by employing the mutant product(s) as catalyst(s) for the synthesis of the native replicator sequence. Detailed analyses have revealed that this novel mode of sequence selection arises as the result of self-organization into networks composed of two or three interconnected (auto)catalytic cycles. These networks are among the first examples of biopolymer-based nonlinear chemical systems in which catalytic and autocatalytic processes are cooperatively coupled.[2]

The present study describes an unprecedented response of a self-replicating peptide system to the spontaneous generation of mutations by self-organizing into networks of cooperative autocatalytic and catalytic cycles that upregulates the production of the native sequence. The system is based on the recently reported sequence of a peptide replicator[3] and is composed of a maximum of four peptide fragments: the native electrophilic **E** and nucleophilic **N** fragments and their single alanine mutants $\mathbf{E_{9A}}$ and $\mathbf{N_{26A}}$, respectively (Figure 1). These peptides undergo competitive ligation reactions to produce four products: the native sequence **T** along with the single mutant peptides $\mathbf{T_{9A}}$ and $\mathbf{T_{26A}}$ and the double mutant peptide $\mathbf{T_{9/26A}}$. Thus addition of the mutant fragments to the initial mixture simulates the spontaneous formation of errors during the self-replication process. Furthermore, the mutations were chosen to be conservative replacements for the native amino acid residues (alanine in place of valine 9 or leucine 26) in order to simulate the production of a mutant population with a closely related informational content,[4] previously termed quasi-species.[5]

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