

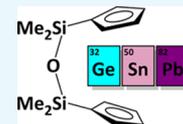
Synthesis, Structure, and Reactivity of Disiloxa[3]tetrelocenophanes

Lisa Wirtz, Matthias Jourdain, Volker Huch, Michael Zimmer, and André Schäfer*^{ib}

Faculty of Natural Sciences and Technology, Department of Chemistry, Saarland University, Campus Saarbrücken, 66123 Saarbrücken, Federal Republic of Germany

Supporting Information

ABSTRACT: Tetramethyldisiloxa[3]metalloenophanes of the heavy group 14 elements germanium, **2a**, tin, **2b**, and lead, **2c**, (tetrelocenophanes) have been synthesized by the reaction of dilithiated ligand, **1**, with the corresponding element(II) chloride. The plumbocenophane, **2c**, forms one-dimensional coordination polymers in the solid state, while the germanocenophane, **2a**, and the stannocenophane, **2b**, are monomeric. Furthermore, the reactivity of the stannocenophane, **2b**, and the plumbocenophane, **2c**, toward N-heterocyclic carbenes was explored. Although the coordination of carbene is reversible in solution at room temperature, the corresponding carbene complexes, **3a,b**, could be structurally characterized, illustrating the Lewis acidity of the central atom in these metalloenophanes.

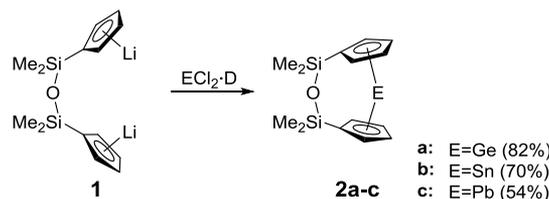


INTRODUCTION

Metallocenes with interlinked cyclopentadienyl moieties, so called *ansa*-metallocenes or metalloenophanes, have been known for over half a century, with examples for various transition metals.¹ They have attracted wide attention for their applications as catalysts in homogeneous catalysis or as monomers in ring-opening polymerization reactions.^{2,3} In contrast, metalloenophanes of p-block elements are much less common, with only a handful of structurally characterized examples, mostly of group 14 elements (tetrelocenophanes).^{4–10} This is particularly surprising, as the unbridged parent compounds have been known for a long time,^{11–13} with stannocene and plumbocene being the first diorganotetrelene type compounds described in the literature.^{14,15} Furthermore, these species could be of potential interest as precursors in the preparation of p-block metal-containing oligomers and polymers. With the great progress in low-valent group 14 chemistry in recent years,^{16–19} and our group's interest in the main group element-based metalloenophanes, our aim was to investigate the influence of different bridging motifs on the molecular geometry and reactivity of tetrelocenophanes. Whereas previous studies focused on disila[2]-metalloenophanes,^{9,10,20} we now report the first synthesis and structural characterization of three-atomic bridged metalloenophanes of p-block elements, in the form of disiloxa[3]-tetrelocenophanes of group 14 elements germanium, tin, and lead, **2a–c**. Although the tetramethyldisiloxa[3] bridging motif has been employed in transition metal-based metalloenophanes in the past,^{21–26} no p-block metalloenophanes with three-atomic bridging motifs have been reported, so far.

RESULTS AND DISCUSSION

The reaction of dilithiated ligand **1** with the corresponding element(II) chloride proceeds smoothly at 173 K to give the corresponding [3]tetrelocenophanes, **2a–c**, in good yields (Scheme 1). Stannocenophane, **2b**, and plumbocenophane, **2c**, exhibit very upfield-shifted NMR resonances in the ¹¹⁹Sn and ²⁰⁷Pb NMR spectra, respectively, ($\delta^{119}\text{Sn}(\mathbf{2b}) = -2124$;

Scheme 1. Synthesis of Tetramethyldisiloxa[3]tetrelocenophanes, **2a–c** [a: E = Ge, D = 1,4-dioxane; b: E = Sn, D = thf; c: E = Pb, D = thf]

$\delta^{207}\text{Pb}(\mathbf{2c}) = -4795$), as is typical for tin(II)- and lead(II)-based metallocenes.^{9,10}

Crystals suitable for single crystal X-ray diffraction analysis were obtained from hexane solutions at 248 K, allowing for a structural characterization of tetrelocenophanes **2a–c** (Figure 1).

While germanocenophane, **2a**, and stannocenophane, **2b**, are monomeric in the solid state, plumbocenophane, **2c**, exhibits a one dimensional polymeric structure in the crystal in which each lead atom is coordinated by three cyclopentadienyl ligands, similar to what is found for plumbocene (Cp_2Pb) in the solid state,^{27–29} and unlike what was reported earlier for a permethylated $\text{Si}[2]$ plumbocenophane.⁹ The intermolecular $\text{Pb}-\text{C}^{\text{Cp}}$ distances are longer (337.9–395.1 pm) than the intramolecular ones (243.0–256.0 pm), suggesting rather weak intermolecular interactions, which is in line with the assumption that plumbocenophane, **2c**, is monomeric in solution. The metal–Cp bonds in **2a–c** are within normal ranges for group 14 metallocenes.¹⁰ When comparing the dihedral angles of the Cp planes, α , in [3]tetrelocenophanes **2a–c** to the angles α found in the previously reported permethylated [2]tetrelocenophanes,⁹ one conspicuous differ-

Received: August 13, 2019

Accepted: September 30, 2019

Published: October 21, 2019

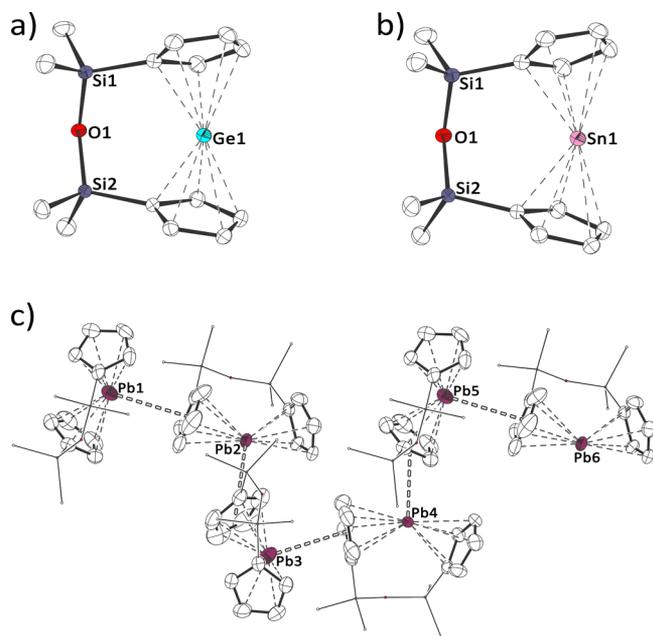


Figure 1. Molecular structures of (a) **2a**, (b) **2b**, and (c) **2c** in the crystal (thermal ellipsoids at 50% probability level, except for the *ansa*-bridge of **2c** in (c); H atoms omitted for clarity).

ence is that [3]tetrelocenophanes **2a–c** exhibit a more bent geometry, much like the unbridged parent compounds germanocene (Cp_2Ge),³⁰ stannocene (Cp_2Sn),³¹ and plumbocene (Cp_2Pb).^{27–29} This is because of the stereochemically active lone pair at the central atom. The influence of the Si–O–Si *ansa*-bridge in tetrelocenophanes **2a–c** on the dihedral angle of the Cp-planes, α , is comparably small (Table 1). This

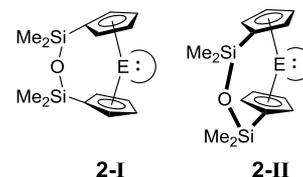
Table 1. Selected Bond Lengths and Angles in **2a–c**, **3a,b** and $\text{Cp}_2(\text{Ge/Sn/Pb})^a$

	E–Cp [pm]	α^b [deg]	β^c [deg]	γ^d [deg]
Cp_2Ge	223.4	50.2	156.9–157.4	
Cp_2Sn	237.0–243.7	45.9–46.7	146.9–147.4	
Cp_2Pb	244.1–252.7	53.6	131.0–134.6	
2a	222.1–225.3	44.9	157.1	143.9
2b	239.2–241.6	49.8	147.7	144.5
2c	243.0–256.0	36.3–54.2	137.1–151.5	143.7–149.8
3a	257.0	37.6	140.9	148.0
3b	260.5	37.0	140.5	150.8

^aRange values given because multiple molecules are found in the asymmetric unit and/or the bond is found more than once in the molecule. ^bDihedral angle of Cp planes ^c $\text{Cp}^{\text{centroid}}\text{–E–Cp}^{\text{centroid}}$ angle ^dSi–O–Si angle.

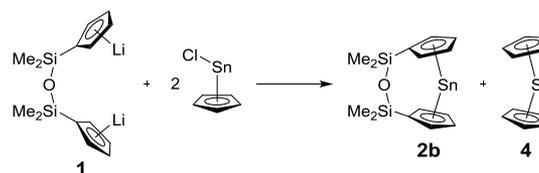
is because of the fact that the Si–O–Si moiety is very flexible and that the *ansa*-bridge is not bound to be positioned on the far side relative to the lone pair of the central atom (Chart 1, 2-I), but can be located laterally (Chart 1, 2-II). This is more pronounced in germanocenophane, **2a**, with shorter Ge–Cp bonds and a larger dihedral angle α between the Cp planes, and less pronounced in stannocenophane, **2b** (**2a**: $\phi^{32} = 56.1^\circ$; **2b**: $\phi^{32} = 51.1^\circ$), and indicates that the lone pair has a stronger effect on the dihedral angle α than the *ansa*-bridge in tetrelocenophanes **2a–c**. In all cases, however, packing effects in the crystal have to be taken into consideration as well.

Chart 1. Illustration of Different Orientations of the *ansa*-Bridge Relative to the Lone Pair at the Central Atom in Disiloxa[3]tetrelocenophanes **2**



As tetrelocenophanes **2a–c** could be of interest as monomers in the preparation of the corresponding poly-metallocenylsiloxanes, we explored the possibility to prepare an analogous disiloxanyl-bridged distannocene, which would be a two-repeat-unit model compound of such a polymer. This is in analogy to a report of Zuckerman and co-workers on the synthesis of a xylyl-bridged distannocene.⁶ However, when dilithiated ligand, **1**, was reacted with two equivalents of cyclopentadienyltin(II) chloride, the ^1H , ^{13}C , and ^{119}Sn NMR spectra showed exclusive formation of stannocenophane, **2b**, and stannocene, **4** [$\delta^{119}\text{Sn} = -2124$ (**2b**), -2199 (**4**)] (Scheme 2). It remains unclear, whether a bridged

Scheme 2. Reaction of Dilithiated Ligand, **1**, with Cyclopentadienyltin(II) Chloride, To Give Stannocenophane, **2b**, and Stannocene, **4**



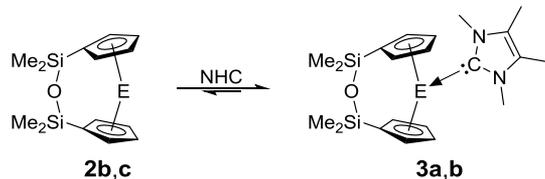
distannocene is initially formed and undergoes a subsequent redistribution reaction to give **2b** and **4**, or if cyclopentadienyllithium is eliminated from a monosubstituted intermediate, giving **2b** and reacting with cyclopentadienyltin(II) chloride to give **4**. In either case, entropic effect might be the driving force for the formation of **2b** and **4** as the sole products of the reaction.

In light of these results, it remains unclear if Zuckerman and co-workers had actually obtained a xylyl-bridged distannocene, as no ^{119}Sn NMR chemical shifts or structural characterization were reported.⁶

Polymetallocenes are most commonly prepared by ring-opening polymerizations starting from the corresponding metallocenophanes, by cleavage of either the metal–Cp bond or the *ansa*-bridge–Cp bond.² Because previous studies of stannocene carbene complexes revealed that the coordination of a strong σ donor can weaken the metal–Cp bond,³³ this was further explored as a potential mechanism for metal–Cp bond activation in tetrelocenophanes, by reacting stannocenophane, **2b**, with 1,3,4,5-tetramethyl-imidazole-2-ylidene. Upon mixing stannocenophane **2b** and NHC in benzene at room temperature and examining the mixture by multinuclear NMR spectroscopy, a downfield shift of the ^{119}Sn resonance was observed ($\delta^{119}\text{Sn} = -1761$; $\Delta\delta^{119}\text{Sn} = 363$ vs **2b**), along with a resonance of $\delta^{13}\text{C} = 200.3$ for the carbene carbon atom. These findings clearly indicate a coordination of NHC to the tin atom in stannocenophane **2b**. Likewise, when plumbocenophane **2c** was reacted with 1,3,4,5-tetramethyl-imidazole-2-ylidene in

toluene at room temperature, a similar coordination was observed (Scheme 3).³⁴

Scheme 3. Reaction of Disiloxa[3]tetrelocenophanes, 2b,c, with NHC To Give NHC Complexes 3a,b (2b/3a: E = Sn; 2c/3b: E = Pb; NHC = 1,3,4,5-Tetramethyl-imidazole-2-ylidene)



Crystals of complexes 3a,b suitable for single crystal X-ray diffraction analysis, could be obtained from thf (3a) and toluene (3b) solutions at 248 K, allowing for structural characterization (Figure 2). Noteworthy, plumbocenophane

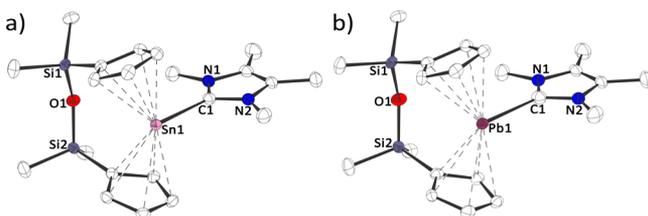


Figure 2. Molecular structure of (a) stannocenophane NHC complex 3a and (b) plumbocenophane NHC complex 3b in the crystal (thermal ellipsoids at 50% probability level, H atoms omitted for clarity).

NHC complex 3b represents the first example of a carbene adduct of a bis(cyclopentadienyl)lead compound. The Sn–C^{NHC} bond in complex 3a is 245.7 pm, the Pb–C^{NHC} bond in complex 3b is 258.2 pm. This is comparably long (e.g.,: $\{(Me_3Si)_3Si\}_2Sn-NHC$: 228.7 pm;³⁵ $\{(Me_2Si)_2((Me_3Si)_2Si)_2\}Sn-NHC$: 229.5 pm;³⁵ $Ter(H)Pb-NHC$: 233.2 pm³⁶), but similar to what has been observed previously for stannocene carbene complexes.³³ The E–Cp bonds in complexes 3a,b are significantly elongated compared to stannocenophane 2b and plumbocenophane 2c, respectively (Table 1), which indicates a weakening of the metal Cp bonds upon coordination of NHC. This is in line with the previous observations in stannocene carbene complexes³³ and can be rationalized by the donation of the carbene into the antibonding lowest unoccupied molecular orbital (LUMO) of the metallocene (Figure 3).

The LUMO of stannocenophane 2b and plumbocenophane 2c, as is typical for tetrelcenophanes in general, corresponds to an antibonding interaction of a p-orbital at the central atom with the cyclopentadienyl ligand orbitals.^{12,13,33} Therefore, the NHC coordinates to the metal atom in 3a,b. In a “side-on” fashion and donation of electron density into the LUMO weakens the E–Cp bond. This is further illustrated by the fact that complex 3a is extremely reactive and decomposes in solution at room temperature within hours. The fact that only a weakening and no cleavage of the E–Cp bonds is observed, might be due to the fact that the carbene coordination is relatively weak. This is in line with calculated complexation energies of $\Delta E = -65.9 \text{ kJ mol}^{-1}$ ($\Delta G^{298} = -5.3 \text{ kJ mol}^{-1}$) for 3a and $\Delta E = -72.2 \text{ kJ mol}^{-1}$ ($\Delta G^{298} = -17.9 \text{ kJ mol}^{-1}$) for 3b

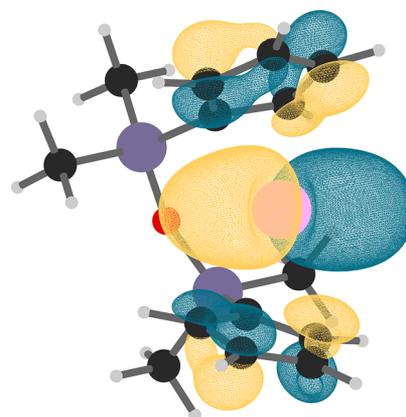


Figure 3. Isosurface plot of the LUMO (Kohn–Sham orbital) of stannocenophane 2b (B3LYP-D3/def2-TZVP, isovalue = 0.035).

(complexation energies refer to the reactions 3a,b \rightarrow 2b,c + NHC and are calculated at B3LYP-D3/def2-TZVP³⁷). Therefore, 3a,b might exist in a dissociative equilibrium in solution and an averaged set of signals is observed in the NMR spectra at room temperature.

To probe this further, solid state ¹³C and ¹¹⁹Sn CP/MAS NMR measurements of complex 3a were conducted (Figure 4). Stannocenophane NHC complex 3a exhibits a ¹¹⁹Sn NMR

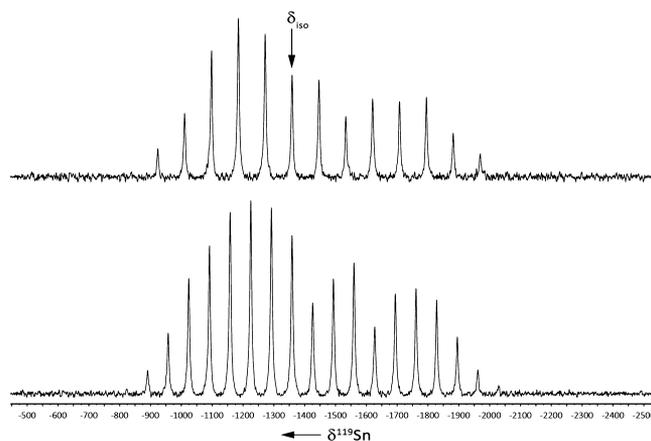


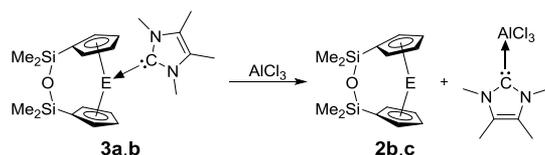
Figure 4. ¹¹⁹Sn{¹H} CP/MAS NMR spectra of stannocenophane NHC complex 3a. Upper trace: 13 kHz MAS, lower trace: 10 kHz MAS [$\delta_{iso} = -1360$; $\delta_{11} = -907(\pm 7)$; $\delta_{22} = -1210(\pm 6)$; $\delta_{33} = -1962(\pm 1)$; $\Omega(\delta_{11}-\delta_{33}) = 1055$].

chemical shift in the solid state of $\delta^{119}Sn = -1360$, which is downfield shifted by $\Delta\delta^{119}Sn = 401$ compared to what is observed in solution at room temperature. The carbene-carbon atom exhibits a ¹³C NMR chemical shift of $\delta^{13}C = 196.5$ in the solid state, with a C–Sn coupling constant of $^1J_{C,Sn} = 587 \text{ Hz}$. This clearly indicates that an averaged set of signals is observed in solution at room temperature and that stannocenophane NHC complex 3a in fact exists in a dissociative equilibrium with stannocenophane 2b + NHC.

To further verify this, the stoichiometry of the reaction was varied. When two equivalents of stannocenophane, 2b, are mixed with one equivalent of NHC, only one set of signals is observed in the ¹H and ¹³C NMR spectra, along with one signal in the ¹¹⁹Sn NMR spectra at $\delta^{119}Sn = -1976$. This is upfield shifted by $\Delta\delta^{119}Sn = 215$, compared to what was observed for solutions derived from 3a ($\delta^{119}Sn = -1761$),

indicating a fast equilibrium between carbene complex, **3a**, and uncoordinated **2b** + NHC.³⁸ In addition, when a solution of **3a** or **3b** is treated with aluminum chloride, almost instantaneous formation of NHC·AlCl₃ and metallocenophanes **2b,c** is observed by multinuclear NMR spectroscopy (Scheme 4).³⁹

Scheme 4. Reaction of NHC Complexes 3a,b with AlCl₃ (2b/3a: E = Sn; 2c/3b: E = Pb; NHC = 1,3,4,5-Tetramethylimidazole-2-ylidene)



This further supports the assumption that the NHC coordination is reversible and that **3a,b** exist in a dissociative equilibrium with **2b,c** + NHC.

CONCLUSIONS

In summary, the synthesis and structural characterization of tetramethyldisiloxa[3]germanocenophane, **2a**, tetramethyldisiloxa[3]stannocenophane, **2b**, and tetramethyldisiloxa[3]plumbocenophane, **2c** is reported. In case of stannocenophane, **2b**, it was shown that it can also be obtained by treatment of dilithiated ligand **1**, with two equivalents of cyclopentadienyltin(II) chloride, which might reveal Zuckerman's report of a distannocene in a different light. Furthermore, stannocenophane **2b**, and plumbocenophane **2c** react with 1,3,4,5-tetramethylimidazole-2-ylidene (NHC) to give the corresponding carbene complexes **3a,b**. These complexes are believed to exist in a dissociative equilibrium in solution at room temperature, as indicated by comparison of solution and solid state CP/MAS ¹¹⁹Sn NMR spectroscopy in case of **3a**, as well as abstraction of NHC by treatment of **3a,b** with aluminum chloride and calculated complexation energies (ΔE) of just -65.9 kJ mol⁻¹ (**3a**) and -72.2 kJ mol⁻¹ (**3b**).

EXPERIMENTAL SECTION

All manipulations were carried out under an inert gas atmosphere (argon 5.0), using either Schlenk line techniques of a glovebox. Dilithiated ligand **1**,^{21–24,26} 1,3,4,5-tetramethylimidazole-2-ylidene,⁴⁰ and cyclopentadienyltin(II) chloride^{41–43} were synthesized according to literature-known procedures. NMR-spectra were recorded on Bruker AVANCE III 300 (solution NMR), Bruker AVANCE III 400 (solution NMR), and Bruker Ascend 400WB (solid state NMR) spectrometers. ¹H and ¹³C NMR spectra were referenced using the solvent signals [$\delta^1\text{H}$ (C₆H₆) = 7.16; $\delta^{13}\text{C}$ (C₆D₆) = 128.06]. ²⁹Si, ¹¹⁹Sn, and ²⁰⁷Pb NMR spectra were referenced using external standards [$\delta^{29}\text{Si}$ (SiMe₄) = 0; $\delta^{119}\text{Sn}$ (SnMe₄) = 0; $\delta^{207}\text{Pb}$ (PbMe₄) = 0]. Elemental analysis was performed on an Elementar vario MICRO cube (in some cases low carbon values were repeatedly reproducibly observed, presumably because of the formation of silicon carbide). Single crystal X-ray diffraction analysis was carried out at low temperatures on Bruker AXS X8 Apex CCD and Bruker AXS D8 Venture diffractometers operating with graphite monochromated Mo K α radiation. Structure solution and refinement were performed using SHELX.⁴⁴ Crystal structures have been deposited with the Cambridge Crystallographic Data Centre

(CCDC) and are available free of charge from the Cambridge Structural Database (reference numbers: 1903471, 1903472, 1903473, 1903474, 1941170).

Synthesis of 2a–c. Dilithiated ligand **1** (500 mg, 1.82 mmol) and the respective element dichloride (GeCl₂, 1,4-dioxane: 421 mg, 1.82 mmol; SnCl₂: 346 mg, 1.82 mmol; PbCl₂: 507 mg, 1.82 mmol) were added to a Schlenk flask and cooled to 173 K. Precooled thf was added and the solution was stirred at 173 K for 90 min. Subsequently, the mixture was allowed to warm to room temperature and stirred for an additional 150 min. All volatiles were removed in vacuo and the residue was suspended in hexane. After filtration, the solution was concentrated and stored at 248 K to obtain **2a–c** as crystalline solids.

Yields: **2a**: 500 mg/82%; **2b**: 490 mg/70%; **2c**: 460 mg/54%.

2a: ¹H NMR (400.13 MHz, 296 K, C₆D₆): δ 0.35 (s, 12H, Si–CH₃), 6.02 (t, ³J_{HH} = 2 Hz, 4H, Cp), 6.28 (t, ³J_{HH} = 2 Hz, 4H, Cp); ¹³C{¹H} NMR (100.62 MHz, 296 K, C₆D₆): δ 1.6 (Si–CH₃), 113.7 (Cp), 118.3 (Cp), 121.7 (Cp); ²⁹Si{¹H} INEPT NMR (79.49 MHz, 296 K, C₆D₆): δ –4.5. Elemental analysis for C₁₄H₂₀GeOSi₂: Calcd: 50.48%, C; 6.05%, H. Found: 49.41%, C; 6.11%, H.

2b: ¹H NMR (400.13 MHz, 297 K, C₆D₆): δ 0.37 (s, 12H, Si–CH₃), 6.06 (t, ³J_{HH} = 2 Hz, ²J_{Hsn} = 20 Hz, 4H, Cp), 6.25 (t, ³J_{HH} = 2 Hz, 4H, Cp); ¹³C{¹H} NMR (100.62 MHz, 297 K, C₆D₆): δ 1.8 (Si–CH₃), 115.2 (Cp), 116.9 (Cp), 118.2 (Cp, ¹J_{Csn} = 49.5 Hz, 51.7 Hz); ²⁹Si{¹H} INEPT NMR (79.49 MHz, 297 K, C₆D₆): δ –5.6; ¹¹⁹Sn{¹H} NMR (148.89 MHz, 297 K, C₆D₆): δ –2124. Elemental analysis for C₁₄H₂₀OSi₂Sn: Calcd: 44.35%, C; 5.32%, H. Found: 43.75%, C; 5.34%, H.

2c: ¹H NMR (300.13 MHz, 299 K, C₆D₆): δ 0.41 (s, 12H, Si–CH₃), 6.04 (m, 4H, Cp), 6.24 (m, 4H, Cp); ¹³C{¹H} NMR (75.48 MHz, 299 K, C₆D₆): δ 1.9 (Si–CH₃), 116.8 (Cp), 117.7 (Cp), 118.9 (Cp); ²⁹Si{¹H} NMR (59.63 MHz, 299 K, C₆D₆): δ –7.1; ²⁰⁷Pb{¹H} NMR (62.51 MHz, 299 K, C₆D₆): δ –4795. Elemental analysis for C₁₄H₂₀OPbSi₂: Calcd: 35.95%, C; 4.31%, H. Found: 36.4%, C; 4.93%, H.

Synthesis of 3a. Stannocenophane **2b** (50.0 mg, 132 μ mol) and 1,3,4,5-tetramethylimidazole-2-ylidene (16.0 mg, 129 μ mol) were mixed, 2 mL of thf, precooled to 193 K, were added, and the resulting mixture was stirred for 10 min at 193 K. Storage of the solution at 248 K yielded yellow crystals of stannocenophane carbene complex **3a**.

Yield: 10 mg/17%. ¹H NMR (400.13 MHz, 296 K, C₆D₆): δ 0.54 (s, 12H, Si–CH₃), 1.34 (s, 6H, C–CH₃), 3.13 (s, 6H, N–CH₃), 6.30–6.36 (m, 8H, Cp); ¹³C{¹H} NMR (100.62 MHz, 296 K, C₆D₆): δ 2.3 (Si–CH₃), 8.1 (C–CH₃), 33.6 (N–CH₃), 115.9 (Cp), 116.7 (Cp), 123.3 (C–CH₃), 200.3 [carbene-C (detected by ¹H–¹³C-HMBC)]; ¹³C{¹H} CP/MAS (13 kHz) NMR (100.67 MHz, 295 K): δ 2.6 (Si–CH₃), 3.3 (Si–CH₃), 7.6 (C–CH₃), 10.2 (C–CH₃), 34.2 (C–CH₃), 111.3, 112.9, 117.8, 120.1, 123.2, 125.3, 196.5 (carbene-C, ¹J_{Csn} = 587 Hz); ²⁹Si{¹H} NMR (79.49 MHz, 296 K, C₆D₆): δ –5.7; ¹¹⁹Sn{¹H} NMR (111.68 MHz, 299 K, C₆D₆): δ –1761; ¹¹⁹Sn{¹H} CP/MAS (13 kHz) NMR (149.05 MHz, 295 K): δ_{iso} –1360. Elemental analysis for C₂₁H₃₂N₂OSi₂Sn: Calcd: C, 50.11%; H, 6.41%; N, 5.57%. Found: C, 50.11%; H, 6.40%; N, 5.72%.

Synthesis of 3b. A solution of Plumbocenophane **2c** (80.0 mg, 171 μ mol) in 3 mL of toluene was added to a solution of 1,3,4,5-tetramethylimidazole-2-ylidene (21.0 mg, 169 μ mol) in 3 mL of toluene and the mixture was stirred for 5 min.

Storage of the solution at 248 K yielded large yellow crystals of plumbocenophane carbene complex **3b**.

Yield: 38 mg/38%. ^1H NMR (400.13 MHz, 293 K, C_6D_6): δ 0.64 (s, 12H, Si- CH_3), 1.32 (s, 6H, C- CH_3), 3.04 (s, 6H, N- CH_3), 6.34 (m, 4H, Cp), 6.39 (m, 4H, Cp); $^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, 293 K, C_6D_6): δ 2.4 (Si- CH_3), 8.2 (C- CH_3), 34.3 (N- CH_3), 114.4 (Cp), 117.0 (Cp), 119.2 (Cp), 123.7 (C- CH_3); $^{29}\text{Si}\{^1\text{H}\}$ INEPT NMR (79.49 MHz, 293 K, C_6D_6): δ -7.0; ^{207}Pb NMR (62.51 MHz, 295 K, C_6D_6): no signal could be detected in the ^{207}Pb NMR spectrum in a range of -2000 to -6800 ppm.

Elemental analysis for $\text{C}_{21}\text{H}_{32}\text{N}_2\text{OPbSi}_2$: Calcd: C, 42.62%; H, 5.45%; N, 4.73%. Found: C, 43.06%; H, 5.59%; N, 4.40%.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02605.

NMR spectra, computational details, and references (PDF)

Optimized geometries (XYZ)

Crystallographic details of **2a** (CIF)

Crystallographic details of **2b** (CIF)

Crystallographic details of **2c** (CIF)

Crystallographic details of **3a** (CIF)

Crystallographic details of **3b** (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: andre.schaefer@uni-saarland.de.

ORCID

André Schäfer: 0000-0002-5969-6618

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Prof. Dr. Guido Kickelbick is thanked for his support. Susanne Harling is thanked for performing elemental analysis. Funding of this research by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation, SCHA 1915/3-1) and Fonds der Chemischen Industrie (FCI) is gratefully acknowledged. We acknowledge support by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) and Saarland University within the funding program Open Access Publishing.

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