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Addition of Lappert's Stannylenes to Carbodiimides, Providing a New Class of Tin(II) Guanidinates

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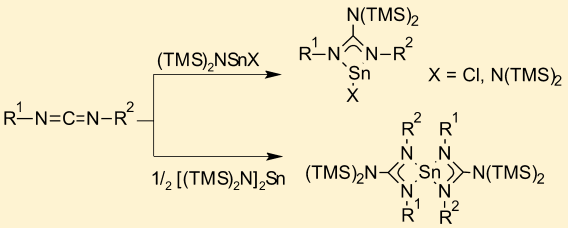
Supporting Information

ABSTRACT: Reactions of bis[bis(trimethylsilyl)amino]tin and the dimer of [bis(trimethylsilyl)amino]tin chloride with various carbodiimides give pure corresponding tin(II) guanidinates in essentially quantitative yields. Heteroleptic bis(trimethylsilyl)amido ({R-NC[N-(SiMe$_3$)$_2$]N-R}SnN(SiMe$_3$)$_2$)- and chloro-substituted ({R-NC[N-(SiMe$_3$)$_2$]N-R}SnCl) tin(II) guanidinates were obtained from reactions of *N*,*N*′-diisopropyl-, *N*,*N*′-dicyclohexyl-, *N*,*N*′-bis(4-methylphenyl)-, and *N*-[3-(dimethylamino)propyl]-*N*′-ethylcarbodiimides, respectively. Homoleptic tin(II) guanidinates {R-NC[N(SiMe$_3$)$_2$]N-R}$_2$Sn were obtained from the *N*,*N*′-bis(4-methylphenyl)- and *N*-[3-(dimethylamino)propyl]-*N*′-ethyl-substituted carbodiimides. Similar reactions of *N*,*N*′-bis(2,6-diisopropylphenyl)- and *N*,*N*′-bis(trimethylsilyl)carbodiimide, respectively, having the bulkiest substituents of the series, failed to take place under various conditions. The complexes prepared were characterized as monomers in solution by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy in C$_6$D$_6$ and THF-*d*$_8$. The solid-state NMR spectra were recorded for structure comparison. X-ray diffraction studies of one homoleptic monomer, two heteroleptic chloro complexes with the structures of two different types of dimers, and the oxidation product of the heteroleptic bis(trimethylsilyl)amido-substituted guanidinate—a centrosymmetric (guanidinato)tin(IV) oxide—were performed on appropriate crystals. Attempts to prepare homoleptic types of isopropyl- and cyclohexyl-substituted tin(II) guanidinate complexes were unsuccessful. The structures were also evaluated by DFT methods.



1. INTRODUCTION

The discovery of steric and electronic stabilization of low-valent species of group 14 metals by bis(trimethylsilyl)amido ligands, in particular the preparation of Lappert's stannylenes,[1] led to major developments in this class of chemistry.[2] Many reactions of these compounds, including mainly oxidation,[3] oxidative addition reactions,[4] reduction to metal clusters,[5] C−H bond or small molecule activation,[6] complexation,[7] reactions with heterocumulenes,[8] and others, have been studied mainly in order to explore analogous reactions of higher congeners of carbenes.[9] The renaissance of this class of chemistry started with the preparation of very bulky,[10] chelating,[11] or spectator ligands, as for example *β*-diketiminato,[12] amidinato,[13] and guanidinato[14] complexes, which stabilize the metal center by their rich *π*-electron systems, thus forming metallaheterocycles.[15]

The reactivity of tin(II) amides with heterocumulenes (CO$_2$, RN═C═O)[8] provided mainly products where the tin atom is bonded to three oxygen atoms, as for example [Me$_3$SiOSn(*μ*-OSiMe$_3$)$_2$]$_2$, Me$_3$SiN═C═O, and carbodiimides. On the other hand s-block,[16] f-block[17] and electron deficient d-block[18] metal amides react with carbodiimides to give the corresponding guanidinates, which are often quite impure or are present in mixtures with amides and other species. There are two patents and a single paper on the reactivity of p-block metals with carbodiimides producing guanidinate, in particular of antimony[19] and germanium.[20] Two additional papers describe the reactivity of (*β*-diketiminato)tin(II) hydride[21] and dimeric di-*tert*-butyltin(IV) imide[22] with carbodiimide producing (*β*-diketiminato)tin(II) formamidinate or cyclic di-*tert*-butyltin(IV) imide-guanidinate, respectively.

The tin(II or IV) guanidinates,[23] which could have interesting properties similar to those found for related amidinates to be single-source precursors for thin films of tin metal or tin(II and IV) compounds,[19] are surprisingly a small group of compounds. Tin(IV) guanidinates were described by Lappert[24] in 1965. Four decades later, the first tin(II) guanidinates, both the homoleptic and heteroleptic chlorides, were prepared by salt elimination from lithium guanidinate and tin dichloride. Jones et al. used their (guanidinato)tin(II) chlorides for coordination of phosphaheterocycles[25] or Ga(I)[26] anionic complexes.

In this paper we describe the family of tin(II) guanidinates with various sterically protecting moieties at the tin center,

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prepared with high atom economy by the facile reaction of Lappert stannylenes with different carbodiimides.

2. RESULTS AND DISCUSSION

2.1. Synthesis. The tin(II) guanidinates prepared are presented in Figure 1. Heteroleptic bis(trimethylsilyl)amido

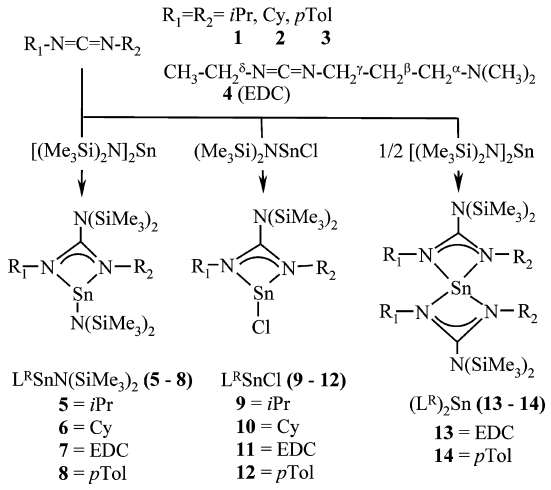


Figure 1. Numbering and preparation of target compounds **5**–**14**. Reagents and conditions: Et_2O, room temperature.

tin(II) guanidinates **5**–**8** were prepared by the reaction of the Lappert's stannylene $[(Me_3Si)_2N]_2Sn$ with *N*,*N*′-diisopropyl-, *N*,*N*′-dicyclohexyl-, *N*,*N*′-bis(4-methylphenyl)-, and *N*-[3-(dimethylamino)propyl]-*N*′-ethylcarbodiimides, respectively, in essentially quantitative yield, at room temperature in Et_2O and with a 1:1 stoichiometric ratio of the reagents.

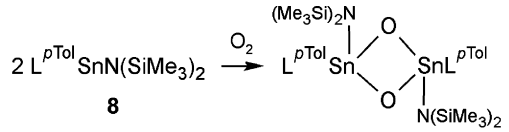
Chlorides **9**–**12**, bearing the same guanidinate units, were prepared in a similar way from $(Me_3Si)_2NSnCl$ dimer with the related carbodiimide under the same reaction conditions. Reactions of *N*,*N*′-bis(2,6-diisopropylphenyl)- and *N*,*N*′-bis(trimethylsilyl)carbodiimide, respectively, with both stannylenes in the stoichiometric ratio 1:1 failed to provide the desired guanidinates, most probably due to the higher steric demand of the carbodiimide substituents. For the reaction of *N*,*N*′-bis(2,6-diisopropylphenyl)carbodiimide with both stannylenes, various reaction conditions—changing the solvents, raising the reaction temperature up to 90 °C, increasing the reaction time up to a few days, and adding various species in catalytic amounts such as acetic acid and hexamethyldisilazane in order to catalyze the reaction under basic or acidic conditions—give virtually no yield of the desired tin(II) guanidinates. Several attempts to react the (guanidinato)tin(II) amide **5** or **8** with *N*,*N*′-bis(4-methylphenyl)- or *N*,*N*′-bis(propan-2-yl)carbodiimide in order to prepare an unsymmetrical heteroleptic compound bearing two different guanidinate ligands also failed, only starting compounds being observed in the NMR spectra.

The homoleptic guanidinate compounds containing *N*,*N*′-bis(4-methylphenyl) and *N*-[3-(dimethylamino)propyl]-*N*′-ethyl substituents were prepared as the only compounds of this type in quantitative yield at room temperature. The attempts to prepare the remaining members of this series containing *N*,*N*′-diisopropyl and *N*,*N*′-dicyclohexyl substituents were not successful, even when **5** or **6** was heated with the respective carbodiimide in various solvents such as THF, Et_2O, and toluene.

Generally, the successful reactions leading to hetero- and homoleptic tin(II) guanidinates **5**–**14** reveal high atom economy, essentially quantitative yields, high selectivity, and fast reaction times (less than 1 h) at room temperature.

Except for the oxidation of the ligand in $[Pb(Cy^G)Cl]_2$ (Cy^G = *N*,*N*″-bis(2,6-diisopropylphenyl)-*N*′,*N*′-dicyclohexylguanidinate), thus forming an alcoholate,[14a] no oxidation product of group 14 guanidinates is known. The compound $\{(L^{pTol})[(Me_3Si)_2N]SnO\}_2$ (**8a**) was obtained as the oxidation product of **8** (Scheme 1) by slow diffusion of air into the Schlenk tube

Scheme 1



through its insufficiently greased stopcock. The process is fully reproducible and is described in the Experimental Section. The oxidation of various tin(II) guanidinates is presently under further investigation in our laboratory.

2.2. NMR Studies in Solution. Solution-state NMR studies were performed with all the investigated series of compounds, not only for solution structure determinations but also in order to monitor the reactions and further reactivity of the target compounds. All compounds studied reveal resolved ^1H NMR spectral patterns assignable to structures with mutually symmetric (C_2) ligands, except for the cyclohexyl-substituted compounds, which are usually complex. Complex signals with usually anisochronous or broad patterns for aliphatic protons were observed in the spectra of EDC-substituted guanidinates **7**, **11**, and **13** (see the Experimental Section). This phenomenon is very likely caused by the presence of a stereogenic center at the central ipso carbon atom which induces a diastereotopic character of methylene groups. Two different signals were found for geometrically nonequivalent trimethylsilyl groups of the amido function in the ^1H NMR spectra of heteroleptic amides **5**–**8**. On the other hand, all compounds reveal only one signal for the trimethylsilyl group substituting the guanidinato ligands, which could be explained by a free rotation of the amido group. The ^1H NMR chemical shifts of the NCH_2 group found for compounds where the EDC ligand fragment is used (**7**, **11**, and **13**) are shifted downfield, in comparison to the chemical shifts found for starting carbodiimide **4**, but it could not be established whether there is a coordination of the nitrogen atom of this group to the tin atom.

The ^{13}C NMR spectra are more informative, especially in cases of the signal of the middle quaternary carbon atom (see Table 1). Its ^{13}C chemical shift value (160–164 ppm) suggests that the tin atom is coordinated by the guanidinato and terminal bis(trimethylsilyl)amido ligands in the cases of amides **5**–**8**, two guanidinato ligands for **13** and **14**, and guanidinato and chloride for **11**. The same parameter for chlorides **9**–**12** was found around 168 ppm in benzene solution, which is shifted about 4 ppm downfield in comparison to the amides **5**–**8** and homoleptic stannylenes **13** and **14**. On the other hand, the chemical shift of the ipso carbon atom in the ^{13}C NMR spectrum of **11** in THF solution reveals a 5 ppm upfield shift in comparison to the spectrum measured in benzene, which is probably caused by a structural change by an interaction with

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Table 1. Selected NMR Spectral Parameters

compd	solvent	param (ppm) $\delta(^{13}C_{ipso})$	$\delta(^{119}Sn)$
$L^{iPr}SnN(SiMe_3)_2$ (**5**)	C_6D_6	160.4	−115.7
	THF-d_8	161.9	−119.5
$L^{Cy}SnN(SiMe_3)_2$ (**6**)	C_6D_6	160.8	−126.9
	THF-d_8	161.5	−127.5
$L^{EDC}SnN(SiMe_3)_2$ (**7**)	C_6D_6	163.8	−144.6
$L^{pTol}SnN(SiMe_3)_2$ (**8**)	C_6D_6	163.6	−87.2
	THF-d_8	164.0	−93.0
$\{(L^{pTol})[(Me_3Si)_2N]SnO\}_2$ (**8a**)	THF-d_8	*a*	−612.8
$L^{iPr}SnCl$ (**9**)	C_6D_6	167.9	−30.4
	THF-d_8	168.0	−51.1
$L^{Cy}SnCl$ (**10**)	C_6D_6	167.8	−34.9
	THF-d_8	168.0	−51.0
$L^{EDC}SnCl$ (**11**)	C_6D_6	166.9	−250.6
$L^{pTol}SnCl$ (**12**)	C_6D_6	168.3	−108.2
	THF-d_8	163.5	−220.0
$(L^{EDC})_2Sn$ (**13**)	C_6D_6	163.2	−377.3
$(L^{pTol})_2Sn$ (**14**)	C_6D_6	163.2	−432.0
	THF-d_8	163.5	−427.8

[a]Not observed.

THF molecule(s). Almost the same ^{13}C chemical shifts as in benzene solution were found for the model series of single-crystal compounds containing the *p*Tol groups **8**, **12**, and **14** (see the Supporting Information, Figures S1−S3; see below for structures determined by X-ray diffraction) in the ^{13}C CP/MAS NMR solid-state spectra. Unfortunately, no literature ^{13}C NMR data are available for the same type of guanidinates.

As can be seen in Table 1, the ^{13}C and ^{119}Sn NMR chemical shifts are nearly solvent independent, which is evidence of the same structure in noncoordinating as well as in coordinating solvents as THF. On the other hand, the tin atom in **12** appears to coordinate the THF molecule(s), resulting in chemical shift reduction by ca. 110 ppm and also the in the change of the ^{13}C NMR shift of the ipso carbon (see above).

Comparison of ^{119}Sn NMR shift values for **9**, **10**, and **12** in benzene with literature values for monomeric heteroleptic guanidinato tin chlorides substituted by bulky aromatic groups (−55 ppm[25]) indicate monomeric structures of all three compounds. The large ^{119}Sn chemical shift decrease for chloride **11** indicates strong coordination by the pendant amino group.

Differences in ^{119}Sn NMR chemical shift values for all three types of tin guanidinates are observed. The amidotin guanidinates **5**−**8** reveal virtually three subtypes: (i) amidotin guanidinates with aliphatic substituents **5** and **6**, which display ^{119}Sn chemical shifts around −120 ppm, (ii) compound **7** with possible adjacent coordination from the amino donor group, with the value at −144.6 ppm, and (iii) the aromatic group substituted amidotin guanidinate **8** with ^{119}Sn NMR chemical shift values around −90 ppm.

The ^{119}Sn chemical shift values around −400 ppm for the homoleptic compounds **13** and **14** indicate four-coordination of the tin atoms in coordinating as well as noncoordinating solvents, resulting in the configuration of the central atom to be pseudo square pyramidal. The difference in chemical shift values of **13** and **14** is assigned to the presence of different types of ligand substituents. There is no literature comparison, because no ^{119}Sn NMR data were mentioned for the only existing homoleptic bis(guanidinato)tin(II) complex described so far.[24b] Both homo- and heteroleptic (amidinato)tin complexes display ^{119}Sn chemical shifts[13h] lower by ca. 80−200 ppm than for the guanidinates investigated.

The ^{119}Sn NMR spectrum of the oxidation product of **8**, **8a**, reveals a 500 ppm shift to lower frequency in comparison to **8**, indicating the presence of five-coordinate tin(IV). Unfortunately, the ^{13}C chemical shift in solution for the ipso carbon as well as ^{119}Sn NMR shifts in the solid state could not be located, probably because of very broad resonances collapsing into the baseline noise. The reasons for that remain unclear but might be due to large chemical shift anisotropy.

2.3. Crystal Structure Determination by X-ray Diffraction. To the best of our knowledge the only two crystal structures determined for heteroleptic (guanidinato)tin-

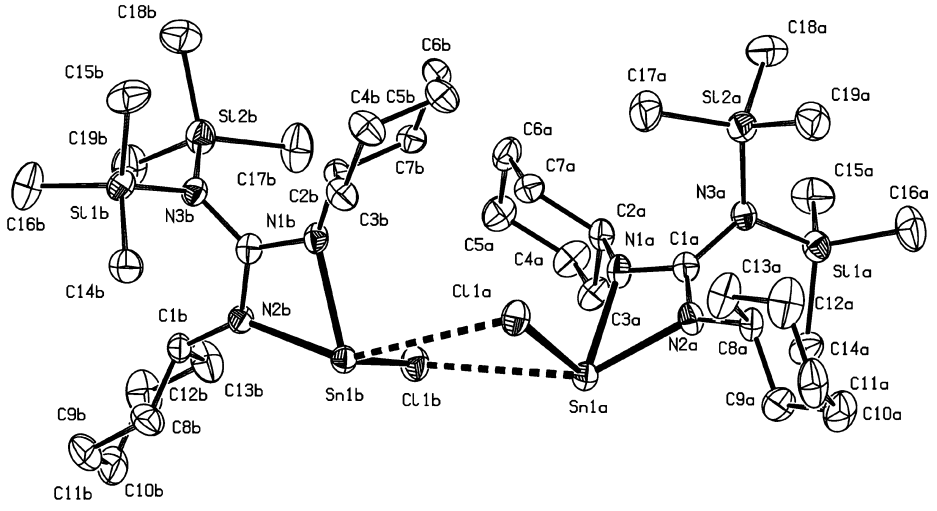

Figure 2. Molecular structure of $L^{Cy}SnCl$ (**10**) (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg), with computed values given in italics: N1−C1 = 1.344(4), *1.344*; N1−C2 = 1.455(5), *1.446*; N2−C1 = 1.319(5), *1.335*; N2−C8 = 1.451(5), *1.447*; N3−C1 = 1.411(5), *1.404*; N1−Sn1a = 2.198(3), *2.232*; N2−Sn1a = 2.211(3), *2.232*; Sn1a−Cl1a = 2.4698(11), *2.468*; Sn1a−Cl1b = 3.3495(9); C2−C1−C8 = 167.29(19), *167.5*; N1−C1−N2 = 111.5(3), *111.9*; C1−Sn1a−Cl1a = 97.76(8), *92.5*; N1−Sn1a−N2 = 59.90(11), *59.3*; Sn1a−Cl1a−Sn1b = 94.92(3).

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(II) chlorides revealed monomeric structural units.[25] The crystal structures of the guanidinatotin chlorides **10** and **12** were determined by X-ray diffraction (Figures 2 and 3). Both

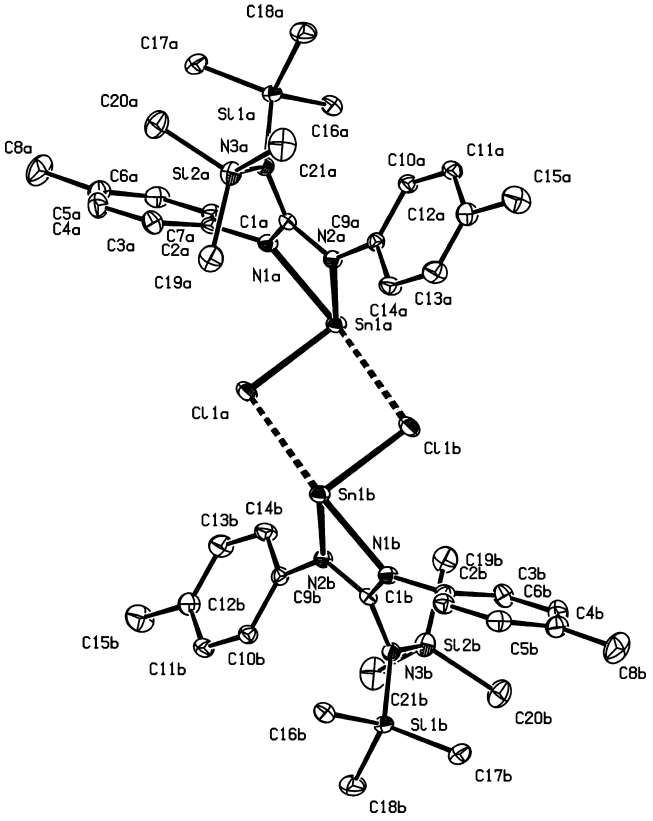

Figure 3. Molecular structure of $L^{pTol}SnCl$ (**12**) (ORTEP view, 50% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg), with computed values given in italics: N1−C1 = 1.331(2), *1.343*; N1−C2 = 1.408(3), *1.410*; N2−C1 = 1.343(2), *1.346*; N2−C9 = 1.414(2), *1.406*; N3−C1 = 1.395(2), *1.380*; N1−Sn1a = 2.2277(16), *2.247*; N2−Sn1a = 2.2019(16), *2.253*; Sn1a−Cl1a = 2.4732(6), *2.454*; Sn1a−Cl1b = 3.1099(7); C2−C1−C9 = 164.99(10), *165.2*; N1−C1−N2 = 111.12(15), *111.4*; C1−Sn1a−Cl1a = 92.02(4), *89.9*; N1−Sn1a−N2 = 59.72(6), *59.1*; Sn1a−Cl1a−Sn1b = 100.75(2).

compounds reveal centrosymmetric dimers with a central Sn_2Cl_2 ring generated by interactions of the tin atoms with chlorine atoms of the second monomeric unit (Sn1a−Cl1b = 3.3495(9) Å for **10** and Sn1a−Cl1b = 3.1099(7) Å for **12**). In both cases these contacts are rather weak in comparison to that in the dimeric amidotin(II) chloride $\{Sn[N(C_6H_3iPr_2\text{-}2,6)(SiMe_3)](\mu\text{-}Cl)\}_2$ (2.765(3) Å[5a]). On the other hand, other amidotin(II) (3.149(2) Å[27] or 3.425(3) Å[28]), (β-diketiminato)tin (3.900(3) Å[29]), or (amidinato)tin(II) chlorides[30] reveal similar or even longer distances. The distances Sn1a−Cl1a = 2.4698(11) Å for **10** and 2.4732(6) Å for **12** are slightly longer by ca. 0.03 Å in comparison to the corresponding distances in tin(II) chlorides mentioned, with one exception, $\{Sn[N(C_6H_3iPr_2\text{-}2,6)(SiMe_3)](\mu\text{-}Cl)\}_2$, at 2.582(3) Å.[5a] The planarity and distances between the atoms forming the four-membered heterocyclic rings N1−C1, N2−C1, N1−Sn1, and N2−Sn1 indicate a high degree of π-electron delocalization within the guanidinato unit, also reflected in the planar N_3C moiety and short N3−C1 distances. Other distances and angles are in line with the literature data[26] for related (amidinato)-tin(II) as well as (guanidinato)tin(II) chloride complexes. The main difference between structures of **10** and **12** is the planarity of the Sn_2Cl_2 ring in the case of **12** and the orientation of the guanidinato ligands to the same side of the Sn_2Cl_2 ring in the case of **10** and an anti orientation in the case of **12**. In **10**, the Sn1b atom deviates from the Sn1a−Cl1a−Cl1b plane by 0.956 Å. On the other hand, the monomeric structures of **10** and **12** were determined using density functional theory calculations, starting from the crystal structures. Selected computed equilibrium distances and geometries are also listed in the caption of Figures 2 and 3. As can be seen, for both **10** and **12**, the computed equilibrium geometries are in very good agreement with the experimental geometries, confirming, among others, the π delocalization in the guanidinato unit. The Sn1 atoms are only slightly above the N_3C plane (0.326(3) Å for **10** and 0.114(4) Å for **12**), and the greatest deviation is in the value of C1−Sn1a−Cl1a angles caused by the short contacts of C1a with Sn1b in the solid state.

The structure of one of the homoleptic bis(guanidinato)tin-(II) complexes (**14**) was also determined by X-ray diffraction (Figure 4) and turned out to exist as two different solvato

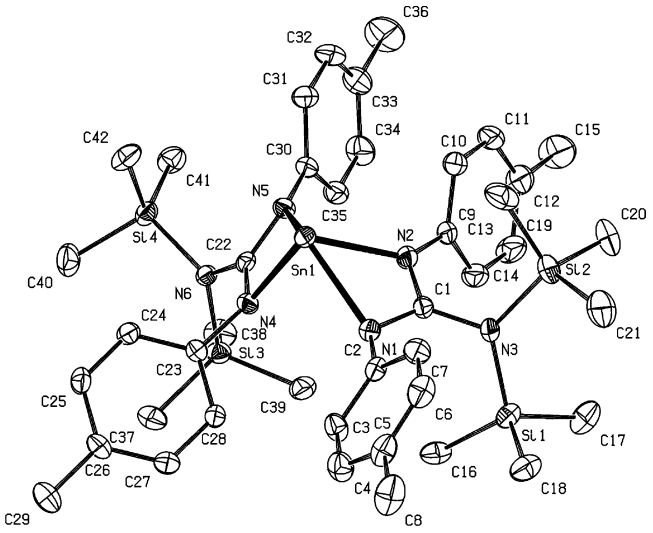

Figure 4. Molecular structure of $(L^{pTol})_2Sn$ (**14**) (ORTEP view, 50% probability level, appropriate parameters for **14′** are given in Supporting Information). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg), with computed values given in italics: N1−C1 = 1.330(3), *1.333*; N1−C2 = 1.415(3), *1.408*; N2−C1 = 1.339(3), *1.347*; N2−C9 = 1.410(3), *1.409*; N3−C1 = 1.403(3), *1.393*; N1−Sn1 = 2.399(2), *2.424*; N2−Sn1 = 2.164(2), *2.222*; N4−Sn1 = 2.201(2), *2.250*; N5−Sn1 = 2.358(2), *2.395*; N4−C23 = 1.416(3), *1.408*; N4−C22 = 1.346(3), *1.349*; N5−C22 = 1.320(3), *1.329*; N5−C30 = 1.407(3), *1.401*; N6−C22 = 1.400(3), *1.395*; C2−C1−C9 = 167.46(14), *166.6*; N1−C1−N2 = 112.1(2), *112.4*; C23−C22−C30 = 166.58(14), *167.6*; N4−C22−N5 = 112.1(2), *112.2*; N1−Sn1−N4 = 91.54(7), *89.7*; N2−Sn1−N5 = 84.91(8), *84.1*; C1−Sn1−C22 = 109.33(7), *105.4*.

polymorphs (**14** and **14′**), one isolated from a diethyl ether and the second from a hexane solution, where the hexane molecule is cocrystallized with **14′**, having no significant interaction with the atoms of **14′**. Only negligible differences between the structures of these solvato polymorphs are found as far as interatomic distances and angles are concerned, but there is a rather large difference in the mutual orientation of both ligands (see Figure S5 in the Supporting Information). The mutual

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distortion of both ligands in **14** from the ideal geometry is probably caused by the strong $\pi-\pi$ aromatic stacking interaction. The tin atom in **14** is four-coordinated with a distorted pseudo square pyramidal configuration, with the largest bonding angle value being 127.7(3)°, in contrast to the C_2 symmetry homoleptic bis(guanidinato)tin(II) complex described by Richeson as distorted pseudo trigonal bipyramidal with a pseudoaxial vector with an angle of 140.4(3)°.[24b] In comparison to the heteroleptic stannylenes (**10** and **12**) discussed above, the bonds N1−Sn1 and N5−Sn1 in **14** are elongated by ca. 0.2 Å, indicating a higher steric demand of ligands or π-electron delocalization decrease in the N_3C system which is nearly planar with a sum of angles around nitrogen atoms of 350.62(8)° for N1, 359.83(9)° for N2, 350.67(8)° for N4, and 358.41(7)° for N5 atoms, respectively. The interplanar (bite) angle between these rings is 77.1(2)°, which is typical for metal complexes of guanidinates as well as of amidinates.[31]

The equilibrium structure of **14** and **14′** were also determined using DFT calculations, again starting from the crystal structures; selected optimized bond lengths and angles are given in the caption of Figure 4 and Figure S6 (Supporting Information). These computed geometrical parameters are in good agreement with the experimental data obtained from the crystal structures. At the level of theory used in the calculations, **14** is only marginally more stable than structure **14′** (about 0.6 kcal mol^{-1}); in view of the possible underestimation of the strength of the $\pi-\pi$ stacking interaction in compound **14** at the current level of theory, this value probably represents a lower bound to the energy difference between the two structures **14** and **14′**.

The oxidation product of **8**, **8a**, crystallizes in the triclinic crystal system $P\bar{1}$. The compound is formed by the central Sn_2O_2 ring with a rather short interatomic distance between the tin atoms of 3.0039(4) Å, which is caused by short interatomic angles inside the ring (Figure 5). The angle between the plane defined by this ring and the guanidinato unit is 67.19(9)°. In contrast with the aforementioned tin(II) guanidinates, the tin atom in **8a** is located out of the guanidinato unit plane (0.407(3) Å). The angle between the amido and guanidinato substituents of the tin atom is rather wide (N4−Sn1−C1 = 115.46(9)°), defining the configurations of the tin atoms as distorted square pyramids, with these atoms located 0.769(3) Å above the bases of the pyramids each defined by two oxygen atoms and two nitrogen atoms of the guanidinato ligands. The mutual orientation of the amido substituents is pseudo trans with respect to the central ring. The distances between tin and nitrogen atoms of the amido substituents are quite short, 2.033(4) Å, and thus comparable to those in simple tin amides.[27] Also, the Sn−O distances are within the range found in the Cambridge Structural Database for tin(IV) compounds with an Sn_2O_2 ring. Similar N−C distances within the N_3C guanidinato moiety again indicate a π-electron delocalization for this system.

3. CONCLUSION

Eight heteroleptic, both amido- and chloro-substituted, and two homoleptic monoanionic tin(II) guanidinates were prepared by reactions of the appropriate carbodiimides with Lappert's stannylenes with high atom economy and yields under very mild conditions. The structures of four of them were determined by X-ray diffraction methods, showing broad differences. The first oxidation product (oxidizing the metal from the +II to +IV state) in group 14 metal guanidinates was prepared and structurally characterized. Because of the relatively easy synthesis of the studied compounds they could be applied in materials chemistry or in the preparation of various metal guanidinates by transmetalation.

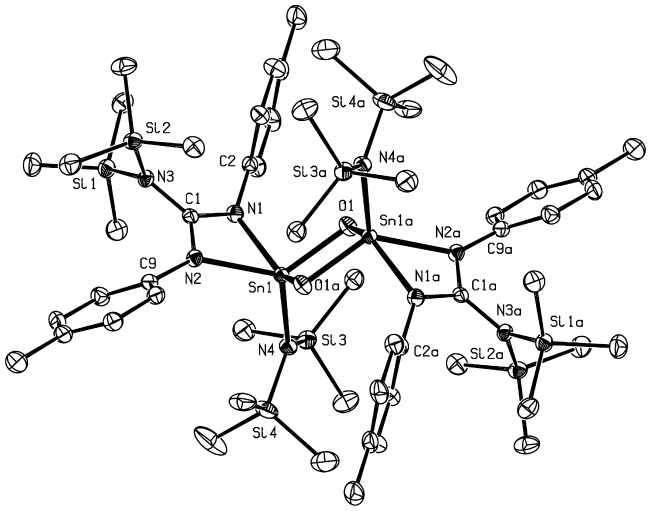

Figure 5. Molecular structure of $\{(L^{pTol})[(Me_3Si)_2N]SnO\}_2 \cdot C_4H_{10}O$ (**8a**) (ORTEP view, 40% probability level). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): N1−C1 = 1.336(7); N1−C2 = 1.431(5); N2−C1 = 1.338(5); N2−C9 = 1.414(7); N3−C1 = 1.402(6); N1−Sn1 = 2.225(4); N2−Sn1 = 2.172(4); C1−Sn1 = 2.646(5); N4−Sn1 = 2.033(4); Sn1−O1 = 1.992(3); Sn1−O1a = 1.998(3); Sn1−Sn1a = 3.0039(4); C2−C1−C9 = 166.5(3); N1−C1−N2 = 111.1(4); N1−Sn1−N2 = 60.16(15); C1−Sn1−Sn1a = 121.77(9); O1−Sn1−O1a = 82.33(14); C1−Sn1−N4 = 115.46(14); Sn1−O1−Sn1a = 97.67(17).

4. EXPERIMENTAL SECTION

4.1.1. General Methods. *NMR Spectroscopy.* NMR spectra were recorded from solutions in benzene-d_6 or THF-d_8 on a Bruker Avance 500 spectrometer (equipped with *Z*-gradient 5 mm probe) at frequencies for ^1H (500.13 MHz), $^{13}C\{^1H\}$ (125.76 MHz), and $^{119}Sn\{^1H\}$ (186.50 MHz) at 295 K. All deuterated solvents were degassed and then stored over K-mirror under an argon atmosphere. Solutions were obtained by dissolving approximately 40 mg of each compound approximately in 0.5 mL of deuterated solvents. Values of ^1H chemical shifts were calibrated to an internal standard, tetramethylsilane ($\delta(^1H)$ 0.00), or to residual signals of benzene ($\delta(^1H)$ = 7.16) and THF ($\delta(^1H)$ 3.58 or 1.73). Values of ^{13}C chemical shifts were calibrated to signals of THF ($\delta(^{13}C)$ 67.6) and benzene ($\delta(^{13}C)$ 128.4). The ^{119}Sn chemical shift values are referred to external neat tetramethylstannane ($\delta(^{119}Sn)$ 0.0 ppm). Positive chemical shift values denote shifts to higher frequencies relative to standards. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode. All ^{13}C NMR spectra were measured using standard proton-decoupled experiments, and CH and CH_3 vs C, and CH_2 were differentiated with the help of the APT method.[32]

The solid-state ^{13}C spectra were recorded under cross-polarization at 6.5 dB power and BB ^1H decoupling on an Avance 250 Bruker instrument resonating at 62.5598 MHz for ^{13}C nuclei, under magic angle spinning at 4 kHz. The sweep width was 300 ppm, the relaxation delay 4 s, the number of scans 2000, and the CP contact time 1500 μs.

4.1.2. Elemental Analyses. The compositional analyses were determined under an inert atmosphere of argon on an EA 1108 automatic analyzer by FISONS Instruments.

4.1.3. Crystallography. The X-ray data (Table 2) obtained from colorless crystals for all compounds were acquired at 150 K using an Oxford Cryostream low-temperature device on a Nonius KappaCCD

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Table 2. Crystallographic Data for 10, 12, 14, 14′, and 8a

	$L^{Cy}SnCl$ (**10**)	$L^{pTol}SnCl$ (**12**)	$(L^{pTol})_2Sn$ (**14**)	$(L^{pTol})_2Sn{\cdot}C_6H_{14}$ (**14′**)	$\{(L^{pTol})[(Me_3Si)_2N]SnO\}_2{\cdot}C_4H_{10}O$ (**8a**)
chem formula	$C_{19}H_{40}ClN_3Si_2Sn$	$C_{21}H_{32}ClN_3Si_2Sn$	$C_{42}H_{64}N_6Si_4Sn$	$C_{48}H_{78}N_6Si_4Sn$	$C_{58}H_{110}N_8O_3Si_8Sn_2$
formula wt	520.86	536.82	884.04	970.21	1429.64
cryst syst	tetragonal	triclinic	monoclinic	monoclinic	triclinic
a/Å	17.8950(4)	9.9640(5)	24.0972(12)	12.4960(9)	12.6030(9)
b/Å	17.8950(19)	11.0551(5)	11.3390(7)	27.177(3)	12.7420(7)
c/Å	16.1841(2)	13.6129(5)	17.7010(8)	15.6270(12)	14.1991(11)
α/deg	90	68.420(3)	90	90	79.350(5)
β/deg	90	77.555(3)	100.487(4)	95.929(7)	64.789(6)
γ/deg	90	68.335(4)	90	90	75.427(5)
unit cell volume/Å^3	5182.7(7)	1290.37(11)	4755.8(4)	5278.6(8)	1988.8(3)
temp/K	150(1)	150(1)	150(1)	150(1)	150(1)
space group	$P\bar{4}2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
no. of formula units per unit cell, Z	8	2	4	4	1
abs coeff, μ/mm^{-1}	1.190	1.198	0.672	0.611	0.789
no. of rflns measd	41 238	25 206	35 302	56 294	39 820
no. of indep rflns	5916	5902	10 377	12 078	8833
R_{int}[a]	0.0612	0.0456	0.0470	0.0461	0.0499
final R1 values ($I > 2\sigma(I)$)[b]	0.0322	0.0223	0.0356	0.0423	0.0545
final wR2(F^2) values ($I > 2\sigma(I)$)	0.0557	0.0504	0.0657	0.0736	0.1200
goodness of fit on F^2[c]	1.177	1.094	1.098	1.126	1.181

[a] $R_{int} = \sum|F_o^2 - F_{o,mean}^2|/\sum F_o^2$. [b] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$. $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{1/2}$. [c] $S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffr} - N_{param})]^{1/2}$.

diffractometer with Mo Kα radiation (λ = 0.710 73 Å) and a graphite monochromator, in the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.[33] The absorption was corrected by integration methods.[34] Structures were solved by direct methods (Sir92)[35] and refined by full-matrix least squares based on F^2 (SHELXL97).[36] Hydrogen atoms were mostly localized on a difference Fourier map, but in order to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $U_{iso}(H) = 1.2U_{eq}$(pivot atom) or $1.5U_{eq}$ for the methyl moiety with C−H = 0.96, 0.97, 0.98, and 0.93 Å for methyl, methylene, methine, and hydrogen atoms in aromatic rings, respectively.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, www: http:// www.ccdc.cam.ac.uk). CCDC deposition numbers are 847157 for **10**, 847156 for **12**, 847155 for **14**, and 847158 for **8a**.

4.1.4. Computations. All structures were optimized at the MO6-2X[37]/cc-pVDZ[38] level of theory (cc-pVDZ-PP)[39] on Sn, which uses a cc-pVDZ like basis set for the valence region, together with a small-core relativistic pseudopotential; the Cartesian coordinates of the resulting gas-phase optimized geometries can be found in the Supporting Information. All computations were performed using the Gaussian 09 program.[40]

4.2. Synthesis. All syntheses were performed using standard Schlenk techniques under an inert argon atmosphere. Solvents and reactants were purchased from commercial sources. Solvents were distilled over K/Na alloy, degassed, and then stored over a K-mirror under an argon atmosphere. Single crystals suitable for XRD analyses were obtained under argon from corresponding saturated solutions of products in Et_2O or hexane cooled to −30 °C. Melting points were measured in inert perfluoroalkyl ether and were uncorrected. NMR spectra in benzene-d_6 of starting N,N′-disubstituted carbodiimides were measured for comparison and studies of chemical shifts of prepared compounds. The parameters for *N,N′*-diisopropylcarbodiimide (**1**) and *N,N′*-dicyclohexylcarbodiimide (**2**) are reported elsewhere.[41] NMR data for *N,N′*-bis(4-methylphenyl)carbodiimide (**3**) are as follows. ^{1}H NMR (500 MHz, 295 K): δ 7.03 (d, ^3J = 8.2 Hz, 4H, Ar*H*); 6.81 (d, ^3J = 8.0 Hz, 4H, Ar*H*); 2.00 (s, 6H, C*H*$_3$). ^{13}C NMR (125 MHz, 295 K): δ 136.9 (Ar); 136.7 (N═C═N); 135.6 (Ar); 130.8 (Ar); 124.7 (Ar); 21.2 (*C*H$_3$). Data for *N*-[3-(dimethylamino)propyl]-*N′*-ethylcarbodiimide (**4**, known as EDC) are as follows. ^{1}H NMR (500 MHz, 295 K): δ 3.11 (t, ^3J = 6.7 Hz, 2H, α-C*H*$_2$); 2.97 (q, ^3J = 7.1 Hz, 2H, δ-C*H*$_2$); 2.14 (t, ^3J = 6.9 Hz, 2H, γ-C*H*$_2$); 2.00 (s, 6H, (C*H*$_3$)$_2$N); 1.53 (m, 2H, β-C*H*$_2$); 0.99 (t, ^3J = 7.2 Hz, 3H, C*H*$_3$). ^{13}C NMR (C_6D_6, 125 MHz, 295 K): δ 140.9 (N═*C*═N); 57.1 (α-*C*H$_2$); 45.8 ((*C*H$_3$)$_2$N); 44.9 (δ-*C*H$_2$); 41.7 (γ-*C*H$_2$); 30.8 (β-*C*H$_2$); 17.2 (*C*H$_3$).

*General Procedure of Preparation of Heteroleptic Tin(II) Guanidinates $L^RSnN(SiMe_3)_2$ (**5**−**8**).* To a solution of bis[bis(trimethylsilyl)amino]tin in Et_2O at room temperature was added 1 equiv of starting N,N′-disubstituted carbodiimides **1**−**4** dissolved in Et_2O. Reaction mixtures were stirred for 2 h, and there was a slight color fading from orange to pale yellow. Subsequently, the crude products were filtered and Et_2O was evaporated under vacuum to give pure products of heteroleptic tin(II) guanidinates **5**−**8** in almost quantitative yields.

*General Procedure of Preparation of Heteroleptic Tin(II) Guanidinates L^RSnCl (**9**−**12**).* To a yellow suspension of [bis(trimethylsilyl)amino]tin chloride in Et_2O at room temperature was added 1 equiv of starting N,N′-disubstituted carbodiimides **1**−**4** in Et_2O. Reaction mixtures were stirred until complete disappearance of the initial yellow color. The colorless crude products were filtered, and then Et_2O was evaporated under vacuum. The pure heteroleptic tin(II) guanidinates **9**−**12** were obtained.

*General Procedure of Preparation of Homoleptic Tin(II) Guanidinates $(L^R)_2Sn$ (**13** and **14**).* To a solution of bis[bis(trimethylsilyl)amino]tin in Et_2O at room temperature was added 2 equiv of starting N,N′-disubstituted carbodiimides **1**−**4** in Et_2O. Reaction mixtures were stirred for $^1/_2$ h, with complete color disappearance from orange to colorless. Subsequently, the crude products were filtered and Et_2O was evaporated under vacuum to give colorless pure products of homoleptic tin(II) guanidinates **13** and **14** in almost quantitative yields.

*4.2.1. Preparation of Heteroleptic Tin(II) Guanidinate $L^{iPr}SnN(SiMe_3)_2$ (**5**).* 1.31 g of **1** (10.3 mmol, 0.815 g/cm^3, 1.59 mL), 4.53 g of $[(Me_3Si)_2N]_2Sn$ (10.3 mmol), 40 mL of Et_2O. Yield: 5.44 g (93%) of pale yellow oily material of **5**. ^{1}H NMR (C_6D_6, 500 MHz, 295 K): δ 3.91 (sep, 2H, C*H*); 1.23 (d, ^3J = 6.4 Hz, 6H, (C*H*$_3$)$_2$); 1.20 (d, ^3J =

6.4 Hz, 6H, $(CH_3)_2$); 0.41 (s, 18H, $(CH_3)_3Si$); 0.22 (s, 9H, $(CH_3)_3Si$); 0.14 (s, 9H, $(CH_3)_3Si$). ^{13}C NMR (C_6D_6, 125 MHz, 295 K): δ 160.4 (N=C(N)N); 46.0 (CH); 26.0 ($(CH_3)_2$); 25.8 ($(CH_3)_2$); 6.0 ($(CH_3)_3Si$); 2.4 ($(CH_3)_3Si$); 2.2 ($(CH_3)_3Si$). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K): δ −115.7. ^1H NMR (THF-d_8, 500 MHz, 295 K): δ 4.00 (sep, 2H, C*H*); 1.25 (d, ^3J = 7.2 Hz, 6H, $(CH_3)_2$); 1.24 (d, ^3J = 6.7 Hz, 6H, $(CH_3)_2$); 0.31 (s, 9H, $(CH_3)_3Si$); 0.27 (s, 9H, $(CH_3)_3Si$); 0.19 (s, 18H, $(CH_3)_3Si$). ^{13}C NMR (THF-d_8, 125 MHz, 295 K): δ 161.9 (N=*C*(N)N); 47.2 (*C*H); 28.4 ($(CH_3)_2$); 26.6 ($(CH_3)_2$); 6.6 ($(CH_3)_3Si$); 3.2 ($(CH_3)_3Si$); 2.9 ($(CH_3)_3Si$). ^{119}Sn NMR (THF-d_8, 186 MHz, 295 K): δ −119.5. Anal. Calcd for $C_{19}H_{50}N_4Si_4Sn$: C 40.34; H, 8.91; N, 9.90. Found: C, 40.26; H, 8.80; N, 10.00.

*4.2.2. Preparation of Heteroleptic Tin(II) Guanidinate $L^{Cy}SnN(SiMe_3)_2$ (**6**).* 1.70 g of **2** (8.3 mmol), 3.63 g of $[(Me_3Si)_2N]_2Sn$ (8.3 mmol), 30 mL of Et_2O. Yield: 5.16 g (96%) of pale yellow solid of **6**. Mp: 81−83 °C. ^1H NMR (C_6D_6, 500 MHz, 295 K): δ 3.57−3.53 (m, 2H, Cy*H*); 1.93 (br s, 4H, Cy*H*); 1.73−1.41 (br m, 10H, Cy*H*); 1.23−1.06 (m, 6H, Cy*H*); 0.48 (s, 18H, $(CH_3)_3Si$); 0.25 (s, 9H, $(CH_3)_3Si$); 0.17 (s, 9H, $(CH_3)_3Si$). ^{13}C NMR (C_6D_6, 125 MHz, 295 K): δ 160.8 (N=C(N)N); 55.2 (Cy); 39.3 (Cy); 37.3 (Cy); 26.9 (Cy); 26.4 (Cy); 26.3 (Cy); 7.0 ($(CH_3)_3Si$); 3.2 ($(CH_3)_3Si$); 2.9 ($(CH_3)_3Si$). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K): δ −126.9. ^1H NMR (THF-d_8, 500 MHz, 295 K): δ 3.48−3.43 (m, 2H, Cy*H*); 1.93−1.88 (m, 4H, Cy*H*); 1.79−1.71 (m, 4H, Cy*H*); 1.65−1.60 (m, 4H, Cy*H*); 1.41−1.17 (br m, 8H, Cy*H*); 0.30 (s, 9H, $(CH_3)_3Si$); 0.25 (s, 9H, $(CH_3)_3Si$); 0.19 (s, 18H, $(CH_3)_3Si$). ^{13}C NMR (THF-d_8, 125 MHz, 295 K): δ 161.5 (N=*C*(N)N); 55.5 (Cy); 39.6 (Cy); 37.6 (Cy); 27.2 (Cy); 26.8 (Cy); 26.6 (Cy); 6.7 ($(CH_3)_3Si$); 3.2 ($(CH_3)_3Si$); 2.8 ($(CH_3)_3Si$). ^{119}Sn NMR (THF-d_8, 186 MHz, 295 K): δ −127.5. Anal. Calcd for $C_{25}H_{58}N_4Si_4Sn$: C, 46.50; H, 9.05; N, 8.68. Found: C, 46.70; H, 9.30; N, 8.45.

*4.2.3. Preparation of Heteroleptic Tin(II) Guanidinate $L^{EDC}SnN(SiMe_3)_2$ (**7**).* 2.16 g of **4** (13.9 mmol, 0.877 g/cm^3, 2.46 mL), 6.12 g of $[(Me_3Si)_2N]_2Sn$ (13.9 mmol), 50 mL of Et_2O. Yield: 7.52 g (91%) of pale yellow oily material of **7**. ^1H NMR (C_6D_6, 500 MHz, 295 K): δ 3.60−3.56, 3.45−3.41 (m, 2H, α-CH_2, anisochronous signals); 3.26 (q, 2H, δ-CH_2); 2.28−2.24, 2.18−2.14 (m, 2H, γ-CH_2, anisochronous signals); 2.08 (s, 6H, $(CH_3)_2N$); 1.67−1.63, 1.61−1.57 (m, 2H, β-CH_2, anisochronous signals); 1.19 (t, ^3J = 7.1 Hz, 3H, CH_3); 0.40 (s, 18H, $(CH_3)_3Si$); 0.21 (s, 9H, $(CH_3)_3Si$); 0.16 (s, 9H, $(CH_3)_3Si$). ^{13}C NMR (C_6D_6, 125 MHz, 295 K): δ 163.8 (N=*C*(N)N); 59.7 (α-CH_2); 46.7 ($(CH_3)_2N$); 45.9 (δ-CH_2); 40.7 (γ-CH_2); 30.8 (β-CH_2); 18.6 (CH_3); 6.4 ($(CH_3)_3Si$); 2.7 ($(CH_3)_3Si$); 2.5 ($(CH_3)_3Si$). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K): δ −144.6. Anal. Calcd for $C_{20}H_{53}N_5Si_4Sn$: C, 40.39; H, 8.98; N, 11.78. Found: C, 40.58; H, 9.05; N, 11.63.

*4.2.4. Preparation of Heteroleptic Tin(II) Guanidinate $L^{pTol}SnN(SiMe_3)_2$ (**8**).* 4.23 g of **3** (19.1 mmol), 8.37 g of $[(Me_3Si)_2N]_2Sn$ (19.1 mmol), 50 mL of Et_2O. Yield: 11.80 g (93%) of pale yellow solid of **8**. Mp: 77−78 °C. ^1H NMR (C_6D_6, 500 MHz, 295 K): δ 7.05 (d, ^3J = 8.2 Hz, 4H, Ar*H*); 6.95 (d, ^3J = 8.1 Hz, 4H, Ar*H*); 2.11 (s, 6H, CH_3); 0.27 (s, 18H, $(CH_3)_3Si$); 0.03 (s, 9H, $(CH_3)_3Si$); −0.12 (s, 9H, $(CH_3)_3Si$). ^{13}C NMR (C_6D_6, 125 MHz, 295 K): δ 163.6 (N=*C*(N)N); 142.4 (Ar-C_{ipso}); 134.1 (Ar-C_{ipso}); 129.9 (Ar-CH); 127.8 (Ar-CH); 21.3 (CH_3); 6.2 ($(CH_3)_3Si$); 2.3 ($(CH_3)_3Si$); 2.2 ($(CH_3)_3Si$). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K): δ −87.2. ^1H NMR (THF-d_8, 500 MHz, 295 K): δ 7.11 (d, ^3J = 8.2 Hz, 4H, Ar*H*); 6.99 (d, ^3J = 8.2 Hz, 4H, Ar*H*); 2.30 (s, 6H, CH_3); 0.05 (s, 9H, $(CH_3)_3Si$); 0.00 (s, 18H, $(CH_3)_3Si$); −0.17 (s, 9H, $(CH_3)_3Si$). ^{13}C NMR (THF-d_8, 125 MHz, 295 K): δ 164.0 (N=C(N)N); 142.7 (Ar-C_{ipso}); 134.6 (Ar-C_{ipso}); 130.1 (Ar-CH); 128.0 (Ar-CH); 21.1 (CH_3); 5.4 ($(CH_3)_3Si$); 2.9 ($(CH_3)_3Si$); 1.9 ($(CH_3)_3Si$). ^{119}Sn NMR (THF-d_8, 186 MHz, 295 K): δ −93.0. Anal. Calcd for $C_{27}H_{50}N_4Si_4Sn$: C, 49.00; H, 7.62; N, 8.47. Found: C, 48.85; H, 7.50; N, 8.65.

*4.2.5. Preparation of $\{(L^{pTol})[(Me_3Si)_2N]SnO\}_2$ (**8a**).* After standing of 500 mg of **8** in 20 mL of Et_2O in a Schlenk tube with an insufficiently greased stopcock at −30 °C for 3 weeks, about 50 mg of **8a** has been reproducibly crystallized. Mp: 150−152 °C. ^1H NMR (THF-d_8, 500 MHz, 295 K): δ 7.04 (d, ^3J = 8.0 Hz, 8H, Ar*H*); 6.84 (d, ^3J = 8.1 Hz, 8H, Ar*H*); 2.26 (s, 12H, CH_3); 0.11 (s, 18H, $(CH_3)_3Si$); 0.05 (s, 36H, $(CH_3)_3Si$); −0.23 (s, 18H, $(CH_3)_3Si$). ^{119}Sn NMR (THF-d_8, 186 MHz, 295 K): δ −612.8. Anal. Calcd for $C_{42}H_{64}N_6O_2Si_4Sn_2$: C, 48.75; H, 6.23; N, 8.12. Found: C, 48.62; H, 6.46; N, 8.34.

*4.2.6. Preparation of Heteroleptic Tin(II) Guanidinate $L^{iPr}SnCl$ (**9**).* 0.82 g of **1** (6.5 mmol, 0.815 g/cm^3, 1.01 mL), 2.05 g of $(Me_3Si)_2NSnCl$ (6.5 mmol), 30 mL of Et_2O. Yield: 2.55 g (89%) of colorless oily material of **9**. ^1H NMR (C_6D_6, 500 MHz, 295 K): δ 3.88 (sep, 2H, C*H*); 0.97 (br s, 12H, $(CH_3)_2$); 0.16 (s, 18H, $(CH_3)_3Si$). ^{13}C NMR (C_6D_6, 125 MHz, 295 K): δ 167.9 (N=C(N)N); 45.5 (CH); 26.4 (br signal $(CH_3)_2$); 2.5 ($(CH_3)_3Si$). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K): δ −30.4. ^1H NMR (THF-d_8, 500 MHz, 295 K): δ 4.02 (sep, 2H, C*H*); 1.16 (d, ^3J = 6.3 Hz, 12H, $(CH_3)_2$); 0.11 (s, 18H, $(CH_3)_3Si$). ^{13}C NMR (THF-d_8, 125 MHz, 295 K): δ 168.0 (N=*C*(N)N); 46.1 (CH); 26.4 ($(CH_3)_2$); 2.5 ($(CH_3)_3Si$). ^{119}Sn NMR (THF-d_8, 186 MHz, 295 K): δ −51.1. Anal. Calcd for $C_{13}H_{32}ClN_3Si_2Sn$: C, 35.43; H, 7.32; N, 9.53. Found: C, 35.73; H, 7.54; N, 9.28.

*4.2.7. Preparation of Heteroleptic Tin(II) Guanidinate $L^{Cy}SnCl$ (**10**).* 1.26 g of **2** (6.1 mmol), 1.92 g of $(Me_3Si)_2NSnCl$ (6.1 mmol), 30 mL of Et_2O. 3.05 g (96%) of white solid of **10**. Mp: 125−127 °C. Single crystals suitable for XRD analyses were obtained under argon from a saturated solution of **10** in a mixture of Et_2O and hexane (2:1) cooled to −30 °C. ^1H NMR (C_6D_6, 500 MHz, 295 K): δ 3.55−3.51 (m, 2H, Cy*H*); 2.15−1.79 (br m, 4H, Cy*H*); 1.62 (br s, 6H, Cy*H*); 1.45−1.14 (br m, 6H, Cy*H*); 1.06−0.91 (m, 4H, Cy*H*); 0.16 (br s, 18H, $(CH_3)_3Si$). ^{13}C NMR (C_6D_6, 125 MHz, 295 K): δ 167.8 (N=*C*(N)N); 53.5 (Cy); 37.6 (br signal Cy); 26.2 (Cy); 26.1 (Cy); 2.4 (br signal $(CH_3)_3Si$). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K): δ −34.9. ^1H NMR (THF-d_8, 500 MHz, 295 K): δ 3.44 (s, 2H, Cy*H*); 1.68 (s, 4H, Cy*H*); 1.59 (br s, 4H, Cy*H*); 1.44 (br s, 2H, Cy*H*); 1.18−1.05 (br m, 10H, Cy*H*); 0.16 (s, 18H, $(CH_3)_3Si$). ^{13}C NMR (THF-d_8, 125 MHz, 295 K): δ 168.0 (N=*C*(N)N); 55.0 (Cy); 37.3 (Cy); 26.6 (Cy); 26.5 (Cy); 2.2 ($(CH_3)_3Si$). ^{119}Sn NMR (THF-d_8, 186 MHz, 295 K): δ −51.0. Anal. Calcd for $C_{19}H_{40}ClN_3Si_2Sn$: C, 43.81; H, 7.74; N, 8.07. Found: C, 43.92; H, 7.80; N, 8.18.

*4.2.8. Preparation of Heteroleptic Tin(II) Guanidinate $L^{EDC}SnCl$ (**11**).* 1.15 g of **4** (7.4 mmol, 0.877 g/cm^3, 1.31 mL), 2.33 g of $(Me_3Si)_2NSnCl$ (7.4 mmol), 30 mL of Et_2O. Yield: 3.15 g (90%) of colorless oily material of **11**. ^1H NMR (C_6D_6, 500 MHz, 295 K): δ 3.38, 3.21 (br s, 2H, α-CH_2, anisochronous signals); 3.24 (br s, 2H, δ-CH_2); 2.52, 1.97 (br s, 2H, γ-CH_2, anisochronous signals); 1.97 (s, 6H, $(CH_3)_2N$); 1.30 (br s, 2H, β-CH_2); 1.11 (t, ^3J = 7.2 Hz, 3H, CH_3); 0.21, 0.13 (br s, 18H, $(CH_3)_3Si$). ^{13}C NMR (C_6D_6, 125 MHz, 295 K): δ 166.9 (N=*C*(N)N); 60.2 (α-CH_2); 46.2 ($(CH_3)_2N$); 46.1 (δ-CH_2); 40.7 (γ-CH_2); 27.5 (β-CH_2); 17.3 (CH_3); 2.6 (br signal $(CH_3)_3Si$); 2.1 (br signal $(CH_3)_3Si$). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K): δ −250.6. Anal. Calcd for $C_{14}H_{35}ClN_4Si_2Sn$: C, 35.79; H, 7.51; N, 11.93. Found: C, 35.81; H, 7.26; N, 11.68.

*4.2.9. Preparation of Heteroleptic Tin(II) Guanidinate $L^{pTol}SnCl$ (**12**).* 5.13 g of **3** (23.1 mmol), 7.27 g of $(Me_3Si)_2NSnCl$ (23.1 mmol), 60 mL of Et_2O. Washed with 10 mL of hexane. Yield: 10.63 g (86%) of white solid of **12**. Mp: 69−73 °C. Single crystals suitable for XRD analyses were obtained under argon from a saturated solution of **12** in Et_2O cooled to −30 °C. ^1H NMR (C_6D_6, 500 MHz, 295 K): δ 7.02 (d, ^3J = 8.1 Hz, 4H, Ar*H*); 6.95 (d, ^3J = 8.1 Hz, 4H, Ar*H*); 2.10 (s, 6H, CH_3); −0.04 (s, 18H, $(CH_3)_3Si$). ^{13}C NMR (C_6D_6, 125 MHz, 295 K): δ 168.3 (N=*C*(N)N); 141.6 (Ar-C_{ipso}); 134.3 (Ar-C_{ipso}); 130.2 (Ar-CH); 126.9 (Ar-CH); 21.3 (CH_3); 1.5 ($(CH_3)_3Si$). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K): δ −108.2. ^1H NMR (THF-d_8, 500 MHz, 295 K): δ 7.09 (d, ^3J = 8.0 Hz, 4H, Ar*H*); 6.99 (d, ^3J = 8.1 Hz, 4H, Ar*H*); 2.27 (s, 6H, CH_3); −0.03 (s, 18H, $(CH_3)_3Si$). ^{13}C NMR (C_6D_6, 125 MHz, 295 K): δ 163.5 (N=*C*(N)N); 142.6 (Ar-C_{ipso}); 134.0 (Ar-C_{ipso}); 130.3 (Ar-CH); 127.1 (Ar-CH); 21.2 (CH_3); 1.6 ($(CH_3)_3Si$). ^{119}Sn NMR (THF-d_8, 186 MHz, 295 K): δ −220.0. Anal. Calcd for $C_{21}H_{32}N_3Si_2Sn$: C, 46.98; H, 6.01; N, 7.83. Found: C, 47.03; H, 7.54; N, 8.10.

*4.2.10. Preparation of Homoleptic Tin(II) Guanidinate $(L^{EDC})_2Sn$ (**13**).* 1.47 g of **4** (9.5 mmol, 0.877 g/cm^3, 1.67 mL), 2.08 g of $[(Me_3Si)_2N]_2Sn$ (4.8 mmol), 30 mL of Et_2O. Yield: 3.42 g (96%) of

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colorless oily material of **13**. ^{1}H NMR (C_6D_6, 500 MHz, 295 K): δ 3.47−3.37 (m, 8H, α-CH_2 + δ-CH_2); 2.35 (t, ^3J = 7.0 Hz, 4H, γ-CH_2); 2.15 (s, 12H, $(CH_3)_2N$); 1.88 (quin, 4H, β-CH_2); 1.27 (t, ^3J = 7.5 Hz, 6H, CH_3); 0.24 (s, 36H, $(CH_3)_3Si$). ^{13}C NMR (C_6D_6, 125 MHz, 295 K): δ 163.2 (N=C(N)N); 59.0 (α-CH_2); 46.3 ($(CH_3)_2N$); 45.9 (δ-CH_2); 41.1 (γ-CH_2); 32.3 (β-CH_2); 19.0 (CH_3); 2.4 ($(CH_3)_3Si$). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K): δ −377.2. Anal. Calcd for $C_{28}H_{70}N_8Si_4Sn$: C, 44.84; H, 9.41; N, 14.94. Found: C, 44.88; H, 9.57; N, 14.80.

*4.2.11. Preparation of Homoleptic Tin(II) Guanidinate (L^{pTol})$_2$Sn (**14**).* 4.76 g of **3** (21.4 mmol), 4.71 g of $[(Me_3Si)_2N]_2Sn$ (10.7 mmol), 50 mL of Et_2O. Yield: 9.21 g (97%) of white solid of **14**. Mp: 83−86 °C. Single crystals suitable for XRD analyses were obtained under argon from a saturated solution of **14** in Et_2O cooled to −30 °C. ^{1}H NMR (C_6D_6, 500 MHz, 295 K): δ 6.94 (d, ^3J = 7.7 Hz, 8H, Ar*H*); 6.81 (d, ^3J = 7.8 Hz, 8H, Ar*H*); 2.19 (s, 12H, CH_3); −0.04 (s, 36H, $(CH_3)_3Si$). ^{13}C NMR (C_6D_6, 125 MHz, 295 K): δ 163.2 (N=C(N)N); 144.1 (Ar-C_{ipso}); 132.7 (Ar-C_{ipso}); 129.6 (Ar-CH); 127.3 (Ar-CH); 21.3 (CH_3); 2.1 ($(CH_3)_3Si$). ^{119}Sn NMR (C_6D_6, 186 MHz, 295 K): δ −432.0. ^{1}H NMR (THF-d_8, 500 MHz, 295 K): δ 6.93 (d, ^3J = 8.0 Hz, 8H, Ar*H*); 6.63 (d, ^3J = 8.1 Hz, 8H, Ar*H*); 2.28 (s, 12H, CH_3); −0.16 (s, 36H, $(CH_3)_3Si$). ^{13}C NMR (THF-d_8, 125 MHz, 295 K): δ 163.5 (N=C(N)N); 144.3 (Ar-C_{ipso}); 133.0 (Ar-C_{ipso}); 129.7 (Ar-CH); 127.4 (Ar-CH); 21.1 (CH_3); 1.94 ($(CH_3)_3Si$). ^{119}Sn NMR (THF-d_8, 186 MHz, 295 K): δ −427.8. Anal. Calcd for $C_{42}H_{64}N_6Si_4Sn$: C, 57.06; H, 7.30; N, 9.51. Found: C, 57.28; H, 7.54; N, 9.19.

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, and CIF files giving NMR spectra, comparisons of compounds **10** and **12** and of compounds **14** and **14′**, the molecular structure of **14′**, computed optimized structures of **10**, **12**, and **14**, and crystallographic data for **8a**, **10**, **12**, **14**, and **14′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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