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Octahedral Alkylbis(phenoxy-imine)tin(IV) Complexes: Effect of Substituents on the Geometry of the Complexes and Their Reactivity Toward Ionizing Species and Ethylene

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The synthesis and characterization of the organo-tin compounds L_2SnR_2 [L = *N*-(3,5-dichlorosalicylidene)aniline; R = CH_3 (**1**), R = CH_2Ph (**2**)] and L'_2SnR_2 [**3**: L′ = *N*-(3-*tert*-butylsalicylidene)aniline, R = CH_2Ph] are described herein. NMR studies showed a highly symmetric structure for complex **1**, with the alkyl groups in a *trans* configuration, and the presence of at least two isomers in fluxional equilibrium for compounds **2** and **3**. Single-crystal X-ray characterization for compound **2** showed an octahedral geometry with the alkyl groups in *trans* relationship. The reactivity of the synthesized compounds toward ionizing agents was studied by NMR spectroscopy. For compounds **1** and **2** formation of cationic species through alkyl abstraction by $B(C_6F_5)_3$ was observed. For compound **3**, a cationic species was obtained by reaction with 1 equiv. of $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$; in this species a η^n coordination of the benzyl group with the metal centre was recognized by NMR solution study. All the obtained cationic species promoted ethylene oligomerization under mild conditions, producing oligomers with saturated end groups and methyl branches. Oligoethylene end-group NMR analysis and deuteriolysis experiments excluded the migratory-insertion mechanism.

Introduction

The activity in olefin polymerization of compounds based on metals beyond group 13 has never been reported in the literature.[1] Recently we reported the oligomerization of ethylene in the presence of bis(phenoxy-imine)dialkyltin(IV) complexes.[2] The latter compounds showed octahedral geometry with alkyl groups in a *cis* configuration and underwent alkyl abstraction reaction with the carbenium salt $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$. The obtained cationic species exhibited low activity in ethylene oligomerization under mild conditions, producing oligomers with saturated end groups and methyl branches. To the best of our knowledge, the oligomerization of ethylene by a group 14 compound is unprecedented in the literature.

These results prompted us to persist in exploring the reactivity of different salicylaldiminatotin(IV) complexes, in order to ascertain the mechanism involved in the formation of branched oligoethylenes. Therefore we studied the synthesis and the structural properties of novel dialkyl bis(salicylaldiminato)tin(IV) complexes, bearing electronically and sterically different ligands. These complexes revealed some interesting features that will be discussed here and compared with the previously reported results.

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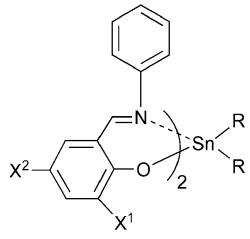
Results and Discussion

Synthesis of the Complexes

The synthesized bis(phenoxy-imine)tin(IV) complexes are described in Scheme 1. The *N*-(3-*tert*-butylsalicylidene)-aniline[3] and *N*-(3,5-dichlorosalicylidene)aniline[4] ligands were synthesized by a condensation reaction between the aldehyde and the aniline according to literature procedures. Complexes were prepared by a metathesis reaction of the sodium salt of the ligands with the corresponding dialkyltin(IV) chloride in tetrahydrofurane, producing compounds **1**–**3** with high yields (73–91%), as yellow or orange solids. The products are stable in an inert atmosphere, but easily underwent hydrolysis with formation of the free ligand in the presence of traces of adventitious water.



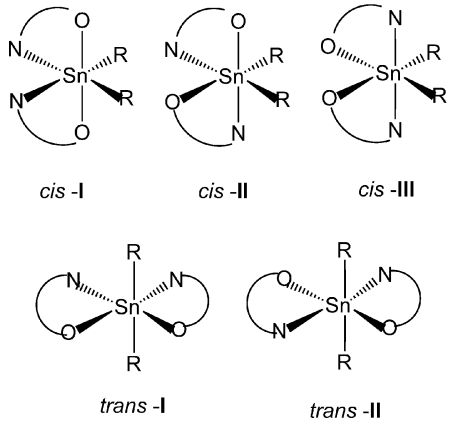
1 X^1 = Cl X^2 = Cl R = CH_3
2 X^1 = Cl X^2 = Cl R = CH_2Ph
3 X^1 = *t*Bu X^2 = H R = CH_2Ph

Scheme 1.

NMR Characterization of the Complexes

All the synthesized compounds were characterized by ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy, and mass spectroscopy. Compound **2** was also characterized by single-crystal X-ray diffraction analysis.

The ^{119}Sn NMR spectrum of the dimethyl compound **1**, bearing the chlorinated phenoxy-imine ligands, showed one signal at –306.5 ppm, compatible with the presence of a single organometallic species. The ^{1}H NMR spectrum showed very sharp signals and a pattern compatible with the presence of a highly symmetric structure in solution. Characteristic signals were the singlet at δ = 0.79 ppm ($^{2}J_{Sn,H}$ = 90.7 Hz) for the methyl groups, and the singlet at δ = 8.02 ppm ($^{3}J_{Sn,H}$ = 12.1 Hz) for the imine hydrogen atoms (C*H*=N). It is known from the literature that the coupling constants $^{2}J(^{119}Sn–^{1}H)$ and $^{1}J(^{119}Sn–^{13}C)$ can be used to estimate the methyl–tin–methyl angle.[5,6] For the previously reported bis(phenoxy-imine)tin(IV) dimethyl complexes, by using the equation specifically developed by Nelson for octahedral dialkyltin compounds,[6] we calculated a methyl–tin–methyl angle of 106(6)°, suggesting a structure with the methyl groups in a *cis* configuration; this result was nicely in agreement with the value disclosed by single-crystal X-ray analysis (107.4°). For compound **1** the value of the coupling constant $^{2}J_{Sn,H}$ for the methyl group bonded to tin is significantly higher than the value observed for previously reported compounds,[2] and the calculated angle C–Sn–C is of 160° (±6), in the expected range for a structure with the methyl groups in a *trans* configuration. For octahedral bis(phenoxy-imine) dialkyl complexes, five isomers are possible, as displayed in Scheme 2. In the present case, therefore, two isomers, "*trans*-**I**" and "*trans*-**II**", are compatible with the NMR spectroscopic data in solution.



Scheme 2.

The dibenzyl compound **2** showed two broad signals, at –425.6 and –426.9 ppm, in the ^{119}Sn NMR spectrum at room temperature, thus indicating the presence of different tin species in solution. In addition, in the ^{1}H NMR spectrum broad signals were also observed. Characteristic resonances are a singlet at δ = 2.56 ppm ($^{2}J_{Sn,H}$ = 105.1 Hz) for the methylene hydrogen atoms (CH_2Ph) and a singlet at δ = 7.84 ppm for the imine protons (C*H*=N). By using the Nelson equation,[6] from the value of the coupling constant $^{2}J_{Sn,H}$ for the methylene hydrogen atoms (CH_2Ph), the calculated angle for the C–Sn–C bonds was of 193° (±6), in the expected range for a structure with the benzyl groups in a *trans* configuration. As above, of the five possible isomers, the two "*trans*" ones are compatible with the NMR spectroscopic data in solution. Single-crystal X-ray diffraction analysis revealed that compound **2** crystallized in the "*trans*-**II**" isomeric form (vide infra).

In order to investigate the fluxional equilibrium between different isomers in solution, variable temperature ^{1}H NMR experiments were performed between 278 and 188 K. Lowering the temperature, the broad signals split (see electronic supporting information). At 203 K the signal of the methylene hydrogen atoms CH_2Ph split up into a well defined AB pattern at about 1.9 ppm, two broad signals at δ = 2.72 ppm ($^{2}J_{Sn,H}$ = 27.3 Hz) and 2.93 ppm, and a minor AB pattern (δ = 2.45 ppm). At lower field three main singlets (δ = 8.00, 7.74 and 7.66 ppm) and a minor one (δ = 7.56 ppm), attributable to the imine protons, were observed. Such observations are compatible with the presence of at least two main isomeric species and a minor one involved in fluxional equilibria.

The dibenzyl compound **3**, bearing the *N*-(3-*tert*-butylsalicylidene)aniline ligands, displayed an intricate ^{1}H NMR spectrum at room temperature (Figure 1). The compound must exist in solution in two isomeric forms, as evidenced by the presence, in the ^{119}Sn NMR spectrum, of two resonances at –456.5 ppm and –457.9 ppm (1:1 molar ratio). In the ^{1}H NMR spectrum, two sets of signals, attributable to two different species in a 1:1 ratio, were also recognized. The first signal set (one singlet at δ = 1.07 ppm for the *t*Bu group, one signal with AB pattern at 2.5 ppm for the diastereotopic methylene hydrogen atoms CH_2Ph and one singlet at δ = 7.99 ppm for the imine proton, with a $^{3}J_{Sn,H}$ of 33.65 Hz) is compatible with a highly symmetric species (**I**). The second signal set, compatible with a nonsymmetric species (**II**), consists of two singlets at δ = 1.28 ppm and 1.41 ppm for the *t*Bu groups, two signals with AB pattern for the CH_2Ph at 2.4 ppm and 2.7 ppm and two singlets for the imine hydrogen atoms at δ = 7.69 ppm and 7.89 ppm. The ^{13}C NMR spectrum of compound **2** coherently displayed two signals sets, one compatible with a symmetric species **I**, the second one compatible with a nonsymmetric species **II**. Variable-temperature ^{1}H NMR experiments, performed between 273 and 353 K, indicated the presence of a fluxional equilibrium between species **I** and **II**. On increasing the temperature the signals of species **II** collapsed into one signal set, attributed to the symmetric species **I** (Figure 2). At 333 K only one AB signal set for the CH_2Ph hydrogen atoms, centred at δ = 2.70 ppm, and only one singlet at δ = 7.83 ppm ($^{3}J_{Sn,H}$ = 16.20 Hz) for the imine hydrogen atoms (C*H*=N) were observed. Unfortunately, we were not able to measure the coupling constants ^{2}J(Sn–H) for the methylene H atoms CH_2Ph, and consequently to estimate the geometry of the benzyl ligands around the tin. We were unable to observe the coalescence temperature for the two species up to 373 K. The ^{119}Sn NMR spectrum, performed

at this temperature in C_6D_5Cl, still showed two resonances at –456.2 and –457.6 (in 1:0.45 ratio). We previously observed a fluxional equilibrium between two different isomeric species for the analogous bis[*N*-(3-*tert*-butylsalicylidene)anilinato]dimethyltin(IV) compound through NMR spectroscopy.[2] In that case two species (a C_2-symmetric one and a C_1-symmetric one) were frozen out at 195 K, while the coalescence temperature T_c was observed at 278 K in the ^{1}H NMR spectra and at 333 K in the ^{119}Sn NMR spectra. It is worth noting that the presence of bulkier benzyl ligands in compound **3** instead of methyl groups slows down the fluxional equilibrium, freezing out the isomers already at room temperature.[7]

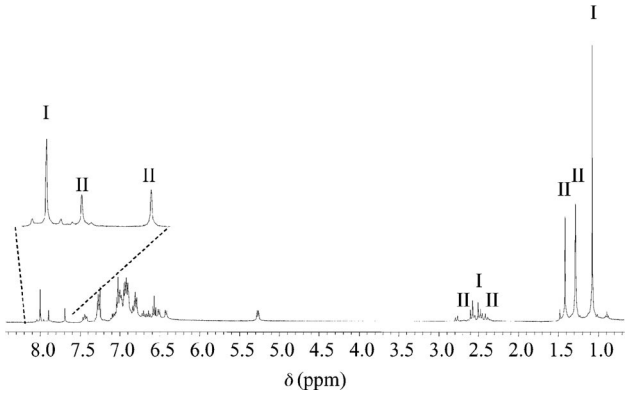


Figure 1. ^{1}H NMR spectrum ($CDCl_3$, 298 K) of compound **3**.

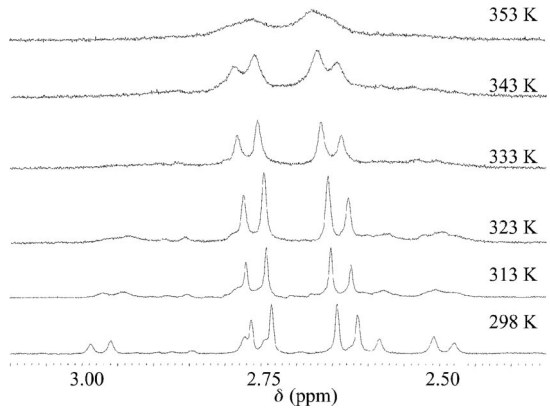


Figure 2. ^{1}H NMR spectra of aliphatic regions of compound **3** at variable temperature (ClC_6D_5).

X-ray Diffraction Analysis

Compound **2** was crystallized from methylene chloride/hexane at room temperature. Crystal data are given in the Experimental Section and selected bond lengths and angles are listed in Table 1. A distorted octahedral geometry with the alkyl group in a *trans* configuration and the two oxygen atoms in *trans* position was disclosed (Figure 3). The tin atom is located on a crystallographic inversion centre and the benzyl moieties coordinated in a η^1 mode. The six-atom ring Sn1–N1–C1–C2–C7–O1 is quite planar (rmsd 0.073) with an envelope angle (between the five-atom plane N1–C1–C2–C7–O1 and the Sn1–N1–C1 plane) of 9.39(14)°.

Table 1. Selected bond lengths [Å], bond angles and torsion angles [°] for compound **2**. Symmetry equivalent atoms are indicated with an asterisk.

Sn1–C14	2.165(3)	N1–C8	1.439(3)
Sn1–O1	2.142(2)	C1–C2	1.446(4)
Sn1–N1	2.339(2)	C2–C7	1.415(4)
N1–C1	1.292(3)	O1–C7	1.299(3)
C14–Sn1–O1	93.13(11)	C14–Sn1–N1	92.06(11)
C14*–Sn–O1	86.87(11)	C14*–Sn1–N1	87.93(11)
O1–Sn1–N1	82.90(8)	C14–Sn1–C14*	179.998(1)
O1–Sn1–N1*	97.11(8)	Sn1–C14–C15	116.87(19)
O1–Sn1–O1*	180.00	N1–Sn1–N1*	180.00
C1–N1–C8–C13	–49.9(4)		

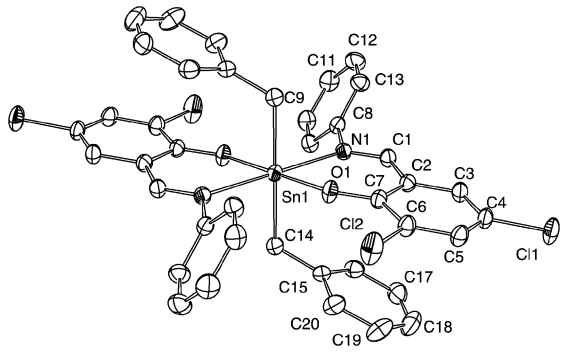


Figure 3. Molecular structure of compound **2**. Thermal ellipsoids are drawn at 30% probably level. Hydrogen atoms have been omitted for clarity.

It is worth noting that the analogous bis[*N*-(3-*tert*-butylsalicylidene)aniline]tin(IV) dialkyl complexes and the bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroaniline]tin(IV) dimethyl compound were crystallized in the *cis*-**I** isomeric structure, displaying the two oxygen atoms *trans* to each other and the alkyl ligands and the nitrogen atoms in a *cis* relationship.[2] Steric factors could explain the difference in the coordination environment at the central tin atom. The presence of chlorine atoms *ortho* to oxygen atoms of the phenoxy-imine ligand probably plays a role, and could favour ligand disposition in the plane.

Notably there are very few structurally characterized octahedral bis(phenoxy-imine)MR_2 compounds (M = any metal, R = alkyl or halogen atom) presenting the R ligands in a *trans* relationship.[8]

Generation of Cationic Species

The synthesis of free cationic species of group 14 elements is a tricky task, because of their high reactivity. In the literature, examples of organotin cations are quite rare. Among them are the remarkable crystal structures of Lambert et al.'s trismesityl stannylium cation displaying a trigonal planar geometry around tin,[9] Sekiguchi et al.'s "stable and free" tin cation bearing three tris(alkyl)silyl ligands[10] and Michl et al.'s tributylstannylium carboranate.[11] On the contrary, organotin cationic compounds stabilized by the

ligand's intramolecular interactions or by external donor atoms are well known and have also been structurally characterized.[12]

In previous work, in order to mimic the active species in homogeneous olefin polymerization catalysis, we pursued cationic species with the formula L_2SnR^+ (L = phenoxy-imine; R = alkyl). For this purpose we used ionizing reagents, such as $[(C_6H_5)NH(CH_3)_2]^+[B(C_6F_5)_4]^-$, $B(C_6F_5)_3$ and $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$, traditionally used in homogeneous Ziegler–Natta catalysis. The alkyl abstraction reaction from the dimethyl- and dibutyl-bis(phenoxyimine)tin(IV) compounds was successfully obtained by the carbenium salt $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$. Reactions with $[(C_6H_5)NH(CH_3)_2]^+[B(C_6F_5)_4]^-$ and $B(C_6F_5)_3$ led instead to degradation products. The obtained cationic species exhibited some activity in the oligomerization of ethylene under mild conditions, producing short-chain oligomers, with saturated end groups and methyl branches.[2] Now these studies have been extended to the new synthesized complexes, and are reported herein.

Reactions of complexes **1**–**3** with $[(C_6H_5)NH(CH_3)_2]^+[B(C_6F_5)_4]^-$ led to decomposition, producing free phenoxy-imine ligands.

Compounds **1** and **2**, bearing the chlorinated phenoxy-imine ligand, displayed similar reactivity toward ionizing agents. Actually, reaction with $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ resulted invariably in mixtures of decomposition products, while the reaction with $B(C_6F_5)_3$ produced the abstraction of an alkyl group. For instance, the reaction of compound **1** with 1 equiv. of $B(C_6F_5)_3$ rapidly produced a cationic species (**1a**) by methyl abstraction, as indicated by the presence in the ^{1}H NMR spectrum of a resonance at δ = 0.42 ppm attributable to the methyl group of the "free" anion $[CH_3B(C_6H_5)_3]$.[13] The ^{119}Sn NMR spectrum of species **1a** showed only one signal at –394.0 ppm. The pattern of signals in the ^{1}H NMR spectrum was compatible with the presence in solution of one symmetric species, having a ligand/methyl signals integral ratio consistent with a 2:1 formulation. According to the formation of a stannylium cation, all the resonances were downfield shifted, if compared with the corresponding resonances for the neutral compound **1** in the same condition. Characteristic resonances are the singlet at 1.042 ppm for $SnCH_3$ ($^2J_{SnH}$ = 101.8 Hz) and the singlet at δ = 8.54 ppm for the imine proton ($^3J_{SnH}$ = 22.3 Hz).[14]

Reaction of compound **2** with 1 equiv. of $B(C_6F_5)_3$ produced a new mono-benzyltin species (**2a**), characterized by a signal at –500.0 ppm in the ^{119}Sn NMR spectrum. In the ^{1}H NMR spectrum characteristic resonances are a singlet at δ = 3.28 ppm for $SnCH_2Ph$ ($^2J_{SnH}$ = 117.0 Hz) and a singlet at δ = 8.47 ppm due to imine proton ($^3J_{SnH}$ = 18.2 Hz). However, in the ^{1}H NMR spectrum of species **2a** the signals for the expected byproduct $[PhCH_2B(C_6F_5)_3]^-$ were absent. In addition, the ^{19}F NMR spectrum showed a large number of resonances of comparable intensity, clear indication of the existence of more than one fluorinated species in solution, probably generated by aryl/alkyl group exchange reactions.[15]

Compound **3** displayed a different behaviour from compounds **1** and **2**. Reaction of compound **3** with $B(C_6F_5)_3$ led to degradation, while reaction with 1 equiv. of $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ produced abstraction of one benzyl group and formation of the cationic species **3a**. Consistently, in the ^{1}H NMR spectrum (Figure 4), the species $PhCH_2C(C_6H_5)_3$ was identified as a byproduct.[16] In the ^{119}Sn NMR only one resonance at –448.7 ppm was observed. In the ^{1}H NMR spectrum, characteristic resonances are one singlet at δ = 1.34 ppm for the *tert*-butyl hydrogens, one singlet at δ = 3.27 ppm ($^2J_{SnH}$ = 118.84 Hz) for the methylene H atoms and one singlet at δ = 8.53 ppm ($^3J_{SnH}$ = 14.92 Hz) for the imine hydrogen C*H*=N. The signal pattern is compatible with the presence of one symmetric species in solution, and shifted at higher frequency, if compared with the corresponding resonance for the neutral compound **3** in the same solvent.

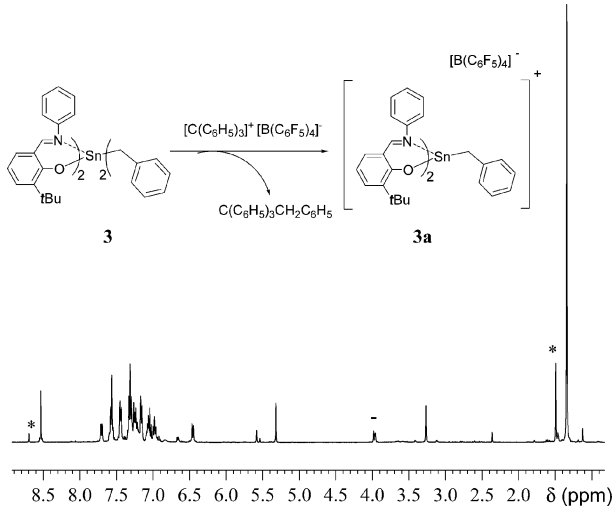


Figure 4. ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of compound **3a**: (*) "free" ligand impurities; (■) $C(C_6H_5)_3CH_2C_6H_5$.

The benzyl ligand can interact with electron-deficient metal centres also through the π-aromatic system. The η^n ($n > 1$) coordination is typical of transition metals;[17] among main group elements, η^3 interaction has been observed, in the solid state, for benzyl lithium.[18] Latesky et al. found NMR spectroscopic evidence to detect this type of interaction in solution.[19] In particular, η^n benzyl ligands are characterized by a high-field shift for the *ortho* hydrogen resonance ($\delta < 6.8$ ppm) in the ^{1}H NMR, and by large $^1J_{CH}$ values for the CH_2 group ($J > 130$ Hz). The increase of the coupling constant can be explained with an increased "sp^2" character of the α-carbon, involving a decrease of the Mt–C–Ph angle. Interestingly, in the NMR spectra of cationic species **3a** we observed an upfield shift of the *ortho* benzyl hydrogens' resonance (δ = 6.44 ppm), and a $^1J_{CH}$ value for the methylene carbon of 139.8 Hz. The value observed is higher than that observed in tetrabenzyltin ($^1J_{CH}$ = 133 Hz), usually taken as a model for a normal σ bond (η^1) benzyl ligand.[20] These spectroscopic features thus suggest that in the cationic species **3a** the benzyl ligand interacts with the tin also through the π-aromatic system. Therefore

a η^n ($n > 1$) coordination for the benzyl ligand can be hypothesized.

In order to study the influence of the temperature on the coordination of the benzyl to the tin atoms, ^{1}H NMR spectra were recorded at lower temperature (between 278 K and 193 K). The aliphatic regions of the ^{1}H NMR spectra for the cationic species **3a** are shown in Figure 5. On decreasing the temperature, the singlet of the methylene hydrogen atoms SnCH_2Ph split up into an AB pattern, indicating that they are diastereotopic. At 233 K the doublet attributable to the *ortho* benzyl hydrogen atoms at δ = 6.44 ppm showed satellite peaks due to the tin–hydrogen spin–spin coupling with J_{SnH} of 33.7 Hz. Similar NMR control experiments performed for the tetrabenzyltin compound at 233 K displayed a singlet for the methylene hydrogen atoms SnCH_2Ph at δ = 2.16 ppm ($^1J_{CH}$ = 132.6 Hz) and a doublet for the *ortho* benzyl hydrogen atoms at δ = 6.60 ppm with a J_{SnH} of 14.9 Hz.

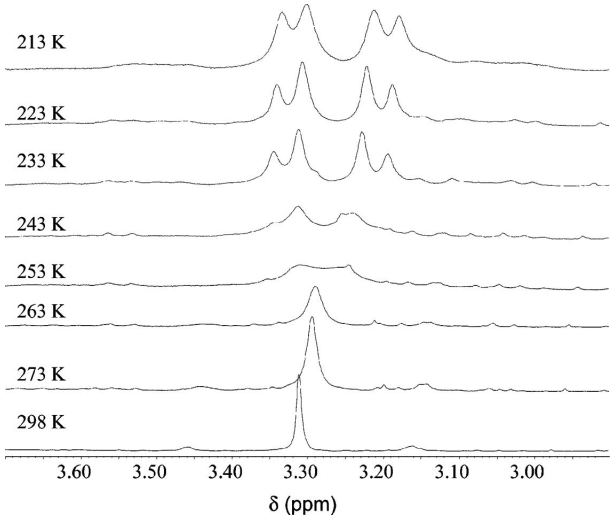


Figure 5. ^{1}H NMR spectra of aliphatic region of compound **3a** at variable temperature (CD_2Cl_2).

In conclusion, these observations (i.e., the AB pattern for the methylene hydrogen atoms and the unusually high value of J_{SnH} for the *ortho* benzyl hydrogen atoms) support the hypothesis that η^n coordination of the benzyl to tin is fluxional (probably through a suprafacial metal shifting) and slows down at low temperature.

It is worth nothing that the cationic species **1a** and **2a** displayed an upfield shift for the ^{119}Sn NMR signals in comparison with the resonances of the corresponding neutral compounds **1** and **2**. A similar behaviour was previously observed for the analogous bis[*N*-(3-*tert*-butylsalicylidene)anilinato]dimethyltin(IV) compound.[2] On the contrary, the ^{119}Sn NMR resonance for **3a** displayed a downfield shift (about 10 ppm) in comparison with the resonance of the corresponding neutral compound **3**. This peculiar feature could be attributed to the different coordination sphere, because of the presence in **3a** of the intramolecular coordination of the benzyl aromatic ring.

A π interaction of the benzyl group to the tin centre was previously recognized by NMR for the cationic species Tip_2SnBz^+ (Tip = 2,4,6-triisopropylphenyl).[21]

Reactivity Toward Ethylene

We disclosed that the ethylene oligomerization reaction is promoted by dimethyl- and dibutyl-bis(phenoxy-imine)-tin(IV) complexes, activated by the carbenium salt.[2] The obtained oligoethylene oily product had short chains, with saturated end groups and methyl branches. This result constituted the first example of oligomerization of ethylene by a group 14 compound, and prompted us to investigate the reactivity of different bis(phenoxy-imine)tin(IV) complexes toward ethylene.

Compound **3** in combination with $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ and compounds **1** or **2** in combination with $B(C_6F_5)_3$ were able to oligomerize ethylene under mild conditions, affording short-chain oligomers (40–60 carbon atoms, estimated by NMR), with saturated end groups and methyl branches. The activities were always very low, and comparable with those observed with previously reported compounds.[2] These results suggest that the structural and electronic properties of the salicylidene-aniline ligands, while influencing the structure of the complexes and their reactivity toward ionizing agents, do not control the ethylene oligomerization activity, at least in the presence of the used catalysts, and under the explored experimental conditions.

Chain end-group analysis was used as a tool to understand the initiation and termination steps of the oligomerization mechanism. Actually, the initiation step is not the olefin insertion into the Sn–alkyl bond. In fact, the obtained oligomers always had saturated *n*-propyl end groups, even when the oligomerization tests were performed in the presence of compounds **2** and **3**, for which a benzyl end group would have been expected on the basis of the ethylene insertion in the Sn–CH_2Ph bond. Moreover, the absence of unsaturated end groups in all the sample indicated that the β-hydrogen elimination mechanism is not involved in the termination step.

In order to gain deeper insight into the termination step, some oligomerization runs were quenched with CH_3OD. Incorporation of deuterium was not observed; therefore the main termination step is not the hydrolysis of the metal–(growing chain) bond.

End-group NMR analysis and deuteriolysis experiments therefore seem to exclude the migratory-insertion mechanism typical of Ziegler–Natta polymerization catalysis.

In order to establish if a different mechanism could be involved in the formation of branched oligoethylenes, further oligomerization tests were performed in the presence of radical additive and proton-trapping agents. The yields and nature of the products were unaffected by the presence of the radical initiators (dicumyl peroxide, dibenzoyl peroxide) or of the radical inhibitor 2,2,6,6-tetramethylpiperidine *N*-oxide. Analogously, the presence of the proton-trapping

2,6-di-*tert*-butylpyridine did not have an effect on the oligomerization results.

While the insertion mechanism can be definitely excluded, at the moment a conclusive answer on the origin of the branched oligoethylenes cannot be given.

Conclusions

Three new octahedral bis(phenoxy-imine)tin(IV)dialkyl complexes have been synthesized and fully characterized by ^{1}H, ^{13}C and ^{119}Sn NMR and mass spectroscopy. Single-crystal X-ray analysis was obtained for compound **2**, showing an octahedral geometry with alkyl groups in *trans* relationship. Compounds **1** and **2** reacted with $B(C_6F_5)_3$ by alkyl abstraction producing cationic species, identified by NMR spectroscopy. For complex **3**, bearing the *N*-(3-*tert*-butylsalicylidene)aniline ligands, cationic species were instead obtained by reaction with $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$. Interestingly, in this latter species η^n coordination of the benzyl group with the metal centre was recognized by NMR study. The obtained cationic species promoted ethylene oligomerization under mild conditions. Mechanistic studies, based on chain end-group NMR analysis and deuteriolysis experiments, excluded a migratory-insertion mechanism typical of Ziegler–Natta olefin polymerization catalysis.

Experimental Section

General Procedure: Manipulation of sensitive materials was carried out under nitrogen using Schlenk or glove-box techniques. Hexane, tetrahydrofuran (THF) and toluene were refluxed over sodium/benzophenone, dichloromethane over calcium hydride, then distilled under nitrogen prior to use. $CDCl_3$, CD_2Cl_2 and ClC_6D_5 were dried with CaH_2 and distilled prior to use. $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ was purchased from Boulder SPA Company and $B(C_6F_5)_3$ from Strem Chemicals. $Cl_2Sn(CH_2C_6H_5)_2$ was synthesized according to the literature.[20] The phenoxy-imine ligands *N*-(3-*tert*-butylsalicylidene)aniline[3] and *N*-(3,5dichlorosalicylidene)aniline[4] were synthesized according to literature procedures. NMR spectra were recorded with a Bruker Advanced 400 MHz spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{119}Sn, 149 MHz; ^{19}F, 376 MHz). The ^{119}Sn NMR were measured relative to $Sn(CH_3)_4$. EI-MS data were obtained with a Finnigan Thermoquest GCQ Plus 200 spectrometer using a direct insertion probe. Elemental analyses were recorded with a Thermo Finnigan Flash EA 1112 series C,H,N,S Analyzer.

Synthesis of Bis[*N*-(3,5-dichlorosalicylidene)anilinato]dimethyltin-(IV) (1): A solution of *N*-(3,5-dichlorosalicylidene)aniline (1.4 g, 5.26 mmol, in 60 mL of THF) was added dropwise to a stirred solution of NaH (252 mg, 10 mmol) in THF (10 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 3 h. The resulting light yellow solution was added to a stirred solution of $Cl_2Sn(CH_3)_2$ (577 mg, 2.63 mmol) in 20 mL of THF at 0 °C. The mixture was warmed to room temperature and stirred overnight. Removal of the solvent in vacuo gave a brown powder. The crude product was extracted with toluene; the solution was concentrated to 15 mL and stored at –20 °C. An orange solid deposited overnight (1.6 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.01 (s, $^{3}J_{SnH}$ = 12.1 Hz, 2 H, N=C*H*) 6.90–7.34 (m, 14 H, Ar*H*), 0.79 (s, $^{2}J_{SnH}$ = 90.7 Hz, 6 H, SnCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 164.8 (N=*C*H), 159.2, 150.2, 134.2, 132.2, 129.9, 129.1, 127.0, 122.8, 121.6, 120.8 (Ar-*C*), 8.7 (Sn-CH_3) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 25 °C): δ = –306.5 (s) ppm. EI-MS: *m*/*z* (%) 664 (10) [$M^+ - CH_3$], 649 (27), 614 (33), 413 (100). $C_{28}H_{22}Cl_4N_2O_2Sn$ (679.014): calcd. C 49.52, H 3.26, N 4.12; found C 49.98, H 3.31, N 3.99.

Synthesis of Bis[*N*-(3,5-dichlorosalicylidene)anilinato]dibenzyltin-(IV) (2): This compound was prepared as illustrated above, but using $Cl_2Sn(CH_2C_6H_5)_2$ (768 mg, 2.06 mmol in 20 mL of dry THF), 1.1 g of *N*-(3,5-dichlorosalicylidene)aniline (4.13 mmol in 50 mL of dry THF) and 150 mg of NaH (2.06 mmol) (yield 1.55 g, 43%). Yellow crystals, suitable for single-crystal X-ray diffraction analysis were grown from dichloromethane/hexane at room temperature. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 7.84 (br. s, 2 H, N=C*H*), 6.78–7.35 (m, 24 H, Ar*H*), 2.56 (br. s, $^{2}J_{SnH}$ = 105.1 Hz, 4 H, CH_2Ph) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 169.07 (N=*C*H), 119.6–150.4 (Ar-*C*), 37.5 (Sn-CH_2Ph) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 25 °C): δ = –425.6 (s), –426.9 (s) ppm. EI-MS: *m*/*z* (%) 740 (35) [$M^+ - CH_2Ph$], 565 (43), 530 (100). $C_{40}H_{30}Cl_4N_2O_2Sn$ (831.209): calcd. C 57.8, H 3.63, N 3.37; found C 60.05, H 3.70, N 3.45.

Synthesis of Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]dibenzyltin(IV) (3): A solution of *N*-(3-*tert*-butylsalicylidene)aniline (1.34 g, 5.28 mmol in 50 mL of THF) was added dropwise to a stirred solution of NaH (270 mg, 11.4 mmol) in THF (10 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 3 h. The resulting light orange solution was added to a stirred solution of $Cl_2Sn(CH_2C_6H_5)_2$ (980 mg, 2.64 mmol) in THF (20 mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight. Removal of the solvent in vacuo gave a brown powder. The crude product was extracted with toluene; the solution was concentrated to 10 mL and stored at –20 °C. A yellow solid deposited overnight (1.55 g, 73%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 7.99 (s, $^{3}J_{SnH}$ = 33.65 Hz, 2 H, N=C*H*), 7.89 (s, $^{3}J_{SnH}$ = 22.30 Hz, 1 H, N=C*H*), 7.69 (s, 1 H, N=C*H*), 5.25–7.27 (br. m, 32 H, Ar*H*), 2.4–2.7 (3dd, 8 H, CH_2Ph), 1.41 (s, 9 H, *t*Bu), 1.28 (s, 9 H, *t*Bu), 1.07 (s, 18 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 174.3, 172.0, 169.0 (N=*C*H), 152.5–115.3 (Ar-*C*), 35.3, 35.1 (*C*-CH_3), 36.1, 34.8, 33.8 (Sn-CH_2Ph), 30.0, 29.6, 29.5 (C-CH_3) ppm. ^{119}Sn NMR (149 MHz, $CDCl_3$, 25 °C): δ = –456.5 (s), –457.9 (s) ppm. EI-MS: *m*/*z* (%) 714 (12) [$M^+ - CH_2Ph$], 683 (20), 460 (48), 343 (100). $C_{48}H_{50}N_2O_2Sn$ (805.64): calcd. C 71.56, H 6.25, N 3.47; found C 71.69, H 6.34, N 3.52.

Generation of {Bis[*N*-(3,5-dichlorosalicylidene)anilinato]methyltin(IV)}$^+$ [MeB$(C_6F_5)_3]^-$ (1a): Compound **1** (15 mg, 22 μmol) was dissolved in dry CD_2Cl_2 (0.5 mL). $B(C_6F_5)_3$ (11 mg, 22 μmol) was added to the yellow solution. The solution was analyzed by NMR spectroscopy at room temperature. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 8.54 (s, $^{3}J_{SnH}$ = 22.3 Hz, 2 H, N=C*H*), 6.9–7.7 (br. m, 14 H, Ar*H*), 1.04 (s, $^{2}J_{SnH}$ = 101.8 Hz, 3 H, Sn-CH_3), 0.42 (br. s, 3 H, -BCH_3) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 171.8 (N=*C*H), 119–150 (Ar*C*), 10.8 (BCH_3^-), 3.73 (Sn-CH_3) ppm. ^{119}Sn NMR (149 MHz, CD_2Cl_2, 25 °C): δ = –394.0 (s) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ = –168.2 (t, 2 F, *m*-F), –165.6 (t, 1 F, *p*-F), –133.6 (d, 2 F, *o*-F) ppm. The side-product $Sn(CH_3)_4$ was also identified.

Generation of {Bis[*N*-(3,5-dichlorosalicylidene)anilinato]benzyltin(IV)}$^+$ (2a): Compound **2** (15 mg, 18 μmol) was dissolved in dry CD_2Cl_2 (0.5 mL). $B(C_6F_5)_3$ (9 mg, 18 μmol) was added to the yellow solution. The resulting solution was analyzed by NMR spectroscopy at room temperature. Selected resonances ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 1.04 (s, $^{2}J_{SnH}$ = 117.0 Hz, 2 H, Sn-

CH_2Ph), 6.5–7.7 (br. m, 14 H, Ar*H*), 8.47 (s, $^3J_{SnH}$ = 18.2 Hz, 2 H, N=C*H*) ppm. ^{119}Sn NMR (149 MHz, CD_2Cl_2, 25 °C): δ = –500.0 (s) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ = –169 to –123.6 ppm.

Generation of {Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]benzyltin(IV)}$^+$ [B(C$_6$F$_5$)$_4$]$^-$ (3a): $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ (25 mg, 27 μmol) was added to a yellow solution of compound **3** (22 mg, 27 μmol) in dry CD_2Cl_2 (0.5 mL). The resulting brown solution was analyzed by NMR spectroscopy at room temperature. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 8.53 (s, $^3J_{SnH}$ = 14.92 Hz, 2 H, N=C*H*), 6.9–7.6 (br. m, 19 H, Ar*H*), 6.44 [d, $^4J_{SnH}$ = 33.75 Hz, 2 H, *o*-$CH_2(C_6H_5)$], 3.26 (s, $^2J_{SnH}$ = 118.84 Hz, 2 H, Sn-CH_2Ph), 1.34 (s, 18 H, *t*Bu) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 174.0 (N=*C*H), 124.2 [*o*-$CH_2(C_6H_5)$], 35.5 (*C*-CH_3), 32.0 (Sn-*C*H$_2$Ph), 29.8 (C-*C*H$_3$) ppm. ^{119}Sn NMR (149 MHz, CD_2Cl_2, 25 °C): δ = –448.7 (s) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ = –168.0 (t, 2 F, *m*-F), –164.1 (t, 1 F, *p*-F), –133.6 (d, 2 F, *o*-F) ppm. $(C_6H_5)_3CH$ and $(C_6H_5)_3CCH_2Ph$ were also identified as side-products.

Oligomerization Tests: A typical oligomerization test was carried out in a 100-mL, magnetically stirred, glass flask, which was conditioned under dynamic vacuum, thermostated at 25 °C and then charged with a solution of the tin compound (30 μmol) and $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ or $B(C_6F_5)_3$ (30 μmol) in ClC_6H_5 or $CH_3C_6H_5$ (15 mL). Ethylene was fed continuously at a pressure of 1 atm; after 24 h, the reaction mixture was poured into acidified methanol (50 mL). The solution was treated with water and hexane (3 × 30 mL). The organic phase was dried with Na_2SO_4 and the solvents distilled off. An oily product was obtained; typically yields are of 200 mg. The products were analyzed by ^{13}C NMR analysis; the oligomer structure was determined according to the literature.[22]

Additional oligomerization tests were performed as above, but adding into the oligomerization mixture 1 equiv. of one of the following compounds: 2,2,6,6-tetramethylpiperidine *N*-oxide, 2,6-di-*tert*-butylpyridine, dicumyl peroxide or dibenzoyl peroxide. Yields and products were unaffected by the presence of the additives. The products were analyzed by ^{1}H and ^{13}C NMR analysis; the oligomer structures were determined according to the literature.[22]

Oligomerization Quenched with CH_3OD: An oligomerization run was performed as described above, but at the end of the reaction time (24 h), a solution of CF_3COOD (2 mL) and CH_3OD (4 mL) was added to the reaction mixture. After two hours, the mixture was poured into methanol (50 mL). The solution was treated with water and hexane (3 × 30 mL). The organic phase was dried on Na_2SO_4 and the solvents stilled off. An oily product was obtained (yield: 130 mg). The product was analyzed by ^{13}C, ^{1}H, ^{2}H NMR spectroscopy. Incorporation of deuterium into the oligomers was not detected.

X-ray Crystallography. Crystal Data for 2: Formula: $C_{40}H_{30}Cl_4N_2O_2Sn$, FW = 831.15, triclinic, space group $P\bar{1}$ (no. 2), Z = 1, a = 9.429(4) Å, b = 12.030(5) Å, c = 8.630(3) Å, α = 90.11(3)°, β = 99.52(3)°, γ = 113.04(3)°, V = 886.0(7) Å^3, D_{calcd} = 1.558 g cm^{-3}, μ_{calcd} = 1.062 mm^{-1}.

Suitable crystals of **2** were selected and mounted in Lindemann capillaries under an inert atmosphere. Diffraction data were measured at room temperature with a Rigaku AFC7S diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). Data reduction was performed with the crystallographic package CrystalStructure.[23] The structure was solved by direct methods using the program SIR92[24] and refined by means of full-matrix least-squares based on F^2 using the program SHELXL97.[25] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and included in structure factor calculations but not refined.

A total of 223 refinable parameters were finally considered. Maximum and minimum residual density were respectively 1.20 e Å^{-3} and –0.89 e Å^{-3}. Final disagreement indices: R_1 = 0.037 for 4476 reflections with $F_o > 4\sigma(F_o)$, wR_2 = 0.091 for all 5170 data. Atomic coordinates, thermal factors, bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre (see below). ORTEP drawings were performed by means of the program ORTEP32.[26]

CCDC-641608 contains the supplementary crystallographic data (excluding structure factors) for compound **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif/.

Supporting Information (see also the footnote on the first page of this article): NMR characterization of compounds **1**, **2**, **3**, **1a**, **2a**, **3a** and of the ethylene oligomerization products.

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