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Octahedral Bis(phenoxy-imine)tin(IV) Alkyl Complexes: Synthesis, Characterization, and Reactivity toward Ionizing Species and Ethylene

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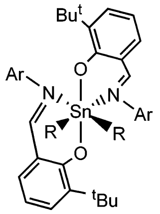
The synthesis of new organotin compounds of the general formula L_2SnR_2 (L = *N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroaniline; R = CH_3 (**1**), *n*-C_4H_9 (**3**)) and L'_2SnR_2 (L′ = *N*-(3-*tert*-butylsalicylidene)aniline; R = CH_3 (**2**), *n*-C_4H_9 (**4**)) is described herein. The compounds were characterized by ^{1}H, ^{13}C, and ^{119}Sn NMR in solution; in some cases a fluxional behavior was observed by variable-temperature experiments. Characterization by single-crystal X-ray diffraction analysis has been obtained for compounds **1**, **2**, and **4**. The reactivity of the synthesized compounds toward ionizing agents was studied by an NMR-tube reaction. Compounds **2** and **4** underwent an alkyl abstraction reaction with the carbenium salt $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$. 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.

Introduction

The field of olefin polymerization catalysis has experienced a great momentum in the past few years, with many new catalyst systems being reported across and also beyond the transition series.[1] Actually, the polymerization of ethylene has been achieved in the presence of transition-metal-free homogeneous Al catalysts, albeit with low activity.[2] In this regard, for instance, we recently described new neutral and cationic salicylaldiminato[3] and 2-anilinotroponato[4] aluminum alkyl complexes and investigated their ethylene polymerization activity.

To our knowledge, however, no examples have been reported in the literature concerning the activity in olefin polymerization of compounds based on metals beyond group 13. In this regard, bearing in mind the similarities between titanium and tin,[5] we thought to explore this potentiality. In general, olefin polymerization catalytic precursors consist of a metal center, bearing ancillary ligand(s) and two alkyl groups located in mutually cis positions; the active species are obtained from the precursors by reactions with suitable ionizing agents. Following the recent results in olefin polymerization with bis(phenoxy-imine) group 4 transition-metal catalysts,[6] our first goal was the synthesis of analogous bis(phenoxy-imine)tin complexes carrying two alkyl groups in cis positions.

Chart 1



1 Ar = C_6F_5 R = CH_3
2 Ar = C_6H_5 R = CH_3
3 Ar = C_6F_5 R = *n*-C_4H_9
4 Ar = C_6H_5 R = *n*-C_4H_9

Although the tetradentate Schiff base Salen ligands have been largely used for the preparation of several complexes of group 14,[7] no reports concerning related bis(salicylaldiminato)tin(IV) compounds have appeared in the literature. Murray et al. described the formation of a 1:2 adduct of tin tetrachloride with *N*-*p*-tolylsalicylaldimine; attempts to deprotonate the Schiff base with triethylamine were unsuccessful.[8] Using a metathesis reaction approach, however, we succeeded in the preparation of new octahedral organotin compounds of the general formula L_2SnR_2 (L = phenoxy-imine; R = alkyl) (Chart 1). In this paper we report on their synthesis and structural characterization and some

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(2) See ref 1 and references therein.

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(6) (a) Tian, J.; Hustad, D.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 5134−5135. (b) Saito, J.; Mitani, M.; Mohri, J.; Ishii, S.; Yoshida, Y.; Matsugi, T.; Kojoh, S.; Kashiwa, N.; Fujita, T. *Chem. Lett.* **2001**, 576−577.

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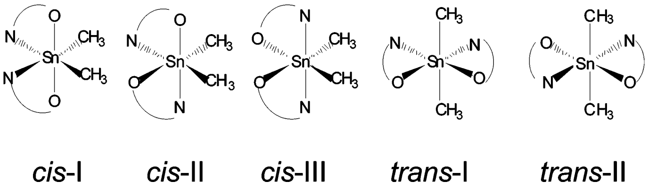
(8) Van den Bergen, A.; Cozens, R. J.; Murray, K. S. *J. Chem. Soc. A* **1970**, 3060−3064.

10.1021/om0491084 CCC: $30.25

Chart 2



preliminary data on their reactivity with ion-generating activators and toward ethylene.

Results and Discussion

Synthesis of the Complexes. The bis(phenoxy-imine)tin complexes were prepared via metathesis reaction of the sodium salt of the ligand with the corresponding dialkyltin(IV) chloride in rigorously dry tetrahydrofurane solvent. Reaction proceeds cleanly with good yields, producing compounds **1**−**4** as yellow or orange solids. The products are very stable as solids in an inert atmosphere, but easily underwent hydrolysis reaction with formation of the free ligand in the presence of traces of adventitious water.

NMR Characterization of the Complexes. Compounds **1**−**4** were characterized via ^{1}H, ^{13}C, and ^{119}Sn NMR in solution, exhibiting interesting spectroscopic features.

Compound **1** showed a clear ^{1}H NMR spectrum in $CDCl_3$ at room temperature, with very sharp peaks: one signal for the $SnCH_3$ protons at 0.37 ppm, one singlet for the ^{t}Bu protons at 1.16 ppm, one signal for the iminic proton at 8.06 ppm, and finally two doublets and one triplet in the aromatic region, accounting for the remaining Ar H protons, were observed. The ^{13}C NMR spectrum coherently displayed only one signal for the methyl groups bound to Sn and only one signal for the methyl groups of the ^{t}Bu substituents on the aromatic rings. The ^{119}Sn NMR spectrum showed one signal at −309 ppm, thus indicating the existence of a single tin species in solution. Additional information came from the observations of the proton−tin and carbon−tin coupling constants. For the iminic protons a ^{3}J(Sn−H) value of 15.9 Hz was measured, thus indicating the coordination of the nitrogen atoms to tin. This picture is compatible with a highly symmetric structure in solution. It is worth noting that for octahedral bis(phenoxy-imine) dialkyl complexes five isomers are possible, as displayed in Chart 2. On the basis of the ^{1}H and ^{13}C NMR signal patterns, the C_1-symmetric structure *cis*-II can be definitely ruled out. According to the equations developed by Lockhart[9] and by Nelson,[10] the coupling constants $^{2}J(^{119}\text{Sn}-^{1}\text{H})$ and $^{1}J(^{119}\text{Sn}-^{13}\text{C})$ can be used to estimate the methyl−tin−methyl angle. In our case the methyl groups bound to Sn exhibited a $^{2}J(^{119}\text{Sn}-^{1}\text{H})$ value of 67.1 Hz; using the equation specifically developed by Nelson for octahedral dialkyltin complexes,[10] the calculated angle for C−Sn−C is 106(6)°, in the expected range for a structure with the methyl groups in a cis configuration. Therefore, the "*trans*-I" and "*trans*-II" isomeric forms of Chart 2 can be also excluded, the two possible isomers in solution remaining *cis*-I and *cis*-III.

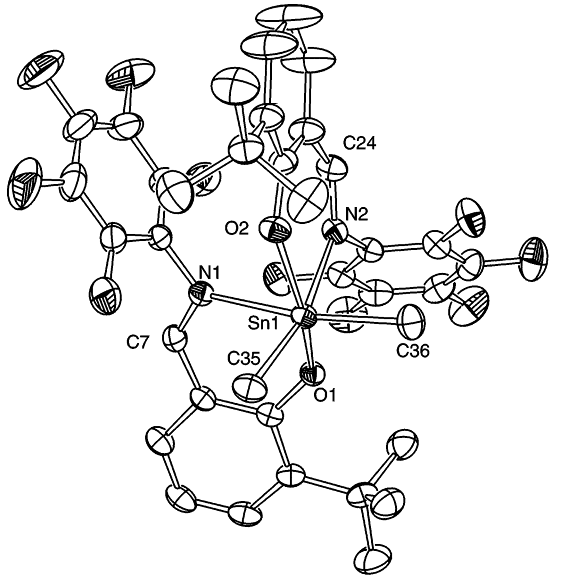


Figure 1. ORTEP diagram of compound **1**. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at the 30% probability level.

The structure was finally elucidated by single-crystal X-ray analysis (Figure 1; vide infra), showing an octahedral arrangement around the tin atom, with the methyl groups in a cis configuration (angle C−Sn−C = 107.4°), and the oxygen atoms in trans positions.

The tin methyl compound **2**, bearing the nonfluorinated *N*-(3-*tert*-butylsalicylidene)aniline ligand, showed, at variance with compound **1**, very broad ^{1}H NMR signals. In addition, in the ^{119}Sn NMR spectrum two broad signals at −352.8 and −342.7 ppm were observed. These observations suggested the existence of different tin species in dynamic equilibrium in solution at room temperature and prompted us to explore the behavior of the compound at lower temperatures. Consequently, several ^{1}H and ^{119}Sn NMR spectra were recorded between 25 and −85 °C in CD_2Cl_2 solution. Upon a temperature decrease, the two resonances in the ^{119}Sn NMR spectra become sharper; at −85 °C the relative ratio is about 3:2.[11] More information came from the ^{1}H NMR spectra (Figure 2); actually, upon lowering the temperature, the broad signals split up. At −85 °C the ^{1}H NMR spectrum of compound **2** exhibited two sets of signals, attributable to two different isomeric species, a C_2-symmetric one and a C_1-symmetric one, respectively, in about a 3:2 ratio. Diagnostic signals for the C_2-symmetric isomer are the singlet relative to the Sn−CH_3 groups (6H, ^{2}J(Sn−H) = 68.12 Hz) at 0.16 ppm, the *t*Bu singlet (18 H) at 0.97 ppm, and the CH═N singlet at 8.11 ppm (^{3}J(Sn−H) = 30.8 Hz). According to the Nelson equation,[10] the measured ^{2}J(Sn−H) value is compatible with a structure showing the methyl groups bound to Sn in mutually cis positions.

For the C_1-symmetric isomer, instead, we observed two signals belonging to the Sn−CH_3 groups, respectively, at 0.33 ppm (3H, ^{2}J(Sn−H) = 65.5 Hz) and −0.21 ppm (3H, ^{2}J(Sn−H) = 65.9 Hz) and two signals (over-

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[9] (a) Lockhart, T. P.; Manders, W. F.; Schlemper, E. O. *J. Am. Chem. Soc.* **1985**, *107*, 7. (b) Lockhart, T. P.; Manders, W. F. *Inorg. Chem.* **1985**, *25*, 892−895.

[10] Howard, W. F.; Crecely, R. W.; Nelson, W. H. *Inorg. Chem.* **1985**, *24*, 2204−2208.

[11] In the ^{119}Sn NMR spectrum at −85 °C a minor resonance at −368 ppm was also detected, but it accounts for less than 5%.

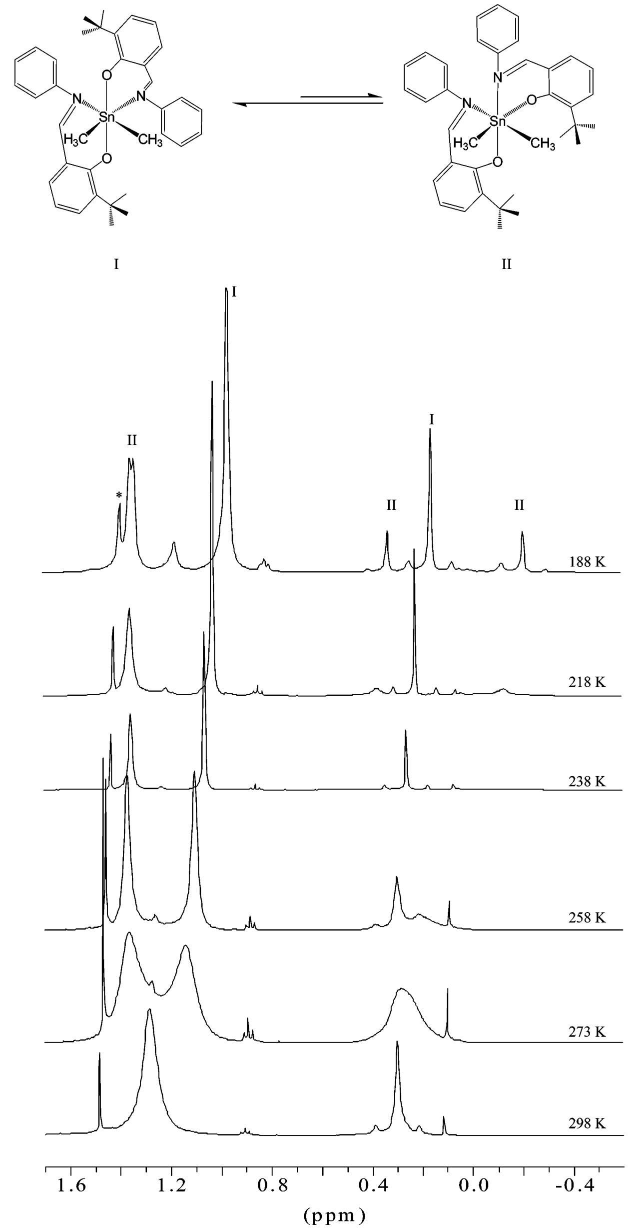

Figure 2. ^1H NMR spectra in the aliphatic regions of compounds **2** at variable temperature (CD_2Cl_2).

lapped, 18 H) for the *t*Bu groups at 1.35 and 1.34 ppm. The resonances for the CH=N hydrogen atoms, instead, at −85 °C still appear as a broad singlet and account for two hydrogen atoms. Several ^1H NMR experiments were also performed between 25 and 60 °C: when the temperature is increased, the signals sharpen, indicating a faster equilibrium between the C_2 and the C_1 species.

The equilibrium between the two isomers does not seem to be concentration dependent: integration of ^{119}Sn NMR signals measured at different concentrations (0.3 and 0.05 M) gave identical results.

For compound **2**, crystals suitable for an X-ray crystal structure determination were grown from hexane at −20 °C and displayed a distorted-octahedral geometry with the alkyl group in a cis configuration and the two oxygen atoms in trans positions.

The tin dibutyl compounds **3** and **4** displayed NMR behavior similar to that of the corresponding dimethyl compounds (**1** and **2**). Compound **3**, bearing the fluorinated phenoxyimine ligand, displayed at room temperature a single ^{119}Sn NMR resonance at −337.4 ppm and clean ^1H and ^{13}C NMR spectra, compatible with the existence, in solution, of a single C_2-symmetric species. As in the case of the previously analyzed compounds, the CH=N hydrogen atoms appear as a singlet at 8.02 ppm, accounting for two H, with a $^3J(Sn-H)$ value of 14.3 Hz, thus indicating the coordination of the N atoms to the tin center.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1, 2, and 4

	1	2	4
Sn−N1	2.397(3)	2.349(3)	2.378(4)
Sn−N2	2.366(3)	2.386(3)	2.373(4)
Sn−O1	2.083(2)	2.086(2)	2.092(3)
Sn−O2	2.077(2)	2.080(2)	2.086(3)
Sn−C35	2.124(3)	2.143(4)	2.157(5)
Sn−C36/C39	2.137(4)	2.144(4)	2.156(4)
N1−C1/C7	1.291(4)	1.291(4)	1.288(6)
N2−C18/C24	1.294(4)	1.289(4)	1.290(6)
N1−C12/C8	1.429(4)	1.436(3)	1.440(5)
N2−C29/C25	1.428(4)	1.441(4)	1.439(6)
C1−C2/C7−C6	1.434(4)	1.438(4)	1.431(6)
C18−C19/C23−C24	1.430(5)	1.443(4)	1.431(6)
N1−Sn−N2	78.06(9)	79.89(9)	80.03(13)
O1−Sn−O2	155.71(9)	161.24(9)	159.06(12)
C35−Sn−C36/C39	107.39(15)	108.79(15)	111.1(2)

The tin dibutyl compound **4**, instead, displayed at room temperature two resonances in the ^{119}Sn NMR spectrum and very broad signals in the ^1H NMR spectrum. As observed for compound **2**, variable-temperature ^1H NMR experiments evidenced the presence of at least two isomeric species, in fluxional equilibrium, while a single-crystal X-ray structure determination revealed that compound **4** crystallizes in the C_2-symmetric form *cis*-I.

X-ray Diffraction Analysis. Suitable crystals for X-ray analysis were obtained from hexane at −20 °C for compounds **1**, **2**, and **4**. The three compounds have a similar molecular structure, displaying a distorted-octahedral geometry; the two oxygen atoms are trans to each other, while the alkyl ligands and the nitrogen atoms are in a cis relationship. Selected bond lengths and angles are listed in Table 1. Notably, the O1−Sn−O2 angle deviates substantially from 180° and the largest deviation is observed in compound **1** (155.71(9)°). This means that in compound **1** the Sn atom is more exposed away from the ligand coordination sphere. The same deviation effect can be observed for the analogous bis(phenoxy-imine)titanium complexes; in particular the angle O1−Ti−O2 is significantly smaller if the N-aryl group is perfluorinated.[12]

To determine if the *cis*-I isomeric structure belonged merely to the particular analyzed crystals or, rather, to all the crude solids, an X-ray powder diffraction analysis was performed on a sample of compound **4**. The Rietveld analysis, based on the single-crystal X-ray structure of compound **4**, disclosed the same structure also for the powder sample, thus indicating the existence of a single isomer in the solid state.

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(12) Cf.: (a) Mitani, M.; Mohri, J.; Yoshida, Y.; Saito, J.; Ishii, S.; Tsuru, K.; Matsui, S.; Furuyama, R.; Nakano, T.; Tanaka, H.; Kojoh, S.; Matsugi, T.; Kashiwa, N.; Fujita, T. *J. Am. Chem. Soc.* **2002**, *124*, 3327−3336. (b) Makio, H.; Kashiwa, N.; Fujita, T. *Adv. Synth. Catal.* **2002**, *344*, 477−493. (c) Tohi, Y.; Makio, H.; Matsui, S.; Onda, M.; Fujta, T. *Macromolecules* **2003**, *36*, 523−525 and references therein.

Similar results were obtained by Coates for analogous bis(phenoxy-imine)titanium compounds: while X-ray data always indicated a C_2-symmetric structure in the solid state, in some cases both C_2- and C_1-symmetric isomers were observed in solution by NMR analysis. The factors influencing the C_2/C_1 ratio were not fully understood, but it was observed that C_1 species were disfavored by the presence of fluorine substituents at the ortho position of the N-aryl rings.[13] These observations nicely agree with our experimental results concerning the closely related tin compounds. We have not explored the mechanism responsible for the isomerization in solution, but it probably operates via a nitrogen dissociation mechanism, as hypothesized for related bis(phenoxy-imine) group 4 transition-metal compounds.[12c]

Generation of Cationic Species and Their Reactivity toward Ethylene. The search for free cations of heavier group 14 elements has recently achieved important results. Lambert et al., for instance, reported the crystal structure of a remarkable triphenylstannylium cation displaying a trigonal-planar geometry around tin.[14] Almost contemporaneously, Sekiguchi also reported the crystal structure of a "stable and free" tin cation bearing three bulky tris(alkyl)silyl ligands.[15]

To mimic the active species in homogeneous olefin polymerization, we were instead interested in generating cationic species with the formula L_2SnR^+ (L = phenoxy-imine; R = alkyl). Actually, the active species in homogeneous olefin polymerization catalysts are believed to be cationic complexes of group 4 metals bearing at least an alkyl group σ-bonded to the metal center, where the polymer chain can grow via olefin insertion. Therefore, we explored the reactivity of the synthesized compounds toward 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, via NMR tube reactions.

Reactions of compounds **1** and **3** with any ionizing reagent resulted invariably in mixtures of decomposition products. In the case of **2** and **4**, reaction with $[(C_6H_5)NH(CH_3)_2]^+[B(C_6F_5)_4]^-$ and $B(C_6F_5)_3$ also led to degradation, while the use of $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ produced abstraction of an alkyl group.

For instance, the reaction of compound **2** with $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ clearly proceeded by methyl abstraction, as indicated by the presence, in the ^1H NMR spectrum, of a resonance at 2.2 ppm attributable to the methyl group of $CH_3C(C_6H_5)_3$ (Figure 3). Characteristic resonances for the cationic species are a singlet at 0.60 ppm for $SnCH_3^+$ and a singlet at 8.16 ppm due to C*H*=N. The imine resonance shows a downfield shift, if compared with the corresponding resonance of compound **2** in the same solvent (7.75 ppm). It is worth noting that in analogous experiments performed with bis(phenoxy-imine) group 4 transition-metal compounds, a cationic character was attributed to the species displaying a similar downfield shift of the imine hydrogen.[16,17]

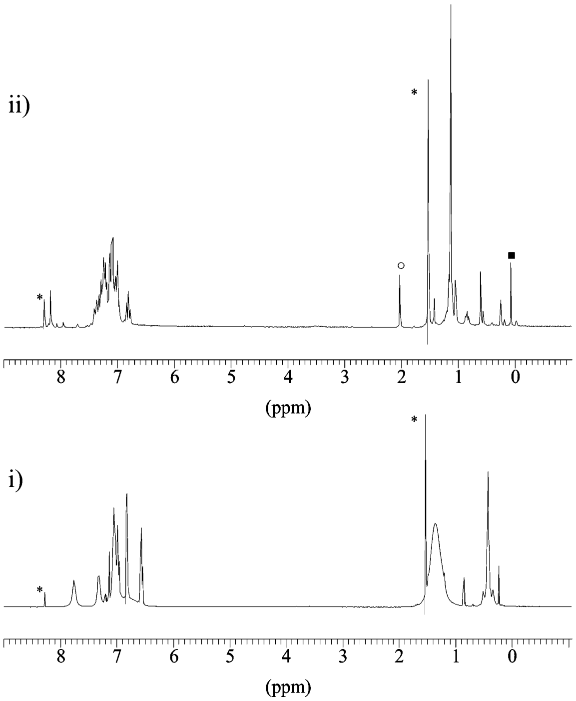

Figure 3. ^1H NMR spectra (ClC_6D_5, 25 °C) of compounds **2** (i) and **2a** (ii): (*) "free" ligand impurities; (○) $C(C_6H_5)_3CH_3$; (■) $Sn(CH_3)_4$ impurities.

The reactivity of the synthesized compounds toward ethylene was explored in preliminary tests. Interestingly, compounds **2** and **4**, in combination with 1 equiv of $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$, displayed some activity, although very low, in the oligomerization of ethylene under mild conditions. In contrast, control experiments, performed under identical conditions but in the presence of compound **2** alone, or in the presence of $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ alone, did not give any product.

The obtained oily products were analyzed by ^{13}C NMR spectroscopy in $CDCl_3$ solution. Interestingly, in addition to the main resonance of polyethylene sequences at 29.98 ppm, minor resonances are detected at 19.97, 24.73, 33.01, and 37.36 ppm. According to literature data, these resonances are diagnostic of the presence of methyl branches.[18] Resonances for saturated end groups are also observed. From the ^{13}C NMR spectrum, the amount of branching was estimated to be 1.5–3 units per chain, while the chain length was between 40 and 60 carbons.

The mechanism responsible of the methyl branches is presently unknown. Formation of methyl-branched polyethylene was previously observed, e.g. with α-diimine Ni and Pd catalysts, for which a "chain walking" mechanism was hypothesized,[19] or with supported vanadium–magnesium catalysts, for which an intramolecular isomerization mechanism of a growing chain was posited.[20]

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(13) Mason, A. F.; Tian, J.; Hustad, P. D.; Lobkovsky, E. B.; Coates, G. W. *Isr. J. Chem.* **2002**, *42*, 301–306.

(14) Lambert, J. B.; Lin, L.; Keinan, S.; Muller, T. *J. Am. Chem. Soc.* **2003**, *125*, 6022–6023.

(15) Sekiguchi, A.; Fukawa, T.; Lee, V. Ya.; Nakamoto, M. *J. Am. Chem. Soc.* **2003**, *125*, 9250–9251.

(16) Makio, H.; Fujita, T. *Macromol. Symp.* **2004**, *213*, 221–233.

(17) The NMR ^{119}Sn spectrum showed a resonance at 394.26 ppm, upfield in comparison with the neutral compound **2**. An opposite behavior, observed by Ružička et al. in five-coordinated Sn cationic compounds, could be probably ascribed to the different coordination environment of tin. Cf.: Ružička, A.; Jambor, R.; Císařová, I.; Holeček, J. *Chem. Eur. J.* **2003**, *9*, 2411–2418.

(18) De Pooter, M.; Smith, P. B.; Dohrer, K. K.; Bennet, K. F.; Meadows, M. D.; Smith, C. G.; Schouwenaars, H. P.; Geerards, R. A. *J. Appl. Polym. Sci.* **1991**, *42*, 399–408.

(19) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415.

It is worth noting that with our system ethylene oligomers were produced only in the presence of the tin compounds **2** and **4**, for which the formation of relatively stable cationic species has been detected. Further work is in progress in order to ascertain the mechanism responsible for ethylene oligomerization and for the branch formation.

Conclusions

A new family of octahedral bis(phenoxy-imine)tin(IV) dialkyl complexes has been synthesized. These compounds have been fully characterized by NMR and single-crystal X-ray analysis. For the compounds bearing the nonfluorinated *N*-(3-*tert*-butylsalicylidene)aniline ligands, the formation of cationic species via alkyl abstraction by $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ has been detected by NMR monitoring. Interestingly, the obtained cationic species promote ethylene oligomerization under mild conditions. To our knowledge, the oligomerization of ethylene by a group 14 compound is unprecedented in the literature.

Experimental Section

General Procedure. Manipulations of sensitive materials were carried out under nitrogen using Schlenk or glovebox techniques. Hexane and THF were refluxed over sodium/benzophenone and distilled under nitrogen prior to use. $CDCl_3$, CD_2Cl_2, and ClC_6D_5 were dried over CaH_2 and distilled prior to use. The carbenium salt $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ was purchased from Boulder SPA Co. and used as received. The phenoxy-imine ligands *N*-(3-*tert*-butylsalicylidene)aniline[21] and *N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroaniline[22] were synthesized according to literature procedures. NMR spectra were recorded on a Bruker Advance 400 MHz spectrometer (^1H, 400 MHz; ^{13}C, 100 MHz; ^{119}Sn 149 MHz; ^{19}F, 376 MHz). The ^{119}Sn NMR spectra 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 analysis were recorded on a Thermo Finnigan Flash EA 1112 series C,H,N,S analyzer.

Synthesis of Bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]dimethyltin(IV) (1). To a stirred solution of NaH (155 mg, 6.45 mmol) in THF (10 mL) at 0 °C was added dropwise a solution of *N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroaniline (1.0 g, 3.23 mmol) in 35 mL of THF. The mixture was warmed to room temperature and stirred for 3 h. The resulting light orange solution was added to a stirred solution of $Cl_2Sn(CH_3)_2$ (350 mg, 1.62 mmol) in 10 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 hexane, and the solution was concentrated to 15 mL and stored at −20 °C. A yellow solid deposited overnight (yield 1.14 g, 85%). Crystals suitable for an X-ray crystal structure determination were grown from hexane at −20 °C. ^1H NMR ($CDCl_3$, 293 K): δ 0.37 (6H, s, $^2J(Sn-H) = 67.1$ Hz, $Sn-CH_3$), 1.16 (18H, s, *t*-Bu), 6.68 (2H, t, Ar H), 7.03 (2H, d, Ar H), 7.39 (2H, d, Ar H), 8.06 (2H, s, $^3J(Sn-H) = 15.9$ Hz, N=CH). ^{13}C NMR ($CDCl_3$, 293 K): δ 6.7 ($^1J(Sn-C) = 645$ Hz, $Sn-CH_3$), 29.2 ($C-CH_3$), 35.1 ($C-CH_3$), 116.9, 119.1, 134.0, 134.8, 142.4, 167.8 (Ar *C*), 176.4 (N=*C*H). ^{119}Sn NMR (CD_2Cl_2, 293 K): δ −308.9. EI MS *m/z* 818 $[M - CH_3]^+$. Anal. Calcd for $C_{36}H_{32}F_{10}N_2O_2Sn$ (833.35): C, 51.89; H, 3.87; N, 3.36. Found: C, 51.7; H, 3.67; N, 3.49.

Synthesis of Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]dimethyltin(IV) (2). This compound was prepared as illustrated above, but using $Cl_2Sn(CH_3)_2$ (1.75 g, 7.9 mmol in 15 mL of dry THF), 4.04 g of *N*-(3-*tert*-butylsalicylidene)aniline (15 mmol in 45 mL of dry THF) and 0.57 g of NaH (24 mmol) (yield 4.7 g, 91%). Crystals suitable for an X-ray crystal structure determination were grown from hexane at − 20 °C. ^1H NMR ($CDCl_3$, 293 K): δ 0.30 (6H, br s, $^2J(Sn-H) = 67.3$ Hz, $Sn-CH_3$), 1.27 (18H, br s, *t*-Bu), 6.58−7.34 (16H, br m, Ar H), 7.95 (2H, br s, N=CH). C_2 isomer: ^1H NMR (CD_2Cl_2, 188 K) δ 0.15 (6H, s, $^2J(Sn-H) = 68.1$ Hz, $Sn-CH_3$), 0.96 (18H, s, *t*-Bu), 6.54−7.45 (16H, br m, ArH), 8.11 (2H, s, $^3J(Sn-H) = 30.8$ Hz, N=CH). C_1 isomer: ^1H NMR (CD_2Cl_2, 188 K) δ −0.21 (3H, s, $^2J(Sn-H) = 65{,}9$ Hz, $Sn-CH_3$), 0.33 (3H, s, $^2J(Sn-H) = 65{,}5$ Hz, $Sn-CH_3$), 1.34 and 1.35 (18H, two singlets overlapped, *t*-Bu), 6.54−7.45 (16H, br m, Ar H), 7.86 (2H, br s, N=CH). ^{13}C NMR ($CDCl_3$, 293 K): δ 7.4 ($Sn-CH_3$), 29.5 ($C-CH_3$), 35.1 ($C-CH_3$), 115.4, 118.5, 123.4, 126.2, 128.9, 132.1, 134.1, 142.4, 151.7, 167.4 (Ar−*C*), 170.5 (N=*C*H). ^{119}Sn NMR (CD_2Cl_2, 293 K): δ −352.8 (s), −342.7 (s). EI MS *m/z* 654 $[M]^+$. Anal. Calcd for $C_{36}H_{42}N_2O_2Sn$ (653.44): C, 66.17; H, 6.48; N, 4.29. Found: C, 67.0; H, 6.80; N, 4.50.

Synthesis of Bis[*N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]dibutyltin(IV) (3). This compound was prepared as above but using $Cl_2Sn[(CH_2)_3CH_3]_2$ (1.27 g, 4.2 mmol) in 10 mL of dry THF, *N*-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroaniline (2.87 g, 8.4 mmol) in 45 mL of THF, and NaH (0.30 g, 12 mmol) (yield 3.0 g, 80%). ^1H NMR ($CDCl_3$, 293 K): δ 0.75 (6H, t, $-CH_3$), 1.20 (30 H, br s, 3 CH_2 and *t*-Bu), 6.64 (2H, t, Ar H), 6.96 (2H, d, Ar H), 7.36 (2H, d, Ar H), 8.02 (2H, s, $^3J(Sn-H)= 14.3$ Hz, N=CH). ^{13}C NMR ($CDCl_3$, 293 K): δ 13.7 ($Sn(CH_2)_3CH_3$), 26.3, 27.2, 28.3 ($Sn-(CH_2)_3CH_3$), 29.5 ($C-CH_3$), 35.2 ($C-CH_3$), 116.6, 119.8, 134.0, 135.0, 141.9 (Ar *C*), 176.8 (N=*C*H). ^{119}Sn NMR (CD_2Cl_2, 293 K): δ −337.4 (s). EI MS *m/z* 917 $[M]^+$. Anal. Calcd for $C_{42}H_{44}F_{10}N_2O_2Sn$ (917.51): C, 54.98; H, 4.83; N, 3.05. Found C, 54.62; H, 5.12; N, 3.24.

Synthesis of Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]dibutyltin(IV) (4). This compound was prepared as above but using $Cl_2Sn[(CH_2)_3CH_3]_2$ (2.7 g, 8.9 mmol) in 20 mL of dry THF, *N*-(3-*tert*-butylsalicylidene)aniline (4.5 g, 17.5 mmol) in 45 mL of THF, and NaH (0.70 g, 29 mmol) (yield 5.9 g, 90%). Crystals suitable for an X-ray crystal structure determination were grown from dried hexane at −20 °C. ^1H NMR ($CDCl_3$; 293 K): δ 0.74 (6H, br t, $-CH_3$), 1.15−1.40 (30 H, br m, 3 CH_2 and *t*-Bu), 6.55−7.30 (16H, br m, Ar H), 7.90 (2H, br s, N=CH). ^{13}C NMR ($CDCl_3$; 293 K): δ 13.7 ($Sn(CH_2)_3CH_3$), 26.4, 27.3, 28.5 ($Sn(CH_2)_3CH_3$), 29.6 ($C-CH_3$), 35.2 ($C-CH_3$), 115.1, 119.9, 123.3, 126.1, 128.8, 132.1, 134.3, 152.2 (Ar *C*), 170.6 (N=*C*H). ^{119}Sn NMR (CD_2Cl_2, 293 K): δ −369.7 (s), −375.8 (s). EI MS *m/z* 737 $[M]^+$. Anal. Calcd for $C_{42}H_{54}N_2O_2Sn$ (737.6): C, 68.39; H, 7.38; N, 3.80. Found: C, 69.12; H, 7.79; N, 3.40.

Generation of Bis[*N*-(3-*tert*-butylsalicylidene)anilinato]methyltin(IV) Tetrakis(perfluorophenyl)borate (2a). Compound **2** (10 mg, 15 μmol) was dissolved in dry ClC_6D_5 (0.5 mL). To the yellow solution was added $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ (14 mg, 15 μmol). An orange solution was obtained and analyzed by NMR spectroscopy at room temperature. ^1H NMR (ClC_6D_5, 293 K): δ 0.60 (3H, s, $Sn-CH_3$), 1.23 (18H, s, *t*-Bu), 6.78−7.39 (16H, br m, Ar H), 8.16 (2H, s, $^3J(Sn-H) = 14{,}9$ Hz, N=CH). ^{13}C NMR (ClC_6D_5, 293 K): δ 3.8 ($Sn-CH_3$), 29.2 ($C-CH_3$), 35.0 ($C-CH_3$), 172.3 (N=*C*H). ^{119}Sn NMR (CD_2Cl_2, 293 K): δ −394.26. ^{19}F NMR (ClC_6D_5, 293 K): δ −131.9 (2F, d, *o*-F), −162.6 (1F, t, *p*-F), −166.4 (2F, t, *m*-F). The

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Table 2. Crystal Data and Refinement Details for Compounds 1, 2, and 4

	1	2	4
mol formula	$C_{36}H_{32}F_{10}N_2O_2Sn$	$C_{36}H_{42}N_2O_2Sn$	$C_{42}H_{54}N_2O_2Sn$
mol wt	833.33	653.43	737.59
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/n$	$P2_12_12_1$
a (Å)	8.757(5)	13.265(6)	16.551(6)
b (Å)	25.021(3)	9.651(4)	18.233(5)
c (Å)	16.603(5)	26.01(1)	12.590(3)
β (deg)	97.49(4)	94.18(4)	
V (Å^3)	3606.6(2)	3320(2)	3799(2)
Z	4	4	4
D_c (g/cm^3)	1.53	1.31	1.29
F(000)	1672	1352	1544
abs coeff (cm^{-1}) ($\lambda = 0.7107$ Å)	7.9	8.0	7.1
transmissn factors	0.753−0.853	0.749−0.786	0.66−0.753
decay (%)		7.7	8.5
decay cor		polynomial	polynomial
scan type	ω	ω	$\omega/2\theta$
$2\theta_{max}$ (deg)	55	50	55
no. of rflns	8299	6130	4829
no. of rflns ($I > 2\sigma(I)$)	4990	5854	3792
no. of variables	460	370	424
R1 ($I > 2\sigma(I)$)	0.031	0.027	0.028
wR2 (all data)	0.082	0.081	0.076
goodness of fit	0.98	1.02	1.02
max, min diff Fourier (e/Å^3)	0.39, −0.39	0.34, −0.55	0.38, −0.39

byproduct $(C_6H_5)_3CCH_3$ was identified according to the literature.[23] The side product $Sn(CH_3)_4$ was also identified.

Polymerization Tests. A typical polymerization test was carried out in a 500 mL magnetically stirred glass autoclave, which was conditioned under dynamic vacuum, thermostated at 25 °C, and then charged with a solution of the tin compound (45 μmol) and $[C(C_6H_5)_3]^+[B(C_6F_5)_4]^-$ (45 μmol) in ClC_6H_5 (50 mL). Ethylene was fed continuously at a pressure of 6 atm; after 6 h, the autoclave was vented and the reaction mixture was poured into acidified methanol. The solution was treated with water and hexane (3 × 30 mL). The organic phase was dried on Na_2SO_4, and the solvents were stilled off. An oily product was obtained; typically yields are about 200 mg. The products were analyzed by ^{13}C NMR analysis; the oligomer structure was assigned according to the literature.[18]

X-ray Diffraction Analysis. Single-Crystal X-ray Crystallography. Suitable crystals 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 Kα radiation ($\lambda = 0.710\ 69$ Å). Data reduction was performed with the crystallographic package TEXSAN.[24] Absorption and intensity decay corrections were applied to the data.

The structures were solved by direct methods using the program SIR92[25] and refined by means of full-matrix least squares based on F^2 using the program SHELXL97.[26]

For all compounds non-hydrogen atoms were refined anisotropically and hydrogen atoms were positioned geometrically and included in structure factor calculations but not refined.

Crystal structures were drawn by means of the program ORTEP32.[27]

Crystal data and refinement details are listed in Table 2.

X-ray Powder Diffraction. A 0.5 mm Lindemann capillary was filled with the air-sensitive powder of **4** and sealed in a drybox under an argon atmosphere.

X-ray powder diffraction data of **4** were collected by means of a Bruker D8 diffractometer equipped with a Goebel mirror using Cu Kα radiation, step size 0.05° in 2θ, and step time 40 s.

Data reduction was performed using the program GUFI.[28] The background was modeled manually using GUFI. Rietveld refinement was accomplished with the program GSAS.[29] The peak profile was described by a pseudo-Voigt function, in combination with a special function that accounts for the asymmetry due to axial divergence.[30] No absorption correction was applied to the data. The atomic parameters were taken from the structure model obtained from the single-crystal X-ray diffraction data and were not refined. Final indices are $R_p = 0.035$ and $R_{wp} = 0.046$.

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Supporting Information Available: Figures giving ^{1}H and ^{13}C NMR spectra of compounds **1**−**4**, ^{1}H and ^{119}Sn NMR spectra of compound **2** at variable temperature, ^{1}H NMR spectra of compound **4** at variable temperature, ORTEP diagrams of compounds **2** and **4**, observed and calculated X-ray powder diffraction pattern of compound **4**, and a ^{13}C NMR spectrum of the ethylene oligomers and CIF files giving crystallographic data for compounds **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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