Organometallic Compounds of Group 13, 55[≠]

Novel Organoaluminum Lewis Acids via Selective Aluminum-Tin Exchange Processes – Electrophilic Initiation by the Aluminum Halide and Ensuing Complexation by the Resulting Tin Halide

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Dedicated to the memory of our most esteemed colleague, the late Professor Wilhelm P. Neumann, master of organotin chemistry[c]

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With the goals of preparing novel carbaluminating reagents and mono- and bidentate organoaluminum Lewis acids, the scope and limitations of synthesizing the requisite organoalanes by the aluminum-tin exchange between an aluminum halide and the appropriate organostannane have been examined in detail. The interactions of such tin precursors as 1,2-bis(trimethylstannyl)ethyne, allyltri-*n*-butyltin, benzyltrimethyltin, and 1,2-bis(trimethylstannyl)benzene and various aluminum chlorides of the type, R_nAlCl_{3-n} (R = Me, Et), gave selective aluminum-tin exchange at the sp- or sp^2-hybridized carbon–tin bond and produced such organoalanes as allyl(methyl)aluminum chloride, benzylaluminum dichloride, 1,2-bis(diethylalumino)ethyne, 1,2-bis(dimethylalumino)benzene, 1,2-bis[chloro(methyl)alumino]benzene, and 1,2-bis(dichloroalumino)benzene in high yield. A complicating factor was the tendency of the R_3SnCl by-product to complex with the resulting organoalane. In some cases, exemplified by allyl(methyl)aluminum chloride, such complexation did not interfere with the carbaluminating action of the reagent; in other cases, exemplified by 1,2-bis[chloro(methyl)alumino]benzene, the R_3SnCl could be removed by means of π-bases and reduced pressures; and in still other structures, as with 1,2-bis(dichloroalumino)benzene, the tin chloride could not be dislodged at moderate temperatures. The structure and bonding in such tin halide–aluminum halide complexes in solution were investigated with the 1:1 adducts of $AlCl_3$ with Me_3SnCl and with nBu_3SnCl, respectively, by means of multinuclear NMR spectroscopy. Furthermore, an XRD of the solid complex, $Me_3SnCl \cdot AlCl_3$, was carried out. Such complexes were shown to consist of 1:1 ion pairs of the type $[R_3Sn^+][AlCl_4^-]$ in dilute solution and of a chiral polymeric helix in the solid state wherein planar Me_3Sn^+ units are linked to each other via bridging tetrachloroaluminate anions, Cl–($AlCl_2$)–Cl^-. Treatment of such complexes with either benzyltriethylammonium chloride (one or two equivalents) or tetramethylphosphonium chloride leads to the displacement of Me_3SnCl and the formation of the expected ionic complexes. Finally, the importance of such novel reagents and chelating Lewis acids to organic synthesis and olefin polymerization is discussed and elucidated.

In continuing investigations directed toward the synthesis of novel Group 13 Lewis acids suitable as cocatalysts with cyclopentadienyl transition metal derivatives for Ziegler−Natta olefin polymerization catalysis, we have sought ways of preparing unsymmetrical organometallics of Group 13 whose Lewis acidity might be enhanced either by the electron-withdrawing nature of the substituent E in **1** or by the chelating effect of two proximally arrayed Lewis acid metal centers M in **2**. In the previous article of this series the possible effect of such Lewis acidity enhancing factors in selected organoboranes was examined.[1] This present study has explored the Lewis acidity of analogous unsymmetrical organoaluminum compounds in the well-established expectation that such organoaluminum analogs would exhibit greater Lewis acidities than their boron counterparts for steric and electronic reasons:[2] the smaller covalent radius of boron versus aluminum (B, 81 pm versus Al, 125 pm) increasing the steric hindrance or F-strain upon complexation (**3**) and any $p_\pi-p_\pi$ back-bonding from ligands (E) on the boron center, such as unshared electron pairs (E = X, RO, or R_2N), decreasing the boron center′s Lewis acidity.

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[c] Professor W. P. Neumann was born in Würzburg, Germany, on October 29, 1926. Upon the completion of studies on pyrimidopyrimidines with Professor F. G. Fischer at the University of Würzburg in 1952, he was awarded the degree Dr. rer. nat. Thereafter, he was postdoctoral research associate with Nobel Laureate Karl Ziegler with whom he embarked on his lifelong study of organotin chemistry. After habilitation on this theme at the University of Gießen in 1960, he served on the same faculty as Außerplanmäßiger Professor until 1968. He joined the faculty of the University of Dortmund in 1969 as Ordinary Professor of Organic Chemistry and until his formal retirement in 1992 he was chiefly responsible for developing the Organic Chemistry Institute of this new university. His research and scholarly work on the organometallic chemistry of tin and germanium and on organic intermediates, such as free radicals and carbenes, were reported in over 250 articles and reviews. At the time of his death on August 3, 1993 he was still at the forefront of the organic chemistry of tin, a research area on which he had composed a monograph as a young scientist (1970, Wiley) and whose high relevance to the whole field of organic chemistry his career in research has made manifest. We, his colleagues, will always fondly remember his great scientific zest and his extraordinary human warmth.

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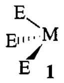
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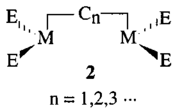
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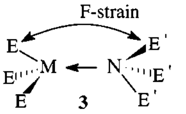
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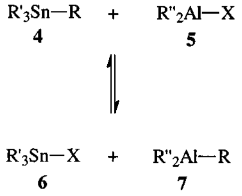
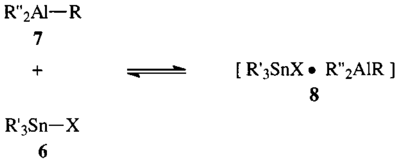
As a preparative route to such unsymmetrical organoaluminum reagents, we have availed ourselves of the selective exchange occurring between organotin compounds and aluminum halides (Equation 1).[3] Such exchanges are potentially reversible depending on the nature of the organyl substituents and on experimental conditions. Where R, R′, and R′′ are alkyl, the reaction proceeds to the left and produces tetraalkyltin compounds.[4] In the present case of interest, the reaction has been found to lead selectively to the right, producing **7**, when R in **4** is an organyl group more electronegative than alkyl, such as allyl, benzyl, aryl, or 1-alkynyl. Furthermore, the extent of tin-aluminum exchange can in some instances be feasibly controlled by removing one of the components of the equilibrium in Equation 1 from the reaction zone by volatization or complexation, in accord with LeChatelier's principle.[5]



$$\underset{\mathbf{4}}{R'_3Sn{-}R} + \underset{\mathbf{5}}{R''_2Al{-}X} \rightleftharpoons \underset{\mathbf{6}}{R'_3Sn{-}X} + \underset{\mathbf{7}}{R''_2Al{-}R} \qquad (1)$$

Because of the greater Lewis acidity of such organoaluminum derivatives, compared with their organoboron analogs, a serious complication occurs when utilizing such tin-aluminum exchanges for preparing unsymmetrical organoalanes (**7**, Equation 1): namely the organoalane **7** usually complexes more or less firmly with the organotin halide byproduct **6** (Equation 2). Such complexation (**8**) generally does not interfere in preparative tin-boron exchanges,[1] most likely because of destabilizing F-strain in such complexation (cf. **3**). This complexation in tin-aluminum exchanges (**8**) has been of dual interest to us: not only did we seek mild experimental conditions to disrupt such complexation and to isolate **7** in satisfactory yield, but also we wished to elucidate the structure and bonding in complex **8**.



$$\underset{\mathbf{7}}{R''_2Al{-}R} + \underset{\mathbf{6}}{R'_3Sn{-}X} \rightleftharpoons \underset{\mathbf{8}}{[\,R'_3SnX \bullet R''_2AlR\,]} \qquad (2)$$

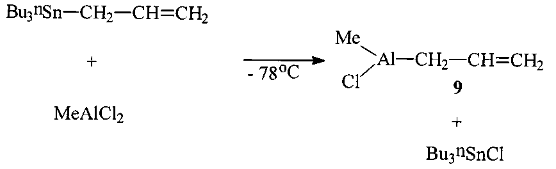
Results

Preparation of Organoalanes by Aluminum−Tin Exchange Reactions

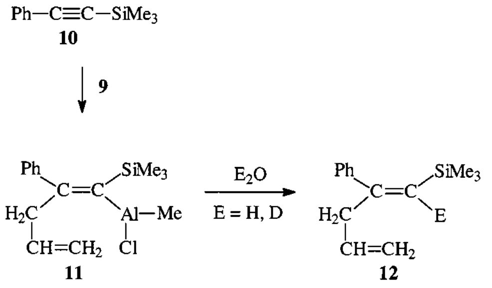
Previous studies on generating organoboranes by boron-tin exchange processes had revealed that selective exchange of groups is achievable when the C−Sn bond is attached to an sp- or sp^2-hybridized group.[1] In addition, by combining what has been established by Neumann in his pioneering work on aluminum-tin exchanges[6] with what is known about lithium-metal exchanges,[7] it was considered likely that aluminum-tin exchanges would proceed selectively at C−Sn bonds to allylic and benzylic groups as well. The driving force for such exchanges appears to lead to the more electropositive metal atom (Li, Al) being bonded to the more electronegative carbon atom (sp-, sp^2-, or allylic-bonded organyl group) in the favored product.

Allyl(methyl)aluminum Chloride (9)

This reagent could be readily generated from the interaction of allyltri-*n*-butyltin with methylaluminum dichloride at −78 °C but the high autoreactivity of such allylic alanes precluded its isolation at room temperature (Equation 3). Hence, reagent **9** was generated at −78 °C in the presence of trimethyl(phenylethynyl)silane (**10**); subsequent hydrolytic work-up led to a high yield of (*Z*)-2-phenyl-1-trimethylsilyl-1,4-pentadiene (**12**). Work-up with D_2O yielded **12** deuteriated at C-2. The exclusive formation of **12** establishes that **9** had carboaluminated **10** with regio- and stereo-selectivity to form precursor **11** (Equation 4).[8]

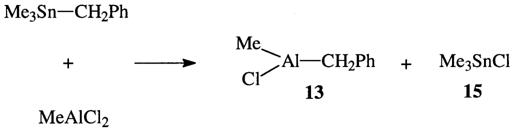


$$Bu_3{}^nSn{-}CH_2{-}CH{=}CH_2 + MeAlCl_2 \xrightarrow{-78^\circ C} \underset{\mathbf{9}}{Me(Cl)Al{-}CH_2{-}CH{=}CH_2} + Bu_3{}^nSnCl \qquad (3)$$


(4)

Benzylaluminum Dichloride (14)

The attempted exchange between benzyltrimethyltin and methylaluminum dichloride to produce benzyl(methyl)aluminum chloride (**13**, Equation 5) took an unexpected course when the separation of **13** from its complex with **15** was undertaken. Under the conditions expected to lead to the dissociation of the complex, **13** · **15**, and the selective volatilization of **15** (100 °C in mesitylene), further tin-aluminum exchange occurred with the formation of pure **14** and the volatilization of tetramethyltin (Equation 6).[9]



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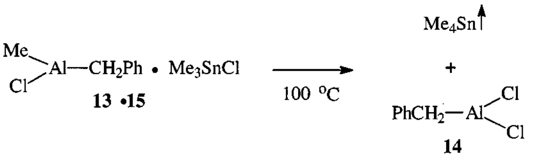
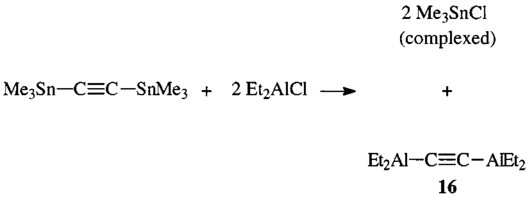


(6)

1,2-Bis(diethylalumino)ethyne (16)

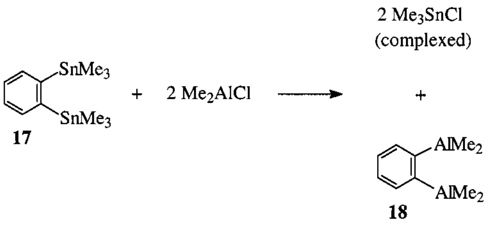
The interaction of 2 equivalents of diethylaluminum chloride with one equivalent of bis(trimethylstannyl)ethyne in pentane at −30°C led to the deposition of 95% of the pale yellow **16**, which was highly pyrophoric and insoluble in benzene or chloroform. The ^{1}H-NMR spectrum of **16** from the reaction mixture from Equation 7 in THF is consistent with complexation of **16** with the ether solvent and the liberation of free Me_3SnCl: The triplet and quadruplet ethyl signals of **16** are shifted downfield from those of unsolvated Et_3Al and the singlet due to free Me_3SnCl is visible at $\delta = 1.2$.



$$\mathrm{Me_3Sn{-}C{\equiv}C{-}SnMe_3} + 2\,\mathrm{Et_2AlCl} \longrightarrow \underset{\mathbf{16}}{\mathrm{Et_2Al{-}C{\equiv}C{-}AlEt_2}} + \underset{\text{(complexed)}}{2\,\mathrm{Me_3SnCl}} \qquad (7)$$

1,2-Bis(dimethylalumino)benzene (18)

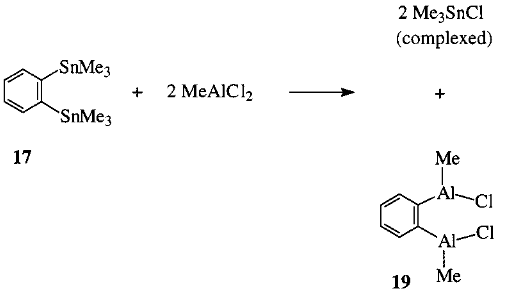
The interaction of 1,2-bis(trimethylstannyl)benzene (**17**) with 2 equivalents of dimethylaluminum chloride in hexane at 25°C produced the *ortho*-dimethylalumino derivative **18** as its 1:1 and 1:2 complexes with Me_3SnCl (Equation 8), as evidenced by Me_3Sn group singlets in the $\delta = 0.02$ to -0.02 region in the ^{1}H NMR, as well as by extra aromatic doublets in the $\delta = 7.0-8.0$ region. Such Me_3SnCl was largely removed by warming under reduced pressure and by the distillative removal of added heptane at ordinary pressure to yield essentially free **18**.



(8)

1,2-Bis[chloro(methyl)alumino]benzene (19)

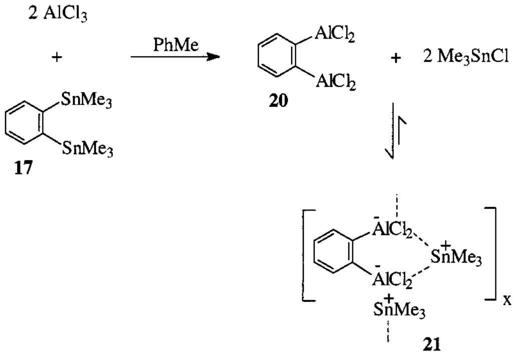
Similarly, the interaction of **17** with 2 equivalents of methylaluminum dichloride in toluene at 25°C yielded the analogous *ortho*-dichloro(methyl)alumino derivative **19**, which was even more strongly complexed with the Me_3SnCl by-product than was **18**. Here the use of the π-base, toluene, for the reaction aided the dissociation and removal of Me_3SnCl from **19**. Evaporation of the toluene solvent and repeated evaporation of several added portions of toluene under vacuum served to chase off almost all of the remaining Me_3SnCl (Equation 9).[8]



(9)

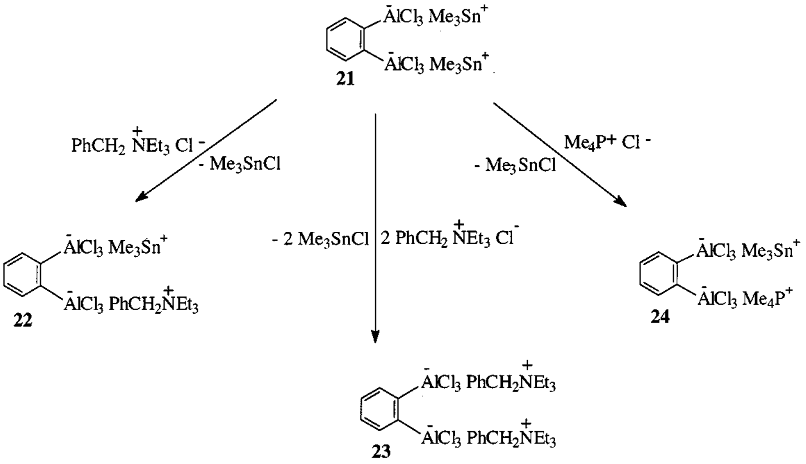
1,2-Bis(dichloroalumino)benzene (20)

Finally, the interaction of **17** with 2 equivalents of aluminum trichloride in toluene suspension led to the aluminum-tin exchange product, **20**, but in this situation the Me_3SnCl by-product remained firmly complexed with **20** to form a polymeric ion pair **21** (Scheme 1).



Scheme 1

The presence of the trichloroaluminate anion is consistent with a ^{27}Al-NMR resonance signal at $\delta = 105$, as is the presence of a planar trimethylstannyl cation supported by the low-field ^{119}Sn-NMR peak at $\delta = 357.5$. (More structural information on such ion-pairs follows below). Thermal dissociation of **21** under high vacuum or by use of π-basic solvents under 100°C has thus far proved to be ineffectual in removing the complexed Me_3SnCl.[8]



Scheme 2

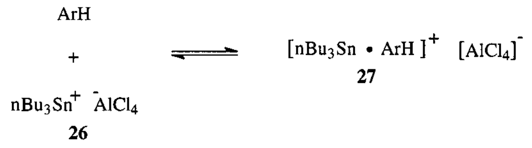
Complexation of Organotin Halides with Aluminum Halides

Trimethyltin Chloride with 1,2-Bis(dichloroalumino)benzene in a 2:1 Ratio (21)

Although Me_3SnCl is difficult to remove from complex **21**, the trimethylstannyl cation can readily be displaced either singly or dually by the benzyltriethylammonium ion (**22** and **23**, Scheme 2) or by the tetramethylphosphonium ion (**24**). In all cases, the ^{27}Al-NMR spectra display a resonance peak in the $\delta = 103$ region; in **22** and **24** the ^{119}Sn-NMR spectra have a peak in the $\delta = 317-320$ region; and in each complex the appropriate ^{1}H- and ^{13}C-NMR peaks corroborate the ionic structures and compositions.

Complexes of Trimethyltin Chloride with Aluminum Chloride (Complex 25) and of Tri-*n*-butyltin Chloride with Aluminum Chloride (Complex 26)

These 1:1 complexes were first described by Neumann, Schick, and Köster almost 35 years ago and upon the basis of the relatively high electrical conductivity of such complexes and their formula weight in dilute solution, they were depicted as ion pairs. Above 1 mol/L concentrations higher degrees of association (2−6) became significant.[9] To add to our insight into the structure of complexes **25** and **26**, a multinuclear NMR study was undertaken in solution. Noteworthy are the following observations: 1) the ^{27}Al-NMR signals occur at $\delta = 104-105$, almost identical with the reported peak for $AlCl_4^-$;[10] 2) the ^{119}Sn-NMR peaks are displayed at $\delta = 358$ and 380, respectively, consistent with the presence of a planar R_3Sn^+ cation;[11][12] and 3) the ^{119}Sn-NMR signal of complex **26** shows a significant upfield shift with increasing π-basicity of the medium: $\delta = 380$ ([D$_6$]benzene), 375 (toluene), 356 (mesitylene), and 338 (saturated solution of hexamethylbenzene in pentane). This last observation is consistent with such increasing π-basicity enhancing the coordination and hence the shielding of the $n\mathrm{Bu}_3\mathrm{Sn}^+$ cation (**27** in Equation 10).



$$\mathrm{ArH} + n\mathrm{Bu_3Sn^+}\ {}^-\mathrm{AlCl_4} \rightleftharpoons [n\mathrm{Bu_3Sn \cdot ArH}]^+\ [\mathrm{AlCl_4}]^- \quad (10)$$

X-ray Crystallographic Structure of $[Me_3SnCl\cdot AlCl_3]_n$, Complex 25, and Its Formulation as Polymeric Trimethyltin Cationic-Tetrachloroaluminate Anionic Pairs

As shown in Figure 1 $[Me_3SnCl\cdot AlCl_3]_n$ (**25**) consists in the solid state of trigonal bipyramidal trimethyltin fragments and tetrahedral coordinated tetrachloroaluminate fragments forming a chiral polymeric helix.[13] The three equatorial methyl groups bonded to the tin atoms are completely planar, the Sn−C bond lengths (average, 2.109 Å, compare Tables 1−3) are within the usual range for $Sn-CH_3$ bonds.[14−22] The two axial positions are occupied by chlorine atoms of the tetrachloroaluminate fragments. The Sn−Cl distances are much longer than usual,[16,17,20,21] especially more than 0.30 Å longer than the Sn−Cl bond in Me_3SnCl (2.430 Å).[16][17] These values show that **25** can best be understood as a contact ion pair of trimethyltin cations and tetrachloroaluminate anions, as was already indicated by the results of the NMR-spectroscopic measurements. Therefore it would be more accurate to write an ionic formula like $[Me_3Sn^+][AlCl_4^-]$ for compound **25**. Furthermore it is worth mentioning that the Sn−Cl distances alternate, each tin atom [except Sn5 with equal distances of 2.790(4) Å] has a short (average, 2.772 Å) and a long bond length (average, 2.832 Å) to a chlorine atom. The Cl−Sn−Cl angles are on an average 172.9° instead of 180°

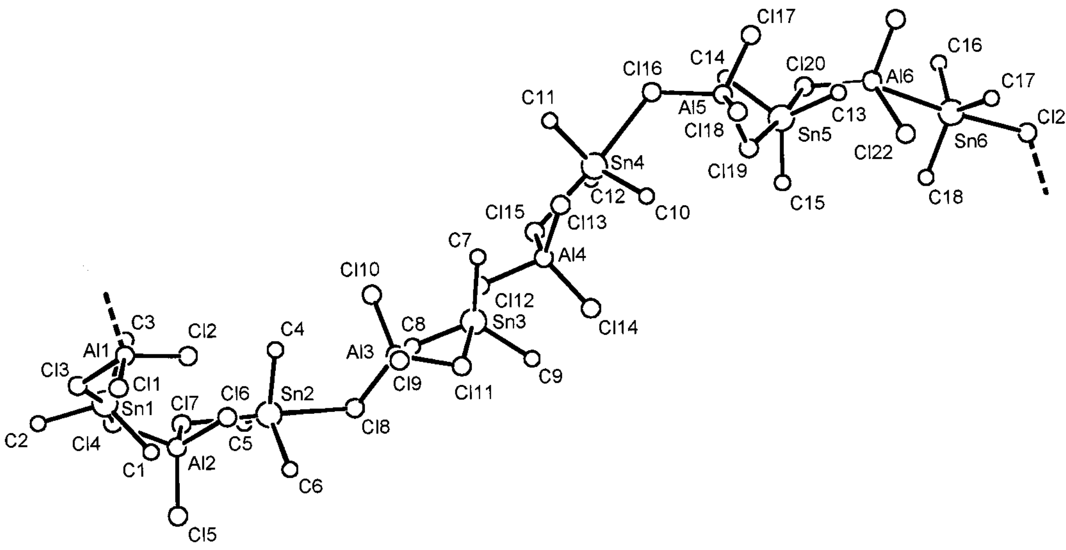


Figure 1. Structure of the polymeric chiral helix of [$Me_3SnCl\cdot AlCl_3$] (**25**)

Table 1. Selected bond lengths and angles of [$Me_3SnCl\cdot AlCl_3$] (**25**)

	Minimum value	Maximum value	Average value
Bond lengths [Å]			
Sn−C	2.02(2)	2.15(2)	2.109
Sn−Cl (short)	2.738(4)	2.792(5)	2.772
Sn−Cl (long)	2.800(4)	2.887(4)	2.832
Sn−Cl terminal	2.065(8)	2.109(6)	2.090
Sn−Cl bridging	2.143(7)	2.205(6)	2.171
Bond angles [°]			
C−Sn−C	116.4(7)	123.6(7)	120.0
Cl−Sn−Cl	168.1(1)	175.7(1)	172.9
Cl(terminal)−Al−Cl(terminal)	114.0(3)	116.8(3)	114.9
Cl(bridging)−Al−Cl(bridging)	103.4(2)	106.6(2)	104.8
Sn−Cl−Al	111.1(2)	122.1(2)	115.8

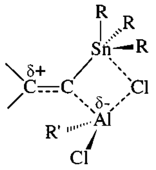
as one would expect for an ideal trigonal bipyramidal configuration.

The tetrachloroaluminate fragments show different distances from the aluminum atoms to its chlorine atoms (average, 2.090 Å) and to the bridging chlorine atoms (average, 2.171 Å), but both bonds are only 0.04 Å shorter or longer than those found for $NaAlCl_4$ (2.13 Å).[23] Also the Cl−Al−Cl angles are slightly different. The angles including the terminal chlorine atoms are on average 114.9°, whereas the Cl−Al−Cl angles for the bridging chlorine atoms are on average 104.8° compared to 109.5° for an ideal tetrahedral configuration. These structural differences at the tetrachloroaluminate fragments in this particular complex can be explained by the interactions of the bridging chlorine atoms with the trimethyltin fragments.

Discussion

Selectivity of Aluminum-Tin Exchange

With organotin derivatives having both sp- or sp^2-hybridized and sp^3-hybridized carbon−tin bonds, such as 1,2-bis(trimethylstannyl)ethyne (**28**) and 1,2-bis(trimethylstannyl)benzene (**17**), attack by the aluminum chloride, R'_nAlCl_{3-n} (**29**), occurs cleanly and exclusively at the carbon−tin bond of higher *s*-character (Equations 7−9 and Scheme 1). This preference for aluminum-tin exchange at such sites accords with a fostered electrophilic attack of **29** at such sites through transition states similar to **30**. Attack of **29** at the α-carbon atom of the C−Sn bond is favored by the σ-bond hyperconjugation stabilizing the positive charge at the β-carbon atom.[25]



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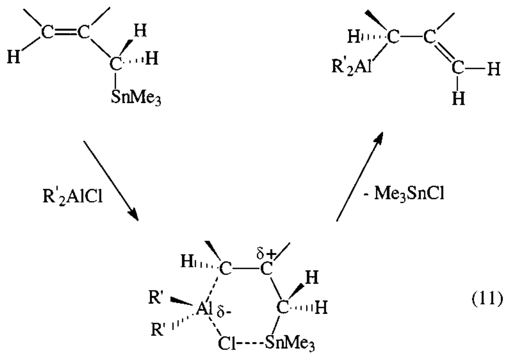
The preferential reactivity of allylic or benzylic C−Sn bonds over alkyl C−Sn bonds can be explained by similar electrophilic attack by R'_nAlCl_{3-n} (**29**) (Equations 4 and 5) except that such attack occurs at the γ-carbon atom with rearrangement (**31**, Equation 11). Here again, the favored transition state **31** is dually stabilized by σ-bond hyperconjugation of the β-carbon atom's positive charge.



(11)

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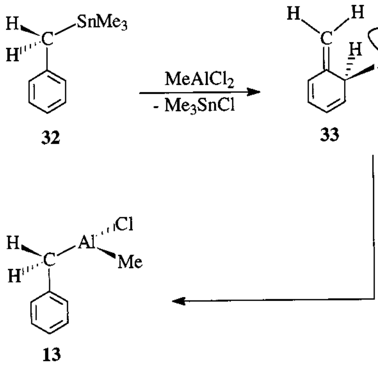
Applicability of this mechanism to the reaction of benzyltrimethyltin (**3**) with $MeAlCl_2$ (Equation 5) would require that the initial reaction product **33** would have to undergo facile rearrangement to **13** (Scheme 3). Transformation of **33** to **13** would involve a 1,3-suprafacial sigmatropic rearrangement which should be thermally allowed via the available p-orbital on the sp^2-hybridized aluminum atom in **33**.[25]



Scheme 3

Lewis Acidity of Aluminum Halides towards Trialkyltin Chlorides and the Structure of the Resulting Lewis Complexes

From the evidence on the spectral properties of complexes **25** and **26**, $R_3SnCl \cdot AlCl_3$, in solution (R = Me, Bu), it is clear that $AlCl_3$ can heterolyze the tin−chlorine bond completely to form the ion pair, $[R_3Sn]^+[AlCl_4]^-$. In dilute solutions of π-basic hydrocarbons such as arenes, the trialkyltin cation is probably solvated by arenes and exists as a simple solvated ion pair with the tetrachloroaluminate anion, as corroborated by ^{119}Sn- and ^{27}Al-NMR spectroscopy. The decreasing chemical shift of the ^{119}Sn signal of **26** as the π-basicity of the arene solvent increases, from $\delta = 380$ in [D$_6$]benzene to 375 in toluene to 356 in mesitylene to 338 in hexamethylbenzene dissolved in pentane, is consistent with an increasing complexation of the Bu_3Sn^+ with the arene π-electron cloud and thus an increasing diamagnetic shielding of the tin cation by the π-electrons. In more concentrated solutions (> 0.01 mol/L) and especially in the solid state, planar R_3Sn cations are linked to each other by $AlCl_4$ anions through $Cl-(AlCl_2)-Cl$ bridges (Figure 1), whereby the bridging Sn−Cl separations are some 30 pm longer (12%) than the Sn−Cl bond in the original Me_3SnCl (at $\delta = 243$). Such relatively weak coordination by the two chlorine atoms means that the planar R_3Sn unit is essentially still cationic.

The stability of the complex **21** between 1,2-bis(dichloroalumino)benzene (**20**) and 2 equivalents of Me_3SnCl demonstrates that an arylaluminum dichloride is still a strong enough Lewis acid to heterolyze Me_3SnCl completely. Presumably the structure of viscous **21** consists of intramolecular and intermolecular bridging of Me_3Sn^+ units between arene $AlCl_3^-$ sites (Scheme 1). The 1,2-bis(dimethylalumino)benzene (**18**) and 1,2-bis[chloro(methyl)alumino]benzene (**19**) are clearly weaker Lewis acids than **20** because the complexed Me_3SnCl can be removed by use of high vacuum and the addition of π-basic arenes (Equations 8 and 9).

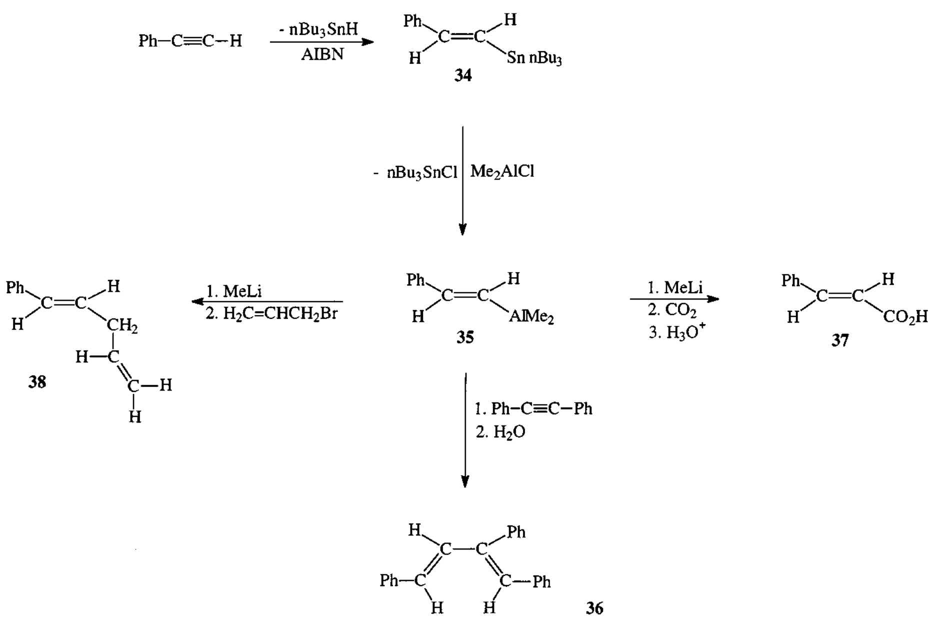
However, there is one structural feature of compounds **18**, **19**, and **20** that make them especially appealing as novel Lewis acids, and this is their potential as structurally rigid, chelating Lewis acids in Ziegler−Natta olefin polymerization. This attractive prospect motivates our continuing efforts to prepare **19** and **20** free of any complexation with Lewis bases. In the final section our recent progress in this research is outlined.

Novel Applications of Unsymmetrical Organoalanes in Organic Synthesis and Polymerization

Such aluminum-tin exchange processes constitute a most useful selective route to vinylic, allylic, acetylenic, aryl, and benzylic organoalanes in their unsolvated form. Illustrative are the preparations depicted in Equations 3, 5, 7, 18, and 19. Since the requisite organotin precursor reacts readily with $RAlCl_2$ or R_2AlCl in alkanes, toluene or dichloromethane, the organoalane can be generated free of any coordinated ether solvent and despite its auto-association, in its more electrophilic form. The weakly coordinated R_3SnX by-product can often be removed by a combination of π-basic hydrocarbons and high vacuum. In some cases, as with allyl(methyl)aluminum chloride (**9** in Equation 3), the presence of the R_3SnX does not interfere with the carbaluminating action of the organoalane.

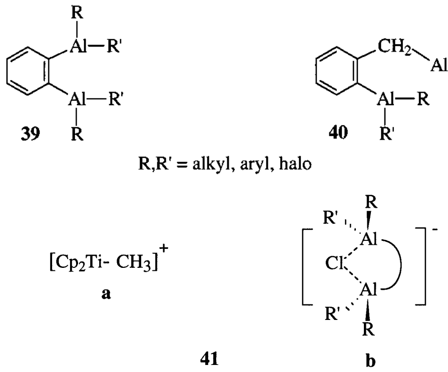
Since many organotin derivatives can be prepared by Grignard and organolithium reactions or by hydrostannations, subsequent aluminum-tin exchanges permit access to the more reactive organoalanes (Scheme 4).[26] Typical is the stereoselective generation of organoalane **35** from organotin precursor **34**. Reagent **35** can carbaluminate alkynes with selective *syn* addition (**36**),[27] undergoes carboxylation via an ate complexation with retention of configuration (**37**)[28][29] and yields the corresponding allyl derivative (**38**) by ate-complex-assisted allylation.[30] These selective reactions at the vinylic C−Al bonds, rather than at the methyl C−Al bonds, highlight the great utility of such vinylalanes in organic synthesis.

Finally, the first successful synthesis of the structurally rigid, chelating Lewis acids of types **39** and **40** from the corresponding organotin precursors has led to their evaluation as potential cocatalysts with transition metal metallocenes for the polymerization of olefins. Indeed, such cocatalysts, when employed with titanocene methyl chloride, $Cp_2Ti(Me)Cl$, in a 1:8 Ti/Al ratio, have been found decidedly superior to other aluminum cocatalysts such as $MeAlCl_2$ and even MAO, in polyethylene productivity numbers at comparable Ti/Al ratios. Productivity numbers (PN) of 2000−3000 g of polyethylene per g Ti × per h × per atm are attained with **39** and **40**, compared with PN values of 800 for MAO and 200 for $MeAlCl_2$.[31] The greater cocata-



Scheme 4

lytic efficacy of **39** and **40** may well stem from the greater binding of the chloride ion through their chelating ability (**41b**) and thus the cleaner generation and separation of the solvent-separated cation **41a**, which has been established as the active site in the metallocene polymerization of olefins.[32−34]



Experimental Section

General Techniques: All preparations and purification procedures involving manipulations with oxygen- and moisture-sensitive reagents were carried out under anhydrous, oxygen-free argon or nitrogen employing Schlenk techniques.[35] Those procedures which did not require a protective atmosphere but involved working with toxic chemicals (such as boron and tin compounds) were carried out in an exhaust hood evacuating air at 100 cubic ft/min. For the operations under reduced pressure the required vacuum was provided either by a rotary vacuum oil pump (down to 0.1 Torr) or by a water pump (down to 10 Torr) and toxic volatiles were condensed in cold traps. Commercially available solvents of reagent grade were purified according to the recommended methods.[35] Solvents used in reactions were always freshly distilled under argon or nitrogen from the appropriate drying agents: aliphatic hydrocarbons from $LiAlH_4$; toluene from sodium; dichloromethane from CaH_2; and ethers from sodium/benzophenone combinations. Deuteriated solvents (Cambridge Scientific) for NMR measurements of oxygen- and moisture-sensitive substances were vacuum-transferred to the Schlenk glass vessels and stored over Molecular Sieves (4 Å) under argon. Gas chromatographic analysis (GC) was performed with a Hewlett-Packard Chromatograph, model 5880A, with helium as the carrier gas. The ^{1}H- (360.1 MHz) and ^{13}C- (90.6 MHz) NMR spectra were recorded with a Bruker AM 360 spectrometer and the ^{27}Al- (78.2 MHz) and ^{119}Sn- (111.9 MHz) NMR spectra with a Bruker AC 300 spectrometer. Solid-state NMR spectra were recorded with a Bruker AC 300 spectrometer at 75.4 (^{13}C), 78.2 (^{27}Al) and 111.9 MHz (^{119}Sn). The ^{1}H- and ^{13}C-NMR chemical shifts are referred to resonances of the solvent [D$_6$]benzene. For ^{27}Al-NMR spectra aqueous $AlCl_3$ (δ = 0) and for ^{119}Sn-NMR spectra Me_3SnCl (16.4% in C_6D_6: δ = 159.7[28]) were used as external reference standards.

Preparation of Aluminum-Tin Complexes with Trialkyltin Chlorides

Complex 25 of Trimethyltin Chloride and Aluminum Trichloride in a 1:1 Ratio: To a suspension of 1.94 g (14.5 mmol) of aluminum trichloride in 20 mL of toluene was added 7.95 mL (7.95 mmol) of a 1.0 M solution of trimethyltin chloride in toluene via a syringe at room temperature. The resulting suspension was stirred for 3 d, filtered, and the solvent removed under reduced pressure. The remaining yellow crystals were washed with 10 mL of pentane, the pentane layer was decanted and the product dried in vacuo. In this way 2.55 g (7.7 mmol) of the crude product was obtained (97%). For further purification the crystals of **25** were again dissolved in 10 mL of toluene, the solution was filtered and cooled to −78°C. After standing overnight the solvent was decanted at a temperature of −78°C and the crystalline product was washed at room temperature with a mixture of 8 mL of pentane and 4 mL of toluene and finally dried in vacuo. − ^{1}H NMR (C_6D_6): δ = 0.88 (s, $SnCH_3$, $^2J_{Sn\text{-}H}$ = 56.2/58.5 Hz). − ^{13}C NMR (C_6D_6): δ = 5.7 ($SnCH_3$, $^1J_{Sn\text{-}C}$ = 334.4/350.1 Hz). − ^{27}Al NMR (C_6D_6): δ = 104.6 ($W_{1/2}$ = 960 Hz). − ^{119}Sn NMR (C_6D_6): δ = 342.0.

Complex 26 of Tri-*n*-butyltin Chloride and Aluminum Trichloride in a 1:1 Ratio: To a suspension of 1.94 g (14.5 mmol) of aluminum trichloride in 20 mL of pentane was added 1.5 mL (5.5 mmol) of tributyltin chloride via a syringe at room temperature. The resulting suspension was stirred for 2 d, filtered, and the solid was extracted three times with 10 mL of pentane. The solvent of the combined extracts and filtrate was removed in vacuo to leave 2.38 g of a yellow oil which was identified as the pure complex **26** by NMR spectroscopy (94%). − ^{1}H NMR (C_6D_6): δ = 0.86 (t, CH_3, 3 H), 1.29 (sext, CH_2, 2 H), 1.72 (m, CH_2, 4 H). − ^{13}C NMR (C_6D_6): δ = 13.6 (CH_3), 25.7 (CH_2, $^{1}J_{\text{Sn-C}}$ = 266.0/278.3 Hz), 27.0 (CH_2, $^{2}J_{\text{Sn-C}}$ = 75.9 Hz), 28.0 (CH_2, $^{3}J_{\text{Sn-C}}$ = 27.7 Hz). − ^{27}Al NMR (C_6D_6): δ = 103.7 ($W_{1/2}$ = 3000 Hz). − ^{119}Sn NMR (C_6D_6): δ = 380.4.

Complex 21 of Trimethyltin Chloride and 1,2-Bis(dichloroalumino)benzene (20) in a 2:1 Ratio: To a suspension of 4.43 g (33.2 mmol) of aluminum trichloride in 25 mL of toluene was added 2.03 g (5.0 mmol) of 1,2-bis(trimethylstannyl)benzene[1] via a syringe at room temperature. The resulting yellow reaction mixture was stirred for 3 d and then filtered. The solvent was evaporated from the filtrate. In order to remove all volatile material the residue was heated in vacuum up to 50°C. The resulting yellow oil was washed with 10 mL of pentane, the pentane layer was decanted and the residual oil dried in vacuum. In this way 3.25 g (4.8 mmol) of the pale yellow oil of **21** was obtained in 97% yield. − ^{1}H NMR (360.1 MHz, C_6D_6, 25°C): δ = 0.86 (s, 6 H, $SnCH_3$, $^{2}J_{\text{Sn-H}}$ = 58.1 Hz), 6.98 (d, 2 H, C_6H_4, $J_{\text{H-H}}$ = 7.8 Hz), 7.08 (d, 2 H, C_6H_4, $J_{\text{H-H}}$ = 7.8 Hz). − ^{13}C NMR (90.6 MHz, C_6D_6, 25°C): δ = 5.9 ($SnCH_3$, $^{1}J_{\text{Sn-C}}$ = 346.3/331.7 Hz), 125.6 (C_6H_4), 128.6 (C_6H_4), 129.4 (C_6H_4). − ^{27}Al NMR (78.2 MHz, C_6D_6, 25°C): δ = 105 ($W_{1/2}$ = 20000 Hz). − ^{119}Sn NMR (111.9 MHz, C_6D_6, 25°C): δ = 357.5.

Displacement of Trimethyltin Chloride from Complex 21

Displacement of One Equivalent of Me$_3$SnCl by Benzyltriethylammonium Chloride. − Complex 22: To 211 mg (0.93 mmol) of benzyltriethylammonium chloride was added 3.1 mL of a 0.3 M of solution of the 2:1 complex of Me_3SnCl and 1,2-bis(dichloroalumino)benzene (**21**) (0.93 mmol) at room temperature. Stirring of the reaction mixture overnight resulted in the formation of two layers. While the upper layer was a clear yellow solution, the lower layer was a brown oil. After removal of solvent, the residue was heated in vacuum up to 40°C in order to remove all volatile material. Addition of C_6D_6 resulted again in the formation of the two layers which were separately investigated by NMR spectroscopy. The spectra of the upper layer showed no signals corresponding to starting materials or to an adduct of bis(dichloroalumino)benzene with benzyltriethylammonium chloride, but did exhibit signals for Me_3SnCl. In the spectra of the lower layer signals corresponding to the presence of the benzyltriethylammonium cation and consistent with the formation of the complex **22** were observed. − ^{1}H NMR (360.1 MHz, C_6D_6, 25°C): δ = 0.65 (t, CH_3CH_2N), 1.08 (s, $SnCH_3$), 2.13 (q, CH_3CH_2N), 3.27 (s, $C_6H_5CH_2N$), 6.80−6.90 (m, C_6H_4), 7.14−7.25 (m, C_6H_4). − ^{13}C NMR (90.6 MHz, C_6D_6, 25°C): δ = 5.9 ($SnCH_3$), 7.5 (CH_3CH_2N), 52.4 (CH_3CH_2N), 60.5 ($C_6H_5CH_2N$), 125.6 (C_6H_5), 128.5 (C_6H_4), 129.3 (C_6H_4), 129.8 (C_6H_5), 131.3 (C_6H_5), 132.0 (C_6H_5).

Displacement of Two Equivalents of Me_3SnCl by Benzyltriethylammonium Chloride. − Complex 23: To a suspension of 340 mg (1.50 mmol) of benzyltriethylammonium chloride in 2 mL of toluene was added 2.5 mL of a 0.3 M solution (0.75 mmol) of the 2:1 complex of Me_3SnCl and 1,2-bis(dichloroalumino)benzene (**21**) in toluene at room temperature. Stirring of the reaction mixture overnight resulted in the formation of two layers. While the upper layer was a pale yellow solution, the lower layer was a bright yellow oil. The separated upper layer was shown by NMR spectroscopy to contain only Me_3SnCl. The separated lower layer was washed with pentane and the residue was then heated in vacuum up to 40°C in order to remove all volatile materials. The remaining yellow residue was treated with C_6D_6 which caused again the formation of two layers, which were individually investigated by NMR spectroscopy. The spectra of the lower layer showed all signals corresponding to the reaction product, namely bis(benzyltriethylammonium) 1,2-phenylenebis(trichloroaluminate) (**23**). − ^{1}H NMR (360.1 MHz, C_6D_6, 25°C): δ = 0.75 (t, CH_3CH_2N), 2.28 (q, CH_3CH_2N), 3.46 (s, $C_6H_5CH_2N$), 6.92−6.95 (m, C_6H_5), 6.98−7.10 (m, C_6H_4), 7.22−7.26 (m, C_6H_5). − ^{13}C NMR (90.6 MHz, C_6D_6, 25°C): δ = 7.6 (CH_3CH_2N), 52.5 (CH_3CH_2N), 60.5 ($C_6H_5CH_2N$), 125.5 (C_6H_4), 125.9 (C_6H_5), 128.5 (C_6H_4), 129.2 (C_6H_4), 129.7 (C_6H_5), 131.0 (C_6H_5), 132.2 (C_6H_5). − ^{27}Al NMR (78.2 MHz, C_6D_6, 25°C): δ = 103.5 ($W_{1/2}$ = 14 Hz).

Displacement of One Equivalent of Me_3SnCl by Tetramethylphosphonium Chloride. −Complex 24: To 152 mg (1.2 mmol) of tetramethylphosphonium chloride was added 4 mL of a 0.3 M solution of complex **21** (1.2 mmol) at room temperature. Stirring the reaction mixture overnight resulted in the formation of two layers: the upper layer was a clear yellow solution and the lower layer was a golden-colored oil. After evaporating the solvent, the residue was heated in vacuum up to 40°C in order to remove all volatile materials. Addition of C_6D_6 resulted in the formation of the two layers which were individually investigated by NMR spectroscopy. The spectra of the upper layer showed only signals corresponding to Me_3SnCl, while in the spectra of the lower layer the signals of the reaction product were found, namely the 1:1 complex of tetramethylphosphonium trichloro(2-dichloroaluminophenyl)aluminate with Me_3SnCl (**24**). − ^{1}H NMR (360.1 MHz, C_6D_6, 25°C): δ = 0.82 (d, CH_3P, $^{2}J_{\text{P-H}}$ = 14.1 Hz), 1.04 (s, CH_3Sn, $^{2}J_{\text{Sn-H}}$ = 58.8 Hz), 6.96−7.22 (m, C_6H_4). − ^{13}C NMR (90.6 MHz, C_6D_6, 25°C): δ = 5.9 (CH_3Sn, $^{1}J_{\text{Sn-C}}$ = 345.0/358.2 Hz), 9.3 (CH_3P, $^{1}J_{\text{P-C}}$ = 56.0 Hz), 130.1 (C_6H_4), 134.3 (C_6H_4), 139.6 (C_6H_4). − ^{27}Al NMR (78.2 MHz, C_6D_6, 25°C): δ = 103 ($W_{1/2}$ = 1500 Hz). − ^{13}P NMR (121.4 MHz, C_6D_6, 25°C): δ = 21.4. − ^{119}Sn NMR (111.9 MHz, C_6D_6, 25°C): δ = 317.0 ($W_{1/2}$ = 30 Hz).

Aluminum-Tin Exchange Reactions

1,2-Bis(diethylalumino)ethyne (16): To a stirred solution of 0.80 g (2.3 mmol) of 1,2-bis(trimethylstannyl)ethyne (**28**), dissolved in 20 mL of dry pentane and cooled to −30°C, was added 5.0 mmol of diethylaluminum chloride in 30 mL of hexane. A pale yellow precipitate appeared almost immediately. The reaction suspension was stirred and brought to room temperature over 60 min. After removal of the volatiles in vacuo, the residue was found to be insoluble in alkanes, benzene or $CDCl_3$ but readily dissolved in THF or ether. The ^{1}H-NMR spectrum in THF showed the absence of **28** and the presence of free Me_3SnCl. Furthermore, in [D$_8$]THF the broaded triplet and quadruplet of the ethyl groups of **16** appeared at δ = 1.3 and 0.8, consistent with coordination of THF, rather than Me_3SnCl, at aluminum.

1,2-Bis(dimethylalumino)benzene (18): To a solution of 6.0 g (14.9 mmol) of 1,2-bis(trimethylstannyl)benzene (**17**)[1] in 20 mL of heptane was added 2.76 g (29.8 mmol) of pure dimethylaluminum chloride by syringe. The resulting solution was stirred at room temperature for 72 h and thereupon the solvent and the Me_3SnCl by-product were evaporated in vacuo without heating. The residue was redissolved in heptane and volatiles again removed under reduced pressure; this addition and evaporation of heptane was repeated to remove all traces of residual Me_3SnCl. The residual viscous pale yellow oil was essentially pure 1,2-bis(dimethylalumino)benzene (**18**) in 89% yield, as evidenced by spectral data. − ^{1}H NMR (360.1 MHz, C_6D_6, 25°C): δ = −0.41 (br., 6 H, $AlCH_3$), −0.32 (br., 6 H,

$AlCH_3$), 6.96 (dd, 2 H, C_6H_4), 7.96 (2 H, dd, C_6H_4). − ^{13}C NMR (90.6 MHz, C_6D_6, 25°C): $\delta = -7.7$ ($AlCH_3$), 6.4 (br., $AlCH_3$), 129.7 (C_6H_4), 144.9 (C_6H_4), 160.3 (C_6H_4). − ^{27}Al NMR (78.2 MHz, C_6D_6, 15°C): $\delta = 174$ ($W_{1/2} = 3200$ Hz); (−8°C): $\delta = 179$ ($W_{1/2} = 5200$ Hz).

1,2-Bis[chloro(methyl)alumino]benzene (19): To a solution of 6.0 g (14.9 mmol) of 1,2-bis(trimethylstannyl)benzene in 20 mL of toluene were added 29.8 mmol of a solution of methylaluminum dichloride in hexane at room temperature. After stirring for 72 h, the solvents were evaporated in vacuo. In order to remove the more tightly complexed Me_3SnCl, the procedure of adding 20 mL of toluene to the reaction residue and evaporating all volatiles at 25°C in high vacuum had to be performed four times. The residue thus obtained was a pale yellow waxy substance (85% yield) whose NMR spectra corroborate that it is rather pure **19**, existing as a bridging isomeric mixture. − ^1H NMR (360.1 MHz, C_6D_6, 25°C): $\delta = 0.25$ (br., $AlCH_3$, 2 H), 0.8 (br., $AlCH_3$, 4 H), 6.8−7.3 (m, br., C_6H_4, 2 H), 7.4−7.9 (m, br., C_6H_4, 2 H). − ^{13}C NMR (90.6 MHz, C_6D_6, 25°C): $\delta = -6.6$ ($AlCH_3$), 4.3 (br., $AlCH_3$), 129.5 (br., C_6H_4), 137.0 (C_6H_4), 150.4 (C_6H_4). − ^{27}Al NMR (78.2 MHz, C_6D_6, 25°C): $\delta = 101$ ($W_{1/2} = 5000$ Hz).

Benzylaluminum Dichloride (14):[36] A solution of 7.6 g (30.0 mmol) of benzyl(trimethyl)tin in 200 mL of mesitylene was treated with 30 mL of a 1.0 M solution of methylaluminum dichloride in hexane and the resulting clear solution was stirred at 20°C for 15 h and then heated at 100−110°C for 3 h. The mesitylene was slowly evaporated at 100°C under a low pressure and caught in a cold trap. By ^1H- and ^{13}C-NMR spectroscopy the mesitylene was shown to contain tetramethyltin but not trimethyltin chloride. Spectral analysis of the residual viscous oil showed it to be pure benzylaluminum dichloride (**14**), free of any organotin by-product. − ^1H NMR (C_6D_6): $\delta = 2.15$ (s, 2 H), 6.71 (br. s, 2 H), 6.95 (t, 1 H), 7.10 (t, 2 H). − ^{13}C NMR (C_6D_6): $\delta = 29$ (CH_2 by DEPT), 123.6, 127.8, 127.86, 127.93.

Allyl(methyl)aluminum Chloride (9):[37] To a solution of 1.87 mL (6.0 mmol) of allyltri-*n*-butyltin and 1.13 mL (5.8 mmol) of trimethyl(phenylethynyl)silane (**10**) in 6.0 mL of toluene, cooled to −78°C, was added dropwise 6.1 mL of a 1.0 M solution of $MeAlCl_2$ in hexane. The reaction mixture was slowly brought to 0°C over 4 h. Hydrolytic work-up with aqueous NaOH and ether extraction of the organic product allowed the isolation of a mixture of tri-*n*-butyltin chloride and (*Z*)-2-phenyl-1-trimethylsilyl-1,4-pentadiene; no starting tin compound or **10** remained. The adduct **12** was cleanly separated from the nBu_3SnCl by column chromatography on silica gel with hexane eluent (90% yield). − ^1H NMR ($CDCl_3$): $\delta = -0.15$ (s, 9 H), 3.15 (d, 2 H), 5.00 (m, H), 5.59 (s, H), 5.84 (m, H), 7.15−7.35 (m, 5 H).[7] − ^{13}C NMR ($CDCl_3$): $\delta = 0.0$, 46.76, 116.41, 126.97, 127.75, 127.98, 135.91, 144.06, 157.43. − When a similar reaction mixture was worked up with NaOD in D_2O, the ^1H singlet at $\delta = 5.59$ was absent in the spectrum of **12**.

X-ray Crystallographic Study of Trimethylstannyl Tetrachloroaluminate, $Me_3SnAlCl_4$ (25). − Crystal Mounting and Data Collection: A pale yellow-brown crystal of **25**, 0.25 × 0.53 × 0.42 mm in size, was mounted with a perfluorinated polyether oil on the tip of a glass fiber on the goniometer head and cooled immediately by an argon current to −173°C. Intensity data were collected with an Enraf-Nonius CAD4 diffractometer by a coupled ω-2θ scan technique with speeds varying from 1.0 to 10.0°/min depending on the standard deviation to intensity ratio of a preliminary 10°/min scan. The radiation employed was Mo-K_α with a graphite monochromator. The crystals of molecular weight 332.6 g mol^{-1} have 6 molecules per unit cell and have a calculated density of 1.97 g cm^{-3}; they belong to the triclinic crystal system and the space group of *P*l, No. 1. The absorption corrections were made by the ψ-scan method. Observed reflections were defined as those reflections with $I \geq 2\sigma(I)$. Only these were used in the solution and refinement of the structure (*F* refinement). For refinement based on F^2 all reflections were used. Refinement was done by least-squares; the quantity minimized was $\Sigma\, w(|Yo| - |Yc|)^2$, with $Y = F$ or F^2. Computations were done using VAX, Sun4, and Silicon Graphics computers. In addition to several locally written programs, the following software was used: S. L. Lawton, R. A. Jacobson, *TRACER* (cell reduction), United States Energy Commission, Report IS-1141, Iowa State University, USA, **1965**. P. Coppens, L. Leiserowitz, D. Rabinovich, *DATAP* (data reduction), *Acta Crystallogr.* **1965**, *18*, 1035. G. M. Sheldrick, *SHELXS-86* (crystal structure determination), *Crystallographic Computing 3* (Eds:. G. M. Sheldrick, C. Krüger, R. Goddard), Clarendon Press, Oxford, **1985**, dp. 175. G. M. Sheldrick, *SHELXL-93* (least-squares refinement), University of Göttingen, **1993**. E. Egert, G. M. Sheldrick, *PATSEE* (structure solution), *Acta Crystallogr.* **1985**, *A41*, 262. P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, M. M. Woolfson, *MULTAN80* (structure solution), University of York, England and Louvain, Belgium, **1980**. W. R. Busing, K. O. Martin, H. A. Levy, *GFMLX, a highly modified version of ORFLS* (full-matrix least-squares refinement), Report ORNL-TM-305, Oak Ridge National Laboratory, Tennessee, USA, **1962**; H. D. Flack, (enantiomorph-polarity estimation), *Acta Crystallogr.* **1983**, *A39*, 876. P. Roberts, G. M. Sheldrick, *XANADU* (calculation of best planes, torsion angles and idealized hydrogen atom positions), University of Cambridge, England, **1976**. R. E. Davis, D. R. Harris, *DAESD* (calculation of distances and angles), Roswell Park Mem. Inst., USA, **1970**. V. Schomaker, K. N. Trueblood, *RIGID* (rigid-body analysis) *Acta Crystallogr.* **1968**, *B24*, 63. C. K. Johnson, *ORTEP* (thermal ellipsoid plot program), Report ORNL-5138, Oak Ridge National Lab., Tennessee, USA, **1976**. E. Keller, *SCHAKAL* (molecular drawing), *Chem. Unserer Zeit* **1986**, *20*, 178. B. W. van der Waal, *FSYN* (slant plane Fourier syntheses), Technical University of Enschede, Netherlands, **1975**. *SYBYL* (molecular calculations), Tripos Associates, Inc., St. Louis. *INSIGHT/DISCOVER*, Biosym Technologies, San Diego, USA. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103346. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk]

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[9] This method of removing the most volatile component, here Me_4Sn, from such aluminum-tin exchange equilibria has great promise for the synthesis of a variety of uncomplexed $RAlCl_2$ reagents from $RSnMe_3$ and $MeAlCl_2$, such as **20**.

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[13] The helical sinuosity in the structure of solid **25** has prompted one of us (C. K.) to view such a structure as a “DNA strand for tin soldiers”.

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[36] Dr. Jürgen Weber conducted this experiment and established the unexpected aluminum-tin exchange depicted in Equation 6.

[37] An undergraduate research assistant in our research group, Leza Luchetta, was first in realizing this novel generation of the allylating agent **9**.

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