446 *Organometallics* **2004,** *23,* 446−453

Decomposition of $[2\text{-Pyr}(SiMe_3)_2C]_2SbCl$ into the Stibaalkene $[2\text{-Pyr}(SiMe_3)_2C{-}Sb{=}C(SiMe_3)2\text{-Pyr}]$: Solid, Solution, and ab Initio Study

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Received October 9, 2003

The disubstituted antimony chloride complex $[2\text{-Pyr}(SiMe_3)_2C]_2SbCl$ (Pyr = C_5H_4N), formed from the 2:1 reaction of $[2\text{-Pyr}(SiMe_3)_2CLi{\cdot}tmeda]$ with $SbCl_3$, readily decomposes into the stibaalkene species $[2\text{-Pyr}(SiMe_3)_2CSb{=}C(SiMe_3)2\text{-Pyr}]$ via β-elimination of Me_3SiCl. The stibaalkene species is an intensely colored, highly air and moisture sensitive, deep red oil. In thf solution the elimination of Me_3SiCl occurs at temperatures ca. −40 °C; however, orange crystals of $[2\text{-Pyr}(SiMe_3)_2C]_2SbCl$ were obtained from an Et_2O solution maintained at −25 °C and the structure was determined by single-crystal X-ray diffraction. ^1H and ^{13}C NMR spectra of the crystals of $[2\text{-Pyr}(SiMe_3)_2C]_2SbCl$ have been obtained in d_8-toluene at −30 °C, and its decomposition to the stibaalkene was followed by recording spectra as the sample was warmed to 30 °C. DFT ab initio calculations have been conducted to investigate the role of the pyridyl groups in Me_3SiCl elimination as well as the structure and stability of the final stibaalkene. These indicate that the formation of strong Sb−N bonds effectively localizes much of the double-bond character in a C=C rather than Sb=C bond, increasing its overall stability.

Introduction

Stable, localized E=C double bonds of heavier group 15 elements are exemplified by the phosphaalkenes, which are now a well-established family of compounds with their methods of formation many and varied.[1] Though fewer examples are known, the synthesis and stabilization of arsaalkenes is also becoming more established.[2] However, there is still significant difficulty in forming compounds which contain stable, localized Sb=C bonds, and in fact only three examples have to date been structurally characterized in the solid state by single-crystal X-ray diffraction.[3] Two of these are the 2,3-distibabutadienes $[(R)(Me_3SiO)C{=}SbSb{=}C(Me_3SiO)(R)]$ (R = Mes, Mes*), produced in low yield as a byproduct in the synthesis of stibadionates.[4] The other is a stibaenol, [(Mes*)C(=O)-Sb=C(OH)(Mes*)], formed on treatment with HCl of the lithiated stibadianato complex obtained from the reaction of $[(SiMe_3)_2SbLi]$ with (Mes*)COCl.[4] We have previously established that the stable stibaalkene $[2\text{-Pyr}(SiMe_3)_2CSb{=}C(SiMe_3)\text{-}2\text{-Pyr}]$ (**1**) can be readily formed on β-elimination of Me_3SiCl from $[2\text{-Pyr}(SiMe_3)_2C]_2SbCl$ (**2**; Pyr = C_5H_4N) as an intensely colored air- and moisture-sensitive red oil. The stibaalkene nature of this red oil, which is stable under an inert atmosphere at room temperature, was established from mass spectrometry studies and from the mixed group 13/15 *geminal* organodimetallic compounds formed on carbometalation with Me_3M (M = Al, Ga)[5,6] and Et_3In.[7] Previous attempts at using this route to form stibaalkenes from $[(Me_3Si)_3CSbCl_2]$, $[(Me_3Si)_2CHSbCl_2]$, and $[\{(Me_3Si)_2CH\}_2SbCl]$ had all proved unsuccessful.[8] While bulky ligands are an obvious prerequisite for the kinetic stability of stibaalkenes, what has been surprising is the thermal robustness of the compounds described above; the two stibabutadienes have relatively high decomposition points (>200 °C), while the red oil **1** was observed in EI-MS intact at 200 °C.

The formation of **1** from **2** can be clearly observed in the reaction mixture at temperatures above −40 °C, indicating that the decomposition of **2** is extremely facile in thf solution. This had previously hindered any attempt at structural characterization of the precursor to the red oil; however, we have now finally crystallized, isolated, and obtained the solid-state structure of $[2\text{-Pyr}(SiMe_3)_2C]_2SbCl$ by single-crystal X-ray diffraction. This has enabled us to conduct an NMR study of the decomposition of the crystals and the coincident forma-

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10.1021/om034229+ CCC: $27.50

tion of the stibaalkene **1**. As such, we now report the NMR spectra of **1** and **2** and the transition between them, while the crystal structure analysis of **2** has allowed us the opportunity to study the geometric and electronic factors which allow the facile elimination of Me_3SiCl and the stabilization of **1** by high-level DFT calculations.

Experimental Section

All compound manipulations were carried out under dry inert-atmopshere conditions (Ar gas) using standard Schlenk techniques and a recirculating glovebox. All solvents were dried by reflux over Na/K alloy and degassed prior to use. d_8-Toluene was dried over 4 Å molecular sieves. $SbCl_3$ was purchased from Aldrich and was purified by sublimation. ^nBuLi (15% solution in hexanes) was purchased from Merck-Schuchardt and standardized before use. 2-Pyr$(Me_3Si)_2CH$ was synthesized according to the literature procedure.[9] Elemental analyses were conducted by CMAS, Melbourne, Australia. All ^1H and ^{13}C NMR spectra were recorded on a Bruker AM400 MHz spectrometer with chemical shifts referenced internally to d_8-toluene.

Crystallography Details. Crystallographic data were collected on an Enraf Nonius KappaCCD diffractometer with graphite-monochromated Mo Kα ($\lambda_o = 0.71073$ Å) radiation. A single crystal of **2** of suitable quality for X-ray analysis was mounted on a glass fiber under oil.[10] Data were collected at 123(2) K and processed using Nonius software. Structures were solved and refined by full-matrix least squares on F^2 and expanded using direct methods with all calculations performed by the SHELXS 97 software[11] and XSEED interface.[12] All H atoms were placed in calculated positions (C−H = 0.95 Å) and included in the final least-squares refinement. All other atoms were located and refined anisotropically.

Computational Details. All hybrid density functional calculations were performed using the ONIOM method[13] as implemented in the Gaussian 98 program, revision A.7.[14] The B3LYP functional[15] was used throughout, and the Sb, Si, and Cl atoms were modeled using the LANL2 effective core potential and associated basis set,[16] augmented by a d polarization function in each case (α = 0.218, 0.284, and 0.64 for Sb, Si, and Cl, respectively).[17] The 6-31G* basis set was used for the remainder of the QM partition, which consisted of all atoms other than the methyl substituents on silicon. The MM partition was treated using the universal force field (UFF).[18] Optimizations were performed without constraint, and the nature of the stationary points was confirmed by calculation of vibrational frequencies.

Synthesis of 2. A cooled (−78 °C) deep orange Et_2O solution (30 mL) of [2-Pyr$(SiMe_3)_2$CLi·tmeda][19] (5 mmol) was added slowly to a cooled (−78 °C) rapidly stirring Et_2O (25 mL) solution of $SbCl_3$ (2.5 mmol, 0.57 g). The yellow reaction mixture was stirred at −60 °C for 2 h, at which point it was quickly filtered into a precooled Schlenk flask via a glass frit to remove LiCl. The now pale orange reaction mixture was stabilized at −35 °C and at least 40% of the volume of Et_2O removed in vacuo. The solution was placed in the freezer at −25 °C. Pale orange crystals of **2** were obtained over several days from a now red solution and isolated at −25 °C by removal of solvent via cannela and washed with cold Et_2O. Yield: 28% (0.44 g). Mp: 72−74 °C to a red melt. ^1H NMR (400 MHz, d_8-toluene, −30 °C): δ 6.96 (br, 1H), 6.93 (d, 1H), 6.73 (dd, 1H), 6.21 (dd, 1H), 0.45 (s, 9H, Me_3Si), 0.41 (s, 9H, Me_3Si). ^{13}C NMR (100.6 MHz, d_8-toluene, −30 °C): δ 167.3, 146.2, 136.0, 124.3, 118.8, 50.1 (*C*−Sb), 4.5 (Me), 2.3 (Me). Anal. Found (calcd): C, 45.6 (45.7); H, 7.2 (7.0); N, 4.6 (4.5). Chemical shift assignments are shown in Figure 5.

NMR Data for **1**. ^1H NMR (400 MHz, d_8-toluene, 30 °C): δ 7.81 (d, 1H), 7.16 (d, 1H), 6.93 (d, 1H), 6.74 (dd, 1H), 6.54 (d,1H), 6.35 (dd, 1H), 6.15 (dd, 1H), 5.50 (dd, 1H), 0.27 (s, 9H, Me_3Si), 0.25 (s, 9H, Me_3Si), 0.12 (s, 9H, Me_3Si). ^{13}C NMR (100.6 MHz, d_8-toluene, 30 °C): δ169.3, 168.4, 146.2, 143.0, 137.2, 124.8, 119.3, 118.0, 101.7, 80.0 (*C*═Sb), 40.9 (*C*−Sb), 3.2 (Me), 2.3 (Me), 1.6 (Me). NMR data for **Me_3SiCl**: ^1H, δ 0.19; ^{13}C, δ 2.9. Chemical shift assignments are shown in Figure 5.

Crystallographic Data for 2: $C_{24}H_{44}N_2Si_4SbCl$; M = 630.17; crystal 0.22 × 0.15 × 0.1 mm; monoclinic, $P2_1/c$; a = 11.607(2) Å, b = 15.809(3) Å, c = 17.269(4) Å; β = 105.80(3)°; V = 3049.1(11) Å^3; $D_c(Z = 4)$ = 1.373 g cm^{-3}; $F(000)$ = 1304 $\mu_{\mathrm{Mo\ K}\alpha}$ = 1.165 mm^{-1} (no correction); $2\theta_{\max}$ = 56.7°; Mo Kα radiation; final R, R_w = 0.034, 0.063; R(all data) = 0.055; GOF 1.03; N_{ind} = 7507 "observed" ($I > 2\sigma(I)$) reflections out of N = 23 601 unique; no. of data/restraints/parameters 7507/0/301.

Results and Discussion

The difficulty in the synthetic procedure was to synthesize and crystallize **2** in a solvent mixture, and at low enough temperatures to inhibit both decomposition to the stibaalkene and/or reduction of the complex to Sb^0. This latter process has been observed when thf was not used as the reaction medium or when tmeda was not used in complexing the lithium alkyl precursor. The synthetic procedure for the formation of the red oil has been described previously,[5] and so a modification of this was used in an attempt to isolate crystalline **2**, depicted in Scheme 1. A cold (−78 °C), dilute diethyl ether solution of [2-Pyr$(SiMe_3)_2$CLi·tmeda] was transferred slowly by cannula to a rapidly stirred dilute diethyl ether solution of $SbCl_3$ maintained at −78 °C. The reaction mixture was warmed to −60 °C, at which temperature it was stirred for ca. 2 h. The yellow reaction mixture was then filtered quickly through a frit in vacuo to a precooled Schlenk flask (at −60 °C). The reaction mixture was raised to −35 °C, at which point the Et_2O volume was reduced by approximately 40% under high vacuum. The now pale orange solution was placed in the freezer and stored at −25 °C. While the

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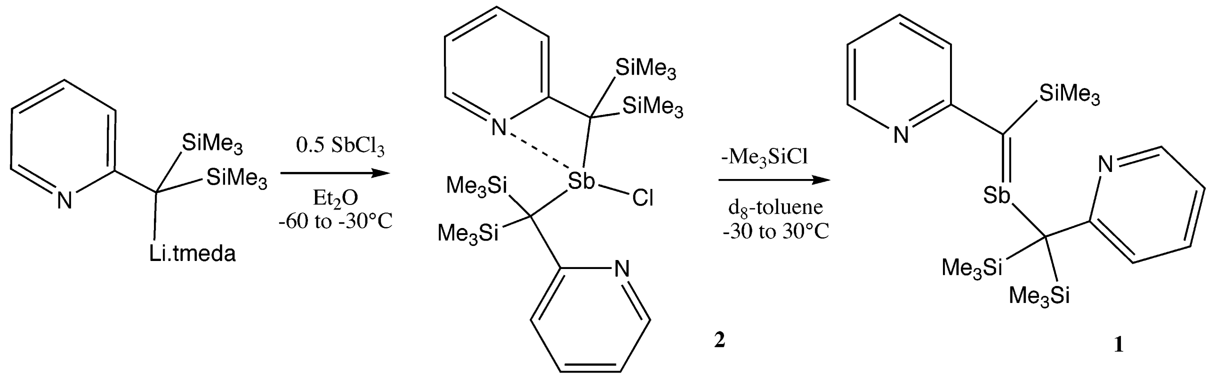
Scheme 1. Synthesis of Crystalline [2-Pyr(SiMe$_3$)$_2$C]$_2$SbCl (2) and the Decomposition of the Crystals to the Stibaalkene [2-Pyr(SiMe$_3$)$_2$CSb=C(SiMe$_3$)-2-Pyr] (1) in the NMR Solvent



solution takes on the typical red color of the stibaalkene, orange crystals of **2** suitable for X-ray diffraction studies were obtained overnight in 28% yield. NMR, elemental analysis, and X-ray studies confirmed the crystals to be [2-Pyr(SiMe$_3$)$_2$C]$_2$SbCl (**2**).

Once isolated from solution, the crystals were found to be stable over long periods when stored at freezer temperature. In fact, in determinations of the melting point the crystals did not undergo any substantial visible change until they decomposed into a deep red melt at 72−74 °C. Therefore, it appears that the formation of the stibaalkene is highly state dependent, which is consistent with previous studies on stibaalkene formation from [2-Pyr(Me$_3$Si)$_2$C]SbCl$_2$ and its subsequent spontaneous polymerization.[25] These crystals could be sublimed intact in vacuo between 200 and 210 °C;[24] however, they readily undergo Me$_3$SiCl elimination in thf and in toluene at relatively low temperatures.

Crystal Structure Studies. The crystals of **2** were found to exist in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Study of the crystal packing indicates there are no strong close intermolecular connections between the individual molecules, and the discrete structure is shown in Figure 1. The crystallographic data are given in the Experimental Section with selected bond lengths and angles in Table 1.

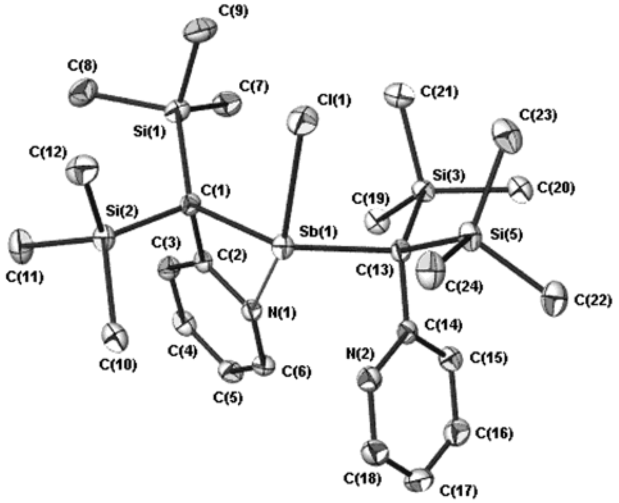


Figure 1. Crystal structure of [2-Pyr(SiMe$_3$)$_2$C]$_2$SbCl (**2**). Selected bond lengths and angles are given in Table 1.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in 2

Sb(1)-C(1)	2.327(2)	N(1)−C(2)	1.350(3)
Sb(1)−C(13)	2.269(2)	C(1)−C(2)	1.496(3)
Sb(1)−N(1)	2.4558(18)	C(13)−Si(3)	1.905(2)
Sb(1)−Cl(1)	2.5074(7)	C(13)−Si(5)	1.938(2)
C(1)−Si(1)	1.908(2)	C(13)−C(14)	1.518(3)
C(1)−Si(2)	1.935(2)	N(2)−C(14)	1.351(3)
N(1)−C(6)	1.346(3)	N(2)−C(18)	1.343(3)

C(13)−Sb(1)−C(1)	120.17(8)	C(2)−C(1)−Sb(1)	94.67(14)
C(13)−Sb(1)−N(1)	85.87(7)	Si(1)−C(1)−Sb(1)	128.57(11)
C(1)−Sb(1)−N(1)	59.30(7)	Si(2)−C(1)−Sb(1)	98.17(10)
C(13)−Sb(1)−Cl(1)	93.33(6)	C(14)−C(13)−Si(3)	114.32(16)
C(1)−Sb(1)−Cl(1)	95.28(6)	C(14)−C(13)−Si(5)	102.97(15)
N(1)−Sb(1)−Cl(1)	148.79(5)	Si(3)−C(13)−Si(5)	112.55(11)
C(6)−N(1)−Sb(1)	147.09(15)	C(14)−C(13)−Sb(1)	100.25(14)
C(2)−N(1)−Sb(1)	93.19(13)	Si(3)−C(13)−Sb(1)	118.90(11)
C(6)−N(1)−C(2)	119.71(19)	C(14)−C(13)−Sb(1)	100.25(14)
C(2)−C(1)−Si(1)	115.29(16)	Si(3)−C(13)−Sb(1)	118.90(11)
C(2)−C(1)−Si(2)	104.40(14)	Si(5)−C(13)−Sb(1)	106.02(10)
Si(1)−C(1)-Si(2)	112.07(11)		

The importance of obtaining the crystal structure was to allow a comparison with other similar systems which have the potential to undergo Me$_3$SiCl elimination. Although we cannot make a direct structural extrapolation from the solid state to that which is present in solution, there may be significant gross features which help explain the ease, or otherwise, of the stibaalkene formation. It also gives a sound basis for computational studies of the decomposition process, which we describe later. Table 2 contains a comparison of all the relevent bond length and angle parameters which may have some significance in understanding the β-elimination process; the importance of the stabilization gained from close N···Sb interactions, the proximity of the Si and Cl atoms, and the strength of Sb−Cl bonds. From Figure 1 it can be seen that in **2** one of the pyridyl groups is oriented such as to allow a close dative contact between the pyridyl N and the Sb center, thus forming the near-planar C2−N1···E−C1 ring, which is coplanar with the

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Table 2. Comparison of Relevant Bond Lengths (Å) and Angles (deg) in Compounds Analogous to 2 in the Solid State

compd	Sb−C	Sb···N	Sb−Cl	C−Sb−Cl	Si−C−Sb−Cl	Me$_3$Si···Cl	ref
[(Me$_3$Si)$_2$CH]SbCl$_2$	2.136(4)		2.355(1)	99.8(1)	22.8	3.62	20[a]
			2.358(2)	102.8(1)			
[(Me$_3$Si)$_2$CH]SbCl$_2$	2.132(4)		2.368(1)	100.5(1)			21
			2.400(1)	96.3(1)	16.0	3.62	
[(Me$_3$Si)$_2$CH]$_2$SbCl	2.171(2)		2.3979(12)	101.08(7)	43.9	3.75	22
	2.167(2)			95.99(7)	39.0	3.72	
[(6-Me-Pyr)(SiMe$_3$)$_2$C]SbCl$_2$	2.218(3)	2.391(3)	2.366(2)	102.9(1)	26.7	3.79	23
			2.466(1)	96.39(9)			
[(2-Pyr)(SiMe$_3$)$_2$C]SbCl$_2$	2.213(5)	2.371(7)	2.373(2)	101.4(1)	32.4	3.81	24
			2.469(2)	98.4(2)			
[(6-Me-Pyr)(SiMe$_3$)CH]SbCl$_2$	2.177(4)	2.418(3)	2.393(1)	99.6(1)	26.4	3.81	23
			2.494(1)	95.0(1)			
[(2-Pyr)(SiMe$_3$)$_2$C]$_2$SbCl	2.327(2)	2.456(2)	2.5074(7)	95.28(6)	51.9	3.56	
	2.269(2)			93.33(6)	30.1	4.01	

[a] Bond angles and lengths in the CSSD differ from those reported in this paper.

pyridyl ring and is typical for this family of complex (E = P, As, Sb). The N···Sb distance of 2.456(2) Å is longer in comparison with the analogous bond distances of 2.418(3) Å in {[(6-Me-2-Pyr)(SiMe$_3$)CH]SbCl$_2$}$_2$, 2.391(3) Å in [(6-Me-Pyr)(SiMe$_3$)$_2$C]SbCl$_2$, and 2.371(7) Å in [(2-Pyr)(SiMe$_3$)$_2$C]SbCl$_2$, which is understandable on the basis of the increased sterics and reduced $\delta+$ charge on the Sb center. The rotation of the other pyridyl ring away from a similar in-plane arrangement places N2 2.844 Å away from the Sb center with a torsion angle for N2−C14−C13−Sb1 of 31.2°. Therefore, while this distance is exactly that observed for one of the two N···Sb distances in the five-coordinate Sb(III) complex [{2-C$_6$H$_4$C(CF$_3$)$_2$O}Sb{2-C$_6$H$_4$(CH$_2$NMe$_2$)$_2$}],[26] the slight rotation precludes a direct dative bond and the Sb center in **2** is four-coordinate in the solid state in a distorted-square-based-pyramidal geometry. There is, however, clearly the possibility of fluxionality and formation of a transient five-coordinate species in solution, which could contribute to the facile stibaalkene formation through imparting conformational rigidity and/or lengthening and weakening of the Sb−Cl bond. Interestingly, as Table 2 illustrates, **2** exhibits, though only marginally, the longest Sb−Cl bond of any of the analogous compounds. Table 2 also indicates that **2** displays the shortest Si···Cl distance, defined by Si5−C13−Sb1−Cl1, of 3.562 Å, which is well within the sum of the van der Waals radii for the two elements (3.85 Å). However, the torsion angle is greater at 51.9° than the 30.1° for Si(1)···Cl(1) which are separated by 4.01Å, a distance outside the sum of the van der Waals radii. All the other complexes listed in Table 2 with similar torsion angles have shorter Si···Cl distances, but of these, only [2-Pyr(Me$_3$Si)$_2$C]SbCl$_2$ has thus far been confirmed as undergoing the β-elimination process. In this case, however, the putative stibaalkene product, [Cl−Sb═C(SiMe$_3$)-2-Pyr], immediately undergoes a [2 + 2] cycloaddition process, resulting in the formation of a two-dimensional polymer with the residual chloride ligands occupying bridging positions.

NMR Studies. Due to the rapid formation of the stibaalkene in thf solution, NMR studies were carried out in d_8-toluene. Crystals of **2** were transferred under argon into a chilled NMR tube standing in an acetone/dry ice bath, and d_8-toluene, which had been precooled to −60 °C, was added quickly by syringe. The orange solution which formed was stable at −30 °C, at which temperature the first ^{1}H and ^{13}C spectra were recorded. In contrast, **2** cannot be successfully synthesized in situ in toluene solution, as reduction to Sb^0 occurs even at very low temperatures. Spectra were then recorded on the sample at 0 °C and 30 °C and finally after 2 days (again at 30 °C), by which time quantitive decomposition had occurred. Assignment of the signals belonging to the individual compounds was achieved using ^{1}H/^{1}H and ^{1}H/^{13}C correlation spectroscopy (HMQC and HMBC). Figure 3 charts the formation of [2-Pyr(SiMe$_3$)$_2$CSb═C(SiMe$_3$)-2-Pyr] (**1**) from [2-Pyr(Me$_3$Si)$_2$C]$_2$SbCl (**2**), with the final spectrum also containing the eliminated Me$_3$SiCl.

At −30 °C the standard ^{1}H spectrum for the 2-Pyr(Me$_3$Si)$_2$C$^-$ moiety is observed, though the signal for the proton in the 6-position of the pyridyl ring is significantly broadened. At 0 °C this becomes a distinct doublet. This would tend to indicate an asymmetry in the bonding of the two 2-Pyr(Me$_3$Si)$_2$C$^-$ moieties to the Sb center at the lower temperature and most likely results from one datively bonding pyridyl ring and one not, as observed in the crystal structure. As the temperature increases to 0 °C, the bonding modes are indistinguishable and suggests that the N···Sb bonds either are no longer present or, more likely, are exchanging rapidly at the Sb center. The sample was maintained at 0 °C for 60 min, during which time there was no visible decomposition of **2**. In the ^{13}C spectrum at −30 °C the carbon atoms bonded to Sb appear at δ 50.7 and, not unexpectedly, do not change significantly when the sample is warmed to 0 °C.

Warming to 30 °C facilitates Me$_3$SiCl elimination, and over the 15 min period it took to warm from 0 °C, the ^{1}H spectrum indicated an approximate 25% conversion to the stibaalkene (Figure 2). In addition to the appearance of the new pyridyl protons, the Me$_3$Si signals from **2** broaden significantly and the new signals from the Me$_3$Si groups **1** and Me$_3$SiCl (^{1}H, δ 0.19; ^{13}C, δ 2.9) appear distinct at lower frequencies; see Figure 3.

When the sample was allowed to fully convert over a 48 h period, a clean spectrum of the stibaalkene was obtained. The ^{1}H spectra are shown in Figures 2 and 3, and the ^{13}C spectrum is shown in Figure 4. Of interest is the chemical shift of the C atom involved in the C═Sb double bond, which appears at δ 80.0, while that

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(26) Yamamoto, Y.; Chen, X.; Kojima, S.; Ohdoi, K.; Kitano, M.; Doi, Y.; Akiba, K. *J. Am. Chem. Soc.* **1995**, *117*, 3922.

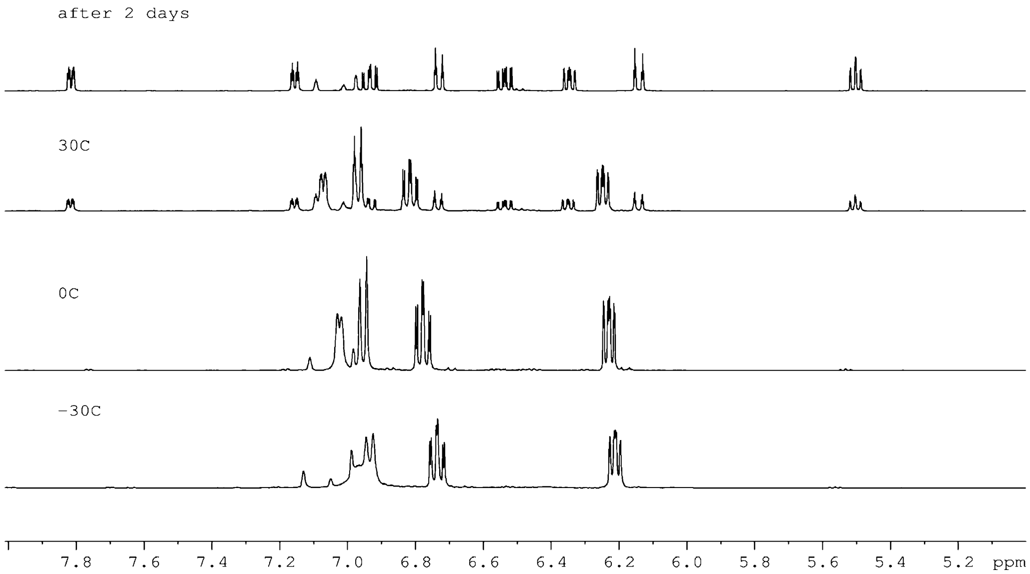

Figure 2. ^{1}H NMR (d_8-toluene) pyridyl region: temperature-dependent formation of stibaalkene **1** from [2-Pyr(Me$_3$Si)$_2$C]$_2$SbCl (**2**).

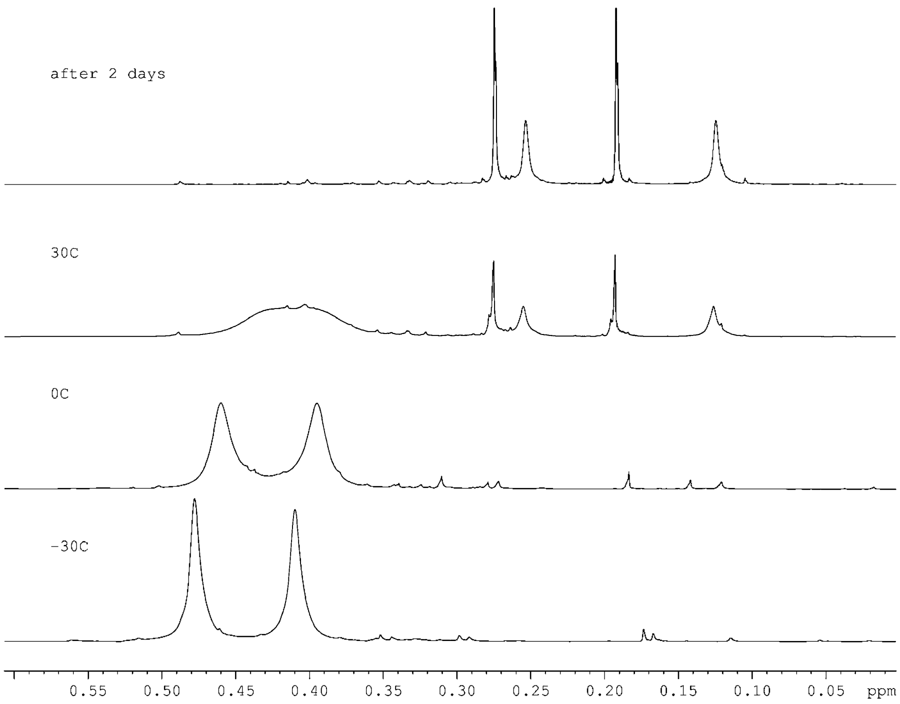

Figure 3. ^{1}H NMR (d_8-toluene) Me$_3$SiCl region: temperature-dependent formation of stibaalkene **1** from [2-Pyr(Me$_3$Si)$_2$C]SbCl (**2**).

from the remaining C−Sb single bond is now evident at δ 40.9. In comparison with the only other reported chemical shifts for a C=Sb bond in stibabenzene, δ 178.3,[27] and [(Mes*)C(=O)Sb=C(OH)(Mes*)], δ 211.8,[4] it might be concluded that there is a comparatively large $\delta-$ charge located on the C in **1** induced by the Sb and Si centers. Figure 5 shows all the ^{1}H and ^{13}C shifts for **1** and **2**.

Theoretical Analysis. The experimental results summarized thus far pose a number of questions that can be usefully addressed computationally, the most obvious being the structure of the red oil **1**. Mass spectrometric data are consistent with its formulation as a monomeric stibaalkene, an observation that contrasts markedly with the corresponding reaction of [2-Pyr(Me$_3$Si)$_2$C]SbCl$_2$, where a polymeric material is formed, presumably from [2 + 2] cycloaddition of a transient stibaalkene. The very different natures of the two elimination products suggests that the structures of the two stibaalkenes may also be rather different. As an initial test of the computational methodology, the structures of the two saturated antimony chloride complexes [2-Pyr(SiMe$_3$)$_2$C]$_2$SbCl (**2**) and [2-Pyr(SiMe$_3$)$_2$C]SbCl$_2$ were optimized. Selected structural parameters are collected in Figure 6, where crystallographic values are given in parentheses for comparison. In both cases,

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[27] Ashe, A. J., III; Sharp, R. R.; Tolan, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 5451.

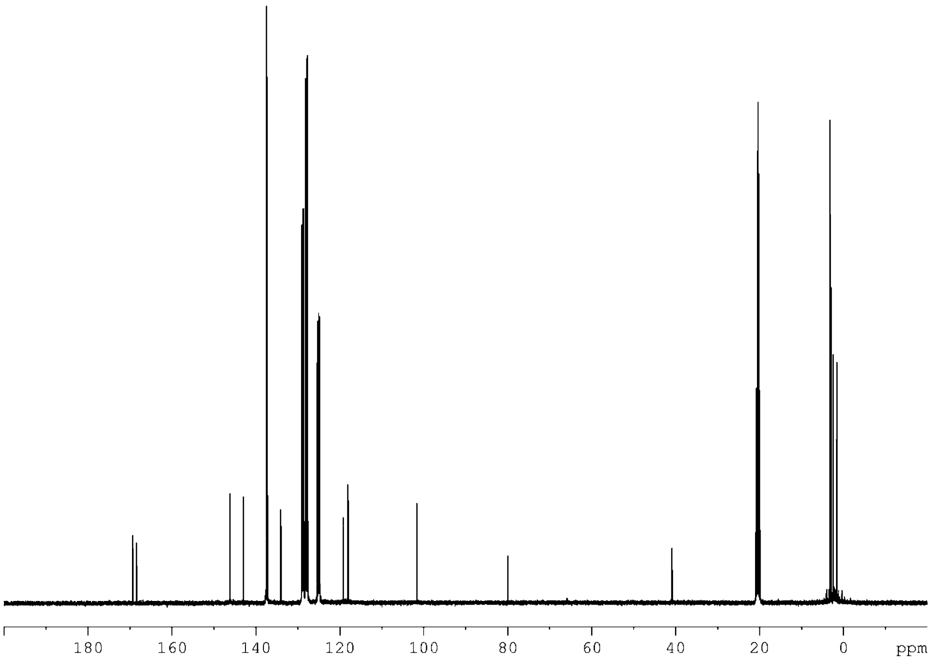


Figure 4. ^{13}C NMR (d_8-toluene, 30 °C, 2 days) of the stibaalkene **1** derived from from [2-Pyr(Me$_3$Si)$_2$C]$_2$SbCl (**2**).

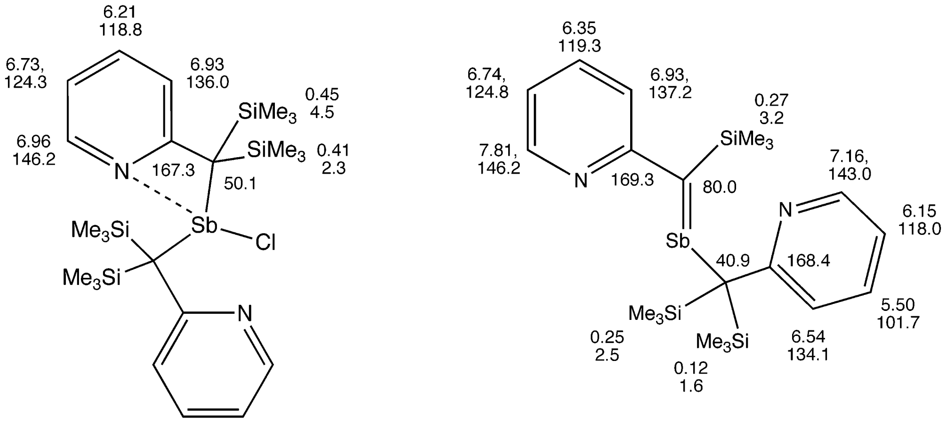


Figure 5. NMR chemical shifts (δ) in d_8-toluene for **2** at −30 °C and the stibaalkene **1** at 30 °C. ^1H shifts are given as the upper numbers and ^{13}C shifts as the lower numbers.

the Sb−C and Sb···N separations are overestimated by between 0.1 and 0.15 Å, while the optimized Sb−Cl bond lengths are somewhat shorter than experiment, discrepancies that probably reflect the limitations of the chosen basis set on Sb. Nevertheless, the gross features of the experimental structures, most significantly the presence of short Sb···N contacts, are well reproduced.

Turning to the stibaalkene elimination products, we are immediately faced with the problem that there are a large number of possible conformations of the terminal methyl groups and, without a crystal structure available to inform the intial guess, it is impossible to guarantee that the global minimum has been located. We have therefore started the optimizations from a number of initial conformations and, although subtle differences in the final bond lengths do occur, the key features of the Sb coordination sphere remain unaltered. Optimized structures of the two monomeric stibaalkenes [ClSb=C(SiMe$_3$)-2-Pyr] and [2-Pyr(SiMe$_3$)$_2$CSb=C(SiMe$_3$)-2-Pyr], are shown in Figure 6. The stibaalkene [ClSb=C(SiMe$_3$)-2-Pyr] has a very short Sb−C distance (2.03 Å compared to values in the region of 2.40 Å for the Sb−C single bond), and there is no evidence of any interaction between the pyridyl nitrogen and the antimony center (Sb···N = 2.71 Å). The structural evidence is therefore consistent with the presence of a localized Sb=C double bond, and the intrinsic weakness of this bond presumably leads to the facile polymerization observed experimentally. In marked contrast, the structure of the stibaalkene **1**, [2-Pyr(SiMe$_3$)$_2$C−Sb=C(SiMe$_3$)-2-Pyr], is not consistent with the presence of a classical Sb=C double bond. The Sb=C bond is substantially longer, at 2.11 Å, and the nitrogen centers on *both* pyridyl rings coordinate to the antimony center, giving rise to a four-coordinate structure, rather, with a vacant site occupied by a lone pair, not dissimilar to those structures adopted by the starting complexes. Given the general tendency to *overerestimate* Sb···N bond lengths noted above, we are confident that these interactions are not an artifact of the computational method. Moreover, there is a marked asymmetry in the Sb−N bond lengths, with the pyridyl group attached to the Sb=C bond (N$_B$) forming a much stronger bond (2.28 Å). Associated with this, significant changes occur

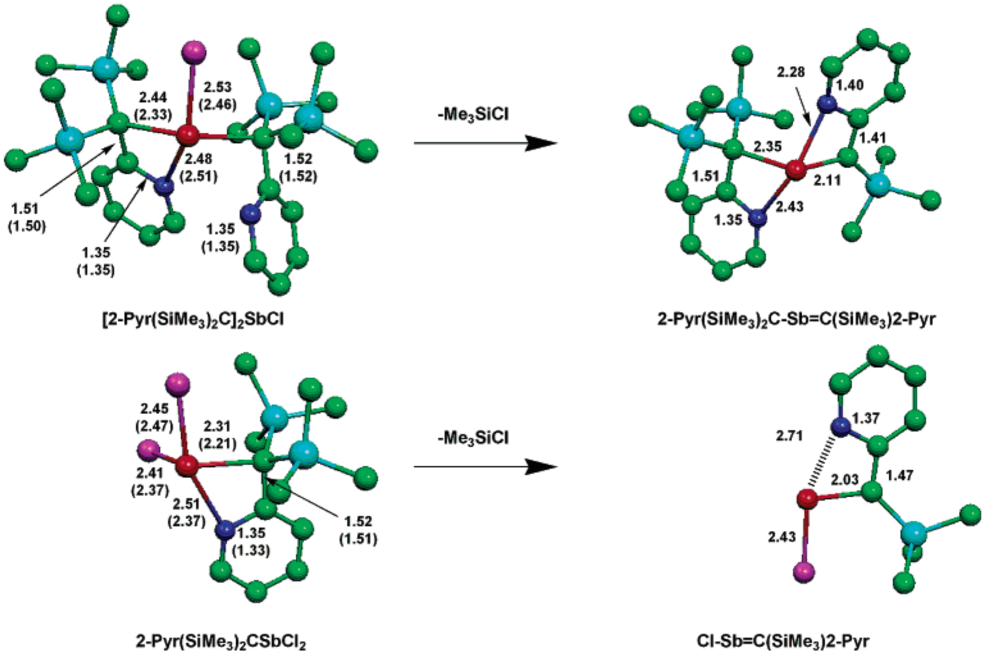
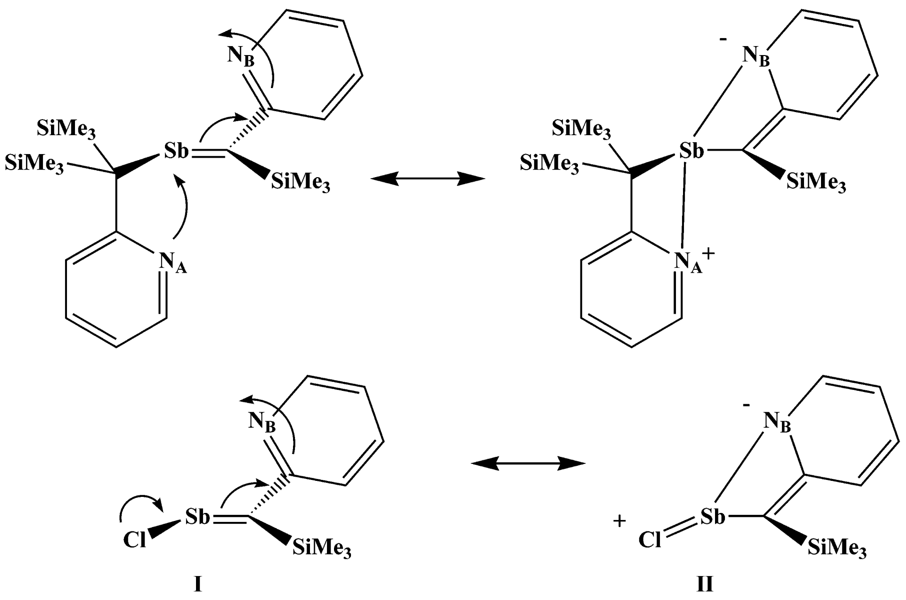


Figure 6. Optimized structures of [2-Pyr(SiMe$_3$)$_2$C]$_2$SbCl, 2-Pyr(SiMe$_3$)$_2$CSbCl$_2$, 2-Pyr(SiMe$_3$)$_2$CSb=C(SiMe$_3$)-2-Pyr, and [ClSb=C(SiMe$_3$)-2-Pyr].

Scheme 2. Resonance Forms for Stibaalkenes 2-Pyr(SiMe$_3$)$_2$CSb=C(SiMe$_3$)-2-Pyr and [ClSb=C(SiMe$_3$)-2-Pyr]



within the =C(SiMe$_3$)-2-Pyr group, most notably a contraction and expansion of the C−C and C=N bonds, respectively.

The rather unexpected structure of **1** can be rationalized by noting that the interaction between Sb and N$_A$ involves donation of electron density from the Pyr lone pair into the π* LUMO of the newly formed Sb=C bond, which in turn will polarize the Sb=C bonding orbital toward the carbon center. The developing charge at the carbon center can then be delocalized onto the pyridyl nitrogen, N$_B$, leading to a strong N$_B$−Sb bond (Scheme 2, resonance form **II**). The short C−C and long C=N$_B$ bonds in the optimized structure, along with the unusually low chemical shift at the unsaturated carbon, are certainly indicative of a strong contribution from resonance form **II**. The crucial stabilizing role of the N$_A$−Sb interaction in **1** is illustrated by the absence of a similarly short Sb···N separation in [ClSb=C(SiMe$_3$)-2-Pyr], despite the presence of an equivalent Sb=C-2-Pyr group. In [ClSb=C(SiMe$_3$)-2-Pyr], donation of electron density into the Sb=C π* orbital can only occur via the lone pairs of the Cl ligand, and the less efficient π overlap leads to a much reduced contribution from resonance form **II**. Thus while there is some contraction and elongation of the C−C and C=N bonds, respectively, the effect is much less dramatic than in **1**. The lower stability of the stibaalkene is reflected in the calculated energy change for elimination of Me$_3$SiCl, which is +22.5 kcal mol^{-1} for [2-Pyr(Me$_3$Si)$_2$C]SbCl$_2$ but only +7.1 kcal mol^{-1} for 2-Pyr(SiMe$_3$)$_2$C]$_2$SbCl.[28] In the absence of effective stabilization of the Sb=C π* orbital by the chloride ligand, the alternative is to form an inter- rather than intramolecular Sb···N bond, consistent with the observed polymeric structure.

Conclusions

The disubstituted antimony chloride compound [2-Pyr-$(SiMe_3)_2C]_2SbCl$ decomposes readily into the stibaalkene [2-Pyr$(SiMe_3)_2CSb{=}C(SiMe_3)$-2-Pyr] (**1**), the decomposition process having now been followed by NMR. In toluene solution this process occurs at temperatures above 0 °C and gives a stable, intensely colored red solution. Theoretical studies have revealed that the origin of the unusual stability of the stibaalkene, **1**, is the formation of strong Sb−N bonds from the pyridyl groups, which effectively localizes much of the double-bond character in a C═C, rather than Sb═C, bond.

Acknowledgment. We thank the Australian Research Council and Monash University for financial support.

Supporting Information Available: Crystallographic data in electronic form as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Although the enthalpy change remains endothermic in both systems, the entropy gain on elimination of Me_3SiCl is more likely to dominate in this case.