X-ray Crystallographic Study of 2,2-Dimethyl-7-methylene-4-phenyl-3-azonia-6-thiabicyclo[3.2.1]octa-3-ene Hexachloroantimonate (**3**-$SbCl_6$):

Crystal data: Empirical formula: $C_{15}H_{18}Cl_6NSSb$; M = 578.85 g mol^{-1}; crystal size: (0.53 × 0.33 × 0.20) mm^3 as orange plate; triclinic; space group P$\bar{1}$(2); unit cell dimensions: a = 9.7815(13), b = 10.6819(14), c = 12.195(2) Å; α = 112.326(11), β = 93.809(11), γ = 109.714(11)°; V = 1081.6 (3) Å^3; Z = 2, ρ = 1.777 g mL^{-1}; μ(Mo-K$_\alpha$) = 2.112 mm^{-1}; empirical absorption correction with Ψ-scans yields T_{min} = 0.8866 and T_{max} = 0.9994; F(000) = 568. – *Data collection and analysis*: NONIUS-CAD-4-Diffraktometer, λ = 0.71073 Å, T = 21(2) °C, ω-2Θ-scan, Θ-range 2.49–23.97°; 3606 reflections collected, 3381 independent reflections (R_{int} = 0.86 %), 3102 observed reflections (I>2σI). *Structure solution and refinement*: Solution with SHELXS-86-program system; refinement of 219 variables with SHELXL-93 converged at R1[F^2] = 0.0276 [wR2(F^2) = 0.0677] for 3606 data (I>2σI) and R1[F^2] = 0.0314 [wR2(F^2) = 0.0703] for all data; final rest electron density: 0.689/–0.668 e/ Å^3.

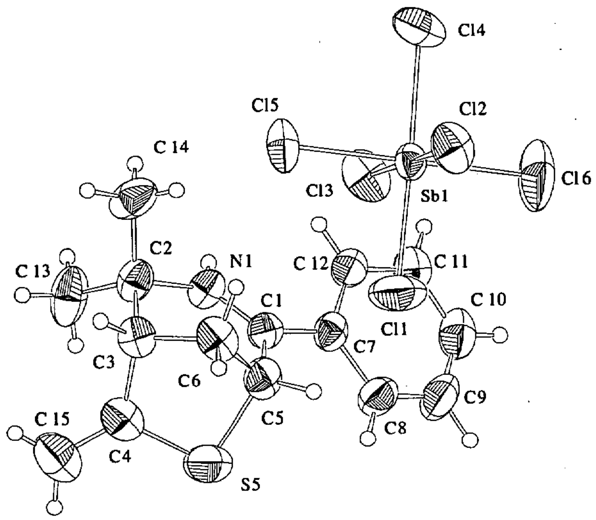

Figure S1. ORTEP diagram of **3**-$SbCl_6$.

Table S1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for **3**-$SbCl_6$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Sb(1)	9285(1)	8265(1)	7183(1)	38(1)
Cl(1)	10321(2)	9151(2)	5806(1)	99(1)
Cl(2)	11638(1)	9485(1)	8537(1)	65(1)
Cl(3)	6915(1)	6995(2)	5788(1)	68(1)
Cl(4)	8292(1)	7301(1)	8541(1)	71(1)
Cl(5)	9758(1)	6144(1)	6194(1)	64(1)
Cl(6)	8684(2)	10296(2)	8120(1)	108(1)
S(1)	7537(2)	6321(2)	914(1)	72(1)
N(1)	5459(3)	4650(3)	2309(3)	43(1)
C(1)	6012(4)	6047(4)	2605(3)	41(1)
C(2)	6218(4)	3595(4)	1904(4)	48(1)
C(3)	7790(4)	4395(4)	1760(3)	46(1)
C(4)	7788(4)	4669(5)	631(4)	55(1)
C(5)	7595(4)	6719(4)	2521(4)	53(1)
C(6)	8502(4)	5940(4)	2804(4)	53(1)
C(7)	5118(4)	6925(4)	2995(3)	42(1)
C(8)	5427(5)	8204(4)	2816(4)	56(1)
C(9)	4571(6)	9016(5)	3177(4)	68(1)
C(10)	3447(5)	8620(5)	3741(4)	63(1)
C(11)	3140(5)	7380(5)	3940(4)	56(1)
C(12)	3968(4)	6536(4)	3569(3)	47(1)
C(13)	5235(5)	2328(5)	724(5)	72(1)
C(14)	6325(5)	3069(5)	2902(5)	70(1)
C(15)	8052(6)	3889(6)	-403(4)	82(2)

Table S2. Bond lengths [Å] for **3**-$SbCl_6$.

Sb(1)-Cl(6)	2.3297(13)
Sb(1)-Cl(5)	2.3461(11)
Sb(1)-Cl(1)	2.3513(13)
Sb(1)-Cl(2)	2.3571(11)
Sb(1)-Cl(4)	2.3624(11)
Sb(1)-Cl(3)	2.3897(12)
S(1)-C(4)	1.770(5)
S(1)-C(5)	1.833(4)
N(1)-C(1)	1.293(5)
N(1)-C(2)	1.501(5)
C(1)-C(7)	1.463(5)
C(1)-C(5)	1.500(5)
C(2)-C(13)	1.512(6)
C(2)-C(14)	1.532(6)
C(2)-C(3)	1.545(5)
C(3)-C(4)	1.513(6)
C(3)-C(6)	1.529(5)
C(4)-C(15)	1.319(6)
C(5)-C(6)	1.508(6)
C(7)-C(12)	1.393(5)
C(7)-C(8)	1.401(5)
C(8)-C(9)	1.377(6)
C(9)-C(10)	1.367(7)
C(10)-C(11)	1.374(6)
C(11)-C(12)	1.381(5)

Table S3. Bond Angles [°] for **3**-$SbCl_6$.

Cl(6)-Sb(1)-Cl(5)	177.01(5)
Cl(6)-Sb(1)-Cl(1)	91.90(7)
Cl(5)-Sb(1)-Cl(1)	89.00(6)
Cl(6)-Sb(1)-Cl(2)	91.05(5)
Cl(5)-Sb(1)-Cl(2)	91.80(4)
Cl(1)-Sb(1)-Cl(2)	90.02(5)
Cl(6)-Sb(1)-Cl(4)	90.47(6)
Cl(5)-Sb(1)-Cl(4)	88.67(5)
Cl(1)-Sb(1)-Cl(4)	177.57(6)
Cl(2)-Sb(1)-Cl(4)	89.37(4)
Cl(6)-Sb(1)-Cl(3)	89.94(5)
Cl(5)-Sb(1)-Cl(3)	87.21(4)
Cl(1)-Sb(1)-Cl(3)	89.68(5)
Cl(2)-Sb(1)-Cl(3)	178.98(4)
Cl(4)-Sb(1)-Cl(3)	90.88(4)
C(4)-S(1)-C(5)	91.3(2)
C(1)-N(1)-C(2)	127.9(3)
N(1)-C(1)-C(7)	121.0(3)
N(1)-C(1)-C(5)	117.2(3)
C(7)-C(1)-C(5)	121.8(3)
N(1)-C(2)-C(13)	107.0(3)
N(1)-C(2)-C(14)	106.4(3)
C(13)-C(2)-C(14)	110.7(4)
N(1)-C(2)-C(3)	109.6(3)
C(13)-C(2)-C(3)	112.4(3)
C(14)-C(2)-C(3)	110.5(3)
C(4)-C(3)-C(6)	103.9(3)
C(4)-C(3)-C(2)	113.9(3)
C(6)-C(3)-C(2)	109.2(3)
C(15)-C(4)-C(3)	126.8(5)
C(15)-C(4)-S(1)	122.7(4)
C(3)-C(4)-S(1)	110.3(3)
C(1)-C(5)-C(6)	110.9(3)
C(1)-C(5)-S(1)	106.1(3)
C(6)-C(5)-S(1)	104.9(3)
C(5)-C(6)-C(3)	103.0(3)
C(12)-C(7)-C(8)	118.4(4)
C(12)-C(7)-C(1)	121.4(3)
C(8)-C(7)-C(1)	120.2(4)
C(9)-C(8)-C(7)	119.8(4)
C(10)-C(9)-C(8)	121.1(4)
C(9)-C(10)-C(11)	120.0(4)
C(10)-C(11)-C(12)	119.9(4)
C(11)-C(12)-C(7)	120.8(4)