Carbene–Antimony Adducts

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One-, Two-, and Three-Electron Reduction of a Cyclic Alkyl-(amino)carbene–$SbCl_3$ Adduct**

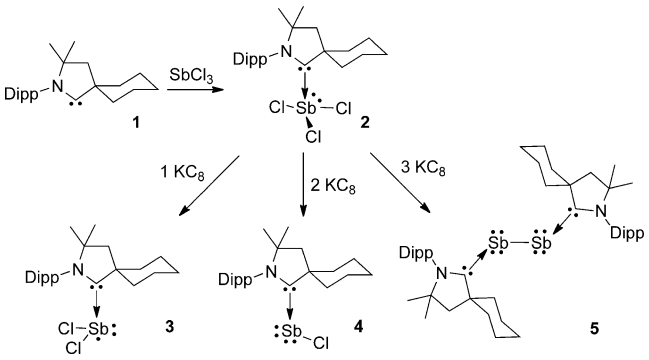
*Robert Kretschmer, David A. Ruiz, Curtis E. Moore, Arnold L. Rheingold, and Guy Bertrand**

Dedicated to Professor Hans-Ulrich Reißig on the occasion of his 65th birthday

Abstract: *A cyclic alkyl(amino)carbene readily reacts with $SbCl_3$ to form the corresponding Sb^{III} adduct. One-electron reduction gives rise to the first example of a neutral antimony-centered radical characterized in solution. Two-electron reduction affords a Lewis base stabilized chloro-stibinidene, whereas three-electron reduction gives an antimony diatomic species capped by two carbenes. The radical has been characterized by EPR spectroscopy, while the structure of the other three species has been ascertained by single-crystal X-ray diffraction. In these four species, the formal oxidation state of the metalloid diminishes from III, to II, to I, and finally 0.*

The chemistry of antimony has expanded substantially in recent years, and it has found numerous applications in CO_2 fixation, O_2 capture, and catalysis.[1] Progress with this element is mainly due to the development of sterically demanding and/or polydentate ligands. Surprisingly, the use of N-heterocyclic carbenes (NHCs)[2] has been limited to the preparation of NHC–SbF_5[3] and NHC–$SbCl_3$.[4] In contrast, NHCs have been widely used for stabilizing lighter Group 15 element derivatives, featuring unusual binding modes, atoms in low oxidation states, and paramagnetic species.[5] Among these findings, reports on NHC-stabilized diatomic main-group allotropes[6] can be considered as breakthroughs in zero-oxidation state main-group chemistry, with N_2,[7] P_2,[8] and As_2[9] being the representatives of Group 15 elements. Although the analogous NHC–antimony and NHC–bismuth derivatives are predicted to be stable,[10] their attempted synthesis by reduction of NHC–$SbCl_3$[4] and NHC–$BiCl_3$[11] were reported to fail. Recent studies have shown that, because of their smaller HOMO–LUMO gap,[12] cyclic alkyl-(amino)carbenes (CAACs)[13,14] allow for the isolation of species when NHCs cannot.[15] Encouraged by these results, we decided to prepare a CAAC–$SbCl_3$ complex, and to study its stepwise reduction by one, two, and three electrons.

The desired starting material **2** was readily prepared by the addition of $SbCl_3$ to a diethyl ether solution of CAAC **1**, and it was isolated as a white solid in 94% yield (Scheme 1).



Scheme 1. Synthesis of CAAC–$SbCl_3$ **2**, and stepwise reduction with KC_8, affording the CAAC-Sb complexes **3**–**5** (Dipp = 2,6-diisopropylphenyl).

The $^{13}C\{^1H\}$ NMR spectrum of CAAC–$SbCl_3$ **2** in C_6D_6 shows the carbene peak shifted drastically upfield (228.4 ppm) compared to the free CAAC **1** (316.1 ppm). A single-crystal X-ray diffraction study[16] confirms the four-coordinate nature of the antimony center, and reveals a distorted seesaw geometry (Figure 1), which resembles the structures of the Group 15 NHC homologues (NHC)PCl_3,[8d] (NHC)$AsCl_3$,[9a] and (NHC)$BiCl_3$.[11]

Reduction of **2** with one equivalent of potassium/graphite (KC_8) in benzene yielded a golden colored, NMR-silent solution. Despite several efforts, crystals suitable for an X-ray diffraction study could not be obtained, but the EPR spectrum (Figure 2a) demonstrates the paramagnetic nature of the formed product **3**. Open-shell calculations at the uM05-2X/def2-SVP//uM05-2X/def2-TZVP[17] level of theory located two close energy minima **3a** and **3b**, corresponding to the formal abstraction of Cl2 and Cl1 or Cl3, respectively, from **2**. The DFT calculations reveal different Mulliken-spin density distributions in each molecule. In **3a** the antimony center is in

[*] Dr. R. Kretschmer,[+] D. A. Ruiz,[+] Prof. Dr. G. Bertrand
UCSD-CNRS Joint Research Laboratory (UMI 3555), Department of Chemistry and Biochemistry
University of California, San Diego
La Jolla, CA 92093-0343 (USA)
E-mail: guybertrand@ucsd.edu
Homepage: http://bertrandgroup.ucsd.edu
Dr. C. E. Moore, Prof. Dr. A. L. Rheingold
UCSD Crystallography Facility, University of California, San Diego
La Jolla, CA 92093-0343 (USA)
[+] These authors contributed equally to this work.

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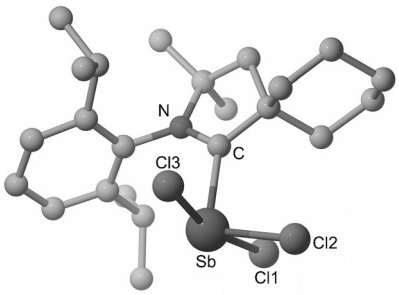

Figure 1. Solid-state structure of **2** (hydrogen atoms and solvent molecules are omitted for clarity). Selected bond lengths [Å] and angles [°]: Sb–Cl1 2.5740(10), Sb–Cl2 2.3760(8), Sb–Cl3 2.4917(9), Sb–C 2.223(3), C–N 1.301(3); N-C-Sb 118.8(2), C-Sb-Cl1 78.69(7), C-Sb-Cl2 99.91(7), C-Sb-Cl3 90.46(7).

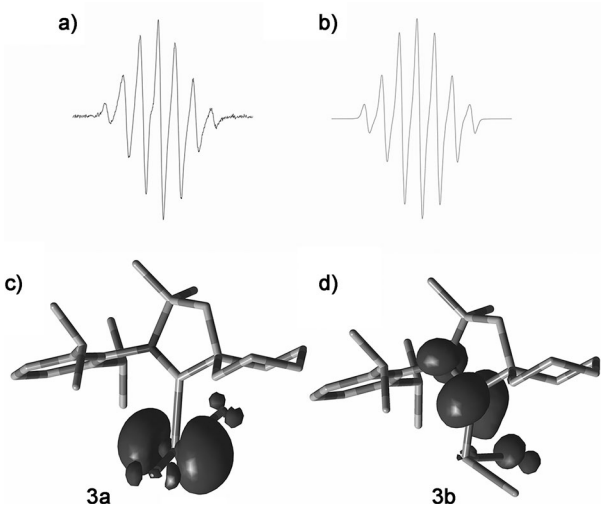

Figure 2. a) X-band EPR spectrum of **3** ($g = 2.0025$) recorded in benzene at room temperature. b) Simulated EPR spectrum[19] of **3** with the following set of hyperfine coupling constants: $a(^{121}Sb) = 0.003$ (57%), $a(^{123}Sb) = 0.003$ (43%), and $a(^{35}Cl) = 4.472$, $a(^{35}Cl) = 4.472$ G (calculated values: $a(^{121}Sb) = 0.004$ (57%), $a(^{123}Sb) = 0.004$ (43%), $a(^{35}Cl) = 3.217$, $a(^{35}Cl) = 3.533$ G). c),d) Representation of the SOMO of **3a** and **3b**, respectively, with isosurfaces at 0.005 a.u.; hydrogen atoms are omitted for clarity.

a distorted T-shaped environment (Figure 2c), and the spin density is almost exclusively located on antimony (90.7%) with minor contributions from the two chlorine atoms (4.6% and 3.9%). In **3b** the antimony is in a trigonal pyramidal environment, and most of the spin density is located on the carbene center (58.7%), with contributions of nitrogen (22.1%), antimony (11.1%), and one chlorine atom (7.3%) (Figure 2d). The calculated hyperfine coupling with Sb is negligible (**3a**: 0.004; **3b**: 0.040 G), which is in line with the absence of coupling observed in the two previously reported Sb-centered radicals, namely $Ar_3Sb^{\bullet+}$[18a] and $ArSbSbAr^{\bullet-}$.[18b] Consequently, owing to the contributions of only two nearly equivalent chlorine nuclei ($S = 3/2$) with significant isotropic hyperfine constants, a septet is expected for **3a**. In contrast, because of the presence of one chlorine and one nitrogen ($S = 1$), **3b** should give a sextet. From the observed EPR spectrum, we can conclude that the observed radical is most likely **3a** with the spin density mainly located on the metalloid. This finding is in contrast with other carbene-stabilized main-group radicals in which the spin density is localized on the carbene fragment.[5d]

Addition of two equivalents of KC_8 to a toluene solution of **2** led, after workup, to **4** that was isolated in 26% yield as an NMR active yellow solid. The carbene NMR signal (241.3 ppm) is shifted downfield compared to **2**. Single crystals of **4**, suitable for an X-ray diffraction study, were grown from a concentrated toluene solution at −20°C (Figure 3). The C-Sb-Cl fragment is severely bent

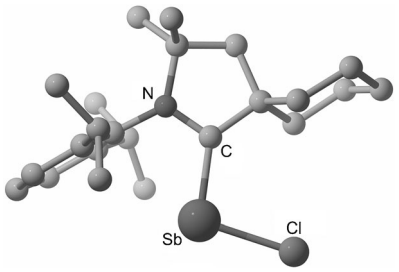

Figure 3. Solid-state structure of **4** (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°] with calculated values (M05-2X/def2-SVP) in square brackets: Sb–Cl 2.4315(13) [2.454], Sb–C 2.082(5) [2.091], C–N 1.336(6) [1.338]; C-Sb-Cl 100.77(13) [98.7], N-C-Sb 117.0(3) [119.3].

(100.77(13)°), with the Sb–C bond (2.082(5) Å) being slightly shorter than that of **2** (2.223(3) Å). DFT calculations at the M05-2X/def2-SVP//M05-2X/def2-TZVP level of theory indicate that the Sb–C interaction has only a partial double-bond character (Wiberg bond index WBI = 1.282). The Sb–C σ-bond results from the carbene lone-pair donation to Sb (Figure 4a), while some pπ back-donation originates from

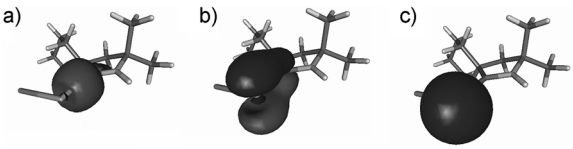

Figure 4. Localized molecular orbitals of a simplified model of **4** (H instead of Dipp): a) Sb–C σ-orbital; b) pπ back-donation from the Sb lone-pair to the empty carbene p-orbital; c) Sb lone-pair orbital.

one of the Sb lone-pair orbital (Figure 4b), which has predominantly p-character (4.22% s, 95.65% p, 0.12% d); the remaining Sb lone-pair orbital has mainly s-character (84.02% s, 15.96% p, 0.01% d; Figure 4c). From these results, it can be concluded that a stiba-alkene resonance form is less relevant than the CAAC-stibinidene form shown in **4**.[20] Note that very few stiba-alkenes are known,[21] and only the stiba-enol [Mes*(CO)Sb=C(Mes*)OH][21a] has been structurally characterized (Sb=C 2.078(3) Å), which prevents any direct comparison for the Sb–C distance.

Last, we carried out the reduction of **2** with three equivalents of KC_8, and isolated **5** in 45% yield. Deep-

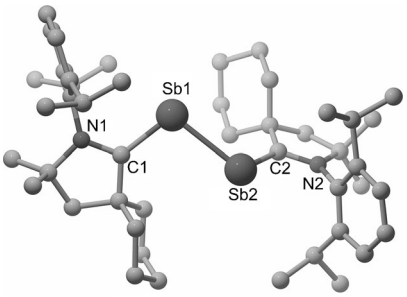

Figure 5. Solid-state structure of **5** (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°] with calculated values (M05-2X/def2-SVP) in square brackets: Sb1–Sb2 2.8125(10) [2.823], Sb1–C1 2.084(11) [2.114], Sb2–C2 2.088(10) [2.114], C1–N1 1.386(13) [1.341], C2–N2 1.359(13) [1.341]; C1-Sb1-Sb2 104.0(3) [106.2], N1-C1-Sb1 120.6(8) [120.2].

purple blocks that were suitable for an X-ray diffraction study were obtained from a concentrated toluene solution at −20 °C (Figure 5). Compound **5** features an anticlinal twisted-bent geometry with a C1-Sb1-Sb2-C2 torsion angle of 122.6(4)°. The C1-Sb1-Sb2 angle (104.0(3)°) falls within the range of values observed for the lighter homologues. The Sb–Sb bond distance (2.8125(10) Å) compares well with those observed in distibanes, for example, in $Ph_2SbSbPh_2$ (2.837(1) Å),[22] and the Sb–C bond distances (2.084(11)–2.088(10) Å) are comparable to the values reported for compounds **A** (2.056(10)–2.065(5) Å; Figure 6).[23] Interestingly, the authors noted that

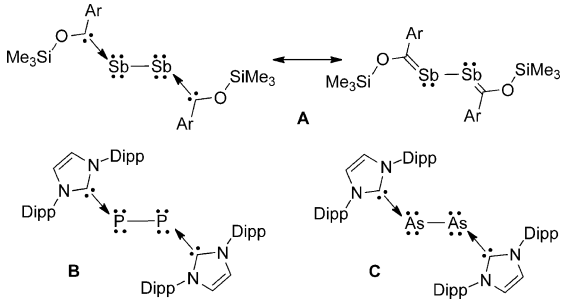

Figure 6. Resonance structures for the known antimony derivative **A**, and previously reported representations of the phosphorus **B** and arsenic **C** analogues of **5** (Ar = Mes or Mes*).

the observed Sb–C distances were longer than computationally predicted for the parent stiba-alkene (2.01 Å).[24] Moreover, one can realize that the substituents in **A** can be regarded as singlet (aryl)(oxy)carbenes. Additionally, calculations found a WBI of only 1.234 for the Sb–C bonds of **5**, a value that is inferior to those reported for the analogous phosphorus and arsenic NHC adducts **B**[8a] and **C**,[9a] 1.397 and 1.341, respectively. Therefore, it can be concluded that the 2,3-stiba-1,3-butadiene resonance form is less relevant than the $(CAAC)_2Sb_2$ form depicted in **5** (Scheme 1).

In summary, the stepwise reduction of a CAAC–Sb^{III} complex allows the preparation of three different antimony species in the formal oxidation states of two, one, and zero. This is a very rare example of a single ligand stabilizing a metal or a metalloid center in four different oxidation states.[25] Compound **3** is the first example of a neutral antimony-centered radical characterized in solution. Derivative **4** can be regarded as a carbene-stabilized stibinidene. Finally, **5** is an example of diatomic antimony species capped with two carbenes. The reactivity of these novel antimony derivatives is under active investigation.

Experimental Section

Synthesis of $CAAC(SbCl_2)^{\bullet}$ **3**, CAAC(SbCl) **4**, and $CAAC_2(Sb_2)$ **5**: One, two, and three equivalents of KC_8 were added in portions over 10 min to a stirred toluene solution (5 mL) of **2** (200 mg, 0.36 mmol). The mixture was stirred for 2 to 3 h, and then the salts were filtered off. Then, the solution was concentrated and stored at −20 °C. **4**: Yellow crystals suitable for an X-ray diffraction study were formed (45 mg, 26 % yield). M.p.: 155 °C (dec.); ^{13}C NMR (125 MHz, [D$_8$]toluene): $\delta = 241.3$ (C-Sb), 147.7 (C_q), 132.2 (C_q), 131.1 (CH_{ar}), 127.3 (CH_{ar}), 82.2 (C_q), 65.4 (C_q), 47.0 (CH_2), 38.1 (CH_2), 30.0, 29.3, 28.7, 25.5, 25.2 (CH_2), 23.8 ppm (CH_2). **5**: Purple block crystals suitable for an X-ray diffraction study were formed (73 mg, 45 % yield). M.p.: 134 °C (dec.); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 233.1$ (C-Sb), 148.0 (C_q), 137.1 (C_q), 129.2 (CH_{ar}), 126.0 (CH_{ar}), 72.7 (C_q), 61.7 (C_q), 49.7 (CH_2), 39.2 (CH_2), 30.0, 29.3, 29.2, 25.2, 23.7 (CH_2), 23.4 ppm (CH_2).

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