

π Interactions

Metal-Free Stabilization of Monomeric Antimony(I): A Carbene-Supported Stibinidene

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Abstract: A diamidocarbene was coordinated to an antimony(III) dichloride Lewis acid. Subsequent reduction with magnesium gave a monomeric, formally antimony(I) fragment that is supported by the diamidocarbene. Spectroscopic, crystallographic, and computational analyses demonstrated that the carbene ligand engages the antimony(I) center in π -backbonding resulting in a short (2.068(7) Å) Sb–C interaction that is comparable to those observed in known stibaalkenes.

Stable carbenes have recently emerged as the preeminent ligands for the stabilization of low-oxidation-state main-group derivatives.^[1] Iconic examples include the carbene-stabilized diatomic allotropes from the groups of Robinson,^[1c,e,g] Bertrand,^[1f] and Braunschweig.^[1h] These unusual compounds exhibit intriguing structural, photophysical, and electrochemical properties when compared to naturally occurring allotropes of the p-block elements. Indeed, many of these derivatives have served as precursors to stable, crystalline main-group-centered radicals. In this context, the cyclic alkyl amino carbenes (CAACs) have been shown to stabilize phosphorus-, carbon-, nitrogen-, silicon-, and boron-centered radicals.^[2]

In addition to the stabilization of formally zero-oxidation-state main-group allotropes, carbenes have been known to stabilize p-block elements in the +1 oxidation state (Figure 1). In a seminal discovery, Arduengo and Cowley demonstrated that N-heterocyclic carbenes (NHCs) are capable of supporting both phosphinidenes (PR, type A) and arsinidenes (AsR, type B).^[3,4] More recently, our group and Bertrand's group independently prepared a wide spectrum of carbene-supported phosphinidenes that utilized the electron-deficient diamidocarbenes (DACs, type C) and CAACs (type D) in addition to NHCs.^[5] Interestingly, when more π -accepting carbenes were used, the ligands were capable of engaging the P(I) center in a backbonding interaction resulting in a shortening of the P–C bond. Specifically, the DAC-supported phosphinidenes exhibited the largest degree of backbonding as indicated by spectroscopic, crystallographic, and computational analyses.^[5b]

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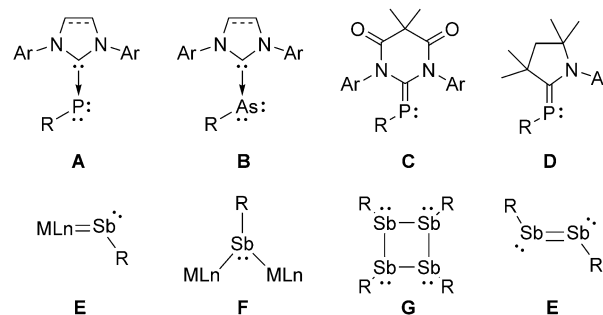
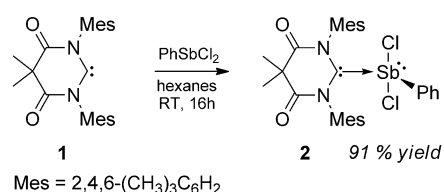


Figure 1. Representative examples of carbene-supported pnictidenes (A–D) and classes of stabilized stibinidenes (E–H).

Surprisingly, there are no reported examples of carbene-supported stibinidenes (SbR), or compounds that contain a formally antimony(I) center. Early examples of stibinidenes come from the groups of Cowley and Huttner, who prepared a variety of transition-metal-supported terminal and bridging stibinidenes (types E and F, respectively; Figure 1).^[6] The field lay fallow for nearly a decade until the groups of Tilley,^[7] Breunig,^[8] and Burford^[9] began exploring the chemistry of stibinidenes. While Tilley continued to research metal-supported stibinidenes, the latter two groups demonstrated that stibinidenes could be isolated as cyclic oligomers (type G) of the general formula (SbR)_n.^[8] In addition to cyclic oligomers, Tokitoh and co-workers and Huttner and co-workers were able to prepare distibenes (type H), or formally stibinidene dimers, by either thermolysis or photolysis of stable stibabismuthenes.^[10,11] Given their wide breadth of reactivity^[12] and propensity to absorb electron density from electron-rich phosphorus centers,^[5b] we questioned whether DACs could support antimony in the +1 oxidation state as well. Herein, we report that monomeric antimony(I) can be stabilized without the use of transition metals by the preparation of the first carbene-supported stibinidene.

To begin our investigation, DAC **1**^[12a] was coordinated to PhSbCl₂^[13] in hexanes to afford the hypervalent carbene-supported Sb^{III} complex **2** (Scheme 1). Throughout the course of



Scheme 1. Synthesis of DAC–SbPhCl₂ compound **2**.

the reaction, **2** precipitated from solution as an orange solid, thus facilitating its isolation (91% yield). Compound **2** was found to be quite thermally stable with a melting point of 110 °C. The identity of **2** was confirmed by ^1H NMR (CDCl_3) and single-crystal X-ray diffraction analyses. The ^1H NMR spectrum of **2** exhibited a single set of peaks that corresponded to equivalent mesityl substituents and upfield signals that corresponded to the antimony–phenyl substituent. These spectroscopic features were indicative of the zwitterionic nature of **2**, in which the carbene is loosely bound to the antimony center, allowing for free rotation about the carbene–antimony bond. In agreement with the ^1H NMR data, the ^{13}C NMR spectrum of **2** (C_6D_6) revealed a highly symmetric structure in solution with equivalent mesityl substituents on the DAC ligand. Additionally, the ^{13}C NMR spectrum exhibited only a single resonance for the two equivalent carbonyl moieties ($\delta = 170.61$ ppm) in the DAC backbone.

Compound **2** crystallized in the triclinic space group $P\bar{1}$ with two unique molecules in the unit cell. In the crystal, the antimony center adopts a truncated trigonal bipyramidal geometry similar to what has been observed for IPr-AsCl_3 , with the chloride ligands occupying pseudo-axial positions (Figure 2).^[19] The

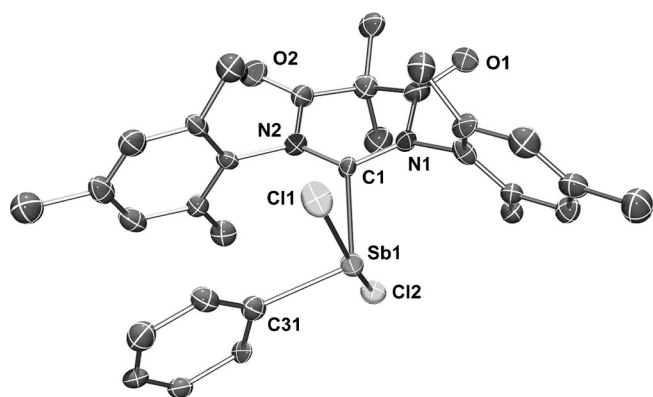


Figure 2. Molecular structure of **2** derived from single-crystal X-ray diffraction analysis (thermal ellipsoids are shown at the 50% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]; second molecule is given in square brackets: C1–Sb1 2.326(4) [2.334(4)], C31–Sb1 2.178(4) [2.186(4)], Sb1–Cl1 2.5269(13) [2.5045(12)], Sb1–Cl2 2.6509(12) [2.6590(12)]; C1–Sb1–C31 104.68(14) [104.80(13)], C1–Sb1–Cl1 90.30(9) [89.16(9)], C1–Sb1–Cl2 75.25(9) [75.47(9)].

carbene ligand appears to be weakly coordinated to the antimony center as evidenced by the long C1–Sb1 distance (2.330 Å, average of both molecules) when compared to the much shorter Sb1–C31 distance (2.182 Å average of both molecules).

With compound **2** in hand, our efforts shifted toward reduction of the Sb^{III} center. The cyclic voltammogram of **2** shows an irreversible redox process at $E_{1/2} = -1.05$ V (vs. Fc^+/Fc , Figure 3) indicating that **2** could be reduced using mild reducing agents (i.e., Mg). The irreversibility of this redox process also indicated that reduction of **2** would result in the formation of a product that could not be electrochemically oxidized back to the starting material. Encouraged by these results, we engaged in the chemical reduction of **2**.

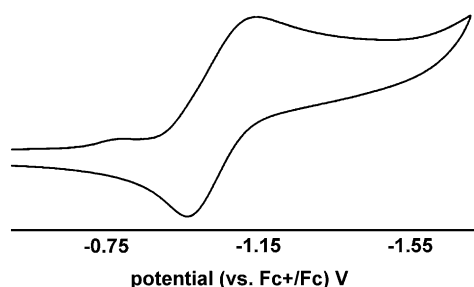
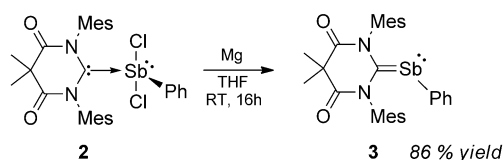


Figure 3. Cyclic voltammogram ($n\text{Bu}_4\text{NPF}_6$ 0.1 M, 100 mV s^{-1} vs. Fc/Fc^+).

Treating a THF solution of **2** with two molar equivalents of magnesium powder resulted in the formation of a dark, fluorescent red solution overnight (Scheme 2). Removal of all volatiles followed by extraction of the dark red residue with hexanes allowed the isolation of compound **3** as an air- and moisture-sensitive bright red orange, thermally stable solid (m.p. 133 °C) in 86% yield. The structure of compound **3** was verified by NMR, X-ray diffraction, and DFT analyses. In contrast to compound **2**, the ^1H NMR of **3** (C_6D_6) exhibited two inequivalent mesityl substituents, which indicated hindered rotation



Scheme 2. Synthesis of DAC–stibinidene compound **3**.

about the carbene–antimony bond. Additionally, the ^1H NMR of **3** is nearly identical to that observed for $1=\text{PPh}$,^[5b] which suggested that there was substantial multiple-bond character between the carbene and antimony centers. In contrast to $1=\text{PPh}$, the carbene nucleus in **3** exhibited a downfield ^{13}C NMR resonance at $\delta = 205.6$ ppm (172 ppm for $1=\text{PPh}$).^[5b] We hypothesize that the lower-field shift observed in **3** may be attributed to the larger antimony atom, which forms a longer bond to the carbene nucleus (see below) when compared to the phosphorus atom in $1=\text{PPh}$ and ultimately shields the carbene ligand to a lesser degree.

Deep red crystals of **3** suitable for X-ray diffraction studies were obtained from a saturated *n*-pentane solution at -30 °C, which allowed us to interrogate the bonding between the carbene ligand and the phenyl stibinidene. As was expected, reduction by two electrons afforded a more electron-rich Sb^{I} , which resulted in a dramatic decrease in the C1–Sb1 bond length from 2.330 Å in **2** to 2.068(7) Å in **3** (Figure 4). The short C1–Sb1 bond is similar to what has been observed for structurally characterized stibaalkenes (2.056–2.078 Å)^[14] and can therefore be regarded as a formal C=Sb double bond. Concomitant with the formation of the π bond is the observed C1–Sb1–C31 angle of $105.5(2)^\circ$ and the N2–C1–Sb1–C31 torsion angle of $-7.5(5)^\circ$, which indicate substantial planarity at the antimony center.

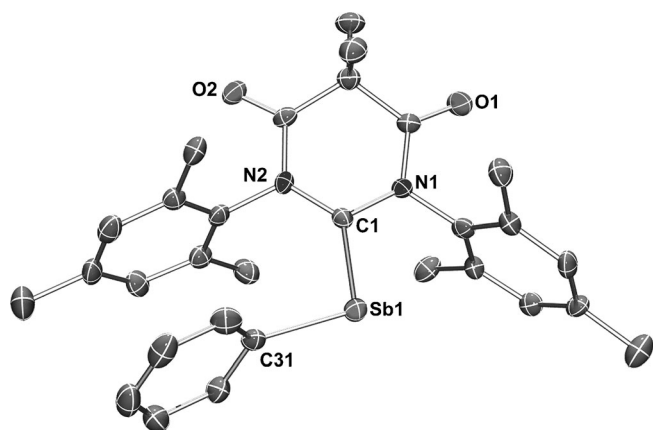


Figure 4. Molecular structure of **3** derived from single-crystal X-ray diffraction analysis (thermal ellipsoids are shown at the 50% probability level, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: C1–Sb1 2.068(7), Sb1–C31 2.160(7), C1–Sb1–C31 105.5(2), N2–C1–Sb1–C31 $-7.5(5)$.

The observed shortening of the C1–Sb1 interaction can be attributed to backbonding from the antimony(III) center into the π -accepting carbene ligand. To gain further evidence for a π -backbonding interaction, we investigated the structure of **3** by using DFT methods.^[15] We first performed a geometry optimization of **3** (B3LYP,^[16] 6-31 g(d,p)^[17] for C, H, N, O and Stuttgart RLC ECP^[18] for Sb) for comparison to the solid-state structure (Figure 5A). The computed structure appeared to be well modelled, with similar metric parameters. Importantly, the computed C1–Sb1 distance of 2.116 Å, C1–Sb1–C31 angle of 107.50°, and N2–C1–Sb1–C31 torsion angle of -8.76° compared well to the X-ray structure data (2.068(7) Å, 105.5(2)°, and $-7.5(5)^\circ$, respectively). Inspection of the frontier orbitals revealed that the HOMO is dominated by a π -bonding orbital that is polarized toward the antimony(III) center (Figure 5B), whereas the LUMO is primarily an antibonding π orbital that is also localized on the carbene ligand (Figure 5C).

The nature of the C1–Sb1 interaction was further examined by using a natural bonding orbital (NBO) analysis.^[19] The NBO

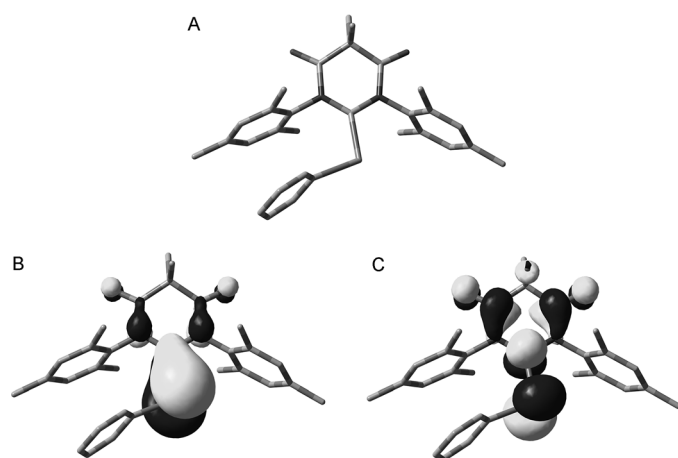


Figure 5. a) Optimized structure of **3**; and b) frontier molecular orbitals: HOMO and c) LUMO for **3** (0.04 isovalue).

analysis revealed that the C1–Sb1 bond was comprised of both σ and π bonding interactions. From the NBO output file, we also determined the C and Sb localization (%) of the π -bonding orbital. This data concluded that there is a well-developed π bond present in the stibinidene complex with near equal localization on the C1 and Sb1 centers (42.5 and 57.5%, respectively). When compared to the DAC-supported phosphinidene 1=PPh (%C 46.3, %P 53.7), it is apparent that the antimony(III) center participates in a weaker backbonding interaction to the carbene ligand. This can be attributed to the poorer overlap of the antimony 5p orbital with the carbene empty 2p orbital when compared to the phosphorus 3p orbital.

From the NBO analysis, the Wiberg bond index (WBI) for the antimony center in **3** was computed to be 2.842, and compared well with 1=PPh, which had a calculated WBI of 2.900.^[5b] This value demonstrates that the Sb^{III} center forms three bonds, two of which are σ bonds and one π bond.

In summary, we reported that monomeric, formally antimony(III) can be stabilized by coordination to an electrophilic diamidocarbene. The DAC-supported stibinidene **3** was characterized by elemental analysis, single-crystal X-ray diffraction, and NMR spectroscopy. The characterization data coupled with DFT analyses indicate that the electron-deficient nature of the carbene ligand further stabilizes the stibinidene moiety by engaging the electron-rich antimony(III) center in a π -backbonding interaction. To our knowledge, **3** represents the first example of a monomeric stibinidene that is stable outside of the coordination sphere of a transition metal. Furthermore, the isolation of **3** obviates the need for transition metals in the stabilization of heavy main-group elements in low-oxidation states. We believe that these findings further demonstrate that stable, singlet carbenes can mimic the chemical behavior of transition-metal centers, a property that we and others are currently exploring.

Experimental Section

Synthesis of **2**

In a nitrogen-filled glovebox, a round bottom flask (250 mL) was charged with the **1** (2.00 g, 5.31 mmol), PhSbCl₂ (1.434 g, 5.31 mmol), a magnetic stirring bar, and 100 mL of hexanes. The resulting slurry was stirred at RT in the glovebox for 18 h. During the course of the reaction, the white solid was replaced by a light orange solid, which was isolated by filtration over a medium-porosity glass frit inside the glovebox. The solid was washed with hexanes (3 × 20 mL) and dried to give compound **2** as a light orange solid.

Synthesis of **3**

In a nitrogen-filled glovebox, a Schlenk flask (50 mL) was charged with **2** (1.5 g, 2.32 mmol), magnesium powder (0.130 g, 5.35 mmol), a magnetic stirring bar, and THF (40 mL). The flask was removed from the glovebox and stirred at RT for 12 h. During the course of the reaction, the majority of the magnesium disappeared, and the solution became a dark, fluorescent red color. After 12 h, all volatiles were removed in vacuo, and the dark red

residue was extracted with hexanes (100 mL) then filtered over a Celite pad to remove precipitated magnesium salts. The Celite pad was washed with hexanes (50 mL), and the combined organic solutions were concentrated to dryness to give compound **3** as a bright red solid.

For explicit experimental data, including spectroscopic data, elemental analyses, and yields, see the Supporting Information.

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