A trimetallic bismuth-based allyl cation

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Abstract

The chemistry of low-valent bismuth compounds has recently unlocked new concepts in catalysis as well as unique electronic structure fundamentals. In this work, we describe the synthesis and characterization of a highly-reduced bismuth salt featuring a cationic core based on three contiguous Bi(I) centers. The triatomic bismuth-based core holds an electronic situation that mimics the description of the archetypical carbon-based π-allyl cation. Structural, spectroscopic and theoretical analyses validate the unique π-delocalization between the bismuth's highly diffused 6p-orbitals, resulting in a 1.5 bond order between the Bi atoms. This electronic situation places this complex as the heaviest and non-radioactive π-allyl cation of the periodic table. Furthermore, we demonstrate that the newly synthesized complex is able to act as a synthon for the transfer of a Bi(I) cation to forge other low-valent organobismuth complexes.

Main text

The π-allyl cation is one of the most recognizable intermediates in organic chemistry, and represents a text-book example to explain molecular orbital theory, resonance, and chemical bonding.[1-7] The unique allylic system of the triatomic carbon arrangement has been the object of study of numerous research groups and served as guiding principle to develop a plethora of synthetic transformations.[8-12] From the electronic point of view, the π-allyl cation is comprised of three carbon atoms (C1, C2 and C3, Figure 1, left), where the C1 is connected to C2 and C3 in a 1.5 bond order. More specifically, these carbons are sp^2 hybridized and are united through two σ bonds. In addition, the three available 2p-orbitals allow the delocalization of the two additional electrons, thus conforming the characteristic delocalized π-system.[13,14] Fascinated by its structure, chemists have looked at synthesizing heavier analogues of the π-allyl cation; yet, the analogues reported can be described as cyclopropenium-type structures[15-17] or, in some cases, as vinylogous systems which

capitalize on the delocalization of the positive charge into neighboring heteroatoms.[18,19] Hence, a genuine π-allyl cation analogue based on heavier elements still remains elusive. Due to its privileged place in the periodic table as the last stable element, we envisaged that the heaviest analogue of this cationic structure should be within reach using bismuth. A direct comparison of the frontier orbitals involved in bonding leads to the realization that a cationic triatomic complex of bismuth with formal oxidation state +1 for the three contiguous Bi atoms $(Bi)_3^+$ would be analogous to that of the carbon-based allyl cation (Figure 1, right). This seemingly simple analogy presents an enormous synthetic challenge: examples of unsupported neutral or cationic di-coordinated bismuth(I) compounds are rare.[20] Siddiqui *et al.* developed a cationic Bi(I) supported by two sterically encumbered CAAC which resembled the heaviest analogue of a carbone.[21] Recently, the group of Driess and Frenking developed a similar structure with germylenes as supporting ligands.[22] For many years, overlapping of large and diffused orbitals leading to chemical bonding between $5p$ and $6p$ orbitals was regarded as a challenge in organometallic chemistry.[23,24] However, this canonical notion has recently been challenged with several examples of heavy main group elements (HMGE) that form double and triple bonds akin the lightest main group elements.[23-30] Based on our recent findings on mono-coordinated bismuthinidene **1**,[31] here we present the synthesis, structure, characterization and reactivity of a unique cationic complex featuring three contiguously bonded Bi atoms in a low oxidation state. The electronic structure calculations reveal the delocalization of two electrons through the non-hybridized $6p$ orbitals of the trimetallic $(Bi_3)^+$ core —due to the low energy of the buried $6s^2$ orbitals— characteristic of the classical π-allyl cation.
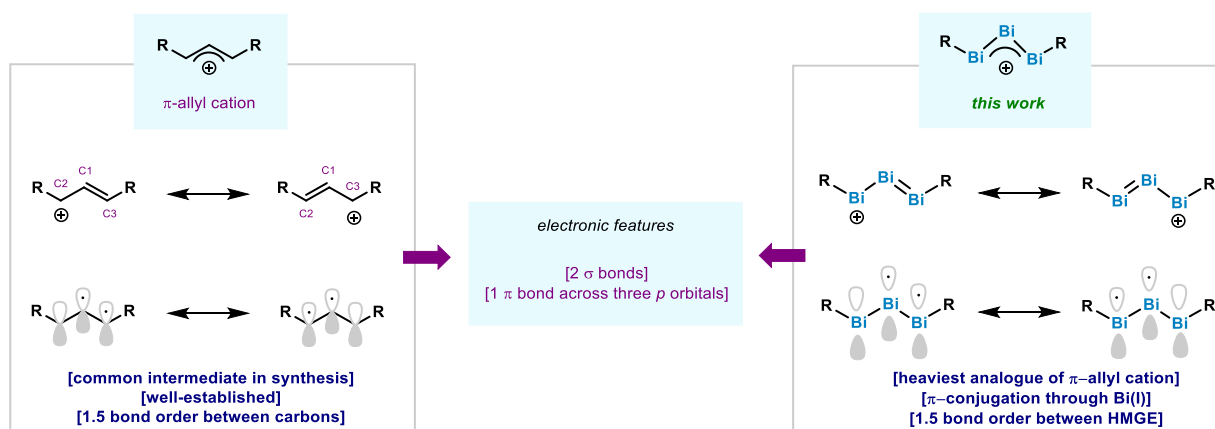
Figure 1. Comparison between the carbon-based π-allyl cation (left) and its heaviest stable analogue based on Bi (right).

When **1** was mixed with mono-hydrated tris(pentafluorophenyl)borane (BCF) in PhMe-d_8 at 25 °C, **2** precipitated from the mixture as an air-sensitive dark brown solid. As by-product, the protonated organic framework was obtained. The structure of **2** was unambiguously determined by single crystal X-ray diffraction (SC-XRD) which revealed its ionic nature. While the cation is constituted by a triatomic bismuth core connected in a linear zig-zag fashion with the bulky organic backbone, a $[(BCF)_2OH]^-$ serves as counter anion. Whereas the distance between Bi_I–Bi_{II} [2.93361(12) Å] is 2% shorter ($\Delta d = 0.0571$ Å) than the Bi–Bi single bond [2.990(2) Å] in **3** (Fig. 2c),[31] it is 3% longer ($\Delta d = 0.08721$ Å) than the Bi=Bi double bond distance in dibismuthene **4** [2.8464(4) Å].[31] Together with previously described bond lengths,[26,31,32,33] the distances in **2** falls in the range between a single and a double bond. At the same time, the Bi_{II}−C(sp^2) distance in **2** suggests a single bond [2.2851(16) Å in **2** *vs* 2.2783(10) in **1**][31,20,34,35] which implies an inexistent delocalization of the charge on the aryl system in the ground state (*vide infra*). The observed C–Bi_I–Bi_{II} and Bi_{II}–Bi_I–Bi_{II} bond angles [(101.29(4)° and 80.637(3)°, respectively] are indicative of the limited ability of Bi to form hybridized sp^2 orbitals, primarily due to the contraction of the 6s orbital as a consequence of relativistic effects.[26,36,37] In solution, compound **2** is stable in dicholoromethane-d_2 and could be fully characterized at 25 °C by NMR. At this temperature, **2** shows C_{2v} symmetry; however, this symmetry is lost at −100°C, in line with the crystal structure (see Supplementary Materials). A single set of Ar_F signals can also be observed at 25 °C, arising from the polyfluorinated anion in **2**. At lower temperatures,

this equivalence is broken and three distinct Ar groups appear, in agreement with previous observations for this anion.[38] Compound **2** appears diamagnetic, and no signal was observed by EPR.
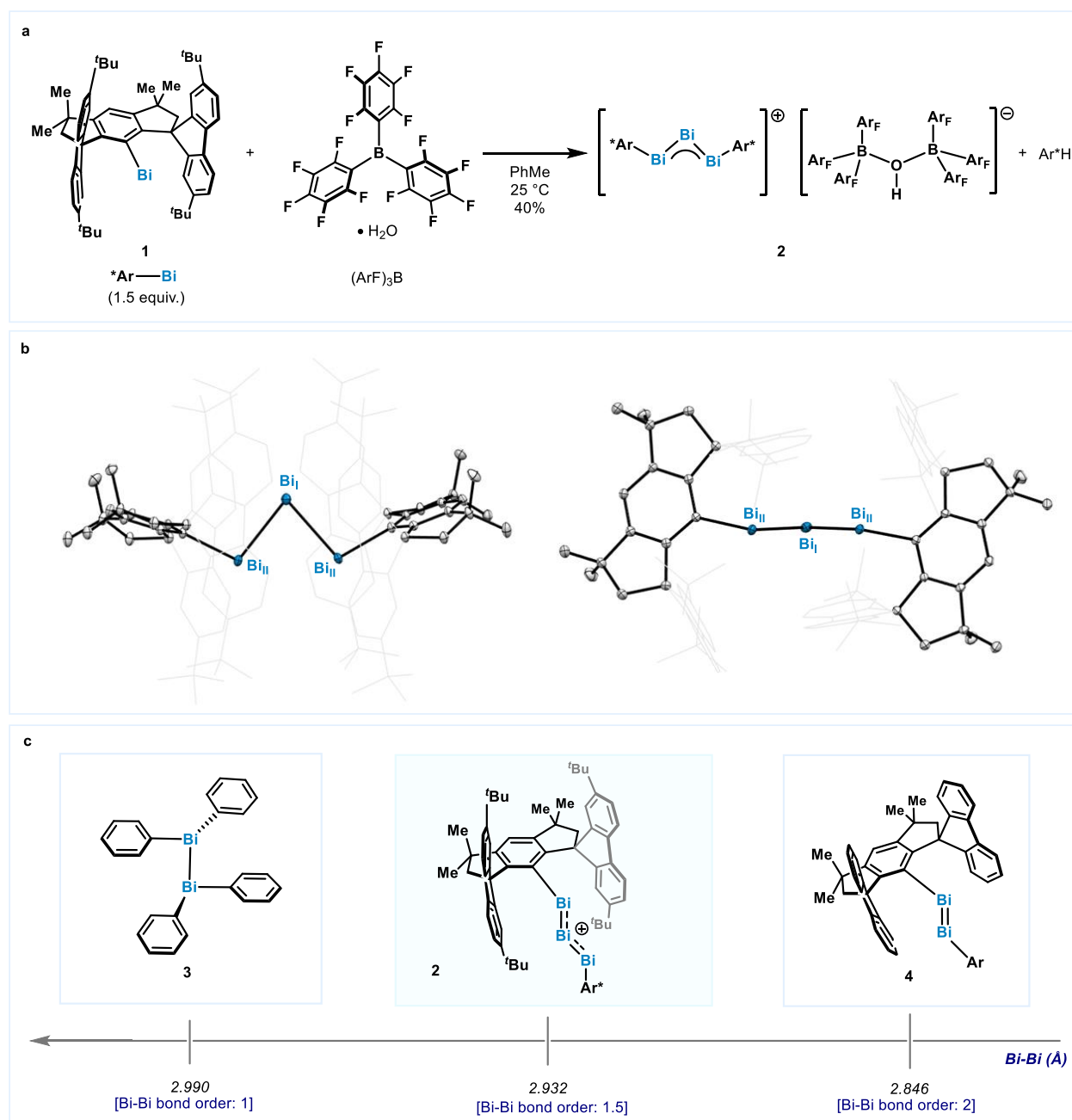
Figure 2. a, Synthesis of **2**. **b**, Solid-state structure of **2** at 100 K in two orientations (anisotropic displacement ellipsoids are displayed at a probability level of 50%, and H atoms, anion, and solvent molecules were omitted for clarity). **c**, Comparison of Bi–Bi bond length.

One the basis of the crystal structure, the geometric structure of **2** was optimized without constraints using the ORCA 5.0[39,] program suite together with the B3LYP functional,[40] the D3(BJ) dispersion correction[41] and the def2-TZVP basis set with associated effective core potentials.[42] The obtained stationary point was

confirmed to be a minimum through the calculation of harmonics frequencies. The calculated Bi_I–Bi_{II} distance of 2.912 Å and the Bi–C distance of 2.295 Å (average) are in overall agreement with the SC-XRD data of 2.93361(12) Å and 2.2851(16) Å, respectively. Given the strong sensitivity of the Bi–Bi distance to the bond order between the two atoms, these results provide evidence for the notion that the electronic situation in the $(Bi)_3^+$ core is properly represented by the calculations. A closer analysis of the electronic structure of the cationic core in **2** confirms that the two Bi_{II} are nearly equivalent and distinct from the bridging Bi_I. As deduced from the analysis of the occupied orbitals, all Bi atoms feature a non-bonding lone pair of electrons corresponding to the inert $6s^2$ (Figure 3a). At the same time, the terminal Bi_{II} atoms further engage in two-electron-two center single bonds with the ligand framework as well as with Bi_I respectively. The central Bi_I atom forges single bonds with the terminal atoms instead. The remaining two valence electrons are delocalized over the three centers in the core (Figure 3b). This defines a bond-order of 1.5 between the Bi_{II}/Bi_I pairs, consistent with the structural parameters and the discussion above. In terms of charge delocalization, the outer Bi_{II} centers carry slightly more positive charge (natural population analysis (NPA) charge ~ +0.7) than the bridging Bi_I (NPA charge ~ 0.15). These charges add up to more than one full positive charge due to the charge transfer of the Bi_{II} centers to the carbon atoms. Overall, this electronic structure resembles the charge distribution typically described in π-allyl cations.
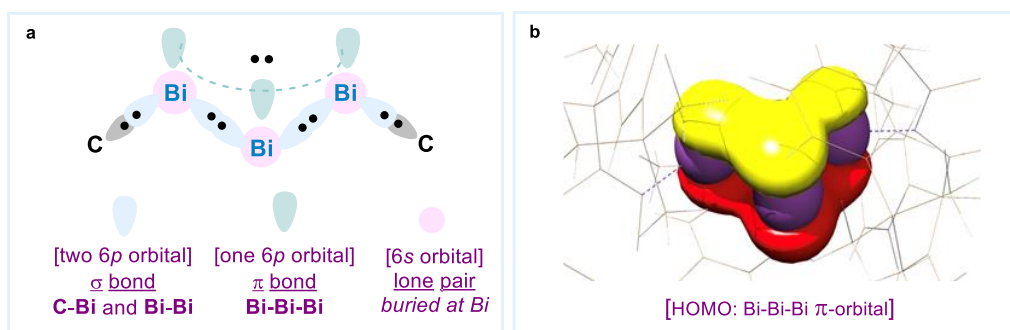
Figure 3. Valence electronic structure of **2**. **a**, Lewis structure representing the $(Bi)_3^+$ core and the electrons involved in bonding. **b**, HOMO orbital containing the delocalized electron pair.

The UV−Vis absorption spectrum of compound **2** shows absorption bands at 27701, 19305, 12887, and 10000 cm^{-1} (Figure 4a, top). This was also calculated using time-dependent DFT (TD-DFT). These all-electron calculations were performed with and without the inclusion of spin-orbit coupling (SOC) using the

X2C-relativistic Hamiltonian[43] and the spin-orbit mean-field (SOMF) operator[44,] together with finite nucleus[45,46] and picture change corrections.[47] Singlet- and triplet excited states calculated from the scalar-relativistic TD-DFT calculation were allowed to interact via the SOC using quasi-degenerate perturbation theory (QDPT). The resulting calculated spectra (Figure 4a, middle and bottom) compares favorably with experiment if the SOC is included. In particular, the trailing intensity observed between 8000 and 12000 cm^{-1} results from a series of singlet- to triplet transitions that borrow intensity via the SOC while the main bands observed around 13000 cm^{-1} and 19000 cm^{-1} are dominantly singlet-singlet based. Interestingly, the calculated spectra predicts that the observed intensities in the UV−Vis spectra derive from transitions that all involve the same acceptor orbital, namely the LUMO of the Bi_3 core. The first two excited states are of $(Bi)_3 \ \sigma \rightarrow (Bi)_3 \ \pi^*$ and $(Bi)_3 \ \pi \rightarrow (Bi)_3 \ \pi^*$ in nature, and account for the bulk of the intensity observed experimentally at 13000 cm^{-1}. The remaining transitions all account for a complex set of ligand-to-metal charge transfer into the $(Bi)_3^+ \ \pi^*$ acceptor orbital.
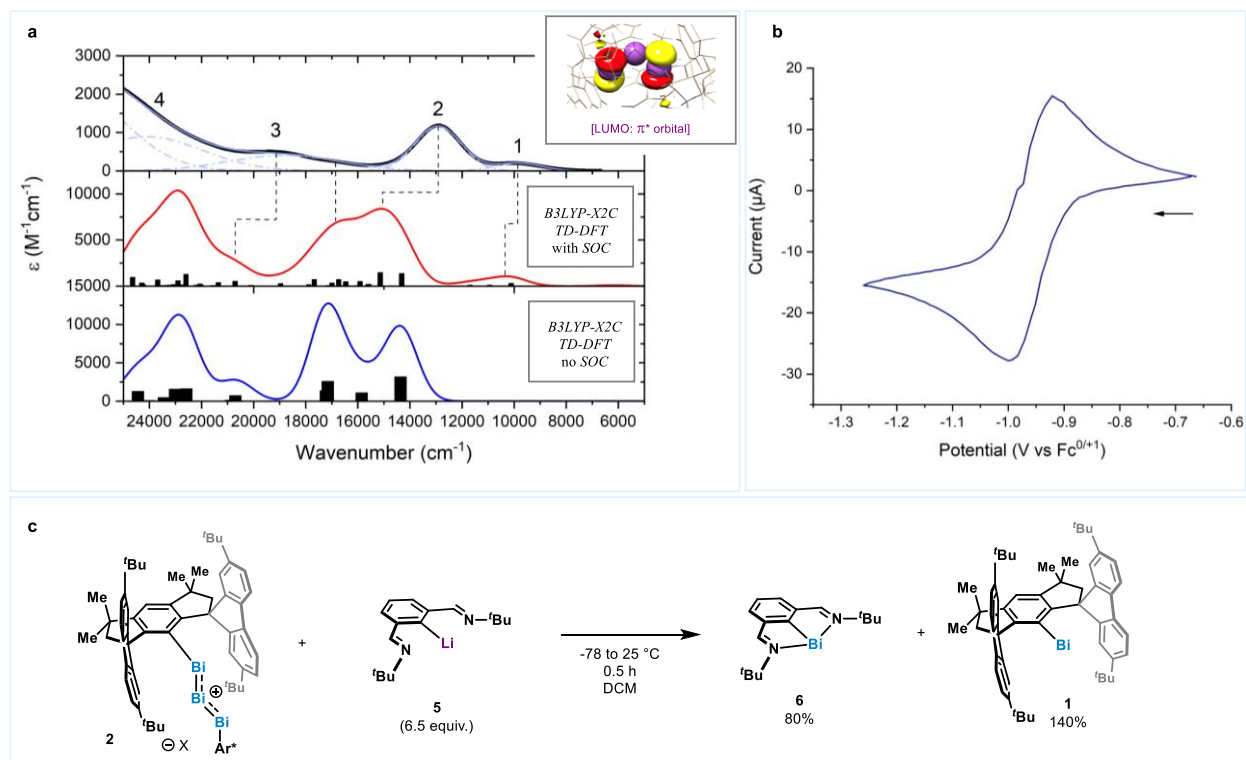
Figure 4. a, Experimental UV−Vis spectrum resolved into individual Gaussian absorption bands labeled 1 to 4 and shown in light purple and calculated UV−Vis absorption spectrum: red profile including SOC; blue profile without SOC. **b**, Cyclic voltammogram of **2** in dichloromethane using 0.1 M [nBu$_4$N][BArF] as supporting electrolyte at ambient temperature; scan rate: 100 mV/s, referenced to Fc$^{0/+}$. **c**, Reaction of **2** as transfer reagent of Bi(I) cations;

Yield and distribution of products **6** and **1** were determined by ^{1}H NMR analysis of the crude mixture using 1,3,5 trimethoxybenzene as the internal standard.

The rich optical spectrum with all transitions having the same LUMO as acceptor points to the $(Bi)_3^+$ core being electrophilic, and hence, facile SET reduction should be within reach. Indeed, cyclic voltammetry of **2** in dichloromethane reveals a reversible reduction wave at $E_{1/2} = –0.95$ versus $Fc^{0/+}$, which we ascribed at the facile reduction to the corresponding fleeting π-allyl radical (Figure 4b, and Supporting Materials). Unfortunately, our attempts to isolate this paramagnetic congener of the starting complex **2** via chemical reduction have proven unsuccessful so far. The very low-lying LUMO and a highly electrophilic $(Bi)_3^+$ core led us to explore complex **2** as a potential electrophilic source of Bi(I) cations. Recently, some main group-based complexes have been used as transfer agents to easily transfer pnictogen atoms.[48,49] When **2** was treated with a solution of organolithium reagent **5**, *N,C,N*-bismuthinidene was obtained in 80% yield, with partial recovery of **1** (Figure 4c). The unique ability to transfer Bi(I) atoms could potentially open new routes for the synthesis of novel low-valent bismuth-based compounds.[34,50]

Conclusions

In conclusion we have synthesized a genuine analogue of the π-allyl cation replacing the typical carbon-based framework with three contiguous bismuth atoms. The synthesis of such a complex demonstrate the ability of very diffuse and large frontier *p* orbitals of heavy main group elements to effectively overlap similarly to their lighter congeners, thus allowing effective π-delocalization of electrons. Intriguingly, the molecular architecture of our bismallyl cation is characterized by two Bi–Bi bonds formally possessing a non-integer bond order. However, as expected when heavy main group elements are involved, the electronic description becomes more entangled due to SOC and relativistic effects. Indeed, according to our interpretation of the absorption spectrum the intensity in the red-region of the spectrum (around 700-900 nm) originates from triplet states that borrow intensity from their singlet counterparts by strong SOC mixing. This situation is highly characteristic of the heavy element bismuth which tends to break the established spin- and space selection rules that govern the properties of most complexes bearing lighter main group elements. In addition, due to the electrophilicity of the highly reduced $(Bi)_3^+$ core, the compound can be used to effectively transfer a Bi(I) atom which provide a blueprint of reactivity for assembling materials and

molecular architectures based on low-valent bismuth compounds. Overall, this complex expands the understanding of chemical bonding in this area of the periodic table and sets novel boundaries in the chemistry of main group elements towards conjugated systems.

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