

## **Abstract for Max-Buchner-Research Scholarship 3771**

### **Neutral and Charged Bismuth Complexes for Synthesis and Catalysis: Alkyl Transfer Reagents via Polar and Radical Pathways**

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#### **Abstract**

This research project has been designed to investigate molecular bismuth compounds in the context of homolytic vs. heterolytic Bi–C bond dissociation. Understanding and deliberately addressing these reaction pathways is a key requirement for the future exploitation of bismuth compounds in synthetic applications for organic synthesis and as precursors for materials science. Unusual and reversible Bi–C bond cleavage reactions have been studied in this work.

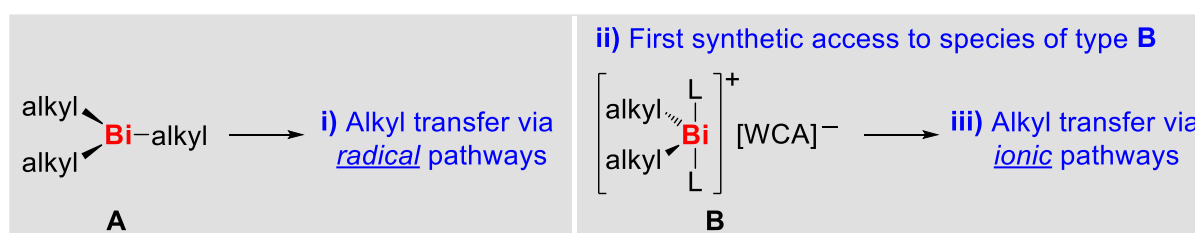
## Neutral and Charged Bismuth Complexes for Synthesis and Catalysis: Alkyl Transfer Reagents via Polar and Radical Pathways

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### 1. Topic and objectives

This research project was situated in the field of well-defined molecular bismuth compounds. Based on their relatively low toxicity,<sup>1</sup> their ability to engage in low-energy homolytic bond dissociation,<sup>2</sup> and the accessibility of Lewis acidic cationic species,<sup>3</sup> the proposal was aiming at the exploitation of neutral and cationic bismuth complexes for synthetic applications. In particular, the homolytic Bi–C bond dissociation of neutral species and heterolytic bond Bi–C bond dissociation of cationic species was targeted (Scheme 1).

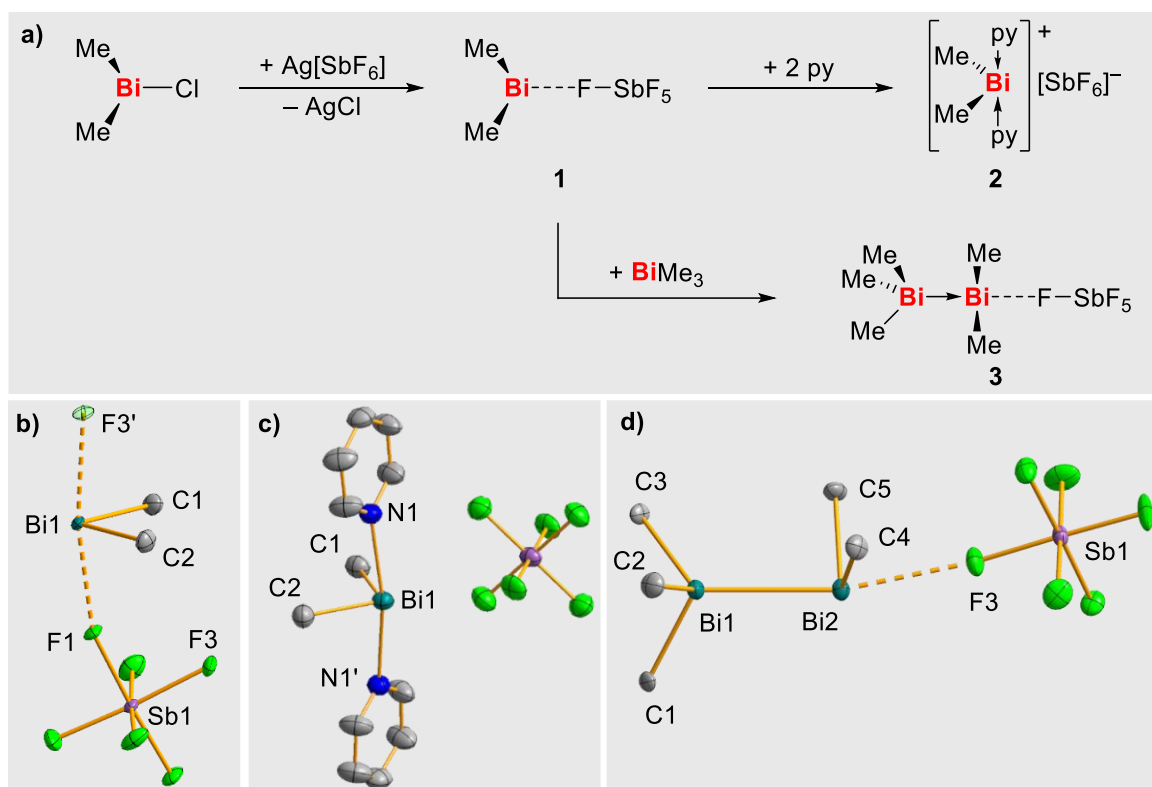


**Scheme 1.** Major goals i-iii of this research project with key compounds of type **A** and **B**. L = substitutionally labile neutral ligand (e.g.: THF), Alkyl = Me, Et, *i*Pr, *t*Bu; WCA = weakly coordinating counter anion.

### 2. Results and outlook

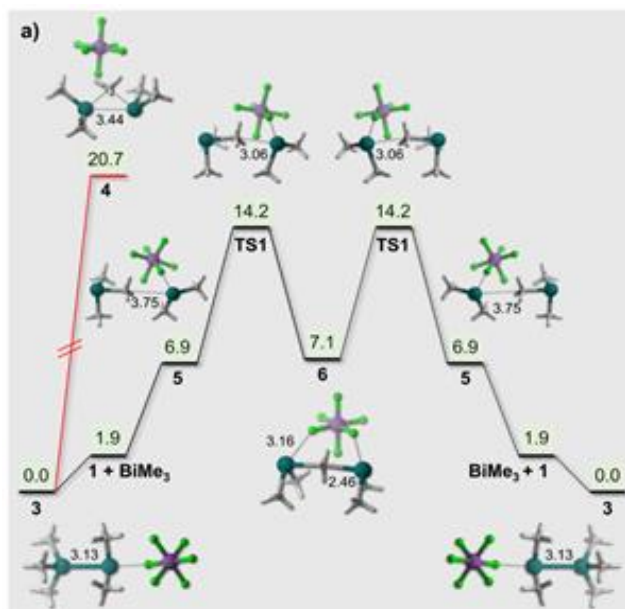
A range of neutral species of the type  $\text{Bi}(\text{alkyl})_3$  and  $\text{Bi}(\text{allyl})_3$  have been synthesized. In the presence of spin traps, the release of alkyl radicals under moderate reaction conditions in solution was demonstrated by EPR spectroscopic experiments. Reactions with radical trapping reagents such as  $(\text{RE})_2$  have been performed and revealed facile alkyl transfer to give heavy ether analogs  $\text{RE}(\text{alkyl})$  ( $\text{R} = \text{aryl}$ ,  $\text{E} = \text{S}, \text{Se}, \text{Te}$ ).

Reactions of  $\text{BiMe}_2\text{X}$  with salts of weakly coordinating anions gave access to the first examples of mononuclear dialkyl bismuth cations.<sup>4,5</sup> Interestingly, compound **1** could be isolated in the absence of neutral donor ligands and was shown to form a contact ion pair in the solid state (Scheme 2). The pronounced and soft Lewis acidity of bismuth cations was also confirmed for the alkyl species **1**: it readily forms Lewis acid/base adducts with a broad range of donor ligands. Compound **2** is one of many examples that result from such adduct formations. Remarkably, even  $\text{BiMe}_3$ , which is an extremely poor donor due to the inert pair effect and relativistic effects, undergoes adduct formation with cationic species **1**. The product of this reaction, compound **3**, shows the first example of a Bi→Bi donor-acceptor bond as an intriguing structural feature.



**Scheme 2.** a) Synthesis of the dimethyl bismuth cation **1** and its Lewis acid/base adducts **2** and **3**. b-d) Solid state structures of 1-3 as determined by single-crystal X-ray analysis (the transparent atom F3' in b) belongs to a neighboring formula unit).

In solution, there were also some unusual properties revealed for compound **3**: it undergoes rapid methyl exchange at ambient temperature. Experimental and theoretical investigations of this phenomenon led to the mechanism shown in Figure 1. Methyl exchange does not proceed via an  $sp^3$ -hybridized methyl group as in local minimum **4**. Instead, a transition state (**TS1**) and a local minimum structure (**6**) with an  $sp^2$ -hybridized methyl anion in a bridging position between two cation  $[BiMe_2]^+$  complex fragments were identified. This corresponds to an  $S_E2$  (back) mechanism for methyl exchange, which has so far only been reported for heterobimetallic late transition metal compounds.<sup>6</sup> Thus, the isolation of the first mononuclear cationic bismuth alkyl species and studies into their reactivity have revealed unusual reaction pathway for heterolytic Bi–C bond cleavage.



**Figure 1.** Energy profile ( $\Delta G$ , kcal·mol<sup>-1</sup>) for methyl exchange reactions in compound **3**: favored (black) and disfavored (red) reaction pathway. Selected calculated interatomic distances are given in Å.

Future investigations will be directed towards the transfer of alkyl radicals and anions from neutral and cationic bismuth compounds in intermolecular reactions for organic and organometallic synthesis and catalysis.

### 3. References

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