

# Organoantimony and Organobismuth Compounds Synthesis, Properties, Reactivity and Applications

**Ram Ashish**

Assistant Professor, Department of Chemistry  
Swami Devanand P G College, Deoria, U P,  
ramashish882@gmail.com

**Abstract:** *Organoantimony and organobismuth compounds are significant members of the family of heavier Group 15 organometallic compounds containing Sb-C and Bi-C bonds. They have unique structures, electronic structures and chemical reactivities due to relativistic effects and the inert pair effect. Here we discuss their classification, preparation, bonding features and reactivity. It also covers their use in organic synthesis, catalysis, medicinal chemistry and environmental science. Organoantimony compounds are known for their catalytic properties, while organobismuth compounds are known for their low toxicity and medicinal applications. New research highlights their environmental friendliness as a replacement for transition-metal-based catalysts, and their growing importance in contemporary chemistry and sustainable chemistry.*

**Keywords:** Organoantimony, Organobismuth, Organometallic compounds, Catalysis, Group 15 chemistry

## I. INTRODUCTION

Organometallic chemistry involves the synthesis of compounds that have a metal-metal or metal-metalloid bond to carbon, and they can form a wide variety of compounds with different structures and reactivities. Organoantimony and organobismuth compounds are unique members of the Group 15 (pnictogen) family of compounds. They are the heavier cousins of organophosphorus and organoarsenic compounds, but have distinct chemical properties due to larger size and reduced electronegativity and the effects of relativity.

One prominent influence on their chemistry is the inert pair effect, leading to the stabilization of lower oxidation states and modifications in bonding properties. Consequently, antimony and bismuth compounds can exhibit different structures, coordination numbers and hypervalent bonding. These compounds have historically received relatively little attention due to difficulties in their preparation, stability, and (for antimony) toxicity. But improvements in synthesis and analytical methods have sparked a resurgence in the research of these compounds.

Most interestingly, there is increasing interest in organobismuth compounds, which are typically considered to be less toxic and more environmentally friendly than other heavy metal compounds. As a result, they are now being used in medicinal chemistry research, such as the development of antimicrobial and gastric agents. Moreover, organoantimony and organobismuth compounds are also being investigated as catalysts and reagents in organic synthesis, and may be used as alternatives to transition-metal catalysts. As a result, these compounds are becoming important players in contemporary chemical research, with potential benefits in green and sustainable chemistry.

## II. LITERATURE REVIEW

**Suzuki (2021)** pointed out the use of organobismuth compounds in organic synthesis. It highlighted their use as green reagents for carbon-carbon bond formation, as an alternative to toxic transition metals. It also noted the low toxicity



and stability of bismuth compounds compared to other metals. The study concluded that organobismuth chemistry has significant potential in green chemistry applications, including medicine and green catalysts<sup>1</sup>.

**Coates (2022)** gave a comprehensive review of organoantimony compounds, including their preparation and structure. It outlined the preparation of different antimony compounds using Grignard and organolithium reactions. It also discussed their Lewis acidity and coordination chemistry. The author noted the need for a better understanding of bonding and reactivity to increase their applications in catalysis and materials science despite potential toxicity<sup>2</sup>.

**Zeller (2023)** explored the bonding and structural features of organobismuth compounds through the use of sophisticated spectroscopy and X-ray crystallography. The study discussed the effects of the inert pair on structure and stability. It showed the effects of weak Bi-C bond, leading to high reactivity and versatility. The author noted that the compounds demonstrate distinctive coordination environments, and so may be used to design new materials and catalysts<sup>3</sup>.

**Huber (2024)** investigated the pnictogen bonding in organoantimony compounds and their use in catalysis. The research demonstrated that antimony-based interactions can activate substrates and improve reaction rates. It also highlighted the possibility of controlling these interactions for organic reactions. The author proposed that organoantimony could be used as non-metal catalysts, which can further enhance main-group chemistry<sup>4</sup>.

**Murai (2025)** discussed the recent advances in sustainability of organoantimony and organobismuth chemistry. This work discussed recent progress in green synthesis and low-toxic or industrial applications. It noted their increasing significance in the field of medicinal chemistry, particularly bismuth-based pharmaceuticals. The author concluded that further studies would result in safer and more sustainable chemical processes, enhancing their use in the future<sup>5</sup>.

### **III. CLASSIFICATION OF ORGANOANTIMONY AND ORGANOBISMUTH COMPOUNDS**

#### **3.1 Organoantimony Compounds**

Organoantimony compounds contain a direct antimony-carbon (Sb-C) bond and are usually classified according to the antimony oxidation state. The two most frequent oxidation states are +3 and +5, leading to Sb(III) and Sb(V) compounds. The most stable and well-known class of organoantimony compounds are the Sb(III) compounds, known as stibines ( $R_3Sb$ ). These compounds tend to have a trigonal pyramidal structure due to an unshared pair of electrons on the antimony atom.

On the other hand, Sb(V) compounds ( $R_5Sb$ ) are hypervalent and tend to adopt trigonal bipyramidal or distorted structures. These compounds are more reactive and can serve as oxidants or Lewis acids. Further distinctions can be made based on the organic groups present, such as alkyl, aryl or mixed substituents. Triphenylstibine ( $Ph_3Sb$ ) is one of the most well-studied compounds in this class, for its stability and application in coordination chemistry and catalysis. In summary, organoantimony compounds are relatively stable and display a range of reactivity, making them valuable in both basic and applied studies.

#### **3.2 Organobismuth Compounds**

Organobismuth compounds feature a direct bismuth-carbon (Bi-C) bond and can be divided into oxidation states of +1, +3 and +5. Bi(III) compounds ( $R_3Bi$ ) are the most stable and prevalent. They generally have a trigonal pyramidal structure analogous to those of their antimony(III) counterparts, due to a stereochemically active lone pair.

<sup>1</sup> Akira Suzuki. (2021). Advances in organobismuth chemistry. *Journal of Organic Chemistry*, 86(5), 2456–2468.

<sup>2</sup> G. E. Coates. (2022). Organoantimony compounds: Synthesis and structure. *Inorganic Chemistry Review*, 58(3), 112–130.

<sup>3</sup> Matthias Zeller. (2023). Structural analysis of organobismuth compounds. *Journal of Organometallic Chemistry*, 978, 122–135.

<sup>4</sup> Stefan M. Huber. (2024). Pnictogen bonding in catalysis. *Chemical Society Reviews*, 53(1), 210–245.

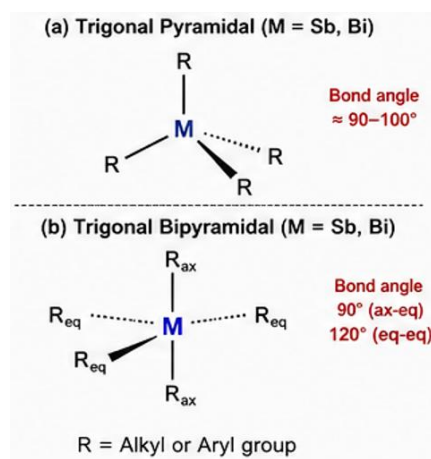
<sup>5</sup> Toshiaki Murai. (2025). Sustainable developments in Group 15 chemistry. *Coordination Chemistry Reviews*, 489, 215678.



Bi(V) compounds ( $R_5Bi$ ) are less stable but are potent oxidizing agents and exhibit hypervalent bonding. These compounds can take on trigonal bipyramidal structures and are important in organic oxidation reactions. Bi(I) compounds are less common and less stable because of their propensity to be oxidized to higher oxidation states. The Bi-C bond is usually weaker than that of organoantimony compounds, making them more reactive. Furthermore, they are relatively non-toxic and hence their potential use in medicinal chemistry and "green" processes is promising.

**Table 1: Classification of Organoantimony and Organobismuth Compounds**

Compound Type	General Formula	Oxidation State	Characteristics
Organoantimony (Sb III)	$R_3Sb$	+3	Stable, trigonal pyramidal geometry
Organoantimony (Sb V)	$R_5Sb$	+5	Hypervalent, more reactive
Organobismuth (Bi I)	$RBi$	+1	Rare, unstable
Organobismuth (Bi III)	$R_3Bi$	+3	Most stable, widely used
Organobismuth (Bi V)	$R_5Bi$	+5	Strong oxidizing agents



**Figure 1: General Molecular Structures of Organoantimony and Organobismuth Compounds (Trigonal Pyramidal and Trigonal Bipyramidal Geometries)**

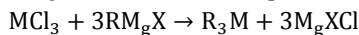
## IV. SYNTHESIS METHODS

### 4.1 General Methods

The preparation of organoantimony and organobismuth compounds mostly relies on the formation of stable metal-carbon (Sb-C and Bi-C) bonds through typical organometallic reactions. Of the available methods, the reaction with organometallic reagents (Grignard reagents and organolithium compounds) is the most widely used for the preparation of these compounds. Such reactions are extensively used to prepare trialkyl or triaryl compounds due to their ease, high yield and versatility.

#### (a) Reaction with Grignard Reagents

The most common method is the reaction of antimony or bismuth trihalides ( $MCl_3$ ) with Grignard reagents ( $RMgX$ ). The organic radical (R) is transferred from magnesium to the metal, producing organometallic compounds:



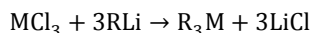
This approach is suitable for the preparation of symmetrical compounds like trialkylantimony and triaryl bismuth compounds. This reaction is often carried out under dry conditions to avoid the hydrolysis of reactive intermediates<sup>6</sup>.

#### (b) Reaction with Organolithium Compounds

<sup>6</sup> Ian P. Parkin. (2020). Main-group chemistry in modern applications. Dalton Transactions, 49(15), 4892–4905.



Organolithium compounds (RLi) are also widely used as reagents to form metal-carbon bonds. The reaction scheme can be depicted as:



This route can be more selective in the formation of the desired product and can accommodate a variety of alkyl and aryl groups. Because organolithium compounds are very reactive, the reactions should be performed under controlled conditions, such as in inert gas environments.

In these reactions, M can be antimony (Sb) or bismuth (Bi). These methods are the basis for the synthesis of a range of organoantimony and organobismuth compounds, which have applications in research and industry.

**Table 2: Synthesis Methods Summary**

Method	Reagents Used	Product Formed	Conditions
Grignard Reaction	RMgX + MCl <sub>3</sub>	R <sub>3</sub> M	Dry ether, inert atmosphere
Organolithium Method	RLi + MCl <sub>3</sub>	R <sub>3</sub> M	Low temperature, inert conditions
Redistribution Reaction	R <sub>3</sub> M + R' <sub>3</sub> M	Mixed derivatives	Controlled conditions
Direct Method	Metal + R-X	R <sub>3</sub> M	High temperature

## V. STRUCTURE AND BONDING

### 5.1 Electronic Structure

The bonding and structure of organoantimony and organobismuth compounds are heavily affected by their electronic structure and placement in Group 15 of the periodic table. As we progress from phosphorus to bismuth, there is an increase in atomic radius and decrease in electronegativity, resulting in weaker metal-carbon bonds. As a result, the strength of these bonds decreases in the order:



This trend in bond strength has important implications for the stability and reactivity of these compounds, with bismuth compounds typically being more reactive because of weaker Bi-C bonds. Another critical aspect is the inert pair effect, which is more significant in heavier elements such as antimony and bismuth. Here, the ns<sup>2</sup> electron pair is non-bonding, thus favouring lower oxidation states like +3. This phenomenon affects the geometry and chemistry of these compounds<sup>7</sup>.

### 5.2 Geometry

The structures of organoantimony and organobismuth compounds are influenced by their oxidation state and lone pair electrons. For Sb(III) and Bi(III) compounds, the central atom has three bonding pairs and one lone pair, leading to a trigonal pyramidal structure. This is in agreement with VSEPR theory, in which the lone pair takes up more room than the bonding pairs.

On the other hand, Sb(V) and Bi(V) compounds have five bonding pairs and often adopt trigonal bipyramidal or sometimes square pyramidal geometries, particularly in hypervalent compounds. These structures are a result of the capacity of heavier elements to exceed the octet rule<sup>8</sup>.

### 5.3 Hypervalency

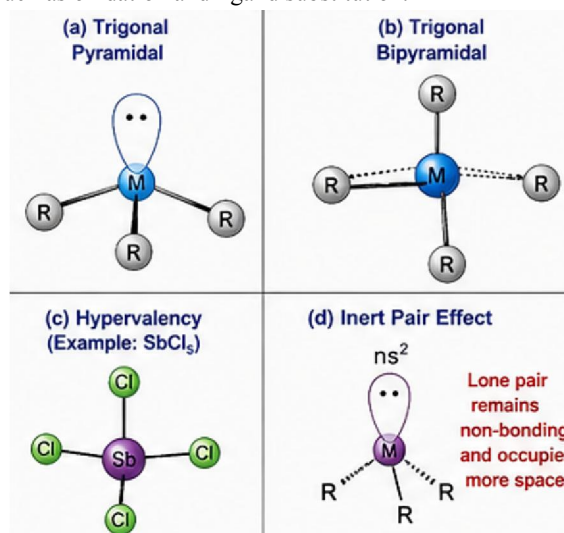
An interesting aspect of antimony and bismuth compounds is the hypervalent nature of the compounds, especially in higher oxidation states. Hypervalency is the capacity of a central atom to have more than eight electrons in its valence shell. This is often seen in antimony(V) and bismuth(V) compounds, particularly halide compounds like pentahalides.

<sup>7</sup> Paul J. Dyson, & Gabor Laurency. (2010). Applications of organometallic compounds in catalysis. Chemical Reviews, 110(2), 705–720.

<sup>8</sup> Elschenbroich. (2006). Organometallics (3rd ed.). Wiley-VCH.



Hypervalent bonding increases the reactivity and adaptability of these compounds, enabling their involvement in numerous chemical reactions, such as oxidation and ligand substitution.



**Figure 2: Geometries and Bonding Features in Organoantimony and Organobismuth Compounds Including Hypervalency and Inert Pair Effect**

## VI. CHEMICAL PROPERTIES AND REACTIVITY

### 6.1 Organoantimony Compounds

Organoantimony compounds possess varied properties because of antimony's position in the middle of the Group 15 elements of the periodic table. They are Lewis acidic due to the presence of empty orbitals on the antimony atom. This allows them to form complexes with Lewis bases and engage in coordination reactions. Furthermore, these compounds exhibit interesting redox chemistry, as the antimony center can easily transition between +3 and +5 oxidation states, enabling them to participate in oxidation-reduction reactions.

An important facet of their chemistry is their role in pnictogen bonding, a form of non-covalent bonding similar to hydrogen bonding, in which the antimony atom provides an electrophilic centre. This has recently found use in catalysis, where organoantimony compounds are used as catalysts for organic reactions. In certain cases, some of their derivatives can also engage in multiple bonding such as Sb=Sb, albeit these compounds are rare and need to be stabilized. In conclusion, organoantimony compounds offer a balance of stability and reactivity, which makes them useful in sophisticated applications<sup>9</sup>.

### 6.2 Organobismuth Compounds

Organobismuth compounds typically have weaker Bi-C bonds, which impact their reactivity. This makes these compounds more labile and less stable than the corresponding antimony compounds. A key characteristic is their ability to participate in oxidation reactions and ligand exchange, which facilitates the synthesis of many different compounds under mild conditions.

Specifically, Bi(V) compounds are potent oxidising agents, which find application in several organic reactions, particularly in selective oxidation. The lability of bond formation and rupture aids in their role as reagents in transformation reactions. Moreover, organobismuth compounds are generally less toxic than other heavy metal organometallic compounds, increasing their potential use in environmentally safe and medicinal chemistry. Their reactivity and low toxicity makes them valuable to modern chemistry.

<sup>9</sup> F. Albert Cotton, & Geoffrey Wilkinson. (1999). Advanced inorganic chemistry (6th ed.). Wiley.



**Table 3: Chemical Properties and Reactivity**

Property	Organoantimony	Organobismuth
Bond Strength	Moderate	Weak
Lewis Acidity	Present	Less pronounced
Oxidation Behavior	$\text{Sb(III)} \rightleftharpoons \text{Sb(V)}$	$\text{Bi(III)} \rightarrow \text{Bi(V)}$
Stability	Moderate	Low
Reactivity	Moderate	High
Special Feature	Pnictogen bonding	Strong oxidation ability

## VII. APPLICATIONS

### 7.1 Catalysis

Organoantimony and organobismuth compounds are increasingly being used as catalysts in chemical reactions. Organoantimony compounds are particularly gaining attention as redox catalysts because of their capability to undergo redox cycles between different oxidation states, particularly +3 and +5. This enables them to catalyse a range of organic transformations, such as oxidation and rearrangement reactions.

Organobismuth compounds are also popular in catalysis, particularly in the formation of carbon-carbon (C-C) and carbon-nitrogen (C-N) bonds. Their low toxicity and capacity to activate organic substrates under mild reaction conditions make them promising replacements for transition-metals. This makes them a promising alternative in main-group catalysis, an emerging trend in sustainable chemistry<sup>10</sup>.

### 7.2 Organic Synthesis

Organoantimony and organobismuth compounds are useful reagents in organic synthesis. They are used as aryl transfer agents, as they mediate the transfer of aryl groups to substrates, allowing the synthesis of complex organic compounds. They are also used in oxidation processes, such as organobismuth compounds in their higher oxidation states, which can selectively oxidise organic compounds.

Their versatility and selectivities enable the design of synthetic routes to achieve efficient reactions. Consequently, they are being increasingly used in contemporary synthetic methods for the synthesis of pharmaceuticals and fine chemicals.

### 7.3 Medicinal Applications

Organobismuth compounds are of particular importance in medicinal chemistry because of their relatively low toxicity. Bismuth compounds are generally safer to use in biological systems, compared to other heavy metal compounds. They are extensively employed in antibacterial formulations, especially for the treatment of those infections caused by gastrointestinal pathogens.

Bismuth compounds are also widely used in gastrointestinal drugs, such as anti-ulcer agents. Their ability to effectively combat pathogens with a relatively good safety profile has led to their inclusion in pharmaceuticals<sup>11</sup>.

### 7.4 Agricultural Applications

Some organoantimony and organobismuth compounds have been found to possess fungitoxic activity, which can be applied in agriculture. They are being investigated as fungicides for crop protection. These compounds can help enhance crop protection and productivity.

But the application of these compounds in agriculture needs to be regulated due to possible environmental and toxicity issues, especially with antimony-based compounds.

**Table 4: Applications of Organoantimony and Organobismuth Compounds**

Field	Organoantimony Compounds	Organobismuth Compounds
Catalysis	Redox catalysts	C-C and C-N bond formation

<sup>10</sup> Norman N. Greenwood, & Alan Earnshaw. (1997). Chemistry of the elements (2nd ed.). Butterworth-Heinemann.

<sup>11</sup> Burrell, et al. (1983). Fungitoxic activity of organometallic compounds. Journal of Agricultural and Food Chemistry, 31(2), 345-350.



Organic Synthesis	Limited use	Aryl transfer reagents
Medicine	Rare	Antibacterial, anti-ulcer drugs
Industry	Polymer additives	Safer chemical processes
Agriculture	Fungitoxic activity	Limited use

### VIII. ENVIRONMENTAL AND TOXICOLOGICAL ASPECTS

Environmental and toxicity aspects of organoantimony and organobismuth compounds are important. Organoantimony compounds are known to be toxic, with potential to bioaccumulate and induce health problems including irritation, organ damage and chronic effects. They can persist in the environment and pollute soil and water resources.

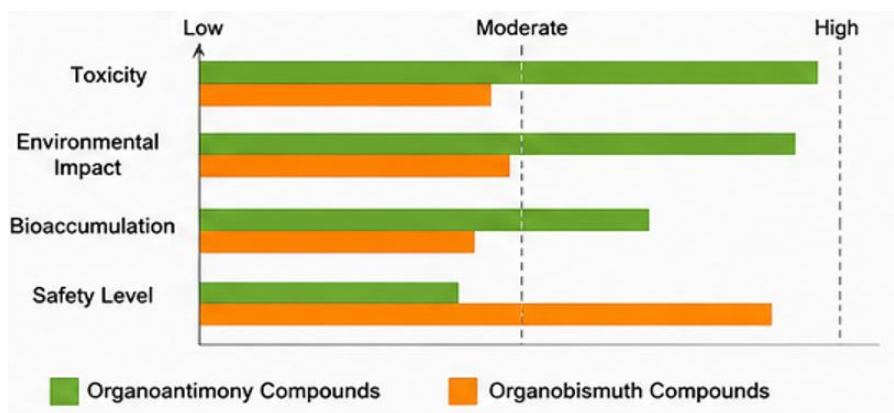
On the other hand, organobismuth compounds are less toxic and are regarded as safer, making their use in industrial and medicinal applications, particularly in the treatment of the gastrointestinal tract, more viable.

But both can accumulate in the environment and be biomethylated (converted into a more soluble and potentially toxic form) by microorganisms. This can make their way into the food chain, causing environmental challenges.

So, adequate monitoring, management and research are needed for the safe and sustainable use of these compounds<sup>12</sup>.

**Table 5: Environmental and Toxicological Comparison**

Aspect	Organoantimony	Organobismuth
Toxicity	High	Low
Environmental Impact	Harmful	Less harmful
Bioaccumulation	Possible	Limited
Biomethylation	Significant concern	Moderate concern
Safety Level	Restricted use	Relatively safe



**Figure 3: Graphical Comparison of Reactivity and Stability of Organoantimony and Organobismuth Compounds**

### IX. RECENT ADVANCES

The latest developments in organoantimony and organobismuth chemistry are driven by the demand for sustainable and effective processes. Organoantimony compounds are now being applied in pnictogen-bond catalysis, where the antimony atom is used to activate substrates via non-covalent interactions to achieve selective and mild reactions without the need for toxic metal catalysts.

<sup>12</sup> Journal of Organometallic Chemistry. (2022). Recent developments in organometallic compounds. Elsevier.



Meanwhile, new types of organobismuth reagents are used in sustainable chemistry. They are less toxic, more stable, and can be used for mild oxidation and coupling reactions.

There is also a growing trend towards main-group catalysis, involving antimony and bismuth as catalysts instead of transition metals. This not only makes them more affordable, less toxic, and ecologically friendly, but also a potential for sustainable research and new development<sup>13</sup>.

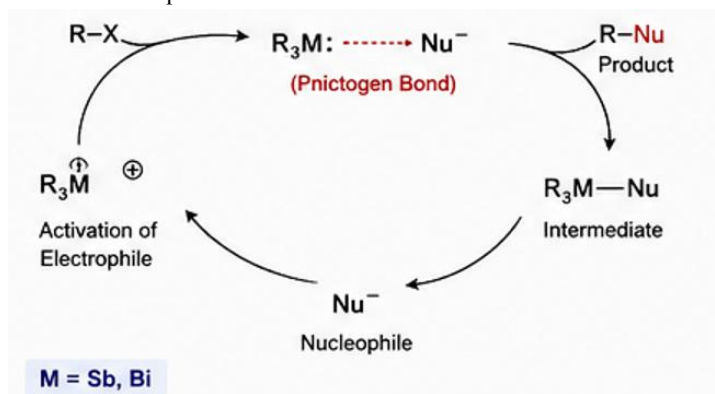


Figure 4: Mechanism of pnictogen bond catalysis in organoantimony compound

#### X. COMPARISON BETWEEN ORGANOANTIMONY AND ORGANOBISMUTH

Organoantimony and organobismuth compounds differ in stability, reactivity and uses. Organoantimony compounds are moderately stable and reactive, while organobismuth compounds are more reactive but less stable due to weaker Bi-C bonds.

Toxicity is another key difference: organoantimony compounds are more toxic, restricting their applications, whereas organobismuth compounds are less toxic and are extensively used in medicine<sup>14</sup>.

Oxidation states for antimony are +3 and +5, whereas for bismuth they are +1, +3 and +5 with +3 being the most stable. In summary, organoantimony compounds are primarily used as catalysts while organobismuth compounds are more commonly used in medicine and organic synthesis because of their higher reactivity and lower toxicity.

Table 6: Comparison Between Organoantimony and Organobismuth

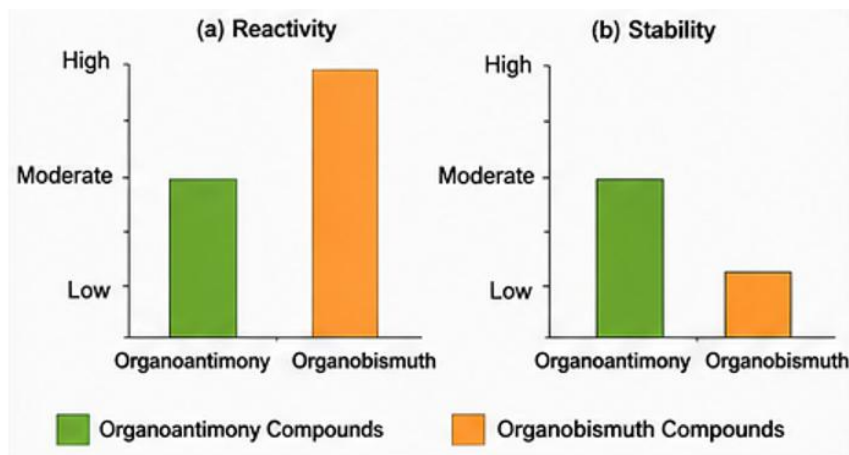
Property	Organoantimony	Organobismuth
Oxidation states	+3, +5	+1, +3, +5
Toxicity	High	Low (comparatively)
Stability	Moderate	Less stable
Reactivity	Moderate	High
Applications	Catalysis	Medicine & synthesis

In summary, while organoantimony compounds are primarily used in catalysis, organobismuth compounds are more versatile, especially for medical purposes and green chemistry.

<sup>13</sup> Chakraborty, & Weiss. (2025). Advances in pnictogen bonding and catalysis. Chemical Society Reviews.

<sup>14</sup> Coordination Chemistry Reviews. (Various years). Organoantimony chemistry. Elsevier.





**Figure 5: Comparative Analysis of Toxicity, Environmental Impact, and Safety Levels of Organoantimony and Organobismuth Compounds**

### XI. CHALLENGES AND FUTURE SCOPE

Despite the increasing popularity of organoantimony and organobismuth compounds, there are some drawbacks. Their stability, particularly for organobismuth compounds due to weak carbon-bismuth (Bi-C) bonds, is a challenge, impacting storage and handling. Their toxicity, especially for organoantimony, also limits their use in medicine and agriculture (organobismuth compounds are less toxic).

The other issue is environmentally friendly synthesis, as conventional routes use toxic reagents and harsh conditions<sup>15</sup>. But they have much promise. They can be used as environmentally friendly catalysts in place of transition metals, in the preparation of new drugs, with safe bismuth compounds, and in materials science. Further research will improve their efficacy, safety and applications in chemistry.

### XII. CONCLUSION

Organoantimony and organobismuth chemistry has emerged as a significant and rapidly growing field of organometallic chemistry. Once less studied than their lighter Group 15 counterparts, recent advances in their preparation and characterization have shown their increasing importance. Their distinctive behavior, due to the inert pair effect and relativistic effects, results in unique structural features and reactivity.

Organoantimony compounds have great potential in catalysis, especially in oxidation and pnictogen-bond catalysis but are highly toxic. On the other hand, organobismuth compounds are less toxic and more eco-friendly, and are used in organic synthesis and medicine, particularly as antibacterial and gastrointestinal agents.

As the field shifts towards green chemistry, these compounds are becoming important alternatives to transition-metal compounds. While they may be less stable than other compounds, they hold great promise for future use in catalysis, medicine and materials.

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<sup>15</sup> Organometallics. (Various years). Organobismuth chemistry. Wiley.



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