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Bismuth Lewis Acids | *Very Important Paper* |

A Dicationic Bismuth(III) Lewis Acid: Catalytic Hydrosilylation of Olefins

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Abstract: Lewis acid promoted activation of inert chemical bonds is central to catalysis. The presence of a highly electrophilic central atom having minimum interactions with anions and solvent molecules is a requisite for a reactive Lewis acid. This requirement for a strong Lewis acid is met with by designing a reactive cation of a heavy element, bismuth, bearing the tridentate trispyrazolylborate ligand. The coordination sphere of the electrophilic bismuth dication is stabilized by very weak interactions with the halogen atoms of the weakly nucleophilic tetrakis(pentafluorophenyl)borate anion, chlorobenzene, and *ortho*-dichlorobenzene in the solid state. The high electrophilicity at bismuth is demonstrated by the ability of the dication to efficiently catalyze the addition of Si–H to olefins.

Introduction

The proposition of carbocations as intermediates in important reactions like Friedel-Crafts alkylation[1] and Wagner–Meerwein rearrangement[2] and the discovery of Ph_3C^+[3] marked the beginnings of reactive main group cations. Though Ph_3C^+ itself remained a laboratory curiosity in the beginning of the twentieth century, the advent of weakly coordinating anions (WCAs)[4,5] paved way for the development of numerous examples of reactive main group cations.[6] Noteworthy examples include ArE^+ (E = Pb[7]), R_2E^+ (E = B,[8] Al,[9–11] Ga,[12] Sb[13] and Bi[13]), R_3E^+ (E = Si,[14–17] Ge,[18,19] Sn[18–20] and Pb[18,19]), CpE^+ (E = Si,[21] Ge,[22] Sn[23,24] and Pb[25,26]) and $(C_5Me_5)E^{2+}$ (E = P,[27] As[28]) The strong electrophilicity- and hence reactivity of these cations can be diminished due to their tendency to coordinate to the counter anions as well as the solvents. High reactivity can be maintained by a thoughtful choice of very weakly nucleophilic anions (WCAs) and solvents.[29,30] WCAs like $[B(C_6F_5)_4]^-$, carboranes and $[Al\{OC(CF_3)_3\}_4]^-$ and weakly nucleophilic halogenated hydrocarbon solvents like chlorobenzene, fluorobenzene, *ortho*-dichlorobenzene (ODCB) and *ortho*-difluorobenzene (ODFB) have been employed to isolate highly reactive cationic Lewis acids.[6] Long contacts between the cationic center and the nucleophilic sites on the WCA and solvents are observed in the solid state. A few of the reactive cations have been shown to exhibit exceptional catalytic activity; Et_2Al^+ is known to efficiently catalyze polymerization of ethene,[11] $(C_6H_5F)_2Ga^+$ is demonstrated to catalyze the polymerization of isobutene[31] and Et_3Si^+ is capable of activating C–F bonds in perfluoroalkyl groups.[32,33] The stabilization of these cations by coordination of the WCAs and weakly nucleophilic solvent molecules does not inhibit the catalytic activity.

Cations of the heavy elements mercury(II),[34] thallium(III),[35] and lead(IV)[35] have been employed in the electrophilic C–H bond activation under extreme reaction conditions. Bismuth, a heavy element, exhibits significant Lewis acidity in III oxidation state.[36] Despite the demonstration of activation of sp^2[37–39] and sp^3 C–H bonds,[40] the potential of this non-toxic element as a reactive cation is not well explored. The isolation of such a Lewis acidic dication requires the employment of a WCA and weakly nucleophilic solvents.[4,5,30] Herein, we present the synthesis and electronic structure of the reactive dication $[Tp^{Me2}Bi]^{2+}$ isolated with the WCA $[B(C_6F_5)_4]^-$ anion in chlorobenzene and *ortho*-dichlorobenzene. The reactive nature of $[Tp^{Me2}Bi]^{2+}$ is demonstrated by catalyzing the olefin hydrosilylation.

Results and Discussion

The structural chemistry of bismuth is controlled by 6*p* orbitals; the 6*s* orbital essentially remains as an inert lone pair. *Trans* influence is pronounced in bismuth compounds possessing highly polarized Bi–X bonds. Lewis acidity of such bismuth complexes originates from the highly electrophilic site *trans* to the polarized Bi–X bond (Figure 1).[41] The three polar Bi–X bonds will constitute the primary bonds and the acceptor sites *trans* to these bonds are involved in secondary bonding (Figure 1).[42]

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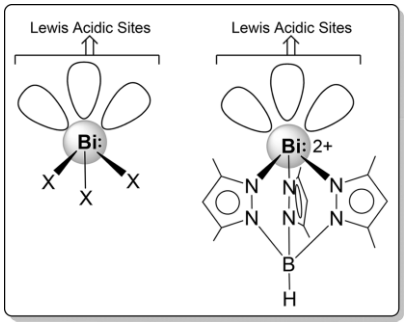
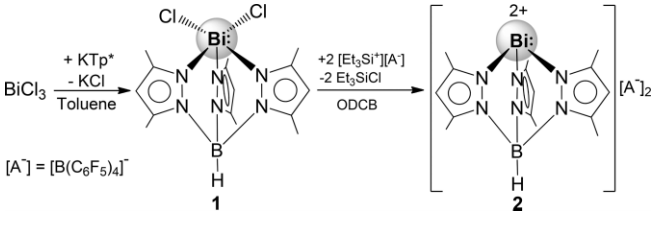


Figure 1. Qualitative representation of Lewis acidic acceptor sites in bismuth compounds bearing polarized Bi–X bonds.

We reasoned that a chelating ligand having three orthogonally faced donor atoms capable of forming a polarized bond with bismuth will leave the acceptor orbitals in *trans* positions Lewis acidic. We selected the mono-anionic hydridotris(3,5-dimethylpyrazolyl)borate (Tp^{Me2}) to meet these demands.[43] The tridentate Tp^{Me2}, (C_{3v} symmetry)[44] can coordinate to Bi^{III} through its three σ-donor nitrogen atoms, thus behaving as a six-electron donor ligand. Absence of favorable π-orbitals, both in terms of energy and effective overlap, in Tp^{Me2},[45,46] should prevent the complete quenching of the positive charge on bismuth thus retaining its electrophilicity. The coordination sites *trans* to the three nitrogen atoms in the $[Tp^{Me2}Bi]^{2+}$ are expected to be highly Lewis acidic (Figure 1).

Tp^{Me2} was introduced on to the bismuth atom by reacting $BiCl_3$ and KTp^{Me2} to obtain $Tp^{Me2}BiCl_2$ (**1**, Scheme 1). The molecular structure of **1**, elucidated by single-crystal X-ray diffraction studies, reveals that three nitrogen atoms of Tp^{Me2} coordinate to the bismuth atom with an average Bi–N distance of 2.405 Å (Figure 2). One of the Bi–N distances [Bi–N2 2.282(9) Å; Table 1] is shorter than the other two similar distances [Bi–N1 2.456(9) and Bi–N3 2.476(10) Å]. The Bi–Cl distances are 2.583(3) (Bi–Cl1) and 2.645(3) Å (Bi–Cl2), in addition to a very long Bi•••Cl contact [Bi•••Cl2′ 3.234(3) Å] in the sixth coordination site with the chlorine atom of the neighboring asymmetric unit. Analysis of the Bi–N and the Bi–Cl distances in **1** reveals *trans* influence around the bismuth center by the donor atoms.



Scheme 1. Synthetic route to prepare Bi^{III} dication.

Abstraction of the two chlorides ions from the bismuth center is expected to result in a highly Lewis acidic dicationic species, $[Tp^{Me2}Bi]^{2+}$. The isolation of the dication and exploration of its potential reactivity critically depend on the choice of the anion and the solvent. We considered employing one of the WCAs, tetrakis(pentafluorophenyl)borate, $[B(C_6F_5)_4]^-$,[47] to set $[Tp^{Me2}Bi]^{2+}$ free. Compound **1** was treated with two equivalents of $[Et_3Si][B(C_6F_5)_4]$ in ODCB at ambient temperature under rigorous air- and moisture-free conditions to obtain $[Tp^{Me2}Bi][B(C_6F_5)_4]_2$ (**2**) (Scheme 1). Compound **2** was crystallized from chlorobenzene and ODCB and the solid-state structure, as established by SCXRD studies, indicated the presence of both the solvents in the unit cell. (Figure 3) $[Tp^{Me2}Bi]^{2+}$ is charge-balanced with two $[B(C_6F_5)_4]$ anions. The average Bi–N distance in $[Tp^{Me2}Bi]^{2+}$ is reduced to 2.201 Å from 2.405 Å in **1**.

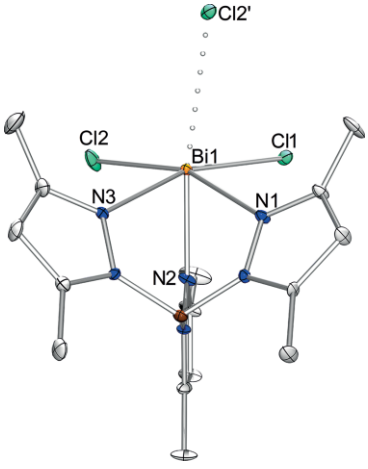


Figure 2. Molecular structure of the asymmetric unit of **1** (CCDC 1410594). Selected geometrical parameters are provided in Table 1.

Table 1. Selected geometrical parameters of **1** and **2** from single-crystal X-ray diffraction and DFT (PBE0 with def2-TZVP basis), in italics below.

	Bond Lengths [Å]			Bond Angles [°]		
	Bi–N1	Bi–N2	Bi–N3	N1–Bi–N2	N2–Bi–N3	N3–Bi–N1
1	2.456(9)	2.282(9)	2.476(10)	78.7(4)	77.4(4)	78.7(3)
	2.527	*2.290*	*2.527*	*75.6*	*77.7*	*77.4*
2	2.117(9)	2.206(9)	2.280(10)	82.5(4)	83.6(4)	86.4(3)
	2.166	*2.166*	*2.167*	*85.2*	*85.2*	*85.2*

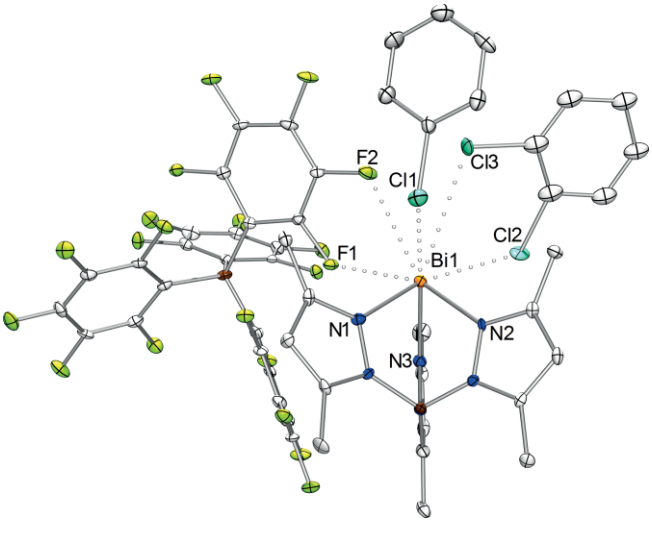


Figure 3. Molecular structure of the $[Tp^{Me2}Bi]$ unit in **2** (CCDC 1847457) exhibiting weak contacts with one of the $B(C_6F_5)_4$ units, chlorobenzene, and *ortho*-dichlorobenzene. Hydrogen atoms are omitted for clarity. Distances [Å] for long contacts: Bi1•••F1 3.01(1), Bi1•••F2 3.16(1), Bi1•••Cl1 3.30(1), Bi1•••Cl2 3.23(4), Bi1•••Cl3 3.55(2).

The bismuth atom in **2** is drawn inside the ligand cavity by 0.226 Å in comparison to **1**. Strikingly, geometrical parameters of Tp^{Me2} are similar for **1** to **2** with respect to C–N, N–N and the two C–C distances; this indicates that there is no change in the electronic structure description of the three pyrazole rings.

Abstraction of two chloride ions from **1** results in the opening up of the coordination sphere around the electrophilic bismuth center spanning a solid angle over 149° in **2**. Very long contacts are observed between the bismuth atom in the $[Tp^{Me2}Bi]$ unit and the weakly nucleophilic halogen atoms of $[B(C_6F_5)_4]$, chlorobenzene and *ortho*-dichlorobenzene (Figure 3). Chlorobenzene and *ortho*-dichlorobenzene coordinate with Bi1 atom through their chlorine atoms with Bi•••Cl contacts ranging from 3.23(4) to 3.55(2) Å [Σr_{cov}(Bi + Cl) = 2.50 Å[48] and Σr_{vdW}(Bi + Cl) = 3.82 Å[49]]. In addition, an *ortho* and a *meta*-F atom of the aryl group belonging to one of the $[B(C_6F_5)]_4$ anions have long contacts with Bi1 atom with distances of 3.01(1) and 3.16(1) Å respectively [Σr_{cov}(Bi & F) = 2.05 Å[48] and Σr_{vdW}(Bi & F) = 3.19 Å[49]]. A search in the Cambridge Structural Database (CSD) revealed that examples of contacts between bismuth atom and weak nucleophiles similar to the ones discussed above are rare.[50] Long contacts with very weak nucleophiles observed in **2** facilitate the isolation of a reactive bismuth dication in the solid state.

Density Functional Theory (DFT) calculations were performed on $[Tp^{Me2}Bi]^{2+}$ at PBE0 with def2-TZVP basis set to elucidate the electronic structure of the dication. Analysis of the molecular orbitals of $[Tp^{Me2}Bi]^{2+}$ indicates that a set of three occupied MOs, consisting of $37a_1$ (HOMO-6) and two degenerate $33e_1$ (HOMO-12, Figure 4), correspond to the three Bi–N bonds. The lowest MO of Figure 4 ($28a_1$, HOMO-29) is the lone pair on the Bi atom with a population of almost two electrons having predominantly s-character of 88 %. LUMOs arise from a linear combination of Bi–N antibonding orbitals. The lower lying degenerate pair, $39e_1$ (LUMO), extend from the Bi atom along the Bi–N axes and are energetically favorable for nucleophilic attack. LUMO+1, $39a_1$, the non-degenerate σ* MO along the C_3 axis, is higher in energy and constitutes the third electrophilic site in $[Tp^{Me2}Bi]^{2+}$. Natural Bond Order (NBO) analysis of $[Tp^{Me2}Bi]^{2+}$ estimates the charge on Bi to be +1.82 a.u. inferring the presence of a nearly di-positive charge on the bismuth center. Energy Decomposition Analysis (EDA) shows that Bi–N bonds have approximately equal electrostatic and covalent contributions. The delocalization of the positive charge to the pyrazole ring is not significant. Tp^{Me2} provides an opportunity to realize the existence of a highly charged heavy element cationic center.

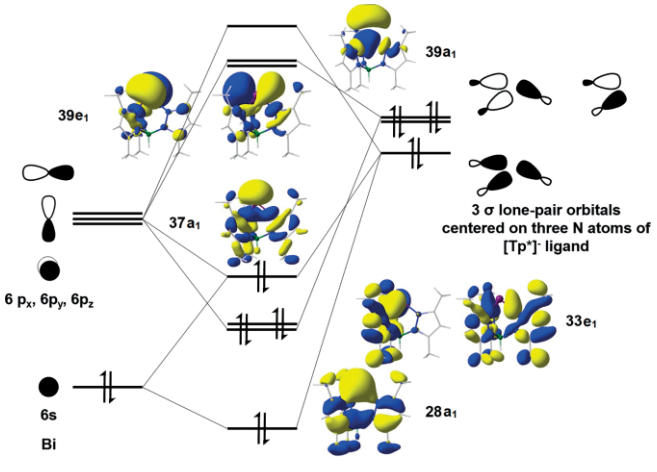


Figure 4. MO interaction diagram for the $[Tp^{Me2}Bi]^{2+}$ dication. Only selected frontier valence orbitals (isovalue = 0.03) which constitute the Bi–N interactions are considered for simplicity, in addition to Bi lone pair($28a_1$).

A modified Gutmann method[51,52] was employed to quantify the Lewis acidity of **2** in solution. Compound **2** was treated with a sub-stoichiometric amount of Et_3PO in ODCB-D_4 resulting in a single sharp peak at δ = 74.8 ppm in the ^{31}P NMR spectrum (Figure 5), a value comparable to the one observed for the benchmark Lewis acid $B(C_6F_5)_3$ (δ = 76.7 ppm in ODCB-D_4, see SI). Further addition of Et_3PO to this solution of **2** led to the appearance of the second peak at δ = 69.6 ppm (Figure 5) reflecting multiple Lewis acidic sites in $[Tp^{Me2}Bi]^{2+}$, thereby confirming the theoretical predictions. An addition of five equivalents of Et_3PO to **2** resulted in a single broad peak at δ = 58.65 ppm (Figure 5) indicating that the binding of Et_3PO to $[Tp^{Me2}Bi]^{2+}$ is highly dynamic contrary to the observation in the case of $B(C_6F_5)_3$ (Figure S9).

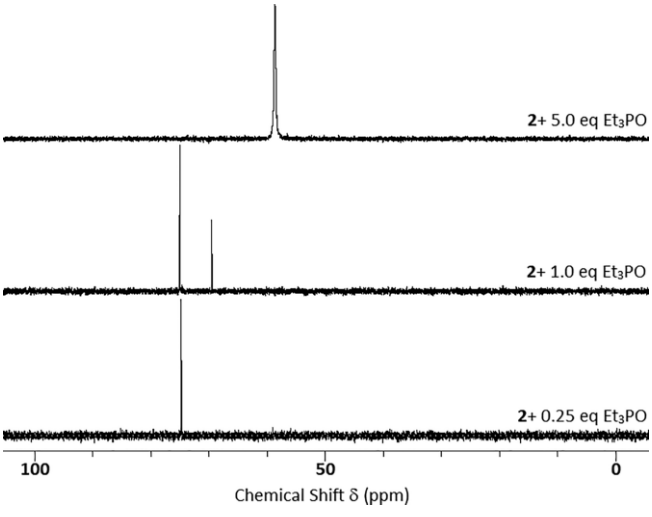
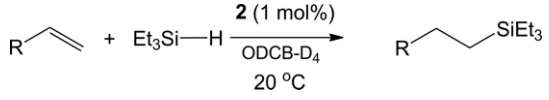


Figure 5. Stacked ^{31}P NMR spectra of solutions ODCB-D_4 solutions of **2** with various amounts of Et_3PO.

With both theoretical and experimental evidence for multiple Lewis acidic sites at the bismuth atom in $[Tp^{Me2}Bi]^{2+}$, we set out to probe the reactivity of **2**. We chose to investigate the hydrosilylation of olefins in the presence of catalytic amounts of **2**. Hydrosilylation of olefins is an important industrial process in the production of a variety of products including lubricants, coatings, cosmetics and adhesives.[53,54] Precious metal catalysts – Speier's catalyst ($[H_2PtCl_6].H_2O$),[55] Karstedt's catalyst [Pt(0) compound bearing vinyl-siloxane ligands][56] and Markó's catalyst (modified Karstedt catalyst bearing NHC ligand)[57] have been traditionally employed to carry out hydrosilylation of alkenes. Recent research in this area has focused on the development of earth abundant transition metal catalysts of Fe, Co and Ni.[58] Due to their Lewis acidity, few *s*-[59] and *p*-block[60–65]

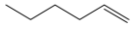
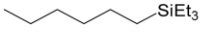
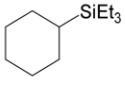
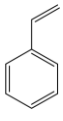
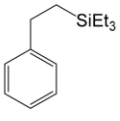
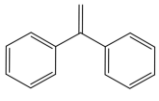
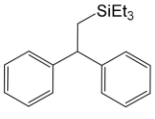
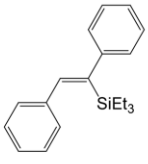
compounds have been explored as possible alternatives to the existing catalysts.

Hydrosilylation of alkenes was performed by employing Et_3SiH as the hydrosilane source in the presence of 1 mol-% of **2** (Scheme 2, see SI Section 4 for experimental details). Addition of $Et_3Si–H$ across double bonds was observed leading to anti-Markovnikov's product under mild conditions and the details of the catalytic hydrosilylation are listed in Table 2. Notably, the undesired side reactions of alkenes like isomerization, polymerization, hydrogenation and dehydrosilylation, a major concern in other catalysts, were not observed. Catalytic hydrosilylation of the alkyne, 1,2-diphenylethyne was also tested and found to proceed efficiently.



Scheme 2. General scheme for the catalytic hydrosilylation of alkenes.

Table 2. Addition of $Et_3Si–H$ to olefins catalyzed by 1 mol-% of compound **2** at 20 °C in ODCB-D_4.

Olefin	Product	Time (min)	Yield (%)
		< 5	> 99
		30	> 99
		180	> 99
		30	> 99
		30	> 99

To understand the mechanism associated with the hydrosilylation in Scheme 2, we tested the reactivity of **2** with alkenes and Et_3SiH separately. While treating **2** with 1-hexene showed no reactivity, reaction between former and Et_3SiH led to the decomposition of **2** and precipitation of elemental bismuth after 12 hours. However, treating **2** with equimolar quantities of 1-hexene and Et_3SiH in ODCB instantaneously resulted in the hydrosilylated product in quantitative yields. These observations indicate that the hydrosilylation of olefins proceeds via Lewis acid promoted activation of $Et_3Si–H$, typically observed in main group Lewis acids.[61,63,66] We resorted to DFT calculations to understand the possible interactions between the dication and the silane. Computations were performed on $[Tp^{Me2}Bi\cdots(H–SiEt_3)_n]^{2+}$ (n = 1–3) and only the complex with n = 2 is discussed (details on complexes with n = 1 and 3 provided in SI). Optimized geometry shows that two $Et_3Si–H$ molecules are weakly interacting unsymmetrically at the di-cationic Bi center through κ^1-Si–H binding mode in $[Tp^{Me2}Bi\cdots(H–SiEt_3)_2]^{2+}$ with Bi···H distances of 2.449 and 2.534 Å [Table 3, Σr_{cov}(Bi + H) = 1.79 Å[48] and Σr_{vdW}(Bi + H) = 3.17 Å[49]]. $Et_3Si–H$ ligands interacts with the two degenerate low-lying LUMOs ($39e_1$ in Figure 4) located *trans*- to the two Bi–N bonds. The dication silane interaction in $[Tp^{Me2}Bi\cdots(H–SiEt_3)_2]^{2+}$ leads to the elongation of the Si–H bond by 0.069 Å compared to that calculated distance for free $Et_3Si–H$ distance (Table 3). This activation of the Si–H bonds is also reflected in substantial decrease in the Wiberg bond indices (WBI) of Si–H bonds (Table 3). The interaction energy between $[Tp^{Me2}Bi]^{2+}$ and two $Et_3Si–H$ is substantial at 118 kJ mol^{-1}(66 and 160 kJ mol^{-1} for one and three $EtSi_3H$, See Figure S32 and Table S3 for details). NBO charges indicate an increase in the polarization in both Si–H bonds up on the complex formation (Table 3). Topological atoms in molecule (AIM) analysis shows the electron density at the bond critical points (BCP) 0.027/0.024 e $Å^{-3}$ for Bi···H1/Bi···H2 and 0.095/0.097 e $Å^{-3}$ for Si1–H1/Si2–H2 bonds (Figure S29). This is in good agreement with the trend shown by bond length, WBI Index and NBO charge analysis (Table 3). No BCP was observed between the Bi and Si atoms. Thus, theoretical investigations provide insights into Si–H bond activation by $[Tp^{Me2}Bi]^{2+}$.

Table 3. Selected interatomic distances [Å], WBI index and NBO charges of $[Tp^{Me2}Bi\cdots(H–SiEt_3)_2]^{2+}$ calculated at PBE0 level with Def2-TZVP basis set for all atoms.

Compound	E–H	Distance [Å]	WBI	NBO Charges
$Et_3Si–H$	Si–H	1.497	0.92	Si: +1.38
				H: –0.19
$[Tp^{Me2}Bi\cdots(H–SiEt_3)_2]^{2+}$	Bi···H1	2.449	0.13	Si1: +1.55
	Bi···H2	2.534	0.10	H1: –0.32
	Si1–H1	1.566	0.72	Si2: +1.53
	Si2–H2	1.559	0.75	H2: –0.31

Conclusions

In summary, we have accessed a reactive Lewis acid of an environmentally benign heavy element, bismuth. A judicious choice of a pure σ-donor ligand and weakly nucleophilic anion and solvents facilitated the isolation of a highly electrophilic bismuth dication. Investigation on the hydrosilylation of olefins has prompted us to explore the potential of **2** in Lewis acid catalyzed hydroelementations to unsaturated bonds. Studies are underway.

CCDC 1410594 (for **1**), and 1847457 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Keywords: Bismuth · Lewis acids · Reactive cations · Weakly coordinating anions · Bond activation · Hydrosilylation

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