The Lewis acidity of bismuth(III) halides: a DFT analysis

Jennifer Sanderson, Craig A. Bayse *

Department of Chemistry and Biochemistry, Old Dominion University, Hampton Boulevard, Norfolk, VA 23529, United States

ARTICLE INFO

ABSTRACT

The Lewis acidity of BiX_3 (X=Cl, Br, I) is explored using density-functional theory (DFT) studies of simple complexes with various alcohol and carbonyl substrates. The calculated relative energies of the complexes follow the trend of hardness for BiX_3 (Cl>Br>I). The observed halogen exchange reaction of $BiCl_3$ with alcohols and alkyl halides is discussed in terms of the computational results as well as theories of hardness and carbocation stability. The DFT results predict similar activation of substrates by molecular BiI_3 relative to $BiBr_3$, which is inconsistent with experimental results, which show no reactivity for the iodide in nonpolar solvents. However, the molecular form is unlikely in these solvents as BiI_3 is an ionic salt in contrast to the chloride and bromide, which are covalent solids.

1. Introduction

Trivalent bismuth halides BiX_3 (X=Cl, Br, I) are useful in organic synthesis as mild Lewis acid catalysts which can be easily recovered from the reaction mixture.[1] These compounds are effective for the removal of a variety of protecting groups including *O,O*-acetals,[2] aminals,[3] silyl ethers,[4] hydrazones, and semicarbazones.[5] BiX_3 and other bismuth salts also catalyze ring-opening reactions of epoxides[6] and a number of bond-forming reactions such as Diels–Alder cyclizations,[7] aldol and Michael reactions,[8] allyl and aryl acylations,[9] sulfonation of arenes,[10] aza-Prins cyclization,[11] tandem cyclization–additions,[12] and the hydroarylation of styrenes and arenes.[13,14] The attraction of these compounds is their low cost and toxicity in comparison to other common Lewis acids.[1] For example, $BiCl_3$ and $BiBr_3$ have replaced $TiCl_4$[8] and $InCl_3$,[12b] respectively, in the Mukaiyama-aldol reaction. The $BiCl_3$-catalyzed Diels–Alder reaction also has higher yields and increased stereoselectivity when compared to Sm-, Ti-, Sc-, and Yb-based Lewis acids[7] as well as prevention of polymerization that can occur with other Lewis acids.[15]

Reaction of various alcohols with BiX_3 (X=Cl, Br, I) in CCl_4 was shown by Keramane et al. to be dependent upon the specific bismuth salt.[16] No reaction was observed in trials including either BiI_3 or primary alcohols. $BiBr_3$ was an effective Lewis acid catalyst, converting secondary and tertiary alcohols to alkenes and benzylic and allylic alcohols to ethers without the formation of alkyl bromides. $BiCl_3$ reacted stoichiometrically to convert secondary alcohols to alkyl chloride and alkene products (70% and 30%, respectively), tertiary alcohols to alkyl chlorides, and benzylic alcohols to ethers and alkyl chlorides. Substantial differences between the BiX_3 salts have also been observed for ring opening of cholesterol epoxides under Ritter conditions:[6a] $BiBr_3$ catalyzes the formation of the *trans*-β-hydroxy acetamide where $BiCl_3$ also produces the chlorohydrin in a 1:1 ratio. Halohydrins of both BiX_3 compounds are formed when the reaction is performed in 1,4-dioxane.

Keramane et al.'s proposed mechanism for reaction from the assumed Lewis acid complex between BiX_3 and the alcohol includes three pathways (Scheme 1). The steps of this mechanism are proposed to occur without carbocation formation. The first pathway involves etherification by S_N2 attack of a second alcohol on the α-carbon of the complexed alcohol. In the second pathway, the oxygen attacks the hydrogen of the adjacent carbon to give an elimination product, driving off water and regenerating BiX_3. The third pathway, available for only $BiCl_3$, is a non-catalytic intramolecular halogen exchange. The bismuth byproduct $BiCl_2OH$ can react further to produce two additional equivalents of RCl. A related halogen exchange reaction occurs between BiX_3 and RX′ under similar conditions when X′ is heavier than X.[17]

To better understand the differences in reactivity of BiX_3 toward alcohols and other substrates, we have performed a series of density-functional theory (DFT) calculations on model complexes of BiX_3 with simple substrates (ethanol, isopropanol, *tert*-butanol, benzyl alcohol, tetrahydrofuran (THF), propenal, and acetone). The actual bismuth species involved in Lewis acid catalysis is unknown. In this study, the simple BiX_3 molecule, known to be trigonal pyramidal in gas phase electron diffraction experiments,[18] is assumed

---

* Corresponding author. Tel.: +1 757 683 4097; fax: +1 757 683 4628.
E-mail address: cbayse@odu.edu (C.A. Bayse).
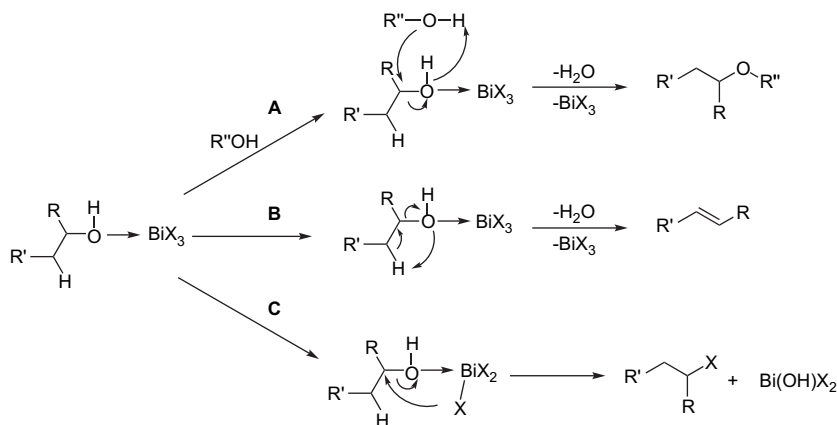
Scheme 1.

to be the active catalyst. These calculations will use one substrate molecule complexed with BiX$_3$, although crystal structures of BiCl$_3$–THF[19] and BiCl$_3$–crown ether complexes[20] show that BiX$_3$ can coordinate up to five ligands.

2. Theoretical methods

Geometry optimizations were performed with Gaussian 03[21] at the DFT/mPW1PW91[22] level. The mPW1PW91 functional has been shown to provide better geometries for BiI$_3$ than B3LYP, HF, or MP2.[23] The Wadt–Hay relativistic effective core potential (RECP)[24] basis sets were used for Bi, Cl, Br, and I. Oxygen, carbon, and hydrogen were represented by the Dunning triple-ζ basis set.[25] Basis sets for Bi, C, and the halogens were augmented with diffuse and polarization functions. For the calculations on the benzyl alcohol complexes, these extended basis sets were used only for the

–CH$_2$OH fragment; all other atoms were described by the Dunning double-ζ basis set.[26] Relative energies of complex formations include the zero-point energy correction (ΔE+ZPE). Analysis of atomic charge and hybridization was performed with Atomic Polar Tensor (APT)[27] and Natural Bond Order (NBO) methods.[28]

3. Results

The DFT-optimized geometries of the trigonal pyramidal (C_{3v}) BiX$_3$ molecules are comparable to experimental electron diffraction data as well as previous computational studies at the HF,[29] MP2,[30] and DFT[31] levels of theory (Table 1). For all methods, the X–Bi–X bond angles increase as a function of the halide in the order of Cl<Br<I due to repulsive interactions between the halides. The Bi–X bond length increases down the halide group corresponding to the sum of the van der Waals radii. The bond lengths for BiCl$_3$ and

Table 1
Bond distances, Bond angles, APT charges (q_{Bi} and q_X), and chemical hardness (η) of BiX$_3$

BiX$_3$		d(Bi–X) (Å)	X–Bi–X (°)	q_{Bi}	q_X	ηBiX$_3$ (eV)	ΔH_{diss}[k] (kcal/mol)
Cl	DFT/mPW1PW91	2.432	98	1.424	−0.475	6.36	200.0
	HF[a]	2.417	97.9				
	MP2[b]	2.453	98.5				
	DFT[c]	2.48	97.3				
	ED[d]	2.424	97.3, 97.5				
	X-ray[e]	2.468, 2.518	94.9, 93.2				
Br	DFT/mPW1PW91	2.598	99.5	1.130	−0.377	5.43	168.1
	HF[a]	2.589	99.1				
	MP2[b]	2.610	99.4				
	DFT[c]	2.63	98.0				
	ED[f]	2.577	98.6				
	X-ray[g]	2.620, 2.690	88.2, 96.3				
I	DFT/mPW1PW91	2.817, 2.802[h]	100.5, 100.5[h]	0.797	−0.266	4.41	129.9
	HF[a]	2.804	100.0				
	MP2	2.842[b], 2.807[h]	100.6[b], 100.4[h]				
	DFT[c]	2.87	99.4				
	DFT/B3LYP	2.828[h]	101.5[h]				
	ED[i]	2.807	99.5				
	X-ray[j]	3.1	90.0				

[a] Ref. 29.
[b] Ref. 30.
[c] Ref. 31.
[d] Ref. 18a.
[e] Ref. 32.
[f] Ref. 18b.
[g] Ref. 33.
[h] Ref. 23.
[i] Ref. 18c.
[j] Ref. 34.
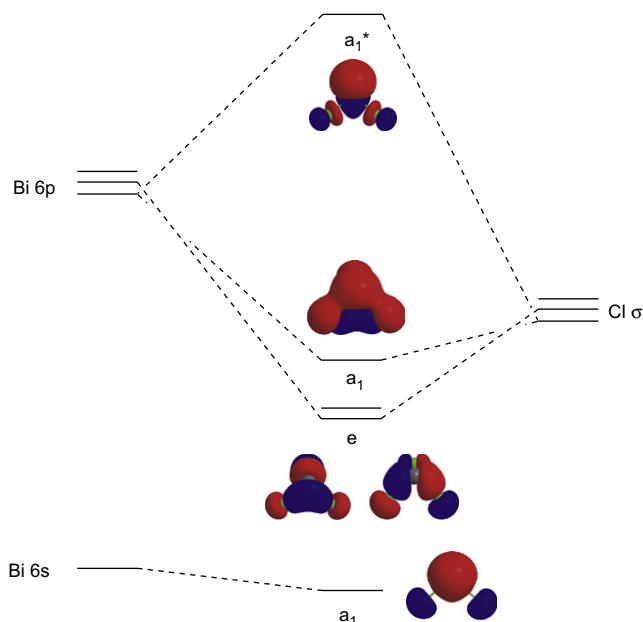[k] Defined as BiX$_3$(g)→Bi(g)+3X(g), see Ref. 38.

BiBr$_3$ from X-ray crystallography[32,33] are larger than the DFT and ED values due to interactions between Bi and the halogens of adjacent molecules within the crystalline lattice. In contrast, the X-ray structure[34] of BiI$_3$ shows a lattice of hexagonal close packed Bi^{3+} and I$^-$ ions rather than the molecular units observed in the gas-phase ED studies. (An ionic polymorph of BiBr$_3$ also exists.[33]) Bi–I distances within the octahedral BiI$_6$ groups are ~0.3 Å longer than the ED distance for BiI$_3$. The ionic nature of BiI$_3$ likely contributes to the differences in reactivity observed by Keramane et al.[16]

The Lewis acidity of BiX$_3$ results from the relativistic contraction of the valence 6s Bi AO.[35,36] The low energy of this AO reduces mixing with the σ-type AOs of the halides, which form bonds through the higher energy bismuth 6p AOs (Fig. 1). The decrease in s character for the bonding MOs also leads to bond angles that are significantly less than 109.5 predicted by VSEPR due to the effective change in hybridization from sp^3 to p^3. NBO analysis gives the contribution of the Bi 6s AO to the Bi–Cl bond as 3.2%. In contrast, the N 2s AO of NCl$_3$ is 13.1%, consistent with sp^3 hybridization and its 110° bond angle. The LUMO of BiX$_3$ is antibonding through the Bi 6p$_z$ AO and the a$_1$ irreducible representation of the halide σ-type AOs. Unlike the electron-deficient boron trihalides, BiX$_3$·L complexes do not form a Bi–L bond along the C$_{3v}$ axis. Complexation of Lewis bases expands octet of bismuth leading to the commonly observed see-saw structures predicted by VSEPR for molecules with four bonds and one lone pair (AX$_4$E).

Although the chloride is the strongest Lewis acid based upon the APT charges for BiX$_3$ (Table 1), analysis of the hardness is important to interpret the reactivity of the bismuth halides. The chemical hardness parameter η is a qualitative measurement of the Lewis acidity defined as the average of the ionization potential and the electron affinity of a species.[37] Using Koopmans' theorem definitions of these properties, the chemical hardness can be written in terms of the HOMO and LUMO energies (Eq. 1):

$$\eta = \frac{1}{2}(\varepsilon_{HOMO} - \varepsilon_{LUMO}) \qquad (1)$$

For BiX$_3$, the HOMO energies increase and the LUMO energies decrease down the halogen group resulting in lower hardness parameters for the heavier halide molecules. The trend in the HOMO–LUMO gap is consistent with the weaker covalent bonds between bismuth and the larger halogens as shown by the homolytic dissociation enthalpy (ΔH_{diss}, Table 1).[38] Comparison of the η values in Table 1 to reported DFT values shows that molecular BiX$_3$ species are significantly softer than BF$_3$ (11.677) or BCl$_3$ (7.294)[39] (Bi^{3+} is commonly listed as a borderline-soft acid). Keramane et al. use the relative hardness of the hydroxide and halide ions to explain the reactivity of BiX$_3$ with both alcohols and alkyl halides: the soft Bi center will preferentially form bonds with the larger halides over the hard OH$^-$ and Cl$^-$ ions. In these terms, the reactivity fits well into the classic formulation of an exchange reaction within hard and soft acid and base (HSAB) theory.[37] BiBr$_3$ and BiI$_3$ do not exchange with alcohols because the hard (R$^+$ and OH$^-$) and soft (Bi^{3+} and X$^-$) components are paired. For reactions with the alkyl halides,[17] the soft bismuth will exchange a halide with the hard carbocation only if bismuth's halide is harder than that of the alkyl halide (e.g., BiCl$_3$ reacts with RBr, but BiBr$_3$ does not react with RCl).

The geometries of several BiX$_3$·L complexes (L=THF, EtOH, *i*-PrOH, *t*-BuOH, BnOH, acetone, and propenal) were calculated to examine the effect of the Lewis acidity of BiX$_3$ on the electronic structure of the substrate molecules (Tables 2 and 3). The overall geometry of the optimized BiX$_3$·L species was the distorted see-saw consistent with AX$_4$E from VSEPR (Fig. 2). Experimental data for simple complexes of BiX$_3$ are not available, but the Bi–O and Bi–Cl$_{trans}$ bond distances for BiCl$_3$·THF (Fig. 2) are comparable to the X-ray structure of BiCl$_3$·3THF (2.63–2.67 and 2.484–2.491 Å, respectively).[19] The similarity between the bond lengths suggests that changes in electronic structure upon formation of the Lewis complex are localized in the hypervalent interaction and can be reproduced in simple BiX$_3$·L complexes. However, these model complexes omit steric interactions between the substrate molecules and may exaggerate changes in electronic structure in the model complexes due to a greater effective q$_{Bi}$ felt by the substrate.

The trend in ΔE+ZPE (Cl>Br>I, Tables 2 and 3) is consistent with the chemical hardness values, which predict that the strongest Lewis complexes with the hard oxygen donors should be formed with the chloride. The complex formation energies for the bromide and iodide are slightly lower than the chloride (~2 kcal/mol for BiI$_3$). The small range for complex formation suggests that the differences in reactivity are due to changes in the electronic structure of the complexed substrate. However, the lack of reactivity in the iodide may be connected to the ionic nature of the solid. Formation of the BiX$_3$·*t*-BuOH complexes is less favorable than that of the EtOH and *i*-PrOH complexes due to the steric interactions between the cis halides and methyl groups.

The stronger interaction between the substrates and BiCl$_3$ is reflected in d(Bi–O) and the change in trans d(Bi–X) bond distance. The weaker BiI$_3$ complexes have Bi–O distances ~0.2 Å longer than the BiCl$_3$·L series. These results are consistent with the valence-bond picture of the three-center-four-electron (3c-4e) bonding described for hypervalent molecules. The resonance structures for the 3c-4e interaction of the trans alcohol and halide of the

Figure 1. Molecular orbital diagram for BiCl$_3$. The chloride p-type lone pair orbitals, including the HOMO, have been omitted for clarity.

Table 2
Selected geometric data, APT charges (q), and NBO data for BiX$_3$·(ketone) complexes (X=Cl, Br, I)

	ΔE+ZPE	d(C–O) (Å)	Δd(C–O) (Å)	d(Bi–O) (Å)	Trans d(Bi–X)	qC
Acetone		1.2072				0.826
BiCl$_3$·acetone	−10.90	1.2206	0.0134	2.6663	2.4698	+0.086
BiBr$_3$·acetone	−9.33	1.2189	0.0117	2.7195	2.6328	+0.079
BiI$_3$·acetone	−8.19	1.2189	0.0117	2.7377	2.8507	+0.067
Propenal		1.2053				0.855
BiCl$_3$·propenal	−10.32	1.2185	0.0132	2.6764	2.4701	+0.068
BiBr$_3$·propenal	−8.84	1.2173	0.0120	2.7273	2.6333	+0.060
BiI$_3$·propenal	−7.72	1.2165	0.0112	2.7551	2.8509	+0.048

Table 3
Selected geometric data, APT charges (q) and NBO data for $BiX_3 \cdot ROH$ (X=Cl, Br, I)

	ΔE+ZPE	d(Bi–O) (Å)	d(C–O) (Å)	Trans d(Bi–X) (Å)	Δd(C–O) (Å)	qC	%s, NBO	%p, NBO
EtOH			1.4157			0.572	23.29	76.60
$BiCl_3 \cdot$EtOH	-11.36	2.6399	1.4337	2.4691	0.0180	−0.045	21.70	78.15
$BiBr_3 \cdot$EtOH	−9.95	2.6839	1.4320	2.6331	0.0163	−0.043	21.86	77.99
$BiI_3 \cdot$EtOH	−7.79	2.7127	1.4312	2.8512	0.0155	−0.049	21.96	77.89
i-PrOH			1.4231			0.566	21.92	77.93
$BiCl_3 \cdot i$-PrOH	−11.49	2.6429	1.4431	2.4705	0.0200	+0.029	20.42	79.42
$BiBr_3 \cdot i$-PrOH	−10.04	2.6874	1.4415	2.6341	0.0184	+0.031	20.56	79.29
$BiI_3 \cdot i$-PrOH	−9.05	2.7203	1.4409	2.8519	0.0178	+0.012	20.64	79.21
t-BuOH			1.4305			0.533	20.65	79.20
$BiCl_3 \cdot t$-BuOH	−11.39	2.6482	1.4514	2.4706	0.0209	+0.069	19.28	80.56
$BiBr_3 \cdot t$-BuOH	−9.87	2.6935	1.4497	2.6342	0.0192	+0.074	19.42	80.42
$BiI_3 \cdot t$-BuOH	−8.82	2.7192	1.4484	2.8522	0.0179	+0.077	19.54	80.30
BnOH			1.4106			0.536	22.73	77.14
$BiCl_3 \cdot$BnOH	−12.44	2.6424	1.4378	2.4702	0.0272	+0.056	20.62	79.25
$BiBr_3 \cdot$BnOH	−10.99	2.6913	1.4348	2.6337	0.0242	+0.049	20.80	79.07
$BiI_3 \cdot$BnOH	−10.05	2.7258	1.4333	2.8515	0.0227	+0.043	20.93	78.94

see-saw-shaped $BiX_3 \cdot ROH$ complex are shown in Eq. 2. As the strength of the Bi–O interaction increases, the right-hand resonance structure becomes more important resulting in a reduction in the overall Bi–X bond order and a longer Bi–X bond. This is consistent with the trend in d(Bi–X) in the order of Cl>Br>I observed for each of the complexes (compare d(Bi–X) in Table 1 to trans d(Bi–X) in Tables 2 and 3).

$$ \underset{H}{\overset{}{>}}\!O\!-\!Bi\!-\!X \longleftrightarrow \underset{H}{\overset{}{>}}\!O^{+}\!-\!Bi \quad X^{-} \qquad (2) $$
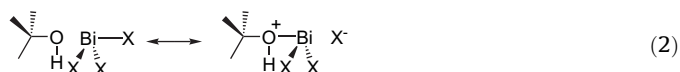
The results for the BiX_3 complexes with carbonyl compounds (acetone and propenal) are listed in Table 2. Activation of aldehydes and ketones by Lewis acid catalysis is important to aldol condensations and other reactions involving nucleophilic attack on the carbonyl group. BiX_3 interacts with the O_{CO} lone pair to increase the positive charge on the carbonyl carbon (Table 2). The effect is primarily inductive as the complexes show only a slight increase in the C–O bond suggesting minor double bond weakening. Lewis acid catalysts accelerate Diels–Alder reactions by lowering the energy of the LUMO to favor interaction with the HOMO of the diene. Propenal was included in the study to show the effect of BiX_3 on a simple dienophile. BiX_3 lowers the LUMO energy of propenal by 0.92–1.04 eV, a limited range reflected in the small changes in the C–O bond distance along the halogen series (Table 2). $BiCl_3$ produces the largest reduction in accordance with the greater electronegativity and inductive effect of chlorine.

The results for the $BiX_3 \cdot$alcohol complexes (Table 3) show increases in the C–O bond distance and the charge on the α-carbon consistent with Lewis acid activation. The Δd(C–O) values in Table 3

are comparable to that for the complex of CF_3CH_2OH with boron trifluoride.[40] $BiCl_3$ produced the largest increase in d(C–O) with smaller differences for the $BiBr_3$ and BiI_3 complexes consistent with their lower Lewis acidity. The increase in the d(C–O) was smallest for the primary alcohol (EtOH, +0.0180 Å, $BiCl_3$) and greatest for benzyl alcohol (+0.0272 Å, $BiCl_3$) with secondary and tertiary alcohols' intermediate following the expected trend for reaction by an S_N1 mechanism. An analysis of the charges for the α-carbon does not reveal clear trends either for the alcohols or for the bismuth halide. However, the decrease in qC for EtOH and the overall increase from i-PrOH to t-BuOH are consistent with the lack of substitution for primary alcohols and the more rapid rates of substitution for tertiary over secondary alcohols.[16] The contribution of the α-carbon p AO to the C–O bond is an alternate measure of activation of the C–O bond. NBO calculations of the free and complexed alcohols (Table 3) show that the percentage of p-character (%p) of the α-carbon in the C–O bond increases as the Lewis acidity of BiX_3 increases and follows the trend in alcohol reactivity for S_N1 reactions (benzyl alcohol>3°>2°>1°). This trend mirrors the decrease in C–O bond order for complexes of alcohols with boron trifluoride calculated at the CNDO level.[41]
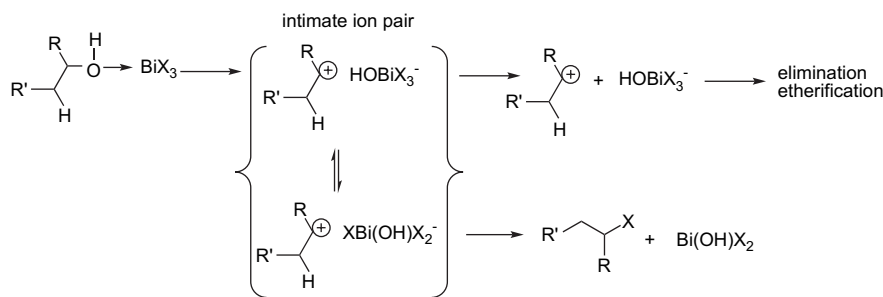
Keramane et al. invoke the S_Ni mechanism[42] to explain the retention of stereochemistry for chlorination of alcohols by $BiCl_3$, but propose that the exchange occurs via a four-centered transition state without formation of an intimate ion pair. Although some of the experimental results suggest that no carbocation forms (disappearance of p-MeBnOH was slower than BnOH), several observed products appear to result from hydride/methyl shifts from an intermediate carbocation. For example, reaction of 2-octanol with $BiCl_3$ leads to 2-, 3-, and 4-chlorooctane as well as 1-, 2-, 3-, and 4-octene. Additionally, the trends in reactivity for the alcohols roughly follow the trend in stability of the carbocation (benzylic/allylic>3°>2°>1°). The concerted transition states for the proposed process have not been determined as part of this computational study, but are necessarily high-energy given strained nature of the four-centered TS and steric interactions with the R groups of the 2° and 3° alcohols. The proposed transition state is also inconsistent with the experimentally observed rates given that no reaction was observed for 1° alcohols where steric interactions would be minimal.

The retention of stereochemistry is consistent with carbocation formation if substitution occurs through an intimate ion pair (Scheme 2). Ion pairing is greatest in nonpolar solvents such as those used in Keramane et al.'s experimental studies and it is possible that intimate ion pairs in Scheme 2 have long enough lifetimes for the observed hydride/methyl shifts within the carbocation. Rearrangement of the $[Bi(OH)X_3]^-$ fragment within the ion pair allows the carbocation to abstract a halide depending upon the relative hardness of the acid and base. This explanation is
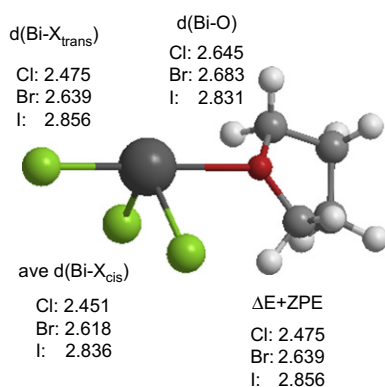
Figure 2. Structure of representative $BiX_3 \cdot L$ complexes (L=THF) with see-saw geometry. Bond distances are in angstroms; ΔE+ZPE is in kcal/mol.

d(Bi–X$_{trans}$)
Cl: 2.475
Br: 2.639
I: 2.856

d(Bi–O)
Cl: 2.645
Br: 2.683
I: 2.831

ave d(Bi–X$_{cis}$)
Cl: 2.451
Br: 2.618
I: 2.836

ΔE+ZPE
Cl: 2.475
Br: 2.639
I: 2.856

Scheme 2.

analogous to that of the retention of stereochemistry in the decomposition of alkyl chlorosulfites via the S_Ni mechanism and requires further experimental studies for confirmation. The similar hardness of chloride and hydroxide allows internal return to RX rather than ROH, but the affinity of Bi for the bromide leads to a stable ion pair that may separate and diffuse into solution. Formation of alkene products may occur by deprotonation of the free or ion-paired carbocation. Etherification may occur via attack of a second alcohol at any stage of the process in Scheme 2 (complex, intimate ion pair, or separated ions).

4. Conclusions

The trend in the Lewis activity of BiX_3 has been examined in terms of chemical hardness and energy of formation. All three BiX_3 molecules are predicted to form Lewis complexes with the model substrates with the strongest interaction for the chloride. Computational measurements of hardness place $BiCl_3$ as the hardest and BiI_3 as the softest in the series. The differences for the reactivity of the chloride and bromide with alcohols can be explained in terms of relative hardness as discussed previously by Keramane et al.[16] The similarity of the hardness of the chloride and hydroxide ions allows these to be exchanged. The higher affinity of Bi for the softer Br prevents side reactions and permits $BiBr_3$ to be an effective Lewis acid catalyst. Indicators of activation (%p, Δd(C–O), etc.) for the $BiI_3 \cdot L$ complexes are only slightly smaller than those of $BiCl_3$ and $BiBr_3$. The lack of activity under Keramane et al.'s reaction conditions is almost certainly due to the ionic nature of the solid given that BiI_3 acts as a Lewis acid catalyst in polar solvents under the same conditions as $Bi(NO_3)_3$[43] where the active species may be the solvated Bi^{3+} ion. Molecular BiI_3 might be expected to be a mild Lewis acid based upon our DFT results, but it is unlikely that BiI_3 molecules are present in solution under Keramane et al.'s reaction conditions.

References and notes

1. (a) Leonard, N. M.; Wieland, L. C.; Mohan, R. S. *Tetrahedron* **2002**, *58*, 8373–8397; (b) Vidal, S. *Synlett* **2001**, 1194–1195.
2. (a) Sabitha, G.; Babu, R.; Reddy, E.; Yadav, J. S. *Chem. Lett.* **2000**, 1074–1075; (b) Bailey, A. D.; Baru; Tasche, K. K.; Mohan, R. S. *Tetrahedron Lett.* **2008**, *49*, 691–694.
3. Cong, X.; Hu, F.; Liu, K.-G.; Liao, Q.-J.; Yao, Z.-J. *J. Org. Chem.* **2005**, *70*, 4514–4516.
4. Bajwa, J.; Vivelo, J.; Slade, J.; Repic, O.; Blacklock, T. *Tetrahedron Lett.* **2000**, *41*, 6021–6024. These authors suggest that HBr produced from the hydrolysis of $BiBr_3$ under the reaction conditions (wet MeCN) may be the active catalyst.
5. Boruah, A.; Baruah, B.; Prajapati, D.; Sandhu, J. *Synlett* **1997**, 1251–1252.
6. (a) Pinto, R. M. A.; Salvador, J. A. R.; Le Roux, C. *Tetrahedron* **2007**, *63*, 9221–9228; (b) McClusky, A.; Leitch, S. K.; Garner, J.; Caden, C. E.; Hill, T. A.; Odell, L. R.; Stewart, S. G. *Tetrahedron Lett.* **2005**, *46*, 8229–8232; (c) Ollevier, T.; Lavie-Compin, G. *Tetrahedron Lett.* **2002**, *43*, 7891–7893.
7. Garrigues, B.; Gonzaga, F.; Robert, H.; Dubac, J. *J. Org. Chem.* **1997**, *62*, 4880–4882.
8. Wada, M.; Takeichi, E.; Matsumoto, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 990–994.
9. Sun, H.-B.; Hua, R.; Chen, S.; Yin, Y. *Adv. Synth. Catal.* **2006**, *348*, 1919–1925.
10. Répichet, S.; Le Roux, C.; Hernandez, P.; Dubac, J. *Tetrahedron Lett.* **1999**, *40*, 9233–9234.
11. Murty, M. S. R.; Ram, K. R.; Yadav, J. S. *Tetrahedron Lett.* **2008**, *49*, 1141–1145.
12. (a) Hinkle, R. J.; Lian, Y.; Litvinas, N. D.; Jenkins, A. T.; Burnette, D. C. *Tetrahedron* **2005**, *61*, 11679–11685; (b) Lian, Y.; Hinkle, R. J. *J. Org. Chem.* **2006**, *71*, 7071–7074.
13. Sun, H.-B.; Hua, R.; Chen, S.; Yin, Y. *Eur. J. Org. Chem.* **2006**, 4231–4236.
14. Bismuth(III) halides have also been implicated as catalysts in the reductive alkylation of silyl ethers, but subsequent experiments showed BiX_3 to be a precursor to the actual catalyst, triethylsilyl halide. Bajwa, J. S.; Jiang, X.; Slade, J.; Prasad, K.; Repič, O.; Blacklock, T. J. *Tetrahedron Lett.* **2002**, *43*, 6709–6713.
15. Laurent-Robert, H.; Gaspard-Iloughmare, H.; Dubac, J. *Synlett* **2000**, 1160–1162.
16. (a) Keramane, E. M.; Boyer, B.; Roque, J.-P. *Tetrahedron* **2001**, *57*, 1909–1916; (b) Keramane, E. M.; Boyer, B.; Roque, J.-P. *Tetrahedron* **2001**, *57*, 1917–1921.
17. Boyer, B.; Keramane, E. M.; Arpin, S.; Montéro, J.-L.; Roque, J.-P. *Tetrahedron* **1999**, *55*, 1971–1976.
18. (a) Toke, O.; Hargittai, M. *Struct. Chem.* **1995**, *6*, 127–130; (b) Haaland, A.; Hougen, J.; Samdal, S.; Tremmel, J. *Acta. Chem. Scand.* **1988**, *A42*, 409–412; (c) Schultz, G.; Kolonits, M.; Hargittai, M. *Struct. Chem.* **1999**, *10*, 321–325; (d) Molnar, J.; Kolonits, M.; Hargittai, M.; Konings, R. J. M.; Booij, A. S. *Inorg. Chem.* **1996**, *35*, 7639–7642.
19. Eveland, J. R.; Whitmire, K. H. *Inorg. Chim. Acta* **1996**, *249*, 41–46.
20. Rogers, R. D.; Bond, A. H.; Aguinaga, S.; Reyes, A. *J. Am. Chem. Soc.* **1992**, *114*, 2967–2977.
21. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02*; Gaussian: Wallingford, CT, 2004.
22. Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664–675.
23. Virko, S.; Petrenko, T.; Yaremko, A.; Wysokinski, R.; Michalska, D. *J. Mol. Struct. (THEOCHEM)* **2002**, *582*, 137–142.
24. Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284–298.
25. Dunning, T. H. *J. Chem. Phys.* **1971**, *55*, 716–723.
26. Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823–2833.
27. Cioslowski, J. *J. Am. Chem. Soc.* **1989**, *111*, 8333–8336.
28. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.
29. Breidung, J.; Theil, W. *J. Comput. Chem.* **1992**, *13*, 165–176.
30. Schwerdtfeger, P.; Hunt, P. In *Advances in Molecular Structure Research*; Hargittai, M., Hargittai, I., Eds.; JAI: Stamford, CT, 1995; Vol. 5, pp 223–262.
31. Atanasov, M.; Reinen, D. *J. Phys. Chem.* **2001**, *105*, 5450–5467.
32. Nyburg, S. C.; Ozin, G. A.; Szymanski, J. T. *Acta Crystallogr.* **1971**, *B27*, 2298–2304.
33. von Benda, H. *Z. Kristallogr.* **1980**, *151*, 271–285.
34. Trotter, J.; Zobel, T. *Z. Kristallogr.* **1966**, *123*, 67–72.
35. Lange, K. C. H.; Klaptoke, T. M. *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; J. Wiley: New York, NY, 1994; p 315.
36. Pyykko, P. *Chem. Rev.* **1988**, *88*, 563–594.
37. Pearson, R. G. *Chemical Hardness*; John Wiley-VCH: Weinheim, 1997.
38. (a) Cubicciotti, D. *J. Phys. Chem.* **1967**, *71*, 3066–3068; (b) Cubicciotti, D. *Inorg. Chem.* **1968**, *7*, 208–211; (c) Cubicciotti, D. *Inorg. Chem.* **1968**, *7*, 211–213.
39. Balawender, R.; Komorowski, L. *J. Chem. Phys.* **1998**, *109*, 5203–5211.
40. (a) Prakash, G. K. S.; Mathew, T.; Marinez, E. R.; Esteves, P. M.; Rasul, G.; Olah, G. A. *J. Org. Chem.* **2006**, *71*, 3952–3958; (b) The C–O bond distance for the $CF_3CH_2OH \cdot BF_3$ complex reported in (a) at the B3LYP/6–31g* level is 1.431 Å. The C–O distance for the uncomplexed alcohol is 1.407 Å;. NB: the Δd(C–O) value is larger than the bismuth complexes because the BF_3 is a harder Lewis acid.
41. Minsker, K. S.; Babkin, V. A.; Zaikov, G. E. *Int. J. Polym. Mater.* **1995**, *28*, 77–81.
42. Smith, M. B.; March, J. *March's Advanced Organic Chemistry*, 6th ed.; Wiley: New York, NY, 2007.
43. Cunha, S.; Rodrigues, M. T. *Tetrahedron Lett.* **2006**, *47*, 6955–6956.