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$BF_3{\cdot}2CF_3CH_2OH$ ($BF_3{\cdot}2TFE$), an Efficient Superacidic Catalyst for Some Organic Synthetic Transformations

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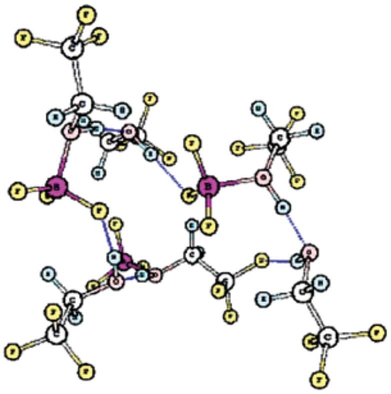

$(BF_3.2TFE)_3$

$BF_3{\cdot}2CF_3CH_2OH$ complex was found to be a very effective superacidic catalyst comparable in acid strength to at least that of 100% anhydrous sulfuric acid for various acid-catalyzed organic transformations such as isomerizations, rearrangements, ionic hydrogenation of various ketones, and aromatics with triethylsilane and nitration of aromatics with metal nitrate. Studies of the pivalaldehyde−methyl isopropyl ketone rearrangement and the benzopinacol to phenanthrene transformation suggest that the complex has an acidity comparable to that of 100% anhydrous sulfuric acid. The structure and properties of the 1:2 boron trifluoride−trifluoroethanol complex have been further studied using NMR (^1H, ^{13}C, ^{19}F, ^{11}B) and DFT calculations at the B3LYP/6-311++G**//B3LYP/6-31G* level.

Introduction

BF_3 has received wide application as a Lewis acid catalyst in a variety of acid-catalyzed reactions. Starting with Meerwein's pioneering work, its remarkable propensity to form coordination compounds with a variety of inorganic and organic bases were also explored.[1] Unlike other boron trihalides, boron trifluoride does not undergo hydrolysis with water under usual conditions to boric acid and hydrofluoric acid.[2−4] Meerwein and collaborators[5,6] found that BF_3 combines with water to form both a monohydrate and a dihydrate.

With organic compounds containing oxygen atoms as n-donors (Lewis bases), boron trifluoride in general forms coordination compounds of 1:1 or 1:2 compositions.[1] With ethers and esters, boron trifluoride forms 1:1 coordination

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complexes. With simple aliphatic ethers, the complexes are stable liquids, which even can be distilled without decomposition. For example, the coordination complexes of BF_3 with dimethyl and diethyl ethers have boiling points of 126.6 and 125.7 °C, respectively, at atmospheric pressure. However, their electrical conductivity is significantly lower than the conductivity of the coordination compounds of boron trifluoride with compounds containing hydroxyl groups.

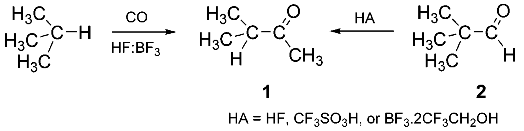
Boron trifluoride forms stable adducts of two types with alcohols: BF_3•ROH and BF_3•2ROH.[7] All of the adducts exhibit strong acidity and show good electrical conductivity but are weaker than boron trifluoride hydrates.[1] Similar to boron trifluoride monohydrate, complexes of the type BF_3•ROH are less stable and cannot be distilled without dehydration or decomposition. However, the complexes BF_3•2ROH are stable and can be distilled under vacuum.

Since fluorine is the most electronegative element, by replacing hydrogen with fluorine the acidity of alcohols can be increased. Due to the strong electron-withdrawing inductive effect of a trifluoromethyl group, the pK_a of 2,2,2-trifluoroethanol (CF_3CH_2OH) is 12.4, thus considerably more acidic[8a] than both methanol ($pK_a = 15.2$) and ethanol ($pK_a = 15.9$).[8b,c] Therefore, we anticipated that the coordination complex of BF_3 with trifluoroethanol would exhibit both increased acidity and higher catalytic activity than the BF_3 complexes of water, alcohols, and others. Herein, we report the preparation and properties of 1:2 complex of BF_3 and 2,2,2-trifluoroethanol and its successful use as a strong acid catalyst in a wide variety of organic transformations.

Results and Discussion

Comparison of Boron Trifluoride−Trifluoroethanol Complex with Boron Trifluoride Hydrates. Physical as well as chemical properties of boron trifluoride monohydrate and dihydrate have been extensively studied. Boron trifluoride dihydrate, BF_3•$2H_2O$, is a colorless liquid that melts at 5.9−6.0 °C with a boiling point of 58.5−60 °C and has a density of 1.65 g/mL.[1,9] It does not etch glass or shows indication of formation of free HF. However, BF_3•H_2O is a less stable colorless liquid that melts at 6.2 °C with a density of 1.80 g/mL. The monohydrate fumes strongly in air and loses boron trifluoride readily when warmed above room temperature. Neither complexes are ionized as solids, but they are highly ionized in the liquid state.[9] The dihydrate exists in the liquid state predominantly in the hydronium ionic form, $[H_3O]^+$, and has a Hammett acidity of $H_o = -6.85$ which is similar to that of 100% nitric acid.[2,3] The monohydrate has a Hammett acidity of $H_o = -11.4$ close to that of 100% anhydrous sulfuric acid ($H_o \approx -12.0$). Boron trifluoride monohydrate was reported to be an efficient acid catalyst in a variety of organic transformations. Some of the well-known examples are oligomerization of 1-alkenes for the manufacture of lubricating oils,[10] alkylation of aromatics with alkenes,[11−15] the Koch−Haaf carbonylation of alkenes or alcohols to carboxylic acids,[16−18] and in the Ritter reaction of alkenes to formamides.[19] Recently, we found that *N*-halosuccinimides in boron trifluoride monohydrate can act as efficient halogenating systems for deactivated aromatics.[20]

SCHEME 1



HA = HF, CF_3SO_3H, or $BF_3.2CF_3CH_2OH$

We found that the BF_3•$2CF_3CH_2OH$ complex could be easily prepared by passing BF_3 into ice-cooled 2,2,2-trifluoroethanol. Since the formation of the complex is highly exothermic, continuous cooling is required. Preparation of the complex can also be carried out by cooling the container in an acetone/dry ice bath. However, precautions have to be taken to avoid freezing (when freezing starts, the frozen complex was taken out from the cooling bath and slowly warmed to ensure melting). The introduction of BF_3 was continued until no further weight increase was observed. The complex has the stoichiometry of BF_3•$2CF_3CH_2OH$ and is a colorless, highly hygroscopic liquid with a density of 1.62 g/mL (since it loses some BF_3 above room temperature, its atmospheric boiling point could not be determined). Similar to other BF_3−alcohol complexes, the ionic form is suggested to be $(CF_3CH_2OH_2)^+(BF_3OCH_2CF_3)^-$ though the structure is not as yet as clearly determined as other BF_3 complexes.[9] It shows high acidity and catalytic activity indicative of a new strong acid system. The OH proton in the proton NMR of the complex is shifted to downfield by 5 ppm showing effective BF_3 complexation making it more acidic. We report the results of a variety of organic transformations using this complex as an effective and a convenient catalyst.

BF_3•$2CF_3CH_2OH$-Catalyzed Synthetic Transformations. (a) Isomerization of Pivalaldehyde to Methyl Isopropyl Ketone. The BF_3•$2CF_3CH_2OH$ complex has been investigated as an acid catalyst in a variety of acid-catalyzed organic transformations. Acid-catalyzed isomerization of epoxides to aldehydes and ketones has been well studied.[21,22] When the isomerization of styrene oxide to phenyl acetaldehyde was attempted with the BF_3•$2CF_3CH_2OH$ complex, the reaction was found to be highly exothermic and generated a mixture of products due to aldol condensation. However, during our studies of various methods for the synthesis of methyl isopropyl ketone **1** (Scheme 1)**,** we found that the pivalaldehyde−methyl isopropyl ketone rearrangement proceeded quantitatively with

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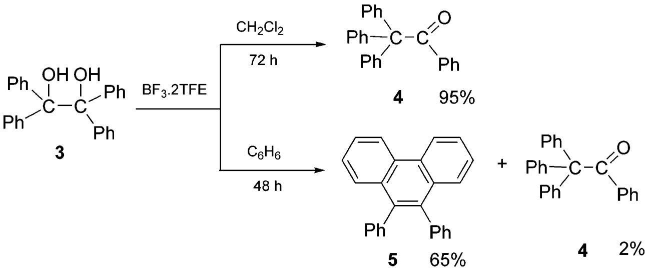
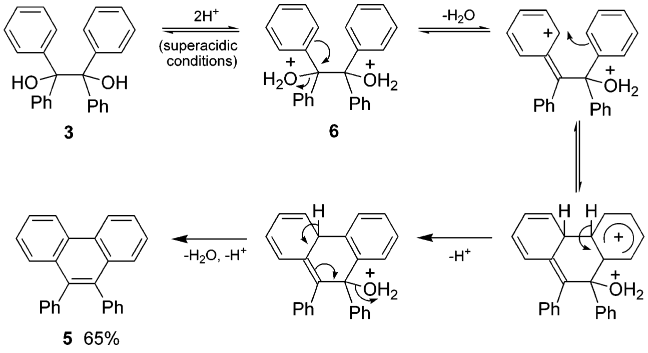
SCHEME 2



SCHEME 3. Mechanism for Phenanthrene Formation

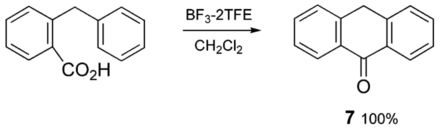


BF_3•$2CF_3CH_2OH$ complex. Since the quantitative rearrangement of pivalaldehyde **2** to methyl isopropyl ketone **1** requires high acidity (optimized at $H_o = -11.3$),[23,24] this indicates that the acidity of the complex is comparably high.

(b) Pinacol−Pinacolone Rearrangement. Pinacol rearrangement was also studied in the presence of BF_3•$2CF_3CH_2OH$. It was found that the products were highly dependent upon the solvent used in the reaction. In dichloromethane, benzopinacol (**3**) afforded benzopinacolone (**4**) in 95% yield. However, in benzene, the major product was 9,10-diphenylphenanthrene (**5**, 65%) along with 2% benzopinacolone (**4**) as shown in Scheme 2.

Recently Olah, Klumpp, et al. have described the preparation of substituted phenanthrenes from aryl pinacols catalyzed by trifluoromethanesulfonic acid in excellent yields.[25] A mechanism was suggested for the formation of phenanthrenes **5** involving the formation of a protosolvated dicationic intermediate **6** from pinacol **3** followed by electrophilic cyclization (Scheme 3). It is known that with weaker sulfuric acid, the rearrangement of benzopinacol **3** produces quantitatively only benzopinacolone **4**, which suggests that superacidity is required for phenanthrene formation. Involvement of possible superelectrophilic activation of electrophiles by protosolvation in superacid-catalyzed reactions was suggested.[26] This could explain the mechanistic pathways for the observed formation of varied products in a wide variety of superacid catalyzed reactions recently studied.[27,28]

SCHEME 4



BF_3•$2CF_3CH_2OH$ is partially soluble in dichloromethane but remains biphasic in benzene. A possible explanation for the formation of benzopinacolone **4** in dichloromethane is that the catalyst is highly diluted due to its partial dissolution, preventing the formation of dicationic intermediate **6** in dichloromethane and thus the rearrangement to benzopinacolone is preferred. Since the catalyst is immiscible with benzene, benzopinacol is highly ionized in the strongly acidic phase resulting in the formation of a highly energetic dicationic intermediate **6** which produces 9,10-diphenylphenanthrene. These results further indicate superacidic nature of the catalyst. On the other hand, when the Fries rearrangement of phenyl acetate was attempted with BF_3•$2CF_3CH_2OH$ the major product was found to be phenol (ester hydrolysis product) with hydroxyacetophenone only as a minor product (<5%). The system is thus not acidic enough to effect the Fries rearrangement at room temperature.

(c) Friedel−Crafts Acylation. Friedel−Crafts acylation reactions were also explored using the BF_3•$2CF_3CH_2OH$ catalyst. Treatment of 2-phenylmethylbenzoic acid (α-phenyl-*o*-toluic acid) gave anthrone (**7**) in quantitative yield through intramolecular Friedel−Crafts acylation (Scheme 4). However, 2-(2-phenylethyl)benzoic acid did not give the expected product, dibenzocycloheptadienone (10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one);, instead, the corresponding ester of trifluoroethanol, trifluoroethyl-2-(2-phenylethyl)benzoate, was obtained. This shows that in the latter the rate of Friedel−Crafts acylation is very slow compared to the esterification by trifluoroethanol. Formation of anthrone (**7**) from 2-phenylmethylbenzoic acid indicates that intramolecular acylation is kinetically more favorable for the formation of the six-membered ring than esterification.

Attempted intermolecular acylation reactions did not give the desired acylated products. During attempted acetylation of benzene with acetic anhydride or acetyl chloride at 0 °C, no acetophenone was observed. Similarly, no methylbenzophenones were formed during attempted benzoylation of toluene with benzoyl chloride. Instead, the product obtained was 2,2,2-trifluoroethylbenzoate in quantitative yield. Based on these observations, it is possible that during the Fries rearrangement of phenyl acetate the intermediate acetyl cation esterified trifluoroethanol to 2,2,2-trifluoroethyl acetate instead of acetylating phenol.

(d) Ionic Hydrogenation of Ketones and Polycyclic Aromatics. Larsen and Chang have described the deuteration of activated aromatics and polycyclic aromatics via a deuteration−deprotonation sequence using BF_3•D_2O.[29] They also found that BF_3•H_2O is an efficient acid catalyst in the ionic hydrogenation of polycyclic atromatics using triethylsilane as the hydride source.[30] Studies by Eckert−Maksic et al. showed that BF_3•H_2O/Et_3SiH system can be used for ionic hydrogenation of aromatic

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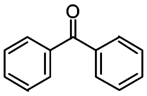
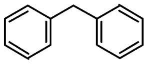
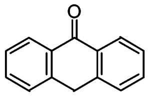
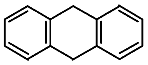
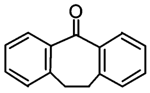
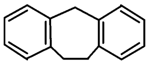
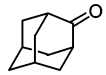
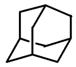
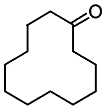
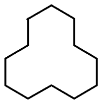
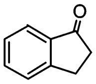
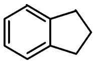
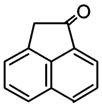
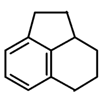
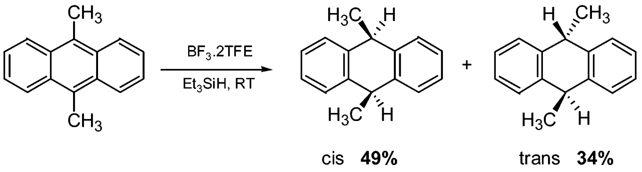
TABLE 1. Reduction of Ketones with Triethylsilane/$BF_3 \cdot 2TFE$

Entry	Ketone	Time (h)	Product	yield (%)
i		2		97
ii		2		78
iii		2		93
iv		3		97
v		2.5		92
vi		4		78
vii		4		82

organosulfur compounds and disubstituted naphthalenes.[31] Reduction of aldehydes and ketones, a crucial step encountered frequently in organic synthesis, has also been carried out by triethylsilane. Aryl ketones and aldehydes with electron-donating ring substituents give the completely deoxygenated products in high yields. However, with aliphatic aldehydes and ketones, the reduction generally stops after the transfer of one equivalent of hydride and a variety of products, including alcohols, esters, silyl ethers, and olefins were obtained depending upon the substrate and the reaction conditions. Due to the high catalytic activity of $BF_3 \cdot 2CF_3CH_2OH$, we studied the ionic hydrogenation with triethylsilane for the reduction of ketones with this catalyst. The reductions proceeded well giving the reduced products in good yields (Table 1). In the case of acenaphthenone (entry vii), not only the carbonyl function but also the aromatic ring closer to the carbonyl function underwent hydrogenation.

The $BF_3 \cdot 2TFE$ catalyst is not only effective for the reduction of aliphatic and aromatic ketones but also for some studied arenes. The yield of the products is significantly higher in comparison with the yield reported for reactions carried out in the presence of $BF_3 \cdot H_2O$. Reduction of 9,10-dimethylanthracene gave both *cis*- and *trans*-9,10-dimethyl-9,10-dihydroanthracenes (59:41) in 83% yield. Both isomers were separated by fractional crystallization. The less soluble *cis* isomer precipitates out first from the solution and was recrystallized from a mixture of hexane and CH_2Cl_2 (9:1). The *trans* isomer could be separated (with some amount of *cis* isomer) from the mother liquor by evaporation of the solvent.

Reduction of benz[*a*]anthracene and dibenz[*a*,*h*]anthracene gave mainly 7,12-dihydrobenz[*a*]anthracene and 7,14-dihydrodibenz[*a*,*h*]anthracene, respectively. Earlier studies by Harvey et al.[32] showed that reduction of anthracene, naphthacene, benz[*a*]anthracene and dibenz[*a*,*h*]anthracene with lithium in liquid ammonia under usual conditions proceeded exclusively in the meso region which was in agreement with Streitwieser's prediction based on molecular orbital calculations of the positions of highest electron density[33] (Table 2). Phenanthrene did not undergo reduction under these conditions.



(e) Nitration of Aromatics. A variety of nitrating agents are known for the nitration of aromatics. Nitric acid or its derivatives and metal nitrates with monodendate and bidendate nitrate ligands have been extensively studied as nitrating agents.[34] Though there are several reports on the use of inorganic nitrates in various acids such as trifluoroacetic acid, polyphosophoric acid, and sulfuric acid, the yields of the nitrated products were found to be low with deactivated aromatic systems.[35] Olah and co-workers reported a homogeneous nitration system using silver nitrate/boron trifluoride in acetonitrile solution.[36] Relatively electron-rich aromatics are nitrated by this system. Later, it has been found that nitration of aromatics with potassium nitrate or nitric acid catalyzed by boron trifluoride monohydrate proceeded with good to excellent yields even for some of the deactivated aromatic systems as well.[37] Since the boron trifluoride−trifluoroethanol complex exhibits the properties of a strong acid as evident from the reactions discussed, we have carried out the nitration of aromatics with potassium nitrate catalyzed by $BF_3 \cdot 2TFE$. In all cases, the catalyst was found to be very efficient and the reaction proceeded in good to excellent yields (Table 3).

DFT Calculations. Density functional theory (DFT) calculations were performed on the BF_3−TFE system in order to get a better understanding of its structure and properties. The structure of a cluster formed by three units of the complex $[CF_3CH_2OH]_2 \cdot BF_3$ was considered in these calculations in order to get an idea of the main interactions that occur within the liquid. A geometry optimization procedure for this system was performed at the B3LYP/6-31G* level. The vibrational analysis showed no imaginary frequencies. NMR chemical shifts calculations were performed at this geometry at the GIAO-B3LYP/6-311++G** level. Energy differences correspond to enthalpies at 298 K and 1 atm, computed at the B3LYP/6-311++G**//B3LYP/6-31G* level. All calculations were performed with the Gaussian 98 package.[38]

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TABLE 2. Reduction of Arenes with Triethylsilane/$BF_3 \cdot 2TFE$

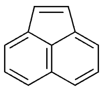
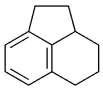
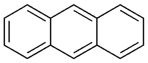
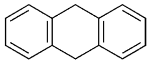
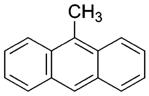
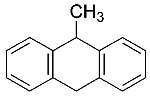
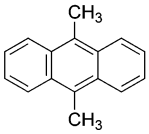
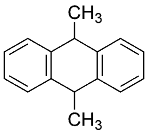
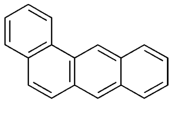
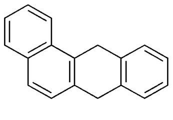
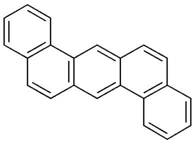
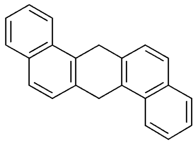
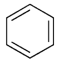
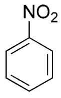
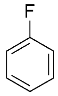
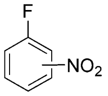
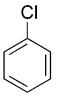
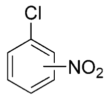
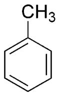
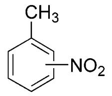
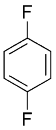
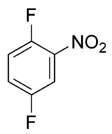
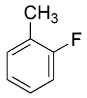
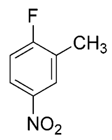
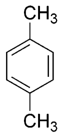
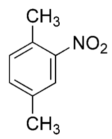
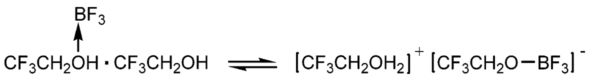
Entry	Arene	Time (h)	Product	yield (%)
i		4		93
ii		5		92
iii		4		90
iv		4		83
v		6		72
vi		5		65

TABLE 3. $BF_3 \cdot 2TFE$-Catalyzed Nitration of Aromatics with KNO_3

Entry	Arene	Time (h)	Product	yield (%)
i		6		82
ii		6	 *o:p 11:89*	88
iii		6	 *o:p 28:72*	87
iv		5	 *o:m:p 44:3:53*	90
v		6		84
vi		5		88
vii		4		92

DFT calculations indicate the complex formation involving bonding of BF_3 to the oxygen atom of CF_3CH_2OH and the prevalence of strong hydrogen bond between this complex with a second trifluorethanol (TFE) molecule. In a limiting case this could lead to complete transfer of the proton to trifluoroethanol in accordance with the equilibrium



$$\overset{BF_3}{\uparrow}CF_3CH_2OH \cdot CF_3CH_2OH \rightleftharpoons [CF_3CH_2OH_2]^+ [CF_3CH_2O{-}BF_3]^-$$

The acidic species can be considered to be the protonated TFE species ($CF_3CH_2OH_2^+$) or, more probably, the solvated $CF_3CH_2OH_2^+$. Experimental gas-phase proton affinity for its conjugated base, TFE, is 167.4 kcal/mol (obtained from the NIST database).[39] The DFT calculations indicate that the proton affinity for TFE is 164.7 kcal/mol, in agreement with the experimental value. This value is an indication of the acidity of the $[CF_3CH_2OH_2]^+$ species in the gas phase. The higher the proton affinity, the lower the ability of the protonated species (conjugate acid) to transfer the proton for another basic species. For comparison, we have tabulated the proton affinities (PA) of TFE and of other acids in Table 4.

TABLE 4. Experimental and Calculated (at B3LYP/6-311++G//B3LYP/6-31G* level) Gas-Phase Proton Affinities for Selected Acids[39]**

	gas-phase proton affinity (kcal/mol)	
acid	exptl	calcd
H_2SO_4	167.2	167.5
FSO_3H		153.4
CF_3SO_3H	167.2	164.6
HF	116	111.9
HCl	133.1	134.4
HBr	139.6	137.1
CF_3CH_2OH (TFE)	167.4	164.7
$(CF_3CH_2OH)_2 \cdot BF_3$		179.4
$[(CF_3CH_2OH)_2 \cdot BF_3]_3$		189.1

Comparing these results, one can see that the acidity of the protonated TFE in the gas phase is comparable to that of triflic acid or sulfuric acid. Since acidity also depends on solvation of the species, we compared some solvation effects. Thermodynamic properties for solvation of the protonated TFE by a second molecule was measured in the gas phase (Scheme 5). Experimental results indicate that the first solvating molecule

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(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

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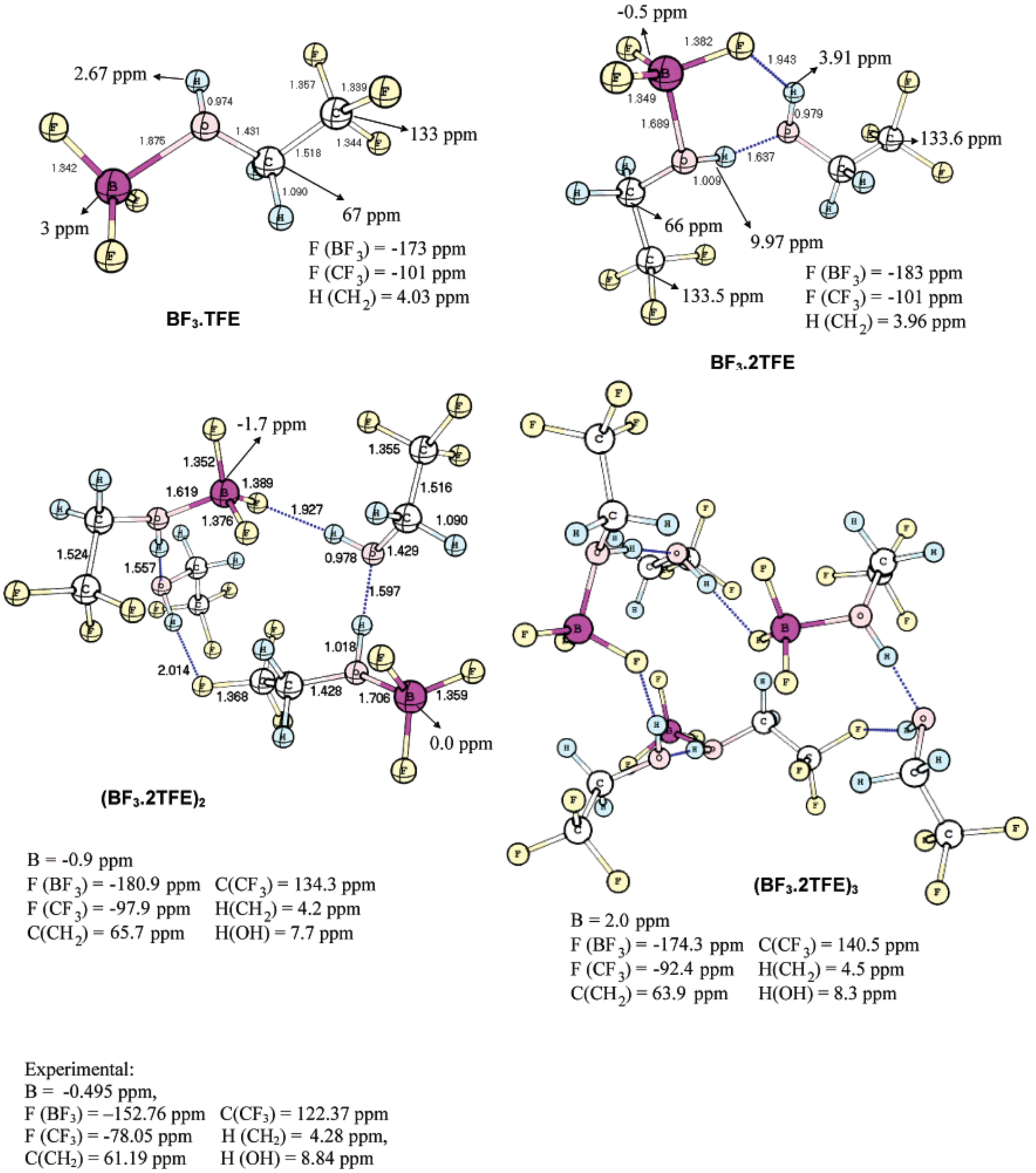

FIGURE 1. Geometries and NMR chemical shifts obtained for complexes BF_3·TFE, BF_3·2TFE and its dimer, $(BF_3$·$2TFE)_2$, and trimer, $(BF_3$·$2TFE)_3$, obtained after energy minimization procedures at the B3LYP/6-31G* level. Indicated chemical shifts refer to the GIAO-B3LYP/6-311++G**/B3LYP/6-31G* level (averaged values, when applicable). References for NMR chemical shifts calculations are BF_3·Et_2O (boron), $SiMe_4$ (carbon and hydrogen), and $CFCl_3$ (fluorine).

SCHEME 5

$$[CF_3CH_2OH_2]^+ + CF_3CH_2OH \longrightarrow CF_3CH_2OH\text{--}H^+\text{--}HOCH_2CF_3$$

$$\Delta H^o_{expt} = -31.8 \text{ kcal/mol};\ \Delta S^o_{expt} = -28.9 \text{ kcal/mol};\ \Delta G^o_{expt} = -23.2 \text{ kcal/mol}$$

stabilizes the system by 31.8 kcal/mol. Results of our DFT calculations for the same reaction give the ΔH value, −26.5 kcal/mol.

As expected, the deprotonation enthalpy for this solvated species is higher (ΔH = 187.6 kcal/mol), if compared with the isolated protonated molecule (ΔH = 164.7 kcal/mol).

The calculations on the 1:1 (BF_3·TFE) and 1:2 (BF_3·2TFE) complexes, considering the latter as a monomer (BF_3·2TFE), a dimer [$(BF_3$·$2TFE)_2$], and a trimer [$(BF_3$·$2TFE)_3$], aiming to give a better understanding of solvation effects, resulted in the structures shown in Figure 1. The structure that shows NMR chemical shifts in best agreement with the experimental values is the trimer. It is noteworthy that there is O- -H- -O and F- -H- -O hydrogen bonding involved in the structure. The hydrogen−fluorine bonding in the complex is especially interesting, suggesting that compounds that are more basic than coordinated BF_3 would potentially be protonated and undergo typical acid-catalyzed reactions as the ones presented in this paper. The calculated proton affinities for the monomer and trimer form are, respectively, 179.4 and 189.1 kcal/mol. These values, higher than the isolated TFE molecule, are compatible with the higher solvation experienced by the excess proton into these more complex systems. Calculated NMR chemical shifts (shown in

Figure 1) agree reasonably with the experimental chemical shifts obtained for the liquid systems. Gas-phase proton affinity data for the $CF_3CH_2OH_2^+$ (the conjugated acid of the TFE) and the calculations on the structure of the trimer suggest the acidity of $BF_3 \cdot 2CF_3CH_2OH$ is in the range between H_2SO_4 and triflic acid, thus being a moderate superacid. This is in agreement with its behavior in acid-catalyzed reactions presented here, which indicate that its acidity is about or higher than acid systems with H_o −11.3.

Conclusion

In conclusion, we have found that a 1:2 complex, $BF_3 \cdot 2CF_3CH_2OH$ ($BF_3 \cdot 2TFE$) formed from BF_3 and CF_3CH_2OH can act as an efficient superacidic catalyst for many organic synthetic transformations. Gas-phase proton affinity data for the $CF_3CH_2OH_2^+$ (the conjugated acid of the TFE) and the calculations on the structure of the trimer $(BF_3 \cdot 2TFE)_3$ suggest the acidity of $BF_3 \cdot 2TFE$ is in the range between H_2SO_4 and triflic acid, thus being a moderate superacid. This is in agreement with its behavior in acid-catalyzed reactions such as pivalaldehyde−methyl isopropyl ketone rearrangement and the benzopinacol to phenanthrene transformation now studied. We expect that $BF_3 \cdot 2TFE$ can serve as an efficient nonoxidizing strong Brønsted acid catalyst for many electrophilic reactions.

Experimental Section

Caution! BF_3 and BF_3 complexes are highly irritating and toxic and can cause severe damages to eyes, skin, and lungs. Precautions have to be taken (chemical safety goggles and rubber gloves) while handling them. Gas masks approved for acid gases or those with an independent supply of oxygen or air should be readily available in convenient locations in the event of an emergency.

Preparation of $BF_3 \cdot 2CF_3CH_2OH$. Freshly distilled 2,2,2-trifluoroethanol (100 g, 1.0 mol) was taken in a dry Nalgene bottle (500 mL), closed, and weighed. The cap of the nalgene bottle was replaced with a cap containing an inlet for the introduction of BF_3 and a safety outlet for the release of excess pressure. The bottle was cooled to 0 °C using an ice bath, and BF_3 was slowly bubbled into 2,2,2-trifluoroethanol with stirring and continuous cooling until the solution was saturated with BF_3 (no further weight increase was observed) and the excess BF_3 was released through the safety outlet. The bottle was closed and weighed again. The solution was found to be a 1:2 complex of BF_3 and 2,2,2-trifluoroethanol with 35 g (0.52 mol) of BF_3 incorporated. The complex was stored in the refrigerator for further use. ^1H NMR (300 MHz, $CDCl_3$ was used as the standard; NMR tube containing the complex was fitted with a capillary containing $CDCl_3$): δ 4.28 (q, 2H, $J_{H-F(\beta)} = 8.12$ Hz); 8.84 (s, 1H). ^{13}C NMR (75 MH_Z, $CDCl_3$ as standard): δ 61.19 (q, CH_2, $J_{C-C-F} = 38.15$ Hz), 122.37 (q, CF_3, $J_{C-F} = 276.50$ Hz). ^{19}F NMR (282.2 MHz, $CFCl_3$ as standard): δ −152.76 (BF_3), −78.05 (t, CF_3, $J_{F-H(\beta)} = 9.16$ Hz. ^{11}B NMR (96 MHz, BF_3−diethyl ether as standard): δ −0.495. Density: 1.62 g/mL.

Acknowledgment. This paper is dedicated to the loving memory of Professor C. P. Joshua, University of Kerala, India. Support of our work by the Loker Hydrocarbon Research Institute is gratefully acknowledged. P.M.E. acknowledges CNPq and FAPERJ (Brazil) for financial support.

Supporting Information Available: ^1H NMR, ^{13}C NMR, ^{19}F NMR, and ^{11}B NMR of $BF_3 \cdot 2TFE$ complex, ^1H NMR of products entries i−vii in Table 1, ^1H NMR of products entries i, ii, and iv−vi in Table 2, ^{13}C spectrum of entry iii in Table 2, ^1H NMR of products entries i−vii in Table 3, and Cartesian coordinates for structures of $TFE \cdot BF_3$, $(TFE)_2 \cdot BF_3$, $[(TFE)_2 \cdot BF_3]_2$, and $[(TFE)_2 \cdot BF_3]_3$ optimized at the B3LYP/6-31G* level. This material is available free of charge via the Internet at http://pubs.acs.org.

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