proven,[3] the absolute configuration of aphanastatin is that shown in **1**. Further evaluation of aphanastatin's antineoplastic properties is in progress.

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Relative Acidity of Superacids: $HF:SbF_5$ Compared with $HSO_3F:SbF_5$

Sir:

Following the pioneering work of Olah and his coworkers from the early sixties up to now, the superacid systems have been used for a variety of applications both in fundamental and applied chemistry.[1] The acidity of a number of superacids has been thoroughly investigated by Gillespie,[2] but the unavailability of weak-enough bases has limited these investigations to HSO_3F containing <11 mol % SbF_5[3] and in HF containing <0.5 mol % SbF_5.[4] With the latter system, a limited number of H_0 measurements showed that HF was weaker than HSO_3F at least in the 0–0.4% SbF_5 region. On the other hand, many experimental results suggested, either on the basis of kinetic measurements[5] or of mechanistic studies,[6,7] that the $HF:SbF_5$ system was by far the strongest and the following classification has been proposed:[5] 1:1 $HF:SbF_5$ > 9:1 $HF:SbF_5$ > 1:1 $HSO_3F:SbF_5$ > 5:1 $HSO_3F:SbF_5$ with the ratio of >500:1: 10^{-1}:10^{-5}. We have shown in a preceding communication[8] how ^1H DNMR and ^1H chemical shift measurements allowed us to evaluate the acidity of HSO_3F containing up to 25 mol % SbF_5, the acidity indicator being monoprotonated *p*-methoxybenzaldehyde ($pK_{BH^{2+}} = -19.5$).

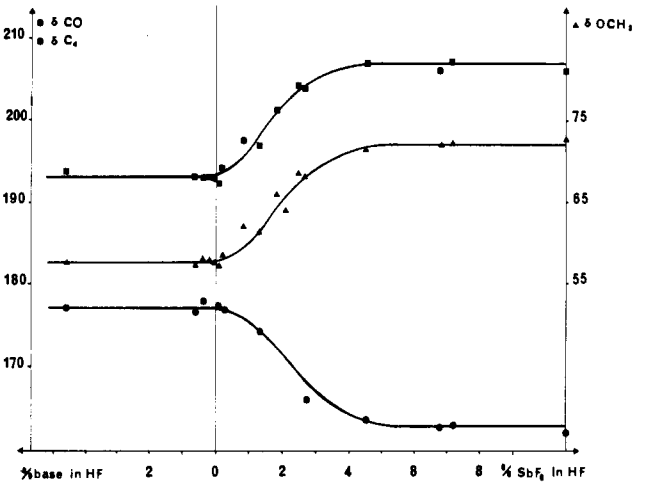
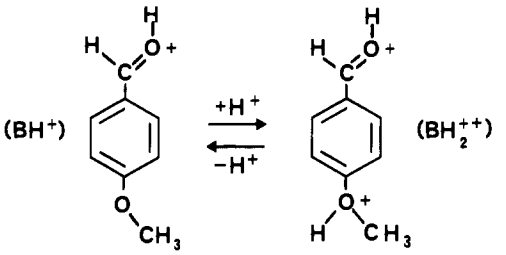


Figure 1. Characteristic chemical shift variation between the BH^+ and BH_2^{2+} forms of the indicator.

We wish now to report our results on the acidity measurement of the $HF:SbF_5$ system with the same indicator which allows us to compare directly the HF with the HSO_3F solvent system. With increasing acidity, the indicator changes from the BH^+ form (monoprotonated on the carbonyl oxygen) to the BH_2^{2+} form (second proton on the ether oxygen). The use



of ^1H NMR[9] was not convenient with the $HF:SbF_5$ system because (1) the $C{=}OH^+$ chemical shift is too much solvent dependent for a fair interpretation of the titration curve and (2) the HF solvent peak overlaps with the aromatic region in the "low" acidity mixtures (SbF_5 < 3%) preventing DNMR measurements. For this reason, we used FT $^{13}C\{^1H\}$ NMR, with the advantage that three characteristic ^{13}C chemical shifts, could be monitored simultaneously for the neutralization curve with an average chemical shift variation $|\Delta(\delta_{BH_2^{2+}} - \delta_{BH^+})|$ of 14 ppm (Figure 1). In protonated aromatic carbonyl compounds the carbonyl ^{13}C chemical shift is known to be very sensitive to the nature of the para substituent;[10] the 4 carbon bearing either the CH_3O- group or the $CH_3O^+(H)$- group and the methoxy carbon itself are the most sensitive to the second protonation. The 1 carbon is also shifted upfield as it correlates well with the σ^+ value of the para substituent.[11] The chemical shifts of BH^+ and BH_2^{2+} can be taken from the limiting values in "low" and high acidity and compared with those measured in the $HSO_3F:SbF_5$ solvent of known acidity as shown in Table I. One can see directly from Figure 1 that half-protonation, $(BH_2^{2+}/BH^+) = 1$, is achieved with ~2 mol % SbF_5 in HF, whereas >15 mol % were necessary in HSO_3F.[8] By measuring the ionization ratio from the neutralization curve and reporting the values in the Hammett equation $H_0 = pK_{BH_2^{2+}} - \log(BH_2^{2+}/BH^+)$ we can follow the acidity as a function of the SbF_5 content. The result is plotted (O) in Figure 2 and compared with earlier data from the literature. Actually we should not call this function an H_0 function as long as

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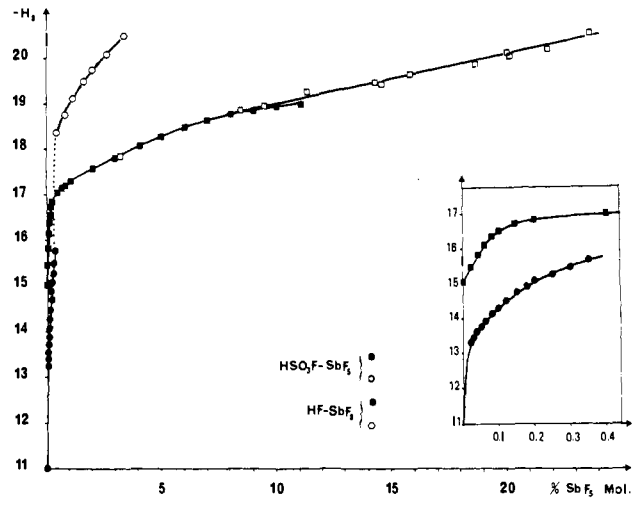

Figure 2. Relative acidities of the HF and the HSO_3F solvent on SbF_5 addition: ■ and ●, ref 3; insert on the right from ref 4; ○, this work; □, our previous work, ref 8.

Table I. ^{13}C Chemical Shifts at −30 °C[a] of Mono- and Diprotonated *p*-Methoxybenzaldehyde[b]

Solvent	C=O	C_4	C_1	CH_3O
HSO_3F	193.4	176.9	121.4	57.4
HF	193.8	177.2	121.9	57.4
HSO_3F:SbF_5 (1:1)	205.5	162.3	128.1	71.8
HF:SbF_5 (1:1)	207.2	162.2	127.9	72.0

[a] Owing to the relative instability of *p*-methoxybenzaldehyde in some of these media all ^{13}C NMR measurements have been carried out at −30 °C. [b] In parts per million from Me_4Si; external capillary with Me_4Si and C_3D_6O lock solvent.

protonated *p*-methoxybenzaldehyde has not been proven to behave like a Hammet base; nevertheless, as our results overlap and are complementary with Gillespie's results, this will not alter significantly the following conclusions. (1) HF:SbF_5 is weaker than HSO_3F:SbF_5 only when the SbF_5 content is below 0.6 mol %. The reason for this is that pure HF is a much weaker acid ($H_0 = -11$) than HSO_3F ($H_0 = -15$). (2) The acidity increase is much stronger in HF than in HSO_3F on SbF_5 addition as can be seen from the slopes on Figure 2. With 4 mol % SbF_5 the HF solvent is already 10^3 times more acidic than HSO_3F with the same SbF_5 concentration. To obtain the same acidity in HSO_3F, one has to add ~20 mol % SbF_5.

This is, to our view, a direct confirmation of the above statement on relative acidities[5] suggested by many indirect experimental data. Considering now the slope of the HF curve, the probable increase to much higher acidities on further SbF_5 addition is not a rash prediction.

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Insertion vs. Addition of Oligomeric Difluorosilylenes. Evidence for the Attack of Oligomeric Difluorosilylenes on the Carbon–Carbon Double Bond as an Initial Step in the Insertion Reactions with *trans*- and *cis*-Difluoroethylene

Sir:

When a comparison between the chemistry of silylenes and carbenes is attempted, as a number of review articles have done,[1-3] the failure to find any evidence for the existence of silacyclopropane in the reactions of SiF_2 with ethylene and fluoroethylenes has greatly confused our understanding of their mechanisms.

While insertion products are found to be the sole type of product in the case of fluoroethylenes,[4,5] the products in the reaction of ethylene are best interpreted as a result of addition.[4] It is generally accepted that in such cases reactions along two paths are likely to occur: SiF_2 attacking either a carbon–carbon double bond or a carbon–fluorine single bond. All identified addition products involve the dimeric unit $\cdot SiF_2SiF_2\cdot$ (and higher units in small yields);[6,7] on the other hand, monomeric SiF_2 has only been found in insertion products.[1,8] From a general mechanistic point of view for reactions with ethylene and fluoroethylenes, it would be hardly conceivable to accept the implication that monomeric SiF_2, being a unique member of the reactive homologue $\cdot(SiF_2)_n\cdot$, reacts only with carbon–fluorine single bonds.

We now report new results of the reactions of silicon difluoride with *trans*- and *cis*-difluoroethylene which provide evidence for the attack on carbon–carbon double bonds by $(SiF_2)_n$ ($n = 1, 2, \ldots$) as an initial step in the insertion reactions.

Silicon difluoride was generated and reacted with *trans*- and *cis*-difluoroethylene in the manner described previously.[9] Products were characterized by their mass, IR, and NMR spectra. The mass spectra clearly indicate that in both reactions 1:3 (difluoroethylene to SiF_2 ratio), 1:2, and small quantities of 1:1 products were formed. The structures of these products are unequivocally determined on the basis of their ^1H and ^{19}F NMR spectra. Some of the NMR parameters are shown in Table I. For all known compounds of insertion products, detailed NMR parameters of the 1:1 and 1:3 types have not been obtained before.

All products are "insertion" products; no silacyclopropanes or disilacyclobutanes are observed. The most interesting result is the fact that both reactions appear to be nonstereospecific. The relative abundances of the various isomers are shown in Table I. Since no trans–cis isomerization of the starting materials was observed, the only reasonable reaction path which leads to both trans and cis isomers in the products of each reaction is an initial attack of $(SiF_2)_n$ on the carbon–carbon double bond, followed by rearrangement. Margrave has proposed a silacyclopropane intermediate for the mechanism of monomeric SiF_2 insertion, which suggested that SiF_2 attacked the carbon–carbon double bond rather than a carbon–fluorine bond;[10] the present work is the first time any relevent evidence has been revealed. However, this evidence does not guarantee

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