

DOI:10.1002/ejic.201300031

The Al(OR^F)₃/H₂O/Phosphane [R^F = C(CF₃)₃] System – Protonation of Phosphanes and Absolute Brønsted Acidity

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Keywords: Acidity / Lewis acids / Frustrated Lewis pairs / Phosphanes / Arsanes / Weakly coordinating anions

The synthesis of the classical, neutral donor–acceptor adducts $Ph_2MeP-/Ph_3P-/Ph_3As-Al(OR^F)_3$ and $H_2O-Al(OR^F)_3$ [1, **2**, **3**, **4**, $OR^F = OC(CF_3)_3$] is reported. The intermediate $H_2O-Al(OR^F)_3$ (**4**) was generated by substitution of PhF in PhF– $Al(OR^F)_3$ with H_2O and was analyzed in a long-term NMR study over 22 days. This Brønsted acidic system was used in orienting experiments to protonate phosphanes such as $PMePh_2$, PPh_3 , PCy_3 , $P(tBu)_3$, and $PCy_2[2,4,6-(iPr)_3C_6H_2]$. Depending on the use of one or two equivalents of PhF–Al- $(OR^F)_3$, the new weakly coordinating anions $[(R^FO)_3Al(\mu-OH)Al(OR^F)_3]^-$ or $[HOAl(OR^F)_3]^-$ were obtained. However, in

Introduction

The importance of a controlled synthesis of alumoxanes and alumoxane hydroxides, which are used, for example, as catalysts for polymerization reactions, has inspired the interest of many research groups.^[1-4] As a completely waterfree environment is almost impossible to realize and sidereactions are often thermodynamically favored, the hydrolysis products cannot be neglected and change the Lewis acid reactivity in many cases.^[5] Thus, Roesky and others systematically analyzed the influence of water on group 13 organometallic compounds, for example.^[2] A special challenge still remains with the synthesis of neutral Lewis acid-base adducts of water and alanes. To the best of our knowledge, only a few neutral adducts with a 1:1 constitution can be cited here: H₂O-AlMes₃,^[6] H₂O-Al(C₆F₅)₃,^[7] H₂O-Al-(OSiPh₃)₃(THF)₂,^[8] H₂O-AlMe(OAr)₂(THF)₂ (-40 °C, THF = tetrahydrofuran),^[9] H_2O-AlX_3 (X = Br, Cl).^[10] Closely related to this type of adducts and intensively studied is the $H_2O-B(C_6F_5)_3$ system, for which a number of water complexes were also structurally characterized (see refs.^[11,12] and literature cited therein). For example, H₂O- $B(C_6F_5)_3$ was used to generate $[M(\eta - C_5H_5)_2]^+$ (M = Cr, Fe, Co),^[11] an In-based triple-decker sandwich complex, or Irdependence of the steric bulk of the phosphanes, stable and unreactive R_3P -Al(OR^F)₃ adducts were also observed in the NMR experiments. The absolute acidity of the key H_2O -Al(OR^F)₃ adduct was evaluated by the relaxed COSMO cluster-continuum (rCCC, COSMO = conductor-like screening model) model in fluorobenzene solution. For a 0.001 M solution of H_2O -Al(OR^F)₃, the medium acidity resulted as -986 kJ mol⁻¹ or a pH_{abs} value of 173. Long-term hydrolysis of H_2O -Al(OR^F)₃ (4), probably to give HOR^F and HOAl-(OR^F)₂ followed by trimerization, gave [HOAl(OR^F)₂]₃ (10), which was identified by X-ray diffraction.

based cationic complexes stabilized by $[(C_6F_5)_3B(\mu-OH)B-(C_6F_5)_3]^{-[13]}$ or $[(C_6F_5)_3BOH\cdots H_2O-B(C_6F_5)_3]^{-[14,15]}$ This system and other donor-acceptor complexes were also studied theoretically by Timoshkin and Frenking.^[5] In these complexes, the Brønsted acidity of H₂O is significantly increased owing to the complexed Lewis acid. Thus, a stronger Lewis acid should further increase the proton acidity. The use of one of the strongest monomeric Lewis superacids, Al(OR^F)₃,^[16,17] should result in one of the highest available Brønsted acidities.

Our route into this topic was indirect. We were inspired by the recent work of Stephan and Erker dealing with the activation of small molecules such as H₂, CO₂, and olefins,^[18-21] and we were interested to test the monomeric Lewis superacid Al(OR^F)₃ [OR^F = OC(CF₃)₃] for FLP-like (FLP = frustrated Lewis pair) chemistry. Closely related FLP systems containing phosphanes and boranes had already been investigated theoretically and experimentally.^[22-24] The great advantage of phosphane bases is the huge variety of available compounds. Also, the mixtures are easy to investigate by NMR spectroscopy. Thus, 1:1 mixtures of various phosphanes and PhF-Al(OR^F)₃ under 1 atm H₂ were analyzed. In all tested reactions, no H₂ activation could be realized. Instead, mainly adduct formation was observed with the sterically less demanding phosphanes such as PPh₃.^[25] Nevertheless, in many reactions protonated phosphonium ions were detected as side-products by NMR spectroscopy. After solving the X-ray structure of a crystalline material that included a protonated $[HPR_3]^+$ phosphonium cation partnered with a new hydroxo aluminate



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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201300031



[HO(Al(OR^F)₃)₂]⁻, it was clear to us that traces of water were present in the reaction mixtures. After determination of the H₂O content of the solvent as 9 ppm by Karl Fischer titration, we systematically studied the influence of water on the phosphane/Al(OR^F)₃ system. Therefore, in initial experiments we protonated phosphanes with intentionally formed H₂O–Al(OR^F)₃ (4). We observed the formation of the two new weakly coordinating anions [HOAl(OR^F)₃]⁻ and [(^FRO)₃Al(μ -OH)Al(OR^F)₃]⁻, which are isostructural to the B(C₆F₅)₃ analogs.^[11,13,15] The formation and hydrolysis of 4 was monitored by NMR experiments. In one of these reactions, the trimerization product [HOAl(OR^F)₂]₃ (10) was characterized by single-crystal X-ray crystallography.

Results and Discussion

The general route to the donor–acceptor systems follows Equation (1). With PMePh₂, PPh₃, and AsPh₃, stable adduct formation was directly observed; the three adducts **1**–**3** were characterized by NMR spectroscopy and single-crystal X-ray crystallography. Furthermore, their calculated dissociation enthalpies of +92, +77, and +60 kJ mol⁻¹ underline the strong Lewis acidity of Al(OR^F)₃ [$\Delta_r H^{o}_{(g)}$, (RI-)BP86/def-TZVP,^[26–31] 298 K, Equation (1)]. As expected for donor ligands, the phosphanes and the arsane aremorestronglycoordinated than the weak bases PhF and SO₂ (–23 and –49 kJ mol⁻¹).

As/PR₃ + Al(OR^F)₃
$$\xrightarrow{\Delta_{\Gamma}H^{\circ}(g)}$$
 R₃As/P-Al(OR^F)₃
PMePh₂ -92 **1**
PPh₃ -77 kJ mol⁻¹ **2**
AsPh₃ -60 **3** (1)

To learn more about the stability of $Al(OR^F)_3$ in the presence of water, we performed an NMR study of 4 in monofluorobenzene, which revealed the unexpected stability of adduct 4. Thus, we dissolved $PhF-Al(OR^{F})_{3}$ in PhF that contained 173 ppm of H₂O as measured by a Karl Fischer titration. In agreement with the hard σ -donor properties of H₂O and the oxophilicity of aluminum, H₂O substituted the weak ligand PhF in the Lewis superacid PhF-Al(OR^F)₃. In NMR spectra of directly prepared 4, as well as in spectra recorded previously of other systems, we observed a sharp singlet at $\delta \approx 6$ ppm, which showed no crosspeaks in an ¹H-¹³C HMBC or ¹H-¹³C heteronuclear single quantum coherence (HSQC) spectra. Thus, we suggest that this signal belongs to a proton bound to a heteroatom. ¹H NMR spectra of the moist PhF solution were recorded directly, and after two, five, 30, and 45 h and 22 days (Figure 1 and Supporting Information). Here, also no crosspeaks in the HMBC and HSOC spectra were detected. Thus, we assigned the main signal in the ¹H NMR spectra at $\delta = 6.03$ ppm to the hydrogen atoms of complexed H₂O. This ¹H NMR signal of H₂O is significantly downfield shifted by 4.9 ppm in comparison to that of free water in PhF (δ = 1.13 ppm). The low-intensity signal at δ = 3.57 ppm (Figure 1) resulted from the free alcohol HOC(CF₃)₃. The intensity of the alcohol signal increased over time, as expected for the slow hydrolysis of Al(OR^F)₃; the signal at δ = 6.03 ppm decreased accordingly. The same tendencies were observed in the ¹⁹F NMR spectra. Further support for our assignment gives the well fitting, DFT-calculated ¹H NMR chemical shift of 4 of δ = 6.32 ppm [(RI-)BP86/def2-TZVPP,^[32,33] reference system H₂O in PhF at δ = 1.13 ppm].



Figure 1. ¹H NMR spectra (400.17 MHz, 298 K, PhF) of **4** measured directly and after 22 days. Spectra were calibrated to the ¹H signal of the *o*-hydrogen atoms of PhF at δ = 7.14 ppm. The signal at δ = 5.39 ppm is so far unidentified.

Protonation of Phosphanes

Sterically demanding phosphanes such as $PCy_2(2,4,6-(iPr)_3C_6H_2)$, PCy_3 , and $P(tBu)_3$ [Tolman cone^[34] angles: $P(tBu)_3$ 182°,^[35] PCy_3 170°^[35]] as well as less crowded ones such as PPh₃ and PMePh₂ (PPh₃ 145°,^[34,35] PMePh₂ 136°^[34,35]) were (partially) protonated with the H₂O/PhF/Al(OR^F)₃ mixture (Table 1) in NMR tube reactions. Depending on the use of one or two equivalents of PhF–Al(OR^F)₃, the terminal hydroxide [HOAl(OR^F)₃]⁻ or the bridged [(^FRO)₃Al(μ -OH)Al(OR^F)₃]⁻ anion formed. The calculated reaction enthalpies agree with the experimental observations. The formation of the hydroxo-bridged anion is more favored at the (RI-)BP86/def-TZVP level (Table 1); values in italics were calculated by using Grimme's D3^[36,37]

Table 1. COSMO-solvated computed Gibbs energies $[kJmol^{-1}]$ for the protonation of phosphanes $[(RI-)BP86/def-TZVP level; \varepsilon_r(PhF) = 5.42]$. Values in italics were calculated by including Grimme's D3 dispersion correction.

 $PR_{3} + H_{2}O-Al(OR^{F})_{3} \frac{n Al(OR^{F})_{3}}{n = 0, 1} [R_{3}PH]^{+} + [HO(Al(OR^{F})_{3})_{1+n}]^{-}$

PR ₃	Compound	$\Delta_{\rm r} G^{\rm o}{}_{\rm (solv)}$ $n = 0$		1	
PMePh ₂	5	11	14	-54	-118
PPh ₃	6	18	21	-47	-111
PCy ₃	7	-44	-40	-108	-172
$P(tBu)_3$	8	-42	-42	-106	-174
$PCy_2[2,4,6-(iPr)_3C_6H_2]$	9	-20	-22	-85	-154



calculated with the conductor-like screening model $(COSMO)^{[38,39]}$ by using $\varepsilon_r(PhF) = 5.42$.^[40]

However, the reaction mixtures always showed several byproducts in the NMR spectra. In particular, the formation of competing adducts was observed for phosphanes such as PPh₃ or PMePh₂ with smaller Tolman cone angle.

All experimental observations are closely related to the known equilibrium behavior of $H_2O-B(C_6F_5)_3$.^[15] They are in good agreement with the theoretically predicted adduct stabilities of the weak donor–acceptor adducts of $B(C_6F_5)_3$ and $Al(C_6F_5)_3$: thus, the gas phase energy for the formation of $H_2O-Al(OR^F)_3$ of -94 kJ mol^{-1} is in the same order of magnitude as that of $H_2O-Al(C_6F_5)_3$ (-112 kJ mol^{-1}) and, as expected, is higher than that of $H_2O-B(C_6F_5)_3$ [-37 kJ mol^{-1} , all calculated at the (RI-)BP86/def2-TZVPP level].^[5,41] In analogy to the exothermic formation of [(C_6F_5)_3X(μ -OH)X(C_6F_5)_3]⁻ {X = Al -199, B -63 kJ mol}^{-1}, (RI-)BP86/def2-TZVPP},^[5] the formation of [(FRO)_3Al(μ -OH)Al(OR^F)_3]⁻ is also thermodynamically favored by a similar amount [-144 kJ mol^{-1} , Equation (2)].

$$[\text{HOAI}(\text{OR}^{\text{F}})_{3}]^{-} + \text{AI}(\text{OR}^{\text{F}})_{3} \quad \frac{\Delta_{\text{F}} \mathcal{H}^{\circ}(\textbf{g})}{-144} [(^{\text{F}}\text{RO})_{3}\text{AI}(\mu-\text{OH})\text{AI}(\text{OR}^{\text{F}})_{3}]^{-}$$
(2)

In a further attempt to crystallize compound **4**, we isolated crystals of the hydrolyzed product $[HOAl(OR^F)_2]_3$ (**10**), which probably resulted from trimerization of the primary hydrolysis product HOAl(OR^F)₂. This is supported by quantum chemical calculations and the similar behavior of HOB(C₆F₅)₂ (Figure 2).^[42]



Figure 2. Hypothetic hydrolysis pathway leading to **10**, and the calculated energies ($\Delta_r G^{\circ}_{(solv)}$) at the (RI-)BP86/def-TZVP level at 298 K, COSMO model ε_r (PhF) = 5.42;^[40] values are given in kJ mol⁻¹, values in *italics* include Grimme's D3 dispersion correction.

NMR Spectroscopy

The NMR spectra of adducts **1** and **2** are as expected and will only be discussed briefly. The ¹⁹F NMR signals at $\delta = -75.4$ and -74.3 ppm as well as the broad ²⁷Al NMR signals at $\delta = 43.9$ and 41.4 ppm are typical for strongly bound Al(OR^F)₃ complexes.^[16] The line-width of the ²⁷Al signal is too broad to show splitting by the P–Al coupling. The ³¹P NMR spectra showed a broad signal at $\delta =$ -26.6 ppm for **1** (cf. free PMePh₂^[43] in THF: -26.1 ppm, in CD₂Cl₂: -27.2 ppm) and a broad signal with two maxima at the borders at $\delta = -11.1$ ppm for **2** (cf. free PPh₃: -6.0 ppm).^[44] The ³¹P NMR chemical shifts are in the same range as those observed for similar Al/B-P complexes $[MePh_2P-BBr_3 \delta(^{31}P) = -9.2,^{[43]} MePh_2P-AlMe_3 \delta(^{31}P) =$ -24.2,^[45] Ph₃P-AlMe₃ δ (³¹P) = -7.3 ppm].^[45] For **2**, the distance between the two maxima in the ³¹P NMR spectra did not change at different magnetic field strengths. This characteristic shape of the ³¹P NMR signal results from P-Al coupling. This proves that the phosphane is covalently bound to the Lewis acid. The complex formation and stability in solution could finally be proven with a ¹H–¹⁹F heteronuclear Overhauser effect spectroscopy (HOESY) experiment (see Supporting Information). The NMR spectroscopic data of 3 in 1,2-F₂C₆H₄ are listed in the Exp. Sect., but the proton chemical shifts can only be assigned to a range of signals. However, NMR measurements of 3 in CD₂Cl₂ solution showed the formation of another compound that is probably $[Ph_3As-CD_2Cl]^+[ClAl(OR^F)_3]^-$. Dissociation of 3 to the weak base AsPh₃ and Al(OR^F)₃ might form an FLP system that attacks CD₂Cl₂ with chloride abstraction and alkylation of the arsane. The signals at δ = 51.2 ppm in the ²⁷Al NMR spectrum and at δ = -75.5 ppm in the ¹⁹F NMR spectrum are indicative of the known [ClAl(OR^F)₃]⁻ anion.^[16] Furthermore, the signals with ¹H chemical shifts of 7.62, 7.78, and 7.92 ppm (ortho, meta, para) are too sharp to result from an adduct (free AsPh₃: one broad signal at 7.34 pm). Consistent with the increased central atom size (P vs. As) and the decreased calculated adduct stability, dissociation of 3 and a further reaction with the solvent CD₂Cl₂ seems to be reasonable. Quantum chemical calculations support this assumption [Equation (3), Gibbs solvation energies were calculated at the (RI-)BP86/def-TZVP level with the COSMO model, $\varepsilon_r(CH_2Cl_2) = 8.93$,^[40] value in *italics* includes Grimme's D3 correction, values are given in kJ mol⁻¹].

AsPh₃ + Al(OR^F)₃ + CH₂Cl₂
$$\xrightarrow{\Delta_{r}G^{\circ}(solv)}_{-115} [Ph_{3}As-CH_{2}Cl]^{*} + [CIAl(OR^{F})_{3}]^{-}_{-149}$$
(3)

A similar chloride abstraction from CD_2Cl_2 was also observed when dissociated $(CF_3)_3COH-Al(OR^F)_3$ was reacted with Me_6C_6 to yield $[Me_6C_6-CD_2Cl]^+[ClAl(OR^F)_3]^-$ and free HOC(CF₃)₃ (NMR discussion, see Supporting Information).

The protonation of the phosphanes with **4** was analyzed with NMR spectroscopy. In all cases, the typical doublet of the ${}^{1}J_{P,H}$ coupling of 400–500 Hz was observed in the ${}^{1}H$ and ${}^{31}P$ NMR spectra (Table 2).

Nevertheless, several side-products, such as unreacted starting materials, neutral competing adducts, or other uncharacterized hydrolysis products, were detected in low-tomedium yields. Although a straight forward characterization of the cations was possible, the anion part was not as easy to interpret. In the ¹H NMR spectra, singlets at $\delta \approx$ 3.5 ppm were observed, which showed no cross-peaks, indicative of hydroxo groups, in ¹H–¹³C HMBC or ¹H–¹³C HSQC spectra. Rather, in a ¹H–¹⁹F HOESY spectrum a





Table 2. Experimental ${}^{31}P$ and ${}^{1}H$ NMR shifts of $[HPR_3]^+$ measured in PhF at room temperature.

Cation	³¹ P δ [ppm], ¹ $J_{P,H}$ [Hz]	$^{1}\text{H} \delta$ [ppm], $^{1}J_{\text{H,P}}$ [Hz]
$\overline{ \{ HPCy_2[2,4,6-(iPr)_3C_6H_2] \}^+ } \\ [HPPh_3]^+ \\ [HP(tBu)_3]^+ \\ [HPCy_3]^+ \\ [HPMePh_2]^+ \\ \label{eq:hermite}$	14.4 (m), 443 7.95 (m), 497 61.2 (m), 426 34.9 (m), 440 2.3 (m), 495	5.95 (m), 443 7.41 (m), 497 4.31 (m), 426 4.38 (m), 440 6.62 (m), 495

cross-peak of the ¹H signal to a ¹⁹F resonance in the range typical for perfluoro tert-butoxy groups was observed. With this ¹H-¹⁹F HOESY spectrum, we can prove the existence of a $[HO(Al(OR^{F})_{3})_{n}]^{-}$ anion, but the exact number of n can be 1 or 2. The calculated ¹H chemical shifts of $[HOAl(OR^{F})_{3}]^{-}$ and $[HO(Al(OR^{F})_{3})_{2}]^{-}$ are 0.89 (0.84) and 3.45 (3.65) ppm [(RI-)BP86/def-TZVP ((RI-)BP86/def2-TZVPP)]; the reference system is H₂O in PhF with $\delta(^{1}\text{H})$ = 1.13 ppm. In agreement with the thermodynamic calculations, which favor the formation of $[HO(Al(OR^{F})_{3})_{2}]^{-}$, the signal is better assigned to the hydroxo-bridged anion. Nevertheless, further investigations dealing with this type of an anion need to be performed. However, according to our experience, almost quantitative conversion was observed with the more sterically hindered phosphanes [e.g., PPh₃ and (tBu)₃P were almost quantitatively protonated] and when the stoichiometry was strictly controlled.

Crystal Structure Determinations

The molecular structures of 1–3, 7, 9, and 10 were characterized by single-crystal structure analysis.

Donor-Acceptor Adducts

The classical phosphane/arsane–alane adducts 1, 2, and 3 are isostructural; the P or As atoms of the ligands are bound to the Al atom (Figure 3), and the OR^F and phosphane/arsane substituents are arranged in a staggered fashion.

The Al–P distances range from 244.1(1) in 1 to 244.7(2) pm in 2 and are significantly shorter than those in other R₃Al-phosphane adducts owing to the strong electronwithdrawing effect of the fluorinated alkoxy ligands at the aluminum atom [R = Me 253.29(6) pm, R = Et 254.13(4) pm,^[46] R = PhSe, 2*Me 251.7(1) pm].^[47] The shortening of the Al–P bond length by 0.6 pm in 1 compared to that in 2 can be explained by the additional inductive effect of the methyl group and the reduced Tolman cone angle (136 vs. 145°).^[34,35] The Al-As distance in **3** of 252.83(4) pm is in the same range as that in (I/Cl)₃Al-AsPh₃ (251.4, 251.9 pm).^[48] Consistent with the increasing ligand size and the weaker σ -donor ability of the ligand, the average Al–O distances decrease from 1 to 2 to 3 (171.8, 171.4, 170.7 pm). However, according to the higher donor strength of the phosphane and arsane ligands, the average Al-O distance increases by about 1.2 to 3.6 pm, if compared to the weaker donor adducts Do-Al(OR^F)₃ with Do = PhF, 1,2-F₂C₆H₄, or SO₂.^[16]

Protonated Phosphonium Salts

The molecular structures of 7 and 9 consist of protonated phosphonium ions stabilized by aluminates with terminal (7) or µ-bridged (9) hydroxo groups (Figures 4 and 5). The terminal Al-O4 bond in 7 of 170.9(2) pm is shorter than that in $[{LAl(OH)}_2(\mu-O)] \cdot 0.5(C_7H_8) \cdot C_6H_{14}$ reported by Roesky [173.8(3) pm^[3]] and the average Al–O distances to the alkoxy ligands. The central Al atom is tetrahedrally coordinated with an average O-Al-O angle of 109.4°. The shortest anion-cation contact is a C-H···F interaction of 248.8 pm. Owing to the presence of a hydrogen bridge, the P···O4 distance of 313.8 pm is considerably smaller than the sum of the van der Waals radii (152 + 180 pm^[49]). However, the hydrogen atom attached to O4 was included in the refinement only at a calculated position. As the proton bound to the phosphorus atom was found in the difference Fourier map and charge equalization is required, this procedure is justified.



Figure 3. Molecular structures of 1 (left) and 2 (right). Thermal ellipsoids are drawn at the 50% probability level. Selected distances [pm]: 1: P–Al 244.1(1), av. Al–O 171.8, av. P–C_{Me/Ph} 182.1. Σ O–Al–O 342.7°; 2: P–Al 244.7(2), av. Al–O 171.4, Σ O–Al–O 343.4°. Adduct 3 is isostructural with 2 and has an As–Al distance of 252.83(4), av. Al–O 170.7, av. As–C_{Ph} 192.8 pm, Σ O–Al–O 342.3°.





Figure 4. Molecular structure of 7. Thermal ellipsoids are drawn at the 50% probability level. Selected distances [pm]: P–H1 128(3), Al–O4 170.9(2), av. Al–O 173.4, av. P– C_{Cy} 182.1, P···O4 313.8, (P)H1···O4 265.9; av. O–Al–O 109.4°.



Figure 5. Molecular structure of **9**. Thermal ellipsoids are drawn at the 50% probability level. Selected distances [pm]: Al1–O7 181.9(4), Al2–O7 182.0(3), P–H1 152.7, av. Al–O 171.2. The Al1–O7–Al2 angle is 148.4°.

As expected, the bridged Al–O distances in **9** are elongated by around 10 pm compared to the Al–O bond lengths in **7** or those to the terminal OC(CF₃)₃ groups, as the O atom is shared between two Al(OR^F)₃ moieties. The position of the hydrogen atom on the hydroxy group was primarily found on the difference Fourier map and was finally restrained by using a DFIX instruction (0.9 Å).^[50] Similar to the Cl analog,^[51] but in contrast to the F analog, the anion exhibits a bend with an Al1–O7–Al2 angle of 148.4°, which is almost 9° larger than that in $[(C_6F_5)_3B(\mu-OH)-B(C_6F_5)_3]^-$ [139.6(5)°].^[15] The shortest anion–cation distance is a C–H···F distance of 249.3 pm. Three intramolecular O–H···F contacts within the anion between 235.0 and 260.6 pm were also observed.

Hydrolysis Product (10)

The trimeric hydrolysis product $[HOAl(OR^F)_2]_3$ (10) consists of an almost planar six-membered ring with alternat-

ing Al(OR^F)₂ and O-H groups and is shown in Figure 6. Compound 10 is isostructural to the fluorine analog, which is known from the decomposition of Al(OR^F)₃.^[16] At two of the three hydroxo groups, H bridging to the fluorine atoms of two PhF molecules can be observed and further supports our assignment. These interactions with O-F separations of 274.0 and 284.2 pm can be classified as rather strong hydrogen bonds (see Figure 6) and even coordinate the weak donor PhF. As expected, these distances are elongated in comparison with the intramolecular hydrogen bonds in $[(B_6F_5)_2BOH]_3$ (O–H to ortho fluorine of C₆F₅ ligand, 267 pm^[42]), but they are in the same range as those in MnF₃·3H₂O (262-276 pm) or the O····N distance in $[(tBu)_2Al(\mu-OH)]_3$ ·2MeCN.^[52,53] Several $[R_2Al(\mu-OH)]_3$ compounds have previously been described. Most of them exhibit a "twist-boat conformation".[53] Also the closely related $[(C_6F_5)_2BOH]_3$ shows a "C₂ twist-boat conformation".^[42] The average Al-O-Al angle in 10 of 138.6° is significantly reduced in comparison to those in $[(tBu)_2Al(\mu-$ OH)]3 (without solvent 142.0°, with coordinated MeCN 141.7°, with THF 140.5°)^[53] or [(^FRO)₂Al(µ-F)]₃ (146.4°).^[16] The average cyclic Al-O bond length in 10 (179.4 pm) lies between those in $[(tBu)_2Al(\mu-OH)]_3$ (184.9 pm)^[53] and [(MCIMP)Al(µ-OH···THF)]₃ (177.7 pm, "almost coplanar")^[4] and is in the same range as those of the tetrameric aluminopolysiloxanes reported by Veith $[R_2Al(\mu-OH)]_4$ (with pyridine av. Al-O 176.9 pm,^[54] with Et₂O av. 180.0 pm^[55]). The difference of the cyclic Al-O bond lengths between coordinated and non-coordinated hydroxo groups is interesting. In all three cases, only two solvent molecules are coordinated and the difference between the non-coordinated and coordinated Al-O bond lengths varies significantly $\{[(tBu)_2Al(\mu-OH)]_3 \cdot 2L: L = THF, \Delta =$ +1.1 pm; L = MeCN, Δ = +1.8 pm; 10: L = PhF, Δ = -1.2 pm}. A possible explanation is that the coordinated solvent molecule in 10 is almost parallel to the $[Al(\mu -$



Figure 6. Molecular structure of **10** with two hydrogen-bonded PhF molecules. Thermal ellipsoids are drawn at the 50% probability level. Disorder in the $C(CF_3)_3$ groups is removed for clarity. Selected distances [pm]: Al1–O10 179.7(2), Al1–O11 180.0(2), Al2–O11 178.9(2), Al2–O12 178.4(3), Al3–O10 180.4(2), Al3–O12 178.7(3), O11…F56 274.0, O10…F55 284.2, O12…F41 292.4. Selected angles [°]: Al1–O10–Al3 137.0(1), Al2–O11–Al1 137.7(1), Al2–O12–Al3 141.2(2).



OH)]₃ plane (29.0 and 22.6° between the [Al–O]₃ plane and the PhF planes), whereas in $[(tBu)_2Al(\mu-OH)]_3\cdot 2L$, L is more vertically positioned.^[53]

Brønsted Acidity Considerations

Gas Phase Acidity of $H_2O-Al(OR^F)_3$

Thermodynamically, the Brønsted acidity of molecules is best expressed by the gas phase acidity (GA = standard Gibbs energy of deprotonation in the gas phase). The lower the GA, the more acidic the molecule. According to our calculated GA value of 1148 kJ mol⁻¹ at the BP86/def-TZVP level of theory, H₂O–Al(OR^F)₃ (4) is more acidic than, for example, HSO₃F (GA = 1233 kJ mol⁻¹), but less acidic than our recently published perfluorinated alcohol adduct H[Al(OR^F)₄] (GA = 1041 kJ mol⁻¹), both calculated at the same level.^[56]

Absolute Acidity of the $H_2O-Al(OR^F)_3|PhF$ System

In agreement with the increased acidity of the coordinated H₂O, experimentally observed by the downfield shift of the protons, we were interested to evaluate the absolute acidity of H₂O–Al(OR^F)₃ (**4**) in regard to the absolute pH scale introduced in 2010.^[57,58] In this medium-independent acidity scale, the absolute chemical potential of the proton $\mu_{abs}(H^+)$, with the gaseous proton as a reference, is used as a universal measure of Brønsted acidity. In a solvent S, $\mu_{abs}(H^+)$ depends on the standard Gibbs solvation energy of the proton $\Delta_{solv}G^{\circ}(H^+,S)$ and the pH of the solution through Equation (4).

$$\mu_{abs}(H^{+}) = \mu_{abs}^{\circ}(H^{+}, S) + RT \ln a(H^{+}, S)$$

= $\Delta_{solv}G^{\circ}(H^{+}, S) - 5.71 \text{ kJ mol}^{-1} \cdot \text{pH}(S)$
with
 $\mu_{abs}^{\circ}(H^{+}, S) = \Delta_{solv}G^{\circ}(H^{+}, S),$
pH = $-\log a(H^{+}, S),$
RT ln10 = 5.71 kJ mol}^{-1}(at 298.15K) (4)

This can be made more comprehendible by the absolute pH_{abs} , defined as in Equation (5).

$$pH_{abs} = -\frac{\mu_{abs}(H^+)}{RT \ln 10} = -\frac{\mu_{abs}(H^+)}{5.71 \, \text{kJ mol}^{-1}}$$
$$= -\frac{\Delta_{solv} G^{\circ}(H^+)}{5.71 \, \text{kJ mol}^{-1}} + pH(S) \text{ (at 298.15 K)}$$
(5)

In other words, with the knowledge of $\Delta_{solv}G^{\circ}(H^+,S)$ as anchor point, one can convert pH(S) in an individual medium into absolute acidity values pH_{abs}, which can be compared over medium boundaries. Single ion Gibbs solvation energies are very difficult to obtain experimentally, but can be computed quantum chemically with an error of 15– 20 kJ mol⁻¹ (\approx 3 pH units).

For fluorobenzene, the standard solvent for this chemistry, the anchor point was hitherto neither experimentally nor computationally investigated. Using our recently established rCCC model,^[58] we calculated $\Delta_{solv}G^{\circ}(H^+,PhF)$, as -887 kJ mol⁻¹ (details in the Supporting Information). This is in line with expectations. As a bulk solvent, according to our calculations, fluorobenzene is more basic than 1,2dichloroethane (-860 kJ mol⁻¹) and is slightly less basic than sulfur dioxide (-898 kJ mol⁻¹).^[58] The comparison with the aqueous system is more spectacular. According to the experimental $\Delta_{solv}G^{\circ}(H^+, H_2O)$ value of $-1105 \text{ kJ mol}^{-1}$ (rCCC model: -1107 kJmol⁻¹), as a bulk solvent water is more basic by 218 kJ mol-1 or 38 pH units, or in other words: a fluorobenzene solution of pH 38 is about as acidic as one molar aqueous hydrochloric acid of aqueous pH 0! By using this anchor point, we calculated the pK_a value of 4 in fluorobenzene solution by constructing the Born-Fajans-Haber cycle (BFHC) shown in Scheme 1. The standard Gibbs solvation energies (COSMO, $\varepsilon_r = 5.42$) of the water adduct (4) and its conjugate base were calculated at the BP86/def-TZVP level of theory.



Scheme 1. Born–Fajans–Haber cycle to calculate the pK_a of 4 in PhF.

According to our calculated pK_a of 31.7, a solution of **4** in pure PhF is only very scarcely dissociated. Using basic chemistry knowledge, the pH of a 1 mM solution of **4** in PhF can then be calculated according to Equation (6).

$$pH(PhF) = \frac{1}{2}[31.7 - \log(0.001)] = 17.4$$
(6)

The absolute acidity is then obtained by inserting this value into Equation (4) to give Equation (7):

$$\mu_{abs}(H^+) = -887 \text{ kJ mol}^{-1} - 5.71 \text{ kJ mol}^{-1} \times 17.4 = -986 \text{ kJ mol}^{-1} \text{ or}$$

 $pH_{abs} = 172.6$ (7)

Thus, according to Equation (7), a millimolar solution of **4** in fluorobenzene has a pH_{abs} of 172.6, which makes it only slightly less acidic than pure H_2SO_4 with a pH_{abs} of 171 (see Supporting Information). An excess of the Lewis acid Al(OR^F)₃, which removes [HO–Al(OR^F)₃]⁻ from the protolysis equilibrium by complexation, should clearly lead to a superacidic solution [cf. to Equation (2) above: $\Delta_r H$ for the complexation is -144 kJ mol^{-1}].

Conclusions

We have described our preliminary attempts to use the superacid $Al(OR^F)_3$ for FLP-like chemistry. Dihydrogen activations with various phosphane/ $Al(OR^F)_3$ systems were not successful. Instead, the activation of the omnipresent, small molecule water was observed even at a low concentra-



tion of 9 ppm. Therefore, $H_2O-Al(OR^F)_3$ (4) was synthesized by substitution of PhF in PhF–Al(OR^F)₃ with H_2O and was analyzed in a long-term NMR study. Over 22 days, the ¹H and ¹⁹F NMR signals of alcohol HOC(CF₃)₃ increased as was expected for hydrolysis to give HOC(CF₃)₃ and HOAl(OR^F)₂. In analogy to the B(C₆F₅)₃ system, a crystalline hydrolysis product **10** was formed, which probably resulted from trimerization of the initially formed HOAl(OR^F)₂. Trimer **10** contains a six-membered ring with bridging hydroxo groups.

The absolute acidity of 4 was evaluated, according to the recently introduced absolute pH scale.[57,58] The absolute chemical potential of a 0.001 M solution of 4 in PhF was established as -986 kJ mol^{-1} and it has a pH_{abs} value of 173. This is nearly as acidic as pure H_2SO_4 (pH_{abs} = 171). The resulting increase of the Brønsted acidity of H2O by complexation with the Lewis superacid $Al(OR^F)_3$ was used to protonate phosphanes. Herein, PMePh₂, PPh₃, PCy₃, $P(tBu)_3$, and $PCy_2(2,4,6-(iPr)_3C_6H_2)$ were protonated and crystallized with the two new weakly coordinating anions $[(^{F}RO)_{3}Al(\mu-OH)Al(OR^{F})_{3}]^{-}$ and $[HOAl(OR^{F})_{3}]^{-}$. However, formation of classical, neutral donor-acceptor adducts between the less encumbered Ph₂MeP, Ph₃P, and Ph₃As and the superacid Al(OR^F)₃ was also observed. The dissolution of 3 in CD₂Cl₂ resulted in the formation of a FLP system, which afforded the activation of CD₂Cl₂ to give the halide abstraction product $[ClAl(OR^{F})_{3}]^{-}$ and alkylated arsane [CD₂ClAsPh₃]⁺. Even if dihydrogen activation has not been achieved, the interesting behavior between water, phosphanes, and Al(OR^F)₃ allows for a better understanding of the undesirable side-reactions of the superacid $Al(OR^{F})_{3}$.

Experimental Section

General: All reactions were performed by using standard Schlenk and vacuum techniques. Chemicals were handled under an argon atmosphere or in a glove box. All phosphanes and AsPh3 were used as provided. PhF, CD₂Cl₂, and perfluorohexane were dried with CaH₂ and distilled afterwards or were directly condensed into the reaction mixtures. PhF-Al(OR^F)₃ was synthesized as previously described.^[17] NMR spectra were measured with special J. Young or flame-sealed NMR tubes with a Bruker Avance II+ 400 MHz WB or Bruker DPX 200 spectrometer. Spectra of CD₂Cl₂ solutions were calibrated to the ¹H signal of CHDCl₂ at δ = 5.32 ppm. Spectra of PhF solutions (without deuterium lock) were calibrated to the ¹⁹F signal at δ = -113.1 ppm with respect to CFCl₃ and the ¹H signal of the *o*-H of PhF at $\delta = 7.14$ ppm. Spectra in 1,2-F₂C₆H₄ solutions were calibrated to the ¹H signal of the *o*-H of the solvent at $\delta = 6.96$ ppm and the ¹⁹F signal at -139.43 ppm (tetramethylsilane, TMS). The field corrections of the ³¹P and ²⁷Al spectra were adjusted to the proton calibration. The Topspin 2.1 software was used.

Crystal structure measurements were performed with a Bruker Quazar APEX2 CCD area detector or a Rigaku R-Axis SPIDER diffractometer with Mo- K_{α} X-ray sources. SHELX,^[50] SIR2004,^[59] and OLEX2^[60] were used to solve and refine the structures. PLA-TON^[61] was used for twin analysis or to change the space group. Graphics of the crystal structures were drawn with ORTEP.^[62]

CCDC-893508 (for 1), -893671 (for 2), -893442 (for 3), -893723 (for 7), -893628 (for 9), and -914824 (for 10) contain the supplementary

crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Structure Data for MePh₂P–Al(OR^F)₃ (1): a = 10.895(3), b = 28.144(7), c = 13.905(3) Å; a = 90, $\beta = 128.759(14)$, $\gamma = 90^{\circ}$; $P2_1/c$, Z = 4, $wR_2 = 0.1028$, $R_1 = 0.0382$. Ph₃P–Al(OR^F)₃ (2): a = 17.691, b = 17.691, c = 19.840 Å; a = 90, $\beta = 90$, $\gamma = 120^{\circ}$; $P\overline{1}$, Z = 6, $wR_2 = 0.1365$, $R_1 = 0.0476$. Ph₃As–Al(OR^F)₃ (3): a = 10.7515(2), b = 17.2947(4), c = 21.1997(5) Å; a = 90, $\beta = 112.4620(10)$, $\gamma = 90^{\circ}$; $P2_1/c$, Z = 4, $wR_2 = 0.0690$, $R_1 = 0.0290$. [HPCy₃][HOAl(OR^F)₃] (7): a = 12.4547(2), b = 17.3208(3), c = 20.0236(3) Å; a = 90, $\beta = 114.5130(10)$, $\gamma = 90^{\circ}$; $P2_1/c$, Z = 4, $wR_2 = 0.1374$, $R_1 = 0.0517$. [HO(Al(OR^F)₃)₂][HPCy₂(2,4,6-(iPr)₃C₆H₂)] (9): a = 12.9204(6), b = 18.1265(9), c = 29.660(2) Å; a = 90, $\beta = 93.603(7)$, $\gamma = 90^{\circ}$; $P2_1/c$, Z = 4, $wR_2 = 0.1887$, $R_1 = 0.0662$. [HOAl(OR^F)₂]₃·2PhF (10·2PhF) a = 12.7572(8), b = 13.7652(10), c = 16.7687(12) Å; a = 83.638(6), $\beta = 79.132(6)$, $\gamma = 76.968(5)^{\circ}$; PV, Z = 2, $wR_2 = 0.1702$, $R_1 = 0.0588$.

Attenuated total reflectance (ATR) IR spectra were recorded with a Nicolet Magna-IR 760 FTIR spectrometer with the software OMNIC. An advanced ATR correction was performed using the standard values. Raman measurements were performed with a Bruker RAM II Fourier transform Raman module for a VERTEX 70 spectrometer with a Nd-YAG laser and the OPUS software. The excitation wavelength was 1064 nm.

General Procedure for Adduct Synthesis: In a special J. Young flask PhF–Al(OC(CF₃)₃)₃ dissolved in PhF or perfluorohexane and phosphane or arsane (1 equiv.) dissolved in PhF or perfluorohexane were mixed at -20 °C. The reaction mixture was stirred for up to two hours and crystallized at -20 or -40 °C. After decantation of the liquid and removal of the residual solvent from the crystalline mass in vacuo, the compounds were isolated as colorless powders in good to almost quantitative yields.

Ph2MeP-Al(OC(CF3)3)3 (1): Ph2MeP (0.033 g, 0.16 mmol) in perfluorohexane, PhF-Al(OC(CF₃)₃)₃ (0.136 g, 0.16 mmol, 1 equiv.). A colorless precipitate appeared immediately, yield 0.07 g, 47%. ¹H NMR (400.17 MHz, CD₂Cl₂, 298 K): δ = 7.59 (m, 2 H, p- C_6H_5), 7.50 (m, 8 H, *olm*- C_6H_5), 1.99 (d, J = 9.3 Hz, 3 H, CH_3) ppm. ¹⁹F NMR (376.54 MHz, CD₂Cl₂, 298 K): $\delta = -75.4$ {s, 27 F, Ph₂MeP-Al(OC(CF₃)₃)₃} ppm. ²⁷Al NMR (104.27 MHz, CD₂Cl₂, 298 K): δ = 43.9 {br. s, 1 Al, Ph₂MeP-Al(OC(CF₃)₃)₃} ppm. ³¹P NMR (161.99 MHz, CD₂Cl₂, 298 K): $\delta = -26.6 \{m, 1 P, Ph_2MeP-$ Al(OC(CF₃)₃)₃) ppm. IR (Diamond ATR): $\tilde{v} = 445$ (w), 538 (w), 573 (w), 692 (w), 727 (m), 739 (w), 854 (w), 894 (w), 955 (w), 974 (s), 1108 (w), 1182 (m), 1218 (s), 1249 (vs), 1266 (s), 1300 (m), 1353 (m), 1442 (w), 3070 (vw) cm⁻¹. FT Raman: $\tilde{v} = 228$ (w), 270 (w), 327 (w), 350 (w), 539 (w), 564 (w), 618 (w), 676 (w), 691 (w), 751 (w), 811 (w), 1002 (s), 1029 (w), 1108 (w), 1164 (vw), 1192 (vw), 1275 (vw), 1425 (vw), 1593 (m), 2756 (w), 2907 (w), 2938 (w), 2971 (vw), 3055 (m), 3072 (m) cm⁻¹.

Ph₃P–Al(OC(CF₃)₃)₃ (2): PhF–Al(OC(CF₃)₃)₃ (0.40 g, 0.48 mmol) in PhF (3 mL), PPh₃ (0.127 g, 0.48 mmol, 1 equiv.) in PhF (2 mL), yield 0.451 g, 94%. ¹H NMR (400.17 MHz, CD₂Cl₂, 298 K): δ = 7.62 (m, 3 H, *p*-H_s), 7.50 (m, 6 H, *m*-H_s), 7.39 (m, 6 H, *o*-H_s) ppm. ¹⁹F NMR (376.53 MHz, CD₂Cl₂, 298 K): δ = -74.3 {s, 27 F, Ph₃P– Al(OC(CF₃)₃)₃). ²⁷Al NMR (104.27 MHz, CD₂Cl₂, 298 K): δ = 41.4 {br. s, Ph₃P–Al(OC(CF₃)₃)₃ ppm. ³¹P NMR (161.99 MHz, CD₂Cl₂, 298 K): δ = -11.1 {m, distance between the two maxima 1060 Hz, Ph₃P–Al(OC(CF₃)₃)₃ ppm. IR (Diamond ATR): \tilde{v} = 434 (w), 497 (w), 537 (w), 565 (vw), 693 (m), 713 (w), 727 (m), 747 (s), 808 (w), 849 (w), 897 (w), 973 (s), 1001 (w), 1027 (w), 1101 (m), 1179 (s), 1215 (vs), 1246 (vs), 1264 (s), 1300 (m), 1350 (w), 1438



(w), 1485 (vw), 1507 (vw), 1540 (vw), 1559 (vw), 3066 (vw) cm⁻¹. FT Raman: $\tilde{v} = 224$ (w), 251 (w), 269 (w), 326 (w), 366 (w), 539 (w), 564 (w), 618 (vw), 691 (vw), 714 (vw), 752 (vw), 809 (w), 1003 (vs), 1029 (m), 1102 (m), 1162 (w), 1187 (w), 1247 (w), 1578 (m), 1590 (vs), 3070 (vs) cm⁻¹.

Ph₃As–Al(OC(CF₃)₃)₃ (3): AsPh₃ (0.037 g, 0.12 mmol), PhF–Al-(OC(CF₃)₃)₃ (0.10 g, 0.12 mmol, 1 equiv.) in PhF (3 mL). Almost quantitative conversion presumed according to NMR analysis. ¹H NMR (400.17 MHz, 1,2-F₂C₆H₄, 298 K): δ = 7.35–7.50 (m, C₆H₅) ppm. ¹⁹F NMR (376.54 MHz, 1,2-F₂C₆H₄, 298 K): δ = -75.4 {s, side-product, probably PhF– or 1,2-F₂C₆H₄–Al(OC(CF₃)₃)₃}, -75.2 {s, 27 F, Ph₃As–Al(OC(CF₃)₃)₃ ppm. ²⁷Al NMR (104.27 MHz, 1,2-F₂C₆H₄, 298 K): δ = 41.9 {br. s, 1 Al, Ph₃As–Al(OC(CF₃)₃)₃}.

NMR Tube Reactions: In special J. Young NMR tubes, 1:1 or 1:2 mixtures of phosphane/PhF–Al($OC(CF_3)_3$)₃ were dissolved in moist PhF (173 ppm water). NMR spectra were measured directly, and the data are included in Table 2 (³¹P and ¹H) and the Supporting Information.

 $PCy_2(2,4,6-(iPr)_3C_6H_2)$ 1:2: $PCy_2(2,4,6-(iPr)_3C_6H_2)$ (0.024 g, 0.06 mmol) and PhF–Al(OC(CF₃)₃)₃ (0.099 g, 0.12 mmol, 2 equiv.) in PhF (1 mL, 173 ppm H₂O).

P(*t***Bu**)₃ **1:2:** P(*t***B**u)₃ (0.012 g, 0.06) and PhF–Al(OC(CF₃)₃)₃ (0.099 g, 0.12 mmol, 2 equiv.) in PhF (1 mL, 173 ppm H₂O).

PCy₃ 1:2: PCy₃ (0.017 g, 0.06 mmol) and PhF–Al(OC(CF₃)₃)₃ (0.099 g, 0.12 mmol, 2 equiv.) in PhF (1 mL, 173 ppm H₂O).

 PCy_3 1:1 (1bar H₂): PCy_3 (0.021 g, 0.07 mmol) and PhF–Al-(OC(CF₃)₃)₃ (0.058 g, 0.07 mmol, 1 equiv.) in PhF (1 mL).

PPh₃ 1:2: PPh₃ (0.01 g, 0.038 mmol) and PhF–Al(OC(CF₃)₃)₃ (0.063 g, 0.076 mmol, 2 equiv.) in PhF (0.8 mL, 173 ppm H₂O).

PMePh₂ 1:2: PMePh₂ (0.02 g, 0.10 mmol) and PhF–Al(OC-(CF₃)₃)₃ (0.16 g, 0.20 mmol, 2 equiv.) in PhF $(0.8 \text{ mL}, 173 \text{ ppm H}_2\text{O})$.

H₂O–Al(OC(CF₃)₃)₃ (4): In a special J. Young NMR tube with a Teflon[®] valve, PhF–Al(OC(CF₃)₃)₃ (0.020 g, 0.024 mmol) was dissolved in PhF (0.6 mL, 173 ppm H₂O). A series of NMR spectra were recorded at various times (Figure 1 and Supporting Information). ¹H NMR (400.17 MHz, PhF, 298 K): $\delta = 6.03$ {s, 2 H, H₂O–Al(OC(CF₃)₃)₃}, 3.57 [s, 1 H, HOC(CF₃)₃] ppm. ¹⁹F NMR (376.54 MHz, PhF, 298 K): $\delta = -74.53$ [s, 9F, HOC(CF₃)₃], -75.53 {s, 27F, PhF–Al(OC(CF₃)₃)₃}, -75.57 {27 F, H₂O–Al(OC(CF₃)₃)₃} ppm. ²⁷Al NMR (104.27 MHz, PhF, 298 K): no signal.

Supporting Information (see footnote on the first page of this article): Details of the quantum chemical calculations, NMR discussions, and crystallographic data.

Acknowledgments

The authors are grateful for financial support by the Fonds der Chemischen Industrie, the Albert-Ludwigs-Universität Freiburg, the Deutsche Forschungsgemeinschaft (DFG) and the European Research Council through the UniChem project.

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Received: January 10, 2013 Published Online: May 10, 2013