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A Very Strong Methylation Agent: $[Me_2Cl][Al(OTeF_5)_4]$

Sebastian Hämmerling, Günther Thiele, Simon Steinhauer, Helmut Beckers, Carsten Müller, Sebastian Riedel*

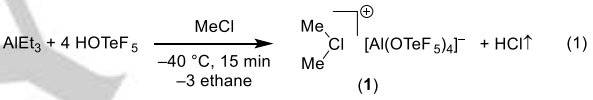
Dedicated to Prof. Dr. Hans-Ulrich Reißig on the occasion of his 70th birthday

Abstract: A new chloronium containing salt $[Me_2Cl][Al(OTeF_5)_4]$ is synthesized on a multigram-scale by means of a simple one-pot procedure. The isolated product can be handled at room temperature and used as a strong electrophilic methylation agent. This is demonstrated by the methylation of the very weak bases $P(CF_3)_3$, PF_3, MeI and MeBr.

Strong and easily-accessible electrophilic methylation agents are rare. The strongest known methylation systems are MeF/SbF_5 in liquid SO_2,[1,2] or *anhydrous* HF,[3] and the *closo*-carborates $Me(CHB_{11}Me_5X_6)$ (X = Cl, Br).[4] It is possible to crystallize methylated SO_2, i.e., $[MeSO_2][SbF_6]$, from a mixture of $MeF/SbF_5/SO_2$.[1,2] However, due to secondary reactions of the strong Lewis acid SbF_5 as oxidizer, its synthetic usability is limited.[5] The application of methyl cations stabilized by *closo*-carborates is limited due to the small-scale accessibility of these compounds.[6] Another class of strong alkylation agents are salts with dialkylhalonium cations.[7,8] Such cations can be prepared by the reaction of $SbF_5{\cdot}MeF$ with MeX (X= I, Br, Cl) in liquid SO_2. Their alkylation strength increases from the iodonium $[Me_2I]^+$ to the chloronium cation $[Me_2Cl]^+$. The elusive fluoronium cation $[Me_2F]^+$ – proposed to be an even stronger methylation agent – is experimentally still unknown. Attempts to detect this elusive species failed so far and yield instead decomposition products such as HF and $C_2F_5^+$ cations.[9] In contrast, a bis-silylated fluoronium salt, $[(Me_3Si)_2F][B(C_6F_5)_4]$,[10] and a cage like C-F-C hydrocarbon based system were described recently.[11]

Another access to the $[Me_2Cl]^+$ cation was reported by using a Brønsted superacid. Addition of chloromethane to $H(CHB_{11}Cl_{11})$ was reported to yield first HCl and $Me(CHB_{11}Cl_{11})$. The latter reacts further with a second chloromethane molecule to the $[Me_2Cl]^+$ cation.[12] We recently reported the synthesis of a new Brønsted superacid, $[ArH][Al(OTeF_5)_4]$ (*Ar*=*ortho*-$C_6H_4F_2$).[13] It is obtained in multi-gram batches by a simple one-step synthesis based on the reaction of triethylaluminium ($AlEt_3$) and pentafluoro-*ortho*telluric acid ($HOTeF_5$) in *ortho*-difluorobenzene (*o*DFB). We were thus interested in the generation of strong methylation agents, starting from this readily-available Brønsted superacid.

Here, we present the simple one-step synthesis of the dimethylchloronium salt $[Me_2Cl][Al(OTeF_5)_4]{\cdot}MeCl$ (**1·MeCl**) using the superacidic system of *in-situ* generated $H[Al(OTeF_5)_4]$ in neat chloromethane (equation 1). Upon addition of pentafluoro-*ortho*telluric acid to a solution of triethylaluminium in chloromethane at –40 °C, the initial reaction mixture changes color, starting from a yellow tinge to a colorless solution within five minutes. Distillation of excess MeCl from the reaction mixture under reduced pressure leads to the formation of a colorless precipitate which still contains solvate MeCl, which can be removed in vacuo at room temperature. Once solvent free, $[Me_2Cl][Al(OTeF_5)_4]$ (**1**) is isolated as a colorless powder and stable for hours at room temperature, where it turns brown within days, however, IR and NMR indicate the absence of impurities or decomposition. The NMR spectra of **1** yields the signal for the methyl groups with the expected chemical shifts and coupling constants ($\delta(^1H)$ = 5.61 ppm; $\delta(^{13}C)$ = 52.7 ppm; $^1J(^{13}C,^1H)$ = 162.1 Hz, ^1H NMR spectrum see Figure S1) and a cross signal in the $^1H,^{13}C$-HMBC due to the $^3J(^{13}C,^1H)$ coupling. Its IR data corresponds well to literature reported values.[7,8,12]



Colorless crystals suitable for X-Ray diffraction where grown from a MeCl/*n*-pentane mixture at –80 °C. **1·MeCl** crystallizes in the monoclinic space group $P2_1/n$ (Figure 1). Both, solvate MeCl and the aluminate anion are disordered as shown in the supporting information (Figure S2). The cation $[Me_2Cl]^+$ has a C1–Cl1–C2 bond angle of 101.0(7) ° with a considerably elongated C–Cl bond (d(C1–Cl1) = 183.9(16) pm, d(C2–Cl1) = 180.1(19) pm) compared to free MeCl (d(C–Cl) = 178.1 pm).[14] The structure of the cation is similar to those in $[Me_2Cl][CHB_{11}Cl_{11}]$.[12] The cation shows a weak contact to the embedded MeCl through a weak C2–H–Cl2 hydrogen bridge[15] (d(C2–Cl2) = 339.2(18) pm) and three further contacts to neighboring anions by weak C–H–F hydrogen bridges (d(C1–F) = 316.7(21) pm, d(C2–F) = 313.2(22) pm and d(C2–F) = 311.2(22) pm, see Figure S3).

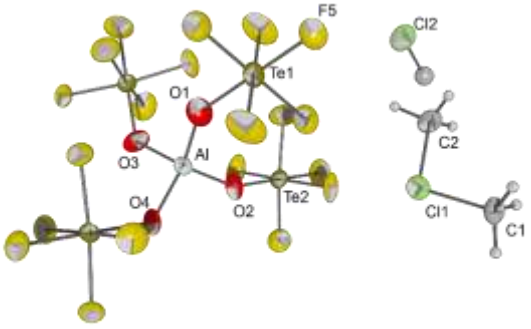


Figure 1. Molecular structure of **1·MeCl** in the solid state. H-Atoms of solvate MeCl are omitted for clarity. Thermal ellipsoids drawn at 50% probability level.

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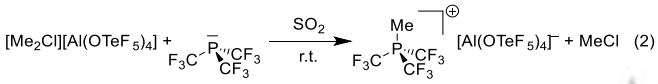
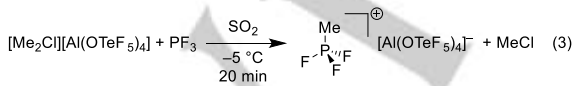
Selected bond length (pm) and angles (°): C1-Cl1 183.9(16), C2-Cl1 180.1(19), C1-Cl1-C2 101.0(7), Al-O1 184.5(14), Al-O2 166.4(14), Al-O3 178.7(14), Al-O4 176.1(14), O1-Te1 180.7(11), O1-Al-O2 112.0(7), O1-Al-O3 107.0(7), O1-Al-O4 110.8(7), O2-Al-O3 114.6(8), O3-Al-O4 105.0(7), O4-Al-O2 107.4(7).

1 is soluble in MeCl, SO_2 and SO_2ClF, but decomposes in solution within days at room temperature, yielding $MeOTeF_5$ from the methylation of the weakly coordinating anion. It can thus be used as Me^+ transfer reagent.

To evaluate this methylation ability, fluorinated phosphorus(III) compounds $P(CF_3)_3$ and PF_3 were chosen as reagent due to their weak nucleophilicity and basicity.[3,16] The reaction of **1** and $P(CF_3)_3$ (equation 2) slowly takes place at room temperature with formation of the previously reported cation $[MeP(CF_3)_3]^+$, as monitored by its characteristic ^{31}P NMR spectrum ($\delta(^{31}P)$ = 40.6 ppm, decet of quartets with $^2J(^{31}P,^{19}F)$ = 127.6 Hz, $^2J(^{31}P,^1H)$ = 15.7 Hz, see Fig. 2).[3] The formation of $[MeP(CF_3)_3]^+$ indicates that the methylation strength of **1** is similar to that of the strongest known methylation system MeF/HF/SbF_5. Furthermore, reaction 2 occurres at room temperature while the reaction of MeF/HF/SbF_5 and $P(CF_3)_3$ requires temperatures below –10 °C to prevent secondary reactions of the phosphonium cation in solution.



An even more challenging cation is $[MePF_3]^+$ which was, so far, only detected in the gas phase by ICR mass spectroscopy.[17] Treatment of PF_3 with **1** in liquid SO_2 at –10 °C leads to the formation of the elusive $[MePF_3]^+$ cation in the salt $[MePF_3][Al(OTeF_5)_4]$ (**2**) (equation 3). This is supported by the observed doublet of quartets in the ^1H NMR spectrum at $\delta(^1H)$ = 3.35 ppm with $^2J(^{31}P,^1H)$ = 18.1 Hz, and $^3J(^{19}F, ^1H)$ = 8.1 Hz. The signal in the ^{31}P NMR at $\delta(^{31}P)$ = 53.1 ppm revealed a smaller $^1J(^{31}P,^{19}F)$ coupling constant of 1277 Hz compared to the signal obtained for PF_3 in SO_2 solution with 1403 Hz. The reaction product was isolated as an off-white powder, but rapidly decomposes at room temperature to a dark brown oil. A 10 mol% excess of **1** within the reaction mixture allows quick handling of **2** at room temperature. The experimental IR spectra of **2**, shown in Table S1, is in good agreement with the calculated spectra at the RI-B3LYP-D3/def2-TZVPP level of theory.



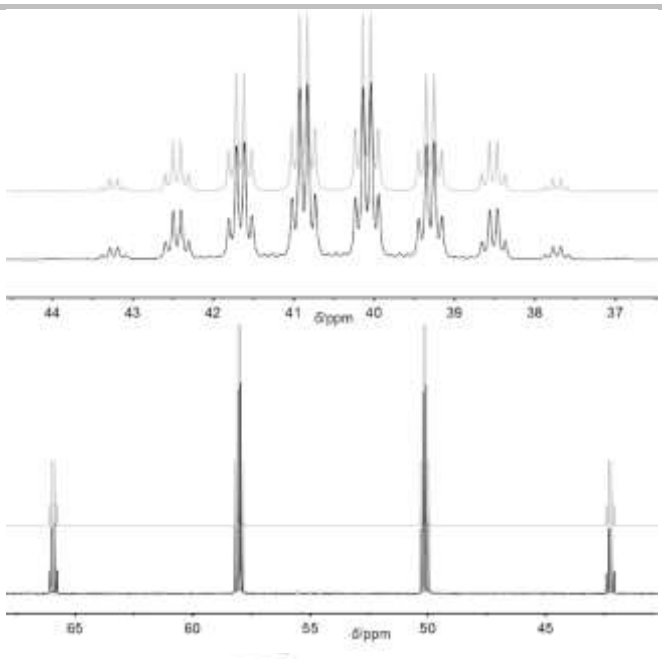


Figure 2. ^{31}P NMR spectra (161.2 MHz, SO_2, 20 °C) of $[MeP(CF_3)_3][Al(OTeF_5)_4]$ (top) and $[MePF_3][Al(OTeF_5)_4]$ (**2**, bottom). Experimental spectra are shown in black, simulated ones are depicted in gray.

The $[MePF_3][Al(OTeF_5)_4]$ salt decomposes in SO_2 solution at room temperature much faster than **1**, forming initially the $[MePF_2(OTeF_5)]^+$ cation which further reacts to $[MePF(OTeF_5)_2]^+$, as observed by NMR spectroscopy. Depending on the number of fluorine substituents in $[MePF_{3-x}(OTeF_5)_x]^+$, $\delta(^{31}P)$ shifts from 53.1 ppm (x = 0), to 45.2 ppm (x = 1) and 37.1 ppm (x = 2). Within this series the $^1J(^{31}P,^{19}F)$ coupling constants decrease from 1277 Hz to 1233 Hz and 1192 Hz, respectively. This decomposition pathway of the aluminate anion indicates the strong Lewis acidic character of the phosphonium cations. We note that the fluoride ion affinity (FIA) of the phosphonium cations $[MePF_{3-x}(OTeF_5)_x]^+$ decrease with increasing the number x of the $OTeF_5$ substituents (Table 1). This observation is surprising as it not only indicates an increase in stability by substitution of F by the $OTeF_5$ group, it also contradicts common consensus, that the $OTeF_5$ substituent has a higher group electronegativity than fluorine.[18] Indeed, the fluoride ion affinity of e.g. $E(OTeF_5)_5$ was proved to be higher than that of EF_5 (E = As, Sb)[19], and this conclusion is in accordance with our result of the increase of the FIA values within the series $PF_{5-x}(OTeF_5)_x$ with x = 0 - 5 (see Fig. S4). These seemingly contradictory results for the two series of the phosphonium cations and the neutral hypervalent species can be attributed to the bonding properties of the $OTeF_5$ group. Our preliminary NBO analysis[20] revealed that substitution of F by the $OTeF_5$ group in $[MePF_{3-x}(OTeF_5)_x]^+$ indeed reduces the NPA charge at the central phosphorus atom and thus, decreases its Lewis-acidity (Fig. S5). This trend is generally found for the series $[MeEF_{3-x}(OTeF_5)_x]^+$ (E = P, As, Sb), $[PF_{4-x}(OTeF_5)_x]^+$ and also for the neutral species $PF_{5-x}(OTeF_5)_x$ (see Fig. S5), which can most probably be attributed to both, a higher ionic character of the P–F bond (Table S3) and a stronger π-bonding of the oxygen lone pairs especially in the 2-center-2-electron bonds of these systems. On the other side, the F_5TeO group preferentially stabilizes 3-center-4-electron bonds in hypervalent species compared to a

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fluorine ligand, because it allows for a more efficient charge delocalization via the σ*(P–O) orbitals than the σ*(P–F) orbitals (Fig. S6). This, most likely result in the higher FIA values for the $OTeF_5$ substituted neutral derivatives.

Based on the very high computed FIA value of $[MePF_3]^+$ (851 kJ·mol^{-1}), this is an even stronger Lewis acid than the previously reported exceptional strong Lewis acid $[FP(C_6F_5)_3]^+$ with a FIA value of 773 kJ·mol^{-1}.[21] The experimental determination of the Lewis acidity of the $[MePF_3]^+$ cation by either ^{31}P NMR spectroscopy using triethylphosphine oxid (Gutmann-Beckett method),[22] or IR spectroscopy using an acetonitrile adduct[23] are not suitable due to the methylation reactions of the substrates.[24] Therefore, a solution of **2** was combined with a solution of either $[^nBu_4N][PF_6]$ (equation 4) or $[^nBu_4N][SbF_6]$ at –70 °C and allowed to warm to room temperature.

$$[MePF_3][Al(OTeF_5)_4] + [^nBu_4N][PF_6] \xrightarrow[\text{r.t.}]{SO_2} MePF_4 + PF_5 + \underset{[Al(OTeF_5)_4]}{[^nBu_4N]} \quad (4)$$

The reaction of **2** with $[PF_6]^-$ anions yields $MePF_4$[25] as observed in the ^{31}P NMR spectrum (quintet of quartets, $\delta(^{31}P)$ = –27.0 ppm, $^1J(^{31}P,^{19}F)$ = 967.9 Hz, $^2J(^{31}P,^1H)$ = 7.2 Hz). In contrast, the $[SbF_6]^-$ anion is stable in the presence of **2**, and it can be concluded that the Lewis acidity of **2** in solution is stronger than that of PF_5, but weaker than SbF_5. The reaction of the chloronium salt **1** with $[^nBu_4N][PF_6]$ or $[^nBu_4N][SbF_6]$ at room temperature in SO_2 yields MeF and PF_5 or SbF_5, respectively (equation 5). This observation exemplifies the high electrophilicity of **1**. $[^nBu_4N][AsF_6]$ reacts with **1** under formation of MeF. The formation of AsF_5 could not be verified as the reaction mixture rapidly forms an insoluble gel – even at –40 °C.

$$[Me_2Cl][Al(OTeF_5)_4] + [^nBu_4N][EF_6] \xrightarrow[\text{r.t.}]{SO_2} \underset{[^nBu_4N][Al(OTeF_5)_4]}{MeCl + MeF + EF_5} \quad (5)$$
$$E = P,\ Sb$$

Table 1. Fluoride ion affinities (FIA) of selected Lewis acids in kJ·mol^{-1}.

Compound	FIA[a]	Compound	FIA[a]
BF_3	356	$[MeP(OTeF_5)_3]^+$	767
PF_5	385	$[MePF(OTeF_5)_2]^+$	782
AsF_5	445	$[MePF_2(OTeF_5)]^+$	811
SbF_5	500	$[MeP(CF_3)_3]^+$	811
$[FP(C_6F_5)_3]^+$	773	$[MePF_3]^+$	851

[a] RI-B3LYP-D3/def2-TZVPP level using TMS^+/TMSF as anchor point.[19]

Iodomethane, and the even less basic molecule bromomethane, are also methylated quantitatively by **1** under formation of $[Me_2I]^+$ or $[Me_2Br]^+$ respectively (equation 6), as proven by IR and NMR spectroscopy ($[Me_2I]^+$: $\delta(^1H)$ = 3.59 ppm; $\delta(^{13}C)$ = 11.7 ppm; $^1J(^{13}C,^1H)$ = 158.7 Hz; $^1H,^{13}C$-HMBC: cross signal; $[Me_2Br^+$: $\delta(^1H)$ = 5.31 ppm; $\delta(^{13}C)$ = 40.2 ppm; $^1J(^{13}C,^1H)$ = 161.4 Hz; $^1H,^{13}C$-HMBC).[7,8] $[Me_2I][Al(OTeF_5)_4]$ was obtained as colorless powder, stable at room temperature and soluble in dichloromethane without decomposition for months, while $[Me_2Br]^+$ is only as stable as **1**.

$$[Me_2Cl][Al(OTeF_5)_4] + MeX \xrightarrow[\text{r.t.}]{SO_2} \begin{matrix} Me \\ X \\ Me \end{matrix}^{\oplus} [Al(OTeF_5)_4]^- + MeCl \quad (6)$$
$$X = Br,\ I$$

According to the proton affinities (PA) SO_2 should be methylated by **1**. However this is not observed as **1** is handled in liquid SO_2 at room temperature. Therefore the methyl cation affinities (MCA) are investigated (see Table 2, more values see Table S2). The MCA predicts the reactivity of **1** in liquid SO_2 – i.e. the not observed methylation of SO_2 with **1** – correctly. Furthermore, even more methylation reaction that are predicted wrongly with the PA, are predicted correctly with the MCA like the methylation of acetonitrile with $[Me_3O]^+$.[26] Hence literature values of PA may be a first reactivity hint for methylation reactions, but calculating the MCA is quit convenient and suggested.

Table 2. Experimental and calculated[a] proton affinities (PA) and methyl cation affinities (MCA)[b] in kJ·mol^{-1}

Compound	PA	MCA
SO_2	672.3 [27]	*229.1*, 254[28]
MeCl	647.3 [27]	*279.2*, 260[28]
MeBr	664.2 [27]	*294.4*, 265[28]
MeI	691.7 [27]	*323.7*
$P(CF_3)_3$	*690.9*	*367.2*
PF_3	695.3 [27], 669±21 [17]	*370.2*
Me_2O	792.0 [27]	*374.0*
MeCN	779.6 [27]	*414.2*

[a] values in *italics* at RI-B3LYP-D3/def2-TZVPP level

[b] MCA = $-\Delta H^0$ for reaction B + Me^+ → BMe^+

In conclusion, we report a simple one-pot synthesis of $[Me_2Cl][Al(OTeF_5)_4]$ (**1**), which is available on a multi-gram scale and can be handled at room temperature and stored for several weeks at –40 °C. The usage of **1** as a strong methylation agent was demonstrated by methylation of very weak bases yielding the $[MeP(CF_3)_3]^+$, $[Me_2Br]^+$ and $[Me_2I]^+$ cations, as well as the first spectroscopic proof of the elusive $[MePF_3]^+$ cation. The methylating agent **1** combines the advantages of $Me(CB_{11}Me_5X_6)$[4] and the MeF/SbF_5[1,2] system: a Lewis acid free, non-oxidizing compound with a large-scale accessibility.

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Keywords: methylation • weakly coordinating anion • pentafluoro-orthotellurates • fluorine chemistry • Lewis acids

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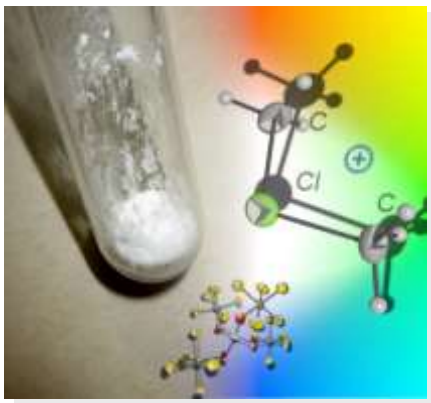

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A Very Strong Methylation Agent: $[Me_2Cl][Al(OTeF_5)_4]$