Supporting Information

The Tris(pentafluorophenyl)methylum Cation: Isolation and Reactivity

K. F. Hoffmann, D. Battke, P. Golz, S. M. Rupf, M. Malischewski, S. Riedel*
Experimental Procedures

All preparative work was carried out using standard Schlenk techniques. Glassware was greased with Tribolfin III. The pentfluoroothioleric acid HOF3\(^{[1]}\) and [Al(OF3)\(_3\)]\(^{[2]}\) were prepared as described elsewhere. All solid materials were handled inside a glove box with an atmosphere of dry argon (O\(_2\) < 0.5 ppm, H\(_2\)O < 0.5 ppm). All solvents were freshly dried with CaH\(_2\) before use and stored on molecular sieves. NMR spectra were recorded on a JEOL 400 MHz ECS or ECZ spectrometer. Chemical shifts and couplings constants of strongly coupled spin systems are given as simulated by gNMR\(^{[3]}\) Crystal data was collected with MoK\(_\alpha\) radiation on a Bruker D8 Venture diffractometer with a CMOS area detector. Single crystals were picked at −40 °C under nitrogen atmosphere and mounted on a 0.15 mm Micromount using perfluoroether oil. The structure was solved with the ShelXT\(^{[4]}\) structure solution program using intrinsic phasing and refined with the ShelXL\(^{[5]}\) refinement package using least squares on weighted F2 values for all reflections using OLEX2.\(^{[6]}\) CCDC 2154970 and CCDC 2153771 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre. Cyclic voltammetry was performed on an Interface 1010 B Potentiostat/Galvanostat/ZRA from Gamry Instruments. The investigations were carried out starting from 0 V going to the reduction first and then to the oxidation. The measurements were performed at a scan rate of 100 mV/s in anhydrous solvents under argon atmosphere without extra supporting and platinum wires as working-, counter-, and quasi-reference electrodes. The voltammograms were internally referenced against Fe\(^{3+}\). The compound was freshly prepared in the cyclic voltammetry cell with a concentration of 0.078 M in ortho-difluorobenzene. The Turbomole program\(^{[7]}\) was used to perform calculations at the unrestricted Kohn-Sham DFT level, using the B3LYP hybrid functional\(^{[8]}\) (with Ri\(^{[9]}\)) in conjunction with the valence triple-ζ basis set with two sets of polarization functions (def2-TZVPP)\(^{[10]}\). Minima on potential energy surfaces were characterized by normal mode analysis. Thermochromic data is provided without counterpoise correction but including zero-point energy correction as obtained from harmonic vibrational frequencies.

C(C\(_6\)F\(_3\))OH

In a Schlenk flask fine magnesium powder (2.43 g, 100 mmol, 3 eq.) was suspended in diethyl ether (150 ml) and cooled to 0 °C. Bromopentfluorobenzene (24.7, 100 mmol, 3 eq.) was added dropwise and the mixture was allowed to warm to room temperature. After 4 hours, methyl chloroformate (3.15 g, 33 mmol, 1 eq.) was added in small portions and the reaction mixture was consecutively stirred for 36 hours at room temperature, finally followed by 4 hours stirring under reflux conditions. Afterwards, the mixture was treated with diluted HCl solution (10%, 20 ml) and then extracted with diethyl ether (3x 30 ml). The collected organic phases were washed with distilled water (3x 30 ml) and Brine solution (3x 30 ml). After drying with MgSO\(_4\), all volatiles were removed under reduced pressure. The resulting crude oil was then refined via fractionated sublimation. The first fraction (50 °C, 1\(\times\)10\(^{-3}\) mbar) belongs to the sideproduct decfluorobenzophenone. The desired product was collected at 100 °C and 1\(\times\)10\(^{-3}\) mbar as yellow crystals (6.73 g, 35%).\(^{[11]}\) 1\(^H\) NMR (400 MHz, CDCl\(_3\), 22 °C): δ = 4.29 (s, 1H, -OH ppm; \(^{19}\)F NMR (377 MHz, CDCl\(_3\), 22 °C): δ = −140.0 (m, 6 ortho-F), −151.0 (m, 3 para-F), −160.2 (m, 6 meta-F) ppm.)
C(C(\(\text{F}_3\))F)_2\text{Cl}

This synthesis is a modified version of an already reported procedure.\[11\]

Tris(pentafluorophenyl)methanol C(C(\(\text{F}_3\))F)_2\text{OH}\] (3.53 g, 7 mmol) was dissolved in thionyl chloride (25.00 g) resulting in a yellow solution. Pyridine (0.49 g, 7 mmol, 1 eq.) and dimethylformamide (0.52 g, 7 mmol, 1 eq.) were added and the mixture was brought to reflux at 80 °C for 48 hours under constant stirring. Afterwards, the mixture was cooled to room temperature and decanted on ice water. It was treated with small portions of saturated NaHCO\(_3\) solution until the formation of gas stopped. The aqueous phase was extracted with dichloromethane (3x 30 ml). The collected organic phases were subsequently washed with saturated NaHCO\(_3\) and Brine solution (each 3x 30 ml), dried with MgSO\(_4\) and finally all volatiles were removed under reduced pressure. After recrystallization in n-pentane at -16 °C the product was obtained as yellow powder (0.95 g, 22 %).

**A stock solution of** C(C(\(\text{F}_3\))F)_2\text{Cl}\[\text{Al(OTeF}_5\)]

Triethylaluminum (41.7 mg, 0.37 mmol, 1 eq.) was dissolved in 4 ml of ortho-difluorobenzene and degassed. Afterwards, pentafluoroorthothielluric acid HOTE\(_2\)F (350 mg, 1.48 mmol, 4 eq.) was condensed onto the frozen solution at -196 °C. Warming the mixture to -30 °C under constant stirring led to a clear yellow solution and gas evolution. After 10 minutes the gas evolution ceased and tris(pentafluorophenyl)methyl chloride (28 mg, 0.05 mmol) was added. Shaking of the mixture led to an intense purple-colored solution, which was analyzed by low-temperature NMR spectroscopy.\[19\] F NMR (377 MHz, CDCl\(_3\), 22 °C): \(\delta = -135.5\) (m, 6 ortho-\(\text{F}\)), -150.0 (m, 3 para-\(\text{F}\), -160.3 (m, 6 meta-\(\text{F}\)) ppm.

These data are in agreement with literature values of C(C(\(\text{F}_3\))F)_2\text{Cl} \[\text{Al(OTeF}_5\]

[C(C(\(\text{F}_3\))F)_2\text{Cl}][\text{Al(OTeF}_5\)]

In a J. Young NMR tube [Al(OTeF\(_5\)]\(_2\) (38 mg, 0.0025 mmol, 0.5 eq) was weighed in and SO\(_2\)Cl\(_2\) was condensed on top at -196 °C. Warming to -30 °C led to a clear, colorless solution. Afterwards, tris(pentafluoro-phenyl)methyl chloride (28 mg, 0.05 mmol) was added. Shaking of the mixture led to an intense purple-colored solution, which was analyzed by low-temperature NMR spectroscopy.\[19\] F NMR (377 MHz, SO\(_2\)Cl\(_2\), ext. [\(\text{D}_2\)]acetone, -60 °C): \(\delta = -38.9\) (m, 1\(\text{F}\)), \(\delta = 176.6\) Hz, -40.0 (m, 1\(\text{F}\)), \(\delta = 182\) Hz, -46.1 (m, 4\(\text{F}\)), \(\delta = 3467\) Hz), -46.5 (m, 4\(\text{F}\)), \(\delta = 3463\) Hz) -112.6 (m, 3 para-\(\text{F}\), -127.7 (m, 6 ortho-\(\text{F}\), -154.3 (m, 6 meta-\(\text{F}\)) ppm.\[27\]Al NMR (78 MHz, C\(_6\)H\(_4\)F\(_2\), ext. [\(\text{D}_2\)]acetone, -40 °C): \(\delta = 47\) (s, [\(\text{Al(OTeF}_5\)]\(_2\)) ppm.

Reaction of [C(C(\(\text{F}_3\))F)_2\text{Cl}][\text{Al(OTeF}_5\)] with isobutane

The reaction was performed in a J. Young NMR tube. To a cooled solution of [Al(OTeF\(_5\)]\(_2\) (44 mg, 0.03 mmol, 0.5 eq.) in SO\(_2\)Cl\(_2\) at -60 °C, tris(pentafluoro-phenyl)methyl chloride (33 mg, 0.06 mmol, 1 eq.) was added under an argon stream, forming a deep purple solution. Finally, isobutane (7 mg, 0.12 mmol, 4 eq.) was condensed on the mixture at -60 °C and further warming was monitored and analyzed with low-temperature NMR spectroscopy.

Reaction of [C(C(\(\text{F}_3\))F)_2\text{Cl}][\text{Al(OTeF}_5\)] with ferrocene

A stock-solution of [C(C(\(\text{F}_3\))F)_2\text{Cl}][\text{Al(OTeF}_5\)] in ortho-difluorobenzene (0.05 mmol/ml) at -30 °C was treated with solid ferrocene (9 mg, 0.05 mmol). Upon contact the solution immediately changed its color to blue and further reacted to a green solution, indicating the successful formation of the ferrocenium cation. The mixture was analyzed by EPR spectroscopy.

Reaction of [C(C(\(\text{F}_3\))F)_2\text{Cl}][\text{Al(OTeF}_5\)] with tris-(4-bromophenyl)amine

A stock-solution of [C(C(\(\text{F}_3\))F)_2\text{Cl}][\text{Al(OTeF}_5\)] in ortho-difluorobenzene (0.052 mmol/ml) at -30 °C was treated with solid tris(4-bromophenyl)amine (13 mg, 0.052 mmol). Upon contact the solution immediately changed its color to a dark blue, indicating the formation of the radical cationic ammoniumyl. The mixture was analyzed by EPR spectroscopy.
NMR Spectra

C(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}OH

Figure S1. ¹⁹F NMR (377 MHz, CDCl\textsubscript{3}, 22 °C).

Figure S2. ¹\textsubscript{H} NMR (400 MHz, CDCl\textsubscript{3}, 22 °C).
$\text{C(C}_\text{6}\text{F}_5)_3\text{Cl}$

Figure S3. $^{19}\text{F}$ NMR (377 MHz, CDCl$_3$, 22 °C).
Figure S4. $^{19}$F NMR (377 MHz, C$_6$H$_4$F$_2$, ext. [D$_6$]acetone, $-40 \, ^\circ\text{C}$).

Figure S5. $^{27}$Al NMR (78 MHz, C$_6$H$_4$F$_2$, ext. [D$_6$]acetone, $-40 \, ^\circ\text{C}$).
Figure S6. $^{19}$F NMR (377 MHz, $\text{SO}_2\text{ClF}$, ext. [D$_6$]acetone, –60 °C). The asterisk marks the signal of the [D$_6$]acetone capillary.

Figure S7. $^{13}$C NMR (101 MHz, $\text{SO}_2\text{ClF}$, ext. [D$_6$]acetone, –60 °C). Asterisks mark the signals of the [D$_6$]acetone capillary.
Figure S8. $^{27}$Al NMR (78 MHz, SO$_2$ClF, ext. [D$_6$]acetone, $-60^\circ$C).
Decomposition of \([\text{C(C}_6\text{F}_5)_3]\)[\text{Al(OTeF}_5)_4]\) in \(\alpha\text{-DFB}\) at room temperature

**Figure S9.** \(^{19}\text{F}\) NMR (377 MHz, \(\text{C}_6\text{H}_4\text{F}_2\), ext. \([\text{D}_6]\text{acetone}, 22^\circ\text{C}\)). Asterisks mark the signals of the \([\text{D}_6]\text{acetone capillary.}\)

**Figure S10.** \(^{19}\text{F}\) NMR (377 MHz, \(\text{C}_6\text{H}_4\text{F}_2\), ext. \([\text{D}_6]\text{acetone, 22 }^\circ\text{C}\)). Asterisks mark the signals of the \([\text{D}_6]\text{acetone capillary.}\)
Variable-Temperature NMR Spectra

After the sample has been warmed for several hours to 0 °C, the sample was measured again at −60 °C. The $^{19}$F NMR spectrum reveals the complete conversion of cation $[\text{C}(\text{C}_6\text{F}_5)_3]^+$ to perfluorotrityl methane. Furthermore, the formation of HOTeF$_5$ was observed in the $^{19}$F and $^1$H NMR spectra, probably occurring due to partial decomposition of $[\text{Al(OTEF}_5)_4]^{-}$ via the protonation of the Bronsted acidic tert-butyl cation. Similar decomposition reactions have been reported by Krossing et al. when they treated AlBr$_3$ with tert-butylbromide.$^{[12]}$ The broadened signals of the isobutane in the $^1$H and $^{13}$C NMR spectra are resolved again, suggesting that the dynamic exchange ceased. Additionally, several signals with low intensity in the range of 1 to 3 ppm in the $^1$H NMR and 0 to 50 ppm in the $^{13}$C NMR are observed, which correspond to isobutene oligomerization products. Still, no clearly assignable signals of the tert-butyl cation are found, which most likely reacted with the excess isobutane of the reaction mixture. Additional experiments were performed in which a slight excess of HOTeF$_5$ is added to the reaction of the Lewis acid Al(OTEF$_5$)$_3$(SO$_2$ClF) and C(C$_6$F$_5$)$_3$Cl in SO$_2$ClF in order to form HCl and therefore remove the chloride source before the isobutane is added. Furthermore, an equimolar amount of isobutane was used. These attempts also resulted in the rapid oligomerization of the formed tert-butyl cation at 0 °C and finally yielded the polymerization of the sample at room temperature.

**Figure S11.** VT $^1$H NMR (400 MHz, SO$_2$ClF, ext. [D$_6$]acetone) spectra of the reaction of $[\text{CPh}_3]^+[\text{Al(OTEF}_5)_3]^{-}$ with isobutane. Asterisk marks the signal of the external deuterated solvent capillary.
Figure S12. VT $^{13}$C NMR (101 MHz, SO$_2$ClF, ext. [D$_6$]acetone) spectra of the reaction of [CPh$_3^+$][Al(OTeF$_5$)$_3$]Cl with isobutane. Asterisk marks the signal of the external deuterated solvent capillary.

Figure S13. VT $^{19}$F NMR (282 MHz, SO$_2$ClF, ext. [D$_6$]acetone) spectra of the reaction of [CPh$_3^+$][Al(OTeF$_5$)$_3$]Cl with isobutane. Asterisk denotes the signal of the external deuterated solvent capillary. Daggers denotes residual CPh$_3^+$Cl.
Figure S14. VT $^{27}$Al NMR (78 MHz, SO:ClF, ext. [D$_6$]acetone) spectra of the reaction of [CPh$^3$][Al(OTeF$_5$)$_3$Cl] with isobutane. Asterisk marks the signal of the external deuterated solvent capillary.
EPR Spectra

\[
\text{SET} \quad \alpha\text{-DFB} \quad -30 \degree \text{C} \rightarrow \text{r.t.} \quad \text{Ph}_{3}\text{C}^{+} + [\text{FeCp}_{2}][\text{Al(OTeF}_{5}\text{)}_{4}]
\]

Figure S15. Experimental EPR spectrum showing the signal of the perfluorinated trityl radical \(\text{CPh}^{+}\)'s at room temperature. The spectrum was recorded using the solution obtained after the reaction of \([\text{CPh}^{+}]\text{[Al(OTeF}_{5}\text{)}_{4}]\) and ferrocene. The experimental \(g\) value is 2.0031.

\[
\text{SET} \quad \alpha\text{-DFB} \quad -30 \degree \text{C} \rightarrow \text{r.t.} \quad \text{Ph}_{3}\text{C}^{+} + [\text{N(C}_{6}\text{H}_{4}\text{Br-4})_{3}\text{][Al(OTeF}_{5}\text{)}_{4}]
\]

Figure S16. Experimental EPR spectrum showing two broad overlapped signals of the perfluorinated trityl radical \(\text{CPh}^{+}\)'s and the ammoniumyl radical cation \([\text{N(C}_{6}\text{H}_{4}\text{Br-4})_{3}\text{][Al(OTeF}_{5}\text{)}_{4}]\) at room temperature. The spectrum was recorded using the solution obtained after the reaction of \([\text{CPh}^{+}]\text{[Al(OTeF}_{5}\text{)}_{4}]\) and the amine \(\text{N(C}_{6}\text{H}_{4}\text{Br-4})_{3}\).
Crystal data

|                      | C(C₆F₁₅)H                  | [C(C₆F₁₅)₃][AlOTeF₅]₄  |
|----------------------|----------------------------|-------------------------|
| **CCDC number**      | 2154970                    | 2153771                 |
| **empirical formula**| C₁₉H₁₅F₁₅                  | AlC₁₉F₅₅O₄Te₄          |
| **formula weight**   | 514.20                     | 1494.57                 |
| **temperature [K]**  | 100                        | 100                     |
| **space group**      | R̅3                         | C2/c                    |
| **a [Å]**            | 3785.7(4)                  | 1383.99(18)             |
| **b [Å]**            | 3785.7(4)                  | 2029.23(18)             |
| **c [Å]**            | 610.10(7)                  | 1400.13(15)             |
| **Z**                | 18                         | 4                       |
| **ρcalcd [g·cm⁻³]**  | 2.030                      | 2.801                   |
| **μ [mm⁻¹]**         | 0.236                      | 3.500                   |
| **refinement**       | R = 0.0463                 | R₁ = 0.0349             |
|                      | wR = 0.1069                | wR = 0.0763             |
| **final R indexes**  | R₁ = 0.0734                | R₁ = 0.0388             |
|                      | wR = 0.1216                | wR = 0.0786             |

**Summary of crystal data and refinement results**

- **CCDC number**: 2154970, 2153771
- **Empirical formula**: C₁₉H₁₅F₁₅, AlC₁₉F₅₅O₄Te₄
- **Formula weight**: 514.20, 1494.57
- **Temperature**: 100 K, 100 K
- **Space group**: R̅3, C2/c
- **Volume [Å³]**: 7572.2(17), 3544.7(7)
- **Z**: 18, 4
- **Density [-]**: 2.030, 2.801
- **Microscope [-]**: 0.236, 3.500
- **Reflection Collected**: 20405
- **Independent Reflections**: 3096 [R₁ = 0.0692], 3642 [R₁ = 0.0467]
- **Data/Refinements/Parameters**: 3096/0/307, 3642/612/363
- **Goodness-of-fit on F²**: 0.993, 1.147
- **Final R Indexes [I > 2σ(I)]**: R₁ = 0.0463, R₁ = 0.0349
- **Final R Indexes [all data]**: R₁ = 0.0734, R₁ = 0.0388
- **Weighted R Indexes**: wR = 0.1069, wR = 0.0763

- **Color**: colorless, colorless
- **Dimension [mm]**: 0.949 x 0.058 x 0.052, 0.459 x 0.164 x 0.03
Figure S17. Molecular structure of C(C₆F₅)₃H.

Table S1. Bond Lengths for C(C₆F₅)₃H.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| F1   | C3   | 1.346(3) | C2   | C3   | 1.382(4) |
| F2   | C4   | 1.335(3) | C2   | C7   | 1.387(4) |
| F3   | C5   | 1.336(3) | C3   | C4   | 1.381(4) |
| F4   | C6   | 1.347(3) | C4   | C5   | 1.377(4) |
| F5   | C7   | 1.344(3) | C5   | C6   | 1.380(4) |
| F6   | C9   | 1.343(3) | C6   | C7   | 1.375(4) |
| F7   | C10  | 1.343(3) | C8   | C9   | 1.388(4) |
| F8   | C11  | 1.342(3) | C8   | C13  | 1.385(4) |
| F9   | C12  | 1.338(3) | C9   | C10  | 1.386(4) |
| F10  | C13  | 1.342(3) | C10  | C11  | 1.370(4) |
| F11  | C15  | 1.342(3) | C11  | C12  | 1.379(4) |
| F12  | C16  | 1.345(3) | C12  | C13  | 1.382(4) |
| F13  | C17  | 1.341(3) | C13  | C14  | 1.383(4) |
| F14  | C18  | 1.337(3) | C14  | C19  | 1.384(4) |
| F15  | C19  | 1.350(3) | C15  | C16  | 1.381(4) |
| C1   | C2   | 1.535(4) | C16  | C17  | 1.374(4) |
| C1   | C8   | 1.527(4) | C17  | C18  | 1.377(4) |
| C1   | C14  | 1.536(4) | C18  | C19  | 1.372(4) |

Table S2. Bond Angles for C(C₆F₅)₃H.

| Atom | Atom | Angle° | Atom | Atom | Angle° |
|------|------|--------|------|------|--------|
| C2   | C1   | 113.5(2)| C11  | C10  | 119.9(3) |
| C8   | C1   | 114.6(2)| F8   | C11  | 120.3(3) |
| C8   | C1   | 113.4(2)| F8   | C11  | 120.1(3) |
| C3   | C2   | 118.7(3)| C10  | C11  | 119.6(3) |
| C3   | C2   | 116.0(3)| F9   | C12  | 120.0(3) |
| C7   | C2   | 125.4(3)| F9   | C12  | 119.4(3) |
| F1   | C3   | 119.8(3)| C11  | C12  | 119.4(3) |
| F1   | C3   | 117.0(3)| F10  | C13  | 119.9(3) |
| C4   | C3   | 123.2(3)| F10  | C13  | 122.2(3) |
### Table S3. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å²×10^3) for C(C₆F₅)₃H.

| Atom | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| H1   | 6442.03 | 5169.25 | 7875.25 | 18    |
[C(C₆F₅)₃][Al(OTeF₅)₄]

Figure S18. Molecular structure of [C(C₆F₅)₃][Al(OTeF₅)₄].

Figure S19. Molecular structure of the disordered anion in [C(C₆F₅)₃][Al(OTeF₅)₄].

Table S4. Bond Lengths for [C(C₆F₅)₃][Al(OTeF₅)₄].

| Atom  | Atom  | Length/Å   | Atom  | Atom  | Length/Å   |
|-------|-------|------------|-------|-------|------------|
| Te2   | F10   | 1.835(3)   | F7    | C10   | 1.333(6)   |
| Te2   | F9    | 1.839(3)   | F5    | C7    | 1.325(6)   |
| Te2   | F13   | 1.820(4)   | F2    | C4    | 1.334(6)   |
| Te2   | O1    | 1.783(3)   | F4    | C6    | 1.323(6)   |
| Te2   | F11   | 1.820(4)   | F8    | C11   | 1.319(9)   |
| Te2   | O4    | 1.88(2)    | F3    | C5    | 1.319(6)   |
| Te2   | F12   | 1.774(19)  | Al1   | O1    | 1.68(3)    |
| Te2   | F14   | 1.85(5)    | Al1   | O4    | 1.718(17)  |
| Te1   | F22   | 1.814(17)  | Al1   | O3    | 1.713(10)  |
| Te1   | O3²   | 1.985(9)   | Al1   | O2    | 1.731(10)  |
Table S5. Bond Angles for [C(OTeF_5)]_2[Al(OTeF_3)].

| Atom | Atom | Angle/° | Atom | Atom | Angle/° |
|------|------|---------|------|------|---------|
| F10  | Te2  | F9      | 85.37(15) | F21  | Te1    | F22   | 90.7(7) |
| F10  | Te2  | O4'    | 175.6(7)  | F21  | Te1    | O3'   | 172.1(5) |
| F10  | Te2  | F14    | 85.1(7)   | F21  | Te1    | F20   | 87.0(5)  |
| F9   | Te2  | O4'    | 93.8(9)   | F21  | Te1    | F24   | 90.9(4)  |
| F9   | Te2  | F14    | 170.5(7)  | F24  | Te1    | O3'   | 87.3(5)  |
| F13  | Te2  | F10    | 88.52(17) | F24  | Te1    | F20   | 86.7(5)  |
| F13  | Te2  | F9     | 88.85(19) | F17  | Te1    | O3'   | 96.0(8)  |
| F13  | Te2  | F11    | 174.99(19)| F17  | Te1    | F16   | 167.0(8) |
| F13  | Te2  | O4'    | 95.8(6)   | F17  | Te1    | O2    | 90.4(5)  |
| F13  | Te2  | F14    | 91.1(13)  | F17  | Te1    | F18   | 83.7(8)  |
| O1   | Te2  | F10    | 94.4(9)   | O1   | Al1   | O4    | 107.9(18) |
| O1   | Te2  | F9     | 176.7(17) | O1   | Al1   | O3    | 114.9(11) |
| O1   | Te2  | F13    | 94.4(17)  | O1   | Al1   | O2    | 107.2(18) |
| O1   | Te2  | F11    | 89.4(17)  | O4   | Al1   | O2    | 110.8(8) |
| F11  | Te2  | F10    | 87.96(18) | O3   | Al1   | O4    | 108.0(11) |
| F11  | Te2  | F9     | 87.3(2)   | O3   | Al1   | O2    | 108.0(5)  |
| F11  | Te2  | O4'    | 87.7(6)   | Al1  | O1    | Te2   | 156.3(3) |
| F11  | Te2  | F14    | 92.1(13)  | C9   | C8    | C9'   | 115.9(6)  |
| F12  | Te2  | F10    | 170.5(6)  | C9   | C8    | C1    | 122.1(3)  |
| F12  | Te2  | F9     | 87.3(8)   | C9'  | C8    | C1    | 122.1(3)  |
| F12  | Te2  | F13    | 85.2(6)   | F6   | C9    | C8    | 120.1(5)  |
| F12  | Te2  | F11    | 97.8(7)   | F6   | C9    | C10   | 117.7(5)  |
| F12  | Te2  | O4'    | 12.3(10)  | C10  | C9    | C8    | 122.1(5)  |
| F12  | Te2  | F14    | 102.2(11) | C3   | C2    | C1    | 121.7(5)  |
| F14  | Te2  | O4'    | 95.7(11)  | C7   | C2    | C2    | 122.3(5)  |
| F22  | Te1  | O3'    | 90.2(7)   | C7   | C2    | C3    | 116.0(4)  |
| F22  | Te1  | F20    | 86.2(6)   | F7   | C10   | C9    | 120.6(5)  |
| F22  | Te1  | F24    | 172.6(7)  | F7   | C10   | C11   | 119.4(5)  |
| O3'  | Te1  | F18    | 162.8(4)  | C9   | C10   | C11   | 120.0(5)  |
| F16  | Te1  | O3'    | 97.0(4)   | C2'  | C1    | C8    | 118.8(3)  |
| F16  | Te1  | F18    | 83.8(4)   | C2   | C1    | C8    | 118.8(3)  |
| O2   | Te1  | O3'    | 77.8(4)   | C2   | C1    | C2'   | 120.5(6)  |
| O2   | Te1  | F16    | 92.0(4)   | F8   | C11   | C10   | 120.1(3)  |
| O2   | Te1  | F18    | 84.9(4)   | F8   | C11   | C10'  | 120.1(3)  |
| F20  | Te1  | O3'    | 85.3(4)   | C10  | C11   | C10'  | 119.7(7)  |
| F15  | Te1  | O3'    | 114.7(5)  | F2   | C4    | C5    | 119.9(5)  |
| F15  | Te1  | F16    | 87.6(4)   | F2   | C4    | C3    | 119.7(5)  |
| F15  | Te1  | O2     | 167.4(5)  | C3   | C4    | C5    | 120.4(5)  |
| F15  | Te1  | F18    | 82.6(5)   | F4   | C6    | C5    | 119.5(5)  |
| F15  | Te1  | F17    | 87.2(5)   | F4   | C6    | C7    | 121.0(5)  |
| F23  | Te1  | F22    | 93.7(6)   | C7   | C6    | C5    | 119.6(5)  |

1^1-X_{x}Y_{3/2}-Z; 2^1/2-X,3/2-Y,1-Z; 3^1-X_{x}Y,1/2-Z
Table S6. Atomic Occupancy for [C(C₆F₅)₃][Al(OTeF₅)₄].

| Atom  | Occupancy | Atom  | Occupancy | Atom  | Occupancy |
|-------|-----------|-------|-----------|-------|-----------|
| A1    | 0.5       | O1    | 0.5       | O4    | 0.5       |
| F22   | 0.5       | O3    | 0.5       | F16   | 0.5       |
| O2    | 0.5       | F18   | 0.5       | F20   | 0.5       |
| F15   | 0.5       | F23   | 0.5       | F19   | 0.5       |
| F21   | 0.5       | F24   | 0.5       | F17   | 0.5       |
| F12   | 0.5       | F14   | 0.5       |       |           |

1¹-X, +Y, 3/2-Z; 2¹/2-X, 3/2-Y, 1-Z; 3²-X, +Y, 1/2-Z
Structure optimizations were performed DFT level using the B3LYP functional together with def2-TZVPP basis set as implemented in the Turbomole V7.3 program.

**Figure S20.** Representation of the B3LYP/def2-TZVPP structure of the CPh₃ radical.

| $r_{ij}$ | $\theta_{ij}$ | $\phi_{ij}$ |
|----------|---------------|-------------|
| 0.12417556615702 | 1.71721899779271 | c |
| 2.23663245826561 | c |
| 2.01265258089143 | c |
| 1.40985456077638 | h |
| 2.49520960704563 | c |
| 2.27732750314509 | h |
| 3.23809910898189 | c |
| 3.62202133278627 | h |
| 2.27732750314509 | h |
| 3.23809910898189 | c |
| 3.62202133278627 | h |
| 2.27732750314509 | h |
| 3.23809910898189 | c |
| 3.62202133278627 | h |
| 2.27732750314509 | h |
| 3.23809910898189 | c |

The total energy is given by $E_{\text{tot}} = -732.8281357854$ H.
Figure S21. Representation of the B3LYP/def2-TZVPP structure of the [CPh₃⁺]⁺ cation.

$coord
-3.130348761389922 -0.01950510799536  1.71921643722896  c
-4.936670970292671  2.00217542925323  2.33427640107620  c
-7.561426157665953  1.549445056711499  2.01312763734952  c
-8.21826237519897  0.27715563159430  2.46909856155231  c
-9.28100926205935  3.46130662601394  2.46909856155231  c
-11.27994157928732 -3.11054280103302  2.3328211175193  h
-8.43716478978566  5.84185041511979  3.2201344183803  c
-9.7902397574937  7.32656650586361  3.6003168544937  h
-5.85934951666082  6.32011054379208  3.4537710270635  c
-5.21673419586087  8.15844246734918  4.1035232144907  h
-4.120284018973  4.39959150273455  2.96729501192002  c
-2.12925208365253  4.80054210010024  3.2299918212504  h
 1.9275959179923  4.4649337237778  -3.8686561416778  h
 1.7935236620714  3.16546307729286 -2.28847003796031  c
-9.04778434529713  2.61531297625470 -1.8520928618285  c
-2.17471022389662  6.64123059357977 -1.7563779751548  h
-0.72080910939945  0.62681974034324  0.5870003611610  c
 1.47681428210423  0.7543591184393  1.2251022376900  c
 1.3660977017015  0.22788590635518  2.6339098436641  h
 3.78225074223847  0.14795412497247  0.1590418664863  c
 5.45963162459643  1.17832116976508  0.7058097958482  c
 3.94521270000484 -1.79872447986049  1.6091850395378  c
 5.74865460182843 -2.25161662103956 -2.45892035451986  c
-1.79184670887454  4.16196133501642  0.68389243669892  c
-2.85942413926063  4.58147718142127  0.80673611408130  c
-5.46926812187654  7.03630027307603  1.38716549501252  c
-2.84051518200988  8.57005673736874  0.17107854811896  c
-4.9047587143507  7.58485289454833  3.53105609781418  c
-5.35577208689562  9.22782704022815  3.9944293152401  h
-5.76277854666247  5.63805622716646  5.08130308691422  c
-6.8453793373683  6.6526602754480  6.7604478635275  h
-5.2191379275807  3.15551796539093  4.4797802318178  c
-5.84196922162223  1.65242629831114  5.71286930674012  c
-3.73618215377697  2.57130648750529  2.3344533225770  c
$end

E_{tot}= -732.6127398496 H
### Supporting Information

**CPh$_3^\text{radical}**

Figure 22. Representation of the B3LYP/def2-TZVPP structure of the CPh$_3^\text{radical}$.  

| coordination | E$_\text{tot}$ | Figure 22 |
|--------------|---------------|------------|
| $0.00012095831423 -0.005869087565973$ | $-2221.462296850$ H |
| $0.00368905955412 -0.580012595665805$ | $-2221.462296850$ H |

E$_\text{tot}$ = $-2221.462296850$ H
Figure S23. Representation of the B3LYP/def2-TZVPP structure of the [CPhF$_3$]$^+$ cation.

$coord$-3.12847519777563 -0.03427606137065 1.72822146454654 c
-4.939707043187294 -2.006291525346993 2.24176378330425 c
-7.571675006988977 -1.63373202801220 1.89721612605944 c
-8.43311375217169 0.54493059177675 1.00250632940774 f
-9.31626289323930 -3.52285053978603 2.32214446182964 c
-11.74329583864015 -3.1377672756079 1.91425183505927 f
-8.48897298953204 -5.86887697891823 3.21654009059876 c
-10.13442534025011 -7.66061877466915 3.66032978459793 f
-5.91947402989705 -6.3125393991908 3.62790083013769 c
-5.16620700503527 -8.52319616055764 4.50571671300607 f
-4.19512200180034 -4.42885981279714 3.1117434147322 c
-1.77922089307287 -4.91241597336640 3.58063012896927 f
1.98668030085786 -4.78764930398260 -4.1991776577930 f
1.82389897630195 -3.07487925705258 -2.40167098406411 c
-0.4623795831801 -2.53657382455660 -1.27258836654440 c
-2.47896441698428 -3.77538471498228 -2.1018817470108 f
-0.71930991579581 -0.6404181502000 0.60525100344119 c
1.52978858760846 0.64239305702560 1.30113332051966 c
1.48662290641729 2.36991152179240 3.1199313319421 f
3.84080214759853 0.07748816878731 0.2388509761327 c
5.90840592237444 1.26364083598099 0.9761123926368 f
3.98916447685892 -1.77947823501118 -1.63631641586980 c
6.16926684157296 -2.26336925926572 -2.6814190042123 f
-1.82391980586644 4.1433322829216 -1.4185952278765 f
-3.0078655081213 4.59123590385150 0.75020154929517 c
-3.60165136180929 7.06685543564855 1.30627131551841 c
-2.96416723170618 8.91035473657836 -0.24669055709049 f
-4.89774393521536 7.61984907940823 3.53780073314571 c
-5.43621440399136 9.95884261456755 4.05949797556257 f
-5.62415200825125 5.6820545665473 5.17274327924609 c
-6.81549428911881 6.23356553529396 7.2976738322198 f
-5.08209316062525 3.20976241928909 4.558453040179 c
-5.75865065892323 3.80203699274708 6.1928142277030 f
-3.7329184915130 2.55605393756551 2.3351250613900 c
$end$

$E_{tot} = -2221.192766570 H$
**Figure S24. Visualization of the NPA charges**

The table below lists the atomic populations from total density:

| atom | charge | n(s)   | n(p)   | n(d)   | n(f)   | n(g)   |
|------|--------|--------|--------|--------|--------|--------|
| 1 c  | 0.22815| 2.90596| 2.85785| 0.00548| 0.00166| 0      |
| 2 c  | -0.207 | 2.92786| 3.2709 | 0.00557| 0.00267| 0      |
| 3 c  | 0.39863| 2.86748| 2.72383| 0.00829| 0.00177| 0      |
| 4 f  | 0.26632| 3.82418| 0.43424| 0.00777| 0.00013| 0      |
| 5 c  | 0.26857| 2.8775 | 2.84235| 0.00967| 0.00191| 0      |
| 6 f  | 0.24373| 3.82387| 0.41166| 0.00806| 0.00014| 0      |
| 7 c  | 0.37481| 2.89338| 2.72071| 0.0094  | 0.00169| 0      |
| 8 f  | 0.22447| 3.82019| 0.3953 | 0.00884| 0.00015| 0      |
| 9 c  | 0.26906| 2.87763| 2.84175| 0.00966| 0.00191| 0      |
| 10 f | -0.24368| 3.82381| 5.41167| 0.00807| 0.00014| 0      |
| 11 c | 0.39892| 2.86712| 2.72388| 0.0083  | 0.00177| 0      |
| 12 f | -0.26632| 3.82416| 5.43426| 0.00777| 0.00013| 0      |
| 13 f | -0.24371| 3.82381| 5.41169| 0.00807| 0.00014| 0      |
| 14 c | 0.26878 | 2.8777 | 2.84193| 0.00968| 0.00191| 0      |
| 15 c | 0.39917 | 2.86763| 2.72315| 0.00828| 0.00177| 0      |
| 16 f | -0.26642| 3.82426| 5.43427| 0.00776| 0.00013| 0      |
| 17 c | -0.20669 | 2.92816| 3.27029| 0.00558| 0.00267| 0      |
| 18 c | 0.3985  | 2.86756| 2.72386| 0.00831| 0.00177| 0      |
| 19 f | -0.26662| 3.82429| 5.43444| 0.00776| 0.00013| 0      |
| 20 c | 0.2691  | 2.87757| 2.84176| 0.00966| 0.00191| 0      |
| 21 f | -0.24366| 3.82383| 5.41163| 0.00806| 0.00014| 0      |
| 22 c | 0.37503 | 2.89337| 2.72047| 0.00943| 0.00169| 0      |
| 23 f | -0.2244 | 3.82016| 5.39526| 0.00884| 0.00015| 0      |
| 24 f | -0.26712| 3.82431| 5.43493| 0.00775| 0.00013| 0      |
| 25 c | 0.39747 | 2.86721| 2.72524| 0.0083  | 0.00177| 0      |
| 26 c | 0.26926 | 2.87758| 2.84159| 0.00966| 0.00191| 0      |
| 27 f | -0.24385| 3.82388| 5.41178| 0.00806| 0.00014| 0      |
| 28 c | 0.37376 | 2.89323| 2.7219 | 0.00942| 0.0017  | 0      |
| 29 f | -0.22485| 3.82017| 5.3957 | 0.00883| 0.00015| 0      |
| 30 c | 0.26909 | 2.87756| 2.84177| 0.00967| 0.00191| 0      |
| 31 f | -0.24389| 3.82383| 5.41186| 0.00806| 0.00014| 0      |
| 32 c | 0.39793 | 2.86734| 2.72467| 0.00829| 0.00177| 0      |
| 33 f | -0.26677| 3.82436| 5.43453| 0.00775| 0.00013| 0      |
| 34 c | -0.20672| 2.9279 | 3.27056| 0.00559| 0.00267| 0      |
**Figure S25.** Representation of the B3LYP/def2-TZVPP structure of HCPh\(_3\).

```plaintext
$coord
-0.43247250805016 0.11287100728542 -1.01694465034275 c
-2.03922444607518 -1.97147748456699 0.18688531523238 c
-4.56318781213606 -2.16573178580534 -0.56172538675342 c
-5.50592046074744 -0.51519441163602 -2.23850245379095 c
-6.1752204512185 -4.00599371412518 0.37377033186685 c
-8.5745283835632 -4.11283501738654 -0.36362889475288 f
-5.2645474365669 -5.74718980062378 2.10934125747594 c
-6.7829965948517 -5.23296019338330 3.0327151842612 f
-2.76161228374391 -5.61741055609950 2.87728256756725 c
-1.87524775217661 -7.27387511178899 4.55376308290948 f
-1.19361834355298 -3.74700264946268 1.91460353496209 c
1.18577059940600 -3.68975019177612 2.76416569249142 f
5.66679847136335 -3.73840607972873 -6.68474798705286 f
5.25788775266411 -2.58674935901642 -5.14396662413502 c
2.8304230996776 -1.90288992408989 -3.8530357976236 c
0.93913925949089 -2.52202989137285 -5.37314293914444 f
2.30422714258549 -0.62917780341081 -1.55964520559647 c
4.36772797027345 -0.07803230144498 -0.02387552962301 c
4.04938722075826 1.09262165442053 2.19291663899325 f
6.82036336628722 -0.72980133960256 -0.88916647305809 c
8.74261365993196 -0.16368541626811 0.83610426678460 c
7.70291218088992 -1.99039727979459 -2.9426256619541 c
9.61319589769076 -2.62674508738355 -3.58879293503998 f
-0.44128468939166 4.57468105473029 -3.81470785010133 c
-0.75698432718067 4.83741818762691 -1.31363956569354 f
-1.08992883108848 7.26050463794448 -0.37522911782999 f
-1.09160325274448 9.24686308057988 -1.92259140054532 f
-1.43195289191594 7.60345149216663 2.2017791000285 f
-1.75348334328894 9.11967367087589 3.13928524164582 f
-1.42966355207435 5.22785261012147 3.79431517486305 c
-1.74182486865912 5.83801019608880 6.27295761217810 f
-1.08222775618332 3.11850056993386 2.8018078998669 c
-1.05702930550292 1.19090821276050 4.43351567373661 f
-0.74367695006078 2.69981501072800 0.22785915311520 c
-1.25198299674452 0.3630046057308 -2.88601229639481 h
$end

\( E_{\text{tot}} = -2222.093075202 \) H
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