Stability of Ag$^{\text{III}}$ towards Halides in Organosilver(III) Complexes

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1. Experimental Section

**General Procedures and Materials.** Unless otherwise stated, the reactions and manipulations were carried out under purified Ar and exclusion of light using Schlenk techniques. Previously degassed solvents were dried using an MBraun SPS800 System (CH$_2$Cl$_2$, Et$_2$O) or over activated 3 Å molecular sieves (MeCN). Compounds [PPh$_4$][CF$_3$AgCF$_3$]$^{[S1]}$ and PhICl$_2$$^{[S2]}$ were prepared using published methods. Silyl reagents Me$_3$SiX (X = Br, I, CN) and AgF were purchased from commercial suppliers and used as received. Elemental analyses were carried out using a Perkin Elmer 2400 CHNS/O Series II microanalyzer. IR spectra were recorded on neat solid samples using a PerkinElmer Spectrum FT-IR spectrometer (4000–250 cm$^{-1}$) equipped with an ATR device. Unless indicated otherwise, NMR spectra were recorded at room temperature on a Bruker ARX 300 spectrometer. NMR parameters associated with the [PPh$_4$]$^+$ cation are unexceptional and are therefore omitted. Chemical shifts ($\delta$F in ppm) are given with respect to CFCl$_3$ as the standard references in use. Chemically inequivalent CF$_3$ groups are indicated as follows: CF$_3$–Ag–CF$_3$ refers to the mutually trans-standing CF$_3$ groups, whereas CF$_3$–Ag–X refers to the CF$_3$ group trans to the anionic X ligand. Multiplicity is indicated as follows: s = singlet, d = doublet, q = quartet, spt = septet, m = multiplet. Standard mass spectra (MS) were registered using negative electrospray ionization (ESI) on Bruker Esquire3000 plus and Bruker MicroTOF-Q spectrometers. Thermogravimetric and differential thermal analyses (TGA/DTA) were performed using a SDT 2960 instrument at a heating rate of 10 °C min$^{-1}$ under N$_2$ atmosphere.

**Caution!** Although we have not encountered any problems working under the conditions detailed below (synthesis of 7), metal azides are potentially explosive, especially by percussion and heating, but sometimes for no obvious reason. Consequently, only small amounts of these materials should be prepared and they should always be handled with great caution.

**Synthesis of [PPh$_4$][CF$_3$$_2$AgF] (1):** A mixture of compound 2 (100 mg, 0.14 mmol) and AgF (109 mg, 0.86 mmol) in dry CH$_3$CN (10 cm$^3$) was stirred in the dark in a quartz Schlenk tube at room temperature for 1 h. The resulting suspension was
Concentrated to dryness and the residue was extracted in CH$_2$Cl$_2$ (3 × 5 cm$^3$) at −78 °C. The colorless filtrate was concentrated and precipitated with dry Et$_2$O (10 cm$^3$) always at −78 °C. A white solid was obtained, which was identified as compound 1 (55 mg, 0.08 mmol, 57% yield).

**IR** (Figure S1): $\tilde{v}$/cm$^{-1}$ = 3063 (w), 3025 (w) 1588 (w), 1487 (m), 1437 (s), 1339 (w), 1191 (w), 1166 (w), 1145 (s), 1107 (s), 1053 (vs), 996 (s), 846 (w), 752 (s), 720 (vs), 616 (w), 524 (vs), 492 (vs; Ag–F), 432 (m), 310 (m).

**19F NMR** (282.231 MHz, CD$_2$Cl$_2$, 193 K; Figure S7): $\delta$/ppm = −24.43 (dm, 3F, 2$^3$J$^{({^{109}}Ag,F)}$ = 75.0 Hz, 3$^2$J(F,F) = 53.7 Hz, 4$^2$J(F,F) = 7.4 Hz; CF$_3$–Ag–F), −37.60 (dq, 6F, 2$^3$J$^{({^{109}}Ag,F)}$ = 29.0 Hz, 2$^3$J(F,F) = 15.0 Hz, 4$^2$J(F,F) = 7.4 Hz; CF$_3$–Ag–CF$_3$), −236.22 (m, 1F, 1$^3$J$^{({^{109}}Ag,F)}$ = 69.9 Hz; Ag–F); the spectrum is simulated in Figure S8.

**MS** (ESI−): m/z = 333 [(CF$_3$)$_3$AgF]$^−$. **Elemental analysis** calcd (%) for C$_{27}$H$_{20}$AgF$_{10}$P: C 48.2, H 3.0; found: C 48.1, H 3.3.

**Synthesis of [PPh$_4$][(CF$_3$)$_3$AgCl] (2):** Portions of PhICl$_2$ (104 mg, 0.41 mmol) were added gradually to a solution of [PPh$_4$][CF$_3$AgCF$_3$] (200 mg, 0.34 mmol) in dry CH$_2$Cl$_2$ (10 cm$^3$) at −55 °C and the mixture was allowed to slowly reach room temperature. The resulting suspension was evaporated to dryness and the residue was extracted in DME (3 × 5 cm$^3$) to remove the [PPh$_4$][AgCl$_2$] salt. After filtration, the solvent in the extract was evaporated to dryness. By treating the resulting residue with Et$_2$O (3 × 5 cm$^3$) and iPrOH (2 × 2 cm$^3$), a pale-yellow solid was obtained, which was identified as compound 2 (119 mg, 0.17 mmol, 75% yield). **IR** (Figure S2): $\tilde{v}$/cm$^{-1}$ = 3060 (w), 1588 (w), 1486 (m), 1436 (s), 1319 (w), 1189 (w), 1164 (w), 1129 (m), 1106 (vs), 1049 (vs), 995 (s), 982 (m), 932 (w), 854 (w), 751 (s), 718 (vs), 687 (vs), 616 (w), 523 (vs), 455 (m), 348 (vs; Ag–Cl), 296 (m). **19F NMR** (282.231 MHz, CD$_2$Cl$_2$, 298 K; Figure S9): $\delta$/ppm = −25.20 (dspt, 3F, 2$^3$J$^{({^{109}}Ag,F)}$ = 72.0 Hz, 4$^2$J(F,F) = 9.0 Hz; CF$_3$–Ag–Cl), −30.20 (dq, 6F, 2$^3$J$^{({^{109}}Ag,F)}$ = 30.4 Hz; CF$_3$–Ag–CF$_3$); the spectrum is simulated in Figure S10. **MS** (ESI−): m/z = 349 [(CF$_3$)$_3$AgCl]$^−$. **Elemental analysis** calcd (%) for C$_{27}$H$_{20}$AgClF$_9$P: C 47.0, H 2.9; found: C 47.3, H 3.2.

**Synthesis of [PPh$_4$][(CF$_3$)$_3$AgBr] (3):** A colourless solution of 1 (50 mg, 0.074 mmol) in MeCN (2 cm$^3$) turned instantly yellow by addition of Me$_3$SiBr (11.6 mm$^3$,
0.089 mmol). After 5 min of stirring in the dark, the reaction medium was concentrated to dryness. By treating the resulting residue with Et₂O (3 cm³), a yellow solid was obtained, which was identified as compound 3 (35 mg, 0.048mmol, 75% yield). IR (Figure S3): ̃ν/cm⁻¹ = 3059 (w), 2921 (w), 1588 (w), 1485 (m), 1436 (s), 1341 (w), 1191 (w), 1163 (w), 1124 (m), 1044 (vs), 995 (s), 849 (w), 750 (s), 718 (vs), 687 (vs), 522 (vs), 454 (m), 313 (m), 293 (s).

19F NMR (282.231 MHz, CD₂Cl₂, 253K; Figure S11): δF /ppm = −26.20 [dm, 3F, 2J¹⁰⁹Ag,F] = 7.15 Hz, 4J(F,F) = 8.6 Hz; CF₃–Ag–Br], −28.39 [dm, 3F, 2J¹⁰⁹Ag,F] = 67.0 Hz; CF₃–Ag–CF₃; the spectrum is simulated in Figure S12. MS (ESI−): m/z = 393 [(CF₃)₃AgBr]. Elemental analysis calcd (%) for C₂₇H₂₀AgBrF₉P: C 44.2, H 2.75; found: C 44.5, H 3.1.

Synthesis of [PPh₄][CF₃₃AgI] (4): A colourless solution of 1 (50 mg, 0.074 mmol) in CH₂Cl₂ (2 cm³) at −78 °C turned instantly orange by addition of Me₃SiI (12.6 mm³, 0.089 mmol). After 5 min of stirring in the dark, the reaction medium was concentrated to dryness. By treating the resulting residue with Et₂O (20 cm³), an orange solid was obtained, which was identified as compound 4 (18.49 mg, 0.023mmol, 32% yield). IR (Figure S4): ̃ν/cm⁻¹ = 3057 (w), 2923 (w), 1588 (w), 1484 (m), 1435 (s), 1340 (w), 1191 (w), 1162 (w), 1108 (m), 1041 (vs), 994 (s), 847 (w), 750 (s), 720 (vs), 687 (vs), 615 (w), 523 (vs), 452 (w), 287 (m). 19F NMR (282.231 MHz, CD₂Cl₂, 253 K; Figure S13): δF /ppm = −20.20 [ dq, 6F, 2J¹⁰⁹Ag,F] = 34.0 Hz, 4J(F,F) = 8.7 Hz; CF₃–Ag–CF₃, −28.39 [dm, 3F, 2J¹⁰⁹Ag,F] = 67.0 Hz; CF₃–Ag–I ; the spectrum is simulated in Figure S14. MS (ESI−): m/z = 441 [(CF₃)₃AgI]. Elemental analysis calcd (%) for C₂₇H₂₀AgBrF₉P: C 41.5, H 2.6; found: C 42.1, H 3.0.

Synthesis of [PPh₄][(CF₃)₃AgCN] (6): Me₃SiCN (11.1 mm³, 0.089 mmol) was added to a solution of compound 1 (50 mg, 0.074 mmol) in MeCN (2 cm³). After 5 min of stirring in the dark, the reaction medium was concentrated to dryness. By treating the resulting residue with Et₂O (3 cm³), a white solid was obtained, which was identified as compound 6 (37 mg, 0.054mmol, 74% yield). IR (Figure S5): ̃ν/cm⁻¹ = 3063 (w), 3025

−S3−
(w), 1588 (w), 1486 (m), 1436 (s), 1341 (w), 1190 (w), 1163 (w), 1136 (s), 1108 (s), 1052 (vs), 996 (s), 888 (vs), 616 (w), 524 (vs), 407 (m), 292 (m).

$^{19}$F NMR (282.231 MHz, CD$_2$Cl$_2$, 298K; Figure S15): $\delta_F$/ppm = $-25.60$ [dq, 6F, $^2J(^{109}\text{Ag,F}) = 36.4$ Hz, $^4J(F,F) = 7.2$ Hz; CF$_3$–Ag–CF$_3$], $-30.40$ [dq, 3F, $^2J(^{109}\text{Ag,F}) = 55.0$ Hz; CF$_3$–Ag–CN]; the spectrum is simulated in Figure S16. MS (ESI–): $m/z$ = 340 [(CF$_3)_3\text{AgCN}]^{-}$. Elemental analysis calcd (%) for C$_{28}$H$_{20}$AgNF$_9$P: C 49.4, H 3.0, N 2.1; found: C 49.7, H 3.4, N 2.45.

Synthesis of [PPh$_4$][(CF$_3$)$_3\text{AgN}_3$] (7): A colourless solution of compound 1 (50 mg, 0.074 mmol) in dry MeCN (2 cm$^3$) turned instantly yellow upon addition of Me$_3$SiN$_3$ (11.7 mm$^3$, 0.089 mmol). After 5 min. of stirring in the dark, the reaction medium was concentrated to dryness and the residue was treated with dry Et$_2$O (3 cm$^3$). A yellow solid was obtained, which was identified as compound 7 (32 mg, 0.52mmol, 65% yield). IR (Figure S6): $\tilde{\nu}$/cm$^{-1}$ = 3061 (w), 2042 (vs, $\nu_a$(NNN) mode), 1585 (w), 1484 (m), 1436 (s), 1339 (w) 1316 (w), 1190 (w), 1165 (w), 1126 (m), 1107 (s), 1057 (vs), 995 (s), 849 (w), 754 (s), 721 (vs), 689 (vs), 615 (w), 523(vs), 452 (w), 396 (m, Ag–N), 305(m). $^{19}$F NMR (282.231 MHz, CD$_2$Cl$_2$, 298K; Figure S17): $\delta_F$/ppm = $-25.76$ [dm, 3F, $^2J(^{109}\text{Ag,F}) = 66.0$ Hz, $^4J(F,F) = 8.2$ Hz; CF$_3$–Ag–N$_3$], $-35.02$ [dq, 6F, $^2J(^{109}\text{Ag,F}) = 31.5$ Hz; CF$_3$–Ag–CF$_3$]; the spectrum is simulated in Figure S18. MS (ESI–): $m/z$ = 356 [(CF$_3$)$_3\text{AgN}_3$]$^{-}$. Elemental analysis calcd (%) for C$_{27}$H$_{20}$AgF$_3$N$_3$P: C 46.6, H 2.9, N 6.0; found: C 46.9, H 3.0, N 6.1.

Multistage Mass Spectrometry (MS$^n$): ESI MS$^n$ spectra were performed in negative ion mode. Sample solutions (5 ppm) were transferred into the ESI source by means of a syringe pump at a flow rate of 4 mm$^3$ min$^{-1}$. Ion-trap MS$^n$ were recorded on a Bruker Esquire 3000+ spectrometer (Bruker Daltonics) with Smart Parameter Settings optimized for each $m/z$ value. The nebulizer (N$_2$) gas pressure, drying gas (N$_2$) flow rate and drying gas temperature were kept at 0.7 bar, 4.0 dm$^3$ min$^{-1}$ and 350 °C, respectively. Spectra were acquired in the $m/z$ 50–1000 range, and the mass axis was
externally calibrated with a tuning mix (from Agilent Technologies). ESI-CID-MS\textsuperscript{n} analyses were carried out using He as the collision gas, an optimal amplitude voltage of 1.9 V and an isolation width for the precursor ion of 5 \textit{m/z} units. The obtained spectra are shown in Figures S19–S30. \textbf{Q-TOF MS}\textsuperscript{n} were recorded on a Bruker MicroTOF-Q Spectrometer (Bruker Daltonics). The nebulizer (N\textsubscript{2}) gas pressure, drying gas (N\textsubscript{2}) flow rate and drying gas temperature were kept at 0.4 bar, 4.0 dm\textsuperscript{3} min\textsuperscript{-1} and 180 °C, respectively. ESI-CID-MS\textsuperscript{n} analyses were carried out using N\textsubscript{2} as the collision gas, 15 eV collision energy and an isolation width for the precursor ion of 5 \textit{m/z} units.
2. IR Spectra

Figure S1. IR spectrum of a powder sample of 1 registered on an ATR device.

Figure S2. IR spectrum of a powder sample of 2 registered on an ATR device.
Figure S3. IR spectrum of a powder sample of 3 registered on an ATR device.

Figure S4. IR spectrum of a powder sample of 4 registered on an ATR device.
Figure S5. IR spectrum of a powder sample of 6 registered on an ATR device.

Figure S6. IR spectrum of a powder sample of 7 registered on an ATR device.
Figure S7. $^{19}$F NMR spectrum (282.231 MHz) of compound 1 in CD$_2$Cl$_2$ solution at 193 K. The observed signals are satisfactorily simulated (Figure S8) with the parameters given in Table S1. Some hydrolysis (ca. 8% here) could not be avoided (minor signals).
Table S1. Coupling constants [Hz] used for the analysis of the $^{19}$F NMR spectrum of compound 1 as shown in Figure S8.$^a$

|          | F   | CF$_3$ | CF$_3$ | $^{107}/^{109}$Ag |
|----------|-----|--------|--------|-------------------|
| F        |     |        | 54.1   |                   |
| CF$_3$   | 15.0| 7.4    |        |                   |
| $^{107}/^{109}$Ag | 60.8/69.9 | 65.2/75.0 | 25.2/29.0 |

$^a$ Labeling color code as in Figure S7.

Figure S8. Experimental (gray traces) and simulated (green traces; linewidth: 2.6 Hz CF$_3$ and 3.5 Hz Ag–F) $^{19}$F NMR spectra (282.231 MHz) of compound 2 in CD$_2$Cl$_2$ solution at 193 K. Full spectrum is shown in Figure S7. The parameters used in the simulation are given in Table S1.
Figure S9. $^{19}$F NMR spectrum (282.231 MHz) of [PPh₄][(CF₃)₃AgCl] (2) in CD₂Cl₂ solution at room temperature. The observed signals are satisfactorily simulated (Figure S10) with the parameters given in Table S2.
Table S2. Coupling constants [Hz] used for the analysis of the $^{19}$F NMR spectrum of compound 2 as shown in Figure S10.$^a$

|        | CF$_3$ | CF$_3$ | CF$_3$ | CF$_3$ | $^{107}/^{109}$ Ag |
|--------|--------|--------|--------|--------|-------------------|
| CF$_3$ | —      | —      | —      | 9.0    | 62.4 / 72.0       |
| CF$_3$ | 9.0    | —      | 107 / 109 Ag | 26.6 / 30.4 | —    |

$^a$ Labeling color code as in Figure S9.

Figure S10. Experimental (gray traces) and simulated (with 1.3 Hz linewidth; yellow traces) $^{19}$F NMR spectra (282.231 MHz) of compound 2 in CD$_2$Cl$_2$ solution at 298 K. The parameters used in the simulation are given in Table S2. Full spectrum is shown in Figure S9.
Figure S11. $^{19}$F NMR spectrum (282.231 MHz) of [PPh$_4$][(CF$_3$)$_3$AgBr] (3) in CD$_2$Cl$_2$ solution at room temperature. The observed signals are satisfactorily simulated (Figure S12) with the parameters given in Table S3.
Table S3. Coupling constants [Hz] used for the analysis of the $^{19}\text{F}$ NMR spectrum of compound 3 as shown in Figure S12.$^a$

|        | CF$_3$ | CF$_3$ | CF$_3$ | CF$_3$ | $^{107}/^{109}\text{Ag}$ |
|--------|--------|--------|--------|--------|--------------------------|
| CF$_3$ | —      | —      | 8.6    | —      | $^{107}/^{109}\text{Ag}$ |
| $^{107}/^{109}\text{Ag}$ | 62.2 / 71.5 | 27.0 / 31.0 | —      | —      |

$^a$ Labeling color code as in Figure S11.

Figure S12. Experimental (gray traces) and simulated (with 3.8 Hz linewidth; orange traces) $^{19}\text{F}$ NMR spectra (282.231 MHz) of compound 3 in CD$_2$Cl$_2$ solution at 298 K. The parameters used in the simulation are given in Table S3. Full spectrum is shown in Figure S11.
Figure S13. $^{19}$F NMR spectrum (282.231 MHz) of [PPh$_4$][(CF$_3$)$_3$AgI] (4) in CD$_2$Cl$_2$ solution at room temperature. The observed signals are satisfactorily simulated (Figure S14) with the parameters given in Table S4.
Table S4. Coupling constants [Hz] used for the analysis of the $^{19}$F NMR spectrum of compound 4 as shown in Figure S14.\(^a\)

|          | CF\(_3\) | CF\(_3\) | CF\(_3\) | 107/109 Ag |
|----------|----------|----------|----------|------------|
| CF\(_3\) | —        | 8.7      | —        | 58.3 / 67.0 |
| CF\(_3\) | 8.7      | —        | 107/109 Ag | 29.6 / 34.0 |
| 107/109 Ag | 58.3 / 67.0 | 29.6 / 34.0 | —       |

\(^a\) Labeling color code as in Figure S13.

Figure S14. Experimental (gray traces) and simulated (with 4.5 Hz linewidth; violet traces) $^{19}$F NMR spectra (282.231 MHz) of compound 4 in CD\(_2\)Cl\(_2\) solution at 298 K. The parameters used in the simulation are given in Table S4. Full spectrum is shown in Figure S13.
Figure S15. $^{19}$F NMR spectrum (282.231 MHz) of [PPh$_4$][(CF$_3$)$_3$AgCN] (6) in CD$_2$Cl$_2$ solution at room temperature. The observed signals are satisfactorily simulated (Figure S16) with the parameters given in Table S5.
**Table S5.** Coupling constants [Hz] used for the analysis of the $^{19}$F NMR spectrum of compound 6 as shown in Figure S16.$^a$

|          | CF$_3$          | CF$_3$          | CF$_3$          | 107 / 109 Ag |
|----------|-----------------|-----------------|-----------------|--------------|
| CF$_3$   | —               | CF$_3$          | 7.2             |              |
| 107 / 109 Ag | 47.8 / 55.0 | 31.7 / 36.4     | —               |              |

$^a$ Labeling color code as in Figure S15.

**Figure S16.** Experimental (gray traces) and simulated (with 1.5 Hz linewidth; red traces) $^{19}$F NMR spectra (282.231 MHz) of compound 6 in CD$_2$Cl$_2$ solution at 298 K. The parameters used in the simulation are given in Table S5. Full spectrum is shown in Figure S15.
Figure S17. $^{19}\text{F}$ NMR spectrum (282.231 MHz) of [PPh$_4$][(CF$_3$)$_3$AgN$_3$] (7) in CD$_2$Cl$_2$ solution at room temperature. The observed signals are satisfactorily simulated (Figure S18) with the parameters given in Table S6.
Table S6. Coupling constants [Hz] used for the analysis of the $^{19}$F NMR spectrum of compound 7 as shown in Figure S18.$^a$

|                | CF$_3$ | CF$_3$ | CF$_3$ | CF$_3$ | 107/109 Ag |
|----------------|--------|--------|--------|--------|------------|
| CF$_3$         | 8.2    | 107/109 Ag |
| 107/109 Ag     | 57.4/66.0 | 27.4/31.5 | —      |

$^a$ Labeling color code as in Figure S17.

Figure S18. Experimental (gray traces) and simulated (with 1.0 Hz linewidth; blue traces) $^{19}$F NMR spectra (282.231 MHz) of compound 7 in CD$_2$Cl$_2$ solution at 298 K. The parameters used in the simulation are given in Table S6. Full spectrum is shown in Figure S17.
4. Multistage Mass Spectrometry (MS\textsuperscript{n})

Figure S19. Quadrupole ion-trap MS\textsuperscript{2} results of the collision-induced dissociation (CID) of the organosilver(III) fluoride complex anion \([\text{[CF}_3\text{AgF]}^-\text{] in 1 showing the typical double-peak pattern.}\textsuperscript{[S5]}

Figure S20. Quadrupole ion-trap MS\textsuperscript{2} results of the collision-induced dissociation (CID) of the organosilver(III) chloride complex anion \([\text{[CF}_3\text{AgCl]}^-\text{] in 2 showing the typical double-peak pattern.}\textsuperscript{[S5]}

Figure S21. Quadrupole ion-trap MS² results of the collision-induced dissociation (CID) of the organosilver(III) bromide complex anion \([\text{[CF}_3\text{AgBr]}^-\] in 3 showing the typical double-peak pattern.\[^{S5}\]

Figure S22. Quadrupole ion-trap MS² results of the collision-induced dissociation (CID) of the organosilver(III) iodide complex anion \([\text{[CF}_3\text{AgI]}^-\] in 4 showing the typical double-peak pattern.\[^{S5}\]
Figure S23. Quadrupole ion-trap MS² results of the collision-induced dissociation (CID) of the organosilver(II) cyanide complex anion \[(\text{CF}_3)_3\text{AgCN}^-\] in 6 showing the typical double-peak pattern.\(^{[55]}\)

Figure S24. Quadrupole ion-trap MS² results of the collision-induced dissociation (CID) of the organosilver(III) azide complex anion \[(\text{CF}_3)_3\text{AgN}_3^-\] in 7 showing the typical double-peak pattern.\(^{[55]}\)
**Figure S25.** Quadrupole ion-trap MS$^3$ results of the collision-induced dissociation (CID) of the organosilver(I) fluoride complex anion [CF$_3$AgF]$^-$ (peak at m/z 195 in Figure S19) showing the typical double-peak pattern.$^{[S5]}$

**Figure S26.** Quadrupole ion-trap MS$^3$ results of the collision-induced dissociation (CID) of the organosilver(I) chloride complex anion [CF$_3$AgCl]$^-$ (peak at m/z 211 in Figure S20) showing the typical double-peak pattern.$^{[S5]}$
Figure S27. Quadrupole ion-trap MS$^3$ results of the collision-induced dissociation (CID) of the organosilver(I) bromide complex anion [CF$_3$AgBr]$^-$ (peak at m/z 255 in Figure S21) showing the typical double-peak pattern.$^{[85]}$

Figure S28. Quadrupole ion-trap MS$^3$ results of the collision-induced dissociation (CID) of the organosilver(I) iodide complex anion [CF$_3$AgI]$^-$ (peak at m/z 303 in Figure S22) showing the typical double-peak pattern.$^{[85]}$
Figure S29. Quadrupole ion-trap MS$^3$ results of the collision-induced dissociation (CID) of the organosilver(I) cyanide complex anion [CF$_3$AgCN]$^-$ (peak at $m/z$ 202 in Figure S23) showing the typical double-peak pattern.$^{[55]}$

Figure S30. Quadrupole ion-trap MS$^3$ results of the collision-induced dissociation (CID) of the organosilver(I) azide complex anion [CF$_3$AgN$_3$]$^-$ (peak at $m/z$ 218 in Figure S24) showing the typical double-peak pattern.$^{[55]}$
5. TGA/DTA Measurements

**Figure S31.** TGA (green trace, vertical scale on the left) and DTA (blue trace, vertical scale on the right) of compound 1 recorded on heating at 10 °C min$^{-1}$. The final residue (24.9%) is appreciably higher than the theoretical silver content (16.0%).

**Figure S32.** TGA (green trace, vertical scale on the left) and DTA (blue trace, vertical scale on the right) of compound 2 recorded on heating at 10 °C min$^{-1}$. The final residue (9.6%) is appreciably lower than the theoretical silver content (15.6%).
Figure S33. TGA (green trace, vertical scale on the left) and DTA (blue trace, vertical scale on the right) of compound 3 recorded on heating at 10 °C min\(^{-1}\). The final residue (10.6%) is appreciably lower than the theoretical silver content (14.6%).

Figure S34. TGA (green trace, vertical scale on the left) and DTA (blue trace, vertical scale on the right) of compound 4 recorded on heating at 10 °C min\(^{-1}\). The final residue (35.4%) is appreciably higher than the theoretical silver content (13.8%).
Figure S35. TGA (green trace, vertical scale on the left) and DTA (blue trace, vertical scale on the right) of compound 6 recorded on heating at 10 °C min$^{-1}$. The final residue (17.3%) nicely approaches to the theoretical silver content (15.8%).

Figure S36. TGA (green trace, vertical scale on the left) and DTA (blue trace, vertical scale on the right) of compound 7 recorded on heating at 10 °C min$^{-1}$. The final residue (29.1%) is appreciably higher than the theoretical silver content (15.5%).
6. Thermolytic Results in the Condensed Phase

**General Procedure:** Each sample (10 mg) was sealed in a glass tube under an inert atmosphere (Ar) and heated for a few minutes at a temperature near that corresponding to the onset of decomposition (TGA/DTA). The soluble fluorinated species were identified by $^{19}$F NMR spectroscopy (Figures S37–S42) with the aid of MS. Full details and individual results are given below.

**Thermolysis of 1:** Heating a 10 mg sample of compound 1 at 140 °C during 2 min rendered a brown residue, which contained some metallic silver and a number of soluble fluorinated species identified as follows (cf. Figure S37). $^{19}$F NMR (282.231 MHz, CD$_2$Cl$_2$): $\delta_F$/ppm = $-32.03$ (dd, $^2J^{^{107/109}Ag,^{19}F} = 35.3/40.9$ Hz; [(CF$_3$)$_4$Ag]),$^{[S1]}$ $-63.2$ to $-64.2$ (several singlets corresponding to trifluoromethylation of the cation at one or two positions of the Ph rings),$^{[S6]}$ $-78.44$ (d, $^2J^{^{1}H,^{19}F} = 79.3$ Hz; CF$_3$H).$^{[S7]}

![Figure S37. $^{19}$F NMR spectrum (282.231 MHz, CD$_2$Cl$_2$) of the residue obtained upon thermolysis of 1 at 140 °C for 2 min. Further details are given in the text.](image-url)
Thermolysis of 2: Heating a 10 mg sample of compound 2 at 135 °C during 2 min rendered a brown residue, which contained some metallic silver and a number of soluble fluorinated species identified as follows (cf. Figure S38). $^{19}$F NMR (282.231 MHz, CD$_2$Cl$_2$): $\delta_F$/pm = −22.0 (dd, $^2J^{107/109}\text{Ag,}^{19}\text{F}$) = 107.6/124.0 Hz; [CF$_3$AgCl$^-$], −26.0 (s; CF$_3$Cl), −32.20 (dd, $^2J^{107/109}\text{Ag,}^{19}\text{F}$) = 35.3/40.9 Hz; [(CF$_3$)$_4$Ag]$^-$) $^{[S1]}$ −63.2 to −64.2 (several singlets corresponding to trifluoromethylation of the cation at one or two positions of the Ph rings), $^{[S6]}$ −78.44 (d, $^2J^1\text{H,}^{19}\text{F}$) = 79.3 Hz; CF$_3$H).$^{[S7]}$

![Figure S38. $^{19}$F NMR spectrum (282.231 MHz, CD$_2$Cl$_2$) of the residue obtained upon thermolysis of 2 at 135 °C for 2 min. Further details are given in the text.](image)
Thermolysis of 3: Heating a 10 mg sample of compound 3 at 130 °C during 2 min rendered a brown residue, which contained some metallic silver and a number of soluble fluorinated species identified as follows (cf. Figure S39). $^{19}$F NMR (282.231 MHz, CD$_2$Cl$_2$): $\delta_{F}$/pm = -18.0 (s; CF$_3$Br), -32.2 (dd, $^2J(^{107/109}$Ag,$^{19}$F) = 35.3/40.9 Hz; [(CF$_3$)$_4$Ag]),[S1] -63.2 to -64.2 (several singlets corresponding to trifluoromethylation of the cation at one or two positions of the Ph rings),[S6] -78.44 (d, $^2J(^1$H,$^{19}$F) = 79.3 Hz; CF$_3$H).[S7]

Figure S39. $^{19}$F NMR spectrum (282.231 MHz, CD$_2$Cl$_2$) of the residue obtained upon thermolysis of 3 at 130 °C for 2 min. Further details are given in the text.
Thermolysis of 4: Heating a 10 mg sample of compound 4 at 75 °C during 2 min rendered a white residue, which contained a number of soluble fluorinated species identified as follows (cf. Figure S40). $^{19}$F NMR (282.231 MHz, CD$_2$Cl$_2$): $\delta_{F}$/pm = $-5.92$ (s; CF$_3$I), $-23.94$ (dd, $^2J(^{107/109}$Ag, $^{19}$F) = 100.4/116.5 Hz; [CF$_3$AgI] $)$, $-25.50$ (dd, $^2J(^{107/109}$Ag, $^{19}$F) = 87.4/100.7 Hz; [CF$_3$AgCF$_3$]$^-$, $^{[S1]}$ $-32.20$ (dd, $^2J(^{107/109}$Ag, $^{19}$F) = 35.3/40.9 Hz; [(CF$_3$)$_4$Ag]$^-$, $^{[S1]}$ $-78.44$ (d, $^2J(^1$H, $^{19}$F) = 79.3 Hz; CF$_3$H).$^{[S7]}

Figure S40. $^{19}$F NMR spectrum (282.231 MHz, CD$_2$Cl$_2$) of the residue obtained upon thermolysis of 4 at 75 °C for 2 min. Further details are given in the text.
Thermolysis of 6: Heating a 10 mg sample of compound 6 at 140 °C during 2 min rendered a white residue, which contained a number of soluble fluorinated species identified as follows (cf. Figure S41). $^{19}$F NMR (282.231 MHz, CD$_2$Cl$_2$): $\delta_F$/pm = −25.60 (ddq, $^2J$(^{107/109}Ag, $^{19}$F) = 31.7/36.4 Hz, $^4J$(^{19}$F, $^{19}$F) = 7.2 Hz; undecomposed 6), −30.40 (ddspt, $^2J$(^{107/109}Ag, $^{19}$F) = 47.8/55.0 Hz; undecomposed 6), −32.20 (dd, $^2J$(^{107/109}Ag, $^{19}$F) = 35.3/40.9 Hz; [(CF$_3$)$_4$Ag]$^-$,[S1] −63.2 to −64.2 (several singlets corresponding to trifluoromethylation of the cation at one or two positions of the Ph rings),[S6] −78.44 (d, $^2J$(^1$H$, $^{19}$F) = 79.3 Hz; CF$_3$H).[S7]

Figure S41. $^{19}$F NMR spectrum (282.231 MHz, CD$_2$Cl$_2$) of the residue obtained upon thermolysis of 6 at 140 °C for 2 min. Further details are given in the text.
**Thermolysis of 7:** Heating a 10 mg sample of compound 7 at 88 °C during 2 min rendered a white residue, which contained a number of soluble fluorinated species identified as follows (cf. Figure S42). \( ^{19}\text{F NMR (282.231 MHz, CD}_2\text{Cl}_2): \delta \text{F/} \text{pm} = -25.80 \text{ (ddspt, } 2J(107/109\text{Ag,}^{19}\text{F}) = 57.4/66.0 \text{ Hz, } 4J(19\text{F,}^{19}\text{F}) = 8.2 \text{ Hz; undecomposed 7),} \)

\[-32.20 \text{ (dd, } 2J(107/109\text{Ag,}^{19}\text{F}) = 35.3/40.9 \text{ Hz; } [(\text{CF}_3)\text{Ag}]^-), \]^{[S1]} \[-35.05 \text{ (ddq, } 2J(107/109\text{Ag,}^{19}\text{F}) = 27.4/31.5 \text{ Hz; undecomposed 7),} \]

\[-63.2 \text{ to } -64.2 \text{ (several singlets corresponding to trifluoromethylation of the cation at one or two positions of the Ph rings),} \]^{[S6]} \[-78.44 \text{ (d, } 2J(1\text{H,}^{19}\text{F}) = 79.3 \text{ Hz; CF}_3\text{H).} \]^{[S7]}

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**Figure S42.** \( ^{19}\text{F NMR spectrum (282.231 MHz, CD}_2\text{Cl}_2) \) of the residue obtained upon thermolysis of 7 at 88 °C for 2 min. Further details are given in the text.
Quantum mechanical calculations were performed with the Gaussian09 package\cite{S8} at the DFT/M06\cite{S9} level of theory with an ultrafine grid option. All atoms (C, N, F, Cl, Br, I, At, and Ag) were described using Ahlrichs’ Def2-TZVPD, a Triple-Zeta-Valence basis set including Polarization and Diffuse basis functions\cite{S10}, as obtained from the Basis Set Exchange webpage\cite{S11}. The potential energy surfaces (PES) of the studied complexes and of the species involved in their fragmentation processes have been examined at this level of theory and their geometries have been optimized in the gas phase with no symmetry restrictions. Frequency calculations have been performed in all the collected stationary points in order to check their nature of either minima or transition states. The optimized structures obtained for the square-planar (d^8) complexes [(CF_3)_3AgX]^− are shown in Figures S43 and S44, and those corresponding to the linear (d^{10}) complexes [CF_3AgX]^− and [FAgX]^− are shown in Figure 7. Atomic coordinates for all the optimized structures are given in a separate .xyz file. Topological analyses of the electron density distribution functions ρ(r) were performed for complexes 1–7 by using the AIMAll program package\cite{S12}, based on the extended wave function obtained by M06 calculations. The topological features of especially relevant critical points (CP) are given in Table 2. Important cross sections in the contour-line ∇^2ρ(r) maps are shown in Figures S45 and S46. Electronic structures and molecular orbital compositions for the halide complexes 1–5 were analyzed by using Chemissian software\cite{13}. The results are shown in Figures S47 and S48 with an abridged version given in Figure 6.
Figure S43. Optimized geometry of the \([(\text{CF}_3)_3\text{AgX}]^–\) anions (X = F, Cl, Br, I, At) in the gas phase calculated at the DFT/M06/Def2-TZVPD level. Calculated Ag–C and Ag–X bond distances [pm] are indicated. The atomic coordinates of each species are given in a separate .xyz file. In the case of the fluoro-complex \([(\text{CF}_3)_3\text{AgF}]^–\), our results compare well with previous calculations by Preiss and Krossing.\(^{[S14]}\)
Figure S44. Optimized geometry of the anions [(CF$_3$)$_3$AgCN]$^-$ (6, left) and [(CF$_3$)$_3$AgN$_3$]$^-$ (7, right) in the gas phase calculated at the DFT/M06/Def2-TZVPD level. Calculated Ag–E bond distances [pm] are indicated. The atomic coordinates of each species are given in a separate .xyz file.
Figure S45. 2D contour-line $\nabla^2 \rho (r)$ diagrams obtained from QTAIM analysis of the optimized [(CF$_3$)$_3$AgX]$^-$ anions 1–5. Cross sections contain the metal coordination plane. Bond critical points (orange spheres) and bond paths (black straight lines) as obtained using non-CP threshold of 0.02.
**Figure S46.** 2D contour-line $\nabla^2 \rho(\mathbf{r})$ diagrams obtained from QTAIM analysis of the optimized anions $[(\text{CF}_3)_3\text{AgCN}]^-(6, \text{left})$ and $[(\text{CF}_3)_3\text{AgN}_3]^- (7, \text{right})$. Cross sections contain the metal coordination plane. Bond critical points (orange spheres) and bond paths (black straight lines) are shown as obtained using non-CP threshold of 0.02.
Figure S47. Energy levels of the frontier orbitals and near lower MO's of the organosilver(III) halide complexes $[(CF_3)_3AgX]^- (X = F, Cl, Br, I, At)$ obtained at DFT/M06 level of theory. An abridged version is shown in Figure 6a.
**Figure S48.** Contour isosurfaces (isovalue: 0.02) of the frontier orbitals and near lower MO's of the organosilver(III) halide complexes $[(\text{CF}_3)_3\text{AgX}]^-$ ($X = \text{F, Cl, Br, I, At}$) obtained at DFT/M06 level of theory. An abridged version is shown in Figure 6b.
Scheme S1. Energy profiles ($\Delta G$ in kcal mol$^{-1}$) calculated at the DFT/M06/TZVPD level for various fragmentation paths, that might be held possible for the $[(\text{CF}_3)_3\text{AgF}]^-$ anion based on our experimental results (Figures S19 and S25). Both primary and secondary dissociation paths are considered. An abridged version is outlined in Scheme 4. The most relevant energy values are given and compared in Table 3.
Scheme S2. Energy profiles ($\Delta G$ in kcal mol$^{-1}$) calculated at the DFT/M06/TZVPD level for various fragmentation paths, that might be held possible for the [(CF$_3$)$_3$AgCl]$^-$ anion based on our experimental results (Figures S20 and S26). Both primary and secondary dissociation paths are considered. An abridged version is outlined in Scheme 4. The most relevant energy values are given and compared in Table 3.
Scheme S3. Energy profiles ($\Delta G$ in kcal mol$^{-1}$) calculated at the DFT/M06/TZVPD level for various fragmentation paths, that might be held possible for the [(CF$_3$)$_3$AgBr]$^-$ anion based on our experimental results (Figures S21 and S27). Both primary and secondary dissociation paths are considered. An abridged version is outlined in Scheme 4. The most relevant energy values are given and compared in Table 3.
Scheme S4. Energy profiles (ΔG in kcal mol$^{-1}$) calculated at the DFT/M06/TZVPD level for various fragmentation paths, that might be held possible for the [(CF$_3$)$_3$AgI]$^-$ anion based on our experimental results (Figures S22 and S28). Both primary and secondary dissociation paths are considered. An abridged version is outlined in Scheme 4. The most relevant energy values are given and compared in Table 3.
Scheme S5. Energy profiles ($\Delta G$ in kcal mol$^{-1}$) calculated at the DFT/M06/TZVPD level for various fragmentation paths, that might be held possible for the [(CF$_3$)$_3$AgAt]$^-$ anion. Both primary and secondary dissociation paths are considered. An abridged version is outlined in Scheme 4. The most relevant energy values are given and compared in Table 3.
Scheme S6. Energy profiles ($\Delta G$ in kcal mol$^{-1}$) calculated at the DFT/M06/TZVPD level for various fragmentation paths, that might be held possible for the [(CF$_3$)$_3$AgCN]$^-$ anion based on our experimental results (Figures S23 and S29). Both primary and secondary dissociation paths are considered. An abridged version is outlined in Scheme 4.
Scheme S7. Energy profiles ($\Delta G$ in kcal mol$^{-1}$) calculated at the DFT/M06/TZVPD level for various fragmentation paths, that might be held possible for the [(CF$_3$)$_3$AgN$_3$]$^-$ anion based on our experimental results (Figures S24 and S30). Both primary and secondary dissociation paths are considered. An abridged version is outlined in Scheme 4.
8. Crystal Data and Structure Refinement

Crystal data and other details of the XRD analysis are presented in Tables S7–S10. Suitable crystals were obtained at −30 °C by slow diffusion of a Et₂O layer (8 cm³) into concentrated solutions of the corresponding complex (~15 mg) in CH₂Cl₂ (1.5 cm³). Crystals were mounted at the end of quartz fibres. Intensity data were collected on a Bruker Apex Duo CCD diffractometer or on a Rigaku/OD Xcalibur CCD diffractometer. The radiation used in all cases was graphite monochromated Mo-Kα (λ = 71.073 pm). The diffraction frames were integrated and corrected for absorption using SAINT together with SADABS, or using CrysAlis Pro.\[S15\] The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares on \(F^2\) with SHELXL.\[S16\] All non-H atoms were assigned anisotropic displacement parameters and refined without positional constraints, except as noted below. All H atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the \(U_{iso}\) values of their attached parent atoms. For compound 3, the Br atom is slightly disordered over two positions in \(trans\) arrangement and the involved CF₃ group is also disordered. The occupancies of these disordered positions were allowed to refine, giving values of 0.954/0.046. The very low occupancy of the minor CF₃ component together with heavy positional overlapping with the major Br atom hindered the reliable location of the corresponding C atom. Nevertheless, the corresponding F atoms were found in the density maps and refined with a common set of anisotropic thermal parameters. For compound 6, the F atoms of one of the CF₃ groups are disordered over two positions which were refined with 0.57/0.43 occupancy. For compound 7 full-body disorder occurred for the anion as described below; even so, it was possible to refine the structure without the use of constraints or restraints. Full-matrix least-squares refinement of these models against \(F^2\) converged to final residual indices given in Tables S7–S10. Full details of the refinement strategies for all of the analyses can be found in the embedded instruction files in the CIF.
**Table S7.** Crystal data and structure refinement for compound 2

| Property                          | Value                        |
|----------------------------------|------------------------------|
| formula                          | C_{27}H_{20}AgClF_{9}P       |
| \( M_r \) [g mol\(^{-1}\)]      | 689.72                       |
| \( T \) [K]                      | 100(1)                       |
| \( \lambda \) [pm]              | 71.073                       |
| crystal system                   | monoclinic                   |
| space group                      | \( P2_1/c \)                 |
| \( a \) [pm]                     | 1153.19(10)                  |
| \( b \) [pm]                     | 1471.34(13)                  |
| \( c \) [pm]                     | 1614.91(15)                  |
| \( \beta \) [°]                 | 103.624(1)                   |
| \( V \) [nm\(^3\)]              | 2.6630(4)                    |
| \( Z \)                          | 4                            |
| \( \rho \) [g cm\(^{-3}\)]     | 1.720                        |
| \( \mu \) [mm\(^{-1}\)]        | 0.997                        |
| \( F(000) \)                     | 1368                         |
| \( 2\theta \) range [°]         | 3.6–61.2                     |
| no. of reflns colltd             | 30249                        |
| no. of unique reflns             | 7349                         |
| \( R_{int} \)                    | 0.0166                       |
| \( R \) indices \([I > 2\sigma(I)]^a\) |                              |
| \( R_1 \)                        | 0.0220                       |
| \( wR_2 \)                       | 0.0550                       |
| \( R \) indices (all data)       |                              |
| \( R_1 \)                        | 0.0266                       |
| \( wR_2 \)                       | 0.0577                       |
| goodness-of-fit\(^b\) on \( F^2 \)| 1.001                         |
| CCDC no.                         | 2084740                      |

\(^a\) \( R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|; \ wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}. \)

\(^b\) Goodness-of-fit = \([\sum w(F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})]^{1/2}.\)
### Table S8. Crystal data and structure refinement for compound 3

| Property                           | Value                                      |
|------------------------------------|--------------------------------------------|
| formula                           | C_{27}H_{20}AgBrF_{9}P                     |
| $M_r$ [g mol$^{-1}$]               | 734.18                                     |
| $T$ [K]                            | 100(1)                                     |
| $\lambda$ [pm]                    | 71.073                                     |
| crystal system                     | monoclinic                                 |
| space group                        | $P2_1/c$                                   |
| $a$ [pm]                           | 1253.25(12)                                |
| $b$ [pm]                           | 1344.86(13)                                |
| $c$ [pm]                           | 1618.21(15)                                |
| $\beta$ [$^\circ$]                | 101.128(1)                                 |
| $V$ [$\text{nm}^3$]               | 2.6761(4)                                  |
| $Z$                                | 4                                          |
| $\rho$ [g cm$^{-3}$]              | 1.822                                      |
| $\mu$ [mm$^{-1}$]                 | 2.385                                      |
| $F(000)$                           | 1440                                       |
| $2\theta$ range [$^\circ$]        | 3.3–62.2                                   |
| no. of reflns colltd               | 24514                                      |
| no. of unique reflns               | 7957                                       |
| $R_{int}$                          | 0.0125                                     |
| $R$ indices $[I > 2\sigma(I)]^a$  |                                            |
| $R_1$                              | 0.0196                                     |
| $wR_2$                             | 0.0498                                     |
| $R$ indices (all data)             |                                            |
| $R_1$                              | 0.0233                                     |
| $wR_2$                             | 0.0512                                     |
| goodness-of-fit$^b$ on $F^2$       | 1.025                                      |
| CCDC no.                           | 2084741                                    |

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$^a R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|; \ wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$

$^b$ Goodness-of-fit = \left[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})\right]^{1/2}.$
Table S9. Crystal data and structure refinement for compound 6

| parameter | value |
|-----------|-------|
| formula   | C_{28}H_{20}AgF_{9}NP |
| $M_r$ [g mol$^{-1}$] | 680.29 |
| $T$ [K]    | 100(1) |
| $\lambda$ [pm] | 71.073 |
| crystal system | monoclinic |
| space group | $P2_1/c$ |
| $a$ [pm] | 1140.13(11) |
| $b$ [pm] | 1494.15(14) |
| $c$ [pm] | 1658.78(15) |
| $\beta$ [$^\circ$] | 106.037(1) |
| $V$ [nm$^3$] | 2.7158(4) |
| $Z$       | 4 |
| $\rho$ [g cm$^{-3}$] | 1.664 |
| $\mu$ [mm$^{-1}$] | 0.882 |
| $F(000)$  | 1352 |
| 2$\theta$ range [$^\circ$] | 3.7–62.2 |
| no. of reflns colltd | 25338 |
| no. of unique reflns | 8105 |
| $R_{int}$ | 0.0188 |
| $R$ indices [$I > 2\sigma(I)$]$^a$ |
| $R_1$ | 0.0255 |
| $wR_2$ | 0.0612 |
| $R$ indices (all data) |
| $R_1$ | 0.0326 |
| $wR_2$ | 0.0646 |
| goodness-of-fit$^b$ on $F^2$ | 1.029 |
| CCDC no. | 2084742 |

$^a$ $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|;$ $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}.$

$^b$ Goodness-of-fit = $\left[\sum w(F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})\right]^{1/2}.$
Table S10. Crystal data and structure refinement for compound 7

| property                      | value                     |
|-------------------------------|---------------------------|
| formula                      | C$_{27}$H$_{20}$AgF$_9$N$_3$P |
| $M_r$ [g mol$^{-1}$]          | 696.30                    |
| $T$ [K]                      | 100(2)                    |
| $\lambda$ [pm]               | 71.073                    |
| crystal system               | monoclinic                |
| space group                  | $C2/c$                    |
| $a$ [pm]                     | 1633.22(5)                |
| $b$ [pm]                     | 750.32(3)                 |
| $c$ [pm]                     | 2237.21(6)                |
| $\beta$ [°]                  | 106.688(3)                |
| $V$ [nm$^3$]                 | 2.62610(15)               |
| $Z$                           | 4                         |
| $\rho$ [g cm$^{-3}$]         | 1.761                     |
| $\mu$ [mm$^{-1}$]            | 0.916                     |
| $F(000)$                     | 1384                      |
| $2\theta$ range [°]          | 6.0–56.6                  |
| no. of reflns colltd         | 10559                     |
| no. of unique reflns         | 2838                      |
| $R_{int}$                    | 0.0304                    |
| $R$ indices [$I > 2\sigma(I)$]$^a$ |                           |
| $R_1$                        | 0.0294                    |
| $wR_2$                       | 0.0693                    |
| $R$ indices (all data)       |                           |
| $R_1$                        | 0.0360                    |
| $wR_2$                       | 0.0739                    |
| goodness-of-fit$^b$ on $F^2$ | 1.033                     |
| CCDC no.                     | 2084743                   |

$^a R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.  
$^b$ Goodness-of-fit = $[\sum w(F_o^2 - F_c^2)^2 / (n_{obs} - n_{param})]^{1/2}$.  


Comments on the disorder in the crystal structure of 7

The structure is divided into well-defined spaces occupied by the cation \([\text{PPh}_4]^+\) and the anion \([\{(\text{CF}_3)_3\text{Ag(N}_3\}_3^-=\), with little in the way of directional contacts between them (*vide infra*). The crystallographic unit cell contains four formula units of the cation–anion pair; *i.e.*, \(Z = 4\) for \([\text{PPh}_4]((\text{CF}_3)_3\text{Ag(N}_3\)).

The central P atom of the cation lies on a two-fold axis, at \((1/2, y, 1/4)\) for the reference asymmetric unit. Refinement in the centric space group \(C2/c\) requires no disorder for this fragment. The ten unique H atoms of the two unique Ph groups were initially placed at calculated positions with \(d(C-H) = 95\) pm and \(U_{iso}(H) = 1.2U_{eq}(C)\). For the final stages of the refinement the constraints were removed and the H atoms were refined independently, each with its own positional and isotropic displacement parameters.

As the cation conforms, without disorder, to the symmetry of space group \(C2/c\), so also do the boundaries of the voids defined by the peripheries of the packed cations — that is, the voids that contain the anions are subject to interactions with their surroundings that conform to this symmetry. These voids are located around crystallographic inversion centers at \((3/4, 3/4, 1/2)\) for the reference asymmetric unit, and its symmetry relatives. The anion is not, however, centrosymmetric; and thus, some form of disorder can be expected, in the absence of symmetry lowering of the whole structure, when the anion occupies the voids formed by the packing of the cation (Figure S49).

In the actual event, we observed whole-body disorder for the anion. Using IUCr terminology, we can describe the disorder assembly as consisting of two disorder groups, each of which is a half-occupied instance of \([\{(\text{CF}_3)_3\text{Ag(N}_3\)]^-.\) The two fragments are related to each other by the inversion center. The distance between the
two half-occupied Ag1 sites is 52.70 (9) pm, which is twice the distance of each Ag1 site from the center of inversion (Figure S50).

Considering only the central Ag atom of the anion and the four atoms coordinated to it, this fragment has approximate $C_{2v}$ symmetry — polar and non-centric. When this group occupies a crystallographic site with centric surroundings, it is not unreasonable to expect the type of disorder that we observe.

The part of the reference asymmetric unit consisting of the anion could have been chosen in any of several ways. The most convenient for the purpose of structure refinement and presentation is that in which the asymmetric unit consists of a complete fragment, but with chemical occupation of 0.5. The center of symmetry generates the other congener, which occupies much of the same space as the reference fragment, but without pronounced atomic-site overlap. This arrangement, together with software controls, makes it possible to suppress the generation of spurious bond distances and angles involving atoms belonging to both fragments. It also makes it easier to apply restraints, if needed. In this case the refinement was stable and convergent without any restraints.

Although the presence of an important level of disorder has a cogent explanation, we nevertheless attempted to solve and refine the structure using the acentric space group $Cc$. All of our attempts in this regard yielded the same disordered pattern conforming to space group $C2/c$. These attempts included ab initio structure solution using $Cc$ and also an attempt to arrive at a structural description in $Cc$ by reduction of symmetry beginning with the disordered model of the structure in $C2/c$. The latter approach is expected to be less prone to false structure mirroring caused by phase bias in a case of severe pseudosymmetry.

As mentioned, there is little in this structure in the way of directed non-covalent interactions. Using default criteria [Program ShelxL2018/3; DH···A < r(A) + 200 pm;
D is the hydrogen bond donor atom, A is the acceptor atom, and \( r(A) \) is its covalent radius, we find three marginal interactions in which the donor is a phenyl H atom of the cation and the acceptor a disordered F atom of the anion: \( \text{C}(\text{sp}^2)-\text{H} \cdots \text{F} \). The donor\( \cdots \)acceptor distances, \( \text{C}(\text{sp}^2) \cdots \text{F} \), fall in the range 315.1(3)–329.5(10) pm with D–H\( \cdots \)A angles between 125.5(16)–133.6 (16)°. These interactions are not expected to be structure-directing. Full details can be found in the CIF.

**Figure S49.** Packing in the crystal structure of 7: unit cell viewed along the \( b \)-axis. Separate cations and anions are arranged in alternating layers parallel to (100).
Figure S50. Drawing (c view) of the two symmetry-related orientations of the [(CF$_3$)$_3$Ag(N$_3$)]$^-$ anion involved in the whole-body disorder found in single crystals of 7 (see Figure S49).
9. References

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