

Synthesis and Lewis Acid Properties of Neutral Silver(III) Adducts Containing the $\text{Ag}^{\text{III}}(\text{CF}_3)_3$ Moiety

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In Memory of Dr. M. Pilar (Piluka) del Río

The acetonitrile Ag^{III} complex $[\text{Ag}^{\text{III}}(\text{CF}_3)_3(\text{NCCH}_3)]$ (**2**) has been reported independently by Eujen and Naumann in the last century, albeit with intriguing NMR discrepancy. In their reports, **2** was claimed to be obtained starting from either $[\text{Ag}^{\text{III}}(\text{CF}_3)_3\text{Cl}]^-$ (**3_{Cl}**) or $[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^-$ (**1**) via halide abstraction using AgNO_3 or acidic treatment, resp. These two synthetic routes are herein reinvestigated. The feasibility of Naumann's method is demon-

strated, thus providing **2** yet accompanied by its *s*-triazinyl derivative $[\text{Ag}^{\text{III}}(\text{CF}_3)_3(\text{C}_6\text{H}_5\text{N}_3)]$ (**2'**). The formation of **2'** is unprecedented and was thereby investigated. Both **2** and **2'** were isolated in pure fashion and fully characterized. In turn, halide extraction from **3_{Cl}** leads to the $\text{Ag}^{\text{III}}\text{-ONO}_2$ anion **5** instead of **2**, as evidenced by NMR spectroscopy, EA and Sc-XRD.

Introduction

Oxidation state III signifies the highest known oxidizing form of silver,^[1] making organosilver(III) species highly prone to get reduced and commonly out of reach.^[2] Nonetheless, Ag^{III} intermediates are frequently invoked to take part within catalytic cycles despite the scarcity of authenticated organosilver(III) case examples.^[3,4] An original strategy to stabilize high-valent metals lies with their bonding to trifluoromethyl anions,^[5] owing to the remarkable $\text{M}-\text{CF}_3$ bond strength and the " σ -non-innocence" of CF_3 ligands.^[6] Indeed, trifluoromethyl Ag^{III} derivatives were synthesized in 1986 by Naumann^[7] using $\text{Cd}(\text{CF}_3)_2$, a toxic and explosive source of trifluoromethylation that has impeded the progress of $\text{Ag}^{\text{III}}\text{CF}_3$ chemistry.^[8] This boundary was circumvented using CF_3SiMe_3 as trifluoromethyl source and $\text{PhI}(\text{OAc})_2$ ^[9a] or air ^[9b,c] as suitable oxidant, thus providing a safe entry to the homoleptic Ag^{III} anion, $[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^-$ (**1**).^[10] The reactivity of **1** was studied by

Naumann and Eujen last century,^[11] leading to novel heteroleptic anions $[\text{Ag}^{\text{III}}(\text{CF}_3)_3\text{X}]^-$ (**3_X**) or neutral complexes $[\text{Ag}^{\text{III}}(\text{CF}_3)_3\text{L}]$ (**4_L**). Amongst them, the $\text{Ag}^{\text{III}}\text{-NCCH}_3$ species **2** stands for the simplest $\text{Ag}^{\text{III}}(\text{CF}_3)_3\text{L}$ synthon described to date. Its synthesis was first notified by Eujen in 1997^[11a] through halide abstraction from $[\text{Ag}^{\text{III}}(\text{CF}_3)_3\text{Cl}]^-$ (**3_{Cl}**) using AgNO_3 in CH_3CN (Figure 1A right). Later on, it was prepared by Naumann^[11b] upon acidic treatment of **1** (Figure 1A left), who described **2** as a yellowish oil. Their strong NMR discrepancy^[11c] and the lack of crystallographic characterization^[11a,b] suggests that **2** has never been purely isolated and further investigation becomes necessary. In fact, the Ag^{III} species **2** has been recently authenticated by us,^[12a] being isolated from **3_{Cl}** and TIClO_4 as a crystalline and colourless material (Figure 1B), which displays identical NMR spectroscopic pattern to the one disclosed by Naumann.^[11b] It also constitutes an ideal organometallic synthon to build neutral complexes of the type $[\text{Ag}^{\text{III}}(\text{CF}_3)_3\text{L}]$ (**4_L**),^[12a] while keeping acidic enough to spontaneously coordinate σ -donor ligands in axial position (Figure 1B).^[12a] Now, we reinvestigate the ongoing transformation of the homoleptic Ag^{III} anion $[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^-$ (**1**) upon acidic treatment (Figure 1C),^[11b] and subsequently interrogate the nature of the complex arising from **3_{Cl}** and AgNO_3 , originally studied by Eujen and co-workers.^[11a]

Results and Discussion

In 2021, Shen reported the reactivity of $[\text{Bu}_4\text{N}][\text{Ag}^{\text{III}}(\text{CF}_3)_4]$ and HBF_4 in CH_2Cl_2 conducting to a surprisingly stable T-shaped $\text{Ag}^{\text{III}}(\text{CF}_3)_3$ motif that evolved to $[\text{Ag}^{\text{III}}(\text{CF}_3)_3(\text{phen})]$ (**4_{phen}**) upon addition of 1,10-phenanthroline.^[13] Intrigued by this observation, coupled to the long-standing controversy on the real nature of the acetonitrile derivative **2**, we tentatively hypothesized that **K-1** and HBF_4 may likewise react in pure acetonitrile, thus providing an ideal entry to **2**. Accordingly, the synthesis of

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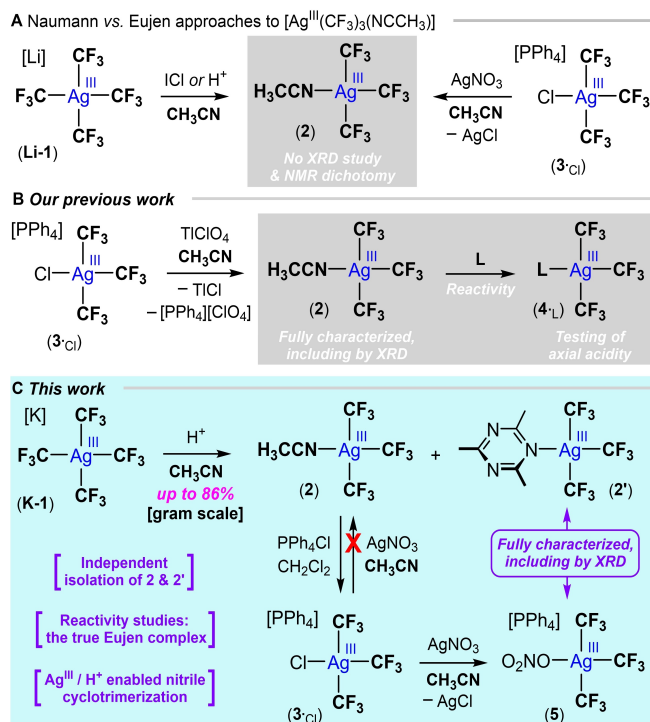


Figure 1. State of the art and focus of this work. (A) Reported synthesis of **2** through acidic treatment of **1** (Naumann, left)^[11b] or halide abstraction from **3-Cl** using AgNO_3 (Eujen, right).^[11a] (B) Authentication of $[\text{Ag}^{\text{III}}(\text{CF}_3)_3(\text{NCCH}_3)]$ (**2**) and the probing of axial acidity in neutral, square planar $\text{Ag}^{\text{III}}\text{CF}_3$ compounds.^[12] (C) **This work:** revisiting Naumann and Eujen approaches to $\text{Ag}^{\text{III}}\text{-NCCH}_3$ species **2**.

2 from **K-1** mediated by Brønsted acid was tackled (Figure 2A). Subsequent additions of HBF_4 in gentle excess to acetonitrile solutions of **K-1** efficiently provoked the α -fluorine elimination step giving rise to a unique pattern of unresolved signals in the ^{19}F NMR spectrum of the crude [δ_{ppm} -20.6 (br, 3F) and -32.5 (br, 6F); Figure 2C top]. This ^{19}F NMR spectroscopic pattern is consistent with a T-shaped $\text{Ag}^{\text{III}}(\text{CF}_3)_3$ entity, and close to the one described for **2** by Naumann^[11b] and us.^[12a] Strikingly, besides a sharp singlet signal resonating at 2.40 ppm, as might be expected for **2**, the ^1H NMR spectrum of bulk material shows a shadowy broad signal around 2.86 ppm (Figure 2D top). Taken together, these observations suggested the coexistence of two distinct $\text{Ag}^{\text{III}}\text{CF}_3$ species being stabilized by different *N*-donor ligands derived from CH_3CN , but equilibrated in solution. Indistinguishable colourless crystals corresponding to both $\text{Ag}^{\text{III}}\text{CF}_3$ compounds **2** and **2'** were grown upon slow evaporation of a dichloromethane solution containing bulk material. The structure of **2'** was definitely determined by Sc-XRD analysis allowing to identify the *s*-2,4,6-trimethyltriazine scaffold (Figure 2B), which accounts for the broad signal resonating at ca. 2.86 ppm in ^1H NMR (*vide infra*). **2'** crystallizes in square planar (*SP*-4) geometry bearing three trifluoromethyl ligands with av. $\text{Ag}^{\text{III}}\text{-CF}_3$ bond length of 2.093 Å (within the typical range for $\text{Ag}-\text{CF}_3$ bonds),^[9,12–14] and having the *s*-2,4,6-trimethyltriazine orthogonally coordinated to the $\text{Ag}^{\text{III}}(\text{CF}_3)_3$ plane (torsion angle of 88.7(2)°).

Selective cyclotrimerization of nitriles to build *s*-triazines mediated by Brønsted acids is quite puzzling.^[15–17] On one hand, owing to its stability and apparently unreactive character, acetonitrile is reluctant to trimerization and exclusively undergoes protonation by superacids ($\text{HSO}_3\text{F-SbF}_5$, HF-AsF_5 or HF-SbF_5).^[16] As a result, metallic compounds bearing monodentate coordination of *s*-triazines are rare,^[18] and **2'** represents the first coordination compound crystallographically characterized featuring the *s*-2,4,6-trimethyltriazinyl motif.^[19] Conversely, the building of **2'** is consistent with the previously observed trimerization of CH_3CN in acidic media (HOTf).^[17]

To our delight, after full conversion of **K-1** into **2** and **2'**, the 2,4,6-trimethyltriazin-1-ium salt could be efficiently extracted to aqueous phase upon acidification with a cold aqueous solution of H_2SO_4 (1 M) granting the gram scale isolation of **2** in analytically pure fashion and excellent yield (86%). Now, the ^{19}F NMR spectrum of **2** in CD_2Cl_2 displays two distinct and well-resolved signals (δ_{ppm} -20.6 (two dsept, 3F; *cis*- CF_3), -32.5 (two dq, 6F; *trans*- CF_3); Figure 2C middle), while its ^1H NMR spectrum exclusively shows a singlet signal pertaining to coordinated CH_3CN (Figure 2D 2nd row). The collected NMR data, together with crystallographic studies, are fully consistent with our previous characterization of **2** and definitely proves the authenticity of the isolated material.^[12a] In hopes of deliberately reaching the *s*-triazinyl- Ag^{III} derivative **2'**, equimolar amounts of **2** and independently synthesized *s*-2,4,6-trimethyltriazine^[17c] were reacted in CH_2Cl_2 at room temperature. Monitoring by ^{19}F NMR spectroscopy indicates instantaneous ligand substitution and concomitant formation of **2'**, which was quantitatively isolated as a white powder. ^{19}F NMR spectrum of **2'** in CD_2Cl_2 displays the typical pattern for a $\text{Ag}^{\text{III}}(\text{CF}_3)_3$ fragment with both signals slightly up-field shifted (δ_{ppm} -22.0 (two dsept, 3F; *cis*- CF_3), -33.1 (two dq, 6F; *trans*- CF_3); Figure 2C bottom). Meanwhile, its ^1H NMR spectrum in CD_2Cl_2 at room temperature shows a unique broad signal appearing at 2.83 ppm attributed to the three methyl groups (Figure 2D 3rd row), instead of the two foreseeable singlet signals resonating in 1:2 ratio. The observed NMR data clearly point to a fluxional behavior of the *s*-2,4,6-trimethyltriazine in solution, most likely owing to coordination/decoordination of the *s*-triazinyl moiety to the $\text{Ag}^{\text{III}}(\text{CF}_3)_3$ fragment. Further support for an easy dissociation of the *s*-2,4,6-trimethyltriazine is provided by the unique set of signals observed in ^{19}F NMR for mixtures containing **2** and **2'** (Figure 2C top), arguing in favor of fast interconversion from one another. This hypothesis proved right and ligand coordination/decoordination was precluded by freezing the sample (-60°C), thus resulting in the splitting of the broad signal into two different sharp signals resonating at 2.74 and 2.86 ppm in 1:2 intensity ratio and corresponding to the *para*- and *ortho*-methyl substituents, respectively (see Figure 2D bottom).

Mechanistically, the formation of the 1,3,5-triazine via nitrile cyclotrimerization exclusively occurs in an acidic acetonitrile solution simultaneously containing $[\text{Ag}^{\text{III}}(\text{CF}_3)_3(\text{NCCH}_3)]$ (**2**). Such a transformation does not occur in the absence of acid, according to our previous results on the synthesis of **2** from $[\text{PPh}_4][\text{Ag}^{\text{III}}(\text{CF}_3)_3\text{Cl}]$ (**3-Cl**) using TlClO_4 as a chloride scavenger.^[12a] Complementary to this, an additional blank experiment has

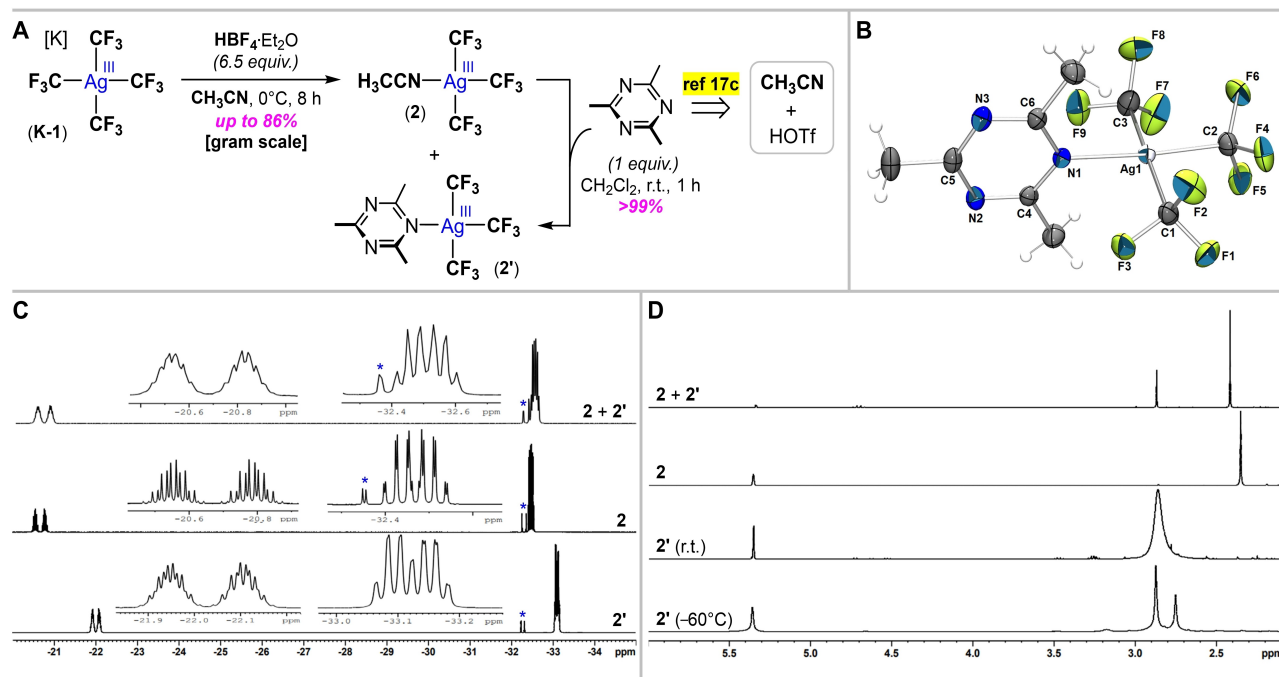


Figure 2. (A) Access to the CH₃CN-Ag^{III} species 2 and its s-triazinyl derivative 2' starting from K-1 and HBF₄, along with an independent synthesis of 2' from 2 and freshly prepared s-2,4,6-trimethyltriazine. (B) ORTEP representation (ellipsoid drawing at 50% probability) of [Ag^{III}(CF₃)₃(s-2,4,6-trimethyltriazine)] (2'). Most significant distances [Å] and angles [°] of 2': Ag1–C1 2.106(2), Ag1–C2 2.069(2), Ag1–C3 2.104(2), Ag1–N1 2.126(2), N1–C4 1.352(3), C4–N2 1.323(3), N2–C5 1.343(3), C5–N3 1.337(3), N3–C6 1.330(3), C6–N1 1.348(3); C1–Ag1–C2 89.87(10), C2–Ag1–C3 88.68(10), C1–Ag1–C3 176.44(10), C1–Ag1–N1 92.02(8), C2–Ag1–N1 175.42(8), C3–Ag1–N1 89.66(9). (C) Stacked ¹⁹F NMR spectra performed in CD₂Cl₂ corresponding to the typical AgCF₃ region for the reaction crude containing 2 and 2' (top), and purely isolated Ag^{III} compounds 2 (middle) or 2' (bottom). The presence of [Ag^{III}(CF₃)₄][−] (1) as a minor impurity (< 3%) is denoted by an asterisk (*). (D) From top to bottom, stacked ¹H NMR spectra in CD₂Cl₂ are shown for the reaction crude containing 2 and 2', purely isolated CH₃CN-Ag^{III} complex 2, and purely isolated s-2,4,6-trimethyltriazinyl derivative 2' either at r.t. or low temperature (−60 °C).

been performed in the absence of silver. Thus, acetonitrile was reacted at 0 °C with HBF₄·OEt₂ (2 equiv.), and the resulting mixture has been stirred for 24 hours at r.t. (see SI for details). Remarkably, no triazine formation is detected by ¹H NMR spectroscopy (Figures S1 and S2). We note here that replacing HBF₄·OEt₂ by HOTf upon otherwise similar conditions enables nitrile cyclotrimerization and leads to 1*H*,3*H*-2,4,6-trimethyl-1,3,5-triazinium triflate, as demonstrated by Acharjya, Thomas *et al.*^[17c] However, based on our reactivity investigations, we state that, under our reaction conditions, the cyclotrimerization process is only triggered by the synergic action of both acids, [Ag^{III}(CF₃)₃] and H⁺. With the starting point of our experimental observations, we have examined the H⁺/Ag^{III} promoted reaction by DFT methods at the M06 level of theory in an SMD modelled acetonitrile solution (see SI), in order to get a picture of the cooperative action of both reagents. A thorough study aiming to unveil the reasons why this transformation occurs with certain Brönsted acids (HOTf) but not with others (HBF₄), although interesting, is out of the scope of this manuscript. Several aspects make this analysis particularly challenging, and need to be carefully taken into account. First, there are three different actors in the reaction, two of them being in low concentration (2, H⁺), while a third one (i.e. CH₃CN) intercedes both as a reagent and solvent; second, the participation of a strong Brönsted acid makes the consideration of discrete solvent molecules mandatory in order to accurately reproduce the proton solvation; and third, each Ag^{III} centre participating

along the reaction may potentially extend its coordination number above four, by additional CH₃CN axial coordination, as proven by us.^[12a] As a result, the discrete additional solvent molecules included in the modelization add to the three acetonitrile molecules that are stoichiometrically required to fulfill the cyclotrimerization reaction. Accordingly, to achieve a reasonable modelization being consistent with the experimental observations, the consideration of (at least) five discrete CH₃CN molecules is necessary.

The trimerization reaction involves three consecutive C–N bond forming processes that can be considered as independent steps of the global transformation. The first C–N bond formation can occur exclusively assisted by H⁺. Interestingly, our calculations show that the simultaneous participation of H⁺ and a [Ag^{III}(CF₃)₃] fragment in this initial step results detrimental. By simplicity, the first C–N bond forming process has been modelled with three acetonitrile molecules and a proton (Figure 3; H⁺ assisted section, black profile). Under these conditions, the energy cost (Δ*G*_{acetonitrile}) to generate an acetonitrile-stabilized cationic imine molecule is 12.3 kcal/mol, and an energy barrier of 20.3 kcal/mol must be overcome. Comparatively, achieving the analogous process involving the Ag^{III} complex [Ag^{III}(CF₃)₃(NCCH₃)₂] (A) and H⁺ requires 28.4 kcal/mol to proceed.

At this point, participation of [Ag^{III}(CF₃)₃] entities becomes essential in the subsequent steps of the cyclotrimerization. As above-mentioned, for consistency with the full process involv-

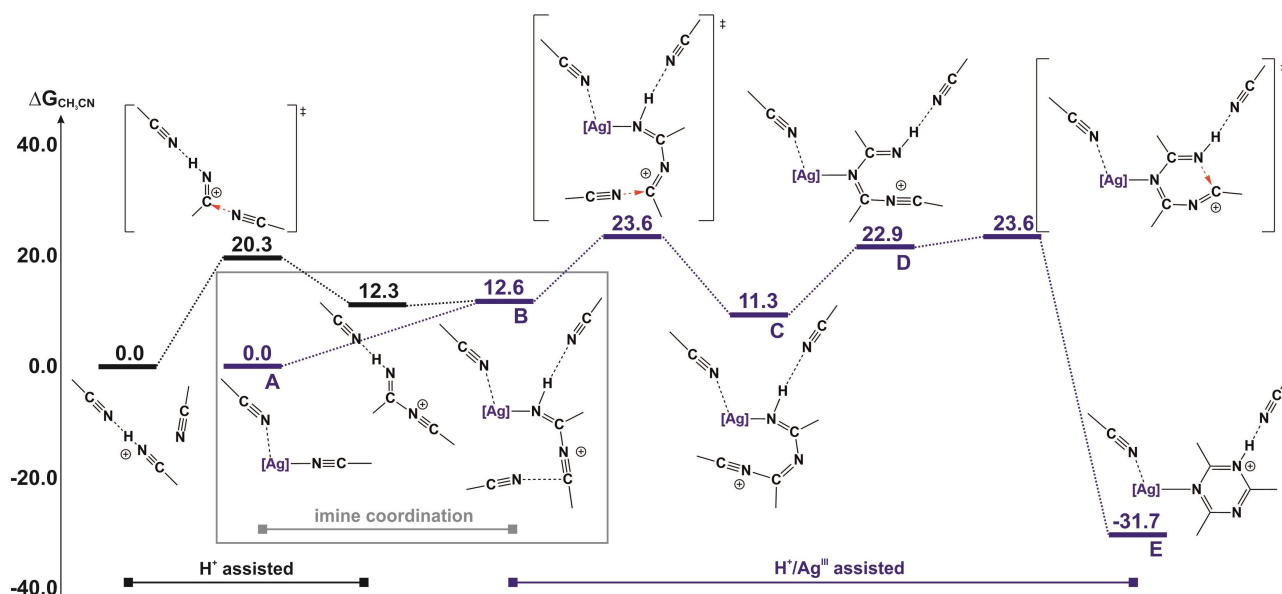


Figure 3. Global ΔG profile (kcal/mol) for the H^+/Ag^{III} promoted trimerization of acetonitrile, calculated at the DFT/M06-GD3/SDD(f),6-311++G**/SMD(acetonitrile) level of theory. For simplicity, [Ag] represents the T-shaped $Ag^{III}(CF_3)_3$ fragment.

ing five discrete acetonitrile molecules, **A** has been considered as the incoming Ag^{III} precursor. The following associative process, giving rise to **B** through the substitution of an acetonitrile ligand by a $[HN=C(CH_3)-NCCH_3]^+$ imine, shows to be enthalpically favoured ($\Delta H_{\text{acetonitrile}} = -14.3$ kcal/mol), although the entropy cost makes this step equilibrated ($\Delta G_{\text{acetonitrile}} = +0.3$ kcal/mol; i.e. +12.6 kcal/mol vs. the initial reagents; Figure 3; *imine coordination* section, grey box). Next step requires the formation of a second C–N bond, and presents a global energy barrier of +23.6 kcal/mol, leading to a new Ag^{III} -imine complex **C**, only +11.3 kcal/mol above in energy with regard to the reactants. This imine ligand in **C** arises from the coupling of three acetonitrile molecules (Figure 3; H^+/Ag^{III} assisted section, blue profile), and presents two nucleophilic N atoms. While the one bearing the H^+ is directly attached to Ag^{III} , the second one is bonded to two distinct C atoms displaying an angular geometry, which suggests a marked nucleophilicity. This favours the decoordination of the NH group and leads to the coordination of the internal N atom, thus affording a new intermediate **D** that is +22.9 kcal/mol above in energy vs. the initial reactants. This step can be seen as a 1,3-shift of the Ag^{III} fragment in the referred imine. Within the resulting species **D**, both the $C\equiv N$ bond and the NH group of the imine are conveniently arranged for rendering the ring closing. Indeed, the third C–N bond forming step requires only additional +0.7 kcal/mol to complete the ring closure (+23.6 kcal/mol relative to the reagents), and finally yields the Ag^{III} triazinium complex **E**, laying as low as –31.7 kcal/mol in the global energy profile (Figure 3; H^+/Ag^{III} assisted section, blue profile). Interestingly, replacing the triazinium ligand in **E** by a solvent molecule is easy, bringing back the Ag^{III} precursor **2**. This is favoured by the lower nucleophilicity of the cationic triazinium ligand compared to that of the corresponding *s*-triazine. In fact, given the marked basic behaviour of the 2,4,6-trimethyl-1,3,5-triazine

skeleton (predicted pK_a for its conjugated acid: 3.41),^[20] the formation of *s*-triazine causes the pH of the mixture to increase as the reaction moves forward. As a direct consequence, the cyclotrimerization process gradually slows down and finally stops.

Once enlightened the access to **2** from the homoleptic Ag^{III} anion **1** in acidic media, we turned our attention back to the seminal report by Eujen.^[11a] Amongst the plethora of elegant syntheses and characterizations carried out for highly unusual $Ag^{III}CF_3$ compounds, two closely related transformations resulted simultaneously intriguing and striking to us, namely: the proposed synthesis of **2** from the chloro-derivative **3_{Cl}** and $AgNO_3$, and the ^{19}F NMR identification of an elusive bimetallic intermediate $\{[(CF_3)_3Ag^{III}]_2(\mu-Cl)\}^-$ (**6** in Figure 4A left). Accordingly, these syntheses were reinvestigated. In first term, **3_{Cl}** has been prepared by mixing equimolar quantities of **2** and $[PPh_4][Cl]$ in CH_2Cl_2 at room temperature to yield **3_{Cl}** as a pale-yellow solid (93%; Figure 4A right and SI) with ^{19}F NMR spectroscopic signature in accordance with reported data (Figure 4B top).^[11a,14] As reported by Eujen,^[11a] stirring a mixture of **3_{Cl}** and $AgNO_3$ in acetonitrile protected from daylight led to the formation of a white precipitate ($AgCl$) accompanied by an assumed unique $Ag^{III}CF_3$ compound. At first sight, this was supported by ^{19}F NMR analysis of the crude, which features the typical spectroscopic pattern for a $Ag^{III}(CF_3)_3$ fragment (δ_{ppm} –21.6 (two dsept, 3F) and –36.4 (two dq, 6F; Figure S13).^[21] However, exhaustive characterization using 1H and ^{31}P NMR spectroscopy evidenced the presence of a PPh_4 cation and the lack of coordinated CH_3CN (see Figures S11 and S14). This was definitely clarified by Sc-XRD analysis on single crystals that confirmed the exact composition and atom connectivity of the $Ag^{III}-ONO_2$ anion **5** (ORTEP representation depicted in Figure 4A). As expected for a d^8 anion, **5** crystallizes in square planar geometry displaying the coordination of three CF_3

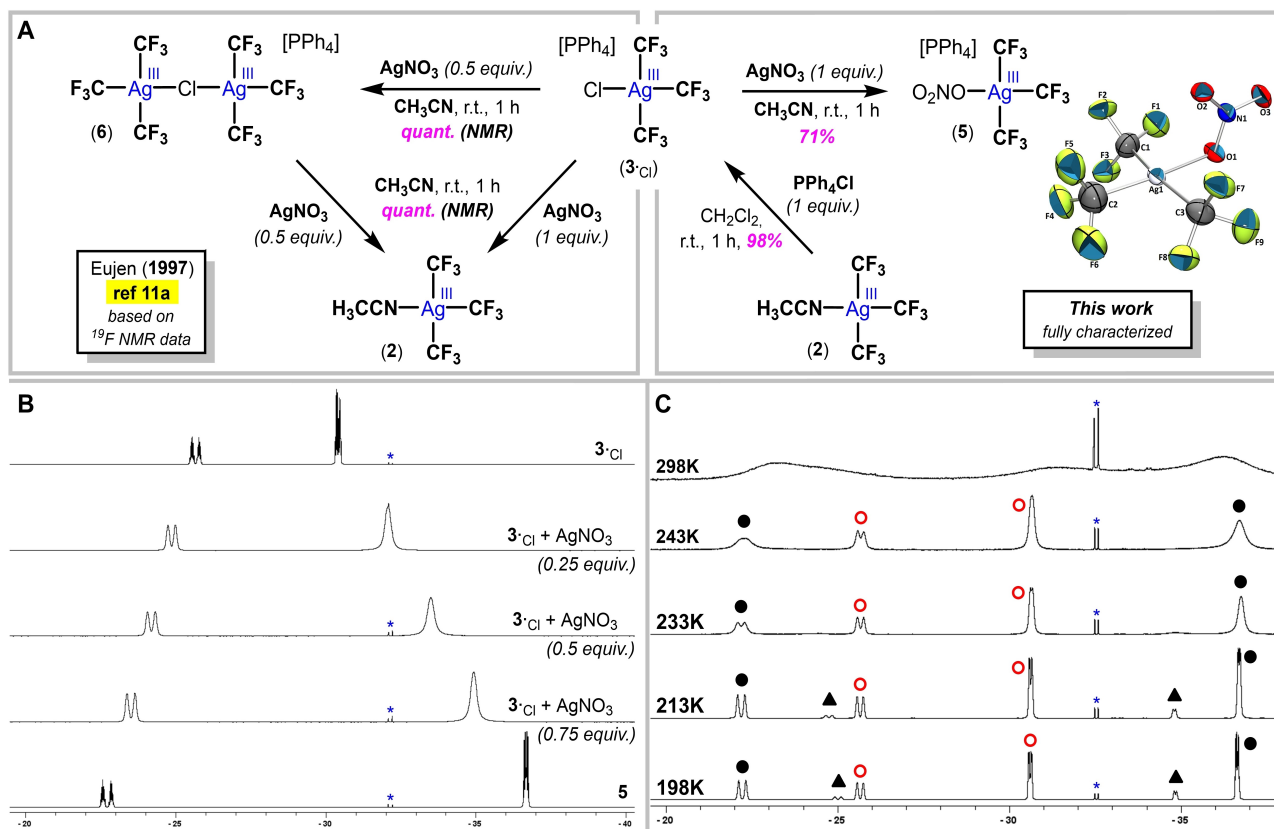


Figure 4. Synthesis, isolation and authentication of the nitrate- Ag^{III} complex, $[\text{Ag}^{\text{III}}(\text{CF}_3)_3(\text{ONO}_2)]^-$ (**5**). (A) Previous interpretations made by Eujen for the chloride abstraction from the $\text{Ag}^{\text{III}}\text{-Cl}$ anion **3_{Cl}** using AgNO_3 (left), and current study including the XRD-determined structure of the $\text{Ag}^{\text{III}}\text{-ONO}_2$ anion **5** (right). For clarity, the PPh_4 cation and disordered atoms are omitted. Most significant distances [Å] and angles [°] of **5**: av. (Ag1-C1) 2.101, av. (Ag1-C2) 2.034, av. (Ag1-C3) 2.105, Ag1-O1 2.097(2), av. (C1-Ag1-C2) 90.0, av. (C2-Ag1-C3) 93.6, av. (C1-Ag1-O1) 88.1, av. (C3-Ag1-O1) 88.3, av. (C1-Ag1-C2) 172.4, av. (C2-Ag1-O1) 174.4. (B) Stacked ^{19}F NMR spectra performed in CD_3CN displaying the typical AgCF_3 region for the addition of AgNO_3 in portions (0.25 equiv. each) to **3_{Cl}**. (C) Stacked VT ^{19}F NMR spectra performed in CD_2Cl_2 corresponding to the typical AgCF_3 region for the reaction crude resulting from **3_{Cl}** and half amount of AgNO_3 going from room temperature (top) to -75°C (bottom). ^{19}F NMR identification of the $\text{Ag}^{\text{III}}\text{-Cl}$ anion **3_{Cl}** (○), the $\text{Ag}^{\text{III}}\text{-ONO}_2$ anion **5** (●), and the putative bimetallic anion $[(\text{CF}_3)_3\text{Ag}^{\text{III}}_2(\mu\text{-Cl})]^-$ (**6**, ▲). The presence of $[\text{Ag}^{\text{III}}(\text{CF}_3)_2]^-$ (**1**) as a minor impurity (< 3%) is denoted by an asterisk (*).

ligands and the monodentate nitrate, as clearly indicated by the significantly shorter distal N1–O bonds (1.228 Å av.) compared to the N1–O1 bond length (1.291(4) Å). Although less pronounced, these crystallographic features are reminiscent of the ones found in the Au^{III}-nitrate anion [Au^{III}(CF₃)₃(ONO₂)][−] reported by Menjón,^[22] the weakened N1–O1 bond enabling NO₂ extrusion in condensed phase and leading to the elusive auroxyl complex [(CF₃)₃AuO][−].^[22]

From another standpoint, at first glance, the *in situ* formation and ^{19}F NMR identification of a presumably bimetallic anion $[(\text{CF}_3)_3\text{Ag}^{\text{III}}]_2(\mu\text{-Cl})^-$ (**6**) from $[\text{Ag}^{\text{III}}(\text{CF}_3)_3\text{Cl}]^-$ (**3-Cl**) and half amount of AgNO_3 in CH_3CN suggested the intermediacy of **6** in the synthesis of the assumed **2**,^[11a] now unequivocally identified as the $\text{Ag}^{\text{III}}\text{-ONO}_2$ anion **5**. A distinct interpretation might arise from the interconversion (faster than NMR timescale) between the starting $\text{Ag}^{\text{III}}\text{-Cl}$ anion **3-Cl** and the resulting $\text{Ag}^{\text{III}}\text{-ONO}_2$ derivative **5**, thus exclusively observing an average pattern of signals by using ^{19}F NMR spectroscopy. Two independent experiments were designed to elucidate whether this bimetallic anion $[(\text{CF}_3)_3\text{Ag}^{\text{III}}]_2(\mu\text{-Cl})^-$ (**6**) may be an intermediate in the formation of the $\text{Ag}^{\text{III}}\text{-ONO}_2$ complex **5**. In a first trial, AgNO_3 was subsequently added in portions (0.25 equiv. each) to a solution

of the $\text{Ag}^{\text{III}}\text{-Cl}$ anion 3-Cl in acetonitrile. In our hands, as substantiated by ^{19}F NMR monitoring (Figure 4B), after addition of equimolar amounts of AgNO_3 , 3-Cl is fully converted into **5**, while partial addition of AgNO_3 originates the formation of a unique set of signals gradually shifting from the starting material 3-Cl to the ones corresponding to the end compound **5** (Figure 4B, 2nd to 4th row). In a second guiding essay, VT ^{19}F NMR experiments were carried out for a sample containing the hypothetical bimetallic anion $[\{(\text{CF}_3)_3\text{Ag}^{\text{III}}\}_2(\mu\text{-Cl})]^-$ (**6**). ^{19}F NMR analysis of the crude at room temperature in CD_2Cl_2 shows very broad signals consistent with the proximity to coalescence (Figure 4C top), thus allowing to freeze the aforementioned interconversion at temperatures below -30°C , concomitantly observing 3-Cl and **5** in equimolar amounts in spite of their unresolved signals (Figure 4C 2nd row). To further scrutinize their identity, one needs to go down in temperature (-60°C) to enhance spectral resolution. As a result, both 3-Cl and **5** resonate not only at their diagnostic chemical shifts, but also displaying the expected multiplicity. By contrast, very surprisingly, a third minor component (*ca.* 5%) appears at temperatures below -60°C giving rise to a typical $\text{Ag}^{\text{III}}(\text{CF}_3)_3$ spectroscopic pattern, resonating at intermediate chemical shifts between the ones

measured for isolated 3_{Cl} and 5 ($\delta_{\text{ppm}} -25.0$ (m, 3F) and -34.8 (m, 6F); Figure 4C 4th row and bottom). The later $\text{Ag}^{\text{III}}\text{CF}_3$ compound, which is equally involved in the equilibrated mixture, is herein tentatively attributed to the bimetallic anion $[(\text{CF}_3)_3\text{Ag}^{\text{III}}]_2(\mu\text{-Cl})^-$ (6). Taking together, when under-stoichiometric amounts of AgNO_3 are employed, immediate conversion of 3_{Cl} into 5 occurs without apparent intermediacy of any chloride bridge bimetallic anion. Accordingly, the solitary NMR spectroscopic pattern observed by Eujen results from the puzzling interconversion of coexisting 3_{Cl} , 5 , and a minor component, most likely 6 . As an ultimate landmark for the fast interconversion of 3_{Cl} and 5 at room temperature, and seeking to ascertain whether or not our claims are right, a dichloromethane solution containing authentic samples of 3_{Cl} and 5 in equimolar amounts was analyzed using ^{19}F NMR spectroscopy at -75°C . Interestingly, this mixture behaves similarly giving rise to a nearly identical product distribution (Figure S17), thus lending additional support to our initial assumptions.

Conclusions

Since the 80's, chemists have explored the access to valuable $\text{Ag}^{\text{III}}\text{CF}_3$ platforms, with 2 representing the simplest example amongst all $\text{Ag}^{\text{III}}(\text{CF}_3)_3\text{L}$ series of compounds. Two inconsistent approaches to 2 were notified by Eujen^[11a] and Naumann^[11b] starting from either $[\text{Ag}^{\text{III}}(\text{CF}_3)_3\text{Cl}]^-$ (3_{Cl}) or $[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^-$ (1) via chloride abstraction using AgNO_3 or acidic treatment, resp. Both approaches are herein revisited proving the feasible synthesis of 2 from K-1 and HBF_4 in CH_3CN , yet partially contaminated by its *s*-triazinyl derivative $2'$. Experiments confirm that the *s*-2,4,6-trimethyltriazinyl core is built through the joint operation of both acids (H^+ , Ag^{III}). Moreover, DFT calculations have provided a plausible mechanism highlighting the synergic action of both acids. Conversely, Eujen's approach leads to the $\text{Ag}^{\text{III}}\text{-ONO}_2$ derivative 5 . Successive additions of AgNO_3 to 3_{Cl} in portions, coupled to VT ^{19}F NMR experiments on the assumed bimetallic intermediate $[(\text{CF}_3)_3\text{Ag}^{\text{III}}]_2(\mu\text{-Cl})^-$ (6), revealed the coexistence and fast interconversion of 3_{Cl} and 5 under sub-stoichiometric additions of AgNO_3 .

Beyond clarifying this long-standing controversy, the availability of 2 from K-1 and HBF_4 highlights its suitability to build a plethora of anionic $[\text{Ag}^{\text{III}}(\text{CF}_3)_3\text{X}]^-$ and neutral $[\text{Ag}^{\text{III}}(\text{CF}_3)_3\text{L}]$ complexes^[12a] with potential utility in organic synthesis and trifluoromethylation.^[4,9b,13,14,23] Applications of these platforms are currently investigated in our laboratories.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

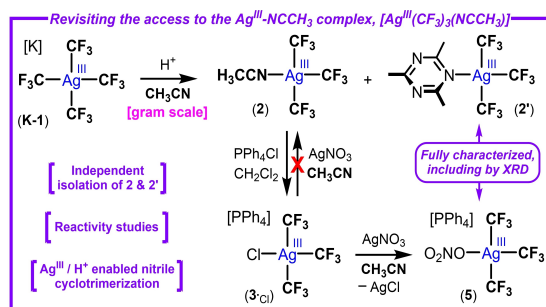
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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- 91.2 Hz, $^2J(^{107}\text{Ag},\text{F}) = 78.9\text{ Hz}$, $^4J(\text{F},\text{F}) = 9.5\text{ Hz}$, 3F; *cis*-CF₃), $-31.6\text{ (q, } ^2J(^{109}\text{Ag},\text{F}) = 22.6\text{ Hz, } ^2J(^{107}\text{Ag},\text{F}) = 19.5\text{ Hz, } ^4J(\text{F},\text{F}) = 9.5\text{ Hz})$, 6F; *trans*-CF₃).
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The synthetic approaches to $[\text{Ag}^{\text{III}}(\text{CF}_3)_3(\text{NCCH}_3)]$ (2) from either $[\text{Ag}^{\text{III}}(\text{CF}_3)_3\text{Cl}]^-$ (3-Cl) or $[\text{Ag}^{\text{III}}(\text{CF}_3)_4]^-$ (1), originally reported by Eujen and Naumann, are herein reinvestigated owing to major inconsistencies. Naumann's method provides 2 from 1 and HBF_4 , yet accompanied by its s-

triazinyl derivative $[\text{Ag}^{\text{III}}(\text{CF}_3)_3(\text{C}_6\text{H}_9\text{N}_3)]$ (2'), which is formed *in situ* through nitrile cyclotrimerization enabled by $\text{Ag}^{\text{III}}/\text{H}^+$. In turn, chloride abstraction from 3-Cl using AgNO_3 leads to $[\text{Ag}^{\text{III}}(\text{CF}_3)_3(\text{ONO}_2)]^-$ (5) instead of 2, as evidenced by NMR spectroscopy, Sc-XRD and EA.

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**Synthesis and Lewis Acid Properties
of Neutral Silver(III) Adducts Con-
taining the $\text{Ag}^{\text{III}}(\text{CF}_3)_3$ Moiety**

