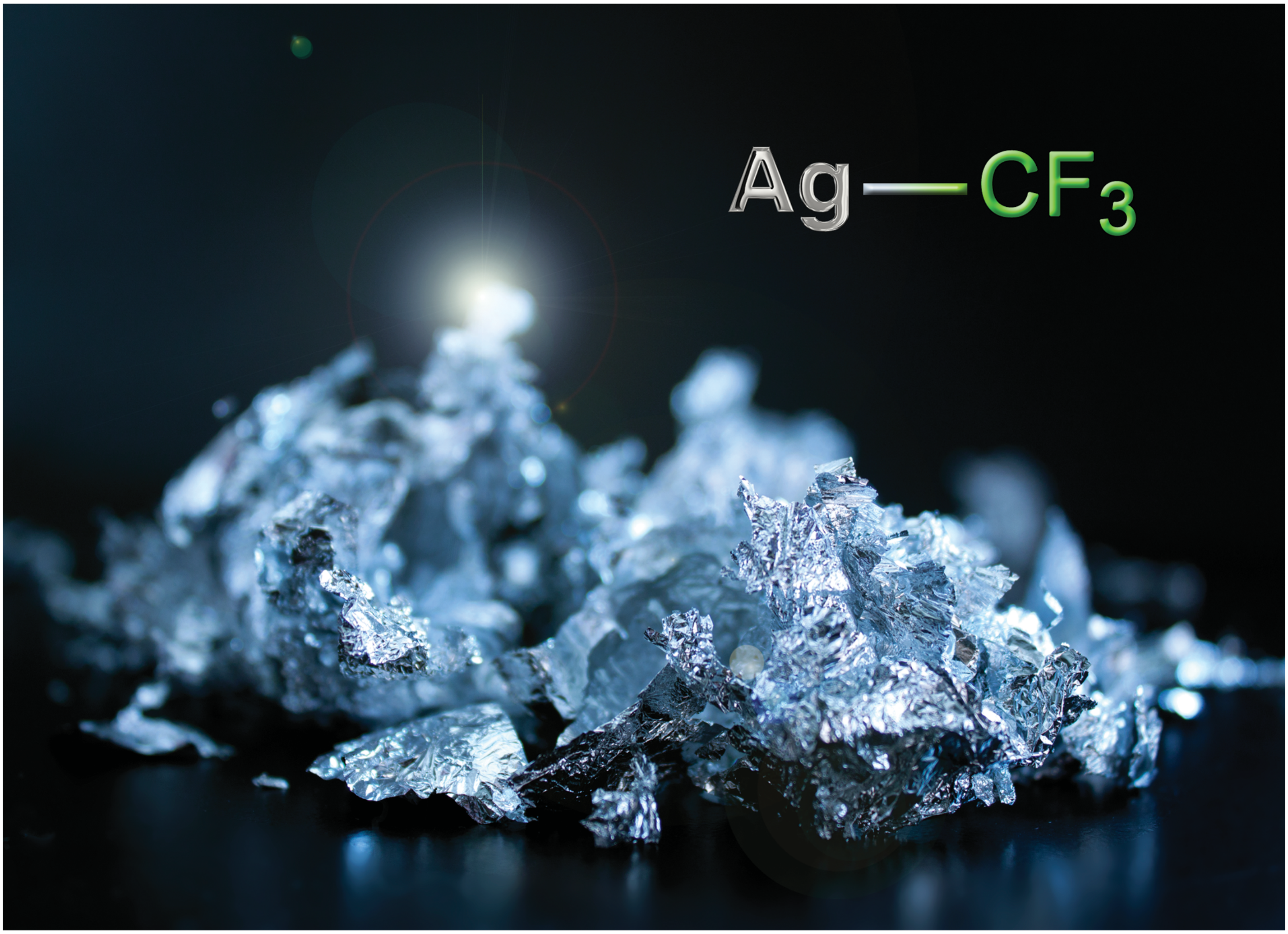

Showcasing joint research from Instituto de Síntesis Química y Catálisis Homogénea (iSQCH), CSIC–Universidad de Zaragoza, Spain, and the Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA), Université Paul Sabatier–CNRS, Toulouse, France.

Electrophilicity of neutral square-planar organosilver(III) compounds

Trifluoromethyl, CF_3, is one of the few ligands able to stabilise Ag(III) complexes. In the neutral frame formed with a series of Group 5 monodentate ligands, the Ag(III) centre still shows substantial acidity favouring coordination of an additional ligand.

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Electrophilicity of neutral square-planar organosilver(III) compounds†

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Neutral Ag(III) complexes stabilised with just monodentate ligands are here unambiguously established. In a series of square-planar $(CF_3)_3Ag(L)$ compounds with hard and soft Group 15 donor ligands, L, the metal center has been found to exhibit substantial acidity favouring apical coordination of an additional ligand under no coordination constraints.

Neutral silver(III) compounds are rare chemical species.[1] Aside from the binary compounds[2,3] AgF_3 and Ag_2O_3—both exhibiting extended structures‡—, all known neutral Ag(III) compounds are stabilised by polydentate ligands (Chart 1). Thus, macrocyclic ligands such as confused porphyrins, carbaporphyrinoids, corroles or carbacorroles are especially suited.[4] Two additional kinds of molecular compounds have been isolated with bidentate ligands: the dithiolate complex $(CF_3)_2Ag(S\&S)$ (S&S = diethyldithiocarbamate) of unknown structure[5] and the five-coordinate $(CF_3)_3Ag(N\&N)$ compounds, where N&N = bpy or phen (Chart 1c).[6,7] In this work, neutral Ag(III) complexes stabilised with just monodentate ligands are exemplified in the solvento-complex $(CF_3)_3Ag(NCMe)$ (**1**) and some of its derivatives with Group 15 donor ligands. Evidence for substantial electrophilic character at the metal centre is also given.

The solvento-complex $(CF_3)_3Ag(NCMe)$ has remained intriguing for more than two decades. Previous efforts to prepare it under different experimental conditions[5,8] gave compounds with significant discrepancies in their ^{19}F NMR spectroscopic properties (Table S1 in the ESI†). In one case,[5] the compound was claimed to have been isolated as a colourless oil in 8.2% estimated yield. This claim, however, is at odds with the observed properties of the gold homologous species $(CF_3)_3Au(NCMe)$, which we isolated as a white solid.[9] Even more intriguing is the purported failure to replace the MeCN molecule by other ligands.[5,8] Here, we provide a reliable procedure to prepare the neutral organosilver(III) compound $(CF_3)_3Ag(NCMe)$ (**1**), which we first isolate as a white solid.

We have found that by treating the anionic chloride complex[10] $[(CF_3)_3AgCl]^-$ with $TlClO_4$ in MeCN (Scheme 1), the neutral organosilver(III) compound $(CF_3)_3Ag(NCMe)$ (**1**) is formed quantitatively on a spectroscopic basis (^{19}F NMR; Fig. S1 in the ESI†). After the appropriate workup, the desired compound is isolated as a deliquescent white solid in moderate yield due to its high solubility in most organic media.

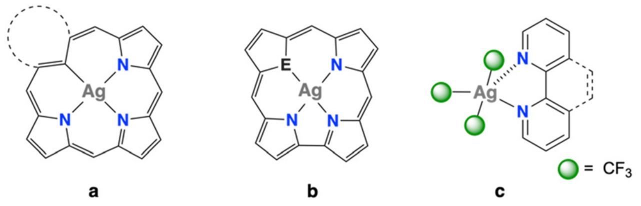
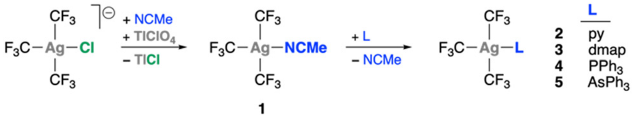


Chart 1 Schematic representation of the neutral Ag(III) complexes stabilised by polydentate ligands: (a) confused porphyrines or carbaporphyrines; (b) corroles (E = N) or carbacorroles (E = CR); (c) bpy or phen. Peripheral substitution may occur at various positions. Confusion may also occur at more than one ring.



Scheme 1 Synthetic procedures to prepare the neutral organosilver(III) compounds **1–5** (dmap = 4-dimethylaminopyridine).

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† Electronic supplementary information (ESI) available: Experimental, spectroscopic, computational and X-ray diffraction details (.pdf); atomic coordinates of the optimized structures (.xyz). CCDC 2226904–2226910. For ESI and crystallographic data in CIF or other electronic format see DOI: **https://doi.org/10.1039/d3cc00493g**

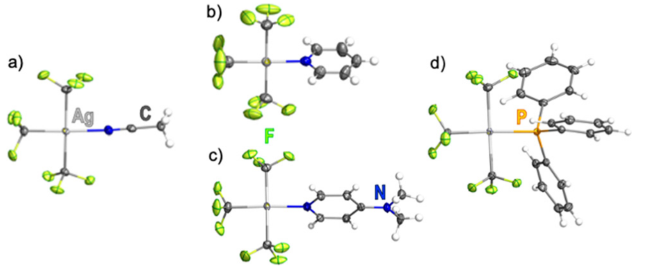

Fig. 1 Displacement-ellipsoid diagram (50% probability) of the *SP*-4 neutral $(CF_3)_3Ag(L)$ complexes as found in single crystals of **1** (a), **2** (b), **3** (c), and **4** (d). Crystallographic details and relevant structural parameters are given in the ESI.†

Compound **1** has square-planar (*SP*-4) geometry (Fig. 1a; Table S3 in the ESI†) as established by single-crystal X-ray diffraction methods (sc-XRD). The observed Ag–N distance (209.05(16) pm) is significantly shorter than those found for the basal Ag–N bonds in the five-coordinate complexes $(CF_3)_3Ag(bpy)$ (214.3(3) pm) and $(CF_3)_3Ag(phen)$ (213.9(2) pm).[6] In addition to the different coordination number (4 *vs.* 5), the bond shortening observed here can also be attributed to the lack of strain in **1** and to the different hybridisation of the N-donor atom in each case (sp *vs.* sp^2).

In contrast to previous reports,[5,8] we found that the MeCN molecule in **1** can be easily replaced by other donors, both soft and hard, as actually expected for a typical labile ligand.[11] Thus, a set of neutral $(CF_3)_3Ag(L)$ compounds [L = py (**2**), dmap (**3**), PPh_3 (**4**), $AsPh_3$ (**5**)] has been prepared by simple exchange processes (Scheme 1). All these new compounds have been isolated and spectroscopically characterised (ESI†). The NMR spectra of the phosphine complex **4** are particularly rich due to the presence of various nuclei with $\frac{1}{2}$ nuclear spin (Fig. S4–S6 in the ESI†). Structural characterisation by sc-XRD (Fig. 1) reveals that these neutral complexes exhibit *SP*-4 structure, as in the parent complex **1**. Except for the phosphine complex **4** (Table S13 in the ESI†), the Ag–C distance *trans* to the neutral L ligand is substantially shorter than in the mutually *trans* Ag–CF_3 due to the different *trans* influence of the CF_3 group and the L ligand.[12] As an example, in the dmap complex **3** (Table S11 in the ESI†), the Ag–C bond distance in the CF_3–Ag–L axis (205.2(4) pm) is significantly shorter than the average value in the CF_3–Ag–CF_3 line: 209.3(4) pm.

The most salient feature in this set of compounds is the observed tendency to associate an additional ligand at the apical position. This feature is clearly seen in the arsine complex $(CF_3)_3Ag(AsPPh_3)\cdot OCMe_2$ (**5**·$OCMe_2$) and exemplified in the case of the pyridine complex $(CF_3)_3Ag(py)$ (**2**), which has also been crystallised as the MeCN and py solvates: **2**·NCMe and **2**·py (Fig. 2). In all these cases, the solvent molecule enters the coordination sphere of silver. The additional bond is substantially longer than a standard covalent bond, but much shorter than the sum of the corresponding van der Waals radii.

This kind of interaction is best described making use of the descriptor recently introduced by Álvarez and coworkers, namely the penetration index.[13] This descriptor§, *p*(AB), provides a measure of the interpenetration of the electron clouds of the involved atoms A/B and is especially suited for interactions lying between typically covalent and van der Waals bonding interactions, *i.e.* somewhere between the intra- and intermolecular dominions. By using this tool, we obtain *p*(AB) values ranging from 70% to 76% for the apical interaction in our solvate-complexes $(CF_3)_3Ag(L)\cdot L'$ (Fig. 2). This means that the apical Ag···E interaction is quite similar in all cases, regardless of the different nature of the donor atom (E = N or O) or its precise hybridisation (sp or sp^2 in the case of N). Of key importance is also the fact that the Ag···E line virtually coincides with the normal to the best basal plane, the deviation being $< 4°$ in all cases (precise values given in the ESI†). Thus, the position of the apical donor atom E matches both metrical and angular criteria to indicate a genuine Ag···E interaction.

We also performed theoretical calculations on various $(CF_3)_3Ag(L)/L'$ systems in the gas phase (L′ = NCMe, Me_2CO) in order to evaluate the influence of the crystal lattice on establishing the apical interaction. The referred systems were modelled under no symmetry or environmental restraints. We found that in these isolated systems, the additional ligand L′ also enters the metal coordination sphere (Fig. S9 and S10 in the ESI†) as the result of a stabilising (exothermic) interaction (Table S16 in the ESI†). In the calculated energy minima, the L′ ligand is also located at the apical site near the basal plane normal. The calculated Ag···L′ distance in the **2**·NCMe molecule (276.0 pm) shows excellent agreement with that experimentally observed in the crystal (278.4(3) pm). The agreement is less satisfactory in the case of **5**·$OCMe_2$ (Ag···L′ = 276.0 (theor.) *vs.* 265.3(1) (exptl.) pm), but still reasonable. Following our calculations, it becomes clear, that the neutral $(CF_3)_3Ag(L)$ complexes exhibit a significant tendency to associate an additional ligand at the apical site. The resulting interaction is not just a solid-state effect, but evidences an intrinsic electrophilic character of the silver(III) centre (Chart 2). The loose apical interaction has little effect on the geometry of the basal unit. This is in contrast with the anionic halide systems $[(CF_3)_2AgX_2]^-$ previously observed, where the association of an additional X^- anion resulted in marked structural changes.[14] Regardless of the extent of distortion observed in each system, it can be concluded that the electrophilic character of the Ag(III) centre seems to be a general feature in *SP*-4 complexes. It would therefore be advisable to take it into account when trying to

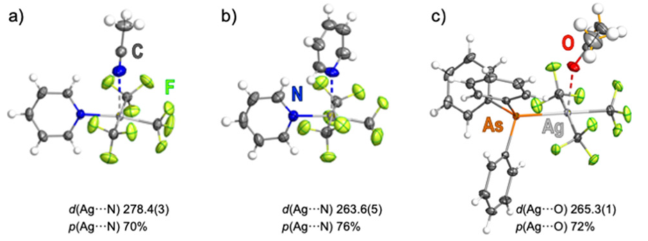

Fig. 2 Displacement-ellipsoid diagram (50% probability) of the solvates $(CF_3)_3Ag(L)\cdot L'$ as found in single crystals of **2**·NCMe (a), **2**·py (b), and **5**·$OCMe_2$ (c). The Ag···L′ distance is indicated in each case together with the corresponding penetration index, *p*(AB).[13] Crystallographic details and relevant structural parameters are given in the ESI.†

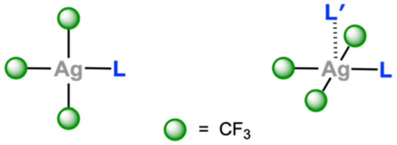

Chart 2 Graphic illustration of the tendency to associate an additional ligand at the apical site observed in the neutral $(CF_3)_3Ag(L)$ complexes, whereby the electrophilic character of the Ag(III) centre is clearly evidenced.

trace reliable reaction mechanisms, as this might lead to a better understanding of the chemical processes.

Compound **2**·py bears an interesting relationship with $(CF_3)_3Ag(bpy)$,[6] since the two pyridine rings are detached in the former, whereas they are linked in the latter. A detailed comparison of their structures is therefore in order. In both cases, the basal Ag–N distance is indistinguishable within the experimental error: 213.1(5) *vs.* 214.3(3) pm. These values are just marginally longer than in the non-solvated *SP*-4 complex **2**: 210.0(6) pm (Table S5 in the ESI†). By contrast, the apical Ag–N distance is substantially longer where the two rings are disconnected, 263.6(5) *vs.* 245.4(3) pm. This shortening can be assigned to the geometric constraint imposed by the chelating bpy ligand and involves an increment in the penetration index *p*(AB) from 76% in **2**·py (Fig. 2b) to 86% in $(CF_3)_3Ag(bpy)$. We can now attribute the apical interaction to a common effect, namely the electrophilicity of the Ag(III) centre (Chart 2). The apical interaction is incipient in **2**·py and tighter in $(CF_3)_3Ag(bpy)$.

In this work, we first isolate the solvento-complex $(CF_3)_3Ag(NCMe)$ (**1**), which has obvious synthetic potential. It provides a convenient entry to a series of $(CF_3)_3Ag(L)$ complexes including the first documented compound with Ag(III)–As bond (**5**: L = $AsPh_3$). These neutral, square-planar Ag(III) complexes show a conspicuous tendency to uptake an additional ligand at the apical position (Fig. 2). Our calculations demonstrate that this feature is not just a solid-state effect, but rather has its origin in an intrinsic electrophilic character of the Ag(III) centre (Chart 2).

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ The structures of AgF_3 (80477-ICSD)[2] and Ag_2O_3 (59193-ICSD)[3] are isomorphous with their corresponding gold homologues.

§ The penetration index, *p*(AB), of two given atoms A and B is defined as follows: $p(AB) = 100\cdot[\nu(A) + \nu(B) - d(AB)]\cdot[\nu(A) + \nu(B) - r(A) - r(B)]^{-1}$, where *d*(AB) is the actual distance between the involved atoms, and *r*(A)/*ν*(A) and *r*(B)/*ν*(B) are their respective covalent/van der Waals radii.[13]

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