

Hot Paper



The Fluoride Method: Access to Silver(III) NHC Complexes

Juan Pueyo,^[a] Daniel Joven-Sancho,^[a] Antonio Martín,^[a] Babil Menjón,^[a] and Miguel Baya*^[a]

Dedicated to the Memory of Dr. Pascal Oulié.

We have synthesized the first silver(III) carbene complexes, $(\text{CF}_3)_3\text{Ag}(\text{NHC})$, by direct reaction of the silver(III) fluoride precursor complex $[\text{PPh}_4][(\text{CF}_3)_3\text{AgF}]$ with different imidazolium salts. This novel methodology circumvents the use of free NHC molecules. The silver(III) carbene complexes thus prepared are unprecedented and show remarkable thermal stabilities. They display square-planar or square-pyramidal geometry. Following our calculations, the electronic structure of a model representa-

tive complex exhibits Inverse Ligand Field (ILF). The compounds reported herein are synthetic analogues of the elusive difluorocarbene and carbonyl species proposed as intermediates in the acidic decomposition of $[\text{Ag}(\text{CF}_3)_4]^-$. The synthetic procedure reported is envisaged to enable access to carbene complexes of other late transition-metals in high oxidation states.

Introduction

Carbene complexes of metals in high oxidation states have earned great relevance in connection to their application as catalysts in various important processes, including methathesis,^[1] carbene transfer,^[2] and oxidation.^[3] Whereas these compounds are well-known for early-transition metals (TMs), for late-TMs this family is largely composed of NHC complexes and is attracting much current interest.^[4]

Focusing on group 11, high-valent metal carbene complexes are underrepresented, especially in the case of the lighter elements, copper and silver. Thus, whilst a good number of Au^{III} -NHC derivatives^[5] are known, just a couple of Cu^{III} -NHC representatives^[6] are to be found (Figure 1a). Most interestingly, and to the best of our knowledge, no Ag^{III} -carbene compound has ever been prepared or even detected so far. This lack is in sharp contrast to the plethora of known Ag^{I} -NHC complexes, which find widespread use as common reagents in organometallic design,^[7] as anticancer agents in medicinal chemistry,^[8] and also as efficient catalysts.^[9] It must be noted, however that the silver(III) difluorocarbene and carbonyl complexes $(\text{CF}_3)_3\text{Ag}(\text{CF}_2)$ and $(\text{CF}_3)_3\text{Ag}(\text{CO})$ were recently suggested as intermediate species in the acidic degradation of the homoleptic $[\text{Ag}(\text{CF}_3)_4]^-$ anion (Figure 1b).^[10] No experimental evidence of their existence was given though. Herein, we report on the preparation

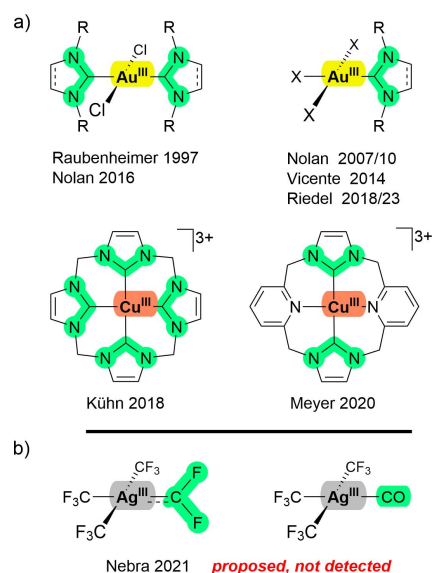


Figure 1. Representative carbene complexes of the coinage metals in oxidation state III: a) firmly established examples of Cu and Au (X and R denoting generic substituents), and b) suggested Ag intermediates.

of a series of Ag^{III} -NHC compounds, by way of the unconventional fluoride derivative $[(\text{CF}_3)_3\text{AgF}]^-$. These unprecedented compounds exhibit marked thermal stability.

Results and discussion

We have recently described a reliable method to prepare the neutral solvento-complex $(\text{CF}_3)_3\text{Ag}(\text{NCMe})$ (**A**).^[11] The ease with which the MeCN ligand is replaced by py, PR_3 or AsR_3 gives ground to consider complex **A** as a convenient synthon of the $(\text{CF}_3)_3\text{Ag}$ moiety.^[11] For this reason, it was quite natural to test its performance towards unsaturated C-donor ligands such as isocyanides, RNC, and free NHC carbenes. To our delight, our starting material **A** cleanly reacted with $^t\text{BuNC}$ giving rise to

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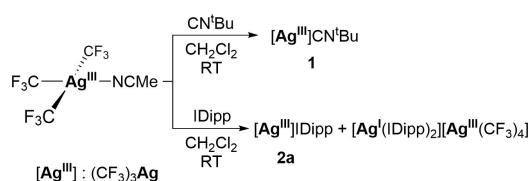
Supporting information for this article is available on the WWW under
<https://doi.org/10.1002/chem.202303937>

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(CF₃)₃Ag(CN^tBu) (**1**, Scheme 1) in quantitative spectroscopic yield (¹⁹F NMR). After the appropriate workup, complex **1** was isolated as an analytically pure white solid in modest yield (38%), owing to its high solubility in most organic media. Complex **1** was characterized by multinuclear NMR (¹H, ¹³C, ¹⁹F) and IR spectroscopic techniques. Furthermore, its molecular structure was established by single-crystal X-ray diffraction (sc-XRD) methods,^[12] which confirmed the typical square-planar (*SP*-4) geometry expected for a four-coordinate metal center with d⁸ electron configuration (see Supporting Information, SI). In fact, the overall structure of **1** is similar to that found in the homologous gold(III) complex (CF₃)₃Au(CN^tBu), which was obtained likewise.^[13] As in the latter case, the M–C distances (Table S2) in the CF₃–Ag–CF₃ axis defined by the mutually *trans*-standing CF₃ groups in **1** (211.7(7) pm *av*) are substantially longer than the M–C distances in the perpendicular CF₃–Ag–CNR axis: Ag–CF₃ 203.4(9) and Ag–CNR 204.8(9) pm. In spite of the structural similarity found in these homologous (CF₃)₃M(CN^tBu) complexes, with undistinguishable M–CNR bond distances (Ag: 204.8(9) pm *vs.* Au: 204.3(5) pm), the ν(CN) stretching frequencies in their corresponding IR spectra differ by 20 cm^{−1} (Ag: 2263 cm^{−1} *vs.* Au: 2283 cm^{−1}).^[13]

In our quest for Ag^{III}-NHC complexes, we first tried to extend the ligand substitution strategy just described by using a free NHC molecule as the incoming ligand. It is worth noting that the procedure had been successfully applied in the homologous gold(III) system.^[5] In our case, however, the reaction of complex **A** with 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IDipp) in dichloromethane as solvent proceeded with partial reduction to Ag^I. As a result, the desired complex (CF₃)₃Ag(IDipp) (**2a**) was always contaminated with variable amounts (*ca.* 25%) of the mixed-valence salt [Ag^I(IDipp)₂][Ag^{III}(CF₃)₄] (Scheme 1). The formation of the latter will be commented later on.

In view of this unexpected difficulty, we sought an alternative and more efficient access. We turned our attention to the fluoride complex [(CF₃)₃AgF][−] (**B**),^[14] where the terminal fluoride ligand shows a marked nucleophilicity. This feature is evidenced by the quantitative reaction with thiols giving rise to the corresponding thiolates [(CF₃)₃Ag(SR)][−].^[14] These reactions are thermodynamically driven by the formation of strong H–F bonds. Thus, we wondered if we could extend the strategy to prepare neutral Ag^{III}-NHC complexes by using easy-to-handle imidazolium salts directly in the reaction pot. This strategy is potentially advantageous as it makes unnecessary the isolation or the *in-situ* generation of a free NHC. It is well known that



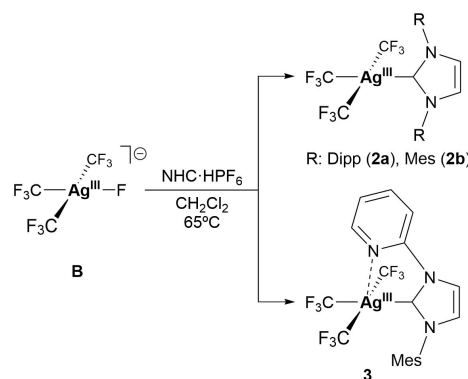
Scheme 1. Ligand replacement strategy for the synthesis of neutral Ag^{III} compounds with C-donor ligands.

some of these species, as for instance IMes, can be tricky to prepare.

With that purpose, complex **B** was reacted with (HIDipp)PF₆ in CH₂Cl₂ at 65 °C in a sealed vessel for 36 h (Scheme 2, above). Under those conditions, the desired product (CF₃)₃Ag(IDipp) (**2a**) was formed almost quantitatively on a spectroscopic basis (¹⁹F NMR), although small amounts (<6%) of the homoleptic [Ag(CF₃)₄][−] anion are still observed. Purification of the resulting solution through a silica plug and subsequent work-up enabled us to isolate the neutral complex (CF₃)₃Ag(IDipp) (**2a**) as an analytically pure white solid in 40% yield. A similar treatment with (HIMes)PF₆ afforded (CF₃)₃Ag(IMes) (**2b**) in 44% isolated yield (Scheme 2, above).

The ¹⁹F{¹H} NMR spectra of **2a** and **2b** are consistent with the described structures, and show the double A₃MX₆ pattern typical of (CF₃)₃AgL compounds, with two doublets of quartets at −28.18 (**2a**) and −28.08 (**2b**) ppm and two doublets of septets at −28.83 (**2a**) and −29.09 (**2b**) ppm (Figures S7 and S9). The ¹H NMR spectra (Figures S8 and S10) present signals consistent with the formation of the corresponding Ag–NHC moieties, as well as with the absence of the H–C(2) proton of the imidazolium salts used as reagents.

Compounds **2a** and **2b** show the typical *SP*-4 geometry, as established by sc-XRD methods (Figures 2a and 2b).^[12] In



Scheme 2. Fluoride strategy for the synthesis of neutral Ag^{III}-NHC compounds.

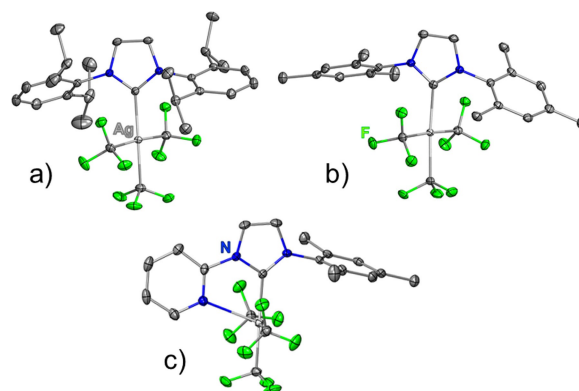


Figure 2. Molecular structures of (CF₃)₃Ag(IDipp) (a, **2a**), (CF₃)₃Ag(IMes) (b, **2b**), and (CF₃)₃Ag(NHC-py) (c, **3**) as established by sc-XRD methods.^[12] Displacement ellipsoids shown at 50% probability, with H atoms omitted for clarity. Relevant geometric parameters are given in SI.

contrast to the structure of compound **1** described previously, all four Ag–C bond lengths in both **2a** and **2b** are very similar, as they lie within very narrow ranges, 209.45(12)–210.71(12) pm for **2a**, and 209.3(2)–210.3(3) pm for **2b** (Tables S4 and S6). The central core of these four-coordinate (CF₃)₃Ag(NHC) complexes is very similar to that found in the related gold(III) derivative (CF₃)₃Au(SIMes). It must be noted, however, that the M–C bond lengths in the latter are slightly shorter, ranging from 207.8(3) to 208.6(3) pm.^[5]

Interestingly, in both structures **2a** and **2b** the NHC ligands bend in a way that one of the H–C bonds in the remote substituents of the NHC ligand approaches the metal center, with the shortest H⋯Ag distances being 291.3 (**2a**) and 291.0 (**2b**) pm. These are too long as to propose agostic interactions, but suggest incipient interactions with the metal centers. In this context, we have recently demonstrated substantial electrophilicity at the metal in *SP*-4 Ag^{III} complexes.^[12] In actual fact, complexes of general formula (CF₃)₃AgL tend to incorporate a fifth ligand in the metal coordination sphere giving rise to square pyramidal structures (*SPY*-5), in which the apical ligand is less tightly bound to the metal than the basal ligands.

Thus, we decided to test the behaviour of a potentially bidentate NHC ligand when coordinated to the (CF₃)₃Ag moiety. The reaction of *N*-(2,4,6-trimethylphenyl)-*N'*-(2-pyridyl)imidazolium hexafluorophosphate with **B** gave rise to the Ag^{III} pyridine-NHC derivative **3** (Scheme 2, below). The structure of **3**, as determined by *sc*-XRD, confirms the *SPY*-5 geometry around the metal center, with a certain elongation at the apical position (Figure 2c).^[12] The basal plane is formed by all four C-donor atoms, whereas the apical position is occupied by the *N*-donor atom of the pendant pyridine group. The Ag–C bond distances in the basal plane lay in the 207.1(3)–210.0(3) pm range (Table S8), not deviating significantly from the observed distances in the four-coordinate complexes **2a** and **2b** (see above). The apical Ag–N bond is substantially elongated (258.9(2) pm) with regard to a regular Ag^{III}–N bond. For comparison, the Ag–N distances in the related (CF₃)₃Ag(py)₂ complex^[11] are 213.1(5) (Ag–N_{bas}) and 263.6(5) (Ag–N_{ap}) pm. In these systems, it is advisable to make use of the penetration index, *p*(AB),^[15] a recently introduced tool to evaluate bonding in-between covalent and van der Waals interactions. The calculated *p*(AgN) involving the apical N atom is 76.6%, which suggests a substantial metal–ligand interaction at the fifth coordination site, thus backing the existence of electrophilicity-at-the-metal in the four-coordinate Ag^{III}–NHC compounds. It is worth noting that, upon apical coordination of the pyridine function, the pendant mesityl ring turns away from the metal, rendering the closest intramolecular H⋯Ag distance (399 pm) much longer than in the four-coordinate complex **2b** (291 pm; see above).

An additional question of interest concerns the electronic structures of the novel Ag^{III}–NHC compounds. Theoretical studies were performed on the model complex (CF₃)₃Ag(Ime) at the DFT-M06 level of theory (see SI). Interestingly, the frontier orbitals are mainly centered at the ligands, whereas the molecular orbitals (MO) mainly based on the silver 4d manifold are much stabilized (Figure 3). Indeed, the metal contribution to

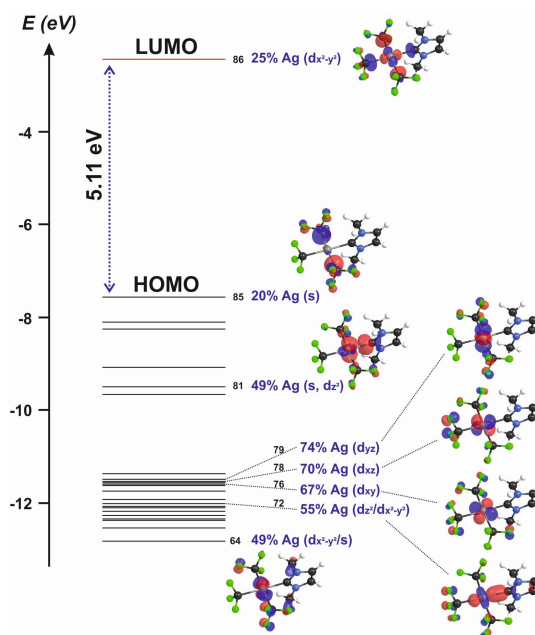


Figure 3. MO diagram calculated at the DFT/M06 level of theory for the model compound (CF₃)₃Ag(Ime).

the HOMO (MO#85) is just a 20%, and the LUMO (MO#86) is contributed by 25% of metal orbitals. Such configuration is typically found in complexes showing Inverted Ligand Field (ILF),^[16] a phenomenon that has been recently noticed and whose implications in chemical properties and reactivity are currently being rationalized.^[17]

The large HOMO–LUMO gap calculated for (CF₃)₃Ag(Ime) (5.11 eV) suggests enhanced stability for this type of compounds. This result prompted us to check experimentally the stabilities of complexes **1**, **2a**, **2b**, and **3** by TGA (see SI). They were found to be remarkably stable with onset temperatures of decomposition following the order: 127 (**1**) < 186 (**2a**) < 196 (**2b**) < 215 (**3**) °C. Complex **1** sharply decomposes at 127 °C (Figure S13) owing probably to the volatility of the CN^tBu ligand (bp 92 °C), which would get lost upon dissociation. The complexes of the less volatile NHC ligands are substantially more stable. Furthermore, they also show richer decomposition patterns with at least one well-defined plateau above the corresponding onset point (Figures S14–S16). In order to ascertain the nature of the species formed upon decomposition of the (CF₃)₃Ag(NHC) complexes under study, we carried out their controlled thermolyses in sealed tubes at temperatures slightly below the corresponding onset decomposition point (see SI). We find it quite remarkable that complexes **2a** and **2b** cleanly afford the mixed-valence compounds [Ag^I(NHC)₂][Ag^{III}-(CF₃)₄] (**4a**, **4b**), with empirical formula (CF₃)₂Ag(NHC). The structure of **4a** was confirmed by *sc*-XRD methods.^[12] The Ag–C distances found in the linear [Ag^I(IDipp)₂]⁺ cation and in the (*SP*-4)-[Ag^{III}(CF₃)₄][−] anion are all quite similar and comprised in the range 208.8(3)–210.7(3) pm (Table S10). The net transformation of **2a/2b** into **4a/4b** involves the formal loss of one CF₃ group per Ag atom and transmetalation. The latter rearrangements are typically promoted by Ag^I species. For this

reason, we believe that in these thermolyses two CF_3 ligands are released from the same metal center rendering the $(\text{CF}_3)_2\text{Ag}^{\text{I}}(\text{NHC})$ intermediate. Subsequent ligand exchange with unreacted $(\text{CF}_3)_3\text{Ag}^{\text{III}}(\text{NHC})$ would lead to the eventually observed compounds. It is worth noting that the overall process takes place with no solvent at all and requires high thermal activation.

Conclusions

We report herein on a novel synthetic route to introduce NHC ligands by reaction of imidazolium salts with a metal fluoride complex (Scheme 2). This procedure has enabled us to access Ag^{III} carbene compounds, which, as far as we know, were unprecedented. The new $(\text{CF}_3)_3\text{Ag}(\text{NHC})$ complexes exhibit unexpectedly high thermal stabilities, evolving into the mixed-valence salts $[\text{Ag}^{\text{I}}(\text{NHC})_2][\text{Ag}^{\text{III}}(\text{CF}_3)_4]$ only at very high temperatures ($> 185^\circ\text{C}$) in the absence of solvent. It can be anticipated that the 'fluoride method' presented here may find wide application in the synthesis of NHC complexes of high-valent coinage-metals and other late-TMs, where the fluoride complexes are particularly reactive.^[18]

Experimental Section

General Procedures and Materials. The reactions and manipulations were carried out under purified Ar and exclusion of light using Schlenk techniques, dried and degassed solvents. Compounds $[\text{PPh}_4][(\text{CF}_3)_3\text{AgF}]^{[14]}$ and $(\text{CF}_3)_3\text{Ag}(\text{NCMe})^{[11]}$ were prepared using published methods. Detailed information on the techniques and equipment used is included in SI. Regarding NMR data, chemical shifts (δ in ppm) are given with respect to the standard references. $\text{CF}_3\text{---Ag---CF}_3$ refers to the mutually *trans*-standing CF_3 groups, whereas $\text{CF}_3\text{---Ag---L}$ refers to the CF_3 group *trans* to the neutral L ligand. Where coupling to the Ag nuclei is observed, only the $^2J(^{109}\text{Ag}, \text{X})$ values are given. Further details are included in SI.

Synthesis of $(\text{CF}_3)_3\text{Ag}(\text{CN}^i\text{Bu})$ (1): To a solution of $(\text{CF}_3)_3\text{Ag}(\text{NCMe})$ (100 mg, 0.28 mmol) in 3 cm^3 of MeCN, CN^iBu (32.3 mm^3 , 0.28 mmol) was added and the mixture was stirred at room temperature for 5 min. After removing the solvent in vacuo and treating the residue with cold *n*-hexane ($2 \times 1\text{ cm}^3$), a white solid was obtained, which was identified as compound **1** (43 mg, 0.11 mmol, 38% yield). IR (Fig. S1): $\tilde{\nu}/\text{cm}^{-1} = 2995$ (w), 2263 (m; CN), 1477 (w), 1456 (m), 1378 (w), 1241 (w), 1121 (vs), 1030 (vs), 998 (vs), 834 (m), 723 (m), 704 (s), 529 (m), 440 (w), 295 (s). $^1\text{H NMR}$ (400.13 MHz, CD_2Cl_2 , 298 K; Fig. S6): $\delta_{\text{H}}/\text{ppm} = 1.63$ (s, Me). $^{13}\text{C NMR}$ (100.61 MHz, CD_2Cl_2 , 298 K): $\delta_{\text{C}}/\text{ppm} = 136.23$ [two d, $^2J(^{109}\text{Ag}, ^{13}\text{C}) = 135.8$ Hz; $\text{CF}_3\text{---Ag---CF}_3$], 127.71 [two d, $^2J(^{109}\text{Ag}, ^{13}\text{C}) = 198.5$ Hz; $\text{CF}_3\text{---Ag---CF}_3$], 127.82 (CN), 60.68 (CMe_3), 29.16 (CH_3). $^{19}\text{F NMR}$ (376.49 MHz, CD_2Cl_2 , 298 K; Fig. S5): $\delta_{\text{F}}/\text{ppm} = -25.34$ [dspt, 3F, $^2J(^{109}\text{Ag}, \text{F}) = 72.7$ Hz, $^4J(\text{F}, \text{F}) = 8.6$ Hz; $\text{CF}_3\text{---Ag---L}$], -25.86 [dq, 6F, $^2J(^{109}\text{Ag}, \text{F}) = 28.61$ Hz, $^4J(\text{F}, \text{F}) = 8.6$ Hz; $\text{CF}_3\text{---Ag---CF}_3$]. **Elemental analysis** (%) calcd for $\text{C}_8\text{H}_9\text{AgF}_9\text{N}$: C 24.14, H 2.27, N 3.51; found: C 24.54, H 2.18, N 3.34. **Single crystals** suitable for X-ray diffraction purposes were obtained by slow diffusion of a *n*-hexane (3 cm^3) layer into a solution of 10 mg of compound **1** in Et_2O (0.5 cm^3) at -30°C .

Synthesis of $(\text{CF}_3)_3\text{Ag}(\text{IDipp})$ (2a): To a solution of 1,3-bis(2,6-diisopropylphenyl)imidazolium hexafluorophosphate, (HIDipp) PF_6 (63.5 mg, 0.12 mmol), in 5 cm^3 of dry CH_2Cl_2 , $[\text{PPh}_4][(\text{CF}_3)_3\text{AgF}]$

(80 mg, 0.12 mmol) was added and the mixture was stirred for 36 h at 65°C , after which time it was extracted using a short silica column and *n*-hexane/ethyl acetate as a carrier (3/1). After the removal of all volatiles under vacuum a white solid was obtained, which was identified as **2a** (33 mg, 0.05 mmol, 40% yield) IR (Fig. S2): $\tilde{\nu}/\text{cm}^{-1} = 2967$ (w), 2170 (w), 1605 (w), 1541 (w), 1449 (m), 1409 (w), 1387 (w), 1351 (w), 1329 (w), 1257 (w), 1136 (s), 1053 (vs), 805 (m), 751 (s), 696 (w), 557 (w), 525 (m), 448 (w), 317 (m), 308 (s). $^1\text{H NMR}$ (400.13 MHz, CD_2Cl_2 , 298 K, Fig. S8): $\delta_{\text{H}}/\text{ppm} = 7.54$ [t, 2H, $^3J(\text{H}, \text{H}) = 7.53$ Hz; *para*-H], 7.39 [d, 4H, $^3J(\text{H}, \text{H}) = 7.53$ Hz; *meta*-H], 7.38 (s, 2H; CH imidazole), 2.85 [spt, 4H, $^3J(\text{H}, \text{H}) = 6.9$ Hz; CHMe_2], 1.34 [d, 6H, $^3J(\text{H}, \text{H}) = 6.9$ Hz; CH_3], 1.11 [d, 6H, $^3J(\text{H}, \text{H}) = 6.9$ Hz; CH_3]. $^{13}\text{C NMR}$ (100.61 MHz, CD_2Cl_2 , 298 K): $\delta_{\text{C}}/\text{ppm} = 174.4$ ($\text{C}^{\text{carbene}}$), 145.6 (*ortho*-C), 136.5 ($\text{CF}_3\text{---Ag---CF}_3$), 133.5 (*ipso*-C), 133.0 ($\text{CF}_3\text{---Ag---L}$), 130.8 (*para*-C), 125.0 (CH imidazole), 124.7 (*meta*-C), 28.3 (CHMe_2), 26.4 (CH_3), 22.0 (CH_3). $^{19}\text{F NMR}$ (376.49 MHz, CD_2Cl_2 , 298 K, Fig. S7): $\delta_{\text{F}}/\text{ppm} = -28.18$ [2 dq, 6F, $^2J(^{109}\text{Ag}, \text{F}) = 34.8$ Hz, $^4J(\text{F}, \text{F}) = 8.8$ Hz; $\text{CF}_3\text{---Ag---CF}_3$], -28.83 [2 dspt, 3F, $^2J(^{109}\text{Ag}, \text{F}) = 51.8$ Hz, $^4J(\text{F}, \text{F}) = 8.8$ Hz; $\text{CF}_3\text{---Ag---L}$]. **Single crystals** suitable for X-ray diffraction purposes were obtained by slow diffusion of a *n*-hexane (6 cm^3) layer into a solution of 10 mg of compound **2a** in CH_2Cl_2 (0.5 cm^3) at -30°C .

Synthesis of $(\text{CF}_3)_3\text{Ag}(\text{IMes})$ (2b): To a solution of 1,3-bis(2,4,6-trimethylphenyl)imidazolium hexafluorophosphate, (HIMes) PF_6 (66.9 mg, 0.148 mmol), in 5 cm^3 of dry CH_2Cl_2 , $[\text{PPh}_4][(\text{CF}_3)_3\text{AgF}]$ (100 mg, 0.148 mmol) was added and the mixture was stirred for 30 h at 65°C , after which time, it was extracted using a short silica column using *n*-hexane/ethyl acetate as a carrier (6/4) to wash off the remainder of the salts in solution. After removal of all volatiles under vacuum, a white solid is obtained, which was identified as **2b** (41 mg, 0.065 mmol, 44% yield). IR (Fig. S3): $\tilde{\nu}/\text{cm}^{-1} = 2099$ (w), 1608 (w), 1484 (m), 1413 (w), 1384 (w), 1328 (w), 1295 (w), 1226 (s), 1114 (m), 1061 (vs), 1032 (vs), 928 (m), 856 (m) 751 (s), 735 (m), 714 (w), 698 (s), 575 (m), 520 (w), 476 (w). $^1\text{H NMR}$ (400.13 MHz, CD_2Cl_2 , 298 K, Fig. S10): $\delta_{\text{H}}/\text{ppm} = 7.30$ (s, 2H; CH imidazole), 6.99 (s, 4H; *meta*-H), 2.28 (s, 6H; *ortho*- CH_3), 2.02 (s, 3H; *para*- CH_3). $^{13}\text{C NMR}$ (100.61 MHz, CD_2Cl_2 , 298 K): $\delta_{\text{C}}/\text{ppm} = 173.0$ ($\text{C}^{\text{carbene}}$), 140.0 (*para*-C Mes), 136.3 ($\text{CF}_3\text{---Ag---CF}_3$), 134.7 (*ipso*-C Mes), 133.4 (*ortho*-C Mes), 132.9 ($\text{CF}_3\text{---Ag---L}$), 130.0 (*meta*-C Mes), 124.8 (CH imidazole), 20.7 (*para*- CH_3 Mes), 18.0 (*ortho*- CH_3 Mes). $^{19}\text{F NMR}$ (376.49 MHz, CD_2Cl_2 , 298 K, Fig. S9): $\delta_{\text{F}}/\text{ppm} = -28.08$ [2 dq, 6F, $^2J(^{109}\text{Ag}, \text{F}) = 35.60$ Hz, $^4J(\text{F}, \text{F}) = 8.6$ Hz; $\text{CF}_3\text{---Ag---CF}_3$], -29.09 [2 dspt, 3F, $^2J(^{109}\text{Ag}, \text{F}) = 52.40$ Hz, $^4J(\text{F}, \text{F}) = 8.6$ Hz; $\text{CF}_3\text{---Ag---NHC}$]. **Elemental analysis** calcd for $\text{C}_{24}\text{H}_{24}\text{AgF}_9\text{N}_2$: C 46.5, H 3.9, N 4.5; found: C 46.9, H 4.0, N 4.4. **Single crystals** suitable for X-ray diffraction purposes were obtained by slow diffusion of a *n*-hexane (6 cm^3) layer into a solution of 10 mg of compound **1** in CH_2Cl_2 (0.5 cm^3) at -30°C .

Synthesis of $(\text{CF}_3)_3\text{Ag}(\text{NHC-py})$ (3): To a solution of 2-(pyridin-2-yl)-3-(2,4,6-trimethylphenyl)imidazolium hexafluorophosphate in 5 cm^3 of dry CH_2Cl_2 , $[\text{PPh}_4][(\text{CF}_3)_3\text{AgF}]$ (100 mg, 0.15 mmol) was added, and the mixture was stirred for 30 h at 65°C , after which time, the mixture was extracted through a short silica column using dichloromethane/ethyl acetate (3/1) as a carrier. The subsequent removal of all volatiles at vacuum yielded a white solid, which was identified as compound **3** (50 mg, 0.09 mmol, 59% yield). IR (Fig. S4): $\tilde{\nu}/\text{cm}^{-1} = 2924$ (w), 2088 (w), 1603 (m), 1582 (w), 1478 (s), 1447 (s), 1384 (w), 1315 (m), 1279 (w), 1249 (w), 1136 (s), 1014 (vs), 855 (s), 803 (w), 778 (s), 737 (s), 715 (m), 688 (s), 628 (w), 590 (w), 523 (m), 403 (w), 353 (m), 310 (s). $^1\text{H NMR}$ (400.13 MHz, CD_2Cl_2 , 298 K; Fig. S12): $\delta_{\text{H}}/\text{ppm} = 8.68$ [dd, 1H, $^3J(\text{H}, \text{H}) = 4.4$ Hz, $^4J(\text{H}, \text{H}) = 1.7$ Hz; H^6 py], 8.10 [td, 1H, $^3J(\text{H}, \text{H}) = 7.6$ Hz, $^4J(\text{H}, \text{H}) = 1.7$ Hz; H^4 py], 7.94 [d, 1H, $^3J(\text{H}, \text{H}) = 1.8$ Hz; CH imidazole], 7.67 [dd, 1H, $^3J(\text{H}, \text{H}) = 7.8$ Hz, $^4J(\text{H}, \text{H}) = 1.0$ Hz; H^3 py], 7.56 [ddd, 1H, $^3J(\text{H}, \text{H}) = 7.6$ Hz, $^3J(\text{H}, \text{H}) = 4.4$ Hz, $^4J(\text{H}, \text{H}) = 1.0$ Hz; H^5 py], 7.29 [d, 1H, $^3J(\text{H}, \text{H}) = 1.8$ Hz; CH imidazole], 7.10 (s, 2H; *meta*-H Mes), 2.42 (s, 3H; *para*- CH_3 Mes), 2.12 (s, 6H; *ortho*- CH_3

Mes). ^{13}C NMR (100.61 MHz, CD_2Cl_2 , 298 K): $\delta_{\text{C}}/\text{ppm} = 173.6$ ($\text{C}^{\text{carbene}}$), 149.0, 148.5, 140.4, 124.3, 112.3 (py), 140.0 136.6 ($\text{CF}_3\text{-Ag-CF}_3$), 135.2, 135.1, 133.0 (*ipso*-C, *ortho*-C, *para*-C Mes), 133.2 ($\text{CF}_3\text{-Ag-NHC}$), 129.5 (*meta*-C Mes), 125.8, 118.0 (CH imidazole), 20.8 (*para*- CH_3 Mes), 17.1 (*ortho*- CH_3 Mes). ^{19}F NMR (376.49 MHz, CD_2Cl_2 , 298 K; Fig. S11) $\delta_{\text{F}}/\text{ppm} = -27.68$ [2 dq, 6F, $^2J(^{109}\text{Ag},\text{F}) = 35.1$ Hz, $^4J(\text{F},\text{F}) = 8.6$ Hz; $\text{CF}_3\text{-Ag-CF}_3$], -28.88 [2 dspt, 3F, $^2J(^{109}\text{Ag},\text{F}) = 53.0$ Hz, $^4J(\text{F},\text{F}) = 8.6$ Hz; $\text{CF}_3\text{-Ag-L}$]. **Elemental analysis** calcd (%) for $\text{C}_{24}\text{H}_{24}\text{AgF}_9\text{N}_2$: C 41.5, H 3.9, N 4.5; found: C 40.8, H 4.0, N 4.4. **Single crystals** suitable for X-ray diffraction purposes were obtained by slow diffusion of a *n*-hexane (6 cm^3) layer into a solution of 10 mg of compound **3** in CH_2Cl_2 (0.5 cm^3) at 4 °C.

Crystal data & Computational details are included in SI. For deposition numbers of the XRD structures, see ref [12].

Supporting Information

Detailed information on general procedures and materials, full characterization data (IR, NMR, TGA, XRD), and computational details.

Acknowledgements

This work was supported by the Spanish MCIU/FEDER (Project PID2021-122869NB-I00) and the Gobierno de Aragón (E17_23R). BIFI (Instituto de Biocomputación y Física de Sistemas Complejos) and CESGA (Centro de Supercomputación de Galicia) are acknowledged for allocation of computational resources. D. J.-S. thanks the Spanish MICIU for a grant (BES-2016-078732).

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: highest oxidation states · inverted ligand field · metal carbenes · silver · trifluoromethyl

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Manuscript received: November 27, 2023
Accepted manuscript online: December 29, 2023
Version of record online: January 15, 2024