Encapsulation of a trinuclear silver(I) cluster by two imido-nitrido metalloligands $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$†

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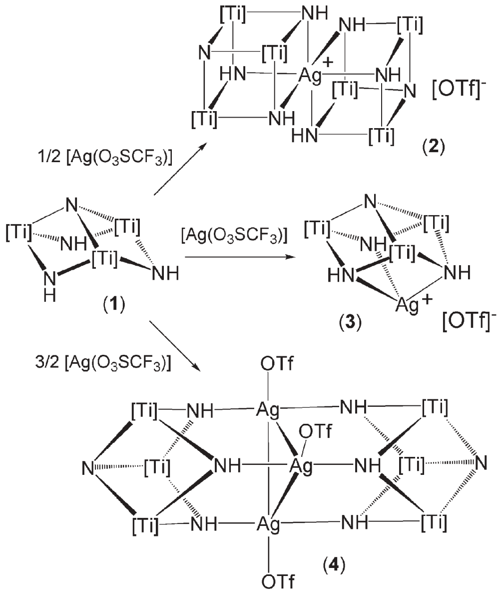
Treatment of the metalloligand $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ with silver(I) trifluoromethanesulfonate in different molar ratios gives the ionic compounds $[Ag\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2][O_3SCF_3]$ and $[Ag\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}][O_3SCF_3]$ or the triangular silver cluster $[(CF_3SO_2O)_3Ag_3\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ in which each face is capped by a metalloligand.

As part of a program related to the synthesis of polynuclear nitrido complexes,[1] we have been studying the coordination chemistry of the trinuclear imido-nitrido complex $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$[2] (**1**) with a variety of main-group and transition metals.[3] In those studies, we have noted that **1** is prone to act as tridentate chelate to a single metal (*e.g.* Ti, Sn, Zn, Cu) through the basal NH imido groups, although in some solid-state structures coordination by only one NH group to the metal center (Sn, Zn, Al, Ga, In) has been observed. In many aspects the metalloligand **1** resembles other well-known tridentate nitrogen ligands in coordination chemistry as tris(pyrazolyl)borates,[4] tris(pyrazolyl)methanes,[5] 1,4,7-triazacyclononanes,[6] and especially 1,3,5-triazacyclohexanes.[7] However, the existence of the μ_3-N nitrido apical group confers a more rigid conformation to **1** when compared with those systems. Here we report the preliminary study about the interactions of silver(I) salts with our metalloligand. The conventional tridentate chelate coordination mode of **1** is observed for several ionic complexes while an unprecedented bridging mode (μ_3-η^1:η^1:η^1) has been structurally characterized in the triangular silver(I) cluster $[(CF_3SO_2O)_3Ag_3\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$.

The results obtained in the treatment of $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) with silver(I) trifluoromethanesulfonate in different ratios are summarized in Scheme 1. The reaction of **1** with a half equivalent of $[Ag(O_3SCF_3)]$ in dichloromethane at room temperature in the absence of light led to the corner-shared double-cube ionic complex $[Ag\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2][O_3SCF_3]$ (**2**). Analogous treatment in a 1 : 1 ratio gave the complex $[Ag\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}][O_3SCF_3]$ (**3**). When the ratio of $[Ag(O_3SCF_3)]$ to the metalloligand was higher than 1.5 : 1 the trinuclear silver(I) compound $[(CF_3SO_2O)_3Ag_3\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2]$ (**4**) was obtained.

Compounds **2–4** were isolated in 50–82% yields as air and light sensitive yellow or orange solids, which are very soluble in halogenated solvents. However, whereas **2** and **3** are scarcely soluble in toluene or benzene, according to an ionic composition, complex **4** exhibits higher solubility in those solvents. The stability of complexes **2–4** in chloroform-d$_1$ was monitored by NMR spectroscopy. Compound **3** is stable for months, but solutions of **2** immediately undergo partial dissociation (*ca.* 5% conversion) to give **3** and **1**. This mixture remains unaltered for long periods of time even after heating at high temperatures. However, addition of $[Ag(O_3SCF_3)]$ (1 equiv.) to this solution at room temperature afforded immediately the complete consumption of **2** and only resonance signals assigned to complex **3** were observed in the NMR spectra. On the other hand, spectra taken after heating of **4** in chloroform-d$_1$ revealed minor resonance signals due to **3**, but only upon leaving the NMR tube at 80 °C for 3 days the spectra showed complete consumption of **4** to give complex **3** along with the precipitation of $[Ag(O_3SCF_3)]$. Stirring of this mixture at room temperature for 1 day regenerated complex **4**.

Compounds **2–4** were characterized by analytical and spectroscopic methods, as well as by X-ray crystal structure determinations for **2** and **4**.‡ IR spectra (KBr) of complexes **2–4** show two ν_{NH} vibrations, between 3357 and 3261 cm^{-1}, in a similar range to the value determined for **1**,[2] 3352 cm^{-1}. Information regarding the possible interaction of the triflate anion with a metal center may be obtained from the solid IR spectra in the 1350–1000 cm^{-1} range.[8] While in **2** the $\nu_{as}(SO_3)$ band is observed at 1274 cm^{-1}, which is



Scheme 1 Reactions of **1** with $[Ag(O_3SCF_3)]$. [Ti] = $Ti(\eta^5\text{-}C_5Me_5)$.

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† Electronic supplementary information (ESI) available: Experimental details and full characterization data for complexes **2–4**. See DOI: 10.1039/b704180b

closely similar to that found for the free $CF_3SO_3^-$ ion,[8b] the analogous stretching mode in **3** splits into two bands at 1276 and 1263 cm^{-1}, indicating some interaction of the triflate ion with the silver cation in the solid state.[8c,d] The splitting in two well-defined bands at 1290 and 1236 cm^{-1} found in compound **4** may agree with the coordination of the triflate groups. The ^1H and $^{13}C\{^1H\}$ NMR spectra in chloroform-d_1 of **2** and **3** at room temperature show resonance signals for equivalent NH and η^5-C_5Me_5 groups, suggesting a highly symmetrical structure or very fast exchange processes in solution, as those observed previously in other adducts of **1**.[3] The NH resonance signals, δ = 12.12 (**2**) and 12.25 (**3**) ppm, in the ^1H NMR spectra are shifted to higher field with respect to that found for **1** (δ = 13.40 ppm), suggesting a tridentate coordination of the ligand to the silver(I) ion.[3d] Thus, the NMR data for **2** would be consistent with a trigonally distorted octahedral geometry around the silver center, as determined previously for other silver(I) ionic complexes with two tridentate nitrogen ligands.[6b,9] However, the solid-state structure of **2** determined by an X-ray analysis reveals a linear two-coordinate environment for the silver center in the cationic fragment (Fig. 1). The silver atom lies on a inversion center and exhibits two silver-nitrogen distances, Ag(1)–N(13) 3.240(4) and Ag(1)–N(12) 2.900(4) Å, clearly longer than that to N(23) 2.205(4) but still shorter than the sum of the van der Waals radii (3.30 Å).[10] Geometrical parameters of the organometallic ligand are similar to those of the parent compound **1**.[2]

Compound **4** is soluble in toluene or benzene, and its ^1H, $^{13}C\{^1H\}$ and ^{19}F NMR spectra in benzene-d_6 or chloroform-d_1 at room temperature are very similar. The spectra show resonance signals for equivalent NH and η^5-C_5Me_5 ligands. The ^1H NMR spectrum in chloroform-d_1 reveals ^1H–$^{107,109}Ag$ couplings ($^2J_{H,Ag}$ = 6 Hz) for the imido groups, suggesting a static structure in solution. $^{13}C\{^1H\}$ NMR spectrum shows a singlet for the ipso-carbon resonance of the C_5Me_5 groups at δ = 127.2 ppm, which is *ca.* 7 ppm shifted downfield with respect to those found in complexes **2** (δ = 119.9 ppm) and **3** (δ = 120.6 ppm). These data are consistent with the solid-state structure determined by X-ray crystallography (Fig. 2). The complex contains an equilateral triangular cluster of Ag^I ions, with Ag–Ag separations of av. 2.978(3) Å; each face of the triangle is capped by a single "$(\mu_3\text{-NH})_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-N})$" metalloligand which binds to each silver center by one NH imido group. Therefore, every Ag^I is coordinated, in addition to the two Ag–Ag interactions, by two NH ligands and one oxygen atom of a triflate group. Thus, the geometry around the silver centers becomes a distorted trigonal-bipyramid with the nitrogen atoms at the axial positions (N–Ag–N 170.7(3)°) and two silver and the oxygen atoms at the equatorial plane (sum of angles = 357(1)°). The Ag–N distances (av. 2.175(7) Å) range between those found for two-coordinate [av. 2.11 Å] and six-coordinate [av. 2.27 Å] Ag^I ions in trinuclear silver complexes with $(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1)$ tris(pyrazolyl)borate ligands[11] and are also similar to that found in complex **2**. The Ag–O distance of av. 2.66(3) Å is smaller than the sum of the van der Waals radii of 3.20 Å,[10] and could be considered to be a coordinative Ag···O interaction,[12] in good agreement with the IR data. The coordination of the metalloligand to three silver atoms in **4** results in a slightly lengthening of the $Ti–N_{imido}$ and Ti···Ti distances, average 2.009(7) Å and 2.879(5) Å respectively, when compared with **1** (average 1.924 Å and 2.802 Å) without any other significant changes in bond lengths and angles.[2]

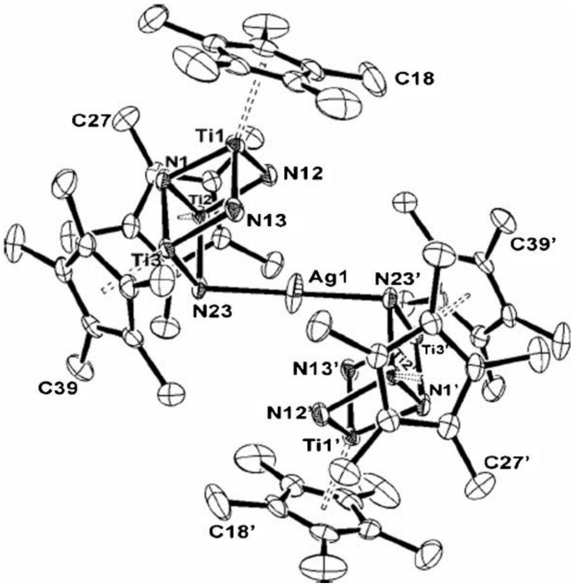

Fig. 1 Cationic fragment of the crystal structure of complex **2** (thermal ellipsoids at the 50% probability level). The prime character in the labels indicates that these atoms are at the equivalent position ($-x,-y,-z$). Selected lengths (Å) and angles (°): Ag(1)–N(23) 2.205(4), Ag(1)–N(13) 3.240(4), Ag(1)–N(12) 2.900(4), Ag(1)···Ti(1) 3.784(1), Ag(1)···Ti(2) 3.102(1), Ag(1)···Ti(3) 3.377(1), averaged values for N(1)–Ti 1.93(1), N_{basal}–Ti 1.96(2), Ti···Ti 2.848(5), N(23)–Ag(1)–N(23)′ 180.0, Ti–N_{basal}–Ti 93(1), Ti–N_{apical}–Ti 94.9(5), N_{basal}–Ti–N_{basal} 106.6(9), N_{basal}–Ti–N_{apical} 85.6(5).

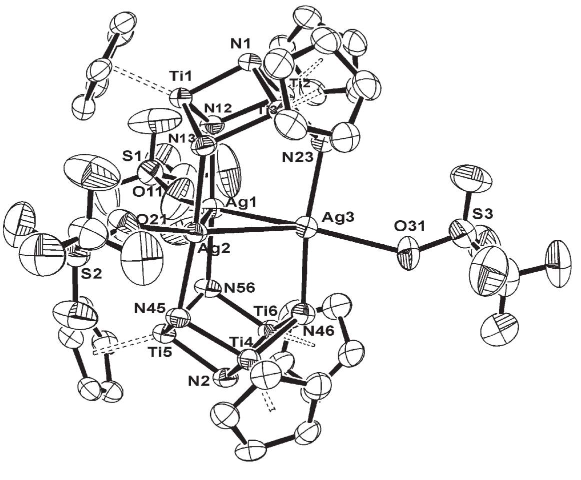

Fig. 2 Crystal structure of complex **4** (thermal ellipsoids at the 50% probability level). The methyl groups of the pentamethylcyclopentadienyl ligands are omitted for clarity. Average of selected lengths (Å) and angles (°): Ag–Ag 2.978(3), Ag–N 2.175(7), Ag–O 2.66(3), Ti–N_{basal} 2.009(7), Ti–N_{apical} 1.922(4), Ti···Ti 2.879(5), Ag–Ag–Ag 60.0(1), Ag–Ag–O 149(1), N–Ag–N 170.7(3), N–Ag–Ag 94(4), N–Ag–O 85(7), Ti–N_{basal}–Ti 91.5(3), Ti–N_{apical}–Ti 96.9(2), N_{basal}–Ti–N_{basal} 110.0(7), N_{basal}–Ti–N_{apical} 85.4(2), Ti–Ti–Ti 60.0(1).

In conclusion, we have demonstrated that $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-N})]$ can interact with both a single silver cation or trinuclear silver clusters through different binding modes. In particular, the unprecedented coordination mode $(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1)$

observed in complex **4** should be common for trinuclear systems containing metal–metal bonds or metallophilic interactions and will be the scope of our next investigations.

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Notes and references

‡ Crystal data for **2**: $C_{61}H_{96}AgF_3N_8O_3STi_6$, $M = 1473.79$, triclinic, $a = 11.6024(18)$, $b = 11.6193(11)$, $c = 14.7433(18)$ Å, $\alpha = 109.264(9)$, $\beta = 111.742(12)$, $\gamma = 95.191(9)$, $U = 1690.8(4)$ Å^3, $T = 200(2)$ K, space group $P\bar{1}$, $Z = 1$, μ(Mo-K$_\alpha$) = 1.042 mm^{-1}, 41498 reflections measured, 7597 unique (R_{int}= 0.057) which were used in all calculations. $R1(F^2) = 0.064$ (for 5044 reflections with $F_o > 4\sigma(F_o)$) and w$R2$ = 0.237 for all data.

Crystal data for **4**·C_7H_8: $C_{70}H_{104}Ag_3F_9N_8O_9S_3Ti_6$, $M = 2079.8$, monoclinic, $a = 16.058(3)$, $b = 20.694(6)$, $c = 37.507(11)$ Å, $\beta = 93.956(19)$, $U = 12434(5)$ Å^3, $T = 200(2)$ K, space group $P2_1/c$, $Z = 4$, μ(Mo-K$_\alpha$) = 0.927 mm^{-1}, 117004 reflections measured, 28264 unique ($R_{int} = 0.076$) which were used in all calculations. $R1(F^2) = 0.051$ (for 16649 reflections with $F_o > 4\sigma(F_o)$) and w$R2$ = 0.146 for all data. CCDC 641160 and 641161. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704180b

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