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**Encapsulation of a trinuclear silver(I) cluster by two imido-nitrido  
metalloligands [ $\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})$ ]**

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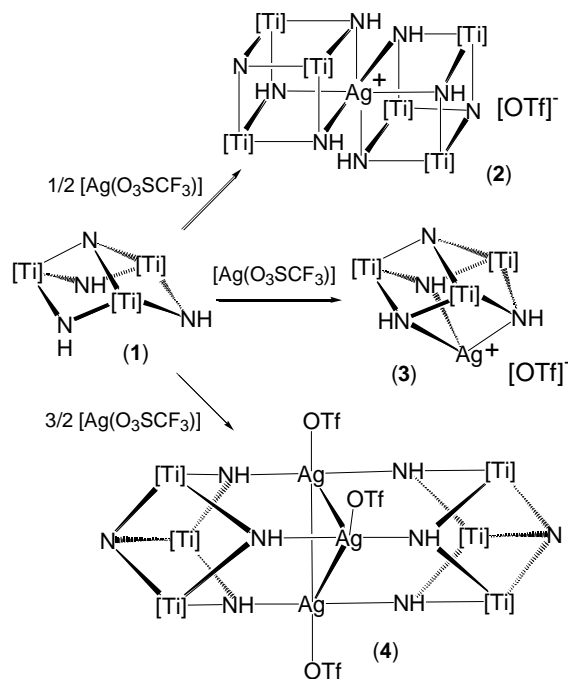
**Abstract:**

Treatment of the metalloligand [ $\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})$ ] with silver(I) trifluoromethanesulfonate in different molar ratios gives the ionic compounds [ $\text{Ag}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2[\text{O}_3\text{SCF}_3]$ ] and [ $\text{Ag}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}][\text{O}_3\text{SCF}_3]$ ] or the triangular silver cluster [ $(\text{CF}_3\text{SO}_2\text{O})_3\text{Ag}_3\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2$ ] in which each face is capped by a metalloligand.

As part of a program related to the synthesis of polynuclear nitrido complexes,<sup>1</sup> we have been studying the coordination chemistry of the trinuclear imido-nitrido complex  $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]^2$  (**1**) with a variety of main-group and transition metals.<sup>3</sup> 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,<sup>4</sup> tris(pyrazolyl)methanes,<sup>5</sup> 1,4,7-triazacyclononanes,<sup>6</sup> and especially 1,3,5-triazacyclohexanes.<sup>7</sup> However, the existence of the  $\mu_3\text{-N}$  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 ( $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$ ) has been structurally characterized in the triangular silver(I) cluster  $[(\text{CF}_3\text{SO}_2\text{O})_3\text{Ag}_3\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$ .

The results obtained in the treatment of  $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$  (**1**) with silver(I) trifluoromethanesulfonate in different ratios are summarized in Scheme 1. The reaction of **1** with half equivalent of  $[\text{Ag}(\text{O}_3\text{SCF}_3)]$  in dichloromethane at room temperature in the absence of light led to the corner-shared double-cube ionic complex  $[\text{Ag}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2][\text{O}_3\text{SCF}_3]$  (**2**). Analogous treatment in a 1:1 ratio gave the complex  $[\text{Ag}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}][\text{O}_3\text{SCF}_3]$  (**3**). When the ratio of  $[\text{Ag}(\text{O}_3\text{SCF}_3)]$  to the metalloligand was higher than 1.5:1 the trinuclear silver(I) compound  $[(\text{CF}_3\text{SO}_2\text{O})_3\text{Ag}_3\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$  (**4**) was obtained.

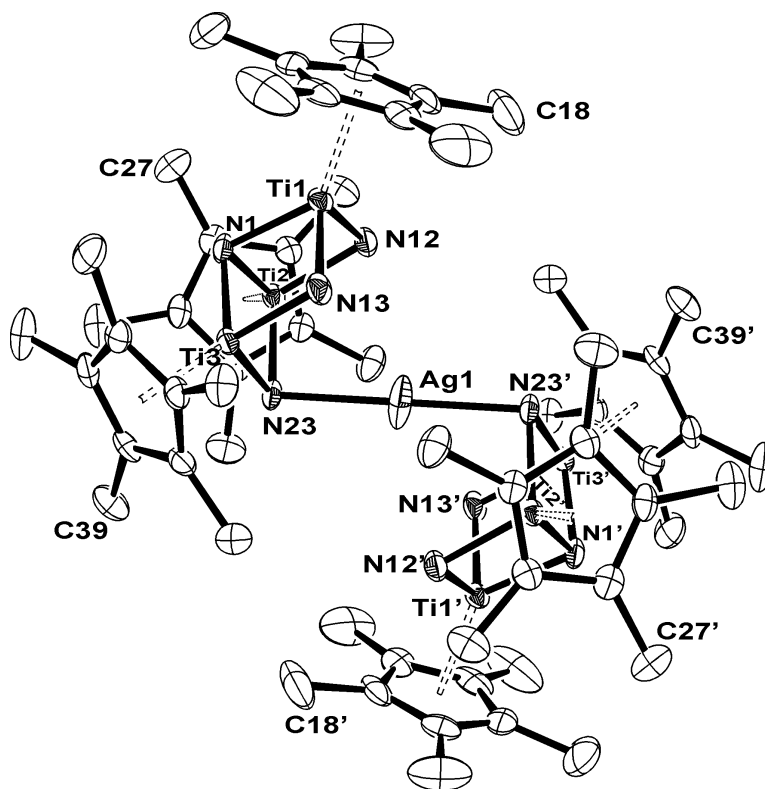
Compounds **2-4** were isolated in 50-82% yield as air and light sensitive yellow or orange solids, which are very soluble in halogenated solvents. However, whereas **2** and **3** are scarcely soluble in toluene or benzene, according to an ionic composition, complex **4** exhibits higher solubility 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  $[\text{Ag}(\text{O}_3\text{SCF}_3)]$  (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  $[\text{Ag}(\text{O}_3\text{SCF}_3)]$ . Stirring of this mixture at room temperature for 1 day regenerated complex **4**.



**Scheme 1.** Reactions of **1** with  $[\text{Ag}(\text{O}_3\text{SCF}_3)]$ .  $[\text{Ti}] = \text{Ti}(\eta^5\text{-C}_5\text{Me}_5)$ .

Compounds **2-4** were characterized by analytical and spectroscopic methods, as well as by X-ray crystal structure determinations for **2** and **4**.<sup>‡</sup> IR spectra (KBr) of complexes **2-4** show two  $\nu_{\text{NH}}$  vibrations, between 3357 and 3261  $\text{cm}^{-1}$ , in a similar range to the value determined for **1**,<sup>2</sup> 3352  $\text{cm}^{-1}$ . 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  $\text{cm}^{-1}$  range.<sup>8</sup> While in **2** the  $\nu_{\text{as}}(\text{SO}_3)$  band is observed at 1274  $\text{cm}^{-1}$ , which is closely similar to that found for the free  $\text{CF}_3\text{SO}_3^-$  ion,<sup>8b</sup> the analogous stretching mode in **3** splits into two bands at 1276 and 1263  $\text{cm}^{-1}$ , indicating some interaction of the triflate ion with the silver cation in the solid state.<sup>8c,d</sup> The splitting in two well-defined bands at 1290 and 1236  $\text{cm}^{-1}$  found in compound **4** may agree with the coordination of the triflate groups. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra in chloroform- $d_1$  of **2** and **3** at room temperature show resonance signals for equivalent NH and  $\eta^5\text{-C}_5\text{Me}_5$  groups, suggesting a highly symmetrical structure or very fast exchange processes in solution, as those observed previously in other adducts of **1**.<sup>3</sup> The NH resonance signals,  $\delta = 12.12$  (**2**) and 12.25 (**3**), in the  $^1\text{H}$  NMR spectra are shifted to higher field with respect to that found for **1** ( $\delta = 13.40$ ), suggesting a tridentate coordination of the ligand to the silver(I) ion.<sup>3d</sup> 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.<sup>6b,9</sup> 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 (Figure 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).<sup>10</sup>

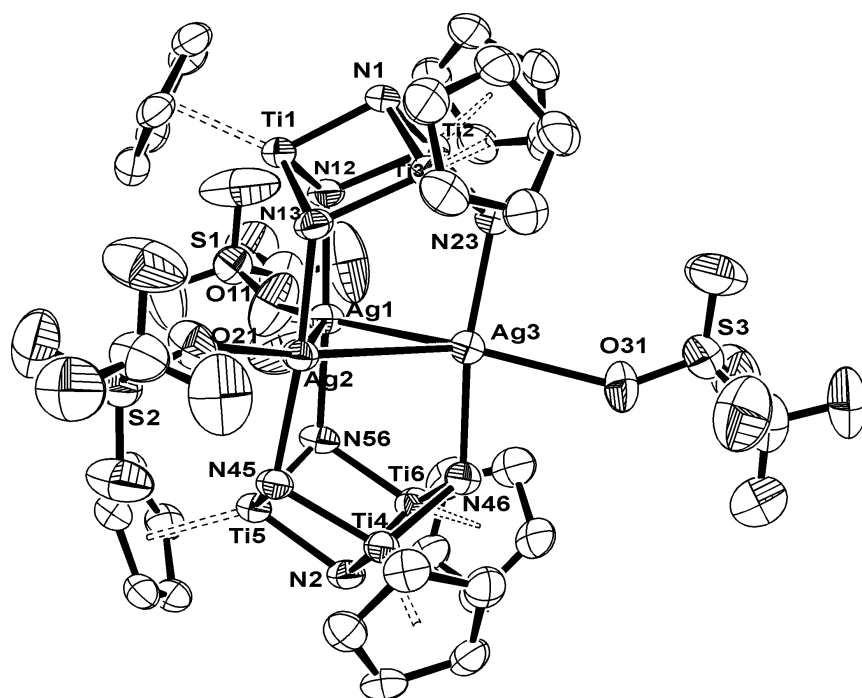
Geometrical parameters of the organometallic ligand are similar to those of the parent compound **1**.<sup>2</sup>



**Figure 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 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<sub>basal</sub>-Ti 1.96(2), Ti···Ti 2.848(5), N(23)-Ag(1)-N(23)' 180.0, Ti-N<sub>basal</sub>-Ti 93(1), Ti-N<sub>apical</sub>-Ti 94.9(5), N<sub>basal</sub>-Ti-N<sub>basal</sub> 106.6(9), N<sub>basal</sub>-Ti-N<sub>apical</sub> 85.6(5).

Compound **4** is soluble in toluene or benzene, and its <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>19</sup>F NMR spectra in benzene-d<sub>6</sub> or chloroform-d<sub>1</sub> at room temperature are very similar. The spectra show resonance signals for equivalent NH and η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub> ligands. The <sup>1</sup>H NMR spectrum in

chloroform-d<sub>1</sub> reveals  $^1\text{H}$ - $^{107,109}\text{Ag}$  couplings ( $^2J_{\text{H,Ag}} = 6$  Hz) for the imido groups, suggesting a static structure in solution.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum shows a singlet for the ipso-carbon resonance of the C<sub>5</sub>Me<sub>5</sub> groups at  $\delta = 127.2$ , which is ca. 7 ppm shifted downfield with respect to those found in complexes **2** ( $\delta = 119.9$ ) and **3** ( $\delta = 120.6$ ). These data are consistent with the solid-state structure determined by X-ray crystallography (Figure 2). The complex contains an equilateral triangular cluster of Ag<sup>I</sup> ions, with Ag-Ag separations of av. 2.978(3) Å; each face of the triangle is capped by a single “(μ<sub>3</sub>-NH)<sub>3</sub>Ti<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>(μ<sub>3</sub>-N)” metalloligand which binds to each silver center by one NH imido group. Therefore, every Ag<sup>I</sup> 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<sup>I</sup> ions in trinuclear silver complexes with (μ<sub>3</sub>-η<sup>1</sup>:η<sup>1</sup>:η<sup>1</sup>) tris(pyrazolyl)borate ligands<sup>11</sup> 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,<sup>10</sup> and could be considered to be a coordinative Ag...O interaction,<sup>12</sup> 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<sub>imido</sub> 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.<sup>2</sup>



**Figure 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<sub>basal</sub> 2.009(7), Ti-N<sub>apical</sub> 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<sub>basal</sub>-Ti 91.5(3), Ti-N<sub>apical</sub>-Ti 96.9(2), N<sub>basal</sub>-Ti-N<sub>basal</sub> 110.0(7), N<sub>basal</sub>-Ti-N<sub>apical</sub> 85.4(2), Ti-Ti-Ti 60.0(1).

In conclusion, we have demonstrated that  $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$  can interact with both a single silver cation or trinuclear silver clusters through different binding modes. In particular, the unprecedented coordination mode  $(\mu_3\text{-}\eta^1:\eta^1:\eta^1)$  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,  $a = 11.6024(18)$ ,  $b = 11.61.93(11)$ ,  $c = 14.7433(18)$  Å,  $\alpha = 109.264(9)$ ,  $\beta = 111.742(12)$ ,  $\gamma = 95.191(9)$ ,  $U = 1690.8(4)$  Å<sup>3</sup>,  $T = 200(2)$  K, space group P-1,  $Z = 1$ ,  $\mu(\text{Mo-K}\alpha) = 1.042$  mm<sup>-1</sup>, 41498 reflections measured, 7597 unique ( $R_{int} = 0.057$ ) which were used in all calculations.  $RI(F^2) = 0.064$  (for 5044 reflections with  $F_o > 4\sigma(F_o)$ ) and  $wR2 = 0.237$  for all data.

Crystal data for **4·C<sub>7</sub>H<sub>8</sub>**:  $C_{70}H_{104}Ag_3F_9N_8O_9S_3Ti_6$ ,  $M = 2079.8$ , monoclinic,  $a = 16.058(3)$ ,  $b = 20.694(6)$ ,  $c = 37.507(11)$  Å,  $\beta = 93.956(19)$ ,  $U = 12434(5)$  Å<sup>3</sup>,  $T = 200(2)$  K, space group P2<sub>1</sub>/c,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 0.927$  mm<sup>-1</sup>, 117004 reflections measured, 28264 unique ( $R_{int} = 0.076$ ) which were used in all calculations.  $RI(F^2) = 0.051$  (for 16649 reflections with  $F_o > 4\sigma(F_o)$ ) and  $wR2 = 0.146$  for all data.

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