Electronic Supplementary Information for:

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

Avelino Martín, Noelia Martínez-Espada, Miguel Mena and Carlos Yélamos*

Departamento de Química Inorgánica, Universidad de Alcalá. 28871 Alcalá de Henares-Madrid (Spain). Tel: (+34) 91-8854898. FAX: (+34) 91-8854683. E-mail: carlos.yelamos@uah.es

Experimental Details and Characterization Data:

General Considerations. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Hexane was distilled from Na/K alloy just before use. Toluene was freshly distilled from sodium. Dichloromethane was dried with P_2O_5 and distilled prior to use. NMR solvents were dried with Na/K alloy (C_6D_6) or calcium hydride ($CDCl_3$) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1×10^{-3} Torr) and subsequently filled with inert gas. Silver(I) trifluoromethanesulfonate was purchased from Aldrich and used as received. $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ (**1**) was prepared according to a published procedure.[1]

Samples for infrared spectroscopy were prepared as KBr pellets. ^1H, $^{13}C\{^1H\}$ and ^{19}F NMR spectra were recorded on a Varian Unity-300 and/or Unity-500 Plus spectrometers. Chemical shifts (δ, ppm) in the ^1H and $^{13}C\{^1H\}$ NMR spectra are given relative to residual protons or to carbon of the solvent. Chemical shifts (δ, ppm) in the ^{19}F NMR spectra are given relative to $CFCl_3$ as external reference. Microanalyses (C, H, N, S) were performed in a Leco CHNS-932 microanalyzer.

Synthesis of [Ag{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$][O$_3$SCF$_3$] (2): A 100 mL amber stained Schlenk flask was charged with **1** (0.30 g, 0.49 mmol), [Ag(O$_3$SCF$_3$)] (0.063 g, 0.24 mmol) and dichloromethane (60 mL). After stirring at room temperature for 20 h, the solution was filtered and the volatile components removed under reduced pressure. The resultant yellow solid was washed with toluene (10 mL) and vacuum-dried to afford **2** as a yellow powder (0.18 g, 50%). IR (KBr, cm^{-1}): 3350 (m), 3334 (w), 2910 (s), 2859 (s), 1490 (w), 1431 (s), 1378 (s), 1274 (vs), 1218 (m), 1139 (vs), 1034 (vs), 716 (vs), 670 (vs), 651 (vs), 636 (vs), 610 (s), 570 (m), 550 (m), 517 (s), 471 (m), 420 (m), 396 (m). ^{1}H NMR (CDCl$_3$, 20 ºC, δ): 12.12 (s broad, 6H; NH), 2.02 (s, 90H; C$_5$Me$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$, 20 ºC, δ): 119.9 (*C*$_5$Me$_5$), 12.3 (C$_5$*Me*$_5$), the *C*F$_3$ carbon atom resonance was not detected. ^{19}F NMR (CDCl$_3$, 20 ºC, δ): -78.2 (C*F*$_3$). Anal. Calcd for $C_{61}H_{96}AgF_3N_8O_3STi_6$ (M$_w$=1473.61) (%): C 49.72, H 6.57, N 7.60, S 2.18. Found: C 49.46, H 6.36, N 7.31, S 2.00.

Synthesis of [Ag{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}][O$_3$SCF$_3$] (3): A 100 mL amber stained Schlenk flask was charged with **1** (0.70 g, 1.15 mmol), [Ag(O$_3$SCF$_3$)] (0.30 g, 1.17 mmol) and dichloromethane (80 mL). After stirring at room temperature for 18 h, the solution was filtered and the volatile components removed under reduced pressure. The resultant yellow solid was washed with hexane (20 mL) and vacuum-dried to afford **3** as a yellow powder (0.82 g, 82%). IR (KBr, cm^{-1}): 3343 (m), 3307 (m), 2911 (s), 2859 (m), 1489 (m), 1428 (s), 1380 (s), 1276 (vs), 1263 (vs), 1224 (s), 1153 (s), 1031 (vs), 803 (s), 726 (s), 654 (vs), 637 (vs), 604 (s), 572 (m), 517 (s), 477 (m), 428 (m), 405 (m). ^{1}H NMR (CDCl$_3$, 20 ºC, δ): 12.25 (s broad, 3H; NH), 2.04 (s, 45H; C$_5$Me$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$, 20 ºC, δ): 120.6 (*C*$_5$Me$_5$), 11.8 (C$_5$*Me*$_5$), the *C*F$_3$ carbon atom resonance was not detected. ^{19}F NMR (CDCl$_3$, 20 ºC, δ): -78.1 (C*F*$_3$). Anal. Calcd for

$C_{31}H_{48}AgF_3N_4O_3STi_3$ (M_w=865.28) (%): C 43.03, H 5.59, N 6.48, S 3.70. Found: C 43.39, H 5.46, N 6.73, S 3.23.

Synthesis of [$(CF_3SO_3)_3Ag_3\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}_2$] (4): A 100 mL amber stained Schlenk flask was charged with **1** (0.30 g, 0.49 mmol), [$Ag(O_3SCF_3)$] (0.25 g, 0.97 mmol) and toluene (70 mL). After stirring at room temperature for 3 days, the solution was filtered and the volatile components removed under reduced pressure. The resultant solid was vacuum-dried to afford **4·C_7H_8** as an orange powder (0.30 g, 59%). The compound was recrystallizated in toluene (20 mL) at –25 ºC to give X-ray quality orange crystals. IR (KBr, cm^{-1}): 3357 (w), 3261 (s), 2914 (s), 2861 (m), 1605 (w), 1495 (m), 1430 (s), 1382 (s), 1290 (vs), 1236 (vs), 1219 (vs), 1155 (vs), 1027 (vs), 807 (m), 772 (s), 731 (m), 695 (w), 652 (vs), 636 (vs), 604 (vs), 572 (m), 516 (s), 465 (s), 407 (m). ^1H NMR ($CDCl_3$, 20 ºC, δ): 12.32 (d broad, $^2J_{H\text{-}Ag}$ = 6.0 Hz, 6H; NH), 2.27 (s, 90H; C_5Me_5). ^1H NMR (C_6D_6, 20 ºC, δ): 12.63 (broad, 6H; NH), 2.16 (s, 90H; C_5Me_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 ºC, δ): 127.2 (C_5Me$_5$), 13.4 (C$_5$$Me_5$), the CF$_3$ carbon atom resonance was not detected. $^{13}C\{^1H\}$ NMR (C_6D_6, 20 ºC, δ): 127.1 (C_5Me$_5$), 13.4 (C$_5$$Me_5$). ^{19}F NMR ($CDCl_3$, 20 ºC, δ): -78.2 (CF_3). ^{19}F NMR (C_6D_6, 20 ºC, δ): -77.8 (CF_3). Anal. Calcd for $C_{70}H_{104}Ag_3F_9N_8O_9S_3Ti_6$ (M_w=2079.63) (%): C 40.43, H 5.04, N 5.39, S 4.63. Found: C 40.34, H 4.87, N 5.42, S 4.55.

X-ray structure determination of 2 and 4. X-ray quality crystals of **2** were grown by careful layering of a dichloromethane solution (20 mL) with hexane (40 mL). Crystals of **4** were grown at –25 ºC from a toluene solution. The crystals were removed from the Schlenk and covered with a layer of a viscous perfluoropolyether (Fomblin®Y). A suitable crystal was selected with the aid of a microscope, mounted on a cryoloop, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit.

Crystallographic data for complexes **2** and **4** are presented in Table 1. The structures were solved, using the WINGX package,[2] by direct methods (SHELXS-97)[3] and refined by least-squares against F^2 (SHELXL-97).[3]

E-stats data for complex **2** showed ambiguous centrosymmetric behavior so the P1 space group was firstly employed to solve and refine the structure. After the metallic core had been located, it could be stated that the triflate anion presented severe disorder and no chemical sensible model could be obtained for it; the Squeeze[4] procedure was then applied to remove the triflate's contribution to the structure factors. On the other hand, the P-1 space group was also tried and the Squeeze procedure had also to be used, surprisingly once the contribution of the triflate anion had been removed it led to a better refinement so this is the space group reported for complex **2**.

Elemental analysis for the pulverized and dried **4** revealed the existence of one molecule of toluene, but once compound **4** was recrystallized not less than four different positions were found for that toluene molecule in the difference Fourier map. Those fragments presented severe disorder and it was not possible to get a chemical sensible model for them, so Squeeze procedure was used to remove their contribution to the structure factors.

In both cases, all non-hydrogen atoms were anisotropically refined and the hydrogen atoms were positioned geometrically and refined by using a riding model.

References

(1) A. Abarca, P. Gómez-Sal, A. Martín, M. Mena, J. M. Poblet, C. Yélamos*, Inorg. Chem.*, 2000, **39**, 642-651.

(2) L. J. Farrugia, *J. Appl. Crystallogr.,* 1999, **32**, 837-838.

(3) G. M. Sheldrick, *SHELX97, Program for Crystal Structure Analysis (Release 97-2)*, Universität Göttingen, Germany, 1998.

(4) SQUEEZE - P. v. d. Sluis, A. L. Spek, *Acta Crystallogr., Sect. A,* 1990, **46**, 194-201.

Table 1.- Crystallographic data for complexes **2** and **4**.

Compound	**2**	**4**·C_7H_8
Empirical formula	$C_{61}H_{96}AgF_3N_8O_3STi_6$	$C_{70}H_{104}Ag_3F_9N_8O_9S_3Ti_6$
Formula weight	1473.79	2079.8
Temperature	200(2) K	200(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P-1	P2$_1$/c
a(Å); α(°)	11.6024(18); 109.264(9)	16.058(3)
b(Å); β(°)	11.61.93(11); 111.742(12)	20.694(6); 93.956(19)
c(Å); γ(°)	14.7433(18); 95.191(9)	37.507(11)
Volume	1690.8(4)	12434(5) Å^3
Z	1	4
Density (calculated)	1.447 Mg/m^3	1.111 Mg/m^3
Absorption coefficient	1.042 mm^{-1}	0.927 mm^{-1}
F(000)	764	4216
Crystal size	0.42 x 0.33 x 0.25 mm^3	0.15 x 0.10 x 0.10 mm^3
Theta range for data collection	3.02 to 27.5°	3.00 to 27.53°
Index ranges	-15 to 14, -14 to 15, -19 to 19	-20 to 20, -26 to 24, -42 to 48
Reflections collected	41498	117004
Independent reflections	7597 [R(int) = 0.057]	28264 [R(int) = 0.076]
Reflections [$I>2\sigma(I)$]	5044	16649
Completeness to theta = 27.5°	98.1	98.7 %
Goodness-of-fit on F^2	1.066	0.944
Final R indices [$I>2\sigma(I)$]	R1 = 0.064, wR2 = 0.189	R1 = 0.051, wR2 = 0.135
R indices (all data)	R1 = 0.101, wR2 = 0.237	R1 = 0.098, wR2 = 0.146
Largest diff. peak and hole (e.Å^{-3})	1.164 and -1.898	0.941 and -0.584