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Electronic Supplementary Information for:

Mercury or Silver Atoms Bridging Trinuclear Titanium Imido-Nitrido Systems

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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. Anhydrous metal halides (HgI_2 (99.999%), AgCl (99.999%), AgI (99.999%)) and $[M\{N(SiMe_3)_2\}]$ (M = Li, K) were 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 and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Unity-300 spectrometer. 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. Microanalyses (C, H, N) for the silver complexes were performed in a Leco

CHNS-932 microanalyzer at the Universidad de Alcalá, while elemental analyses for the mercury derivatives were carried out in a Fisons CHNS-O-EA 1108 microanalyzer at the Universidad de Santiago de Compostela (Spain).

Synthesis of [$I_2Hg\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (2): A 100 mL Schlenk flask was charged with **1** (0.60 g, 0.99 mmol), HgI_2 (0.45 g, 0.99 mmol) and toluene (30 mL). After stirring at room temperature for 3 days, the volatile components were removed under reduced pressure. The resultant solid was washed with toluene (5 mL) and vacuum-dried to give **2** as a yellow powder (0.82 g, 78%). IR (KBr, cm^{-1}): 3354 (w), 3323 (w), 2944 (w), 2909 (m), 2856 (w), 1488 (w), 1427 (m), 1377 (m), 1261 (w), 1066 (w), 1023 (m), 865 (w), 765 (m), 748 (m), 711 (m), 690 (m), 654 (vs), 603 (m), 549 (w), 524 (w), 425 (m). ^1H NMR ($CDCl_3$, 20 ºC, δ): 11.98 (s broad, 3H; NH), 2.08 (s, 45H; C_5Me_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 ºC, δ): 121.1 (C_5Me_5), 12.2 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{30}H_{48}HgI_2N_4Ti_3$ (M_w=1062.73) (%): C 33.91, H 4.55, N 5.27. Found: C 31.84, H 4.66, N 4.46.

Synthesis of [$ClAg\{(\mu_3\text{-}NH)_3Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}$] (3): A 100 mL amber stained Schlenk flask was charged with **1** (0.70 g, 1.15 mmol), AgCl (0.17 g, 1.19 mmol) and dichloromethane (80 mL). After stirring at room temperature for 20 h, the solution was filtered. The volatile components were removed under reduced pressure and the resultant solid was washed with hexane (20 mL) and vacuum-dried to give **3** as an orange solid (0.53 g, 62%). IR (KBr, cm^{-1}): 3359 (m), 3286 (m), 2908 (s), 2856 (s), 1490 (m), 1429 (m), 1377 (s), 1261 (w), 1067 (w), 1025 (m), 795 (s), 746 (s), 711 (s), 657 (vs), 523 (w), 477 (w), 425 (m), 400 (m). ^1H NMR ($CDCl_3$, 20 ºC, δ): 12.34 (s broad, 3H; NH), 2.03 (s, 45H; C_5Me_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 ºC, δ): 120.1 (C_5Me_5), 11.8 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{30}H_{48}AgClN_4Ti_3$ (M_w=751.66) (%): C 47.94, H 6.44, N 7.45. Found: C 47.70, H 6.33, N 7.06.

Synthesis of [IAg{(μ_3-NH)$_3$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (4): In a fashion similar to the preparation of **3**, treatment of **1** (0.30 g, 0.49 mmol) with AgI (0.12 g, 0.51 mmol) in dichloromethane (60 mL) afforded **4** as an orange solid (0.25 g, 61%). IR (KBr, cm^{-1}): 3358 (w), 3289 (m), 2907 (s), 2855 (m), 1488 (w), 1427 (m), 1376 (s), 1066 (w), 1023 (m), 792 (m), 750 (s), 711 (s), 657 (vs), 607 (s), 521 (m), 477 (m), 425 (m), 399 (m). ^{1}H NMR (CDCl$_3$, 20 ºC, δ): 12.36 (s broad, 3H; NH), 2.03 (45 H, s, C$_5$Me$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$, 20 ºC, δ): 120.1 (*C*$_5$Me$_5$), 11.8 (C$_5$*Me*$_5$). Anal. Calcd for $C_{30}H_{48}AgIN_4Ti_3$ (M_w=843.11) (%): C 42.74, H 5.74, N 6.64. Found: C 41.74, H 5.66, N 5.55.

Synthesis of [Hg$_2${(μ_3-N)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)(μ_3-N)}$_2$] (5): A 100 mL Schlenk flask was charged with **2** (0.30 g, 0.28 mmol), [K{N(SiMe$_3$)$_2$}] (0.11 g, 0.55 mmol) and toluene (25 mL). After stirring at room temperature for 2 h, the reaction mixture was filtered and the resultant red solution was concentrated under reduced pressure to ca. 10 mL. Further stirring of this solution at room temperature for 20 h gave the precipitation of **5** as a deep red solid (0.10 g, 45%). X-ray quality crystals of complex **5** were obtained in lower yield upon standing the toluene solution without any stirring. IR (KBr, cm^{-1}): 3353 (w), 2905 (s), 2853 (m), 1492 (w), 1431 (m), 1374 (m), 1261 (w), 1096 (w), 1066 (w), 1022 (m), 865 (w), 766 (s), 716 (s), 673 (vs), 651 (vs), 625 (s), 592 (w), 556 (w), 536 (w), 506 (m), 413 (m). ^{1}H NMR (CDCl$_3$, 20 ºC, δ): 14.12 (s broad, 2H; NH), 2.02 (s, 60H; C$_5$Me$_5$), 1.90 (s, 30H; C$_5$Me$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$, 20 ºC, δ): 117.7, 117.2 (*C*$_5$Me$_5$), 12.3, 12.1 (C$_5$*Me*$_5$). Anal. Calcd for $C_{60}H_{92}Hg_2N_8Ti_6$ (M_w=1613.82) (%): C 44.66, H 5.74, N 6.94. Found: C 45.22, H 6.01, N 6.13.

Synthesis of [Ag$_2${(μ_3-N)(μ_3-NH)Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ-NH)(μ_3-N)}$_2$] (6): A solution of [Li{N(SiMe$_3$)$_2$}] (0.020 g, 0.12 mmol) in toluene (5 mL) was carefully added to **3** (0.080 g, 0.11 mmol) in toluene (20 mL). The system was allowed to react without any stirring for 3 days to give the precipitation of red crystals and a fine white powder. After elimination of the solution by decantation, the crystals were rinsed with several portions of toluene (4 × 5 mL) to remove the powder and were characterized as **6**·C_7H_8 (0.035 g, 42%). IR (KBr, cm^{-1}): 3369 (w), 2907 (m), 2856 (m), 1494 (w), 1437 (m), 1375 (m), 1066 (w), 1023 (w), 808(s), 750 (s), 709 (vs), 645 (vs), 604 (vs), 516 (m), 456 (w), 415(w), 394 (m). Anal. Calcd for $C_{67}H_{102}Ag_2N_8Ti_6$ (M_w=1522.54) (%): C 52.85, H 6.75, N 7.36. Found: C 53.44, H 6.05, N 6.36.

X-ray structure determination of 3, 5 and 6. Crystals of **3** were grown at –25 ºC from a toluene solution. Red crystals of **5** and **6** were grown from the preparative reactions in toluene at room temperature as described in the Experimental Section. 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. DIRAX,[2] COLLECT[3] and EvaldCCD[4] programs were used to determine the unit cell, perform the data collection and data reduction, respectively.

Crystallographic data for complexes **3**, **5** and **6** are presented in Table 1. The structures were solved, using the WINGX package,[5] by direct methods (SHELXS-97[6] for **3** and **6** and SIR2002[7] for **5**) and refined by least-squares against F^2 (SHELXL-97).[6] All non-hydrogen atoms were anisotropically refined. In **3** SIMU and DELU restraints were applied for all the carbon atoms and several carbon atoms were disordered. The disorder was treated for the pentamethylcyclopentadienyl ring C10-C19 and FLAT and ISOR restraints were applied on those atoms. Nevertheless, this disordered ring still gave poor bond length and angle values. In **3** one of the two toluene molecules showed some disorder and some restraints were applied. The disorder observed in this compound could be affecting the poor wR2 value. Hydrogen atoms were geometrically placed and left riding on their parent atoms, except for the hydrogen atom on N3 for **6** that was found in the Fourier map and refined freely, and the hydrogen atoms on C15, C15’, C16, C16’, C17, C17’, C18, C18’, C19, C19’ in **3** and C15, C16, C19 in **6** that were fixed. In **6** both silver atoms were disordered in two positions being the occupancy factor 0.5, the disordered atoms are related by a symmetry plane. Using lower symmetry groups, such as $P2_1/n$, does not lead to a better description of the disorder. Also in **6** a molecule of toluene crystallized with every molecule of the compound, this solvent molecule was found in the difference Fourier map but was very disordered and it was not possible to get a chemical sensible model for it, so Squeeze procedure[8] was used to remove its contribution to the structure factors.

In the case of **5** all non-hydrogen atoms were anisotropically refined and all hydrogen atoms were geometrically placed and left riding on their parent atoms.

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Table 1.- Crystallographic data for complexes **3**, **5** and **6**.

Compound	$\mathbf{3 \cdot 2C_7H_8}$	**5**	$\mathbf{6 \cdot C_7H_8}$
Empirical formula	$C_{44}H_{64}AgClN_4Ti_3$	$C_{60}H_{92}Hg_2N_8Ti_6$	$C_{67}H_{102}Ag_2N_8Ti_6$
Formula weight	936.01	1613.81	1522.71
Temperature (K)	200(2)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	P-1	$P2_1/n$	Pnnm
a(Å); α(°)	11.549(3); 75.127(9)	10.977(2)	14.923(3)
b(Å); β(°)	13.123(2); 74.609(11)	20.139(3); 104.01(2)	15.546(3)
c(Å); γ(°)	17.273(2); 70.225(14)	14.837(2)	16.496(3)
Volume (Å^3)	2334.6(7)	3182.4(9)	3827.0(2)
Z	2	2	2
Density (calculated) (Mg/m^3)	1.332	1.684	1.321
Absorption coefficient (mm^{-1})	0.997	5.560	1.133
F(000)	972	1600	1572
Crystal size (mm^3)	0.42 x 0.41 x 0.29	0.54 x 0.11 x 0.11	0.36 x 0.27 x 0.24
Theta range for data collection	3.53 to 27.50°	3.01 to 27.50°	3.03 to 27.59°
Index ranges	-15 to 14, -17 to 16, -22 to 22	-14 to 14, -26 to 26, -19 to 19	-19 to 19, -20 to 20, -21 to 21
Reflections collected	49737	72220	83765
Independent reflections	10490 [R(int) = 0.0538]	7307 [R(int) = 0.139]	4541 [R(int) = 0.0729]
Reflections [$I>2\sigma(I)$]	5858	4781	3401
Completeness to theta = 27.5°	97.9 %	99.8 %	98.6 %
Goodness-of-fit on F^2	1.100	1.001	1.046
Final R indices [$I>2\sigma(I)$]	R1 = 0.097, wR2 = 0.261	R1 = 0.045, wR2 = 0.086	R1 = 0.051, wR2 = 0.131
R indices (all data)	R1 = 0.166, wR2 = 0.327	R1 = 0.093, wR2 = 0.097	R1 = 0.074, wR2 = 0.141
Largest diff. peak and hole (e.Å^{-3})	2.342 and -2.445	1.645 and -0.945	0.739 and -0.628