Mercury or silver atoms bridging trinuclear titanium imido–nitrido systems†

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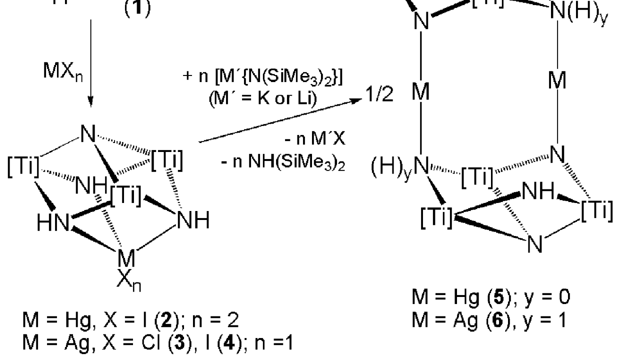
Received (in Cambridge, UK) 28th August 2008, Accepted 14th October 2008
First published as an Advance Article on the web 11th November 2008
DOI: 10.1039/b814982h

The imido–nitrido complex [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] entraps mercury(II) or silver(I) halides MX_n to give cube-type adducts [X_nM{(μ_3-NH)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] which react with alkali metal bis(trimethylsilyl)amide reagents to afford [M_2{(μ_3-N)$_n$(μ_3-NH)$_{2-n}$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$(μ-NH)($\mu_3$-N)}$_2$] (M = Hg, *n* = 2; M = Ag, *n* = 1) where two [Ti_3N_4] cores are linked by two mercury or silver atoms in a linear geometry.

While an extensive chemistry has been developed with mononuclear transition metal complexes bearing nitrido ligands as a terminal functionality, M≡N,[1] the study of polynuclear derivatives containing bridging nitrido ligands remains comparatively scarce.[2] This is mainly a result of the difficult characterization of their singular structures and, maybe more important, the lack of a systematic way of syntheses. Polynuclear nitrido complexes might be of interest as building blocks in the synthesis of metal nitride materials.[3] Furthermore, species with μ_n-nitrido groups are proposed as intermediates in dinitrogen fixation and activation,[4,5] and new structural and electronic data on molecular systems may provide insights into those processes. For instance, new structural data of the FeMo-cofactor of nitrogenase have prompted recent interest in iron nitride clusters of high nuclearity as potential models of the active site.[4,6] Over the last few years we have been involved in the development of a family of heterometallic nitrido complexes with new structural and bonding features. The rational synthesis of these polynuclear systems is based on the incorporation of metal complexes at the μ-NH basal imido groups of the trinuclear titanium derivative [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)][7] (**1**) and posterior N–H activation generating μ_3- or μ_4-nitrido ligands.[8] The existence of the μ_3-N nitrido apical group confers a rigid character to **1** and the structure of the resultant nitrido complexes depends on the geometrical preferences of the incorporated metal. Here we report the preliminary results on the coordination of **1** to mercury(II) or silver(I) halides and the utility of these molecular adducts to prepare nitrido complexes with linear mercury or silver atoms bridging two trinuclear titanium systems.

The synthetic chemistry is outlined in Scheme 1. Treatment of **1** with one equivalent of mercury(II) iodide or silver(I) halide in toluene or dichloromethane at room temperature led to the cube-type adducts [X_nM{(μ_3-NH)$_3$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (M = Hg, *n* = 2, X = I (**2**); M = Ag, *n* = 1, X = Cl (**3**), I (**4**)). The analogous reaction of **1** with mercury(II) chloride gave an intractable mixture of products, presumably by activation of Hg–Cl bonds with generation of reactive HCl. Silver derivatives **3** and **4** are light sensitive in solution and in the solid-state and their preparation and manipulation were carried out in the absence of light.

Compounds **2–4** were isolated as air-sensitive yellow or orange solids in good yields (61–78%) which are very soluble in halogenated solvents. The mercury derivative **2** is poorly soluble in hydrocarbon solvents but silver complexes **3** and **4** exhibit a good solubility in toluene or benzene. Compounds **2–4** were characterized by analytical and spectroscopic methods, as well as by an X-ray crystal structure determination for **3**.‡ IR spectra (KBr) of complexes **2–4** show two ν_{NH} vibrations, between 3359 and 3286 cm^{-1}, in a range similar to the value determined for **1**,[7b] 3352 cm^{-1}. The ^1H and $^{13}C\{^1H\}$ NMR spectra in chloroform-d_1 of **2–4** at room temperature reveal resonance signals for equivalent NH and η^5-C_5Me_5 groups. The NH resonance signals (δ = 12.36–11.98) in the ^1H NMR spectra are shifted to higher field with respect to that found for **1** (δ = 13.40).[7b] These data suggest a tridentate coordination of the titanium metalloligand to the mercury or silver center and are consistent with a very fast exchange process (**2**) or a highly symmetrical structure (**3** and **4**) in



Scheme 1 Synthesis of titanium–mercury/silver nitrido complexes.

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† Electronic supplementary information (ESI) available: Experimental details and full characterization data for complexes **2–6**. CCDC 699910–699912. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814982h

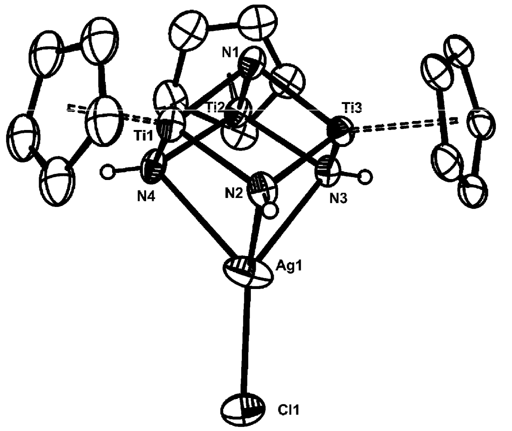

Fig. 1 Crystal structure of complex $\mathbf{3}\cdot 2C_7H_8$ (thermal ellipsoids at the 30% probability level). The methyl groups of the pentamethylcyclopentadienyl ligands and the C_7H_8 solvent molecules are omitted for clarity. Selected lengths (Å) and angles (°): Ag(1)–Cl(1) 2.358(2), Ag(1)–N(2) 2.563(6), Ag(1)–N(3) 2.387(6), Ag(1)–N(4) 2.507(6), N(2)–Ag(1)–N(3) 78.2(2), N(2)–Ag(1)–N(4) 75.7(2), N(3)–Ag(1)–N(4) 79.0(2), Cl(1)–Ag(1)–N(2) 121.4(2), Cl(1)–Ag(1)–N(3) 141.0(2), Cl(1)–Ag(1)–N(4) 135.6(2).

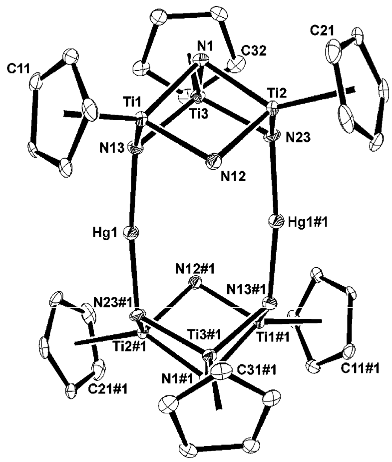

Fig. 2 Crystal structure of complex **5** (thermal ellipsoids at the 30% probability level). The methyl groups of the pentamethylcyclopentadienyl ligands and hydrogen atoms are omitted for clarity. Selected lengths (Å) and angles (°): Hg(1)–N(23)#1 2.041(5), Hg(1)–N(13) 2.038(5), Ti(3)–N(13) 1.925(5), Ti(3)–N(23) 1.945(5), Hg(1)···Hg(1)#1 3.335(1), N(23)#1–Hg(1)–N(13) 173.0(2), Hg(1)–N(13)–Ti(3) 120.6(3), N(13)–Ti(3)–N(23) 105.7(2), Ti(3)–N(23)–Hg(1)#1 114.5(2). Symmetry transformations used to generate equivalent atoms: #1 $-x + 2$, $-y + 2$, $-z$.

solution, as observed previously in other metal halide adducts of **1**.[9] The molecular structure of $\mathbf{3}\cdot 2C_7H_8$ was determined by an X-ray analysis of crystals grown in a toluene solution at −25 °C. The solid-state structure reveals a $[AgTi_3N_4]$ cube-type core (Fig. 1). The silver atom exhibits a distorted tetrahedral geometry with N–Ag–N angles ranging from 75.7(2)–79.0(2)° and N–Ag–Cl angles spanning 121.4(2)–141.0(2)°. The Ag–Cl bond distance, 2.358(2) Å, and the silver–nitrogen bond lengths, 2.387(6)–2.563(6) Å, compare well with those found in $[Ag([9]aneN_2S)Cl]$.[10] Geometrical parameters of the organometallic ligand are similar to those of the parent compound **1**.[7a]

Treatment of the mercury diiodide complex **2** with two equivalents of potassium bis(trimethylsilyl)amide in toluene at room temperature led to $[Hg_2\{(\mu_3\text{-}N)_2Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)(\mu_3\text{-}N)\}_2]$ (**5**) in a 45% yield (Scheme 1). The analogous reaction of **2** with $[Li\{N(SiMe_3)_2\}]$ produced the formation of $[Hg\{N(SiMe_3)_2\}_2]$[11] and the previously described lithium iodide adduct $[ILi\{(\mu_3\text{-}NH)_3\text{-}Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu_3\text{-}N)\}]$.[9] Similar treatment of the silver chloride complex **3** with one equivalent of lithium bis(trimethylsilyl)amide led to the precipitation of red crystals of complex $[Ag_2\{(\mu_3\text{-}N)(\mu_3\text{-}NH)Ti_3(\eta^5\text{-}C_5Me_5)_3(\mu\text{-}NH)(\mu_3\text{-}N)\}_2]\cdot C_7H_8$ ($\mathbf{6}\cdot C_7H_8$) isolated in a 42% yield after workup.

Compounds **5** and **6** were characterized by analytical and spectroscopic methods, as well as by X-ray crystal structure determinations.‡ IR spectra (KBr) reveal one ν_{NH} vibration at 3353 cm^{-1} (**5**) and 3369 cm^{-1} (**6**). The silver derivative **6** is not soluble in common organic solvents precluding its characterization by NMR spectroscopy. In contrast, the mercury complex **5** is not soluble in toluene or benzene but exhibits a good solubility in halogenated solvents. The ^1H NMR spectrum of **5** in chloroform-d$_1$ at room temperature shows resonance signals for two $\eta^5\text{-}C_5Me_5$ ligands in a 2 : 1 ratio and a broad signal for one NH group. The NH resonance signal in the spectrum (δ = 14.12) is shifted to lower field than that found in **1** (δ = 13.40), suggesting the absence of coordination of the NH ligand to the mercury center in solution.[8d] The NMR data for **5** are consistent with the solid-state structure determined by X-ray crystallography (Fig. 2) which is very close to a C_{2h} symmetry. The molecular structure shows two $[Ti_3N_4]$ cores connected by two mercury atoms. There is a center of symmetry at the midpoint between the Hg atoms. Each mercury adopts an almost linear geometry (N(23)#1–Hg(1)–N(13) 173.0(2)°) with Hg–N bond lengths identical within experimental error, 2.041(5) and 2.038(5) Å, which are typical of mercury(II) amido derivatives with this arrangement.[12] The structure of **5** contains a $[Hg_2Ti_2N_4]$ eight-membered ring that adopts a chair conformation with two mercury atoms and four μ_3-N nitrido groups in a plane and the two titanium atoms bent away from the plane. This chair conformation may correspond to the minimization of the steric repulsion of the bulky pentamethylcyclopentadienyl ligands.[13] The mercury(II)–mercury(II) separation of 3.335(1) Å is slightly shorter than the sum of the van der Waals radii (3.46–3.50 Å),[14] and could be indicative of metallophilic interaction.[15] However, the parallel disposition of the L ligands in the $(HgL_2)_2$ fragment suggests the absence of such Hg–Hg attraction according to theoretical studies carried out by Pyykkö and Straka.[14b] Additionally, the mercury–mercury distance in **5** is longer than that between the nitrido groups (N(13)···N(23) 3.086(7) Å) within each Ti_3N_4 core (outward angle N(23)#1–Hg(1)–N(13) 187.0°) indicating Hg–Hg repulsion.

Complex **6** shows a similar structure to that of **5** (Fig. 3). Molecules of **6** lie on an inversion center in the midpoint between the two silver atoms. Each silver exhibits an almost linear two-coordinate environment (N(1)#2–Ag(1)–N(3) 165.1(1)°) with Ag–N bond lengths clearly different, that with the nitrido group, Ag(1)–N(1)#2 2.096(4) Å, shorter than that with the dative imido ligand, Ag(1)–N(3) 2.200(3) Å. Complex **6** contains a $[Ag_2Ti_2N_4]$ eight-membered ring that adopts a chair conformation similar to that of **5** but now the titanium

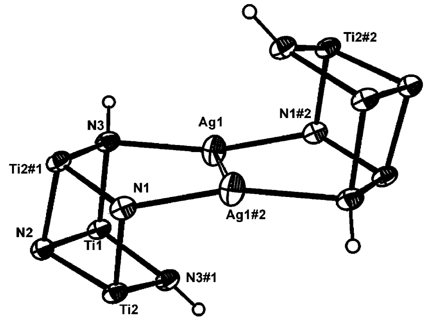

Fig. 3 Crystal structure of complex **6**·C_7H_8 (thermal ellipsoids at the 30% probability level). The pentamethylcyclopentadienyl ligands and the C_7H_8 solvent molecule are omitted for clarity. The disorder of the silver atoms is not shown. Selected lengths (Å) and angles (°): Ag(1)–N(1)#2 2.096(4), Ag(1)–N(3) 2.200(3), Ti(2)#1–N(3) 1.998(3), Ti(2)#1–N(1) 1.874(2), Ag(1)···Ag(1)#2 2.966(1), N(1)#2–Ag(1)–N(3) 165.1(1), Ag(1)–N(3)–Ti(2)#1 108.5(2), N(3)–Ti(2)#1–N(1) 106.6(2), Ti(2)#1–N(1)–Ag(1)#2 131.9(2). Symmetry transformations used to generate equivalent atoms: #1 $x, y, -z + 1$; #2 $-x, -y + 2, -z + 1$.

and μ_3-NH groups are bent away from the plane containing the Ag(1), Ag(1)#2, N(1), N(1)#2 atoms. The Ag(1)–Ag(1)#2 separation of 2.966(1) Å is longer than that in metallic silver (2.89 Å) but clearly shorter than the sum of the van der Waals radii (3.44 Å).[16] Additionally, the silver–silver distance in **6** is shorter than that between N(1) and N(3), 3.100 Å, within each Ti_3N_4 core producing an outward angle N(1)#2–Ag(1)–N(3) of 165.1(1)°. Thus, the metal atoms come closer together which could be indicative of metallophilic attraction.[17] Silver(I) dimers with similar attractive Ag···Ag interactions have demonstrated their ability to act as linking units of polyoxometalate (POM) clusters to construct frameworks of increasing complexity.[18]

In conclusion, we have demonstrated that $[\{Ti(\eta^5\text{-}C_5Me_5)(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$ acts as a tridentate neutral ligand to silver(I) and mercury(II) halides to give molecular adducts. Posterior treatment of these complexes with alkali metal amide reagents results in polynuclear nitrido derivatives with $[M_2Ti_2N_4]$ eight-membered rings in a chair conformation affording the opportunity to evaluate the existence of M···M metallophilic interaction.

We thank the Spanish MEC (CTQ2005-00238), Comunidad de Madrid and the Universidad de Alcalá (CCG06-UAH/PPQ-0665), and Factoría de Cristalización (CONSOLIDER-INGENIO 2010) for financial support of this research. N. M.-E. thanks the MEC for a doctoral fellowship.

Notes and references

‡ Crystal data for **3**·$2C_7H_8$: $C_{44}H_{64}AgClN_4Ti_3$, M = 936.01, triclinic, a = 11.549(3), b = 13.123(2), c = 17.273(2) Å, α = 75.127(9), β = 74.609(11), γ = 70.225(14)°, U = 2334.6(7) Å^3, T = 200(2) K, space group $P\bar{1}$, Z = 2, μ(Mo-K$_\alpha$) = 0.997 mm^{-1}, 49 737 reflections measured, 10 490 unique (R_{int} = 0.0538) which were used in all calculations. $R1(F^2)$ = 0.097 (for 5858 reflections with $F_o > 4\sigma(F_o)$) and w$R2$ = 0.327 for all data. Crystal data for **5**: $C_{60}H_{92}Hg_2N_8Ti_6$, M = 1613.81, monoclinic, a = 10.977(2), b = 20.139(3), c = 14.837(2) Å, β = 104.01(2)°, U = 3182.4(9) Å^3, T = 200(2) K, space group $P2_1/n$, Z = 2, μ(Mo-K$_\alpha$) = 5.560 mm^{-1}, 72 220 reflections measured, 7307 unique (R_{int} = 0.139) which were used in all calculations. $R1(F^2)$ = 0.045 (for 4781 reflections with $F_o > 4\sigma(F_o)$) and w$R2$ = 0.097 for all data. Crystal data for **6**·C_7H_8: $C_{67}H_{102}Ag_2N_8Ti_6$, M = 1522.71, orthorhombic, a = 14.923(3), b = 15.546(3), c = 16.496(3) Å, U = 3827.0(2) Å^3, T = 200(2) K, space group $Pnnm$, Z = 2, μ(Mo-K$_\alpha$) = 1.133 mm^{-1}, 83 765 reflections measured, 4541 unique (R_{int} = 0.0729) which were used in all calculations. $R1(F^2)$ = 0.051 (for 3401 reflections with $F_o > 4\sigma(F_o)$) and w$R2$ = 0.141 for all data. CCDC 699910–699912. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b814982h

1 (*a*) W. A. Nugent and J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley, New York, 1988; (*b*) R. A. Eikey and M. M. Abu-Omar, *Coord. Chem. Rev.*, 2003, **243**, 83–124.
2 (*a*) K. Dehnicke and J. Strähle, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 955–978; (*b*) K. Dehnicke, F. Weller and J. Strähle, *Chem. Soc. Rev.*, 2001, **30**, 125–135.
3 *The Chemistry of Transition Metal Carbides and Nitrides*, ed. S. T. Oyama, Blakie Academic & Professional, London, 1996.
4 (*a*) S. C. Lee and R. H. Holm, *Proc. Natl. Acad. Sci. U. S. A.*, 2003, **100**, 3595–3600; (*b*) S. C. Lee and R. H. Holm, *Chem. Rev.*, 2004, **104**, 1135–1157.
5 (*a*) N. Kuganathan, J. C. Green and H.-J. Himmel, *New J. Chem.*, 2006, **30**, 1253–1262; (*b*) H.-J. Himmel and M. Reiher, *Angew. Chem., Int. Ed.*, 2006, **45**, 6264–6288.
6 (*a*) M. V. Bennet, S. Stoian, E. L. Bominaar, E. Münck and R. H. Holm, *J. Am. Chem. Soc.*, 2005, **127**, 12378–12386; (*b*) M. V. Bennet and R. H. Holm, *Angew. Chem., Int. Ed.*, 2006, **45**, 5613–5616.
7 (*a*) H. W. Roesky, Y. Bai and M. Noltemeyer, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 754–755; (*b*) A. Abarca, P. Gómez-Sal, A. Martín, M. Mena, J. M. Poblet and C. Yélamos, *Inorg. Chem.*, 2000, **39**, 642–651.
8 (*a*) A. Abarca, M. V. Galakhov, J. Gracia, A. Martín, M. Mena, J.-M. Poblet, J. P. Sarasa and C. Yélamos, *Chem.–Eur. J.*, 2003, **9**, 2337–2346; (*b*) A. Martín, M. Mena, A. Pérez-Redondo and C. Yélamos, *Inorg. Chem.*, 2004, **43**, 2491–2498; (*c*) A. Martín, N. Martínez-Espada, M. Mena, A. Pérez-Redondo and C. Yélamos, *Inorg. Chem.*, 2006, **45**, 6901–6911; (*d*) M. García-Castro, A. Martín, M. Mena and C. Yélamos, *Organometallics*, 2007, **26**, 408–416.
9 M. García-Castro, J. Gracia, A. Martín, M. Mena, J.-M. Poblet, J. P. Sarasa and C. Yélamos, *Chem.–Eur. J.*, 2005, **11**, 1030–1041.
10 U. Heinzel and R. Mattes, *Polyhedron*, 1992, **11**, 597–600.
11 H. Bürger, W. Sawodny and U. Wannagat, *J. Organomet. Chem.*, 1965, **3**, 113–120.
12 (*a*) H. Schumann, J. Gottfriedsen, S. Dechert and F. Girgsdies, *Z. Anorg. Allg. Chem.*, 2000, **626**, 747–758; (*b*) Y. Tang, A. M. Félix, B. J. Boro, L. N. Zakharov, A. L. Rheingold and R. A. Kemp, *Polyhedron*, 2005, **24**, 1093–1100.
13 A boat conformation of the ring would place the η^5-C_5Me_5 in an eclipsed position.
14 (*a*) A. J. Canty and G. B. Deacon, *Inorg. Chim. Acta*, 1980, **45**, L225–L227; (*b*) P. Pyykkö and M. Straka, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2489–2493.
15 P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597–636.
16 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441–451.
17 (*a*) P. Pyykkö and F. Mendizabal, *Inorg. Chem.*, 1998, **37**, 3018–3025; (*b*) C. M. Che and S. W. Lai, *Coord. Chem. Rev.*, 2005, **249**, 1296–1309.
18 (*a*) R. Villanneau, A. Proust, F. Robert and P. Gouzerh, *Chem. Commun.*, 1998, 1491–1492; (*b*) S.-M. Chen, C.-Z. Lu, Y.-Q. Yu, Q.-Z. Zhang and X. He, *Inorg. Chem. Commun.*, 2004, **7**, 1041–1044; (*c*) H. Abbas, A. L. Pickering, D.-L. Long, P. Kögerler and L. Cronin, *Chem.–Eur. J.*, 2005, **11**, 1071–1078; (*d*) C. Streb, C. Ritchie, D.-L. Long, P. Kögerler and L. Cronin, *Angew. Chem., Int. Ed.*, 2007, **46**, 7579–7582.