3308 *Organometallics* **2002,** *21,* 3308−3310

Titanium−Group 2 Metal Molecular Nitrides

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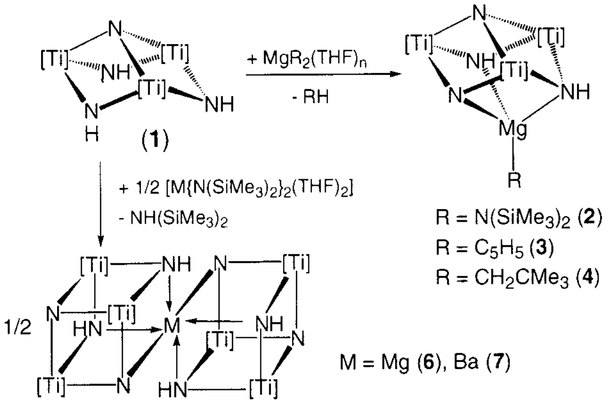
Received May 10, 2002

Summary: Treatment of [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] with magnesium amido/cyclopentadienyl/alkyl derivatives [MgR_2(THF)$_n$] (1 equiv) gives single cube-type molecular nitrides [RMg{(μ_3-N)(μ_3-NH)$_2$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}]. Analogous reactions with 0.5 equiv of [M{N($SiMe_3$)$_2$}$_2$(THF)$_2$] (M = Mg, Ba) afford the corner-shared double-cube nitrido complexes [M{(μ_3-N)(μ_3-NH)$_2$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}$_2$].

Polynuclear nitrido complexes containing different metal centers in a well-defined structure have a potential role as new motifs of ternary metal nitride materials. Among those materials, nitrides with both group 2 and transition metals have very interesting physical properties.[1] As part of a program related to the preparation of nitrido complexes, we have been studying the reactivity of the trinuclear imido−nitrido complex [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] (**1**)[2,3] toward different inorganic metal compounds. Complex **1** shows an incomplete-cube core and is prone to incorporate metal fragments into the structure.[4−7] With these considerations in mind, our attention has been recently focused on alkaline earth−titanium nitrido complexes. Herein we describe the synthesis, structure, and properties of single and corner-shared double cube-type magnesium/barium−titanium molecular nitrides. Those complexes show four- and six-coordinate group 2 metals bearing the monoanionic tridentate "{(μ_3-N)(μ_3-NH)$_2$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}$^-$" ligand. Their structures and thermal stabilities are discussed and compared with other magnesium and barium derivatives.

The synthetic chemistry is outlined in Scheme 1. Treatment of **1** with 1 equiv of the magnesium amido, cyclopentadienyl, or alkyl complexes [MgR_2(THF)$_n$] [R = N($SiMe_3$)$_2$ $n = 2$,[8] C_5H_5 $n = 0$,[9] CH_2CMe_3 $n = 2$[10]] in toluene leads to the solvent-free tetranuclear derivatives [RMg{(μ_3-N)(μ_3-NH)$_2$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}][R=N($SiMe_3$)$_2$ (**2**), C_5H_5 (**3**), CH_2CMe_3 (**4**)] via amine/cyclopentadiene/alkane elimination. The reaction with the amido derivative [Mg{N($SiMe_3$)$_2$}$_2$(THF)$_2$] is very slow at room temperature and was carried out at 50 °C, but the alkyl and cyclopentadienyl analogues [MgR_2(THF)$_n$] reacted almost immediately.

Scheme 1. Synthesis of 2−7 from 1 ([Ti] = Ti (η^5-C_5Me_5))



Complexes **2**−**4** were obtained as orange solids in good yields (77−83%) and characterized by spectral and analytical methods,[11] as well as by an X-ray crystal structure determination for **2**.[12] Complexes **2** and **3** are thermally stable in benzene-d_6 solutions at 150 °C, whereas the neopentyl derivative **4** decomposes within hours at room temperature.[13] Furthermore, **1** reacted with [Mg(CH_2Ph)$_2$(THF)$_2$][10] in benzene-d_6 almost immediately, and the expected complex [($PhCH_2$)Mg{(μ_3-N)(μ_3-NH)$_2$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}] (**5**) was detected by NMR spectroscopy,[14] but despite many attempts we did not obtain a pure sample for a complete characterization. Solutions of **4** and **5** in toluene at room or low temperature decomposed to give red crystals, which were identified as the corner-shared double-cube azaheterometallocubane complex [Mg{(μ_3-N)(μ_3-NH)$_2$$Ti_3$($\eta^5$-$C_5Me_5$)$_3$($\mu_3$-N)}$_2$] ($C_7H_8$)$_2$ (**6**). This compound was also

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[11] Selected spectroscopic data for complexes **2**−**4**. Complex **2**: IR (KBr, cm^{-1}) 3370 (w), 3342 (w); ^{1}H NMR (C_6D_6, 20 °C, δ) 10.91 (s br, 2H; NH), 2.05 (s, 30H; C_5Me_5), 1.89 (s, 15H; C_5Me_5), 0.30 (s, 18H, $SiMe_3$); ^{13}C{^{1}H} NMR (C_6D_6, 20 °C, δ) 119.6 (C_5Me$_5$), 118.3 (C_5Me$_5$), 12.03 (C$_5$*Me*$_5$), 11.98 (C$_5$*Me*$_5$), 6.8 (Si*Me*$_3$). Complex **3**: IR (KBr, cm^{-1}) 3355 (w), 3335 (w); ^{1}H NMR (C_6D_6, 20 °C, δ) 10.31 (s br, 2H; NH), 6.28 (s, 5H, C_5H_5), 2.05 (s, 30H; C_5Me_5), 1.88 (s, 15H; C_5Me_5); ^{13}C{^{1}H} NMR (C_6D_6, 20 °C, δ) 118.9 (C_5Me$_5$), 117.6 (C_5Me$_5$), 106.0 (C_5H_5), 11.8 (C$_5$*Me*$_5$), 11.7 (C$_5$*Me*$_5$). Complex **4**: IR (KBr, cm^{-1}) 3351 (m); ^{1}H NMR (C_6D_6, 20 °C, δ) 11.10 (s br, 2H; NH), 2.06 (s, 30H; C_5Me_5), 1.87 (s, 15H; C_5Me_5), 1.27 (s, 9H, CH_2C*Me*$_3$), 0.17 (s, 2H, C*H*$_2$CMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 20 °C, δ) 119.1 (C_5Me$_5$), 117.9 (C_5Me$_5$), 37.3 (CH_2*C*Me$_3$), 31.9 (CH_2CMe$_3$), 25.3 (*C*H$_2$CMe$_3$), 11.8 (C$_5$*Me*$_5$), 11.7 (C$_5$*Me*$_5$).

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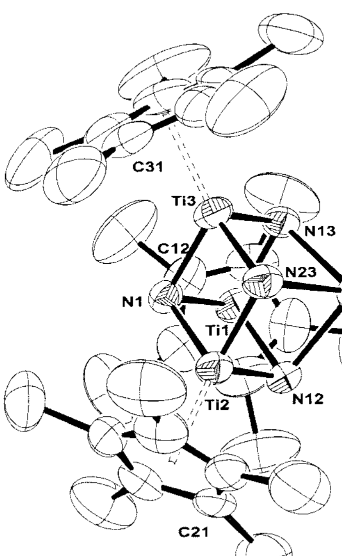

Figure 1. ORTEP of complex **2**.

prepared in higher yield (51%) from the reaction of complex **2** with 1 equiv of **1** in toluene at room temperature or by reaction of [Mg{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] with 2 equiv of **1** at 50 °C in toluene (44%).

Analogous treatment of [Ba{N(SiMe$_3$)$_2$}$_2$(THF)$_2$][8] with 1 or 2 equiv of **1** in toluene at room temperature afforded orange crystals of [Ba{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (**7**) in 58 and 61% yield, respectively. Monitoring the reaction in benzene-d_6 allows the detection of the complex [(Me$_3$Si)$_2$NBa{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] (**8**) by NMR spectroscopy.[15] Complexes **6** and **7** were not soluble in common solvents and were characterized by IR spectroscopy, microanalysis, and X-ray crystal structure determinations.[12] The IR spectra for **6** and **7** revealed ν_{NH} vibrations at 3354 and 3318 cm^{-1}, respectively.

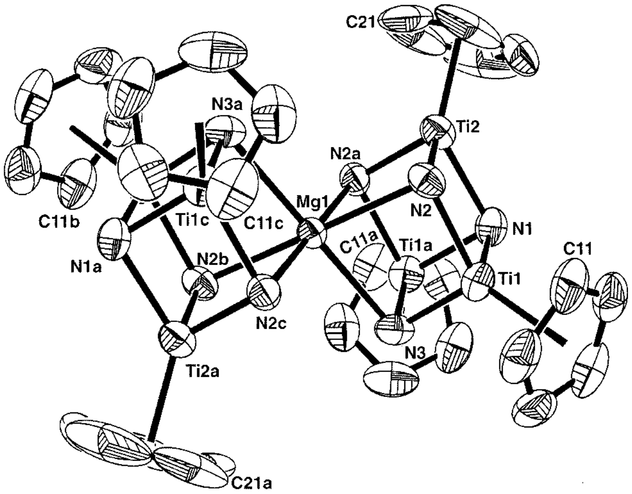

Figure 2. ORTEP of complex **6** without methyl groups.

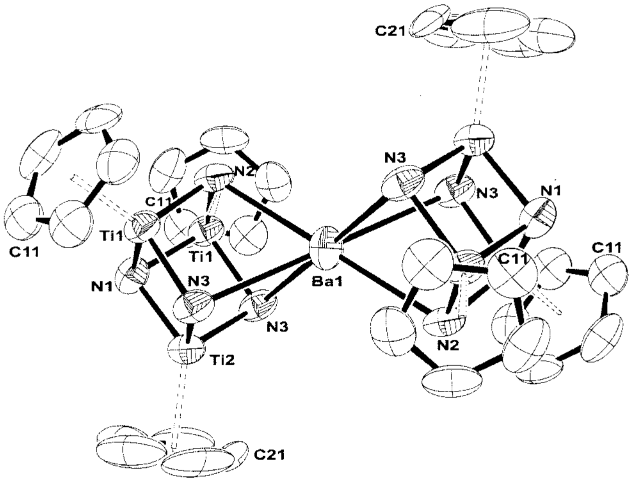

Figure 3. ORTEP of complex **7** without methyl groups.

The molecular structure of **2** confirms the azaheterometallocubane core [MgTi$_3$N$_4$] of the complex and the κ^3-coordination of the "{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$^-$" ligand to magnesium (Figure 1). The geometry about the magnesium center is best described as distorted tetrahedral, with intraligand N−Mg−N angles spanning 81.6(2)−82.9(2)° and interligand N−Mg−N(2) angles in the range 125.9(3)−138.9(3)°. The magnesium−nitrogen bond lengths within the cube core are in the range 2.183(6)−2.211(6) Å and are longer than that to the amido ligand [Mg−N(2) 1.986(6) Å]. The coordination environment around magnesium is similar to those determined for several Tp′MgX derivatives.[16]

Complexes **6** and **7** crystallize with two toluene molecules, and the structures confirm a corner-shared double-cube [MTi$_6$N$_8$] core (Figures 2 and 3). The coordination geometry about the centrosymmetric magnesium and barium centers is best described as trigonally distorted octahedral. The two "{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$^-$" ligands adopt a mutually staggered conformation. Complex **6** shows two clearly different Mg−N bond lengths, 2.251(6) and 2.410(11) Å, intraligand N−Mg−N angles, 73.8(3) and 79.5(3)°, and interligand N−Mg−N angles, 100.5(3)−106.2(3)°. The longer Ba−N bond lengths and narrower N−Ba−N angles found for complex **7** reveal a trigonal antiprism with

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(12) Crystal data for C$_{36}$H$_{65}$MgN$_5$Si$_2$Ti$_3$ (**2**): space group $P\bar{1}$ with a = 11.738(1) Å, b = 11.936(2) Å, c = 18.018(3) Å, α = 84.82(1)°, β = 74.53(1)°, γ = 66.57(1)°, V = 2232.1(6) Å^3, Z = 2, d_{calcd} = 1.179 g·cm^{-3}, μ(Mo Kα) = 0.620 mm^{-1}. Intensity measurements were performed by $\omega-2\theta$ scans in the range 2° < 2θ < 46° at room temperature, 6554 reflections measured (6201 unique). A cutoff $I > 2\sigma(I)$ was used for R factor calculations to give R1 = 0.070, wR2 = 0.177 and GOF = 0.955. Crystal data for C$_{74}$H$_{110}$MgN$_8$Ti$_6$ (**6**): space group $Pnmn$ with a = 14.533(2) Å, b = 15.471(6) Å, c = 16.626(8) Å, V = 3738(2) Å^3, Z = 2, d_{calcd} = 1.265 g·cm^{-3}, μ(Mo Kα) = 0.663 mm^{-1}. Intensity measurements were performed by $\omega-2\theta$ scans in the range 6° < 2θ < 54° at room temperature, 3673 reflections measured (3395 unique). A cutoff $I > 2\sigma(I)$ was used for R factor calculations to give R1 = 0.097, wR2 = 0.257 and GOF = 0.981. Crystal data for C$_{74}$H$_{110}$BaN$_8$Ti$_6$ (**7**): space group $Pnnm$ with a = 15.090(2) Å, b = 15.357(2) Å, c = 16.789(2) Å, V = 3890.6(6) Å^3, Z = 2, d_{calcd} = 1.312 g·cm^{-3}, μ(Mo Kα) = 1.125 mm^{-1}. Intensity measurements were performed by $\omega-2\theta$ scans in the range 0° < 2θ < 48° at room temperature, 3474 reflections measured (3198 unique). A cutoff $I > 2\sigma(I)$ was used for R factor calculations to give R1 = 0.082, wR2 = 0.206 and GOF = 1.022. All the structures were refined by least-squares methods against F^2.

(13) Complex **4** was isolated as a spectroscopically pure orange solid in 83% yield if the reaction and subsequent workup were performed within 1 h.

(14) Selected NMR data for **5**: ^{1}H (C$_6$D$_6$, 20 °C, δ) 10.95 (s br, 2H, NH), 2.02 (s, 30H, C$_5$Me$_5$), 1.86 (s, 15H, C$_5$Me$_5$), 1.65 (s, 2H, CH_2Ph); ^{13}C{^{1}H} (C$_6$D$_6$, 20 °C, δ) 119.3, 117.8 (C_5Me$_5$), 18.9 (CH$_2$Ph).

(15) Selected NMR data for **8**: ^{1}H (C$_6$D$_6$, 20 °C, δ) 12.86 (s br, 2H, NH), 2.11 (s, 30H, C$_5$Me$_5$), 2.00 (s, 15H, C$_5$Me$_5$), 0.24 (s, 18H, SiMe$_3$); ^{13}C{^{1}H} (C$_6$D$_6$, 20 °C, δ) 117.5, 115.8 (C_5Me$_5$), 5.6 (SiMe_3).

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averages Ba−N 2.821(9) Å, intraligand N−Ba−N 63.3(3)°, and interligand N−Ba−N 116.7(3)°. The crystal structures of **6** and **7** compare well with those determined for Tp^{Me2}M (M = Mg,[16] Ba[17]), but showing longer M−N bond lengths and narrower N−M−N intraligand angles.

Thermal stabilities in solution of the single-cube complexes [RM{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}] may be rationalized by the steric crowding about the group 2 metals. If R is relatively small (CH$_2$Ph **5**, CH$_2$CMe$_3$ **4**) or M is large (Ba **8**), compounds undergo ligand redistribution reactions to give the insoluble corner-shared double-cube azaheterometallocubane complexes [M{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$_2$] (**6** and **7**). Analogous ligand redistribution reactions from alkylmagnesium bearing hydrotris(pyrazolyl)borato ligands have been reported by Parkin et al. and compared with the Schlenk equilibrium (eq 1).[16]

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (1)$$

In those studies, the derivatives [{η^3-HB(3,5-Me$_2$pz)$_3$}MgR] suffer ligand redistribution reactions at 80−120 °C, whereas analogous magnesium alkyl derivatives with the more sterically demanding {η^3-HB(3-Bu^{t}pz)$_3$} ligand are stable in that temperature range. We have recently estimated the steric profile of **1** in iridium structures,[7] being between those determined for Tp and Tp^{Me2}. Accordingly, the "{(μ_3-N)(μ_3-NH)$_2$Ti$_3$(η^5-C$_5$Me$_5$)$_3$(μ_3-N)}$^-$" organometallic ligand confers steric crowding on the magnesium center smaller than Tp^{Me2} and their complexes exhibit lower thermal stability.

We are continuing to explore the synthesis of other group 2−titanium azaheterocubane complexes as precursors for a wide range of new chemistry and, in particular, in the context of their potential use as sources of ternary nitrides MTi$_x$N$_y$.

Acknowledgment. We are grateful to the Spanish MCYT (BQU2001-1499), DGICAM (07N/0044/1999), and the Universidad de Alcalá (UAH2002/019) for support of this research.

Supporting Information Available: Experimental details for syntheses of **2**, **3**, **4**, **6**, and **7**, analytical and spectroscopic data for all the complexes, and X-ray structural information on **2**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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