Inorg. Chem. **2008**, *47*, 7077−7079

Inorganic Chemistry
Communication

Yttrium and Erbium Halide Complexes with [{Ti(η^5-C_5Me_5)(μ-NH)}$_3$(μ_3-N)] as a Neutral Tridentate Ligand

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Received June 6, 2008

Treatment of [{TiCp*(μ-NH)}$_3$(μ_3-N)] (**1**; Cp* = η^5-C_5Me_5) with yttrium and erbium halide complexes [$MCl_3(THF)_{3.5}$] and [$MCpCl_2(THF)_3$] (Cp = η^5-C_5H_5) gives cube-type adducts [Cl_3M{(μ_3-NH)$_3$$Ti_3Cp^*_3$($\mu_3$-N)}] and [$CpCl_2M${($\mu_3$-NH)$_3$$Ti_3Cp^*_3$($\mu_3$-N)}]. An analogous reaction of **1** with [{MCp_2Cl}$_2$] in toluene affords [Cp_3M(μ-Cl)ClCpM{(μ_3-NH)$_3$$Ti_3Cp^*_3$($\mu_3$-N)}] (M = Y, Er).

A recent theme in the chemistry of group 3 and lanthanide metals is the synthesis and reactivity of molecular complexes bearing tridentate nitrogen-based ligands as elegant alternatives to the well-established cyclopentadienyl-based complexes. Representative examples of ligands pursued in this vein include facially coordinating six-electron donors as the anionic tris(pyrazolyl)borates[1] and, more recently, the neutral analogous tris(pyrazolyl)methanes and tris(pyrazolyl)silanes.[2,3] Their electronic properties and especially the flexible coordination ability of such tripodal ligands are very different when compared with the planar cyclopentadienyl ligands,[4] permitting the isolation of species whose cyclopentadienyl relatives are highly reactive. More rigid trinitrogen ligands employed in group 3 and lanthanide metal complexes are cyclic triamines such as 1,4,7-triazacyclononanes[3,5] and 1,3,5-triazacyclohexanes.[3b,6] The trinuclear titanium imido−nitrido complex [{TiCp*(μ-NH)}$_3$(μ_3-N)] (**1**; Cp* = η^5-C_5Me_5)[7,8] shows a six-membered [Ti_3(μ-$NH)_3$] ring with three NH electron-donor imido groups and can also be seen as a sophisticated, preorganized, tridentate ligand similar to triazacycloalkanes. However, the existence of the μ_3-N nitrido apical group confers a more rigid conformation to **1** when compared with those systems. Our previous work has shown that **1** is capable of acting as a neutral ligand through the basal NH groups toward transition[9] and main-group[10] metal derivatives. Herein we report on the preliminary study of the coordination of metalloligand **1** to group 3 and lanthanide metals.

The synthetic chemistry is outlined in Scheme 1. Treatment of **1** with 1 equiv of yttrium and erbium trichloride tetrahydrofuran adducts [$MCl_3(THF)_{3.5}$] in a 4:1 toluene−THF mixture at room temperature afforded the precipitation of cube-type complexes [Cl_3M{(μ_3-NH)$_3$$Ti_3Cp^*_3$($\mu_3$-N)}] [M = Y (**2**), Er (**3**)] as yellow solids in good yields (77% and 69%). An analogous reaction of **1** with yttrium and erbium mono(cyclopentadienyl) derivatives [$MCpCl_2(THF)_3$] (Cp = η^5-C_5H_5)[11] gave brown solutions from which the adducts [$CpCl_2M${(μ_3-NH)$_3$$Ti_3Cp^*_3$($\mu_3$-N)}] [M = Y (**4**) 28%, Er (**5**) 23%] were isolated as orange solids after workup. Complexes **4** and **5** were obtained in higher yield (ca. 48%) by the treatment of trihalides **2** and **3** with sodium cyclopentadienide (1 equiv) in toluene at room temperature.

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(1) (a) Santos, I.; Marques, N. *New J. Chem.* **1995**, *19*, 551–571. (b) Marques, N.; Sella, A.; Takats, J. *Chem. Rev.* **2002**, *102*, 2137–2159.

(2) (a) Bigmore, H. R.; Lawrence, S. C.; Mountford, P.; Tredget, C. S. *Dalton Trans.* **2005**, 635–651. (b) Sella, A.; Brown, S. E.; Steed, J. W.; Tocher, D. A. *Inorg. Chem.* **2007**, *46*, 1856–1864.

(3) (a) Lawrence, S. C.; Ward, B. D.; Dubberley, S. R.; Kozak, C. M.; Mountford, P. *Chem. Commun.* **2003**, 2880–2881. (b) Tredget, C. S.; Lawrence, S. C.; Ward, B. D.; Howe, R. G.; Cowley, A. R.; Mountford, P. *Organometallics* **2005**, *24*, 3136–3148.

(4) (a) Kitajima, N.; Tolman, B. W. *Prog. Inorg. Chem.* **1995**, *43*, 419–531. (b) Tellers, D. M.; Skoog, S. J.; Bergman, R. G.; Gunnoe, T. B.; Harman, W. D. *Organometallics* **2000**, *19*, 2428–2432.

(5) (a) Hajela, S.; Schaefer, W. P.; Bercaw, J. E. *J. Organomet. Chem.* **1997**, *532*, 45–53. (b) Bambirra, S.; van Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Chem. Commun.* **2001**, 637–638. (c) Bambirra, S.; Meetsma, A.; Hessen, B. *Acta Crystallogr.* **2006**, *E62*, m314–m316. (d) Bambirra, S.; Meetsma, A.; Hessen, B.; Bruins, A. P. *Organometallics* **2006**, *25*, 3486–3495. (e) Bambirra, S.; van Leusen, D.; Tazelaar, C. G. J.; Meetsma, A.; Hessen, B. *Organometallics* **2007**, *26*, 1014–1023.

(6) Köhn, R. D.; Pan, Z.; Kociok-Köhn, G.; Mahon, M. F. *J. Chem. Soc., Dalton Trans.* **2002**, 2344–2347.

(7) Roesky, H. W.; Bai, Y.; Noltemeyer, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 754–755.

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

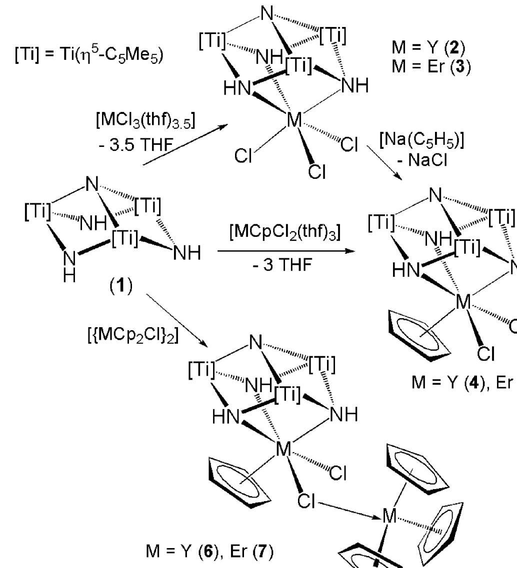
(9) (a) Freitag, K.; Gracia, J.; Martín, A.; Mena, M.; Poblet, J.-M.; Sarasa, J. P.; Yélamos, C. *Chem.−Eur. J.* **2001**, *7*, 3644–3651. (b) Abarca, A.; Galakhov, M.; Gracia, J.; Martín, A.; Mena, M.; Poblet, J. M.; Sarasa, J. P.; Yélamos, C. *Chem.−Eur. J.* **2003**, *9*, 2337–2346. (c) Martín, A.; Martínez-Espada, N.; Mena, M.; Pérez-Redondo, A.; Yélamos, C. *Inorg. Chem.* **2006**, *45*, 6901–6911.

(10) (a) García-Castro, M.; Martín, A.; Mena, M.; Yélamos, C. *Organometallics* **2004**, *23*, 1496–1500. (b) García-Castro, M.; Gracia, J.; Martín, A.; Mena, M.; Poblet, J.-M.; Sarasa, J. P.; Yélamos, C. *Chem.−Eur. J.* **2005**, *11*, 1030–1041. (c) García-Castro, M.; Martín, A.; Mena, M.; Yélamos, C. *Organometallics* **2007**, *26*, 408–416.

(11) (a) Manastyrskyj, S.; Maginn, R. E.; Dubeck, M. *Inorg. Chem.* **1963**, *2*, 904–905. (b) Zhou, X.; Wu, Z.; Ma, H.; Xu, Z.; You, X. *Polyhedron* **1994**, *13*, 375–378.

10.1021/ic8010426 CCC: $40.75

Scheme 1. Reaction of **1** with Yttrium and Erbium $[MCp_{3-n}Cl_n]$ Derivatives



While the trichloride derivatives **2** and **3** are only moderately soluble in halogenated solvents, cyclopentadienyl compounds **4** and **5** are very soluble in chloroform and slightly soluble in toluene or benzene. Complexes **2**−**5** were characterized by spectral and analytical methods, as well as by X-ray crystal structure determination for the erbium derivatives **3** and **5**.[12] IR spectra (KBr) showed one ν_{NH} vibration, between 3330 and 3325 cm^{-1}, in a range similar to that determined for **1** (3352 cm^{-1}).[8] The ^1H and $^{13}C\{^1H\}$ NMR spectra in chloroform-d_1 at room temperature of the diamagnetic yttrium complex **2** reveal resonance signals for equivalent NH and η^5-C_5Me_5 groups and agree with a C_{3v}-symmetric structure in solution. The NH resonance signal in the ^1H NMR spectrum (δ 12.90) is shifted to a higher field than that found in **1** (δ 13.40), suggesting a tridentate coordination of the metalloligand.[9,10] The ^1H NMR spectra in chloroform-d_1 or benzene-d_6 at room temperature of **4** show singlets due to equivalent NH, η^5-C_5Me_5, and η^5-C_5H_5 groups in the expected proportions of 3:45:5. The NMR data for **4** are consistent with the existence of a low-energy exchange process in solution, similar to that studied in detail for the six-coordinate titanium adduct $[Cl_2(ArN)Ti\{(\mu_3\text{-}NH)_3Ti_3Cp^*_3(\mu_3\text{-}N)\}]$.[9b]

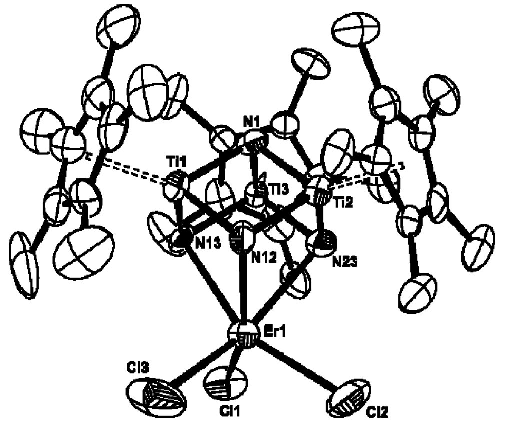


Figure 1. Perspective view of **3** with thermal ellipsoids at the 50% probability level. Ranges for selected lengths [Å] and angles [deg]: Er−Cl 2.537(5)−2.570(4), Er−N 2.552(10)−2.646(11), Cl−Er−Cl 98.2(2)−102.0(2), N−Er−N 69.7(4)−71.7(4).

The crystal structure of **3** shows an $[ErTi_3N_4]$ cube-type core with the neutral ligand $[(\mu\text{-}NH)_3Ti_3Cp^*_3(\mu_3\text{-}N)]$ coordinating in a tripodal fashion (Figure 1). We are not aware of any structure containing a six-coordinate "ErN_3Cl_3" core, but the coordination environment about the erbium atom is comparable to those reported for the yttrium tris(pyrazolyl)silane $[Y\{MeSi(3,5\text{-}Me_2pz)_3\}Cl_3]$[3b] and tris(pyrazolyl)methane $[Y\{HC(3,5\text{-}Me_2pz)_3\}Cl_3]$[2b] derivatives. Thus, in a fashion similar to those complexes, the erbium atom exhibits a trigonal antiprismatic geometry with one tighter triangle defined by the nitrogen atoms and with a more open one defined by the chloride ligands. This is clearly seen by comparing the N−Er−N [ave 70.5(6)°] and Cl−Er−Cl [ave 100(1)°] angles. The Er−Cl bond lengths [ave 2.553(12) Å] are similar to the Y−Cl distances in complexes $[Y\{MeSi(3,5\text{-}Me_2pz)_3\}Cl_3]$ [ave 2.568(1) Å][3b] and $[Y\{HC(3,5\text{-}Me_2pz)_3\}Cl_3]$ [ave 2.555(2) Å],[2b] as expected from the ionic radii of Er^{3+} (1.030 Å) and Y^{3+} (1.040 Å).[13] However, complex **3** shows Er−N bond lengths [ave 2.59(3) Å] clearly longer than the Y−N distances found in those yttrium chloride derivatives, ave 2.464(3) and 2.459(5) Å, suggesting a weaker coordination of the titanium tripodal ligand. This might correspond to the steric repulsion between the bulky pentamethylcyclopentadienyl ligands and the chloride groups placed in an eclipsed position. Accordingly, the distortions in bond distances and angles within the tridentate ligand are small when compared to those of **1**.[7]

The molecular structure of **5** consists of a distorted $[ErTi_3N_4]$ cube-type core (Figure 2) very similar to that of **3**. Erbium is bonded to one η^5-cyclopentadienyl ligand, two chlorides, and three imido groups of the $[Ti_3(\mu\text{-}NH)_3(\mu_3\text{-}N)]$ core. If the centroid (Cp) of the C_5H_5 ligand is considered, the coordination sphere about the erbium atom may also be described as trigonal antiprismatic [average angles: N−Er−N 70.6(3)°, Cl1−Er−Cl2 95.6(1)°, and Cp−Er−Cl 103.5°]. The cyclopentadienyl ligand is bonded in an η^5 fashion to erbium with an Er−Cp(centroid) distance of 2.379 Å, in the range observed for other cyclopentadienyl-containing erbium

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(12) Crystal data for **3**: $C_{30}H_{48}Cl_3ErN_4Ti_3$, $M_w = 882.03$, monoclinic, $a = 11.177(4)$ Å, $b = 17.907(2)$ Å, $c = 37.753(6)$ Å, $\beta = 94.39(2)°$, $V = 7534(3)$ Å^3, $Z = 8$, space group $P2_1/c$ (No. 14), $T = 200(2)$ K, $\lambda = 0.710\,73$ Å, $D_{calcd} = 1.555$ g cm^{-3}, $\mu = 3.055$ mm^{-1}, R1 = 0.088, wR2 = 0.194 [for 5909 reflections with $I > 2\sigma(I)$]. Crystal data for **5**: $C_{35}H_{53}Cl_2ErN_4Ti_3$, $M_w = 911.67$, monoclinic, $a = 11.039(4)$ Å, $b = 18.155(6)$ Å, $c = 19.094(6)$ Å, $\beta = 94.10(2)°$, $V = 3817(2)$ Å^3, $Z = 4$, space group $P2_1/n$ (No. 14), $T = 200(2)$ K, $\lambda = 0.710\,73$ Å, $D_{calcd} = 1.587$ g cm^{-3}, $\mu = 2.95$ mm^{-1}, R1 = 0.062, wR2 = 0.148 [for 5668 reflections with $I > 2\sigma(I)$]. Crystal data for **7**$\cdot 2C_7H_8$: $C_{64}H_{84}Cl_2Er_2N_4Ti_3$, $M_w = 1458.47$, monoclinic, $a = 18.166(4)$ Å, $b = 14.615(3)$ Å, $c = 24.832(5)$ Å, $\beta = 102.40(2)°$, $V = 6439(2)$ Å^3, $Z = 4$, space group $P2_1/c$ (No. 14), $T = 200(2)$ K, $\lambda = 0.710\,73$ Å, $D_{calcd} = 1.505$ g cm^{-3}, $\mu = 3.057$ mm^{-1}, R1 = 0.048, wR2 = 0.080 [for 8524 reflections with $I > 2\sigma(I)$]. The values of R1 and wR2 are defined as follows: $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$.

(13) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.

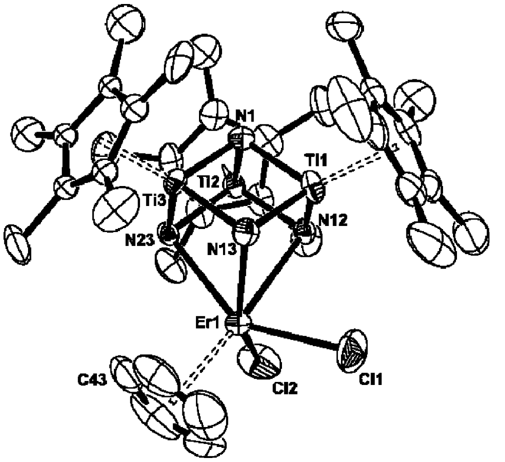

Figure 2. Perspective view of **5** with thermal ellipsoids at the 50% probability level. Ranges for selected lengths [Å] and angles [deg]: Er1−Cl1 2.596(3), Er1−Cl2 2.566(2), Er1−N 2.537(6)−2.630(5), Er1−Cp 2.379, Cl1−Er1−Cl2 95.6(1), N−Er1−N 70.2(2)−71.0(2), Cp−Er1−Cl1 104.4, Cp−Er1−Cl2 102.6, Cp−Er1−N12 175.6, Cp−Er1−N13 105.8, Cp−Er1−N23 106.1.

complexes.[14] The steric bulk of the C_5H_5 ligand produces a slight closing of the Cl1−Er−Cl2 angle [95.6(1)°] with respect to those found in **3**; however, there is not any important distortion in the Er−N bond lengths [ave 2.59(4) Å] and N−Er−N angles [ave 70.6(3)°].

An analogous treatment of **1** with yttrium and erbium di(cyclopentadienyl) derivatives $[\{MCp_2Cl\}_2]$[15] (0.5 or 1 equiv) in toluene at room temperature afforded the precipitation of complexes $[Cp_3M(\mu\text{-}Cl)ClCpM\{(\mu_3\text{-}NH)_3Ti_3Cp^*_3(\mu_3\text{-}N)\}]\cdot C_7H_8$ [M = Y ($\mathbf{6}\cdot C_7H_8$), Er ($\mathbf{7}\cdot C_7H_8$)] (Scheme 1). Compounds **6** and **7** were isolated as orange solids in low yields (18 and 43%) and were characterized by IR spectroscopy and C, H, and N microanalysis, as well as by X-ray crystal structure determination.[12,16] When the yttrium derivative **6** was dissolved in benzene-d_6 or chloroform-d_1, the ^1H and $^{13}C\{^1H\}$ NMR spectra of the resultant orange solutions revealed resonance signals for complexes **1** and $[\{YCp_2Cl\}_2]$ as major products, indicating the decomposition of **6** in solution. Furthermore, the reaction of **4** with $[YCp_3]$ (1 equiv) or the treatment of **4** with $[Na(C_5H_5)]$ (1 equiv) in chloroform-d_1 gave also a mixture of **1** and $[\{YCp_2Cl\}_2]$ according to ^1H NMR spectroscopy. It appears that a presumably derivative $[Cp_2ClY\{(\mu_3\text{-}NH)_3Ti_3Cp^*_3(\mu_3\text{-}N)\}]$ could be too crowded and decomposes in solution. Accordingly, complex **1** did not react with $[YCp_3]$ in benzene-d_6 even after prolonged heating at 100 °C.

The molecular structure of the erbium complex **7** is shown in Figure 3. The overall structure of **7** resembles that described for **5** but with an $[Er(\eta^5\text{-}C_5H_5)_3]$ fragment linked to Er1 via a μ-Cl ligand. The geometry and bond distances about Er2 are comparable to those found in the $[ErCp_3(THF)]$ derivative.[17] The coordination of this additional fragment does not produce significant distortions about the Er1 center when compared to **5**. The donation of electron density from μ-Cl to Er2 results in a lengthening of the Er1−Cl1 bond distance. The μ-Cl group is bridging asymmetrically to the erbium atoms [Er1−Cl1 2.696(2) Å and Er2−Cl1 2.765(2) Å], whereas the terminal Er1−Cl2 and Er1−Cp1 bond distances, 2.582(2) and 2.385 Å, respectively, are almost identical with those of **5**. The Er1−N bond lengths and N−Er1−N angles with the tridentate ligand remain also invariable [ave Er−N 2.612(10) Å and N−Er−N 69.3(5)°] when compared to those of the previous structures of **3** and **5**.

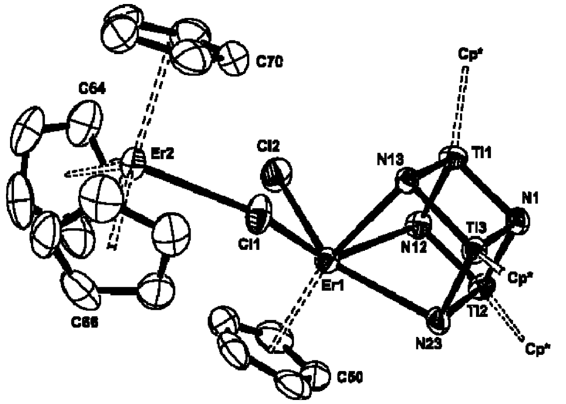

Figure 3. Simplified view of **7** with thermal ellipsoids at the 50% probability level. Ranges for selected lengths [Å] and angles [deg]: Er1−Cl2 2.582(2), Er1−Cl1 2.696(2), Er1−N 2.600(4)−2.624(4), Er1−Cp1 2.385, Er2−Cl1 2.765(2), Er2−Cp2 2.441, Er2−Cp3 2.436, Er2−Cp4 2.460, Cl1−Er1−Cl2 89.9(1), N−Er1−N 68.7(2)−70.0(2), Cp1−Er1−Cl1 101.4, Cp1−Er1−Cl2 104.0, Cp1−Er1−N12 119.9, Cp1−Er1−N13 159.4, Cp1−Er1−N23 96.5, Er1−Cl1−Er2 149.8(1).

In summary, we have shown that the imido−nitrido complex **1** acts as a rigid facially coordinating ligand to yttrium and erbium halide complexes. We are currently exploring the synthesis of other group 3 and lanthanide complexes and studying the reactivity of these systems.

Acknowledgment. We are grateful to the Spanish MEC (Grant CTQ2005-00238/BQU), Comunidad de Madrid and the Universidad de Alcalá (Grant CCG06-UAH/PPQ-0665), and Factoría de Cristalización (CONSOLIDER-INGENIO 2010) for support of this research. J.C. thanks the UAH and MEC for undergraduate fellowships.

Supporting Information Available: Experimental details and full characterization data for complexes **2**−**7**, crystallographic data, perspective view, and selected bond distances and angles for complex **6**, and X-ray crystallographic file in CIF format for the structure determination of **3**, **5**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[14] (a) Day, C. S.; Day, V. W.; Ernst, R. D.; Vollmer, S. H. *Organometallics* **1982**, *1*, 998–1003. (b) Lamberts, W.; Lueken, H.; Hessner, B. *Inorg. Chim. Acta* **1987**, *134*, 155–157. (c) Pfeiffer, D.; Guzei, I. A.; Liable-Sands, L. M.; Heeg, M. J.; Rheingold, A. L.; Winter, C. H. *J. Organomet. Chem.* **1999**, *588*, 167–175.

[15] Maggin, R. E.; Manastyrskyj, S.; Dubeck, M. *J. Am. Chem. Soc.* **1962**, *85*, 672–676.

[16] Full details of the X-ray crystal structure determination, a figure, and parameters of **6** can be found in the Supporting Information.

[17] Chen, W.; Lin, G.; Xia, J.; Wei, G.; Zhang, Y.; Jin, Z. *J. Organomet. Chem.* **1994**, *467*, 75–78.