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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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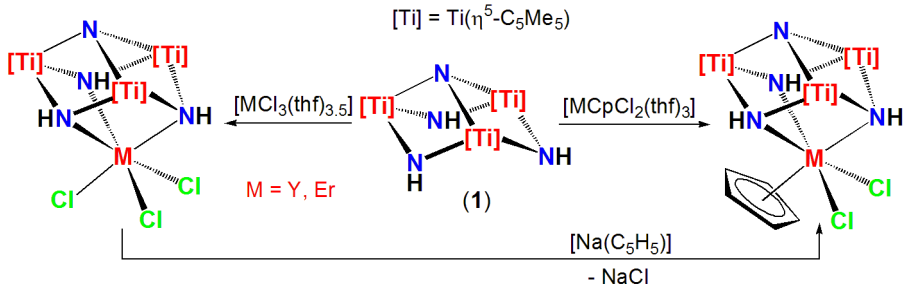
Synopsis:

Cube-type complexes [$Cl_3M\{(\mu_3\text{-}NH)_3Ti_3Cp^*_3(\mu_3\text{-}N)\}$] and [$CpCl_2M\{(\mu_3\text{-}NH)_3Ti_3Cp^*_3(\mu_3\text{-}N)\}$] (M = Y, Er) have been obtained upon treatment of [{$TiCp^*(\mu\text{-}NH)\}_3(\mu_3\text{-}N)$] (**1**) with the tetrahydrofuran adducts [$MCl_3(thf)_{3.5}$] and [$MCpCl_2(thf)_3$]. The metalloligand **1** acts as a rigid facially coordinating six-electron donor to the rare-earth metals.



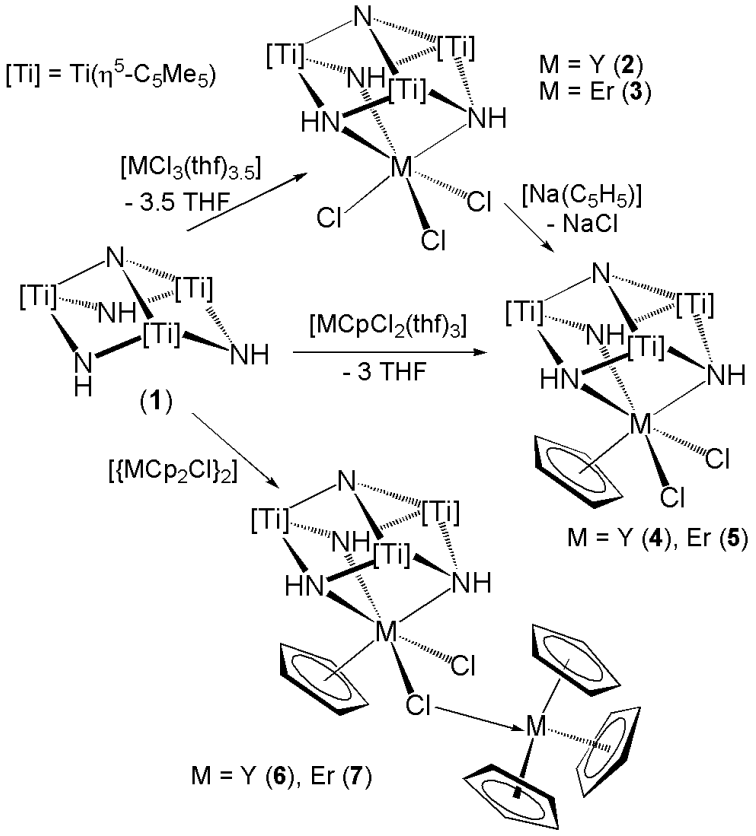
Abstract:

Treatment of [{TiCp*(μ-NH)}$_3$(μ$_3$-N)] (**1**) (Cp* = η^5-C$_5$Me$_5$) with yttrium and erbium halide complexes [MCl$_3$(thf)$_{3.5}$] and [MCpCl$_2$(thf)$_3$] (Cp = η^5-C$_5$H$_5$) gives cube-type adducts [Cl$_3$M{(μ$_3$-NH)$_3$Ti$_3$Cp*$_3$(μ$_3$-N)}] and [CpCl$_2$M{(μ$_3$-NH)$_3$Ti$_3$Cp*$_3$(μ$_3$-N)}]. Analogous reaction of **1** with [{MCp$_2$Cl}$_2$] in toluene affords [Cp$_3$M(μ-Cl)ClCpM{(μ$_3$-NH)$_3$Ti$_3$Cp*$_3$(μ$_3$-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 $[\{TiCp^*(\mu\text{-}NH)\}_3(\mu_3\text{-}N)]$[7,8] ($Cp^* = \eta^5\text{-}C_5Me_5$) (**1**) shows a six-membered $[Ti_3(\mu_3\text{-}NH)_3]$ ring with three NH electron-donor imido groups and can also be seen as a sophisticated, preorganized, tridentate ligand similar to those 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 towards transition[9] and main group[10] metal derivatives. Herein we report the preliminary study about the coordination of the metalloligand **1** to group 3 and lanthanide metals.

The synthetic chemistry is outlined in Scheme 1. Treatment of **1** with one equivalent of yttrium and erbium trichloride tetrahydrofuran adducts $[MCl_3(thf)_{3.5}]$ in a 4:1 mixture toluene-THF at room temperature afforded the precipitation of cube-type complexes $[Cl_3M\{(\mu_3\text{-}NH)_3Ti_3Cp^*_3(\mu_3\text{-}N)\}]$ [M = Y (**2**), Er (**3**)] as yellow solids in good yields (77% and 69%). Analogous reaction of **1** with yttrium and erbium mono(cyclopentadienyl) derivatives

$[MCpCl_2(thf)_3]$[11] (Cp = η^5-C_5H_5) gave brown solutions from which the adducts $[CpCl_2M\{(\mu_3\text{-}NH)_3Ti_3Cp^*_3(\mu_3\text{-}N)\}]$ [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 treatment of the trihalides **2** and **3** with sodium cyclopentadienide (1 equiv) in toluene at room temperature.



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 in toluene or benzene. Complexes **2-5** were characterized by spectral and analytical methods, as well as by X-ray crystal structure determinations for the erbium derivatives **3** and **5**.[12] IR spectra (KBr) showed one ν_{NH} vibration, between 3330 and 3325 cm^{-1}, in a similar range 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 ^{1}H NMR spectrum (δ = 12.90) is shifted to higher field than that found in **1** (δ = 13.40), suggesting a tridentate coordination of the metalloligand.[9,10] The ^{1}H 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 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]

The crystal structure of **3** shows an $[ErTi_3N_4]$ cube-type core with the neutral ligand $[(\mu_3\text{-}NH)_3Ti_3Cp^*_3(\mu_3\text{-}N)]$ 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 (av. 70.5(6)º) and Cl-Er-Cl (av. 100(1)º) angles. The erbium-chloride bond lengths (av. 2.553(12) Å) are similar to the Y-Cl distances in complexes $[Y\{MeSi(3,5\text{-}Me_2pz)_3\}Cl_3]$ (av. 2.568(1) Å)[3b] and $[Y\{HC(3,5\text{-}Me_2pz)_3\}Cl_3]$ (av. 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 erbium-nitrogen bond lengths (av. 2.59(3) Å) clearly longer than the Y-N distances found in those yttrium chloride derivatives, av. 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 **1**.[7]

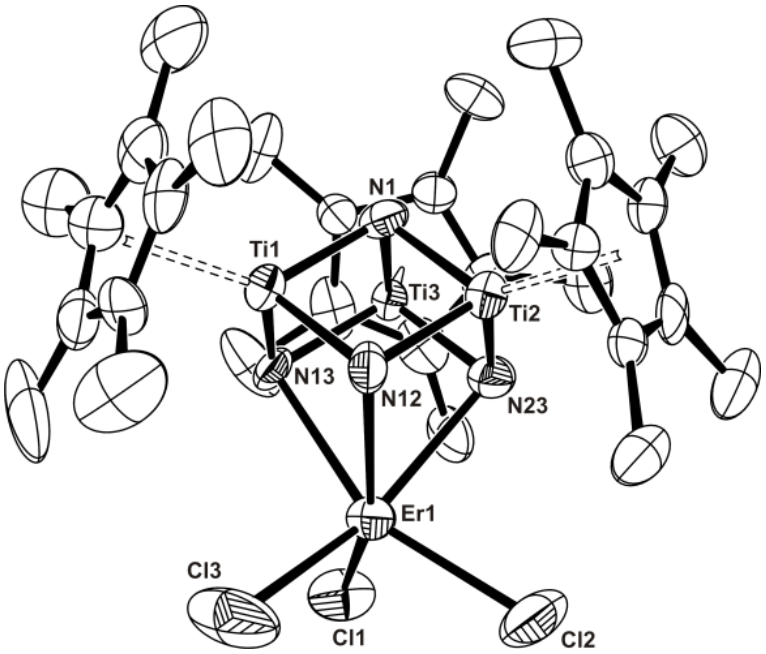


Figure 1. Perspective view of $[Cl_3Er\{(\mu_3\text{-}NH)_3Ti_3Cp^*_3(\mu_3\text{-}N)\}]$ (**3**) with thermal ellipsoids at the 50% probability level. Ranges for selected lengths [Å] and angles [deg]: Er-Cl 2.537(5)-2.570(4), Er-N 2.552(10)-2.646(11), Cl-Er-Cl 98.2(2)-102.0(2), N-Er-N 69.7(4)-71.7(4).

The 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)º, Cl(1)-Er-Cl(2) 95.6(1)º and Cp-Er-Cl 103.5º). 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 complexes.[14] The steric bulk of the C_5H_5 ligand produces a slight closing of the Cl(1)-

Er-Cl(2) angle (95.6(1)º) with respect to those found in **3**, however, there is not any important distortion in the Er-N (av. 2.59(4) Å) bond lengths and N-Er-N (av. 70.6(3)º) angles.

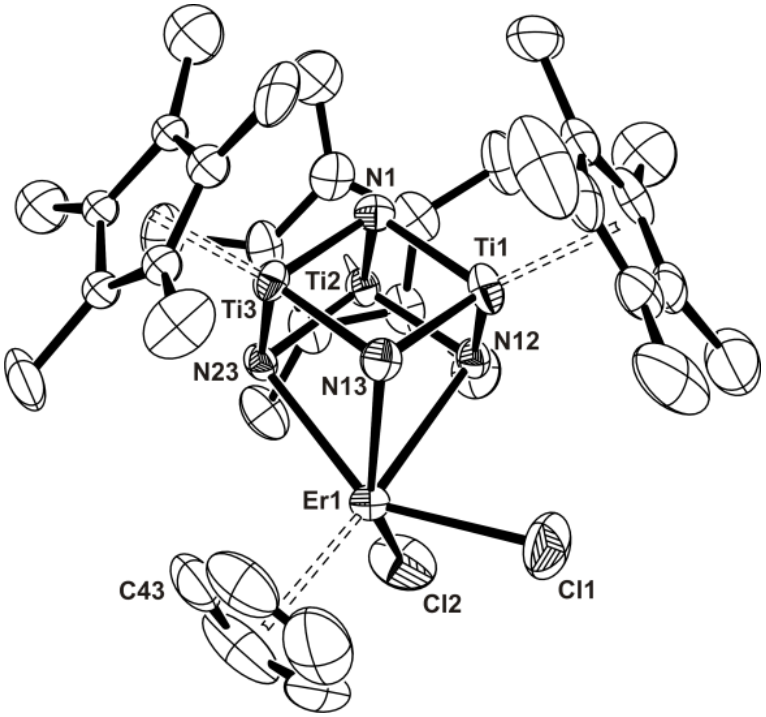


Figure 2. Perspective view of [$CpCl_2Er\{(\mu_3\text{-}NH)_3Ti_3Cp^*_3(\mu_3\text{-}N)\}$] (**5**) with thermal ellipsoids at the 50% probability level. Ranges for selected lengths [Å] and angles [deg]: Er(1)-Cl(1) 2.596(3), Er(1)-Cl(2) 2.566(2), Er(1)-N 2.537(6)-2.630(5), Er(1)-Cp 2.379, Cl(1)-Er(1)-Cl(2) 95.6(1), N-Er(1)-N 70.2(2)-71.0(2), Cp-Er(1)-Cl(1) 104.4, Cp-Er(1)-Cl(2) 102.6, Cp-Er(1)-N(12) 175.6, Cp-Er(1)-N(13) 105.8, Cp-Er(1)-N(23) 106.1.

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 (**6**·C_7H_8), Er (**7**·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, N microanalysis, as well as by X-ray crystal structure determinations.[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 ºC.

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 erbium(1) via a μ-Cl ligand. The geometry and bond distances about erbium(2) 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 erbium(1) center when compared to **5**. The donation of electron density from the μ-Cl to erbium(2) results in a lengthening of the Er(1)-Cl(1) bond distance. The μ-Cl group is bridging asymmetrically to the erbium atoms (Er(1)-Cl(1) 2.696(2) and Er(2)-Cl(1) 2.765(2) Å) whereas the terminal Er(1)-Cl(2) and Er(1)-Cp(1), 2.582(2) and 2.385 Å, bond distances are almost identical to those of **5**. The erbium(1)-nitrogen bond lengths and nitrogen-Er(1)-nitrogen angles with the tridentate ligand remain also invariable (av. Er-N 2.612(10) Å and N-Er-N 69.3(5)º) when compared to those of the previous structures of **3** and **5**.

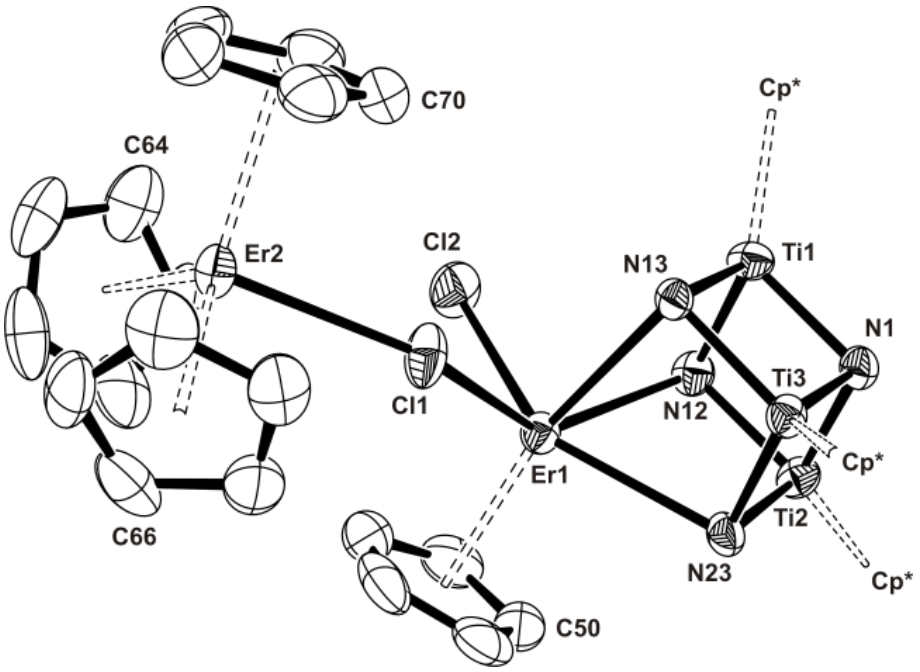


Figure 3. Simplified view of [$Cp_3Er(\mu\text{-}Cl)ClCpEr\{(\mu_3\text{-}NH)_3Ti_3Cp^*_3(\mu_3\text{-}N)\}$] (**7**) with thermal ellipsoids at the 50% probability level. Ranges for selected lengths [Å] and angles [deg]: Er(1)-Cl(2) 2.582(2), Er(1)-Cl(1) 2.696(2), Er(1)-N 2.600(4)-2.624(4), Er(1)-Cp(1) 2.385, Er(2)-Cl(1) 2.765(2), Er(2)-Cp(2) 2.441, Er(2)-Cp(3) 2.436, Er(2)-Cp(4) 2.460, Cl(1)-Er(1)-Cl(2) 89.9(1), N-Er(1)-N 68.7(2)-70.0(2), Cp(1)-Er(1)-Cl(1) 101.4, Cp(1)-Er(1)-Cl(2) 104.0, Cp(1)-Er(1)-N(12) 119.9, Cp(1)-Er(1)-N(13) 159.4, Cp(1)-Er(1)-N(23) 96.5, Er(1)-Cl(1)-Er(2) 149.8(1).

In summary, we have shown that the imido-nitrido complex [$\{TiCp^*(\mu\text{-}NH)\}_3(\mu_3\text{-}N)$] (**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.

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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**. X-ray crystallographic files in CIF format for the structure determinations 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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(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, β = 94.39(2)°, V = 7534(3) Å^3, Z = 8, space group $P2_1/c$ (No. 14), T = 200(2) K, λ = 0.71073 Å, D_{calcd} = 1.555 g·cm^{-3}, μ = 3.055 mm^{-1}, $R1$ = 0.088, w$R2$ = 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, β = 94.10(2)°, V = 3817(2) Å^3, Z = 4, space group $P2_1/n$ (No. 14), T = 200(2) K, λ = 0.71073 Å, D_{calcd} = 1.587 g·cm^{-3}, μ = 2.95 mm^{-1}, $R1$ = 0.062, w$R2$ = 0.148 (for 5668 reflections with $I>2\sigma(I)$). Crystal data for **7**·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, β = 102.40(2)°, V = 6439(2) Å^3, Z = 4, space group $P2_1/c$ (No. 14), T = 200(2) K, λ = 0.71073 Å, D_{calcd} = 1.505 g·cm^{-3}, μ = 3.057 mm^{-1}, $R1$ = 0.048, w$R2$ = 0.080 (for 8524 reflections with $I>2\sigma(I)$). The values of $R1$ and $wR2$ are defined as follows $R1 = \Sigma||F_o| - |F_c||/[\Sigma|F_o|]$ and $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

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

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