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Synthesis, structure, and characterization of lanthanide complexes bearing 1,3-diphenyltriazenido ligands

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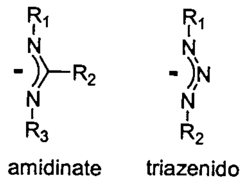
Abstract

Protonolysis reactions between tris(cyclopentadienyl)lanthanide complexes and 1,3-diphenyltriazene were investigated as routes to lanthanide complexes containing 1,3-diphenyltriazenido ligands. There was no detectable reaction between tris(cyclopentadienyl)erbium or tris(cyclopentadienyl)lutetium and excess 1,3-diphenyltriazene at ambient temperature in toluene solvent, due to the insolubility of the polymeric tris(cyclopentadienyl)lanthanide complexes in this medium. The monomeric, toluene-soluble adduct tris(cyclopentadienyl)(4-*tert*-butylpyridine)erbium(III) was obtained in 41% yield upon reaction of tris(cyclopentadienyl)erbium with 4-*tert*-butylpyridine in toluene at ambient temperature. Treatment of tris(cyclopentadienyl)(4-*tert*-butylpyridine)erbium or tris(cyclopentadienyl)(4-*tert*-butylpyridine)lutetium with 1,3-diphenyltriazene (one equivalent) in toluene at ambient temperature afforded bis(cyclopentadienyl)(1,3-diphenyltriazenido)(4-*tert*-butylpyridine)erbium(III) (73%) and bis(cyclopentadienyl)(1,3-diphenyltriazenido)(4-*tert*-butylpyridine)lutetium(III) (81%), respectively, as red–brown solids. Treatment of tris(cyclopentadienyl)lanthanide with 1,3-diphenyltriazene (three equivalents) and pyridine (two or three equivalents) in refluxing toluene afforded tris(1,3-diphenyltriazenido)bis(pyridine)erbium(III)·(pyridine)$_{1.0}$·(toluene)$_{0.5}$ (48%) and tris(1,3-diphenyltriazenido)bis(pyridine)lutetium(III) (63%) were isolated as red–brown solids. The crystal structures of bis(cyclopentadienyl)(1,3-diphenyltriazenido)(4-*tert*-butylpyridine)erbium(III) and tris(1,3-diphenyltriazenido)bis(pyridine)erbium(III)·(pyridine)$_{1.0}$·(toluene)$_{0.5}$ are described. Both complexes are monomeric and contain bidentate 1,3-diphenyltriazenido ligands. The potential utility of lanthanide complexes bearing 1,3-diaryltriazenido ligands as source compounds in chemical vapor deposition processes is discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lanthanides; Erbium; Lutetium; 1,3-Diphenyltriazenido ligands; Nitrogen-containing compounds

1. Introduction

Complexes bearing amidinate ligands (Scheme 1) are the subject of considerable current research activity [1–3]. Desirable attributes of these ligands include excellent thermodynamic stability in resultant complexes due to the formation strong metal–nitrogen bonds, tunable steric profile through choice of substituents on the carbon and nitrogen atoms, as well as their ability to function as spectator ligands in analogy with well-precedented ligands such as cyclopentadienyl and 1,3-diketonates. This combination of properties has led to the use of amidinate ligands to stabilize reactive complexes and to promote the formation of monomeric complexes through steric saturation of the metal coor-



Scheme 1. Structures of amidinate and triazenido ligands.

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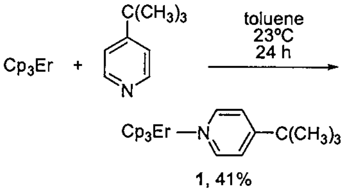
dination sphere. Our group has recently reported the application of a new erbium pyrazolato complex for the deposition of erbium-doped GaAs films using a chemical vapor deposition (CVD) process [4]. Importantly, the use of an erbium complex with an all-nitrogen coordination sphere led to a single, highly emissive erbium center in the films, whereas cyclopentadienyl-based erbium complexes afforded weaker, broad luminescence from many types of erbium sites. Complexes with all-nitrogen coordination spheres are desirable in the CVD of group 13–15 semiconductor materials to minimize the introduction of carbon or other undesired elements into the growing film. As part of the development of erbium source compounds, we became interested in new nitrogen donor ligands that might lead to volatile lanthanide complexes that could be useful in CVD applications. The success that has been achieved with the synthesis of monomeric lanthanide complexes containing amidinate ligands [3,5] suggested that aminidates or structurally related ligands might afford thermally stable, volatile lanthanide complexes. However, the amidinate ligand contains a carbon atom as part of the ligand framework, which could lead to carbon contamination in films derived from amidinate source compounds. We therefore turned our attention to 1,3-diaryltriazenido ligands (Scheme 1), which are related to amidinate ligands through replacement of the carbon atom by a nitrogen atom. 1,3-Diaryltriazenido ligands would not place carbon atoms in the inner coordination sphere, and therefore could be superior to amidinate ligands for the preparation of CVD precursors.

Complexes bearing 1,3-diaryltrizenido ligands have been reported for many main group and d-block metals [1–3]. Coordination modes that have been documented among the d-block metals include monodentate [6], bridging [7], and bidentate [8]. Recent work in the Group 1, Group 2, and Group 13 metals has revealed that the bidentate coordination mode predominates [9,10]. Surprisingly, there have been no reports of structurally characterized lanthanide complexes bearing 1,3-diaryltriazenido ligands. In particular, we envisioned that the bidentate coordination, flexible steric profile of the aryl groups, and strongly basic nitrogen donor atoms might lead to volatile, monomeric complexes that could be used in CVD processes. Herein we describe the synthesis, structure, and properties of a series of erbium and lutetium complexes bearing the 1,3-diphenyltriazenido ligand. Treatment of tris(cyclopentadienyl)lanthanide(III) (lanthanide = erbium or lutetium) with 1,3-diphenyltriazene in toluene at ambient temperature did not result in any detectable reaction, due to the insolubility of the polymeric lanthanide starting complexes. However, the toluene-soluble adducts tris(cyclopentadienyl)(4-*tert*-butylpyridine)lanthanide(III) react smoothly with 1,3-diphenyltriazene in toluene to displace one cyclopentadienyl ligand at ambient temperature and all three cyclopentadienyl ligands under more forcing conditions. The crystal structures of representative complexes demonstrate that the 1,3-diphenyltriazenido ligand coordinates in a bidentate fashion. The potential use of lanthanide complexes bearing 1,3-diaryltriazenido ligands in CVD processes is discussed. This work represents the first description of structurally characterized lanthanide complexes bearing 1,3-diaryltriazenido ligands, and suggests that such ligands promote the formation of monomeric complexes by saturating the coordination sphere of the metal ions.

2. Results

2.1. Synthetic chemistry

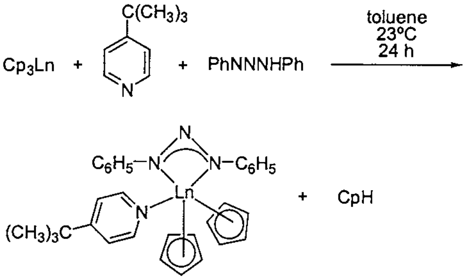
We initially envisioned that homoleptic complexes bearing 1,3-diphenyltriazenido ligands might be accessible by treatment of tris(cyclopentadienyl)lanthanide with three equivalents of 1,3-diphenyltriazene through protonolysis of the cyclopentadienyl ligands. Accordingly, tris(cyclopentadienyl)lutetium and tris(cyclopentadienyl)erbium were reacted with three equivalents of 1,3-diphenyltriazene in toluene at 23°C. Due to the very low solubility of the tris(cyclopentadienyl)lanthanide reactants, there was no detectable reaction over 48 h. We reasoned that if the tris(cyclopentadienyl)lanthanide starting materials could be converted into more soluble species, reaction might proceed smoothly. To probe this point, tris(cyclopentadienyl)erbium was treated with one equivalent of 4-*tert*-butylpyridine in toluene at 23°C, resulting in the slow dissolution of tris(cyclopentadienyl)erbium over 24 h to afford a clear pink solution (Eq. (1)). Sublimation of the pink residue obtained from this reaction yielded tris(cyclopentadienyl)(4-*tert*-butylpyridine)erbium (**1**, 41%) as pink crystals. The formulation of **1** was established by spectral and analytical techniques. The formation of monomeric adducts of tris(cyclopentadienyl)lanthanide(III) complexes similar to **1** is well precedented [11].



(1)

The formation of **1** as a toluene-soluble species suggested that it might serve as an efficient starting material for the synthesis of complexes bearing 1,3-diphenyltriazenido ligands. Accordingly, a suspension of tris(cyclopentadienyl)erbium or tris(cyclopentadienyl)lutetium in toluene was treated with 4-*tert*-

butylpyridine (one equivalent) and 1,3-diphenyltriazene (one equivalent) in toluene for 24 h (Eq. (2)).

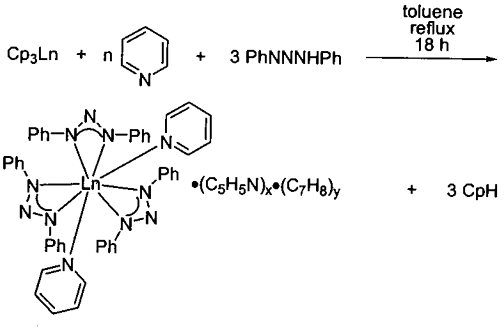


2, Ln = Er, 73%
3, Ln = Lu, 81%

(2)

The workup as described in the Section 4 afforded bis(cyclopentadienyl)(1,3 - diphenyltriazenido)(4 - *tert*-butylpyridine)erbium(III) (**2**, 73%) and bis(cyclopentadienyl)(1,3 - diphenyltriazenido)(4 - *tert* - butylpyridine)-lutetium(III) (**3**, 81%) as red–brown solids. The structures of **2** and **3** were assigned based upon spectral and analytical data. Additionally, the crystal structure of **2** was determined (vide infra). Incomplete displacement of the cyclopentadienyl groups in **3** by 1,3-diphenyltriazenido ligands was obvious from the NMR spectra. Treatment of tris(cyclopentadienyl)erbium or tris(cyclopentadienyl)lutetium with 4-*tert*-butylpyridine (one equivalent) and excess 1,3-diphenyltriazene (three equivalents) at 23°C did not lead to the displacement of additional cyclopentadienyl ligands, and only **2** and **3** were isolated.

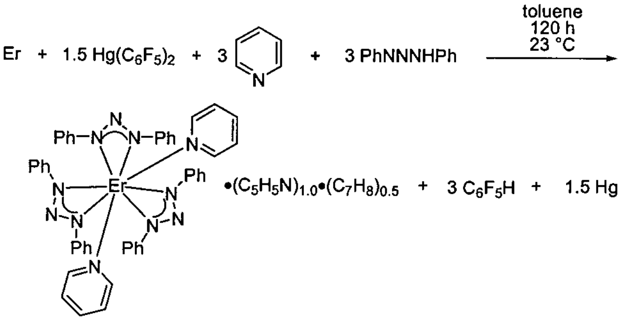
Since only one cyclopentadienyl ligand of tris(cyclopentadienyl)erbium or tris(cyclopentadienyl)lutetium was replaced upon treatment with 1,3-diphenyltriazene at ambient temperature, we sought to conduct the reactions under more forcing conditions. Treatment of tris(cyclopentadienyl)lutetium or tris(cyclopentadienyl)erbium with 1,3-diphenyltriazene (three equivalents) and pyridine (two or three equivalents) in refluxing toluene for 18 h afforded tris(1,3-diphenyltriazenido)bis(pyridine)erbium(III) · (pyridine)$_{1.0}$ · (toluene)$_{0.5}$ (**4**, 48%) and tris(1,3-diphenyltriazenido)-bis(pyridine)lutetium(III) (**5**, 63%) as red–brown solids (Eq. (3)).



4, Ln = Er, n = 3, x = 1.0, y = 0.5, 48%
5, Ln = Lu, n = 2, x, y = 0, 63%

(3)

The structures of **4** and **5** were established from the spectral and analytical data. Additionally, the X-ray crystal structure of **4** was determined (vide infra). The presence of the pyridine and toluene solvates in **4** was determined initially by X-ray crystallography. Carbon, hydrogen, and nitrogen microanalyses for bulk **4** were more consistent with a formulation of tris(1,3-diphenyltriazenido)bis(pyridine)erbium(III)·(pyridine)$_{1.0}$·(toluene)$_{1.0}$, in which one equivalent of toluene is present in the sample. The paramagnetic nature of **4** did not allow collection of its NMR spectra, which would have allowed another determination of the amount of toluene present in the sample. It is possible that the toluene solvate is labile, and slowly volatilizes to give variable toluene content in solid samples. The NMR spectra of **5** showed resonances attributable only to phenyl groups and pyridine, indicating complete substitution of the cyclopentadienyl ligands and no pyridine or toluene solvates. Compound **4** was also obtained in 49% yield by treating erbium metal with bis(pentafluorophenyl)mercury (1.5 equivalents), 1,3-diphenyltriazene (three equivalents), and pyridine (three equivalents) in toluene at ambient temperature for 120 h (Eq. (4)).



4, 49%

(4)

2.2. X-ray crystal structures of 2 and 4

In order to define the bonding of the 1,3-diphenyltriazenido ligands to erbium, the X-ray crystal structures of **2** and **4** were determined. Experimental crystallographic data are summarized in Table 1, selected bond lengths and angles are given in Tables 2 and 3, while perspective views are presented in Figs. 1 and 2.

Complex **2** crystallizes as a monomeric species with two η^5-cyclopentadienyl ligands, one bidentate 1,3-diphenyltriazenido ligand, and one 4-*tert*-butylpyridine donor. There are two independent molecules in the unit cell that are identical within the precision of the experiment. If the cyclopentadienyl ligands are considered to occupy three coordination sites, then the erbium centers in **2** are nine coordinate. The erbium–carbon bond

Table 1
Experimental crystallographic data for **2** and **4**

Compound	**2**	**4**
Empirical formula	$C_{31}H_{33}ErN_4$	$C_{54.5}H_{49}ErN_{12}$
Formula weight	628.87	1039.32
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	13.0820(10)	11.2701(2)
b (Å)	13.2770(10)	13.7089(3)
c (Å)	18.3420(10)	17.5024(3)
α (°)	105.000(10)	102.071(2)
β (°)	107.820(10)	106.4843(8)
γ (°)	96.650(10)	99.232(2)
V (Å^3)	2863.0(3)	2465.0(2)
Z	4	2
T (K)	295(2)	222(2)
λ (Å)	0.71073	0.71073
$D_{calc.}$ (g cm^{-3})	1.459	1.400
μ (cm^{-1})	2.956	17.54
$R(F)$ [a] (%)	5.95	6.43
$Rw(F)$ [a] (%)	10.08	13.48

[a] Quantity minimized: $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$.

lengths associated with the cyclopentadienyl ligands bonded to erbium(1) fall within the range of 2.624(12)–2.668(10) Å, while the erbium–cyclopentadienyl(centroid) distances 2.366(10) and 2.380(10) Å. These values are consistent with idealized η^5-bonding. The cyclopentadienyl(centroid)–erbium - cyclopentadienyl(centroid) angles are 128.4(4) and 129.4(4)°. The erbium–nitrogen bond lengths within the 1,3-diphenyltriazenido ligand are 2.423(6) (N(1)), 2.447(7) (N(3)) and 2.958(7) (N(3)) Å. These values indicate idealized bidentate bonding of the 1,3-diphenyltriazenido ligand, with N(2) not being bonded to erbium. The four-membered ring formed by bonding of the 1,3-diphenyltriazenido ligand to erbium is essentially planar, with nitrogen-nitrogen–nitrogen angles of 108.4(6) and 109.9(6)°. The planar metallacycle, coupled with the fact that the nitrogen–nitrogen–nitrogen angles are less than the idealized angle of 120°, do not indicate any significant bonding between the erbium atoms and the central nitrogen atoms of the 1,3-diphenyltriazenido ligands. The erbium–nitrogen bond lengths associated with the 4-*tert*-butylpyridine ligand are 2.515(7) and 2.525(7) Å.

Table 2
Selected bond lengths (Å) and angles (°) for **2** [a]

Bond lengths (Å)			
Er(1)–C(23)	2.663(9)	Er(1)–C(24)	2.635(10)
Er(1)–C(25)	2.645(12)	Er(1)–C(26)	2.641(10)
Er(1)–C(27)	2.668(10)	Er(1)–C(28)	2.615(10)
Er(1)–C(29)	2.629(10)	Er(1)–C(30)	2.632(11)
Er(1)–C(31)	2.624(12)	Er(1)–C(32)	2.662(11)
Er(1)–Cp(1)	2.380(10)	Er(1)–N(2)	2.958(7)
Er(1)–Cp(2)	2.366(10)	Er(1)–N(3)	2.447(7)
Er(1)–N(1)	2.423(6)	Er(1)–N(13)	2.515(7)
Bond angles (°)			
Cp(1)–Er(1)–Cp(2)	128.4(4)	Cp(1)–Er(1)–N(1)	103.0(4)
Cp(2)–Er(1)–N(1)	98.7(4)	Cp(1)–Er(1)–N(3)	126.9(4)
Cp(2)–Er(1)–N(3)	103.4(4)	Cp(1)–Er(1)–N(13)	97.2(4)
Cp(1)–Er(1)–N(13)	108.0(4)	N(1)–Er(1)–N(3)	51.9(2)
N(1)–Er(1)–N(13)	124.4(2)	N(3)–Er(1)–N(13)	74.5(2)

[a] Cp(1) defines the centroid of the cyclopentadienyl ligand containing C(23)–C(27); Cp(2) defines the centroid of the cyclopentadienyl ligand containing C(28)–C(32).

Table 3
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths (Å)			
Er–N(1)	2.405(6)	Er–N(7)	2.378(6)
Er–N(3)	2.422(6)	Er–N(9)	2.441(6)
Er–N(4)	2.419(6)	Er–N(10)	2.484(6)
Er–N(6)	2.429(6)	Er–N(11)	2.468(6)
Bond angles (°)			
N(1)–Er–N(3)	52.2(2)	N(4)–Er–N(6)	52.5(2)
N(7)–Er–N(9)	52.7(2)	N(1)–Er–N(11)	82.0(2)
N(3)–Er–N(11)	82.0(2)	N(1)–Er–N(10)	99.6(2)
N(3)–Er–N(10)	75.7(2)	N(4)–Er–N(11)	100.1(2)
N(6)–Er–N(11)	76.9(2)	N(4)–Er–N(10)	84.2(2)
N(6)–Er–N(10)	82.5(2)	N(7)–Er–N(11)	133.2(2)
N(9)–Er–N(11)	82.4(2)	N(7)–Er–N(10)	76.3(2)
N(9)–Er–N(10)	127.9(2)	N(10)–Er–N(11)	149.7(2)

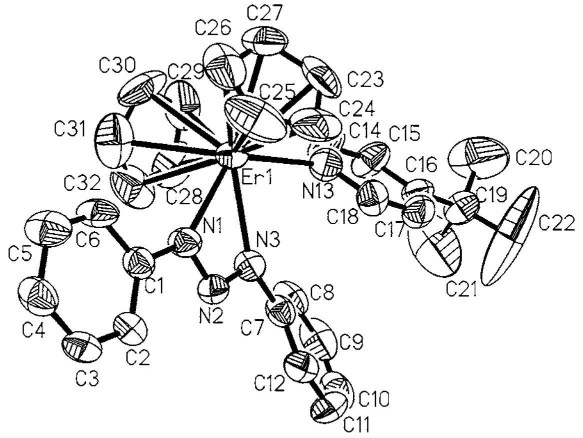


Fig. 1. Perspective view of $(C_5H_5)_2Er(PhNNNPh)(4\text{-}(C(CH_3)_3)\text{-}C_5H_4N)$ (**2**) with thermal ellipsoids at the 50% probability level.

Complex **4** crystallizes as a monomeric complex bearing three bidentate 1,3-diphenyltriazenido ligands and two pyridine ligands. In addition, **4** crystallizes with one pyridine solvate molecule and one-half toluene per erbium atom. The geometry about the erbium atom in **4** can be envisioned as distorted trigonal bipyramidal, if the centers of the 1,3-diphenyltriazenido ligands are considered to be monodentate donors. The 1,3-diphenyltriazenido ligands define the equatorial plane, while the pyridine groups reside in the axial positions. Two of the metallacycles defined by the erbium atom and the N_3-triazenido core are approximately coplanar, while the third metallacycle is approximately perpendic-

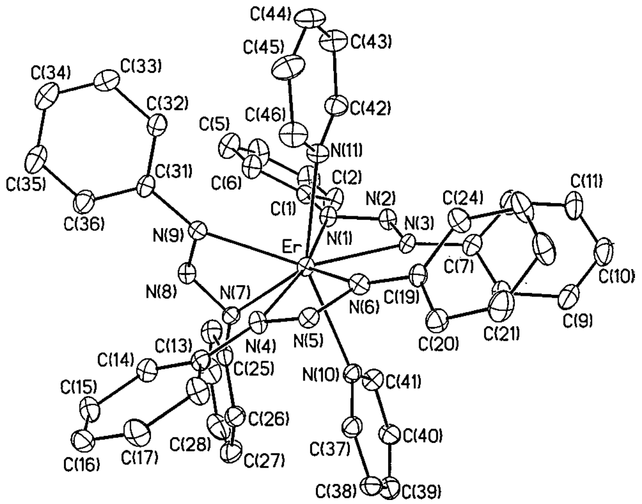


Fig. 2. Perspective view of $Er(PhNNNPh)_3(C_5H_5N)_2(C_5H_5N)_{1.0}\cdot(C_7H_8)_{0.5}$ (**4**) with thermal ellipsoids at the 30% probability level.

ular to the plane formed by the other two metallacycles. The erbium–nitrogen bond lengths associated with the two approximately coplanar 1,3-diphenyltriazenido ligands range between 2.405(6) and 2.429(6) Å, while the values for the 1,3-diphenyltriazenido ligand that is perpendicular to this plane are 2.378(6) and 2.441(6) Å. The large difference in erbium–nitrogen bond lengths associated with the third 1,3-diphenyltriazenido ligand appears to arise from unfavorable steric interactions between the phenyl group bonded to N(9) and the pyridine ligand containing N(11). The erbium–nitrogen bond lengths associated with the pyridine ligands are 2.468(6) and 2.484(6) Å. The nitrogen–erbium–nitrogen angle involving the pyridine ligands is 149.7(2)°.

2.3. Volatility evaluation

Since one of our long-term goals is the preparation of new lanthanide complexes for use as source compounds in CVD processes, the volatility of **2**–**5** was probed. In preparative sublimation experiments, **2**–**5** failed to sublime at temperatures below 250°C at pressures of about 0.1 mmHg. Instead, black residues were obtained, indicating extensive decomposition. Accordingly, **2**–**5** are not suitable precursors for film depositions.

3. Discussion

The syntheses of **2**–**5** deserve special comment. The key innovation that we developed is the use of the monomeric, toluene-soluble adduct **1** to promote cyclopentadienyl ligand protonolysis. Many of the tris(cyclopentadienyl)lanthanide complexes are polymeric by way of intermolecular cyclopentadienyl bridges [12], which leads to insolubility in toluene and other media. As a result of this insolubility, we did not observe any reaction between tris(cyclopentadienyl)erbium or tris(cyclopentadienyl)lutetium at ambient temperature in the absence of a good neutral donor ligand. Apparently, 1,3-diphenyltriazene is not sufficiently basic to break up the polymeric structures of the cyclopentadienyl starting materials. However, treatment of the soluble adduct **1** with one equivalent of 1,3-diphenyltriazene led to the smooth formation of **2** at ambient temperature, while treatment of tris(cyclopentadienyl)lutetium with three equivalents of 1,3-diphenyltriazene and pyridine afforded **4** and **5** upon refluxing in toluene. Presumably, adducts similar to **1** form with tris(cyclopentadienyl)lanthanide that facilitate cyclopentadienyl protonolysis.

The structural features of **2** and **4** can be compared with related erbium complexes that contain cyclopentadienyl ligands and anionic nitrogen donor ligands that are related to 1,3-diphenyltriazenido ligands. In nine-coordinate **2** (considering the cyclopentadienyl ligand as occupying three coordination sites), the erbium–carbon bond lengths ranged between 2.624(12) and 2.668(10) Å with erbium–cyclopentadienyl(centroid) distances of 2.366(10) and 2.380(10) Å, while in ten-coordinate tris(cyclopentadienyl)erbium the erbium–carbon bond lengths were between 2.620(10) and 2.824(8) Å with erbium–cyclopentadienyl(centroid) distances of 2.399, 2.405, and 2.448 Å [12]. The slightly shorter bond lengths in **2** compared with tris(cyclopentadienyl)erbium can be rationalized on the basis of the less crowded metal center in **2**. The erbium–nitrogen distances in **2** and **4** can be compared with the related values in the ytterbium amidinate complex $[p\text{-}MeOC_6H_4C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ [5f], since the sizes of erbium(III) and yttrium(III) ions are very similar. The yttrium–nitrogen bond lengths ranged between 2.325(4) and 2.345(4) Å for the five-coordinate complex. By comparison, the erbium–nitrogen bond lengths associated with the 1,3-diphenyltriazenido ligands ranged between 2.423(6) and 2.447(7) in nine-coordinate **2** and between 2.378(6) and 2.441(6) in eight-coordinate **4**. Clearly, the lanthanide–nitrogen bond lengths in complexes containing 1,3-diaryltriazenido ligands will be strongly affected by the coordination number at the lanthanide center.

The results of the present study demonstrate that 1,3-diphenyltriazenido ligands bond to lanthanide(III) ions in a bidentate fashion, in close analogy with amidinate ligands [1–3]. In particular, the structures of **4** and **5** demonstrate that the 1,3-diphenyltriazenido ligand is sufficiently sterically saturating to promote the formation of monomeric complexes. Accordingly, it is very likely that 1,3-diaryltriazenido ligands will find application as ancillary ligands in lanthanide complexes. It has been established that metal–carbonyl complexes bearing 1,3-diaryltriazenido ligands have slightly higher carbonyl stretches than the analogous complexes bearing amidinate ligands [13]. Accordingly, 1,3-diaryltrizenido ligands are stronger electron-withdrawing ligands than amidinate ligands, and can be expected to confer unique electronic characteristics to the metals to which they are bonded.

The homoleptic complexes **4** and **5** are part of a growing class of lanthanide complexes containing three monoanionic, bidentate nitrogen donor ligands and varying numbers of neutral oxygen or nitrogen donor ligands [1–4,14–16]. Edelmann and co-workers reported the synthesis and structure of $Pr(Me_3SiNC(4\text{-}CH_3OC_6H_4)NSiMe_3)_3$ [5j], which contains three bidentate benzamidinate ligands. The bulky trimethylsilyl substituents on the nitrogen atoms block the coordination of any neutral donor ligands, and the molecule is monomeric and six-coordinate. Accordingly, benzamidinate ligands with silyl substituents on the nitrogen atoms possess a larger steric profile than cyclopentadienyl ligands, since many tris(cyclopentadienyl)-lanthanide complexes are polymeric in the solid state through bridging cyclopentadienyl ligands [11]. Deacon and co-workers described recently a series of lanthanide pyrazolato complexes of the formula $Ln(R_2pz)_3L_2$, where R is an alkyl substituent and L is a neutral oxygen donor ligand [15]. The pyrazolato ligands coordinate in a η^2-fashion, leading to eight-coordinate metal centers. We have found that complexes of the formula $Ln(R_2pz)_3N_2$, where R = *tert–butyl* and N = neutral aromatic nitrogen donor, possess substantially higher thermal stability than the analogous complexes bearing neutral oxygen donors [16] and have described the use of the erbium derivative $Er(tBu_2pz)_3$(4-*tert*-butylpyridine)$_2$ as a source compound for the deposition of erbium-doped GaAs films [4]. The fact that **4** and **5** require two neutral donor ligands to saturate the coordination sphere implies that the steric profile of the 1,3-diphenyltriazenido ligand is similar to that of 3,5-disubstituted η^2-pyrazolato ligands, but is smaller than that of benzamidinate ligands and cyclopentadienyl ligands. Demand for new lanthanide source compounds for use in CVD processes [17] should lead to increasing interest in lanthanide complexes containing all-nitrogen coordination spheres.

The results described herein suggest that complexes containing 1,3-diaryltriazenido ligands do not possess sufficient thermal stability to serve as source compounds in CVD processes, since **2**–**5** decomposed prior to sublimation. Interestingly, tris(cyclopentadienyl)-erbium(III) and tris(cyclopentadienyl)lutetium(III) sublime quantitatively at about 180°C (0.1 mmHg) in our sublimation apparatus. The fact that **2** and **3** decompose under similar conditions suggests that the 1,3-diphenyltriazenido ligand undergoes thermal decomposition at lower temperatures than would be required for vapor transport of **2** and **3**. The decompositions probably involve loss of dinitrogen, which implies that it is the triazenido N_3 core that leads to the low thermal stability. Accordingly, it is likely that substituents on the terminal nitrogen atoms other than phenyl, e.g. alkyl or substituted aryl, would not provide a sufficient increase in thermal stability that would lead to volatile complexes. The search for new ligands for CVD applications should therefore focus on nitrogen donors other than 1,3-disubstituted triazenido ligands.

4. Experimental

4.1. General considerations

All reactions were performed under an atmosphere of argon using Schlenk techniques. Toluene and hexane were distilled from sodium. Pyridine and 4-*tert*-butylpyridine were distilled from calcium hydride. Erbium metal powder (40 mesh) was purchased from Strem Chemicals, Inc. 1,3-Diphenyltriazene was obtained from Aldrich Chemical Co. Tris(cyclopentadienyl)erbium(III) [11], tris(cyclopentadienyl)lutetium(III) [18], and bis(pentafluorophenyl)mercury [19] were synthesized according to literature methods.

^{1}H-NMR and ^{13}C{^{1}H}-NMR were obtained at 300 or 75 MHz in benzene-d_6. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Haake–Buchler HBI digital melting point apparatus and are uncorrected.

4.2. Preparation of tris(cyclopentadienyl)(4-tert-butylpyridine)erbium(III) (1)

A 200-ml Schlenk flask was charged with tris(cyclopentadienyl)erbium (0.200 g, 0.551 mmol), 4-*tert*-butylpyridine (0.0750 g, 0.551 mmol), and toluene (50 ml). The resultant mixture was stirred at ambient temperature for 24 h to give a clear pink solution. The volatile components were removed under reduced pressure and the residue was sublimed (150°C, 0.1 mmHg) to afford pink crystals of **1** (0.551 g, 41%): dec. range 160–170°C; IR (Nujol, cm^{-1}) 3076 (s), 2711 (m), 1770 (w), 1651 (m), 1608 (s), 1541 (m), 1498 (s), 1412 (s), 1274 (m), 1210 (m), 1063 (s), 1011 (vs), 882 (m), 829 (s), 758 (vs), 610 (m).

Anal. Calc. for $C_{24}H_{28}ErN$: C, 57.91; H, 5.67; N, 2.81. Found: C, 57.11; H, 5.49; N, 2.76%.

4.3. Preparation of bis(cyclopentadienyl)(1,3-diphenyltriazenido)(4-tert-butylpyridine)erbium(III) (2)

A 200-ml Schlenk flask was charged with tris(cyclopentadienyl)erbium (0.600 g, 1.65 mmol), 4-*tert*-

butylpyridine (0.338 g, 2.50 mmol), and toluene (50 ml). After all of the solids dissolved (ca. 0.25 h), a solution of 1,3-diphenyltriazene (0.500 g, 2.54 mmol) in toluene (20 ml) was added by cannula to give an orange–red solution. The mixture was then stirred for 24 h at ambient temperature. The resultant solution was filtered through a 2-cm pad of Celite on a coarse glass frit. The filtrate was concentrated to a volume of ca. 40 ml. The flask was stored in a −20°C freezer for 24 h, during which time crystallization proceeded. Removal of the solvent using a cannula, followed by vacuum drying for 1 h, afforded red–brown crystals of **2** (0.755 g, 73%): m.p. 211–213°C; IR (Nujol, cm^{-1}) 3057 (s), 1608 (s), 1589 (s), 1541 (m), 1479 (s), 1412 (s), 1336 (m), 1274 (broad, vs), 1159 (m), 1068 (m), 1011 (s), 901 (m), 839 (m), 782 (broad, vs), 700 (s), 653 (m).

Anal. Calc. for $C_{31}H_{33}ErN_4$: C, 59.21; H, 5.29; N, 8.91. Found: C, 59.10; H, 5.32; N, 9.02%.

4.4. Preparation of bis(cyclopentadienyl)(1,3-diphenyltriazenido)(4-tert-butylpyridine)lutetium(III) (3)

In a fashion similar to the preparation of **2**, tris(cyclopentadienyl)lutetium (0.250 g, 0.676 mmol), 1,3-diphenyltriazene (0.201 g, 1.02 mmol), and 4-*tert*-butylpyridine (0.138 g, 1.02 mmol) were reacted in toluene (70 ml) to afford **3** as an orange–brown solid (0.352 g, 81%): m.p. 193–196°C; IR (Nujol, cm^{-1}) 3009 (m), 1612 (s), 1592 (s), 1481 (s), 1416 (s), 1343 (m), 1275 (broad, vs), 1164 (m), 1068 (m), 1012 (s), 835 (m), 786 (vs), 763 (broad, vs), 700 (s), 656 (m); ^{1}H-NMR (benzene-d_6, δ, 23°C) 8.07 (m, 2 H, 4-*tert*-Bupy C–*H*), 7.36 (m, 2 H, Ph_2N_3 C–*H*), 7.17 (m, 4H, Ph_2N_3 C–*H*), 6.96 (m, 4 H, Ph_2N_3 C–*H*), 6.50 (m, 2 H, 4-*tert*-Bupy C–*H*), 6.03 (s, 10 H, C_5H_5), 0.85 (s, 9 H, 4-*tert*-Bupy, C(C*H*$_3$)$_3$); ^{13}C{^{1}H}-NMR (benzene-d_6, ppm, 23°C) 162.23 (s, 4-*tert*-Bupy *C*–C(CH$_3$)$_3$), 151.26 (s, Ph_2N_3 *C*–N), 150.26 (s, 4-*tert*-Bupy *C*–H), 128.95 (s, Ph_2N_3 *C*–H), 123.48 (s, Ph_2N_3 *C*–H), 121.38 (s, 4-*tert*-Bupy *C*–H), 119.46 (s, Ph_2N_3 *C*–H), 109.51 (s, *C*$_5$H$_5$), 34.59 (s, 4–tert-Bupy *C*(CH$_3$)$_3$), 29.96 (s, 4-*tert*-Bupy C(*C*H$_3$)$_3$).

Anal. Calc. For $C_{31}H_{33}LuN_4$: C, 58.49; H, 5.23; N, 8.80. Found: C, 58.09; H, 5.24; N, 8.90%.

4.5. Preparation of tris(1,3-diphenyltriazenido)bis(pyridine)erbium(III)·(pyridine)$_{1.0}$·(toluene)$_{0.5}$ (4)

A 200-ml Schlenk flask was charged with tris(cyclopentadienyl)erbium (0.200 g, 0.551 mmol), 1,3-diphenyltriazene (0.325 g, 1.65 mmol), pyridine (0.128 g, 1.62 mmol), and toluene (50 ml). The reaction mixture was refluxed for 18 h to give an orange–red solution. After filtration through a 2-cm pad of Celite on a coarse glass frit, the resultant filtrate was layered with ca. 20 ml of hexane. After equilibration for 24 h at ambient temperature, **4** was isolated as a red–brown solid after removing the supernatant solution with a cannula and vacuum drying the crystals for 1 h (0.275 g, 48%): dec. range 115–118°C; IR (Nujol, cm^{-1}) 3045 (m), 1589 (s), 1484 (s), 1442 (s), 1293 (s), 1264 (vs), 1164 (m), 1068 (m), 1035 (m), 896 (m), 758 (s), 691 (s).

Compound **4** was also prepared by charging a 200-ml Schlenk flask with erbium metal (0.619 g, 3.70 mmol), bis(pentafluorophenyl)mercury (1.39 g, 2.60 mmol), 1,3-diphenyltriazene (1.02 g, 5.20 mmol), pyridine (0.276 g, 3.50 mmol), and toluene (50 ml). The reaction mixture was stirred for 120 h to give an orange–red solution with a black precipitate. After filtration through a 2-cm pad of Celite on a coarse glass frit, the resultant clear solution was concentrated under reduced pressure to ca. 30 ml and stored at −20°C for 24 h to afford red–brown crystals of **5** (0.877 g, 49%): dec. range 110–113°C; IR (Nujol, cm^{-1}) 3057 (m), 1589 (s), 1484 (s), 1445 (s), 1297 (s), 1264 (vs), 1159 (m), 1073 (m), 1020 (m), 896 (m), 753 (s), 696, (s).

Anal. Calc. for $C_{46}H_{40}ErN_{11}\cdot(C_5H_5N)_{1.0}\cdot(C_7H_8)_{1.0}$: C, 64.18; H, 4.92; N, 15.49. Found: C, 64.01; H, 5.01; N, 15.12%. Anal. Calc. for $C_{46}H_{40}ErN_{11}\cdot(C_5H_5N)_{1.0}\cdot(C_7H_8)_{0.5}$: C, 62.98; H, 4.75; N, 16.17%.

4.6. Preparation of tris(1,3-diphenyltriazenido)-bis(pyridine)lutetium(III) (5)

In a similar fashion to the preparation of **4**, tris(cyclopentadienyl)lutetium (0.200 g, 0.541 mmol), 1,3-diphenyltriazene (0.319 g, 1.62 mmol), pyridine (0.128 g, 1.62 mmol), and toluene (50 ml) were reacted to afford brown crystals of **5** (0.315 g, 63%): dec. range 112–119°C; IR (Nujol cm^{-1}) 3048 (m), 1579 (m), 1479 (s), 1345 (m), 1326 (m), 1293 (s), 1264 (vs), 1231 (s), 1164 (m), 1063 (m), 1040 (m), 753 (s), 691 (s); ^{1}H-NMR (benzene-d_6, δ, 23°C) 8.67 (m, 4 H, py C–*H*), 7.33 (m, 6 H, Ph_2N_3 C–*H*), 7.02 (m, 12 H, Ph_2N_3 C–*H*), 6.83 (m, 12 H, Ph_2N_3 C–*H*), 6.63 (m, 2 H, py C–*H*), 6.27 (m, 4 H, py C–*H*); ^{13}C{^{1}H}-NMR (benzene-d_6, ppm, 23°C) 150.49 (s, Ph_2N_3 *C*–N), 149.53 (s, py *C*–H), 137.75 (s, py *C*–H), 128.94 (s, Ph_2N_3 *C*–H), 124.51 (s, Py *C*–H), 123.97 (s, Ph_2N_3 *C*–H), 119.83 (s, Ph_2N_3 *C*–H).

Anal. Calc. for $C_{46}H_{40}LuN_{11}$: C, 59.93; H, 4.37; N, 16.71. Found: C, 59.39; H, 4.49; N, 16.41%.

*4.7. X-ray crystallographic structure determinations of **2** and **4***

A yellow flat rod of **2** was sealed in a thin-walled glass capillary tube under a nitrogen atmosphere. The crystal was mounted on a Siemens/Bruker P4/CCD diffractometer equipped with monochromated Mo–K$_\alpha$ radiation and the manufacturer's SMART collection software and SAINT processing software. A hemisphere of data was collected at 10 s per frame with 0.3° between each frame. A total of 15 512 reflections were integrated from the 1390 frames collected. Absorption corrections were applied with the manufacturer's program XPREP and 11 066 reflections were obtained after averaging ($R_{\text{int}} = 0.097$). The structure was solved and refined on F^2 with the programs of SHELXS and SHELXL-93 [20]. Hydrogen atoms were placed in calculated positions. All non-hydrogen atoms were described anisotropically. The asymmetric unit contains two neutral erbium complexes. All atoms occupy general positions in the cell. The *tert*-butyl groups on the 4-*tert*-butylpyridine ligands were severely disordered.

A suitable crystal of **4** was sealed in a thin-walled glass capillary tube under a nitrogen atmosphere. No evidence of symmetry higher than triclinic was observed in the diffraction data. The centrosymmetric space group option $P\bar{1}$ was chosen, which yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix, least-squares procedures. The asymmetric unit contains one erbium complex, a pyridine molecule, and half of a toluene molecule that is disordered over an inversion center. Pyridine is also disordered over two positions and the nitrogen atom cannot be distinguished from the carbon atoms. All pyridine ring atoms were refined as carbon atoms and the rings were refined as rigid planar bodies. All non-hydrogen atoms were refined with anisotropic displacement parameters, except for the carbon atoms of the pyridine solvate molecule. The hydrogen atoms on the solvate molecules were ignored due to the disorder and all other hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.03) program library [21].

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 118422 (**2**) and 118421 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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