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Mono-cyclopentadienyl complexes of lanthanum: synthesis and characterization of anilido derivatives

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Abstract

Use of the bulky cyclopentadienyl ligand $[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]^-$ (Cp‴) allows for the isolation of monomeric, mono-ring lanthanide species. As previously reported, (Cp‴)K reacts with $LaI_3(THF)_4$ (THF = tetrahydrofuran) in THF/pyridine to form the mono-ring complex (Cp‴)$LaI_2(py)_3$ (**1**) (py = pyridine); a minor product of this reaction is the bis-ring species (Cp‴)$_2$LaI(py) (**2**). The solid state structure of **2** reveals a monomeric compound containing a pseudo-tetrahedral metal center exhibiting no unusual intramolecular contacts. Addition of one equiv of KNHAr (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) to complex **1** in THF generates the mono-anilido compound (Cp‴)LaI(NHAr)(THF)$_2$ (**3**), which may be converted to the more stable pyridine adduct (Cp‴)LaI(NHAr)(py)$_2$ (**4**) by the addition of pyridine to **3**. An X-ray crystal structure of **3** indicated a trigonal bipyramidal metal center with the anilido group oriented *trans* to the iodide atom (N1–La1–I1 = 123.1(3)°). A structural study on the bis-pyridine adduct **4** revealed a similar C_s-symmetric structure with a slightly increased $N_{anilido}$–La–I angle of 132.1(2)°. Addition of KNHAr to the di-iodo bipyridine adduct (Cp‴)LaI_2(bipy)(py) (**5**), in which the two iodide atoms are *cis*-disposed, yields the mono-anilido complex (Cp‴)LaI(NHAr)(bipy)(py) (**6**) (bipy = 2,2′-bipyridine); this compound may also be prepared by the addition of bipy to (Cp‴)LaI(NHAr)(py)$_2$ (**4**). An X-ray diffraction study shows that the lanthanum center in **6** is octahedrally coordinated by a Cp‴ ring, an iodide, an anilido group, a pyridine molecule and two nitrogens of a bipy molecule. In this case, the anilido moiety and the iodide ligand are arranged in a *cis* fashion ($N_{anilido}$–La–I = 111.2(2)°), resulting in a complex with C_1 symmetry. Both (Cp‴)LaI(NHAr)(py)$_2$ (**4**) and (Cp‴)LaI(NHAr)(bipy)(py) (**6**) are inactive as catalysts for the hydroamination/cyclization of 2-amino-hex-5-ene.

Keywords: Lanthanum; Bulky cyclopentadienyl; Anilido

1. Introduction

The recent renaissance of organolanthanide chemistry may be directly attributed to the ability of many lanthanide complexes to catalyze organic reactions [1–3]. Metallocene based derivatives have been shown to be effective catalysts for ethylene polymerization, hydrogenation, hydroboration and hydrosilylation. One of the most well studied reactions is the intramolecular hydroamination of alkenes and alkynes to form nitrogen-containing heterocycles [4], which are of interest in natural products synthesis [5,6] and the pharmaceutical industry [7]. Early work by Marks et al. demonstrated that high degrees of stereoselectivity were possible by utilizing asymmetric catalysts incorporating chiral ancillary ligands; however, the organolanthanide complexes often required lengthy and involved syntheses [8–11]. Additionally, epimerization of C_1-symmetric lanthanide-based systems was often observed in the presence of donor molecules, contributing to lowered enantioselectivities. More recently, Livinghouse and coworkers have revealed that non-cyclopentadienyl based systems such as C_2-symmetric bis-amides [12] and chelating bis-thiophosphinic amidates [13] result in improved stereoselectivities and substantially increased catalytic activities, suggesting that complicated multistep syntheses and separation of chiral ligand systems are

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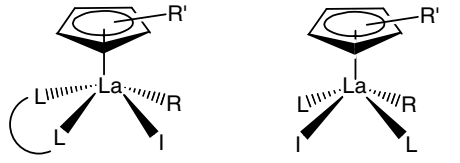
not necessary. Similarly promising results have been communicated for lanthanide systems bearing polydentate Schiff base ligands such as salicylaldimine [14], and this chemistry has recently been extended to include the binaphthyl diamine [15], biphenolate and binaphtholate families [16]. In fact, the cyclization efficiency of many amino-olefins in the presence of the simple tris-amide $Ln[N(SiMe_3)_2]_3$ (Ln = lanthanide) is directly comparable to cyclizations conducted under identical conditions using yttrocene catalysts [17].

We have been interested in the synthesis of lanthanide species complexed by a single bulky cyclopentadienyl ring [18], reasoning that much useful chemistry may have been overlooked by concentrating on the bis-cyclopentadienyl derivatives, $Cp^{\#}_2LnX$ ($Cp^{\#}$ = substituted cyclopentadienyl; X = halide, alkyl, hydride, etc.). In the course of our studies, we realized that simple chiral organolanthanide compounds (**A**) could be readily synthesized by the addition of a bidentate chelating ligand such as 2,2′-bipyridine to a C_s-symmetric precursor such as $Cp^{\#}LnIR(L)_2$ (**B**) (R = anilido; L = Lewis base). In this manner, chiral species could be obtained without the need for synthesizing chiral auxillary ligands and subsequent separation of enantiomers by derivitization and/or chiral chromatography. Here we report the synthesis of new mono-ring organolanthanide species and discuss the possible implications on enantioselective hydroamination.



A **B**

2. Results and discussion

2.1. Synthesis and characterization of $(Cp'''_2LaI(py)$ (2)

We previously reported the synthesis of the mono-ring compound $(Cp''')LaI_2(py)_3$ (**1**) from the reaction of $Cp'''K$ with $LaI_3(THF)_4$ in THF, followed by the addition of pyridine [19]. We have recently discovered that the bis-ring complex $(Cp'''_2LaI(py)$ (**2**) is also formed in this reaction, albeit in low yield (Eq. (1)). Compounds **1** and **2** are easily separated due to their differing solubilities in common organic solvents.

$$LaI_3(THF)_4 + Cp'''K \xrightarrow[-KI]{THF/py} \underset{\mathbf{1}}{(Cp''')LaI_2(py)_3} + \underset{\mathbf{2}}{(Cp''')_2LaI(py)} \quad (1)$$

74% 5%

Complex **2** is soluble in pentane and diethyl ether, in contrast to the mono-ring compound **1**, which is insoluble in these solvents. The ^1H NMR spectrum of **2** in d^5-pyridine is similar to that of complex **1** in the same solvent, with a single peak arising from the four equivalent CpH protons and two singlets in a 2:1 ratio as a result of the $SiMe_3$ groups. The bis-ring compound **2** likely arises from a small excess of $Cp'''K$ used in the reaction. Thermolysis of a d^5-pyridine solution of $(Cp''')LaI_2(py)_3$ (**1**) (80 °C, 48 h) does not result in the formation of **2**, suggesting that the steric bulk of the $C_5H_2(SiMe_3)_3$ ligands is enough to discourage redistribution reactions to form bis-ring and unsubstituted products, although it is possible that such reactions could occur in more weakly coordinating solvents such as THF.

2.1.1. Solid state and molecular structure of $(Cp'''_2LaI$ (py) (2)

Single crystals of **2** that were suitable for an X-ray diffraction study were grown by slow evaporation of a saturated hexanes solution. Selected bond lengths and angles are presented in Table 1. A thermal ellipsoid plot giving the atom-numbering scheme used in the tables is shown in Fig. 1; complete details of the structural analyses of compounds **2**, **3**, **4** and **6** are listed in Table 3. The molecule is monomeric in the solid state, with the La(III) ion coordinated by two $C_5H_2(SiMe_3)_3$ ligands, a single

Table 1
Selected bond distances (Å) and angles (°) for $(Cp'''_2LaI(py)$ (**2**)

La1–Cp1	2.579	La1–Cp2	2.573
La1–N1	2.643(4)	La1–I1	3.1272(9)
Cp1–La1–N1	100.28	Cp1–La1–I1	110.51
Cp1–La1–Cp2	134.37	N1–La1–I1	94.79(11)
N1–La1–Cp2	108.53	I1–La1–Cp2	101.62

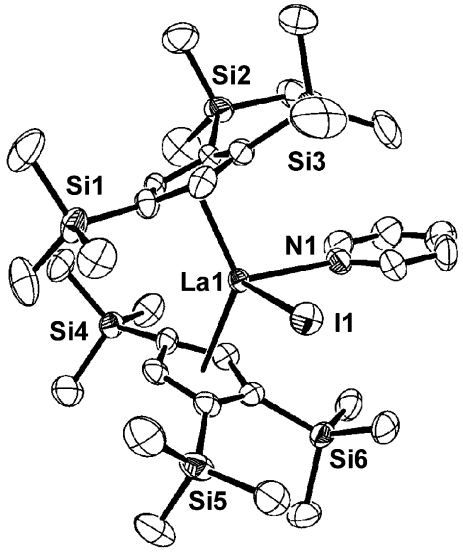


Fig. 1. Thermal ellipsoid view of $(Cp'''_2LaI(py)$ (**2**) drawn with 30% probability ellipsoids.

Table 2
Selected bond distances (Å) and angles (°) for $(Cp''')LaI(NHAr)(THF)_2$ (**3**), $(Cp''')LaI(NHAr)(py)_2$ (**4**) and $(Cp''')LaI(NHAr)(bipy)(py)$ (**6**)

	3	4	6
La1–Cp1	2.596	2.577	2.612
La1–I1	3.1628(18)	3.1980(14)	3.2219(13)
La1–N1	2.324(12)	2.351(10)	2.397(9)
La1–N2	–	2.694(9)	2.712(10)
La1–N3	–	2.721(9)	2.701(10)
La1–N4	–	–	2.777(10)
La1–O1	2.544(11)	–	–
La1–O2	2.575(11)	–	–
Cp1–La1–I1	113.95	120.37	107.88
Cp1–La1–N1	122.47	107.37	104.63
Cp1–La1–N2	–	110.11	98.43
Cp1–La1–N3	–	104.17	99.46
Cp1–La1–N4	–	–	167.66
Cp1–La1–O1	100.59	–	–
Cp1–La1–O2	101.95	–	–
I1–La1–N1	123.1(3)	132.1(2)	111.1(2)
I1–La1–N2	–	83.6(2)	90.3(2)
I1–La1–N3	–	80.6(2)	137.9(2)
I1–La1–N4	–	–	77.3(2)
I1–La1–O1	84.2(3)	–	–
I1–La1–O2	86.5(3)	–	–
N1–La1–N2	–	84.1(3)	145.3(3)
N1–La1–N3	–	84.2(3)	88.1(3)
N1–La1–N4	–	–	87.8(3)
N1–La1–O1	85.3(4)	–	–
N1–La1–O2	83.6(4)	–	–
N2–La1–N3	–	145.6(3)	58.9(3)
N2–La1–N4	–	–	70.0(3)
N3–La1–N4	–	–	66.0(3)
O1–La1–O2	158.4(3)	–	–

iodide ion and a pyridine molecule. The geometry about the lanthanum center is best described as pseudo-tetrahedral, with the largest distortion from idealized geometry found between the two bulky $C_5H_2(SiMe_3)_3$ ligands (Cp1–La1–Cp2 = 134.37°). As found in the less sterically hindered mono-ring derivative, the $SiMe_3$ groups in **2** are bent back approximately 14° from the plane of the cyclopentadienyl ring. The La–I bond length of 3.1272(9) Å is slightly shorter than those found for complex **1** (3.1934(15) and 3.2289(14) Å) [19] as well as other mono-ring lanthanum di-iodide complexes (3.1974(4) and 3.2287(4) Å for $(\eta^5{:}\eta^1{:}\eta^1C_5H_3(CH_2CH_2NMe_2)_2$-1,2)-$LaI_2(THF)$; 3.1696(4) and 3.2681(4) Å for $(\eta^5{:}\eta^1{:}\eta^1$-$C_5H_3(CH_2CH_2NMe_2)_2$-1,3)$LaI_2(THF)$) [20]. The La–C and La–N distances are unremarkable and are similar to those ascribed to other similar complexes.

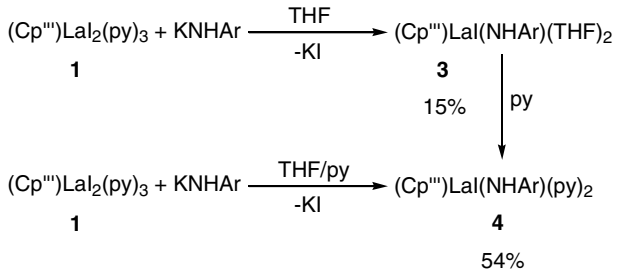
2.2. Synthesis and characterization of $(Cp''')LaI(NHAr)(THF)_2$ (3) and $(Cp''')LaI(NHAr)(py)_2$ (4)

The addition of one equiv of KNHAr (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) to a THF solution of $(Cp''')LaI_2(py)_3$ (**1**) produces the mono-anilido complex $(Cp''')LaI(NHAr)(THF)_2$ (**3**) as a light yellow solid in low yield (Scheme 1). Compound **3** is soluble in toluene, producing an effective avenue for separating the mono anilido complex from unreacted di-iodo species **1**, which is toluene insoluble. We [19,21] and others [20,22,23] have previously shown that reacting potassium salts with iodo lanthanide species is a facile method for the sequential introduction

Table 3
Crystallographic data

Compound	2	3	4	6
Formula	$C_{33}H_{63}ILaNSi_6$	$C_{34}H_{63}ILaNO_2Si_3$	$C_{36}H_{57}ILaN_3Si_3$	$C_{41}H_{60}ILaN_4Si_3$
Molecular weight	908.18	867.94	881.92	959.01
Temperature (K)	203(2)	203(2)	203(2)	203(2)
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
Crystal size (mm)	0.40 × 0.30 × 0.20	0.40 × 0.36 × 0.30	0.45 × 0.22 × 0.20	0.30 × 0.22 × 0.16
a (Å)	10.527(3)	15.006(6)	10.188(4)	11.337(3)
b (Å)	13.180(4)	15.006(6)	19.174(8)	22.703(8)
c (Å)	17.667(5)	38.061(17)	24.476(11)	17.694(6)
α (°)	94.223(7)	90	90	90
β (°)	101.430(6)	90	100.762(9)	92.801(7)
γ (°)	107.708(5)	90	90	90
V (Å^3)	2265.2(12)	8570(6)	4697(3)	4549(3)
Z	2	8	4	4
D_{calc} (g/mL)	1.332	1.345	1.247	1.400
Absorption coefficient (mm^{-1})	1.804	1.827	1.666	1.728
$F(000)$	924	3536	1784	1944
Θ range (°)	1.64–27.87	1.07–23.27	1.36–22.46	1.46–22.46
Total reflections	16,072	45,329	22,098	22,994
Independent reflections	8770	12130	5614	5886
GOF	1.100	1.775	3.726	1.408
$R1$	0.0489	0.0586	0.0771	0.1118
$wR2$	0.1053	0.1623	0.1670	0.1238

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_{2w} = [\sum[\omega(F_o^2 - F_c^2)^2] / \sum[\omega(F_o^2)^2]]^{1/2}$; $\omega = 1/[\sigma^2(F_o^2) + (aP)^2]$, where $a = 0.0394, 0.0711, 0.027$ and 0.0315.



Scheme 1.

of ligands of interest without unwanted redistribution reactions. In this case, there is no evidence for the formation of the bis-anilido or bis-ring species, $(Cp''')La(NHAr)_2$ or $(Cp''')_2La(NHAr)$. This synthetic method also circumvents the formation of salt or "ate" complexes, which is a pervasive problem in f-element chemistry [24–34].

The formulation of **3** with two molecules of coordinated THF was based on the X-ray crystal structure determination (see later); ^1H NMR spectroscopy was consistent with less than two molecules per metal center. We were unable to obtain a suitable microanalysis for this compound, which we ascribe to the extreme sensitivity of this material. As reported for the parent di-iodo species [19], a more stable, higher yielding derivative was obtained by synthesizing the pyridine analog. If the metathesis reaction to form the mono-anilido derivative was performed in the presence of pyridine, the thermally stable, less fluxional bis-pyridine adduct $(Cp''')LaI(NHAr)(py)_2$ (**4**) was isolated in moderate yield. Compound **4** may also be formed by the addition of pyridine to a toluene solution of **3**; the pyridine adduct **4** is isolable as golden yellow needles following evaporation of a saturated hexanes solution. The ^1H NMR spectra of **3** and **4** were consistent with the presence of one anilido group per metal center; additionally, the thermal stability of the pyridine adduct **4** was reflected in the satisfactory microanalysis obtained for this compound.

2.2.1. Solid state and molecular structures of $(Cp''')LaI(NHAr)(THF)_2$ (3) and $(Cp''')LaI(NHAr)(py)_2$ (4)

Colorless crystals of **3** that were amenable to X-ray diffraction studies were grown by slow evaporation of a saturated toluene solution. The solid state molecular structure of **3** is presented in Fig. 2. A comparative listing of relevant bond lengths and angles for the anilido derivatives **3**, **4** and **6** is available in Table 2. The lanthanum metal center is best described as trigonal bipyramidal, with the oxygen atoms of the THF donors occupying axial sites. The Cp ring centroid, N1 and I1 reside in the equatorial plane, with all of the angles anchored by the lanthanum center being close to

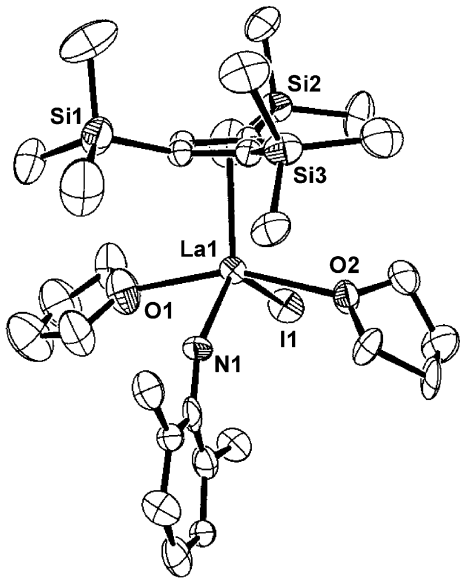


Fig. 2. Thermal ellipsoid view of $(Cp''')LaI(NHAr)(THF)_2$ (**3**) drawn with 30% probability ellipsoids. Isopropyl methyl groups omitted for clarity.

the expected 120°. Due to the steric bulk of the $C_5H_2(SiMe_3)_3$ ligand, the O1–La1–O2 angle deviates from ideal (158.4(4)°). An additional indication of the extent of steric crowding around the metal center is the bending back of the $SiMe_3$ groups from the plane of the Cp ring (~15°). This has been a common feature of all of the mono-ring La complexes we have investigated. Overall, the molecule has C_s symmetry, with a mirror plane containing La1, I1, N1 and the cyclopentadienyl centroid. The La1–I1 distance of 3.1628(18) Å is intermediate between those determined for complexes **1** and **2** and is similar to La–I parameters reported for related cyclopentadienyl-supported compounds. The $La–N_{anilido}$ bond length of 2.324(12) Å may be compared with values of 2.347(4) and 2.360(3) Å for the terminal metal–anilido linkages in dimeric $La_2(NHAr)_6$ and are in agreement with those found in the monomeric base adducts $La(NHAr)_3(THF)_3$ and $La(NHAr)_3(py)_2$ (2.360(3)–2.434(3) Å) [35]. The La–O(THF) distances do not differ greatly from those observed in $La(O\text{-}2,6\text{-}^iPr_2C_6H_3)_3(THF)_2$ (2.52(1) Å ave) [36] as well as other THF adducts of La such as $La(\eta^5\text{-}C_5Me_5)[CH(SiMe_3)_2]_2(THF)$ (2.547(6) Å) [37], $La(\eta^5\text{-}C_5H_5)_3(THF)$ (2.57(1) Å) [38], $(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_3(CH_2\text{-}CH_2NMe_2)_2\text{-}1,2)LaI_2(THF)$ (2.558(3) Å) [20] and $(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5H_3(CH_2CH_2NMe_2)_2\text{-}1,3)LaI_2(THF)$ (2.593(3) Å) [20]. The distances between the metal center and the carbon atoms of the Cp ring are within the expected range for such compounds.

Crystals of **4** were obtained by the slow evaporation of a concentrated hexanes solution. The molecular structure is depicted in Fig. 3 and a partial list of bond

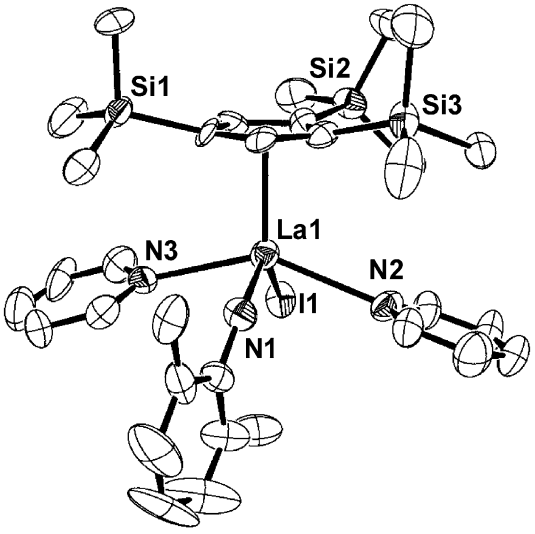
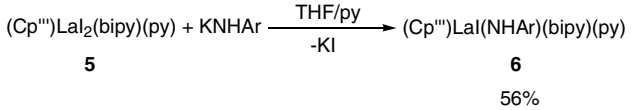


Fig. 3. Thermal ellipsoid view of (Cp‴)LaI(NHAr)(py)$_2$ (**4**) drawn with 30% probability ellipsoids. Isopropyl methyl groups omitted for clarity.

lengths and angles can be found in Table 2. The overall structural features of **4** are the same as those determined for **3**, although the slightly more rigid pyridine donors result in a more distorted coordination sphere (N1–La1–N2 = 145.6(3)°). The bond lengths and angles in **4** are not dissimilar to those established for **3** and will not be discussed in detail aside from the La–$N_{pyridine}$ distances (2.694(9) and 2.721(9) Å), which compare favorably with those in (Cp‴)$LaI_2(py)_3$ (**1**) [19], (Cp‴)$_2$LaI(py) (**2**) and La(NHAr)$_3$(py)$_2$ [35].

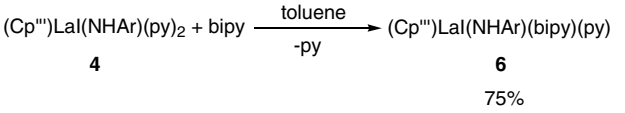
2.3. Synthesis and characterization of (Cp‴)LaI(NHAr)(bipy)(py) (6)

We and others have previously reported that the stereochemistry of mono-ring lanthanide complexes may be controlled by the addition of a bidentate Lewis base such as 1,2-dimethoxyethane [39] or 2,2′-bipyridine [19]. We reasoned that the relative orientation of the iodide and anilido groups may be important in catalytic processes such as intramolecular hydroamination/cyclization reactions, where the catalyst structure plays an important role in determining the stereochemistry of the organic product. Thus, addition of KNHAr to a THF solution of (Cp‴)LaI_2(bipy)(py) (**5**), in which the two iodide atoms are *cis*-disposed, yields the mono-anilido complex (Cp‴)LaI(NHAr)(bipy)(py) (**6**) as an orange solid in moderate yield (Eq. (2))



(2)

Compound **6** is soluble in diethyl ether and common organic solvents such as benzene and toluene. Alternately, **6** may be synthesized by the addition of a toluene solution of 2,2′-bipyridine to a toluene solution of the bis-pyridine adduct (Cp‴)LaI(NHAr)(py)$_2$ (**4**) (Eq. (3))



(3)

The ^{1}H NMR spectrum of **6** in d^5-pyridine confirms the presence of a single bipyridine molecule per lanthanum center, although NMR spectroscopy was not helpful in determining the stereochemistry of the product. In order to establish the configuration of **6**, we turned to X-ray crystallography.

2.3.1. Solid State and Molecular Structure of (Cp‴)LaI(NHAr)(bipy)(py) (6)

X-ray quality crystals of **6** were collected after cooling a concentrated diethyl ether solution to –30 °C. The solid state structure is available in Fig. 4; selected bond lengths and angles are presented in Table 2. Compound **6** exhibits a distorted octahedral geometry, with the cyclopentadienyl centroid and the nitrogen atom of the pyridine molecule occupying axial positions (Cp1–La1–N4 = 167.66°). The iodide ligand resides significantly below the equatorial plane, likely a result of the steric bulk of the iodide, anilido and bipyridine units, as well as an attempt to alleviate any interaction with the $SiMe_3$ groups of the cyclopentadienyl ring. The crowding of the coordination sphere is also evidenced by the La1–I1

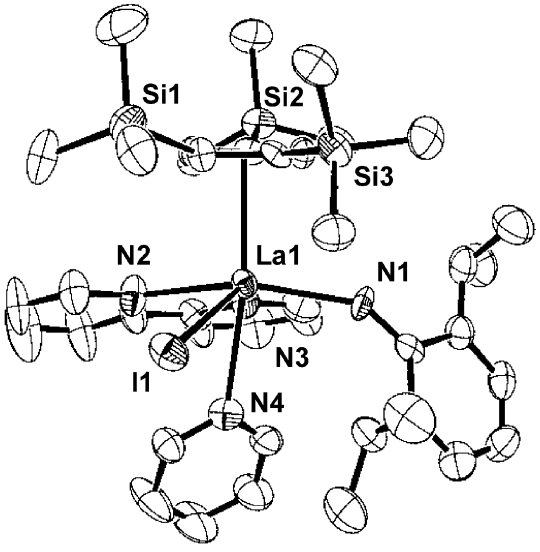


Fig. 4. Thermal ellipsoid view of (Cp‴)LaI(NHAr)(bipy)(py) (**6**) drawn with 30% probability ellipsoids.

bond length of 3.2219(13) Å, which is longer than the equivalent bonds in **2**, **3** and **4**. A slight lengthening of the La–$N_{anilido}$ bond is also observed. The presence of a chelating bipyridine molecule also serves to force the iodide and anilido moieties into closer proximity. In the di-iodo species **1** and **5**, the addition of 2,2′-bipyridine results in a reduction of the I1–La1–I2 angle from 153.90(3)° in **1** to 99.53(4)° in **5**, a change of ~55° [19]. Although the analogous change in I1–La1–$N_{anilido}$ bond angle between the bis-pyridine adduct **4** and the bipyridine adduct **6** is less pronounced (132.1(2)° in **4**, 111.2(2)° in **6**), more important is the formation of a chiral metal center in complex **6** upon the addition of a simple bidentate ligand to **4**.

3. Conclusions

We have shown that mono-cyclopentadienyl complexes of lanthanum are readily accessible via simple, high-yielding reactions, and the relative orientation of the iodide and anilido groups is easily controlled by the appropriate choice of Lewis base, allowing for the isolation of both achiral C_2-symmetric and chiral C_1-symmetric species. All anilido derivatives presented here are inactive for the hydroamination/cyclization of 2-amino-hex-5-ene, which is predicted based on the relative pK_a's of the parent amines ($HN(SiMe_3)_2 > 2$-amino-hex-5-ene $\gg$ 2,6-di-iso-propyl-aniline). Our initial selection of the [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]$^-$ ligand system for this chemistry was based on the ability of bulky cyclopentadienyl ligands to stabilize mono-ring lanthanide complexes, and limit redistribution reactions to generate the more common bis-cyclopentadienyl compounds. Additionally, the presence of three trimethylsilyl groups on the cyclopentadienyl ring increased solubility and provided a convenient NMR handle. From a retrosynthetic perspective, a more suitable target complex for the hydroamination/cyclization of amino-olefins would be the bis(trimethylsilyl)amido species, (Cp‴)LaI- ($N(SiMe_3)_2$)$(py)_2$ and (Cp‴)LaI($N(SiMe_3)_2$)(bipy)(py). However, these compounds have proven to be too soluble to isolate as discrete species, and structural information has not been forthcoming due to their extreme solubility even in aliphatic solvents at –40 °C. In order to investigate the catalytic potential of mono-ring lanthanide species, the [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]$^-$ ligand will have to be replaced with a comparably bulky, but less soluble derivative, such as the fluorenyl or indenyl group. This study has revealed a general approach to the synthesis of mono-cyclopentadienyl, mono-anilido lanthanide species; modification of the complexes with related bulky cyclopentadienyl-based ligands should allow for the generation of viable catalysts for the hydroamination/cyclization of a variety of amino-olefins.

4. Experimental

4.1. General considerations

All manipulations were carried out under an inert atmosphere of oxygen-free UHP grade argon using standard Schlenk techniques or under oxygen-free helium in a Vacuum Atmospheres glovebox. 2,2′-Bipyridine was purchased from Aldrich and used as received. Pyridine was purchased from Aldrich and distilled over sodium benzophenone prior to use. [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]K [40,41], $LaI_3(THF)_4$ [21], KNHAr [42], (Cp‴)$LaI_2(py)_3$ (**1**) [19], (Cp‴)LaI_2(bipy)(py) (**5**) [19] and 2-amino-hex-5-ene (**7**) [43,44] were prepared according to literature procedures. Hexanes, toluene, tetrahydrofuran and diethyl ether were de-oxygenated by passage through a column of supported copper redox catalyst (Cu-0226 S) and dried by passing through a second column of activated alumina [45]. d^8-THF and d^5-pyridine were distilled over sodium benzophenone and degassed prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AMX 300 spectrometer at ambient temperature unless otherwise noted. ^1H chemical shifts are given relative to residual C_4D_7HO ($\delta = 3.58$ ppm) or C_5D_4HN ($\delta = 8.74$ ppm). ^{13}C chemical shifts are given relative to C_4D_8O ($\delta = 67.57$ ppm) or C_5D_5N ($\delta = 150.35$ ppm). Infrared spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer as Nujol mulls between KBr plates. Elemental analyses were performed by the Micro-Mass Facility at the University of California, Berkeley.

4.2. (Cp‴)$_2$LaI(py) (2)

An orange THF solution of [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]K (1.00 g, 3.12 mmol) was added dropwise to a solution of $LaI_3(THF)_4$ (2.50 g, 3.10 mmol) in THF, forming an orange/brown slurry. This was stirred at room temperature overnight. The reaction mixture was then filtered through a frit lined with Celite to remove insoluble KI, yielding an orange solution. The solvent was removed under vacuum and the off-white residue dissolved in toluene. Approximately 1 mL pyridine was added and the slightly cloudy orange solution was stirred for 1 h. The solution was filtered through a frit lined with Celite, and the toluene removed under vacuum. The solid was washed with hexanes to yield (Cp‴)$LaI_2(py)_3$ (**1**) as an off-white solid. The hexanes washings were combined and left to evaporate to give **2** as colorless plates (140 mg, 5% yield). ^1H NMR (d^5-pyridine): δ 8.74 (m, *o*-pyridine), 7.58 (m, *p*-pyridine), 7.30 (s, 4H, Cp*H*), 7.22 (m, *m*-pyridine), 0.46 (s, 18H, Si*Me*$_3$), 0.39 (s, 36H, Si*Me*$_3$). $^{13}C\{^1H\}$NMR (d^5-pyridine): δ 145.47 (Cp‴), 138.78 (Cp‴), 129.12 (Cp‴), 3.24 (Si*Me*$_3$), 2.52 (Si*Me*$_3$) (pyridine peaks obscured by sol-

vent resonances). IR (Nujol, cm^{-1}): 1340 (sh), 1304 (m), 1250 (m), 1220 (m), 1170 (m), 1150 (s), 1090 (m), 1073 (m), 1037 (s), 1005 (s), 992 (m), 967 (w), 933 (m), 891 (m), 842 (s), 753 (m), 723 (s), 623 (w). Anal. Calc. for $C_{33}H_{63}ILaNSi_6$: C, 43.64; H, 6.99; N, 1.54. Found: C, 42.73; H, 7.23; N, 1.58.

4.3. (Cp‴)LaI(NHAr)(THF)$_2$ (3)

Solid [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]K (320 mg, 1.00 mmol) was added to a solution of $LaI_3(THF)_4$ (810 mg, 1.00 mmol) in THF, forming an orange/brown slurry. After stirring overnight, a THF solution of KNHAr was added (215 mg, 1.00 mol). The reaction mixture was then stirred overnight and filtered through a frit lined with Celite to remove insoluble KI. The THF was removed under vacuum and the solid extracted with a minimum of toluene and filtered. The yellow toluene solution was left to evaporate, resulting in large colorless blocks (130 mg, 15% yield). ^{1}H NMR (d^8-THF): δ 6.98 (s, 2H, Cp*H*), 6.79 (d, $^3J_{H-H} = 7.5$ Hz, 2H, *m*-H), 6.36 (t, $^3J_{H-H} = 7.5$ Hz, 1H, *p*-H), 5.27 (s, 1H, N*H*), 3.62 (br m, α-THF), 2.80 (sept, $^3J_{H-H} = 7.2$ Hz, 2H, C*H*Me$_2$), 1.77 (br m, β-THF), 1.17 (d, $^3J_{H-H} = 7.2$ Hz, 12H, CH*Me*$_2$), 0.38 (s, 18H, Si*Me*$_3$), 0.34 (s, 9H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (d^8-THF): δ 152.81 (NH*Ar*), 136.63 (NH*Ar*), 136.12 (Cp‴), 133.73 (NH*Ar*), 129.81 (Cp‴), 129.04 (Cp‴), 123.52 (NH*Ar*), 68.38 (α-THF), 31.04 (*C*HMe$_2$), 26.52 (β-THF), 24.63 (CH*Me*$_2$), 2.68 (Si*Me*$_3$), 1.33 (Si*Me*$_3$). IR (Nujol, cm^{-1}): 3177 (w), 1597 (w), 1305 (w), 1248 (m), 1168 (w), 1018 (m), 890 (m), 837 (m), 722 (m). We were unable to obtain a suitable microanalysis for this compound.

4.4. (Cp‴)LaI(NHAr)(py)$_2$ (4)

To a THF solution of **1** (1.50 g, 1.70 mmol) was added a solution of KNHAr (350 mg, 1.70 mmol) in THF, forming a yellow/orange slurry. The reaction mixture was then stirred overnight and filtered through a frit lined with Celite to remove insoluble KI. The THF was removed under vacuum and the solid dissolved in toluene. Approximately 1 mL of pyridine was added, and the reaction mixture stirred for 1 h, after which time the slightly cloudy solution was filtered through a frit lined with Celite. The solvent was then removed under vacuum, and the yellow solid was extracted with hexanes. The remaining insolubles were filtered off, and the bright yellow hexanes solution left to evaporate, yielding **4** as bright yellow needles (810 mg, 54% yield). ^{1}H NMR (d^5-pyridine): δ 8.74 (m, *o*-pyridine), 7.58 (m, *p*-pyridine), 7.37 (s, 2H, Cp*H*), 7.22 (m, *m*-pyridine), 7.11 (d, $^3J_{H-H} = 7.5$ Hz, 2H, *m*-H), 6.78 (t, $^3J_{H-H} = 7.5$ Hz, 1H, *p*-H), 6.40 (s, 1H, N*H*), 3.09 (sept, $^3J_{H-H} = 7.2$ Hz, 2H, C*H*Me$_2$), 1.22 (d, $^3J_{H-H} = 7.2$ Hz, 12H, CH*Me*$_2$), 0.37 (s, 18H, Si*Me*$_3$), 0.34 (s, 9H, Si*Me*$_3$). ^{13}C{^{1}H}NMR (d^5-pyridine): δ 152.83 (NH*Ar*), 137.16 (NHAr), 136.44 (Cp‴), 134.18 (NHAr), 129.86 (Cp‴), 129.12 (Cp‴), 31.61 (*C*HMe$_2$), 24.67 (CH*Me*$_2$), 2.58 (Si*Me*$_3$), 1.33 (Si*Me*$_3$), (one NHAr peak and pyridine peaks obscured by solvent resonances). IR (Nujol, cm^{-1}): 3173 (w), 1598 (w), 1305 (m), 1250 (w), 1152 (w), 1089 (m), 1064 (w), 1034 (m), 1002 (w), 935 (m), 838 (s), 723 (s), 621 (w). Anal. Calc. for $C_{36}H_{57}ILaN_3Si_3$: C, 49.03; H, 6.51; N, 4.76. Found: C, 48.73; H, 6.74; N, 4.38.

4.5. (Cp‴)LaI(NHAr)(bipy)(py) (6)

Method 1. A THF solution of KNHAr (170 mg, 0.76 mmol) was added to a THF/pyridine solution of (Cp‴)LaI_2(bipy)(py) (**5**) (660 mg, 0.76 mmol), forming a yellow/orange slurry. The reaction mixture was then stirred overnight and filtered through a frit lined with Celite to remove insoluble KI. The solvent was removed under vacuum to give an orange solid. The solid was extracted with diethyl ether, filtered, and cooled to –30 °C to give orange crystals of **5** (810 mg, 56% yield).

Method 2. A toluene solution of 2,2′-bipyridine (110 mg, 0.70 mmol) was added to a yellow toluene solution of **4** (620 mg, 0.70 mmol), forming a deep red solution. The reaction mixture was stirred overnight and the solvent removed under vacuum. The residue was washed with hexanes and dried under vacuum to give **6** as an orange solid (510 mg, 75% yield). ^{1}H NMR (d^5-pyridine): δ 8.74 (m, *o*-pyridine), 8.72 (m, 4H, 3,6-bipy), 7.77 (d of t, 2H, 5-bipy), 7.58 (m, *p*-pyridine), 7.38 (s, 2H, Cp*H*), 7.25 (m, 2H, 4-bipy), 7.22 (m, *m*-pyridine), 7.11 (d, $^3J_{H-H} = 7.5$ Hz, 2H, *m*-H), 6.80 (t, $^3J_{H-H} = 7.5$ Hz, 1H, *p*-H), 6.39 (s, 1H, N*H*), 3.09 (sept, $^3J_{H-H} = 7.2$ Hz, 2H, C*H*Me$_2$), 1.22 (d, $^3J_{H-H} = 7.2$ Hz, 12H, CH*Me*$_2$), 0.37 (s, 18H, Si*Me*$_3$), 0.34 (s, 9H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (d^5-pyridine): δ 156.93 (bipy), 152.80 (NH*Ar*), 137.55 (bipy), 137.15 (NH*Ar*), 136.70 (Cp‴), 134.18 (NHAr), 129.86 (Cp‴), 129.11 (Cp‴), 124.62 (bipy), 121.63 (bipy), 31.60 (*C*HMe$_2$), 24.66 (CH*Me*$_2$), 2.57 (Si*Me*$_3$), 1.33 (Si*Me*$_3$), (one NHAr peak and pyridine peaks obscured by solvent resonances). IR (Nujol, cm^{-1}): 3168 (w), 1598 (m), 1311 (m), 1250 (m), 1211 (w), 1167 (w), 1157 (w), 1088 (m), 995 (m), 935 (m), 834 (s), 723 (s), 640 (m), 623 (m). Anal. Calc. for $C_{36}H_{55}ILaN_3Si_3$: C, 49.14; H, 6.30; N, 4.78. Found: C, 47.62; H, 6.18; N, 4.95.

4.6. General procedures for hydroamination/cyclization

In the glovebox, a screw-cap NMR tube was charged with catalyst (0.015 mmol), C_6D_6 (~0.5 mL) and 2-amino-hex-5-ene (**7**) (0.30 mmol). The NMR tube was then placed in an oil bath maintained at 80 °C, and the conversion followed by ^{1}H NMR spectroscopy.

4.7. Crystallographic studies

Crystals of **2**, **3**, **4** and **6** were mounted on glass fibers using a spot of silicone grease. Due to air sensitivity, the crystals were mounted from a pool of mineral oil under argon gas flow. The crystals were placed on a Bruker P4/CCD diffractometer, and cooled to 203 K using a Bruker LT-2 temperature device. The instrument was equipped with a sealed, graphite monochromatized Mo Kα X-ray source ($\lambda = 0.71073$ Å). A hemisphere of data was collected using φ scans, with 30 s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using SMART [46] software. Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT [47] software. The data were corrected for absorption using the SADABS [48] program. Decay of reflection intensity was monitored via analysis of redundant frames. The structures were solved using Direct methods and difference Fourier techniques. For **3** and **4**, the amido hydrogen atom positions were located on the difference map, and refined with isotropic temperature factor set to 0.08 Å^2. For **2**, **3**, **4** and **6**, all other hydrogen atom positions were idealized, and rode on the atom they were attached to. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. For **3**, the electron density of a disordered THF molecule was removed from the unit cell using PLATON/SQUEEZE [49]. This resulted in two THF molecules per cell being removed (74 e$^-$/cell and 326 Å^3). For **6**, the structure was refined as a racemic twin, with the minor component batch-scale-factor converging to 0.423(8). Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL NT [50]. Additional details of data collection and structure refinement are listed in Table 3.

5. Supporting information available

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre CCDC No. 230910 for compound **2**, No. 230911 for compound **3**, No. 230912 for compound **4** and No. 230913 for compound **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: cdeposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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