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Syntheses and structures of mono-cyclopentadienyl di-iodide complexes of the lanthanides: X-ray crystal structures of $Cp'''LaI_2py_3$ ($Cp''' = [\eta^5 - C_5H_2(SiMe_3)_3\text{-}1,2,4]^-$; py = pyridine) and $Cp'''LaI_2$(bipy)py (bipy = 2,2′-bipyridine)[†]

Garth R. Giesbrecht[1], David L. Clark[2], John C. Gordon[3]* and Brian L. Scott[3]**

[1]Nuclear Materials Technology (NMT) Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA
[2]The Glenn T. Seaborg Institute for Transactinium Science, Los Alamos National Laboratory, Los Alamos, NM 87545, USA
[3]Chemistry (C) Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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$[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]K$ reacts with $LaI_3(THF)_4$ in tetrahydrofuran (THF) to form the mono-ring complex $[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]LaI_2(THF)_x$ (1). Elemental analysis and ^1H NMR spectroscopy indicate that the coordinated THF molecules are labile and are easily removed under vacuum. The THF adduct 1 is readily converted to the more stable pyridine complex $[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]LaI_2py_3$ (2) by the addition of excess pyridine to a toluene solution of 1. Although solid samples of 2 lose pyridine less readily, the pyridine molecules exchange with solvent molecules, and in the presence of a large excess of THF, 1 is re-formed. Complex 2 may be crystallized from toluene, and an X-ray diffraction study revealed a monomeric species with the two iodide ligands *trans* to each other, and three pyridines arranged in a meridional fashion. The addition of one equivalent of 2,2′-bipyridine to a toluene solution of 1 yields the bipyridine adduct, $[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]LaI_2$(bipy) (3). In contrast to 1 and 2, the bipyridine molecule in 3 remains ligated to the lanthanum center in all solvents. Complex 3·py may be crystallized from THF–pyridine; in this case, the presence of bipyridine forces a *cis* orientation of the two iodide ligands.

KEYWORDS: lanthanum; iodide; bulky cyclopentadienyl

INTRODUCTION

The organometallic chemistry of the lanthanides has enjoyed a recent resurgence, due to the highly active nature of many organolanthanide complexes as catalysts for organic transformations.[1–7] The most common ligand framework for organometallic complexes of the rare-earth metals has been the combination of two cyclopentadienyl (C_5H_5) or pentamethylcyclopentadienyl (C_5Me_5) ligands. However, the mono-ring analogues, or half-sandwich complexes, are much less common.[8] These compounds have often been overlooked, primarily for two reasons: (1) due to the electrophilicity of the lanthanides, common synthetic routes often result in the non-stoichiometric incorporation of salt molecules into the coordination sphere of the metal, resulting in 'ate' complexes;[9–19] (2) the high degree of steric unsaturation in these complexes often leads to disproportionation of $CpLnX_2$ species to Cp_2LnX and LnX_3 (Cp = cyclopentadienyl or cyclopentadienyl derivative; Ln = lanthanide; X = halide, alkyl, aryloxide, amide).[17,20,21] Recently, work by us[22] and others[23–25] has shown that, by employing potassium salts of C_5Me_5 and lanthanide tri-iodides, mono-ring species that are free from additional salt complexation may be obtained, although there are still only a handful of $CpLnI_2L_x$ (L = Lewis

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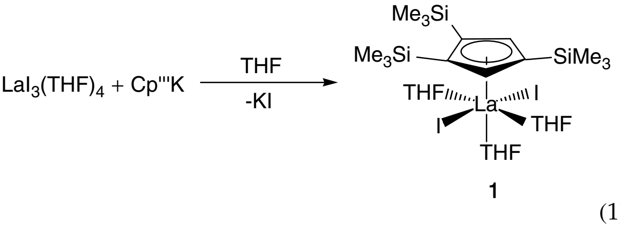
*Correspondence to: John C. Gordon, Chemistry (C) Division, Los Alamos National Laboratory, C-SIC, Mail Stop 5514, Los Alamos, NM 87545, USA.
E-mail: jgordon@lanl.gov
**Correspondence to: Garth R. Giesbrecht, Nuclear Materials Technology (NMT) Division, Los Alamos National Laboratory, NMT-DO, Mail Stop J514, Los Alamos, NM 87545, USA.
[†]Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

base) species that have been reported in the literature.[8] To combat the second problem, and in light of the utilization of the pentamethylcyclopentadienyl ligand to isolate lanthanide dialkyl complexes such as (η^5-C_5Me_5)La[CH($SiMe_3$)$_2$]$_2$[26] and (η^5-C_5Me_5)Gd(CH_2Ph)$_2$(THF) (THF = tetrahydrofuran),[27] it seemed logical to us that the use of a bulkier, yet readily available cyclopentadienyl derivative may serve to expand this interesting class of compounds. Although the alkali metal chemistry of the 1,2,4-C_5H_2($SiMe_3$)$_3$ ligand has been well established,[28–34] organolanthanide complexes bearing this ligand system are limited to a solitary example[35] (the C_5H_2($SiMe_3$)$_3$ ligand has been used previously in organoactinide chemistry[36,37]). Here, we report the synthesis and characterization of mono-ring complexes of lanthanum employing the bulky ligand [1,2,4-C_5H_2($SiMe_3$)$_3$]$^-$, and the control of the stereochemistry of the resultant di-iodide complexes by the appropriate choice of Lewis base.

RESULTS AND DISCUSSION

The addition of a THF solution of the potassium salt [η^5-C_5H_2($SiMe_3$)$_3$-1,2,4]K[33,34] to a slurry of $LaI_3(THF)_4$ in THF results in the substitution of one iodide ligand and the formation of the mono-ring lanthanum complex [η^5-C_5H_2($SiMe_3$)$_3$-1,2,4]$LaI_2(THF)_x$ (**1**):



(1)

Complex **1** is soluble in common organic solvents such as benzene, toluene and THF. The three trimethylsilyl groups impart additional solubility to the complex, as the pentamethylcyclopentadienyl derivative, (η^5-C_5Me_5)$LaI_2(THF)_3$, is insoluble in either toluene or benzene.[23] The formulation of **1** with three equivalents of coordinated THF in Fig. 1 is based on the stoichiometry of the previously reported pentamethylcyclopentadienyl analogues, (η^5-C_5Me_5)$LnI_2(THF)_3$ (Ln = La[23], Ce[23], Nd[22]). As for these complexes, **1** readily loses THF and the elemental analysis of isolated material corresponds to a formulation of [η^5-C_5H_2($SiMe_3$)$_3$-1,2,4]$LaI_2(THF)_{0.3}$. Although compound **1** is soluble in benzene, the ^{1}H NMR spectrum obtained in C_6D_6 consisted of broad resonances consistent with a fluxional process. Sharper peaks were obtained in THF-d^8; two $SiMe_3$ resonances in a 2 : 1 ratio arising from the Cp ring trimethylsilyl groups were apparent, at 0.37 ppm and 0.30 ppm, respectively, and the two CpH protons gave rise to a single resonance at 6.91 ppm. Although the trimethylsilyl peaks are relatively insensitive to the chemical environment, the position of the CpH protons can shift over 1 ppm in response to varying Lewis bases (see later). Integration of the signals arising from coordinated THF (20 °C, THF-d^8) yielded values ranging from 2.5 to <1 THF per lanthanum center, depending on the preparation; in addition to loss of THF upon exposure to vacuum during normal workup, these loosely bound ligands are also likely to undergo rapid exchange with THF-d^8 in solution.

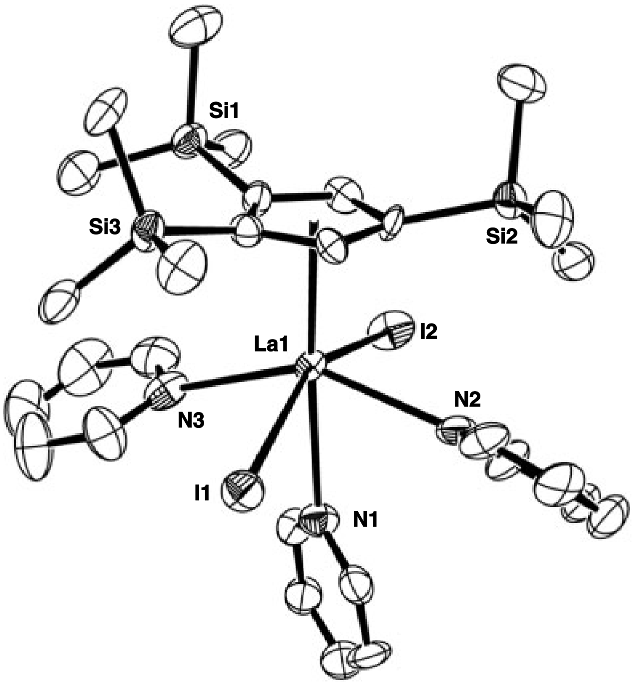
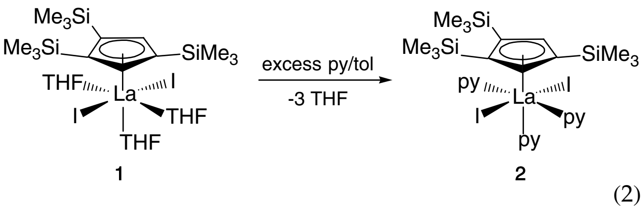


Figure 1. Thermal ellipsoid view of [η^5-C_5H_2($SiMe_3$)$_3$-1,2,4] LaI_2py_3 (**2**) drawn with 50% probability ellipsoids. The interstitial toluene molecule is omitted for clarity.

We have previously reported that ambiguities regarding complex stoichiometry can be avoided by replacing labile THF molecules with more Lewis basic nitrogen-based ligands such as pyridine.[22] The addition of an excess of pyridine to a toluene solution of [η^5-C_5H_2($SiMe_3$)$_3$-1,2,4]$LaI_2(THF)_x$ (**1**) resulted in the complete substitution of the THF groups and the formation of the tris-pyridine adduct, [η^5-C_5H_2($SiMe_3$)$_3$-1,2,4]LaI_2py_3 (**2**):

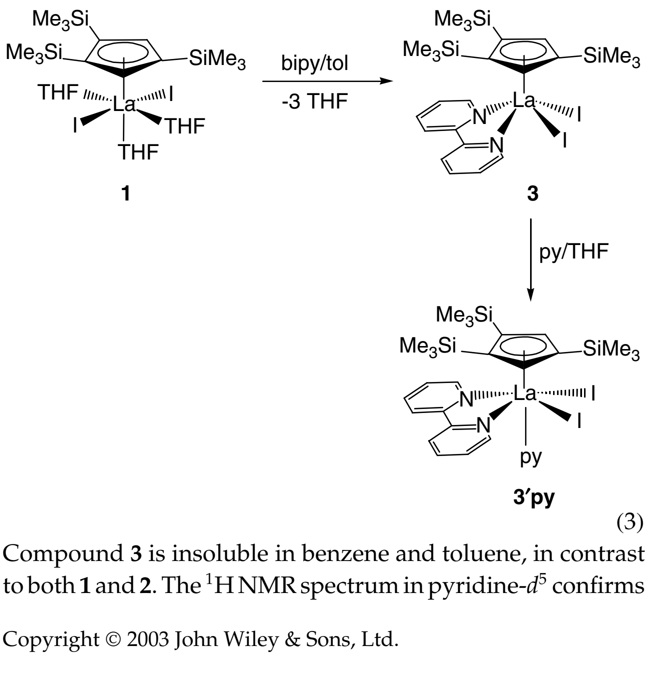


(2)

Compound **2** is less susceptible to solvent loss than the THF adduct **1**; elemental analysis is consistent with the presence of between one and two molecules of pyridine per metal atom. Additionally, the IR spectrum of solid **2** (Nujol mull, KBr plates) shows a band characteristic of coordinated pyridine at 623 cm^{-1}.[38] As for compound **1**, the ^{1}H NMR spectrum of **2** in C_6D_6 is suggestive of a fluxional process, with the $SiMe_3$ groups appearing as a single, broad peak. The ^{1}H

NMR spectrum of **2** in THF-d^8 consists of sharp peaks, indicating either a rigid solution structure or rapid exchange on the NMR time-scale. The resonances arising from pyridine are only minimally shifted from those of free pyridine in THF-d^8; thus, it is difficult to ascertain whether the pyridine molecules are coordinated to the lanthanum center and do not shift significantly upon coordination, or whether, in the presence of a large excess of THF, the pyridine molecules are displaced. However, the CpH protons appear at 6.94 ppm, which is similar to that observed for [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]$LaI_2(THF)_x$ in THF-d^8 (6.91 ppm). The ^{1}H NMR spectrum of **2** in pyridine-d^5 is similar to that in THF-d^8, with pyridine resonances occurring at the same shift as that for free pyridine. In this case, the CpH peak is visible at 7.82 ppm, a downfield shift of ~1 ppm compared with the same sample in THF-d^8. This downfield shift upon dissolution in pyridine-d^5 suggests that the pyridine molecules in **2** are rapidly exchanging in solution, and in the presence of a large excess of THF-d^8, the THF adduct (or more accurately, the THF-d^8 adduct) **1** is re-formed, in spite of THF being the weaker Lewis base. However, the pyridine present in the NMR sample (THF-d^8) of a freshly recrystallized sample integrates for three molecules of pyridine per metal center, implying that the tris-pyridine adduct is formed originally. Prolonged exposure to vacuum results in some loss of coordinated solvent, with the elemental analysis corresponding to approximately 1.5 equivalents of pyridine per metal center, which was confirmed by two independent samples. We have experienced no problems in using the formula [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]LaI_2py_3 to calculate molecular weights for subsequent reactions. This formulation was also confirmed by an X-ray diffraction study (see later).

Addition of a toluene solution of 2,2′-bipyridine (one equivalent) to a toluene solution of [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]$LaI_2(THF)_x$ (**1**) results in the immediate formation of a tan precipitate, which was identified as the bipyridine adduct [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]LaI_2(bipy) (**3**):



(3)

Compound **3** is insoluble in benzene and toluene, in contrast to both **1** and **2**. The ^{1}H NMR spectrum in pyridine-d^5 confirms the presence of a single bipyridine molecule per lanthanum center, which is further supported by the microanalysis of **3**. The CpH protons of **3** resonate at 7.82 ppm, which is the same shift observed for the tris-pyridine adduct **2**. The peaks arising from the bipyridine moiety appear at similar chemical shifts to those of free bipyridine in pyridine-d^5 and are somewhat broadened, indicating that some exchange may occur between a species such as [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]LaI_2(bipy) (or [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]LaI_2(bipy)(py)) and the tris-pyridine adduct [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]LaI_2py_3. Dissolution in THF-d^8 results in an upfield shift of the CpH resonance to 7.05 ppm (a similar shift to that observed for **1**); however, the position and shape of the bipyridine resonances are markedly different than those of free bipyridine in THF-d^8. It is likely that, in the presence of excess pyridine, the mono-pyridine adduct [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]LaI_2(bipy)(py) is formed (see crystal structure), whereas in THF the dominant species in solution is the mono-THF adduct, [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]LaI_2(bipy)(THF).

Single crystals of **2** that were suitable for an X-ray diffraction study were grown by slow evaporation of a saturated toluene 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** and **3·py** are listed in Table 3. Compound **2** co-crystallizes with two molecules of toluene per unit cell. The molecule is monomeric in the solid state, with the lanthanum(III) ion coordinated by two iodide ions, three pyridine nitrogen atoms, and the $C_5H_2(SiMe_3)_3$ ligand. The geometry about the lanthanum center is best described as pseudo-octahedral, with the iodide ligands *trans* to each other (I1–La1–I2 = 153.90(3)°) and a meridional arrangement of pyridine molecules. This *mer,trans* geometry is the preferred arrangement for $CpLnX_2L_3$ species (Cp = substituted cyclopentadienyl; Ln = lanthanide; X = halide; L = Lewis base).[8] In order to relieve a steric interaction between the bulky $C_5H_2(SiMe_3)_3$ group and the iodide

Table 1. Selected bond distances (Å) and angles (deg) for [η^5-$C_5H_2(SiMe_3)_3$-1,2,4]LaI_2py_3 (**2**)

La1–N1	2.830(9)	La1–N2	2.649(10)
La1–N3	2.712(10)	La1–I1	3.1934(15)
La1–I2	3.2289(14)	La1–Cp1	2.557
La1–C1	2.835(10)	La1–C2	2.801(10)
La1–C3	2.840(10)	La1–C4	2.813(10)
La1–C5	2.854(10)	N1–La1–N2	74.7(3)
N1–La1–N3	73.6(3)	N1–La1–I1	77.2(2)
N1–La1–I2	77.2(2)	N1–La1–Cp	175.9
N2–La1–N3	147.7(3)	N2–La1–I1	80.3(2)
N2–La1–I2	88.1(2)	N2–La1–Cp	102.0
N3–La1–I1	86.6(2)	N3–La1–I2	91.0(2)
N3–La1–Cp	110.0	I1–La1–I2	153.90(3)
I1–La1–Cp	104.5	I2–La1–Cp	100.7

ligands, the equatorial groups are bent away from the ring and toward the group in the position *trans* to the ring. This is evident in the angle defined by the *trans* nitrogen atoms of the equatorial pyridine molecules (147.7(3)°). These distortions are similar in magnitude to those determined for $(\eta^5\text{-C}_5\text{Me}_5)\text{NdI}_2\text{py}_3$[22] and $(\eta^5\text{-C}_5\text{Me}_5)\text{CeI}_2(\text{THF})_3$,[23] for which I–Ln–I angles of 153.39(2)° and 152.18(3)° respectively were observed. Also, the SiMe_3 groups in **2** are bent back approximately 14° from the plane of the cyclopentadienyl ring. The methyl groups of the C_5Me_5 ligands in $(\eta^5\text{-C}_5\text{Me}_5)\text{NdI}_2\text{py}_3$ and $(\eta^5\text{-C}_5\text{Me}_5)\text{CeI}_2(\text{THF})_3$ are also bent away from the rest of the molecule. The La–I bond lengths of 3.1934(15) and 3.2289(14) Å are comparable to those determined for other mono-ring lanthanum di-iodide complexes (3.1974(4) and 3.2287(4) Å for $(\eta^5{:}\eta^1{:}\eta^1\text{-C}_5\text{H}_3(\text{CH}_2\text{CH}_2\text{NMe}_2)_2\text{-1,2})\text{LaI}_2(\text{THF})$; 3.1696(4) and 3.2681(4) Å for $(\eta^5{:}\eta^1{:}\eta^1\text{-C}_5\text{H}_3(\text{CH}_2\text{CH}_2\text{NMe}_2)_2\text{-1,3})\text{LaI}_2(\text{THF}))$[25] and also the mono-aryloxide compound [(*R*)-2-(1-naphthol)-1′-naphthoxide)]$\text{LaI}_2(\text{THF})_3$, for which La–I distances of 3.235(2) and 3.268(2) Å were reported.[39] By comparison, the average La–I bond length in seven-coordinate $\text{LaI}_3(\text{THF})_4$ is 3.154(4) Å.[24] The range of La–C distances (2.801(10) to 2.854(10) Å) and the distance from the centroid of the $\text{C}_5\text{H}_2(\text{SiMe}_3)_3$ group to the metal center (2.557 Å) are typical of mono-cyclopentadienyl lanthanum complexes.[23–25,40] The La–N distances are unremarkable and are similar to those ascribed to neutral tri-iodide species such as (tris[(2-pyridyl)methyl]amine)LaI_3(py) (2.712(5) Å).[41]

Single crystals of **3·py** that were amenable to X-ray diffraction were grown by slow evaporation of a saturated THF–pyridine solution. Selected bond lengths and angles are presented in Table 2. A thermal ellipsoid plot giving the atom-numbering scheme used in the tables is shown in Fig. 2. The refinement of **3·py** was limited by twinning and disorder of the pyridine ligand. The final refinement included anisotropic temperature factors on the lanthanum, silicon and iodide atoms only. However, in spite of the large wR_2 value for this structure, a significant amount of high-angle data was collected, which allows for a discussion of the metrical parameters associated with **3·py**. In contrast to compound **2**, the iodide ligands in **3·py** are arranged in a *cis* orientation (I1–La1–I2 = 99.53(4)°), which is a direct result of the coordination of the bipyridine ligand. This is a rare example of a complex of the type CpLnX_2L_3 in which the LnX_2 fragment displays such a geometry, the only other reported cases being the mono-ring compounds $(\eta^5{:}\eta^1{:}\eta^1\text{-C}_5\text{H}_3(\text{CH}_2\text{CH}_2\text{NMe}_2)_2\text{-1,2})\text{LaI}_2(\text{THF})$[25] and $(\eta^5\text{-C}_5(\text{CHMe}_2)_4\text{H})\text{YbCl}_2(\text{DME})$.[42] The iodide ligands and the bipyridine moiety coordinate to the metal center equatorially, with the octahedron about the lanthanum center completed by the $\text{C}_5\text{H}_2(\text{SiMe}_3)_3$ ring and an equivalent of pyridine. As for **2**, the iodides and the bipyridine molecule are bent away from the ring (Cp–La1–N1 = 102.25°; Cp–La1–N2 = 98.17°; Cp–La1–I1 = 108.11°; Cp–La1–I2 = 105.17°) and the steric interaction is further relieved by the SiMe_3 groups of the substituted cyclopentadienyl group residing significantly above the plane of the Cp ring. The La–I distances in **3·py** (La1–I1 = 3.1552(12) Å; La1–I1 = 3.1781(15) Å) are not significantly different than those in **2**; additionally, the La–N and La–C bond lengths in **3·py** are similar to those of the tris-pyridine adduct. It does not appear that the substitution of two pyridine molecules in **2** for a bipyridine molecule in **3·py** has any significant effect on the gross structural features of **3·py**, aside from the orientation of the two iodide ligands.

Table 2. Selected bond distances (Å) and angles (deg) for $[\eta^5\text{-C}_5\text{H}_2(\text{SiMe}_3)_3\text{-1,2,4}]\text{LaI}_2(\text{bipy})\text{py}$ (**3·py**)

La1–N1	2.628(5)	La1–N2	2.614(7)
La1–N3	2.803(5)	La1–I1	3.1552(12)
La1–I2	3.1781(15)	La1–Cp1	2.546
La1–C1	2.794(6)	La1–C2	2.796(6)
La1–C3	2.836(6)	La1–C4	2.842(6)
La1–C5	2.805(7)	N1–La1–N2	60.50(18)
N1–La1–N3	70.57(15)	N1–La1–I1	142.88(12)
N1–La1–I2	92.47(15)	N1–La1–Cp	102.25
N2–La1–N3	73.61(18)	N2–La1–I1	93.97(11)
N2–La1–I2	147.69(11)	N2–La1–Cp	98.17
N3–La1–I1	76.77(9)	N3–La1–I2	81.09(13)
N3–La1–Cp	170.94	I1–La1–I2	99.53(4)
I1–La1–Cp	108.11	I2–La1–Cp	105.17

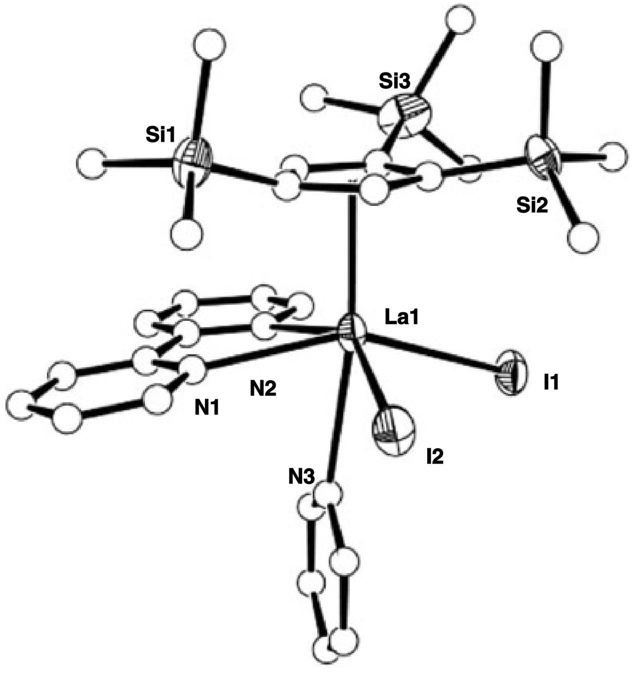


Figure 2. Thermal ellipsoid view of $[\eta^5\text{-C}_5\text{H}_2(\text{SiMe}_3)_3\text{-1,2,4}]\text{LaI}_2(\text{bipy})\text{py}$ (**3·py**) drawn with 50% probability ellipsoids. Atoms that were refined isotropically are depicted as spheres.

CONCLUSIONS

We have demonstrated that by employing the potassium salt of a sterically encumbered cyclopentadienyl ligand and the tri-iodide derivative of a lanthanide metal, monomeric, mono-ring derivatives may be obtained. This approach circumvents the incorporation of salt molecules into the metal coordination sphere, which is often observed when ancillary ligands are introduced to lanthanide metals via salt metathesis reactions with both the smaller halides and/or lighter alkali metals. This problem is often compounded when the syntheses of mono-ligand compounds are attempted, due to the high degree of steric and electronic unsaturation at the metal center. Additionally, the orientation of the two iodide ligands can be controlled by the appropriate choice of Lewis base. Such control of stereochemistry may be desirable in subsequent metathetical reactions, where the relative orientation of two functional groups in $CpLnX_2$ species (X = alkyl, amide) may have some effect on the stability and reactivity of the resultant complexes.

EXPERIMENTAL

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. $[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]K$[33,34] and $LaI_3(THF)_4$[22] were prepared according to literature procedures. Hexane, toluene and THF 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.[43] Pyridine was distilled over sodium benzophenone and degassed prior to use. Pyridine-d^5 and THF-d^8 were distilled over sodium and freeze–pump–thawed three times prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AMX 500 spectrometer at ambient temperature. ^1H chemical shifts are given relative to residual C_5D_4HN ($\delta = 8.74$ ppm) or C_4D_7HO ($\delta = 3.58$ ppm). ^{13}C chemical shifts are given relative to C_5D_5N ($\delta = 150.35$ ppm) or C_4D_8O ($\delta = 67.57$ ppm). IR 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.

$[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]LaI_2(THF)_x$ (1)

An orange THF solution of $[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]K$ (1.00 g, 3.12 mmol) was added dropwise to a slurry 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 to give **1** as an off-white solid (2.22 g, 80% yield). ^1H NMR (THF-d^8): δ 6.91 (s, 2H, Cp*H*), 3.65 (br m, α-THF), 1.78 (br m, β-THF), 0.37 (s, 18H, Si*Me*$_3$), 0.30 (s, 9H, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR (THF-d^8): δ 38.22 (Cp$'''$), 136.52 (Cp$'''$), 134.11 (Cp$'''$), 68.38 (α-THF), 26.51 (β-THF), 2.98 (Si*Me*$_3$), 1.67 (Si*Me*$_3$). IR (Nujol, cm^{-1}): 1346 (w), 1312 (w), 1249 (s), 1198 (w) 1169 (w), 1145 (m), 1093 (s), 1012 (m), 993 (m), 932 (m), 838 (s), 755 (s), 723 (m), 687 (m), 641 (m), 636 (m), 625 (m). Anal. Found: C, 26.32; H, 4.53. Calc. for $C_{14}H_{29}I_2LaSi_3(C_4H_8O)_{0.3}$: C, 26.23; H, 4.55.

$[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]LaI_2py_3$ (2)

$[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]LaI_2(THF)_x$ (**1**) (2.80 g, 3.12 mmol) was dissolved in toluene and 1 ml pyridine was added. After stirring for 1 h, the slightly cloudy orange solution was filtered through a frit lined with Celite, and the toluene removed under vacuum. The solid was washed with hexanes to yield on off-white solid (2.00 g, 70% yield). Slow evaporation of a saturated toluene solution yielded **2** as large, colorless blocks. ^1H NMR (THF-d^8): δ 8.65 (br s, 6H, *o*-pyridine), 7.69 (m, 3H, *p*-pyridine), 7.29 (m, 6H, *m*-pyridine), 6.94 (s, 2H, Cp*H*), 0.33 (s, 18H, Si*Me*$_3$), 0.28 (s, 9H, Si*Me*$_3$). ^1H NMR (pyridine-d^5): δ 8.74 (m, *o*-pyridine), 7.82 (s, 2H, Cp*H*), 7.58 (m, *p*-pyridine), 7.22 (m, *m*-pyridine), 0.52 (s, 18H, Si*Me*$_3$), 0.21 (s, 9H, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR (pyridine-d^5): δ 138.86 (Cp$'''$), 137.67 (Cp$'''$), 136.45 (Cp$'''$), 3.15 (Si*Me*$_3$), 1.59 (Si*Me*$_3$) (pyridine peaks obscured by solvent resonances). IR (Nujol, cm^{-1}): 1600 (m), 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. Found: C, 32.22; H, 4.37; N, 3.08. Calc. for $C_{14}H_{29}I_2LaSi_3(C_5H_5N)_{1.5}$: C, 32.56; H, 4.64; N, 2.65.

$[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]LaI_2bipy$ (3)

An orange THF solution of $[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]K$ (1.00 g, 3.12 mmol) was added dropwise to a slurry 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 to give $[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]LaI_2(THF)_x$ as an off-white solid. This was dissolved in toluene and filtered through a frit lined with Celite. A toluene solution of 2,2′-bipyridine was slowly added, forming an insoluble tan solid. The solid was collected on a frit and washed with toluene to yield on off-white solid (2.04 g, 80% yield). Slow evaporation of a saturated THF–pyridine solution of **3** yielded the pyridine adduct **3·py** as small yellow plates. ^1H NMR (THF-d^8): δ 9.65 (br d, $^3J_{H-H} = 3.9$ Hz, 2H, 3-*H*), 8.50 (d, $^3J_{H-H} = 8.1$ Hz, 2H, 6-*H*), 8.23 (t, $^3J_{H-H} = 7.5$ Hz, 2H, 5-*H*), 7.76 (t, $^3J_{H-H} = 7.5$ Hz, 2H, 4-*H*), 7.05 (s, 2H, Cp*H*), 0.26 (s, 18H, Si*Me*$_3$), −0.13 (s, 9H, Si*Me*$_3$). ^1H NMR (pyridine-d^5): δ 8.76 (br d, $^3J_{H-H} = 2.5$ Hz, 2H, 3-*H*), 8.71 (d, $^3J_{H-H} = 4.5$ Hz, 2H, 6-*H*), 7.82 (s, 2H, Cp*H*), 7.77 (t, $^3J_{H-H} = 7.5$ Hz, 2H, 5-*H*), 7.25 (t, $^3J_{H-H} = 7.5$ Hz, 2H, 4-*H*), 0.52 (s, 18H, Si*Me*$_3$), 0.21 (s, 9H, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR (pyridine-d^5): δ 156.92 (bipy), 138.85 (Cp$'''$), 137.67 (Cp$'''$), 137.56 (bipy), 124.62 (bipy), 121.63 (bipy), 3.16 (Si*Me*$_3$), 1.60

(Si*Me*$_3$), (one Cp‴ and one 2,2′-bipyridine peak obscured by solvent resonances). IR (Nujol, cm^{-1}): 1600 (m), 1593 (m), 1250 (s), 1172 (m), 1156 (m), 1092 (m), 1013 (m), 995 (w), 933 (m), 852 (m), 835 (s), 775 (m), 752 (m), 735 (m), 722 (m), 686 (w), 643 (w), 625 (w). Anal. Found: C, 33.29; H, 4.31; N, 3.19. Calc. for $C_{14}H_{29}I_2LaSi_3(C_{10}H_8N_2)$: C, 34.71; H, 4.49; N, 3.37.

Crystallographic studies

A crystal was mounted onto a glass fiber using a spot of silicone grease. Owing to air sensitivity, the crystal was mounted from a pool of mineral oil under argon gas flow. The crystal was 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[44] software. Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT[45] software. The data were corrected for absorption using the SADABS[46] program. Decay of reflection intensity was monitored via analysis of redundant frames. The structure was solved using direct methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom they were attached to. For **2**, the final refinement included anisotropic temperature factors on all non-hydrogen atoms. For **3·py**, the final refinement included anisotropic temperature factors on the lanthanum, silicon, and iodine atoms. The refinement of **3·py** was limited by twinning and disorder of the pyridine ligand. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL NT.[47] Additional details of data collection and structure refinement are listed in Table 3.

Table 3. Crystallographic data[a]

Compound	**2**(toluene)$_{0.5}$	**3**(pyridine)
Formula	$C_{32.5}H_{48}I_2LaN_3Si_3$	$C_{29}H_{42}I_2LaN_3Si_3$
Molecular weight	957.72	909.64
Temperature, K	203(2)	203(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Crystal size (mm^3)	0.40 × 0.20 × 0.02	0.17 × 0.12 × 0.10
a(Å)	19.131(9)	10.301(5)
b(Å)	10.172(5)	10.822(5)
c(Å)	21.104(10)	19.602(9)
α°	90	88.362(11)
β°	92.842(7)	86.972(9)
γ°	90	66.748(8)
VÅ^3	4102(3)	2004.9(17)
Z	4	2
D_{calc} (g ml^{-1})	1.551	1.507
Absorption coefficient (mm^{-1})	2.657	2.714
F(000)	1876	884
θ range (°)	1.93 to 22.46	1.04 to 22.46
Total reflections	19 258	9389
Independent reflections	5312	4872
GOF	2.334	1.965
R_1	0.0939	0.1162
WR_2	0.1292	0.3733

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ and $R_{2w} = [\Sigma[\omega(F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]]^{1/2}$; $\omega = 1/[\sigma^2(F_o^2) + (aP)^2]$, where $a = 0.0249$ and 0.0392.

Supporting information available

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 203306 for compound **2** and no. 203307 for compound **3·py**. 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: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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