N-aromatic heterocycle adducts of bulky [1,2,4-(Me₃C)₃C₅H₂]₂Sm: synthesis, structure and solution analysis†

Grégory Nocton* and Louis Ricard

The reactions of the bulky samarocene [1,2,4-(Me₃C)₃C₅H₂]₂Sm (1) with several N-aromatic heterocycles, namely, pyridine (3), picoline (4), 4-tert-butyl-pyridine (5), isoquinoline (6) and quinoline (7), are reported. All reactions proceed smoothly in pentane in good yield and crystals of all adducts have been obtained in moderate to good yield and analyzed by X-ray crystallography. The X-ray crystal structures are in agreement with Sm(ii) coordination adducts in which no electrons are transferred to the N-aromatic heterocycle. Magnetic data were recorded for 1 and for all adducts, 3–7, and reinforce the electronic structure of Sm(ii), f⁶ simple coordination adducts. ¹H NMR at different temperatures and visible spectroscopy in toluene show that fast exchange of the N-aromatic heterocyclic ligand (L) occurs in solution according to a ML = M + L equilibrium in which the equilibrium constant is dependent on the bulkiness of L. This fast exchange is stopped below a coalescence temperature Tc, at which the three tert-butyl groups of the cyclopentadienyl are differentiated. The associated rotational barriers have been calculated. Cyclic voltammetry of 1 in THF showed a quasi-reversible wave at a reducing potential of −2.10 V versus the ferricinium/ferrocene couple for the Sm(II)−Sm(III) couple and leads to the conclusion that the non-reduction of L lies in the sterics of 1.

Introduction

The capacity that divalent lanthanides complexes have to transfer a single electron is of great interest since this mono-electronic reduction may lead to interesting chemical reactivity exemplified by the use of SmI₂ as a reducing agent in organic chemistry.¹,³ Moreover, the synthesis and reactivity of organometallic complexes of divalent lanthanides featuring Cp-type ligands has been studied for several decades³–⁸ and, aside from the classical divalent lanthanides Eu,⁹ Yb¹⁰ and Sm,¹¹ non-classical molecular divalent lanthanides have emerged using bulky substituents branched on the cyclopentadienyl to stabilise the divalent metal centre.⁸ These new complexes are not only a synthetic challenge but also lead to interesting reductive reactivity of small molecules, including reduction of N₂,¹² CO₂ and CO.⁶ Another aspect of this reactivity is the reaction with pyridine that features a coupling in the 4,4′-positions of the latter.¹³ The electronic structure of these systems has been largely discussed over the last few years¹⁴–¹⁸ and it seems now relatively well established that both the electronics and the sterics of the ligand set are participating in the stability and reactivity of the metalloocene fragment. It is important since the design of new molecular divalent lanthanide complexes takes both contributions into account in order to predict and dictate the chemical reactivity of these complexes. A related recent study established that the understanding of the electronic structure is key to envisage a mechanistic descriptive approach to the reactivity in ytterbocene complexes.¹⁹ Therefore we became interested in the rationalisation of the different contributing factors of the observed chemical reactivity of organolanthanides.

In a recent work, Nief and Evans started evaluating the influence of the ligand on the reduction properties of samarocene systems using sterically similar but electronically different Cp* and C₅Me₅P π-ligands.¹⁸ From their seminal work, it emerges clearly that the ligand electronics are indeed playing a role in the electron transfer and subsequent reactivity. The present article is the continuing story of these samarocene adducts and we wish to report the reaction of the bulky samarocene fragment [1,2,4-(Me₃C)₃C₅H₂]₂Sm with several N-aromatic heterocyclic ligands including pyridine and quinoline. The use of the 1,2,4-(Me₃C)₃C₅H₂ ligand is of particular
interest since the molecular divalent thulium complex [1,2,4-(Me3C)3C5H2]2Tm was shown to react rapidly with pyridine and form a dinuclear complex of Tm(III) in which the two pyridine ligands are coupled in their 4,4'-position,13 and molecular complexes of divalent neodymium and dysprosium are also reported with this ligand.12,20 Moreover, the THF adduct of [1,2,4-(Me3C)3C5H2]2Sm, reported by Sitzmann and co-workers, shows the presence of only one molecule of THF coordinated to the Sm centre,21 while the presence of two pyridine molecules in Cp2Sm and (CMe3P)2Sm fragments possibly complicates the conclusions on the necessary conditions for electron transfer. In this light, reactions of N-aromatic heterocyclic ligands featuring different bulky groups with [1,2,4-(Me3C)3C5H2]2Sm allow the evaluation of the steric effects that contribute to the electron transfer reaction occurring or not. The synthesis, X-ray structure and magnetic properties of several adducts with increasing bulkiness of [1,2,4-(Me3C)3C5H2]2Sm are herein described along with variable temperature 1H NMR data and visible spectroscopy.

Results

Syntheses

The two complexes [1,2,4-(Me3C)3C5H2]2Sm denoted Cp2Sm (1) and Cp2Sm(thf) (2) were prepared using slight modifications of the published procedure of Sitzmann and co-workers.21 The reaction was performed with isolated dry SmI2 and potassium salt of the tris-tert-butylcyclopentadienyl in THF at low temperature affording a purple solution of the Cp2Sm(thf). After removal of THF and extraction in pentane, one molecule of THF remains and a purple powder of Cp2Sm(thf) was obtained in good yield (75%). The latter complex was sublimed at 123 °C under reduced pressure to yield pure Cp2Sm as purple crystals.

Adducts of Cp2Sm were then prepared by mixing a concentrated pentane solution of Cp2Sm to stoichiometric amounts of pyridine, picoline, 4-tert-butylpyridine, quinoline and isoquinoline for the preparation of 3, 4, 5, 6 and 7, respectively. In the case of 3–6, the solutions turned immediately darker and deposited dark purple crystals of 3, 4, 5 and 6 after standing at room temperature. Complexes 3 and 4 were obtained in good yields while the yields of 5 and 6 were much improved when the pentane solutions were taken to a minimal volume. The case of the quinoline adduct of Cp2Sm is a little different since evaporation to a minimal volume yielded crystals at room temperature that were embedded in an oily brown/yellow residue. Several washings with pentane were necessary in order to obtain crystals of good quality for magnetic measurements. Attempts to crystallize 3–7 at lower temperature (−40 °C) did not lead to much improvement in the yields.

X-Ray structures

The crystal structures of all adducts were obtained by single crystal X-ray analysis. Additionally, the base free Cp2Sm (1) data were collected at low temperature (150 K), which significantly improves the quality of the X-ray crystal structure reported by Sitzmann and coworkers21 (Table 1). An ORTEP of 1 is shown in Fig. 1, while those of 3–7 are shown in Fig. 2. Selected structural parameters and crystallographic data are presented in Table 1 and Table S1,† respectively.

Complexes 3, 4 and 7 crystallized in monoclinic P21/c space group while 5 and 6 are triclinic P1. Complex 5 co-crystallized with a second molecule of 4-tert-butylpyridine in the outer sphere and, in spite of our efforts, only this stoichiometry leads to crystalline material. All adducts have approximately the same symmetry so that the tert-butyl groups of the cyclopentadienyl ligand are staggered. As is suggested by Sitzmann and co-workers, this may be due to the presence of the ligand L that forces the tert-butyl groups to avoid each other for steric reasons.21 The mean C(Cp)–Sm distances range between 2.86(2) Å and 2.88(2) Å and are nearly the same in all adducts 3–7, and compare well with that of Cp2Sm(thf) (2) (2.86 Å) and Cp2Sm(2,6-Me2C6H3NC) (2).21 The Sm–N distances in 3–7 are rather long compared to the THF adduct 2 (2.605(3) Å) and

<table>
<thead>
<tr>
<th>Sm–C (distance range)</th>
<th>Cp2Sm (1)</th>
<th>Cp2Sm(thf) (2)</th>
<th>Cp2Sm(py) (3)</th>
<th>Cp2Sm(4-Me-py) (4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.769(5)–2.839(5)</td>
<td>2.837(6)–2.885(6)</td>
<td>2.821(5)–2.900(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.757(4)–2.835(4)</td>
<td>2.809(5)–2.905(5)</td>
<td>2.828(5)–2.901(5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.802(2)–2.79(3)</td>
<td>2.86(2)–2.87(3)</td>
<td>2.88(2)–2.87(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.526–2.516</td>
<td>2.60–2.60</td>
<td>2.61–2.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.890(5)–2.87(3)</td>
<td>2.86(2)–2.87(3)</td>
<td>2.88(2)–2.87(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.901(5)–2.828(5)</td>
<td>2.86(2)–2.87(3)</td>
<td>2.88(2)–2.87(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.605(3)</td>
<td>2.689(5)–2.768(5)</td>
<td>2.710(5)–2.663(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm–C (distance range)</td>
<td>Cp2Sm(4-4Bu-py)–4-4Bu-py (3)</td>
<td>Cp2Sm(isoquinoline) (6)</td>
<td>Cp2Sm(quinoline) (7)</td>
<td></td>
</tr>
<tr>
<td>2.818(4)–2.918(4)</td>
<td>2.820(7)–2.893(6)/2.835(7)–2.906(7)</td>
<td>2.826(4)–2.912(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.86(4)</td>
<td>2.86(3)/2.86(2)</td>
<td>2.87(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.59</td>
<td>2.59–2.61</td>
<td>2.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>149</td>
<td>149–152</td>
<td>148</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.687(4)</td>
<td>2.70(1)–2.670(6)</td>
<td>2.754(3)</td>
<td></td>
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</tr>
</tbody>
</table>

† From ref. 21.
indicate the presence of a Sm(II)-neutral ligand rather than a Sm(III)-reduced ligand situation.

It is noteworthy that the sterics of the ligands have little influence on the Sm–N distance since pyridine, picoline and 4-tert-butyl-pyridine have similar distances of 2.73(5) Å, 2.69(3) Å, 2.687(4) Å, respectively. On the other hand, isoquinoline and quinoline have Sm–N distances of 2.69(2) Å and 2.754(3) Å that differ by about 0.06 Å, which is not surprising because the lone pair of the quinoline is fairly misdirected for the quinoline to avoid steric bulk of the tert-butyl groups of the cyclopentadienyl. The pyridine in 3, picoline in 4 and 4-tert-butyl-pyridine in 5 are also twisted from the plane formed by the two centroids of the tris-tert-butyl-cyclopentadienyl rings, the samarium atom and the nitrogen atom, so that the dihedral angles between the plane described above and the plane formed by the pyridyl ring are 42° and 59° in 3, 44° and 58° in 4, 78° in 5, 52° and 59° in 6 and 66° in 7. This was also observed for the THF adduct and is likely to be the geometry optimization due to steric bulk. The latter observation is important because it appears as a prelude to the solution behaviour of 3–7 (see the 1H NMR spectroscopy section).

Magnetic data

The magnetic properties of complexes 1–7 were measured in the solid state in the temperature range 5 K–300 K. Available data on solid-state magnetism of molecular Sm(II) and Sm(III) complexes are very limited22,23 although this piece of information may be informative to determine the oxidation state. A plot of $\mu_{\text{eff}}$ vs. temperature is shown in Fig. 3 and the other plots ($\chi$ vs. $T$, $\chi T$ vs. $T$ and $1/\chi$ vs. $T$) are available in ESI.$^+$ The $\chi$ vs. $T$ curves all have the same shape, a monotonic gradual increase with decreasing temperature until a plateau is reached. Such a magnetic behaviour is consistent with a non-magnetic ground state with thermally populated excited states (temperature independent paramagnetism, TIP). Sm(II) complexes, f$_6$, have a 7F ground state that is split into six spin-orbit states 7F$_J$, the non-magnetic 7F$_0$ state being the ground state. Although the ground state is non-magnetic, the first spin-orbit excited states are thermally populated at room temperature.$^{24,25}$ Therefore, the magnetic effective moment values for Sm(II) (and Eu(III) that exhibits the same electronic structure) are generally reported to lie around 3.4–3.8 $\mu_B$ at 300 K.$^{11,23,26}$ In the Van Vleck theory for the free ion, the theoretical magnetic effective moment is calculated with a spin-orbit coupling constant, $\lambda$, of 300 cm$^{-1}$ and therefore only the first two excited states $J = 1$ and $J = 2$ are reasonably populated at 300 K. This leads to a value approaching 3.5$\mu_B$ at 300 K.$^{23,24}$ On top of this, crystal field splitting may lead to several new states (crystal field states), populated according to the Boltzmann law. This leads to a multi-parameter curvature of

![Fig. 1 ORTEP of two different views of 1 with thermal ellipsoids at 50% level. Sm is presented in green and C in dark grey. Hydrogen atoms have been omitted for clarity.](image1)

![Fig. 2 ORTEPs of 3–7 with thermal ellipsoids at 50% level. Sm is presented in green, N in blue and C in dark grey. Hydrogen atoms and eventual co-crystallized solvent molecules have been omitted for clarity. The other figures are available in ESI.$^+$](image2)
Cyclic voltammetric data were recorded for in a 0.1 M [NBu₄][BPh₄]-THF solution, and a cyclic voltammogram is shown in Fig. S15.† Several support electrolytes were used and we found that only [NBu₄][BPh₄] gave reasonable data. The quasi-reversible half-wave potential is −2.10(3) V vs. the ferrocinium/ferro-cene couple and is of the same order of magnitude as that of (C₃Me₂Et)₂Sm(OEt₂) measured in THF (−2.12 V vs. FeC₇/FeC₇).²² Variable scan rates allowed us to trace a plot of the current intensity as a function of the square root of the rate and showed that the redox process is diffusion limited (see Fig. S16†).

This piece of information is important because if the net redox potential of Cp²⁺Sm(thf) lies within the same value as that of (C₃Me₂Et)₂Sm(thf)₂ and presumably that of Cp⁺⁺Sm, the reaction with pyridine shows a different outcome.

### ¹H NMR spectroscopy

The solution behaviour of 1–7 was studied by ¹H NMR spectroscopy in toluene-d₈. At room temperature, all adducts have two ¹Bu resonances in a 18:36 ratio, implying that free rotation of the 1,2,4-(Me₂C₆)₂C₆H₄ groups occurs. The NMR chemical shifts of the hydrogen atoms located on the Cp rings could not be observed. The proton chemical shifts of L (pyridine, Me-pyridine and ¹Bu-pyridine) are shielded (to a small extent) compared to the value of the free ligand. When one equivalent of the free ligand, L, is added to a toluene-d₈ solution of 3–5, the chemical shift values are deshielded toward the free ligand values and the peaks increase in intensity. No free ligand signals appear in accordance with fast exchange of the ligand at the NMR time scale. In the case of the quinoline and isoquinoline ligands, the room temperature shifts of the ligands in 6 and 7 are very close to those of the free ligands and therefore imply that the exchange is not favoured at room temperature. When the temperature is decreased, all adducts, 2–7, present temperature dependence of their chemical shifts in agreement with paramagnetic species. The δ (ppm) vs. 1/T plots are shown in ESI (Fig. S9–S12†). At around −30 °C (243 K), the NMR lines are broadened and tend to disappear, so that only the ¹Bu resonances are followed with confidence. Around this temperature, they split into three distinct resonances in an 18:18:18 ratio. This coalescence implies that the overall free rotation of the 1,2,4-(Me₂C₆)₂C₆H₄ group no longer exists and a barrier for this rotation may be calculated at the temperature of coalescence (Tc) for the adducts 3–6. In the case of 7, no coalescence temperature could be detected because the spectrum is very broad below 250 K. Additionally, the signals for the coordinated ligand in adducts 3–6 appear with a larger chemical shift in agreement with a rigid structure in solution below Tc. Below Tc, no exchange is observed with free ligand (L) in 2–6, as also demonstrated by crossover experiments between 2 and complexes 3–6, respectively. The coalescence temperature was measured using the extrapolation method described by Streitwieser²⁷ and activation barriers were calculated at Tc²⁷ and are shown in Table 2. The values agree well with reported barriers for lanthanide complexes with the

### Table 2 Variable temperature solution ¹H NMR data and rotational barriers calculated at Tc

<table>
<thead>
<tr>
<th>Complex</th>
<th>Tc (K)</th>
<th>Δν (Hz)</th>
<th>ΔG‡ (kcal mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp²⁺Sm(1)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cp²⁺Sm(thf) (2)</td>
<td>234</td>
<td>900</td>
<td>10.0(2)</td>
</tr>
<tr>
<td>Cp²⁺Sm(py) (3)</td>
<td>238</td>
<td>870</td>
<td>10.2(2)</td>
</tr>
<tr>
<td>Cp²⁺Sm(4-Me-py) (4)</td>
<td>240</td>
<td>960</td>
<td>10.3(2)</td>
</tr>
<tr>
<td>Cp²⁺Sm(4-Me-py) (4) (C₇D₁₄)</td>
<td>241.5</td>
<td>1125</td>
<td>10.27(5)</td>
</tr>
<tr>
<td>Cp²⁺Sm(4'-Bu-py) (5)</td>
<td>250</td>
<td>750</td>
<td>10.8(3)</td>
</tr>
<tr>
<td>Cp²⁺Sm(isoquinoline) (6)</td>
<td>238</td>
<td>900</td>
<td>10.2(2)</td>
</tr>
<tr>
<td>Cp²⁺Sm(quinoline) (7)</td>
<td>—</td>
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</table>
Visible spectroscopy

Visible spectra recorded at room temperature in toluene solutions of 1, 3–7 are shown in Fig. 4. Two main features are present at around 550 nm and at around 800 nm. All spectra possess approximately the same shape in agreement with the purple colour of the solutions. Absorption coefficients of both bands are about 1000 cm$^{-1}$ M$^{-1}$ and are in agreement with spin allowed f–d transitions and metal to ligand charge transfer, respectively. f–d Transitions are observed in divalent lanthanides (as opposed to trivalent lanthanides) because the d shell is stabilized and therefore lower in energy so that the transitions appear regularly in the visible range (400–800 nm). Small energy shifts are observed for the band located at around 800 nm but this feature is rather common with f–d transitions since the energy of the d-shell is quite dependent on the ligand set or the solvent. The small differences in this case do not allow unequivocal interpretation. The broadness of the band is also a common feature of divalent lanthanide but is not well documented in the molecular divalent lanthanide chemistry literature. A strong vibronic participation would be an explanation but more work is needed to describe it. The band located at around 550 nm is attributed to the metal to ligand charge transfer Sm $\rightarrow$ Cp$^\ddagger$ as the energy and intensity remain the same in complexes 1 and 3–7. The measurements of visible spectra of 4 in toluene and methylcyclohexane afford almost identical spectra (see SI137) and show that there is almost no solvent effect on these two bands.

The most important feature of this study lies in the band observed at around 450 nm. This indeed constitutes the principal modification observed in the different spectra in the different adducts 3–7 compared to 1, and may therefore be attributed to charge transfer from the metal (M) to the N-aromatic heterocyclic ligand (L), M $\rightarrow$ L, that forms the adduct ML.

The interesting trend in the intensity of this band is in good agreement with the trend observed in the values of the rotational activation barriers in solution. This shows that, at the time scale of the electronic transition, which is faster than the NMR, the exchange in solution between the samarocene fragment, Cp$^\ddagger$Sm, and the ligand L is also exemplified in visible spectroscopy. Under these conditions, a coordination equilibrium forms such as ML $\rightleftharpoons$ M + L, where M is the samarocene fragment Cp$^\ddagger$Sm and L corresponds to pyridine, methylpyridine, tert-butylypyridine, isoquinoline and quinoline in complexes 3, 4, 5, 6 and 7, respectively. If true, temperature will modify this equilibrium as $K_c = [ML]/[M][L]$ is temperature dependent. To test this conjecture, a solution of 4 was studied in toluene while increasing the temperature in small temperature steps. Spectra were recorded in an NMR tube adapted with a J. Young valve previously warmed in a water bath at the given temperature. Corrections for the solvent and the NMR tube were subtracted for each temperature. The results of this experiment are shown in Fig. 5. Because of the rudimentary experimental setup, the error at each temperature is estimated at 2 °C. In spite of this, Fig. 5 displays gradual modifications in spectra with increasing temperature that are in good agreement with a coordination equilibrium displaced toward free samarocene and free ligand at higher temperature. Despite our efforts, we were not able to obtain reliable data at lower temperature in order to check whether the intensity increase at 450 nm stops at the coalescence temperature, ($T_c = 240$ K, $-33$ °C) as is suggested by $^1$H NMR data (the exchange is stopped below $T_c$). A tentative spectrum recorded between $-10$ °C and $-20$ °C is shown in ESI (SI14†). Both experiments are anyhow in good agreement with the
solid state information as well as the $^1$H NMR information and lead us to conclude that 3–7 are simple coordination adducts.

**Discussion**

From solid-state structural and magnetic data, there is no doubt that Cp$^*_2$Sm(L), 3–7, are Sm(n) complexes and L is therefore neutral, i.e. no reduction occurs. In the X-ray structures, the effect of the steric hindrance is not clear because Sm–N distances are within the same order when L is pyridine or 4-tert-butylpyrididine. In solution, visible spectroscopy as well as variable temperature $^1$H NMR spectroscopy are in accordance with a coordination equilibrium ML ⇄ M + L that stops at low temperature without modifying the electronic structure. In these cases, a trend is clearly discernable and shows that the steric hindrance of these complexes. A first explanation would be that it is the presence of a tert-butylpyrididine. This work with the use of picoline and 4-picoline and 4-tert-butylpyrididine. In solution, visible spectroscopy as well as variable temperature $^1$H NMR spectroscopy are in accordance with a coordination equilibrium ML ⇄ M + L that stops at low temperature without modifying the electronic structure. In these cases, a trend is clearly discernable and shows that the steric hindrance of these complexes.

In a previous study, Evans and Nief showed that the Cp$^*_2$Sm fragment allows the reduction of pyridine. A consequence of this reduction is the coupling of two pyridine moieties in the 4–4’ positions to form the corresponding dimer. Pyridine has a net redox potential of −3.2 V vs. Fe$^2$/Fe$^{2+}$ while the Cp$^*_2$Sm fragment has a −2.12 V vs. Fe$^2$/Fe$^{2+}$ redox potential in THF. It is clear from this example that the coordination of pyridine modifies to some extent the redox potential so that reduction is favoured. In this work, we show that the Cp$^*_2$Sm fragment has a redox potential of −2.10 V vs. Fe$^2$/Fe in THF, a similar value compared to Cp$^*_2$Sm. However, the outcome is different: no reduction occurs with pyridine. There are several differences between the two complexes that may explain this result.

First, only one pyridine is coordinated in the Cp$^*_2$Sm fragment. A first explanation would be that it is the presence of a second pyridine that allows the reduction to occur. In this case, an electronic contribution (the change in redox potential when one more pyridine is coordinated) is to invoke, an argument developed in Nief and Evans’ seminal work. In order to get insights into this, adducts of isoquinoline and quinoline were synthesised because their redox potentials are −2.62 V and −2.58 V vs. Fe$^2$/Fe, respectively, a large difference compared to pyridine, i.e. their reduction has to be facilitated from an electronic aspect. However, no reduction occurs with isoquinoline and quinoline in 6 and 7. This experiment shows that the electronics are not likely to be the only contribution to the reduction of L in these systems.

A second explanation would be that the steric constraints of Cp$^*_2$Sm are important and the coordination of pyridine is not facilitated and preclude its reduction. This is shown in this work with the use of picoline and 4-tert-butylpyrididine with the Cp$^*_2$Sm fragment that show different visible spectra at room temperature. Additionally, from X-ray structures and $^1$H NMR data at low temperature, it seems clear that L does not lie in a plane of symmetry but is twisted from this ideal geometry. Yet, the question remains whether it is a purely steric problem in terms of proximity between the Sm metal centre and the nitrogen atom of L that disallows the reduction or whether a symmetrical condition (in terms of orbital symmetry) is needed for the electron to leave Sm toward L. Both arguments constitute the steric and the symmetrical contributions. Previous studies of Nief and Evans have raised the question of electronics in these organolanthanides, while Andersen and some of us pursued the question of the symmetry contribution to explain the reactivity of the ytterbocene adduct of 4,5-diazfluorene. This work brings some new indications concerning the steric aspects of these complexes.

**Conclusion**

The reaction of the bulky samarocene with L (L = pyridine, picoline, 4-tert-pyrididine, isoquinoline, quinoline) in pentane allowed the synthesis of the adducts Cp$^*_2$Sm(L), 3–7, in moderate to good yield. All adducts have been characterized by X-ray, temperature dependent magnetic data and $^1$H NMR, Vis-NIR spectroscopy. All these data are in agreement with Cp$^*_2$Sm(L), 3–7, being Sm(n) simple neutral coordination complexes in both solution and solid state. These data contrast with precedents in the literature of Cp$^*_2$Sm, in which pyridine was reduced. The measurement of the redox potential of Cp$^*_2$Sm in a THF solution indicates that the electronics are similar to that of Cp$^*_2$Sm and do not explain the absence of reduction of L in this case. However, at room temperature, L exchange is fast in solution and the equilibrium ML ⇄ M + L is dependent on the steric hindrance of L. This led to the conclusion that it is the stericity of Cp$^*_2$Sm that do not allow us to gather the conditions for the reduction of L to occur. Several hypotheses were discussed to understand this result and work is in progress in order to bring more insights into these electron transfer reactions in organolanthanides. Indeed, their interesting reactivity begets the question of the necessary conditions that have to be fulfilled to dictate this reactivity. From this and previous work, it is clear that the contributions are multiple (symmetry, steric and electronics), much like in d-transition metals, which is more surprising in 4f-element complexes.

**Experimental**

**General considerations**

All reactions were performed using standard Schlenk-line techniques or in a glovebox (MBraun). All glassware was dried at 120 °C for at least 12 h prior to use. [1,2,4-{Me$_3$C}(C$_5$H$_2$)$_2$]Sm(THF) was prepared according to a published procedure with slight modifications (see the Syntheses section). Toluene, toluene-d$_8$, C$_6$D$_6$, C$_5$D$_{14}$ and pentane were dried over sodium and transferred under reduced pressure in a cold flask. All solvents were degassed prior to use. Pyridine, 4-methyl-pyrididine, isoquinoline and quinoline were degassed and stirred on molecular sieves for 24 h, transferred under reduced pressure in a cold flask and stored on molecular sieves in the glovebox. NMR spectra were recorded on a Bruker 300 MHz Avance III spectrometer. Chemical shifts are expressed relative to TMS in
ppm. Visible spectra were recorded in the range 300–1100 nm at room temperature on an Agilent Cary 60 Spectrometer in 10 mm quartz cuvettes. The solvent background was corrected. Elemental analyses were obtained from the London Metropolitan University Science Centre. Cyclic voltammetry studies were conducted in a N2 filled glovebox using a Princeton Applied Research VersaSTAT4 potentiostat. Measurements were performed in a 5 mL THF solution of 5 mM of the complex and ~0.1 M of [NBu4][BPh4] with a 5 mm platinum disk working electrode and a silver wire as a quasi-reference electrode. Redox potentials were calibrated with ferrocene and cobaltocene. We estimated the errors on the measured redox potential to be within 30 mV with multiple measurements. Magnetic measurements were performed using a Cryogenic SX600 SQUID magnetometer and samples were prepared in sealed tubes. Diamagnetic contribution was corrected using the Pascal contents.

Syntheses

[1,2,4-(Me3C)3C5H2]2Sm (1). This molecule was prepared by Sitzmann and coworkers21 using an in situ synthesis of SmI2 by the method of Kagan.35 For this work, the procedure was modified a little with no improvement in the yield (the yield reported by Sitzmann is 79%). A green powder of SmI2 (710 mg, 1.75 mmol) was combined in the drybox with K[1,2,4-(Me3C)3C5H2] (952 mg, 3.50 mmol) and THF was condensed to be within 30 mV with multiple measurements. Magnetic measurements were performed using a Cryogenic SX600 SQUID magnetometer and samples were prepared in sealed tubes. Diamagnetic contribution was corrected using the Pascal contents.

[1,2,4-(Me3C)3C5H2]2Sm (50 mg, 0.081 mmol). The dark purple mixture was stirred for 1 minute at room temperature and was concentrated to a minimum to obtain a viscous dark purple solution (<1 mL) that was allowed to stand for 3 days at room temperature to yield large dark crystals. These crystals were washed with pentane two times (32 mg, 52%). During the last operation the yield decreased dramatically but washings were necessary for the analytical purity of the crystals. The crystals were then dried at 80 °C for 16 h. In spite of our efforts to use a 1 : 1 stoichiometry, crystals of 5 only crystallized with one free ligand in the lattice. This is also shown by NMR spectroscopy. Crystallization at −35 °C led to the same result. To increase the yield a 2 : 1 stoichiometry was then used. 1H NMR: (toluene-d8, 293 K) δ (ppm) 13.63 (18H), 7.36 (br, 4H, 4'-Bu-py), 6.02 (br, 4H, 4'-Bu-py), 5.28 (36H), 0.82 (18H, 4'-Bu-py). Anal. calcd for C52H84N2Sm: C, 70.37; H, 9.54; N, 3.16. Found: C, 70.28; H, 9.43; N, 2.97.

[1,2,4-(Me3C)3C5H2]2Sm(isoquinoline) (6). Isoquinoline (0.011 g, 0.094 mmol) was added to a 5 mL pentane solution of [1,2,4-(Me3C)3C5H2]2Sm (55 mg, 0.089 mmol). The dark purple mixture was stirred for 1 minute at room temperature and was concentrated to a minimum to obtain a viscous dark purple solution (<1 mL) that was allowed to stand for 3 days at room temperature to yield large dark crystals. These crystals were washed with pentane two times and the pure crystals were dried (31 mg, 48%). As for 5, the washing of the crystals with pentane decreased dramatically the yield but was necessary to obtain pure crystals. 1H NMR: (toluene-d8, 293 K) δ (ppm) 12.56 (18H), 7.90 (br, 1H, isoquinoline), 7.57 (br, 1H, isoquinoline), 7.30 (br, 1H, isoquinoline), 7.28 (br, 2H, isoquinoline), 6.65 (br, 1H, isoquinoline), 6.41 (br, 1H, isoquinoline), 5.17 (36H). Anal. calcd for C54H86N2Sm: C, 69.20; H, 8.78; N, 1.88. Found: C, 69.12; H, 8.86; N, 2.02.

[1,2,4-(Me3C)3C5H2]2Sm(quinoline) (7). Quinoline (15 g, 0.128 mmol) was added to a 5 mL pentane solution of [1,2,4-(Me3C)3C5H2]2Sm (50 mg, 0.081 mmol). The dark purple mixture was stirred for 1 minute at room temperature and was concentrated to a minimum to obtain a viscous dark purple solution (<0.2 mL) that was allowed to stand for 3 days at room temperature to yield large dark crystals and a yellowish oil. These crystals were washed with pentane two times and the pure crystals were dried (35 mg, 54%). 1H NMR: (toluene-d8, 295 K) δ (ppm) 10.80 (18H), 8.77 (s, 1H, quinoline), 8.27 (d, J = 8 Hz, 1H, quinoline), 7.47 (d, J = 8 Hz, 1H, quinoline), 7.37 (m, 1H, quinoline), 7.33 (d, J = 7 Hz, 1H, quinoline), 7.16 (d, J = 8 Hz, 1H, quinoline), 6.77 (dd, J = 8 Hz, 2 Hz, 1H, quinoline), 4.72 (36H). Combustion analysis was not satisfactory after repeated trials. The [1,2,4-(Me3C)3C5H2]2Sm : quinoline ratio of 1 : 1 was checked in 1H NMR.
X-Ray crystallography

Single crystals of compounds 1, 3–7 were mounted on a kapton loop using Paratone® oil and cooled to 150 K in a nitrogen stream for X-ray structure determination. The loop was transferred to a Nonius Kappa diffractometer using a MoKα (\(\lambda = 0.71073 \, \text{Å}\)) X-ray source, a graphite monochromator and a Brucker APEX-II detector. Preliminary orientation matrices and cell constants were determined by collection of 20 s frames, followed by spot integration and least-squares refinement. Data were integrated and corrected for Lorentz and polarization effects. The crystal structures were solved in SIR97\(^{37}\) and refined in SHELXL-97\(^{38}\) by full-matrix least-squares using anisotropic thermal displacement parameters for all non-hydrogen atoms. All hydrogen atoms were placed at geometrically calculated positions. CIF files were deposited at the Cambridge Data Base Centre under the reference CCDC numbers: 961767 (1), 961768 (3), 961769 (4), 961770 (5), 961771 (6) and 961772 (7).

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Notes and references