

New base-free metallocenes of samarium and neodymium, an approach to stereoelectronic control in organolanthanide chemistry

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New unsolvated metallocenes of early lanthanides, (Cp⁴ⁱ)₂Sm, COTSmCp⁴ⁱ, and COTNdCp⁴ⁱ (Cp⁴ⁱ = C₅HⁱPr₄) have been prepared and fully characterised, including X-ray structural analysis: the absence of ancillary base in these complexes is not only the consequence of steric effects; these results bring up the debated question of electronic control in organolanthanide chemistry.

It is an acknowledged fact that, considering their ionic character, the stability of organometallic complexes of lanthanides is mainly governed by electrostatic factors and steric requirements.^{1–3} Some geometrical preferences have been rationalised with models excluding electronic factors.^{4,5} Nevertheless, these models have shown their limitations^{6–8} and a degree of covalence in the lanthanide–ligand bond might be involved in some cases.^{9,10}

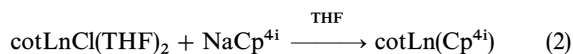
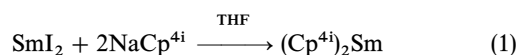
Organolanthanides are becoming more and more implicated in the field of homogeneous catalysis.^{11–13} Potentially active compounds are undercoordinated and soluble in non-polar solvents, but the rules of their formation and stability are still not completely defined. The ubiquitous pentamethylcyclopentadienyl (Cp* = C₅Me₅) ligand, which limits ligand exchange reactions,¹¹ has been used extensively¹⁴ to synthesise half-metallocenes and metallocenes. But this ligand does not allow undercoordinated complexes of the early lanthanides to be easily isolated, the base-free structurally characterised derivatives being limited to Cp*₂Ln¹⁵ and C₅Me₄RLn–cot–LnC₅Me₄R (Ln = Sm,⁶ Eu;⁷ R = Me, Et)[†]. For trivalent lanthanides, metallocenes are accessible using the cyclooctatetraenyl dianionic ligand cot^{2–} = C₈H₈^{2–}). Base-free structures have been reported mainly for the late series.^{14,17}

Very recently, we were able to obtain undercoordinated complexes of early lanthanides, bearing the tetraisopropylcyclopentadienyl [Cp⁴ⁱ = C₅Hⁱ(Pr)₄] ligand and active in polymerisation catalysis.¹⁸ We wanted to extend the use of this ligand to the preparation of metallocenes of (II) and (III) lanthanides.

We report here the synthesis, complete characterisation, and structural behaviour of three new metallocenes of early lanthanides. We will attempt to show that not only the steric hindrance but also the electronic donation of the ligand are related to their base-free structures, with the underlying question arising from all these observations: is it possible to demonstrate some electronic control in organolanthanide chemistry?

The syntheses were all conducted in THF. (Cp⁴ⁱ)₂Sm (**1**) is obtained from the reaction of 2 equiv. of NaCp⁴ⁱ with SmI₂ [eqn. (1)]. cotLnCl(THF)₂ (Ln = Sm, Nd) in the presence of 1

equiv. of NaCp⁴ⁱ affords in high yield the corresponding lanthanide(III) metallocenes cotLnCp⁴ⁱ (Ln = Sm, **2**; Nd, **3**) [eqn. (2)]. Each compound is free of THF according to its ¹H NMR spectrum.



Suitable crystals for an X-ray study were collected from pentane (**1**, **2**) or diethyl ether (**3**) solutions.

As seen in the ORTEP view reported in Fig. 1, **1** is a THF-free bent samarocene. The Sm–CP distance (CP is the ring centroid) is 2.51 Å, which is equivalent to that in the samarium(II) metallocenes Cp*₂Sm (2.53 Å) and triple-decker C₅Me₄RSm–cot–SmC₅Me₄R (2.51 and 2.47 Å for Sm–CP). The Cp–Sm–Cp angle is 152° in **1** which is 12° more than in its permethylated analogue.¹⁵ Such a straightening, reasonably due to steric hindrance, is also observed in the alkaline earth series: 162.3° [(Cp⁴ⁱ)₂Ca] vs. 147.0° (Cp*₂Ca) and 154.3° [(Cp⁴ⁱ)₂Ba] vs. 131.0° (Cp*₂Ba).^{19,20} The CP–Ln distance is

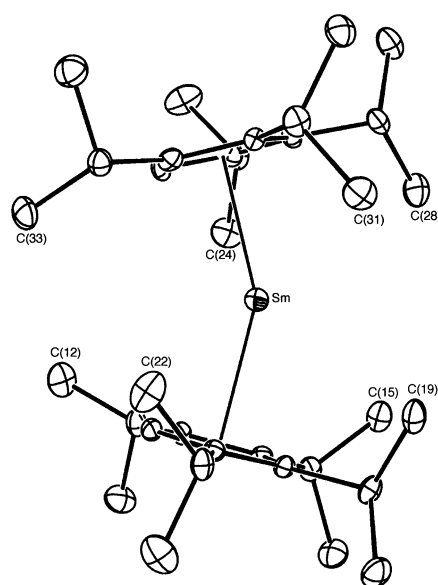


Fig. 1 Molecular structure of **1** showing the atom numbering scheme. Thermal ellipsoids scaled at 30% probability. Selected bond lengths (Å) and angles (°) include: Sm–CP1 2.51, Sm–CP2 2.51, Sm–C(19) 3.54, Sm–C(31) 3.58, CP1–Sm–CP2 152.0. CP1 and CP2 are the geometric centers of the C(1)–C(5) and C(6)–C(10) rings, respectively.

2.40 Å in **2** and 2.45 Å in **3** (Fig. 2), while the COT–Ln distance (COT is the ring centroid of cot) is 1.84 Å in **2** and 1.90 Å in **3**. The molecular structures of **2** and **3** also show a slight bending: 170.4° for the CP–Ln–COT angle in **2**, 165° in one independent conformer of **3** and 173° in the other. Only two analogous examples are available in the literature, $\text{cotTb}(\text{C}_5\text{H}_3'\text{Bu}_2)^{17a}$ and the very recently reported cotSmCp^* .^{17b} In the Tb complex, the more pronounced steric effect [Tb belongs to the late family: $r_i(\text{Tb}^{3+}) = 0.92$ vs. 0.97 Å (Sm^{3+}) and 1 Å (Nd^{3+})²¹] forces a quasi-parallel structure, with an angle of 177.8°. The bending is in the same range in **2** as for the Sm compound (164°).^{17b}

It is clear that the presence of the very bulky Cp^{4i} ligand induces a straightening of the normal bent structure. It can be recalled that the reasons of the bending have until now not been definitely established. The ionic nature of the bonding in the metallocenes of lanthanides(III)⁸ and of alkaline earths (Ca, Ba) was the postulated reason.^{5,8,19,20} Nevertheless, according to a recent paper,⁸ organolanthanide chemistry cannot be thought of as being purely ionic, and the molecular orbital model cannot account for the bending observed in metallocenes of divalent lanthanides. The van der Waals attractive model also does not give a definitive explanation for the bending found in **2** and **3**, as well as in the $\text{Cp}^*\text{Ln} - \text{cot} - \text{LnCp}^*$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$) and cotLnCp^* ($\text{Ln} = \text{Sm}, \text{Dy}, \text{Er}, \text{Yb}$)^{17b} series.

The three metallocenes **1**, **2** and **3** are not solvated, even though their synthesis proceeds in the presence of the coordinating THF. One might assume that the bulky Cp^{4i} ligand precludes the coordination of an ancillary molecule; nevertheless, with Ca(II), smaller than Sm(II) ($r_i = 1.06$ Å vs. 1.11 Å²¹), adducts are invariably obtained.‡ In addition, when 1 equiv. of THF is added to a C_6D_6 solution of **1**, the THF signals are observed at their diamagnetic position. Also, as does Cp^*Sm ,²² **1** efficiently polymerises ϵ -caprolactone:§ obviously there is room for both the growing chain and the coordinated monomer. The related cyclopentadienyl complex decamethylsamarocene is obtained as a bis-THF adduct²³ and desolvated in vacuum (4×10^{-5} torr, 100 °C).²⁴ The obtention of the unsolvated **1** is an unexpected, original obser-

vation. Complexes **2** and **3** also exhibit unprecedented (for the early lanthanide series, except for the very recently reported cotSmCp^* ^{17b}) structures. They display a real monomeric structure—the intermolecular $\text{Sm} \cdots \text{CH}_3$ distances are larger than 5.79 Å—whereas the related complexes cotLaCp^* ²⁵ and cotCeCp^* ²⁶ are considered as oligomeric. $\text{cotSmC}_5\text{Me}_4\text{R}$, synthesised by oxidation with cot ($\text{R} = \text{Me}, \text{Et}$),⁶ and $\text{cotLnC}_5\text{Me}_4\text{PMe}_2$ ($\text{Ln} = \text{Sm}, \text{Nd}$) are associated ($\text{Ln} = \text{Nd}$) in non-coordinating solvents.²⁸ None of these have been structurally characterised; actually $\text{cotTb}(\text{C}_5\text{H}_3'\text{Bu}_2)^{17a}$ is the only bis-polyhapto trivalent lanthanide complex, bearing a sterically hindered cyclopentadienyl ligand, whose structural data can be compared with those of **2** and **3** (ionic radius bigger than 0.9 Å) but terbium is not an early lanthanide. Concerning the cotLnCp^* series Evans *et al.* reported that with metals larger than samarium, solvates are isolated.^{17b}

If **1** is unsolvated, it is obviously not only for steric reasons. The steric hindrance of a bulky cyclopentadienyl ligand is, moreover, not always sufficient to preclude coordination on a large early lanthanide: in $\text{cotSm}\{2,5\text{-di}^i\text{Bu}\text{pyrrolyl}\}(\text{THF})$,²⁹ the pyrrolyl ligand is disubstituted, and yet a THF molecule is coordinated on the same side as one *tert*-butyl substituent. The presence of the THF may here be the consequence of the electronic deficiency of the samarium atom (pyrrolyl is known to be a poor electron donor). Furthermore, the coordination shell of a lanthanide ion is large enough to accept three peralkylcyclopentadienyls³⁰ and the recently published synthesis of the neutral $(\text{Cp}^{4i})_2\text{LnBH}_4$ ($\text{Ln} = \text{Sm}, \text{Nd}$) shows that it is possible to coordinate an additional ligand close to two very bulky tetraisopropylcyclopentadienyl rings.¹⁸ That must be *a fortiori* the case for the larger Sm(II) cation.

An original feature is also observed in **1**: the shortest intramolecular $\text{Sm} \cdots \text{CH}_3(^i\text{Pr})$ distance (the tertiary carbon is located 0.04 Å under the cyclopentadienyl ring) is 3.54 Å. With the assumption of a C–H distance of 0.96 Å³¹ the $\text{Sm} \cdots \text{H}$ separation is evaluated at 2.70 Å, which is compatible with an agostic interaction;¹⁵ a comparable interaction was found in $\text{C}_5\text{Me}_4\text{EtSm} - \text{cot} - \text{SmC}_5\text{Me}_4\text{Et}$ ⁶ [intramolecular $\text{Sm} \cdots \text{CH}_3(\text{Et group})$ distance of 3.40 Å] and an agostic $\text{Sm} \cdots \text{H}$ bond was evidenced in $\text{Sm}(\text{Tp}^{i\text{Bu},\text{Me}})_2$, with a $\text{Sm} \cdots \text{H}$ separation of 2.52 Å.³²

The same and more pronounced phenomenon was also found in $(\text{Cp}^{4i})_2\text{NdBH}_4$, whose structure was published recently by some of us,¹⁸ and in $(\text{Cp}^{4i})_2\text{SmBH}_4$: a very short $\text{Ln} \cdots \text{CH}_3(^i\text{Pr})$ distance (3.41 Å) could be observed [the tertiary carbon being located 0.15 (Sm) and 0.13 Å (Nd) under the cyclopentadienyl ring] for one of the Cp ligands. The resulting evaluated $\text{Ln} \cdots \text{H}$ distances are 2.50 (Sm) and 2.57 Å (Nd). Thus, the electron deficiency of the metal is compensated by this slight internal interaction. But when the borohydride is replaced by an isosteric chloride ligand, the homologous complex adopts an “ate” structure $[(\text{Cp}^{4i})_2\text{NdCl}_2] - [\text{Na}(\text{OEt}_2)]^+$.³³ This is another illustration of the structural diversity in these complexes, in which electronic control plays a role.

On the other hand, the Lncot derivatives **2** and **3** do not display such interactions [a Nd(1) \cdots C(82) distance of 3.47 Å, for a shift of the tertiary carbon of only 0.01 Å is found in the most bent conformer; this could be the result of the packing, as this deformation is absent in the other conformer of **3**]. The same is true for $\text{cotTb}(\text{C}_5\text{H}_3'\text{Bu}_2)^{17a}$ which does not need a supplementary internal $\text{Ln} \cdots \text{CH}_3(^i\text{Bu})$ compensation, such as that found in $(^i\text{Bu}_2\text{C}_5\text{H}_3)_2\text{Yb}$.⁸ The cot–Ln distances, the shortest ones observed, lie in the same range for these three complexes: 1.84 (**2**), 1.90 (**3**), 1.77 and 1.85 Å (Tb).^{17a}

To summarise, the presence of THF on a metallocene may be related to the electronic demand. As evidenced in **2** and **3**, an early lanthanide cation may be sufficiently stabilised by bearing just one cot and one Cp^{4i} ligand. No additional ligand is needed; this is in accordance with Ephritikhine *et al.*,

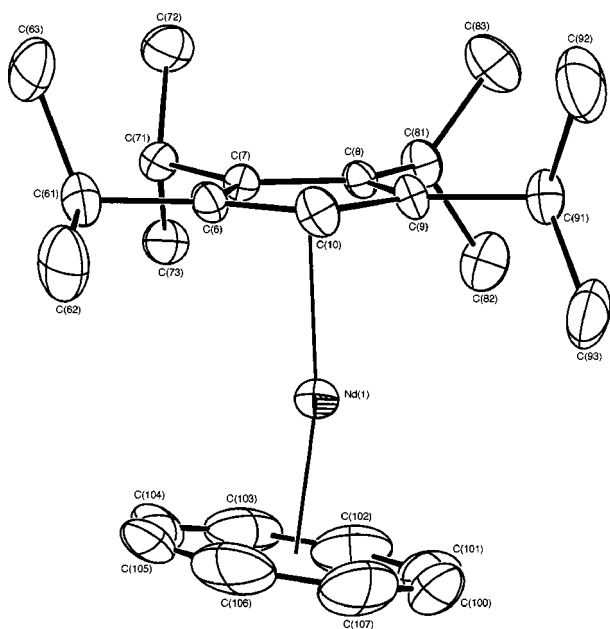


Fig. 2 Molecular structure of one of the independent molecules of **3** showing the atom numbering scheme. Thermal ellipsoids scaled at 30% probability. Selected bond lengths (Å) and angles (°) include: Nd(1)–CP1 2.45, Nd(1)–COT1 1.90, CP1–Nd(1)–COT1 165. CP1 and COT1 are the geometric centers of the C(6)–C(10) and C(100)–C(107) rings, respectively.

who postulated that a cot ligand makes the cation less electrophilic than two Cp* ligands.³⁴ Thus, we believe that **2** and **3** are under electronic rather than steric control. In **1**, the electron deficiency of the metal is fully compensated by a slight internal interaction, which can be rationalised as an electronic control of the coordination sphere of the lanthanide atom. This electronic stabilisation of an early organolanthanide complex can also be evidenced in the mono-tetraisopropylcyclopentadienyl series: we observed that for the two isostructural undercoordinated complexes (Cp⁴ⁱ)Ln(THF)(BH₄)₂ (Ln = Sm, Nd), the residual space around the metal is filled with 2 BH₄ and one THF only.¹⁸ The tetrahedral geometry observed, extremely unusual as all monocyclopentadienyl homologous derivatives are octahedral, is the result of the electronic donation of one electron-rich Cp, one THF and two BH₄ (more electron-donating than a halogen ligand). This last example supports the general idea, beyond the steric hindrance of the Cp⁴ⁱ ligand, of the electronic contribution to the stability of early organolanthanides, and shows the limits of the space-filling alkaline earth metals model. In other words, it is possible to suggest electronic control of the coordination sphere around the lanthanide atom. This aspect is worth noting and calls for urgent studies.

Experimental

Syntheses

Complex 1. SmI₂ (600 mg, 1.48 mmol) and NaCp⁴ⁱ,³⁵ (760 mg, 2.96 mmol) were dissolved in 20 ml of THF. The dark green solution was stirred at ambient temperature for 12 h. The solvent was removed under dynamic vacuum and the purple residue extracted with pentane (20 ml). After filtration the volume of solvent was reduced and upon cooling the solution to -20 °C, purple crystals of **1** were formed. Yield: 78% (714 mg). Spectroscopic data for **1**: ¹H NMR (200 MHz, C₆D₆, 343 K): δ 22.37 (s, 2H, HC₅ⁱPr₄), 14.75 (s, 12H, HC₅ⁱPr₄), 4.72 (br, 12H, HC₅ⁱPr₄), 2.93 (br, 12H, HC₅ⁱPr₄ + 4H, HC₅ⁱPr₄), -3.84 (s, 12H, HC₅ⁱPr₄ + 4H, HC₅ⁱPr₄). C₃₄H₅₈Sm requires C, 66.16; H, 9.47. Found C, 66.63; H, 9.51%.

Complex 2. A solution of NaCp⁴ⁱ (208 mg, 0.80 mmol) in 20 ml of THF was added by fractions, at room temperature, to a suspension of cotSmCl(THF)₂ [synthesised according to the published procedure³⁶ with solid K₂(cot) reagent³⁷] (365 mg, 0.84 mmol) in THF (20 ml). After stirring for 6 h at ambient temperature and evaporation of the THF in vacuum, the crude brown solid was extracted with toluene (35 ml). The resulting solution was filtered and concentrated to dryness to yield 247 mg (62.8%) of **2**. Recrystallisation from pentane and cooling to -20 °C afforded X-ray quality crystals. Spectroscopic data for **2**: ¹H NMR (200 MHz, C₆D₆, 298 K): δ 10.73 (s, 1H, HC₅ⁱPr₄), 8.72 (s, 8H, cot), 2.43 (br, 2H, HC₅ⁱPr₄), 2.19 (br, 2H, HC₅ⁱPr₄), 1.47 (d, 6H, HC₅ⁱPr₄), 0.43 (d, 6H, HC₅ⁱPr₄), 0.21 (d, 6H, HC₅ⁱPr₄), -0.26 (br, 6H, HC₅ⁱPr₄). C₂₅H₃₇Sm requires C, 61.54; H, 7.64; Sm, 30.82. Found C, 59.11; H, 7.73; Sm, 29.63%.

Complex 3. The same procedure was followed for the synthesis of **3**, starting from cotSmCl(THF)₂ (352 mg, 0.82 mmol) and NaCp⁴ⁱ (200 mg, 0.78 mmol). Yield: 280 mg (73.8%). Recrystallisation from diethyl ether at room temperature afforded X-ray quality crystals. Spectroscopic data for **3**: ¹H NMR (200 MHz, C₆D₆, 343 K): δ 24.8 (s, 1H, HC₅ⁱPr₄), 8.57 (br, 6H, HC₅ⁱPr₄), -0.4 (br, 2H, HC₅ⁱPr₄), -7.7 (br, 6H, HC₅ⁱPr₄), -12.2 (br, 6H, HC₅ⁱPr₄), -13.3 (br, 6H, HC₅ⁱPr₄), -13.4 (s, 8H, cot); the last signal (br, 2H, HC₅ⁱPr₄) appears at 4.2 at 298 K. C₂₅H₃₇Nd requires C, 62.32; H, 7.74. Found C, 62.42; H, 7.97%.

X-ray crystallographic studies

Data were collected on Nonius KappaCCD (**1**) or Enraf Nonius CAD4 (**2**, **3**) diffractometers, using Mo-Kα graphite-monochromated radiation (λ = 0.71073 Å) for all the complexes. The structures were solved and refined with SHELX-97.^{31,38} Absorption corrections were made by the psi-scan method for complexes **2** and **3**.

Complex 1. C₃₄H₅₈Sm, FW = 617.15, monoclinic, space group C2/c, *a* = 33.672(2), *b* = 12.308(1), *c* = 16.500(1) Å, β = 112.932(4)°, *U* = 6343.3(9) Å³, *Z* = 8, μ = 1.870 mm⁻¹, *T* = 110(2) K, 6811 reflections collected, 3257 independent and 2719 observed reflection [*I* ≥ 2σ(*I*)]. Final *R*(*F*) = 0.026 (observed), 0.034 (all); w*R*(*F*²) = 0.059 (observed), 0.064 (all).

Complex 2. C₂₅H₃₇Sm, FW = 487.90, monoclinic, space group P2₁/n, *a* = 8.498(2), *b* = 28.893(5), *c* = 10.265(1) Å, β = 112.64(1)°, *U* = 2326.2(7) Å³, *Z* = 4, μ = 2.53 mm⁻¹, *T* = 296(2) K, 4895 reflections collected, 4638 independent and 2972 observed reflections [*I* ≥ 2σ(*I*)]. Final *R*(*F*) = 0.042 (observed), 0.080 (all); w*R*(*F*²) = 0.100 (observed), 0.110 (all).

Complex 3. C₂₅H₃₇Nd, FW = 481.79, monoclinic, space group P2₁/a, *a* = 19.021(3), *b* = 8.377(3), *c* = 29.023(3) Å, β = 91.72(2)°, *U* = 4622.4(20) Å³, *Z* = 8, μ = 2.252 mm⁻¹, *T* = 296(2) K, 6485 reflections collected, 6241 independent and 4035 observed reflections [*I* ≥ 2σ(*I*)]. Final *R*(*F*) = 0.031 (observed), 0.099 (all); w*R*(*F*²) = 0.067 (observed), 0.079 (all).

CCDC reference number 440/226. See <http://www.rsc.org/suppdata/nj/b0/b006834i/> for crystallographic files in .cif format.

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Notes and references

† With the smaller late lanthanide ytterbium, desolvated structures are more commonly observed: not only Cp*₂Yb, but also Cp*Yb-cot-YbCp*,⁷ (C₅Me₄H)₂Yb, (tBu₂C₃H₃)₂Yb, [(Me₃Si)₂C₃H₃]₂Yb⁸ and the polymeric unsubstituted Cp₂Yb¹⁶ could be obtained.

‡ The syntheses of the corresponding metallocenes Cp*₂Ae and (Cp⁴ⁱ)₂Ae (Ae = alkaline earth metal) proceed in THF. In some cases, ether adducts were prepared to overcome the problems of desolvation of coordinated THF.^{19,20}

§ Poly(εCL) is obtained in 5 min (RT, yield 90%, monomer/catalyst = 400). A. Hafid, unpublished results.

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