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Lanthanidocenes: Synthesis, Structure and Bonding of Linear Sandwich Complexes of Lanthanides

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ABSTRACT: The article presents the synthesis, structure, and bonding of a series of neutral and linear sandwich compounds with the cyclononatetraenyl (Cnt) ligand and divalent lanthanides. These compounds account for the emergence of the lanthanidocene series in reference to the ferrocene and uranocene. The synthetic strategy uses the solubility difference between two conformational isomers of the ligand as well as their isomerization induced by solvent coordination, yielding to the isomorphous and isostructural, neutral and rigorously linear sandwich complexes. The molecular structures highlight a Cnt-Ln-Cnt angle at 180° and a ring size close to the Cnt-Cnt (centroid) distance. A qualitative molecular orbital diagram is provided in D_{9d} symmetry and DFT calculations enforce the bonding model.

INTRODUCTION.

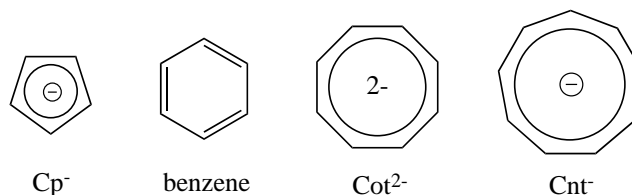
The initial report of a new type of organo-iron compound in 1951¹ has marked the onset of an extensive and fruitful research field devoted to the synthesis and the structural analysis of the so-called metallocenes.²⁻³ The sandwich shape of these molecules is fascinating since it provides a great platform for further substitutions. Additionally, the high symmetry of such molecules is particularly interesting since it confers various reactivity and physical properties to the metal center, depending upon the electron count.⁴ Thus, not only that these compounds broke the fundamental nature of the structural perspectives of the time, but it also fed multiple research fields for more than 60 years.

The cyclopentadienyl (Cp) ligand (Chart 1) that is used for the synthesis of neutral metallocenes is small, Hückel aromatic, mono-anionic, and is therefore particularly well adapted for transition metals of the +II oxidation state.⁴ For the main group metallocenes, the lone-pair p orbital causes a bending in groups 14 and 15 complexes,⁵⁻⁶ while for larger elements with different oxidation states, such as the f-elements, the coordination chemistry studies with the Cp ligand have also led to other geometries than the linear sandwich one.⁷⁻⁹ Thus, Streitwieser proposed to use the cyclooctatetraenyl (Cot) ligand for 5f-elements of +IV oxidation state: in 1968, the synthesis¹⁰ and the structure¹¹ of a neutral and linear sandwich complex of uranium was reported and named uranocene, in reference to ferrocene.²⁻³ For the 4f-elements, the lanthanides, the only element for which the formal +IV oxidation state is well-known is Ce: cerocene, *i.e.* $Ce(Cot)_2$, is the only one of the series that is reported yet,¹² and the numerous reports on its bonding and on the formal oxidation state of cerium¹³⁻¹⁷ highlight the large fundamental interest for this type of molecules.

For the other lanthanides, three Cp ligands surround the metal center with +III oxidation states, leading to Cp_3Ln ,⁷⁻⁸ while with +II oxidation states, a bending is induced because of inter-molecular interactions.¹⁸⁻¹⁹ Furthermore, in Cot chemistry, the anionic nature of the trivalent metal complexes also generally results in a bending and/or in the formation of chain structures, preventing the establishment of a systematic isostructural series of linear sandwich complexes of lanthanides.²⁰⁻²²

An interesting step toward such a series has been done with the report of formal zero-valent bis(arene) lanthanides compounds synthesized in the 1980's with the bulky 1,3,5-*tert*-butylbenzene ligand.²³⁻²⁴ Indeed, in order to reach the desired linear geometry, the preferred solution is to use large substituents, assuming that the sterics will dictate the symmetry.²⁵⁻²⁷ This strategy has proven to be useful in the synthesis of a series of cationic Cp'_2Ln^+ ,²⁸ in which the Cp'_2Dy^+ closely linear geometry allowed to break records in single molecule magnets (SMM) properties,²⁹⁻³¹ but also allowing spontaneous reduction of $Sm^{III/II}$ and extraordinary luminescence of Eu^{II} complexes.³³

Chart 1. Aromatic ligands used for the design of sandwich complexes.



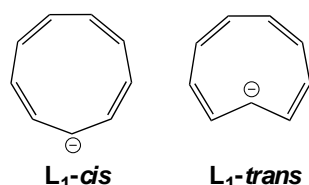
Our strategy is based on the use of divalent lanthanides, whose chemistry expended largely in the last decades,³⁴⁻³⁵ with the next Hückel-aromatic and monoanionic ligand after the Cp ligand, the cyclononatetraenyl anion (Cnt, $C_9H_9^-$, Chart

1).³⁶⁻³⁷ A recent article by Nakajima *et al.* reported the structural and physical properties of the $\text{Eu}(\text{Cnt})_2$ complex,³⁸ while Walter *et al.* have reported the synthesis of the $\text{Ba}(\text{Cnt})_2$ complex.³⁹ In this article, we report the original synthesis, the structure and the bonding of several $\text{Ln}(\text{Cnt})_2$ complexes, a series of neutral and linear sandwich compounds of lanthanides, justifying the name of *lanthanidocenes*.

RESULTS AND DISCUSSION.

Synthesis and Structural Analysis. The KCnt salt has been prepared from a literature procedure,^{37, 40} and can be recrystallized from diethylether, forming yellow X-ray suitable crystals (Figure 1). The structure shows a positional disorder for the C1 carbon atom, indicating the presence of two isomers: the *cis,cis,cis,cis*-cyclononatetraenyl ($\text{L}_1\text{-cis}$), in which all carbon atoms form a regular ring and the *cis,cis,cis,trans*-cyclononatetraenyl ($\text{L}_1\text{-trans}$), in which one carbon atom is moved inside the ring (Chart 2).

Chart 2. Structure of the two isomers of L_1 .



Both isomers are also present in solution (Figure S1): the ^1H NMR spectrum of the crystals in CD_3CN shows the characteristic singlet at 6.94 ppm of $\text{L}_1\text{-cis}$ as well as the characteristic triplet associated with the internal hydrogen atom ($\text{L}_1\text{-trans}$) at -3.54 ppm in a 1:4 ratio. Boche *et al.* measured an activation free-enthalpy of $29.7 \text{ kcal.mol}^{-1}$ in thf at 60°C for the KCnt isomerization process.⁴¹ Thus, if the ring opening reaction time is extended to 3 days instead of several hours, only the symmetrical isomer $\text{L}_1\text{-cis}$ is obtained. However, since the latter is not soluble in diethylether, its purification by crystallization is rendered very difficult.

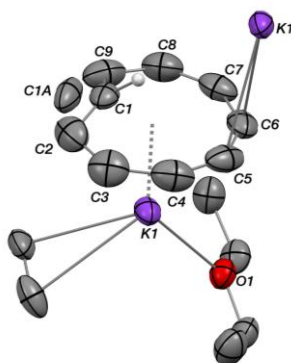


Figure 1. Molecular structure of $\text{KL}_1\cdot\text{OEt}_2$ recorded at 150 K; thermal ellipsoids are shown at 50% probability. C1 and C1A show the positional disorder. Hydrogen atoms have been removed for clarity except that of C1 in order to show its orientation.

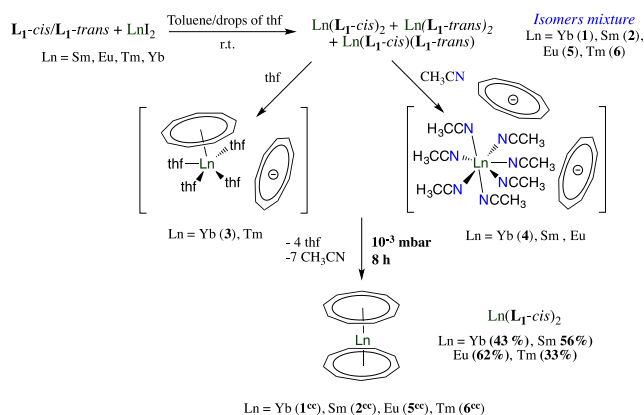
Because of these solubility problems, the reaction of $\text{L}_1\text{-cis}$ with lanthanide diiodide precursors leads, in very low yield (1% - 5%), to powders, which are not greatly soluble in hydrocarbon solvents.³⁴ Therefore, the isomer mixture is preferred for the syntheses. When the synthesis is performed in

diethylether from a suspension of YbI_2 with 2 equivalents of the isomers mixture, the yield remains low (15 %). Performing the reaction in thf does not improve the yield since after evaporation of the solvent and extraction of the residue in toluene it still remains very similar. However, when the salt metathesis reaction is performed directly in toluene with a few drops of thf, the suspension turns immediately green and a good amount (43 %) of the crystals of, $\text{Yb}(\text{Cnt})_2$, **1** can be obtained, after filtration, from the green solution at -35°C .

The ^1H NMR spectrum shows three different complexes in solution: the two homoleptic $\text{Yb}(\text{L}_1\text{-cis})_2$ (**1^{cc}**) $\text{Yb}(\text{L}_1\text{-trans})_2$ (**1^{tt}**) complexes and the heteroleptic $\text{Yb}(\text{L}_1\text{-cis})(\text{L}_1\text{-trans})$ (**1^{ct}**) complex (Figure S2). The characteristic singlet of **1^{cc}** at 7.16 ppm and both characteristic triplets of **1^{ct}** and **1^{tt}** at -3.97 ($J = 15.4 \text{ Hz}$) and -4.13 ppm ($J = 15.5 \text{ Hz}$) allow their identification. The ^{13}C NMR shows only 6 resonances for the two major isomers, one for **1^{cc}**, and 5 for **1^{tt}**. Among them, 5 resonances have $^1J_{\text{CH}}$ coupling constants in a 154-162 Hz range, in good agreement with sp^2 aromatic carbon atoms, while the last one has a $^1J_{\text{CH}}$ of 126 Hz, in agreement with an sp^3 carbon atom (Figure S3-S4) and can be attributed to the carbon away from the ring plane.

A similar synthetic procedure than that of **1** was used to afford $\text{Sm}(\text{Cnt})_2$ (**2**) in better yields (56 %) as brown crystals (Scheme 1). The ^1H NMR shows 12 resonances (three isomers) spanning from 50.3 to -2.35 ppm (Figure S8). All of them can be all identified with a 2D-COSY experiment (Figure S9). The isomerization must be performed at temperatures close to room temperature (25°C) to be optimum since the rate of the reaction slows down when increasing the temperature, preventing to realize an Eyring analysis.³⁷ After several days, the crystallization of yellow (**1^{cc}**) and orange (**2^{cc}**) crystals occurs in unsatisfactory low yields,³⁸ which encouraged us to search for better isomerization solvents.

Scheme 1. Synthetic scheme for **1**, **3** and **4**.



When crystals of **1** are dissolved in thf, red crystals crashed out immediately while the dilute ^1H NMR shows only one broad singlet at 6.92 ppm (Figure S5). The X-ray diffraction analysis of the crystals shows an ion-pair of $[\text{Yb}(\text{L}_1)(\text{thf})_4][\text{L}_1]$ (**3**) with one Cnt ligand coordinated to the ytterbium metal while the second one is not (Figure 2). Four molecules of thf complete the coordination sphere of ytterbium, *viz.* thf is a good donor for lanthanide ions and competes with the Cnt coordination. The Yb-O average distance is $2.44(3) \text{ \AA}$ (Figure 2 and Table S11), in agreement with a divalent metal center.⁴² The Cnt ligand coordinated to the ytterbium also exhibits a disorder between the *cis* and *trans* form in a 1:1 ratio. Howev-

er, the outer-sphere ligand shows only the *cis* form, which means that it has been entirely isomerized. The broad and unique resonance in ^1H NMR at 6.92 ppm accounts for a possible exchange between both ligands. This behavior is very interesting since it means that the isomerization barrier is related to the coordination to a given metal center.⁴¹ Since a fast isomerization process would be very advantageous for the synthesis of 1^{cc} and 2^{cc} , we turned to acetonitrile as a solvent.

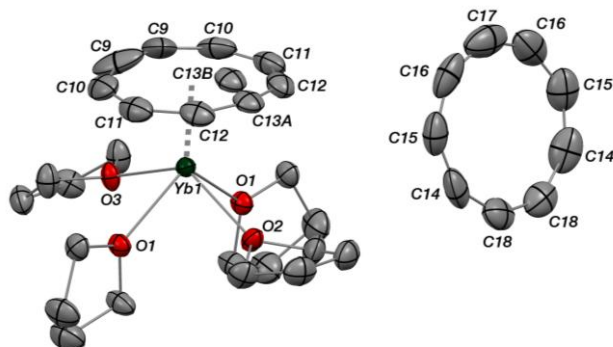


Figure 2. Molecular structure of **3** recorded at 150 K; thermal ellipsoids are shown at 50% probability and the hydrogen atoms are omitted for clarity.

The dissolution of **1** in acetonitrile immediately leads to a color change from green to orange while the ^1H NMR spectrum shows only one resonance at 6.91 ppm (Figure S6). A titration with small amounts of acetonitrile in dichloromethane solutions of **1** and **2** allows following the fast isomerization (Figure S17, Figure S19). Orange crystals can be obtained from a 1:10 room temperature acetonitrile/toluene solution of **1**. They were analyzed as the ion-pair $[\text{Yb}(\text{CH}_3\text{CN})_7][\text{L}_1]_2$ (**4**) (Figure 3). Two independent molecules are present in the unit cell and all ligands are *cis*. The geometry around both ytterbium metal centers is a distorted pentagonal bipyramid and the average Yb-N distances of 2.52(3) Å (Figure 2b and S10) are also in agreement with a divalent center. However, the hepta-

coordination in **4** slightly reduces the average Yb-N distance compared to that of the octa-coordinated acetonitrile complex.⁴³ The key experiment is to expose the crystals of **4** under reduced pressure: after 8 h under 10^{-3} mbar *vacuum*, the yellow powder that is obtained does not contain any trace of acetonitrile and the sharp singlet resonance agrees with the presence of 1^{cc} as a unique isomer.²⁶

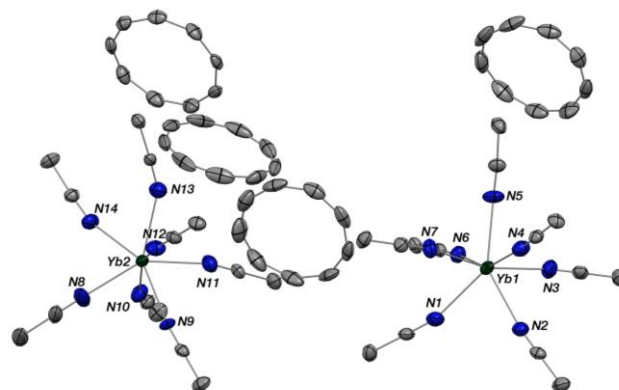


Figure 3. Molecular structure of **4** recorded at 150 K; thermal ellipsoids are shown at 50% probability and the hydrogen atoms are omitted for clarity.

The UV-visible spectra of 1^{cc} and 2^{cc} were compared with those of **1** and **2** in which the Cnt ligand is not entirely isomerized. As expected from the less pronounced color of the symmetrical species, the extinction coefficient is larger in **1** and **2** while the bands' energies are very similar. The light yellow and orange colors of 1^{cc} and 2^{cc} , respectively correspond to a low intense tail from 400 nm to 700 nm (Figure S20-S21).

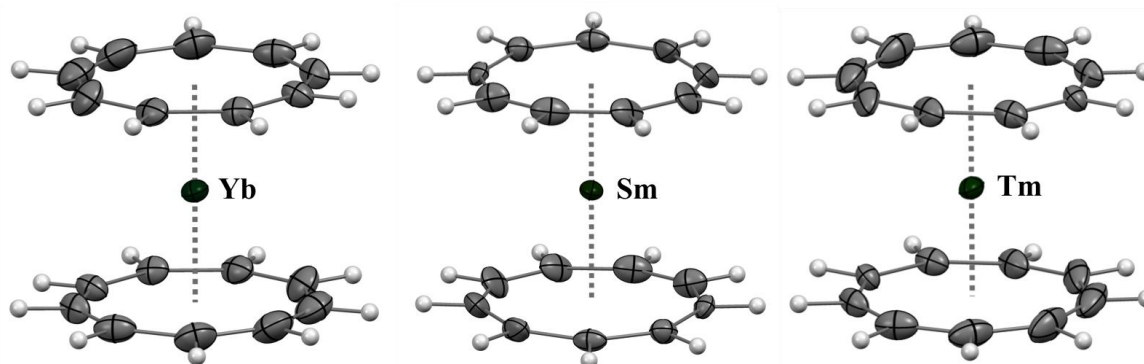


Figure 4. Molecular structure of 1^{cc} , 2^{cc} and 6^{cc} recorded at 150 K; thermal ellipsoids are shown at 50% probability. Disordered carbon atoms are not shown for clarity.

Table 1. Main metric parameters 1^{cc} , 2^{cc} , 5^{cc} , and 6^{cc} . Distances are given in Å and angles in deg, ctr is for centroid.

	1	2	5 from ref ³⁸	6
C-C range in ring	1.33(3)-1.43(3)	1.33(1)-1.47(2)	1.353(15)-1.448(13)	1.32(1)-1.47(2)

Average C-C	1.39(4)	1.39(4)	1.39(2)	1.39(4)
M-C(N) range	2.74(2)- 2.86(2)	2.833(8)- 2.958(6)	2.796(13)-2.957	2.736(8)-2.760(8)
M-C(N) average	2.79(3)	2.88(3)	2.87(4)	2.75(1)
M-L ₁ (ctr)	1.932	2.061	2.065	1.91
ctr-ctr	3.865	4.122	4.131	3.82
Ring size (max C...C-C)	4.06	4.05	4.02	4.02
ctr-Ln-ctr	180	180	180	180

Complexes **1^{cc}** and **2^{cc}** are only sparingly soluble in toluene and benzene but are soluble and stable in dichloromethane. The stability in dichloromethane is rather abnormal for divalent Sm and Yb.⁴⁴ However, this unexpected stability may open new perspectives in the study of their coordination chemistry and reactivity. With a new synthetic procedure in hand, we also performed the synthesis of the europium analogue Eu(L₁)₂ (**5**) in good yield (62 %)³⁸ and more perilously that of the “non-classical” and very reducing divalent lanthanide thulium,⁴⁵⁻⁴⁶ Tm(L₁)₂ (**6**) (33 %), starting from TmI₂(thf)₃.⁴⁷ All compounds **1^{cc}**, **2^{cc}**, **5^{cc}**, and **6^{cc}** are isomorphous and isostructural (Figure 4).

The sandwich complexes **1^{cc}**, **2^{cc}**, **5^{cc}**, and **6^{cc}** crystallize in the P2₁/n space group. The Cnt rings are disordered so that there is an alternation of stacked, D_{9h} and eclipsed D_{9d} symmetry. Interestingly the ring size, measured with the maximal through-space C...C-C distance, is close to that of the centroid-centroid distance. The resulting high symmetry is likely to induce interesting spectroscopic properties.³⁸ The Ln-C and Ln-ctr distances (Table S9) compare similarly with Ln-Cot distances,^{21-22, 48} 1.932 Å in **1**, 2.061 Å in **2**, 2.065 Å in **5**,³⁴ and 1.910 Å in **6**, following the lanthanide contraction trend (Table 1), while they are shorter than that of Ln-Cp typical distances.⁴⁹ The centroid-Ln-centroid angle is of 180°, in agreement with rigorously linear sandwich compounds. The sandwich compounds pack in the solid-state without obvious intermolecular interactions (Figure S32), the shortest carbon-carbon contact being 3.715 Å for **1^{cc}**, 3.694 Å for **2^{cc}** and 3.711 Å for **6^{cc}**. All compounds are air-sensitive although the sandwich complexes are relatively more stable than the thf half-sandwich adduct, **3**, or the heptaacetonitrile complex, **4**.

Bonding Analysis. The structures of the sandwich complexes were optimized in the gas phase using DFT and a qualitative molecular orbital diagram for **1^{cc}** is given in D_{9d} symmetry (Figure 5). The (Cnt)₂ fragments have several symmetry-adapted orbitals mixing with 4f-orbitals: 1_{e_{2u}} and 2_{e_{2u}} are the bonding and anti-bonding combination of the ligands E_{2u} orbitals with the f-δ orbitals and 1_{e_{3u}} is the bonding combination of the ligands E_{3u} orbitals with the f-φ orbitals, similarly to the uranocene and cerocene.^{10, 17} The other f-orbitals do not combine with the ligand. For the ytterbocene and europocene (filled and half-filled 4f-shell) the relative energy and symmetry of the Kohn-Sham highest occupied orbitals (Figure 6) fit very well with the qualitative molecular orbital diagram. The population analysis for all complexes (Tables S1-S3) is of 91 to 96 % 4f and 4 to 8% Cnt in 1_{e_{3u}} and 2_{e_{2u}}, while it is of 91 and 93 % Cnt and 5-8% 4f in 1_{e_{2u}} and 2_{e_{3u}}, in agreement with the expected predominantly ionic bonding.

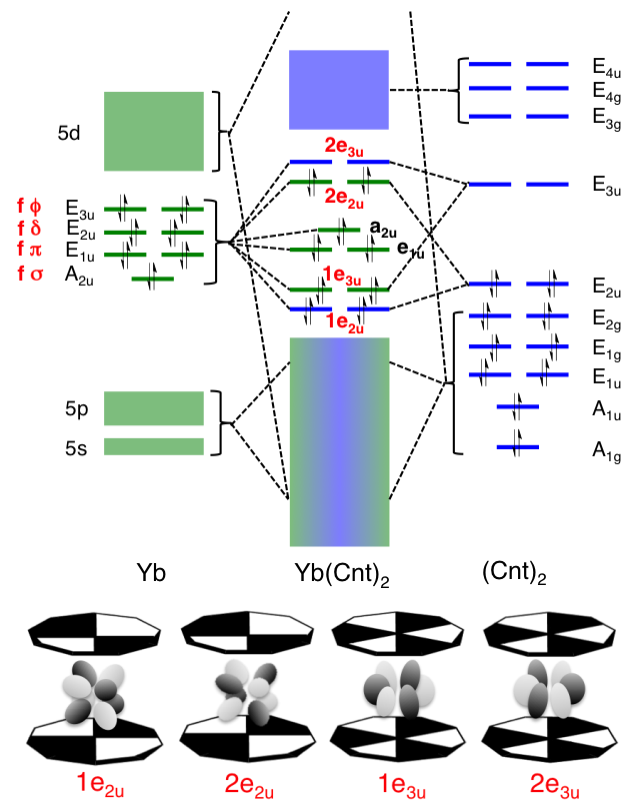


Figure 5. Molecular orbital diagram of Yb(Cnt)₂ (**1**) in D_{9d} symmetry (the blue color is for ligand-based orbitals, the green for metal-based orbitals) and principal molecular orbitals schematic picture.

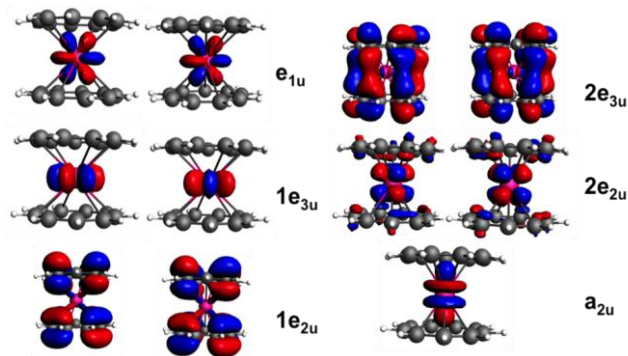


Figure 6. Kohn-Sham highest occupied molecular and LUMO (2_{e_{3u}}) orbitals of Yb(Cnt)₂ (**1**).

CONCLUSIONS.

This work describes the original synthesis, the structure, and bonding of four lanthanidocenes, linear sandwich compounds with the Cnt ligand. The easy access to these compounds in appreciable yields closes the gap between the transition metals metallocenes with the Cp ligand, such as ferrocene, and tetravalent 4f – and 5f metallocenes with the Cot ligand, such as uranocene and cerocene. The molecular structures feature two η^9 -coordinated ligands in a rigorously linear sandwich arrangement. Their simple nature and original symmetry will naturally engage a series of further structural, spectroscopic and theoretical studies along the lanthanide series. Additionally, the formation of a very rare base-free thulium complex, as well as the absence of reactivity with dichloromethane advantageously enlarges the scope of what can be done with very reactive divalent lanthanides compounds. Additionally, the coordination dynamics of the Cnt ligand will also favor rich coordination chemistry and related reactivity.

EXPERIMENTAL SECTION.

General Procedures. All reactions were performed using standard Schlenk-line techniques or in argon or nitrogen filled gloveboxes (MBraun). All glassware was dried at 140°C for at least 12 h prior to use. Thf, diethylether, toluene, CD₃CN, C₆D₆ and toluene-d₈ were dried over sodium (or CaH₂ for CD₃CN), degassed and transferred under reduced pressure in a cold flask. YbI₂ and SmI₂ were prepared following literature procedures^{44, 50} while EuI₂ and TmI₂ were purchased from Aldrich. NMR spectra were recorded in 5 mm tube adapted with a J. Young valve on Bruker 300 MHz Avance III spectrometers. Chemical shifts are expressed relative to TMS in ppm.

Syntheses. Preparation of potassium cyclononatetraenyl (KCnt). The potassium cyclononatetraenyl salt was prepared following a modified literature procedure.^{37, 40} 9-methoxybicyclo[6.1.0]nonatriene was diluted in 30 mL of thf before being added to potassium chunks suspended in 400 mL of thf cooled to -40°C and let under stirring overnight. The brown slurry was then filtered and the solvents removed under reduced pressure to yield a brown solid, which was washed with pentane until the pentane fractions were colorless. Finally the solid was extracted with Et₂O and the obtained solution was cooled to -35°C to yield colorless blocks of (Et₂O)₂.KCnt suitable for X-Ray diffraction. Since these crystals can easily lose their coordinated ether molecule, a great care should be taken while drying them under reduced pressure overnight before using them in order to make sure that no Et₂O molecules are remaining in the ligand salt. ¹H NMR (CD₃CN, 300 MHz, δ /ppm): 7.15 (dd, J =15 Hz, 6Hz, 2H), 6.94 (s, 2.39H), 6.65 (m, 4H), 6.49 (m, 2H), -3.54 (t, J = 15 Hz, 1H).

Preparation of bis(cyclononatetraenyl) ytterbium (1^{cc}). To a solid mixture of KCnt (36.9 mg, 236 μ mol, 2 eq.) and YbI₂ (48.5 mg, 113 μ mol, 1 eq.) prepared in a Schlenk tube, 6 mL of toluene was added followed by 5 drops of thf. The tube was then cautiously protected with paraffin film and the obtained green slurry was stirred for two hours. After, the tube was depressurized and the mixture was stirred under static *vacuum* for a further 14 h before the white solid was filtered off and extracted with 8 mL of toluene (The static *vacuum* is helping to maximize the yield, decreasing the amount of thf in the solution while the reaction proceeds). The obtained deep green fractions were then gathered and concentrated before being cooled to -35°C. The title product was then obtained as small black crystals (19.6 mg, 48.1 μ mol, 43 %) suitable for X-ray diffraction. The composition of the crystals can be evaluated by ¹H NMR, showing the presence of a mixture of 1^{cc}, 1^{cf}, and 1^{cf}. This ratio evolves with the timing of the reaction and work-up. The crystals can, be dissolved in a mixture 1:1 (v:v) of toluene and MeCN and stirred for 24 h before being evaporated and dried under reduced pressure to yield only the 1^{cc} isomer as a yellow powder which can be recrystallized if necessary from hot toluene as small yellow needles. ¹H NMR (CD₂Cl₂, 300

MHz, δ /ppm): 7.16-7.03 (m), 7.16 (s, 1^{cc}), 6.69-6.64 (t), 6.56-6.31 (m), -3.97 (t, J = 14.8 Hz, 1^{cf}), -4.13 (t, J = 14.8 Hz, 1^{cf}). ¹³C {¹H} NMR (CD₂Cl₂, 75.4 MHz, δ /ppm): 127.00 (d, J_{CH} = 126 Hz, 1^{cf}), 121.83 (d, J_{CH} = 162 Hz), 116.39 (d, J_{CH} = 156 Hz), 111.12 (d, J_{CH} = 154 Hz), 108.97 (d, J_{CH} = 156 Hz), 108.40 (d, J_{CH} = 157 Hz, 1^{cf}). Elemental analysis: Calcd. for C₁₈H₁₈Yb: C, 53.09; H, 4.42. Found: C, 52.34; H, 4.44.

Preparation of bis(cyclononatetraenyl) samarium (2^{cc}). To a solid mixture of KCnt (44.0 mg, 281 μ mol, 2 eq.) and SmI₂ (54.3 mg, 134 μ mol, 1 eq.) prepared in a Schlenk tube, 6 mL of toluene was added followed by 5 drops of thf. The tube was cautiously protected with paraffin film and the obtained black slurry was stirred for two hours. After, the tube was depressurized and the mixture was stirred under static *vacuum* for a further 14 h before the white solid was filtered off and extracted with 8 mL of toluene. The obtained deep brown fractions were then gathered and concentrated before being cooled to -35°C. The title product was then obtained as small black crystals (28.8 mg, 74.9 μ mol, 56 %) suitable for X-ray diffraction. The composition of the crystals can be evaluated by ¹H NMR, showing the presence of a mixture of 2^{cc}, 2^{cf}, and 2^{cf}. This ratio evolves with the timing of the reaction and work-up. The crystals can be dissolved in a mixture 1:1 (v:v) of toluene and MeCN and stirred for 24 h before being evaporated and dried under reduced pressure to yield only the 2^{cc} isomer as an orange powder which can be recrystallized if necessary from hot toluene as small orange needles. ¹H NMR (toluene-d₈, 300 MHz, δ /ppm): 50.30 (s, 2^{cf}), 50.28 (s, 2^{cf}), 26.27 (s, 2^{cf}), 23.03 (m, 2^{cf}), 22.89 (s, 2^{cf}), 21.1 (m, 2^{cf}), 20.67 (s, 2^{cc}), 20.01 (m, 2^{cf}), 15.27 (s, 2^{cf}), 6.00 (s, 2^{cf}), -1.12 (t, 2^{cf}), -2.30 (t, 2^{cf}). The ¹³C NMR spectrum was not satisfactory due to too pronounced paramagnetism. Elemental analysis: Calcd. for C₁₈H₁₈Sm: C, 56.22; H, 4.68. Found: C, 55.86; H, 4.87.

Preparation of bis(cyclononatetraenyl) europium (5^{cc}). To a solid mixture of KCnt (34.4 mg, 220 μ mol, 2 eq.) and EuI₂ (54.3 mg, 134 μ mol, 1 eq.) prepared in a Schlenk tube, 6 mL of toluene was added followed by 5 drops of thf. The tube was cautiously protected with paraffin film and the obtained red slurry was stirred for two hours. After, the tube was depressurized and the mixture was stirred under static *vacuum* for a further 14 h before the solid was filtered off and extracted with 8 mL of toluene. The obtained red fractions were then gathered and concentrated before being cooled to -35°C. The title product was then obtained as small black crystals (26.5 mg, 68.6 μ mol, 62 %) suitable for X-ray diffraction. Because of the highly paramagnetic behavior of 5, the composition of the crystals could not be evaluated by ¹H NMR. The crystals have nevertheless been dissolved in a mixture 1:1 (v:v) of toluene and MeCN and stirred for 24 h before being evaporated and dried under reduced pressure to yield only the 5^{cc} isomer as a light orange powder, which can be recrystallized if necessary from hot toluene as small orange needles. The structure was similar to that already reported by Nakajima.³⁸

Preparation of bis(cyclononatetraenyl) thulium (6^{cc}). To a solid mixture of KCnt (12.1 mg, 77.6 μ mol, 2 eq.) and TmI₂(thf)₃ (24.8 mg, 38.8 μ mol, 1 eq.) prepared in a Schlenk tube 8 mL of toluene was added. The tube was cautiously protected with paraffin film and the obtained red slurry stirred for two hours at room temperature. The tube was then depressurized and the mixture was stirred under static *vacuum* for a further 14 h before the brown solid was filtered off and extracted with 8 mL of toluene. The obtained orange fractions were then gathered and concentrated before being cooled to -35°C. The title product was then obtained as a micro-crystalline purple-red powder (5.2 mg, 12.9 μ mol, 33 %). X-Ray suitable deep red crystals can be obtained from the recrystallization of this powder from toluene. The ¹H NMR in toluene-d₈, 300 MHz remains silent. Due to the relative thermal stability of 6^{cc}, the elemental analysis was not tried.

Isomerization of Ln(Cnt)₂ induced by addition of MeCN. To 0.5 mL of a saturated solution of Ln(Cnt)₂ in C₆D₆ (for 1) or in tol-d₈ (for 2) was added 0.1 mL of CD₃CN. A color shift was immediately observed. The reaction was then monitored by ¹H NMR. When only

one isomer was remaining in solution, solvents were removed under reduced pressure yielding a yellow solid (for **1**) or an orange solid (for **2**) which was re-dissolved in hot C₆D₆ and ¹H NMR spectroscopy was performed on the sample.

Theoretical calculations. Geometry optimizations were performed without any symmetry constraints using the scalar relativistic ZORA Hamiltonian at the DFT level with Orca program package.⁵¹ The SARC-TZVP adapted basis sets were used. The structures were checked to correspond to energy minima by calculating frequencies at the optimized geometries. Several functionals were used, *i.e.* PBE, PBE0, SSB-D, TPSSH and were associated to dispersion corrections in the framework proposed by Grimme.⁵² The electronic structure has been found to be qualitatively non-functional dependent. DFT Calculations were performed both in the gas phase and in toluene using the CPCM method but solvent effects did not change the global picture. Consequently, the detailed analyses, in the D_{3d} symmetry, described here were obtained at the SSB-D/TZ2P level based on TPSSH optimized geometries, using the ADF program package.⁵³

X-ray crystal structures. The structure resolution was accomplished using the SHELXS-97⁵⁴ and SHELXT⁵⁵ program and the refinement was done with the SHELXL⁵⁶ program. The structure solution and the refinement were achieved with the PLATON software.⁵⁷ Finally, pictures of the compound structure were obtained using the MERCURY software. During the refinement steps, all atoms- except hydrogen atoms- were refined anisotropically. The position of the hydrogen atoms was determined using residual electronic densities. Finally, in order to obtain a complete refinement, a weighting step followed by multiples loops of refinement was done. The crystal structures of KL₁•OEt₂, **1-4**, and **6** have been deposited in the CCDC with #1861445-1861450.

ASSOCIATED CONTENT

Supporting Information

Additional information on the syntheses, solution NMR data, UV-visible spectroscopy, computations and structural information are given in the supporting information. The Supporting Information is available free of charge on the ACS Publications website.

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