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Synthesis and characterization of a new class of divalent lanthanide complexes $\{[C_5H_4(CMe_2Ph)]_4Ln_2(\mu-X)_2\}[Li(DME)_3]_2$ (Ln = Sm, X = I; Ln = Yb, X = Cl; DME = dimethoxyethane)

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Abstract

Synthesis and characterization of a new class of ion-pairs complexes $[Ln_2(PhMe_2CC_5H_4)_4(\mu-X)_2][Li(DME)_3]_2$ (Ln = Sm, X = I; Ln = Yb, X = Cl) are described. The reaction of $SmI_2(THF)_2$ (THF = tetrahydrofuran) with two equivalents of $PhMe_2C-C_5H_4Li(DME)$ in THF affords the Sm(II) complex $[Sm_2(PhMe_2CC_5H_4)_4(\mu-I)_2][Li(DME)_3]_2$ (**1**), while the Na–K alloy reduction of $(PhMe_2CC_5H_4)_2YbCl$, which was formed in situ by the reaction of $YbCl_3$ and $PhMe_2CC_5H_4Li$ in 1:2 molar ratio, gives Yb(II) complex $[Yb_2(PhMe_2CC_5H_4)_4(\mu-Cl)_2][Li(DME)_3]_2$ (**2**). The single-crystal structural analyses of **1** and **2** reveal that they both comprise two $Li^+(DME)_3$ cations and a new class of dianion, $\{[C_5H_4(CMe_2Ph)]_4Ln_2(\mu-X)_2\}^{2-}$, in which two $[C_5H_4(CMe_2Ph)]_2Ln$ were bridged together by two iodine atoms for Sm and two chlorine atoms for Yb. The coordination geometry of the central metal is best described as a distorted tetrahedral.

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Keywords: Crystal structures; Cyclopentadienyl; Ion-pairs; Dianion

1. Introduction

The chemistry of organolanthanide in low oxidation state has achieved great progress [1,2]. Until now, a variety of organolanthanides in +2 state with cyclopentadienyl and non-cyclopentadienyl ligands have been synthesized. In view of the structures of these complexes, most of them have a neutral or an anionic structure in the solid state [1,3]. The complexes having discrete ion-pairs structures are rare [1b,1e,2e,4] and only one lanthanide(II) complex, $[Yb_6[C_5Me_4(SiMe_2-Bu^t)]_6I_8][Li(THF)_4]_2$, has been structurally characterized to comprise a dianionic structure, $\{Yb_6[C_5Me_4(SiMe_2-Bu^t)]_6I_8\}^{2-}$ dianion [4]. During our study on the synthesis of the homoleptic complex of lanthanide(II)

with the less sterically demanding cyclopentadienyl ligand $C_5H_4(CMe_2Ph)^-$, a new class of ion-pairs complexes $\{[C_5H_4(CMe_2Ph)]_4Ln_2(\mu-X)_2\}[Li(DME)_3]_2$ (Ln = Sm, X = I (**1**); Ln = Yb, X = Cl (**2**)) were obtained, in which the new dianion $\{[C_5H_4(CMe_2Ph)]_2Ln(\mu-X)\}_2$ with chlorine bridges for Yb and iodine bridges for Sm, respectively, in the binuclear species were constructed. To our best knowledge, this is the first dianion that has chlorine bridges or iodine bridges in Ln binuclear species. Here, we would like to report the results.

2. Experimental

All manipulations were performed under argon using the Schlenk technique. Toluene, hexane, and THF were purified by distilling from Na–benzophenone. $PhMe_2C-C_5H_4Li(DME)$ [5a], $SmI_2(THF)_2$ [6], and $YbCl_3$ [7] were prepared by the literature methods. Melting points were

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determined in sealed argon-filled capillaries and are uncorrected. The content of lithium was determined on a Hitachi 180-80 polarized Zeeman atomic absorption spectrophotometer. Lanthanide metal analysis was carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed on a Carlo Erba 1110 analyzer by direct combustion. The $^1\text{H-NMR}$ spectra were obtained on an INOVA-400 MHz apparatus and referenced to TMS.

2.1. Synthesis of $[\text{Sm}(\text{PhMe}_2\text{CC}_5\text{H}_4)_4(\mu\text{-I})_2][\text{Li}(\text{DME})_3]_2$ (**1**)

Into the stirred solution of $\text{SmI}_2(\text{THF})_2$ (1.92 g, 3.5 mmol) in 40 ml THF was added $\text{PhMe}_2\text{CC}_5\text{H}_4\text{Li}(\text{DME})$ (1.96 g, 7 mmol) in 15 ml DME. The mixture was stirred for 12 h at room temperature (r.t.). The dark-brown solution was concentrated under a vacuum to a volume of 10 ml, then cooled at -15°C . Black crystals obtained were recrystallized in DME–toluene to give 1.2 g (37%) of **1**. **1** was decomposed at 230°C . $^1\text{H-NMR}$ (THF-d^8 , 400 MHz, 25°C): δ 7.68–7.18 (m, 10H, C_6H_5), 6.50–6.26 (m, 8H, C_5H_4), 3.60 (s, 12H, DME), 3.44 (s, 18H, DME), 1.69 (s, 6H, $\text{C}(\text{CH}_3)_2$). Anal. Calc. for $\text{C}_{80}\text{H}_{120}\text{O}_{12}\text{I}_2\text{Li}_2\text{Sm}_2$: C, 52.11; H, 6.51; Li, 0.75; Sm, 16.32. Found: C, 51.64; H, 6.87; Li, 0.71; Sm, 15.96%.

2.2. Synthesis of $[\text{Yb}(\text{PhMe}_2\text{CC}_5\text{H}_4)_4(\mu\text{-Cl})_2][\text{Li}(\text{DME})_3]_2$ (**2**)

Addition of $\text{PhMe}_2\text{CC}_5\text{H}_4\text{Li}(\text{DME})$ (3.08 g, 11 mmol) in 25 ml DME to a suspension of YbCl_3 (1.54 g, 5.5 mmol) in 20 ml THF at r.t. yielded a red solution. After stirring for 5 h, into the resulting solution was added excessive Na–K alloy. The reaction mixture was stirred continually for 2 days. A purple solution that formed was filtered and concentrated to 15 ml and cooled to -15°C for crystallization. Dark-red crystals of **2** was obtained (3.42 g, 73%). m.p.: 187°C . $^1\text{H-NMR}$ (C_6D_6 , 400 MHz, 25°C): δ 7.60–7.22 (m, 10H, C_6H_5), 6.48–6.26 (m, 8H, C_5H_4), 3.32 (s, 12H, DME), 3.20 (s, 18H, DME), 1.51 (s, 6H, $\text{C}(\text{CH}_3)_2$). Anal. Calc. for $\text{C}_{80}\text{H}_{120}\text{O}_{12}\text{Cl}_2\text{Li}_2\text{Yb}_2$: C, 56.32; H, 7.04; Li, 0.81; Yb, 20.30. Found: C, 56.14; H, 6.87; Li, 0.79; Yb, 19.56%.

2.3. X-ray structure determination of **1** and **2**

A single crystal suitable for X-ray measurement was sealed in thin-walled glass capillaries under argon and mounted on a Rigaku Mercury CCD area detector with graphite-monochromated Mo– K_α radiation. The structure is solved by direct methods (for **1**), or heavy-atom Patterson methods (for **2**), and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using

the riding model. All calculations were performed using the crystal structure crystallographic software package.

3. Results and discussion

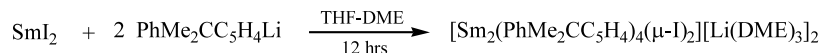
3.1. Synthesis of divalent samarium and ytterbium derivatives

Considering the fact that the $\text{PhMe}_2\text{CC}_5\text{H}_4^-$ used as π -ligand has not been found in the chemistry of organolanthanide complex, even it has been proved to be suitable for the preparation of the transition metal complexes [5], we tried to use the ligand to synthesize the corresponding lanthanide(II) complex. $\text{PhMe}_2\text{C-C}_5\text{H}_4\text{Li}(\text{DME})$ was prepared by the reaction of PhLi with 6,6-dimethylfulvene [5a]. The metathesis reaction of $\text{SmI}_2(\text{THF})_2$ with two equivalents of $\text{PhMe}_2\text{CC}_5\text{H}_4\text{Li}$ in THF at room temperature gives the dark-brown crystals after work up. The crystals were characterized by elemental analysis, $^1\text{H-NMR}$, and X-ray techniques. X-ray determination shows that the complex has a new class of ion-pairs structure, $[\text{Sm}_2(\text{PhMe}_2\text{CC}_5\text{H}_4)_4(\mu\text{-I})_2][\text{Li}(\text{DME})_3]_2$ (Scheme 1). The dianion, $[\text{Sm}_2(\text{PhMe}_2\text{CC}_5\text{H}_4)_4(\mu\text{-I})_2]^{2-}$, is different from that of $\{\text{Yb}_6[\text{C}_5\text{Me}_4(\text{SiMe}_2\text{-Bu}^t)]_6\text{I}_8\}^{2-}$ published [4]. The former is Ln binuclear species and the latter is Ln polynuclear one. However, these two dianions have iodine bridges. In order to see whether the iodine bridge is the special case in the dianion structure, we tested the Na–K alloy reduction reaction of $\text{Yb}(\text{PhMe}_2\text{CC}_5\text{H}_4)_2\text{Cl}$, which was formed in situ by the reaction of YbCl_3 and $\text{PhMe}_2\text{CC}_5\text{H}_4\text{Li}(\text{DME})$ in 1:2 molar ratio. After work up, the dianion complex $[\text{Yb}_2(\text{PhMe}_2\text{CC}_5\text{H}_4)_4(\mu\text{-Cl})_2][\text{Li}(\text{DME})_3]_2$ containing two chlorine bridges was also obtained in good yield (Scheme 2). The results indicated that chlorodianion can also be constructed in organolanthanide(II) complex.

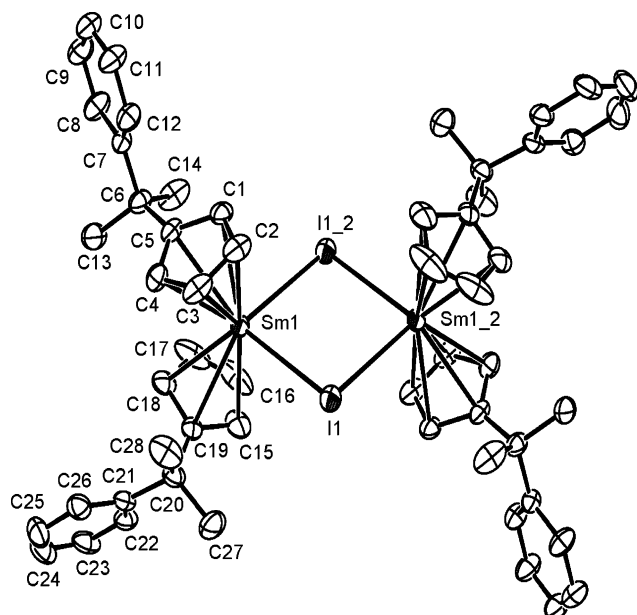
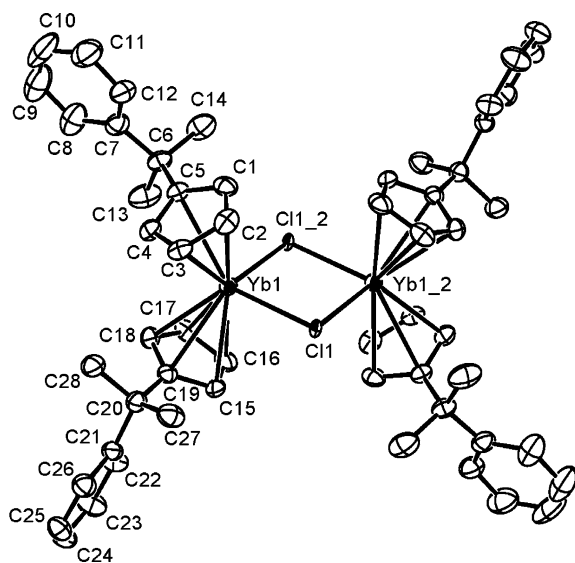
The two complexes are very air- and moisture-sensitive and soluble in donor solvents such as THF and DME; **1** is nearly insoluble in toluene, while **2** is only sparingly soluble in toluene.

3.2. Description of crystal structures of **1** and **2**

Crystals of compounds **1** and **2** suitable for X-ray diffraction determination were grown from a DME–toluene solution at -15°C . The dianion structures of **1** and **2** are presented in Figs. 1 and 2, respectively. The packing diagram of the unit cell in complex **1** indicated that the cations sit out in the lattice oriented toward the lanthanides (see Fig. 3). A partial bond lengths and angles of **1** and **2** are listed in Tables 1 and 2, respectively. Details of the structural analyses for **1** and **2** are given in Table 3.



Scheme 1.

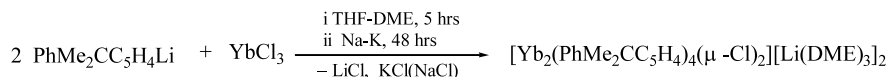
Fig. 1. ORTEP view of $[\text{Sm}_2(\text{PhMe}_2\text{CC}_5\text{H}_4)_4(\mu\text{-I})_2]^{2-}$ (**1**) drawn with 50% probability ellipsoids.Fig. 2. ORTEP view of $[\text{Yb}_2(\text{PhMe}_2\text{CC}_5\text{H}_4)_4(\mu\text{-Cl})_2]^{2-}$ (**2**) drawn with 50% probability ellipsoids.

Molecular structure of **1** and **2** comprise two $\text{Li}^+(\text{DME})_3$ cations and a $\{[\text{C}_5\text{H}_4(\text{CMe}_2\text{Ph})]_4\text{Ln}_2(\mu\text{-X})_2\}^{2-}$ dianion. **1** has two iodoanion, while **2** has two chloroanion. The dianion is the first example of an Ln binuclear species and also the first example with Ln–Cl bridges.

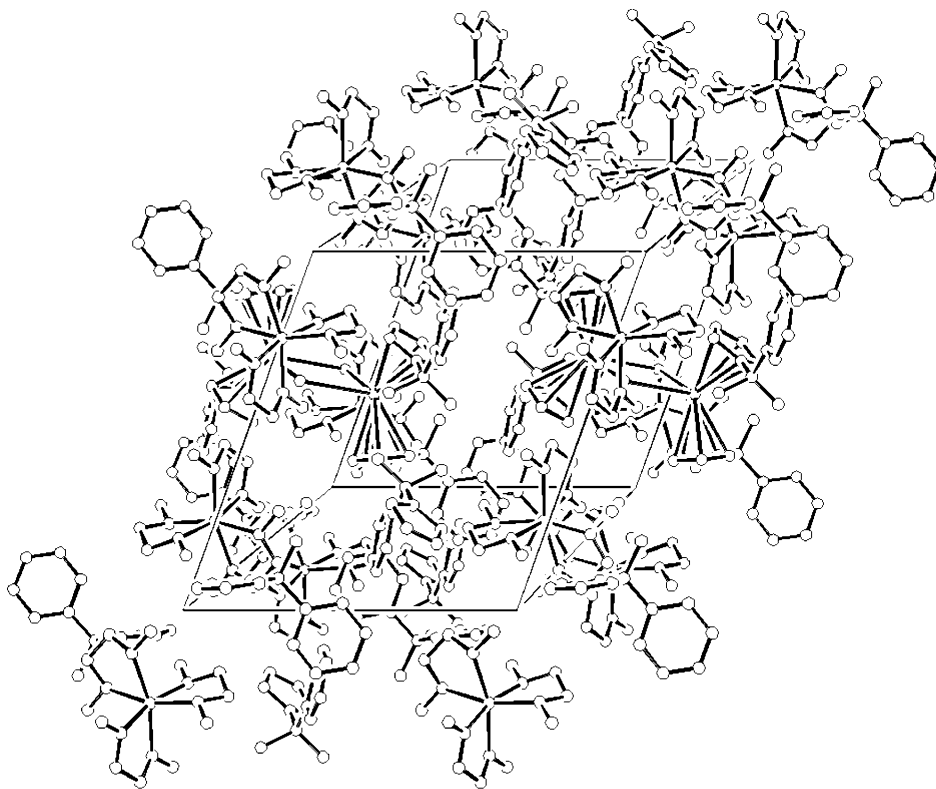
1 and **2** exhibit similar coordination geometries. The central metal is bound to two $\text{C}_5\text{H}_4\text{PhCMe}_2$ in an η^5 -manner and to two halogen atoms (I in Sm; Cl in Yb) to form the formal coordination number of 8. The geometry around the central metal is best described as a pseudo-distorted tetrahedral. The two halides and two lanthanide atoms are exactly coplanar as required by the crystallographic symmetry. Although this coordinated geometry around central metal is common in the trivalent disubstituted cyclopentadienyl lanthanide halides [8], this is the first example in the divalent lanthanide complexes. Each lithium atom in the cations is coordinated to three DME molecules and adopts a distorted octahedral geometry.

The average lanthanide–carbon (ring) bond lengths for **1** and **2** are 2.861 and 2.754 Å, and the Ln–Cent (ring) distances are 2.600 and 2.592 Å in **1**, and 2.476 and 2.466 Å in **2**, respectively. These values are comparable when the general difference of 0.13 Å between the ionic radii of Sm(II) and Yb(II) is considered [9]. The bond distances 2.600 and 2.592 Å in **1** can also be compared with the related value of 2.534 Å reported for $[(\text{C}_5\text{Me}_5)\text{Sm}(\mu\text{-I})(\text{THF})_2]_2$ [10], and the corresponding values in **2** are similar to the distances 2.414(9) Å in $[(\text{C}_5\text{Me}_5)\text{Yb}(\mu\text{-I})(\text{THF})_2]_2$ and 2.38(2) Å in $[(\text{C}_5\text{Me}_5)\text{Yb}(\mu\text{-I})(\text{DME})_2]_2$ [4] when the differences of the ion radii with different coordination number of Yb and Sm are considered. The samarium–iodide bond lengths of 3.281(1) and 3.310(1) Å are shorter than those in $[(\text{C}_5\text{Me}_5)\text{Sm}(\mu\text{-I})(\text{THF})_2]_2$ (3.356(2) and 3.459(2) Å) [10] if the difference of 0.05 Å between the ion radii of eight-coordinated Sm(II) and seven-coordinated Sm(II) is considered [9]. The values are slightly longer than the terminal Sm–I distances 3.216(1) Å in $[\text{C}_5\text{Me}_4\text{Si-Me}_2(\text{iPr}_2\text{-tacn})]\text{SmI}$ [11]. This is reasonable because in general, the terminal bond distance is shorter than that of bridging bond.

Rare examples of the chlorine-bridged lanthanides(II) in a dimeric form are known so far, and only three complexes, $[\text{Yb}(\mu\text{-Cl})(\eta^5\text{-C}_4\text{Me}_4\text{P})(\text{THF})_2]_2$ [12], $\{(\mu\text{-}\eta^1\text{:}\eta^5\text{-Me}_2\text{C}_4\text{H}_2\text{N})_2\text{Yb}(\mu\text{-Cl})[\text{Li}(\text{OEt}_2)]\}_2$, and



Scheme 2.

Fig. 3. Packing arrangement in the unit cell of **1**.Table 1
Selected bond distances (Å) and angles (°) for **1**

Bond distances (Å)	
Sm1–I1	3.281(1)
Sm1–I1_2	3.310(1)
Sm1–C1	2.859(6)
Sm1–C2	2.817(6)
Sm1–C3	2.827(6)
Sm1–C4	2.885(6)
Sm1–C5	2.919(5)
Sm1–C15	2.865(6)
Sm1–C16	2.818(8)
Sm1–C17	2.810(7)
Sm1–C18	2.849(6)
Sm1–C19	2.905(5)
Sm1–Cent1 [#]	2.600
Sm1–Cent2 ^{##}	2.592
Bond angles (°)	
I1–Sm1–I1_2	89.37
C5–C6–C7	111.8(5)
C19–C20–C21	108.8(5)
Sm1–I1–Sm1_2	90.53
I1–Sm1–Cent1	108.2
I1–Sm1–Cent2	106.8
Cent1–Sm1–Cent2	133.1

Table 2
Selected bond distances (Å) and angles (°) for **2**

Bond distances (Å)	
Yb1–Cl1	2.833(1)
Yb1–Cl1_2	2.838(1)
Yb1–C1	2.804(6)
Yb1–C2	2.729(6)
Yb1–C3	2.677(6)
Yb1–C4	2.744(6)
Yb1–C5	2.826(6)
Yb1–C15	2.768(6)
Yb1–C16	2.688(7)
Yb1–C17	2.690(6)
Yb1–C18	2.763(6)
Yb1–C19	2.819(6)
Yb1–Cent1 [#]	2.476
Yb1–Cent2 ^{##}	2.466
Bond angles (°)	
Cl1–Yb1–Cl1_2	89.37
C5–C6–C7	111.8(5)
C19–C20–C21	108.8(5)
Yb1–Cl1–Yb1_2	90.53
Cl1–Yb1–Cent1	108.2
Cl1–Yb1–Cent2	106.8
Cent1–Yb1–Cent2	133.1

{[(μ - η^1 : η^5 -Me₂C₄H₂N)₂Yb(μ -Cl)][Li(THF)(OEt₂)](μ-Cl)Li(OEt₂)}₂ [13], have been reported. The Yb–Cl bond distances 2.833(1) and 2.838(1) Å in **2** are similar to the distances 2.7724(8) and 2.7554(9) Å in [Yb(μ-

Cl)(η^5 -C₄Me₄P)(THF)₂]₂ [12] when the differences of the ion radii between eight-coordinated Yb(II) and seven-coordinated Yb(II) are considered, but are longer than those in {(μ - η^1 : η^5 -Me₂C₄H₂N)₂Yb(μ-

Table 3
Experimental data for the X-ray diffraction study of **1** and **2**

	1	2
Empirical formula	C ₈₀ H ₁₂₀ I ₂ Li ₂ O ₁₂ Sm ₂	C ₈₀ H ₁₂₀ Cl ₂ Li ₂ O ₁₂ Yb ₂
Formula weight	1842.31	1704.69
Temperature (K)	299.9	193.1
λ (Mo–K α) (Å)	0.7107	0.7107
Size (mm ³)	0.50 × 0.30 × 0.10	0.50 × 0.25 × 0.25
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$
Unit cell dimensions		
<i>a</i> (Å)	12.862(4)	12.1615(4)
<i>b</i> (Å)	14.019(4)	14.4829(5)
<i>c</i> (Å)	14.691(5)	14.5171(2)
α (°)	64.09(1)	71.02(1)
β (°)	70.12(2)	65.765(13)
γ (°)	68.09(2)	65.91(1)
<i>V</i> (Å ³)	2160.3(12)	2089.93(10)
<i>Z</i>	1	1
<i>D</i> _{calc} (Mg m ⁻³)	1.416	1.354
Absorption coefficient (mm ⁻¹)	2.116	2.342
<i>F</i> (0 0 0)	932.00	876.00
θ Range for collection (°)	3.0–27.5	5.9–27.5
Number of reflections collected	9423	9328
Number of independent reflections	7168	7297
Variables	502	502
<i>R</i> [<i>I</i> > 3 σ (<i>I</i>)]	0.0520	0.0480
<i>R</i> _{int}	0.027	0.054
<i>R</i> _w	0.1460	0.1160
GOF on <i>F</i> ²	1.097	1.097

Cl)[Li(OEt₂)]₂ (2.711(3) and 2.688(3) Å) and {[(μ - η^1 : η^5 -Me₂C₄H₂N)₂Yb(μ -Cl)]Li(THF)(OEt₂)] [(μ -Cl)Li(OEt₂)]₂ (2.682(3) and 2.744(2) Å) [13]. However, the values can be compared with the corresponding distances in the trivalent chlorine-bridged complexes [(C₅H₅)₂YbCl]₂ (2.639(3) and 2.645(3) Å) [14] and [(MeC₅H₄)₂YbCl]₂ (2.64 Å) [15] when the difference of 0.155 Å between the ion radii of Yb(II) and Yb(III) is considered [9].

4. Conclusion

We demonstrated the straightforward preparation of two new organolanthanide(II) derivatives containing the readily accessible C₅H₄CMe₂Ph⁻ ligand. The single-crystal structural analyses of the two lanthanocene complexes, {[C₅H₄(CMe₂Ph)]₄Ln₂(μ -X)₂}[Li(DME)₃]₂ (Ln = Sm, X = I; Ln = Yb, X = Cl), revealed that they are constructed in the dinuclear species with discrete ion-pairs structures.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 210007 and 210008 for complexes **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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