

JOM 22982

Studies on organolanthanide complexes

XLIV *. Synthesis of bis(2-methoxyethylcyclopentadienyl) divalent organolanthanides (Ln = Sm, Yb) and molecular structure of solvated $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Yb} \cdot \text{OC}_4\text{H}_8$

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(Received April 10, 1992)

Abstract

Bis(2-methoxyethylcyclopentadienyl) divalent solvent-free organolanthanide complexes $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Sm}$ (1) and $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Yb}$ (2) have been synthesized by the interaction of $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)\text{K}$ with LnI_2 (Ln = Sm, Yb). Recrystallization of 2 from THF produced the solvated single crystal $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Yb} \cdot \text{OC}_4\text{H}_8$ (3) which has the coordination number of nine, the highest yet reported for this class of compound. The two ring centroids of the 2-methoxyethylcyclopentadienyl rings, the two oxygen atoms of ether-substituted groups on the rings and the oxygen atom of the THF form a distorted trigonal bipyramid around the central ion of ytterbium.

1. Introduction

In recent years, the chemistry of divalent organolanthanide complexes has yielded particularly remarkable and striking results [1–8]. The major breakthrough in the chemistry of divalent organolanthanides in general and that of Sm^{II} in particular involved the use of the pentamethylcyclopentadienyl ligand, which confers stability, solubility, reactivity and crystallinity on organometallic compounds. Unlike cyclopentadienyl or methylcyclopentadienyl compounds the pentamethylcyclopentadienyl derivatives of Sm^{II} are soluble in aro-

matic and coordinating solvents. Moreover, $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_2$ is capable of unusual transformations of multiple-bonded substrates [6,9].

The useful properties bestowed by pentamethylcyclopentadiene may be attributed to its large size [10,11]. Any such group may be expected to offer similar properties. It was demonstrated [3] that the derivatives of Sm^{II} could also be prepared using bulky *t*-butyl substituted cyclopentadienyl as ligands. The effect of ligand C_5Me_5 and ${}^t\text{BuC}_5\text{H}_4$ is to decrease the acidity of divalent organolanthanide complexes. This effect might also be achieved by using more accessible cyclopentadienyl ligands with donor substituents possessing the properties of a Lewis base.

In the absence of any reports on the use of methoxyethylcyclopentadienyl ligands in the preparation of divalent organolanthanides, we thought it of

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* For Part XLIII, see ref. 26.

** Dedicated to professor Yao-Zeng Huang on the occasion of his 80th birthday.

interest to investigate the reaction between $(\text{CH}_3\text{-OCH}_2\text{CH}_2\text{C}_5\text{H}_4)\text{K}$ and LnI_2 . We describe the synthesis of derivatives of Sm^{II} and Yb^{II} with 2-methoxyethylcyclopentadienyl ligands and report the structural characterization of $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Yb} \cdot \text{OC}_4\text{H}_8$ (**3**).

2. Experimental details

Since the complexes described below are extremely sensitive to air and moisture, all operations were carried out under prepurified argon by Schlenk techniques or in a glovebox. All solvents were refluxed and distilled either over finely divided LiAlH_4 or over blue sodium benzophenone under argon immediately before use. Samarium and ytterbium diiodides were prepared by a published procedure [12]. $\text{K}(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)$ was prepared by the reaction of KH with $\text{MeOCH}_2\text{-CH}_2\text{C}_5\text{H}_5$ [13]. Mass spectra were recorded on a Finnigan 4021 spectrometer. ^1H NMR spectra were obtained on a Varian XL-200 (200 MHz) spectrometer referenced to external Me_4Si , and $\text{THF-}d_8$ was dried over Na/K alloy and degassed by freeze-thaw cycles on a vacuum line.

XPS data were recorded on an NP-1 spectrometer equipped with a $\text{Mg K}\alpha$ X-ray source. The rare earth metals were analyzed by direct complexometric titration with disodium EDTA. Carbon and hydrogen analyses were carried out by combustion in an aluminium tube. Melting points were determined in sealed argon filled capillaries and are uncorrected.

2.1. $(2\text{-MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Sm}$ (**1**)

Complex **1** was produced by the reaction of SmI_2 and $\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4\text{K}$ in the ratio 1/2 in THF. $\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4\text{K}$ (6 mmol) in 20 ml of THF was added to SmI_2 (3 mmol) in 40 ml of THF at room temperature. The solution turned purple and was stirred for 6 h. The Schlenk flask was centrifuged to give a clear THF solution, which was reduced in volume to about 12 ml. Addition of 30 ml of n-hexane gave a product, which was washed twice with 20 ml portions of hexane and then dried at 50°C in vacuum to afford a purple solid (**1**): 0.868 g; Yield 75%. m.p. 120°C (dec.) Anal. Found: C, 47.87; H, 5.77; Sm, 37.99. $\text{C}_{16}\text{H}_{22}\text{O}_2\text{Sm}$ calc.: C, 48.47; H, 5.55; Sm, 37.87%. MS (m/e): 398 $[\text{M}]^+$. χ_{M} (293 K) = 6.0939×10^{-6} (cgs), $\mu_{\text{eff}} = 3.76 \mu_{\text{B}}$.

2.2. $(2\text{-MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Yb}$ (**2**)

The procedure followed was similar to that for **1**. Complex **2** was obtained as an orange-red solid in 80%

yield. Anal. Found: C, 45.47; H, 5.35; Yb, 40.91. $\text{C}_{16}\text{H}_{22}\text{O}_2\text{Yb}$ calc.: C, 45.82, H, 5.25; Yb, 41.20%. MS (m/e): 420 $[\text{M}]^+$.

2.3. $(2\text{-MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Yb} \cdot \text{OC}_4\text{H}_8$ (**3**)

The orange-yellow crystal of complex **3** was obtained when recrystallizing **2** in THF at room temperature. M.p. $172\text{--}174^\circ\text{C}$. Anal. Found: C, 48.97; H, 6.08; Yb, 34.45. $\text{C}_{20}\text{H}_{30}\text{O}_3\text{Yb}$ calc.: C, 48.88; H, 6.11; Yb, 35.23%. ^1H NMR (δ , TMS, ppm): 5.34–5.47 (8H); 3.68–3.62 (8H); 3.37 (6H); 2.73–2.66 (4H); 1.82–1.77 (4H).

2.4. Crystal structure of $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Yb} \cdot \text{THF}$ (**3**)

An orange-yellow single crystal with approximate dimensions $0.2 \times 0.3 \times 0.1$ mm was sealed in a thin-walled glass capillary under argon. Intensity data were collected at 20°C with a Enraf-Nonius CAD4 diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation. 1934 unique reflections were measured in the range $0^\circ < 2\theta < 50^\circ$ with $0 \leq h \leq 16$, $0 \leq k \leq 12$, $-17 \leq l \leq 17$. The correction of LP and absorption was applied for the reflection data. The structure was solved by the Patterson method and by difference Fourier synthesis. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by the full-matrix least squares technique. Final R , R_w and S were 0.026, 0.037, 3.48 respectively, for 1621 observed reflections ($F^2 > 3\sigma(F^2)$). All calculations were performed on a Microvax II computer with *SDF* and *ORTEP* programs. Scattering factors were taken from the *International Tables for X-ray Crystallography* (1974). Table 1 lists the crystal data of **3**. Table 2 lists the final atomic positional and thermal parameters.

3. Results and discussion

3.1. Synthesis

Two equivalents of $\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4\text{K}$ and LnI_2 ($\text{Ln} = \text{Sm}, \text{Yb}$) react in THF at room temperature and deposit on addition of n-hexane the new divalent organolanthanide complexes, which are dried in vacuum to give the purple compound $(\text{MeOCH}_2\text{CH}_2\text{-C}_5\text{H}_4)_2\text{Sm}$ and the orange-red compound $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Yb}$ in good yields (eqn. (1)).

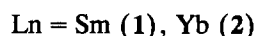
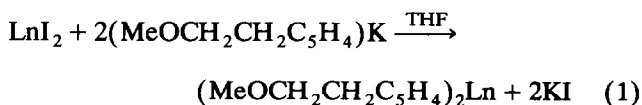
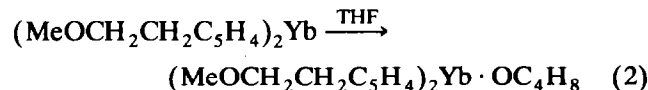


TABLE 1. Crystal data for 3

Compound	(MeOCH ₂ CH ₂ C ₅ H ₄) ₂ Yb·(THF)
Mol. wt.	491.5
Crystal size (mm)	0.2×0.3×0.1
Cell constants	
<i>a</i> (Å)	13.600(4)
<i>b</i> (Å)	10.486(2)
<i>c</i> (Å)	14.326(4)
β (°)	104.03(2)
<i>V</i> (Å ³)	1982.1
Scan range 2 θ (°)	0–50
Number of reflections	1934
Number of reflections for <i>I</i> > 3 σ (<i>I</i>)	1621
Space group	<i>C</i> 2/ <i>c</i>
<i>Z</i>	4
<i>D</i> (g cm ⁻³)	1.647
<i>R</i>	0.026
<i>R</i> _w	0.037
<i>F</i> (000)	976

In these complexes, two cyclopentadienyl rings and two oxygen atoms of ether substituted groups on the rings are coordinated with the central metal. Therefore, the coordination number of central metal for the two complexes is 8. The complex 3, with the coordination number of nine, can be introduced when recrystallizing complex 2 in THF (eqn. (2)).



We believe the coordination number of complex 3 to be the highest yet found for monomeric divalent organolanthanide complexes.

TABLE 3. ¹H NMR data for 3 (δ , TMS, ppm)

Compound ^a	Me–O–	–O–CH ₂ –	–CH ₂ –Cp'	Cp'	THF
Cp' ₂ Yb·THF	3.37 (s, 6H)	3.69–3.62 (t, 4H)	2.73–2.66 (t, 4H)	5.32 (s, 4H) 5.47 (s, 4H)	3.67–3.62 (t, 4H) 1.82–1.77 (t, 4H)
Cp'Na	3.05 (s, 3H)	3.28 (t, 2H)	2.50 (t, 2H)	5.18 (t, 2H) 5.31 (t, 2H)	
$\Delta\delta$ ^b	0.32	0.31	0.22	0.22 0.27	

^a Cp' = MeOCH₂CH₂C₅H₄. ^b $\Delta\delta = \delta(\text{Cp}'_2\text{Yb} \cdot \text{THF})\text{H} - \delta(\text{Cp}'\text{Na})\text{H}$.

TABLE 4. Mass spectral data for 1 and 2^a

Complex	[M] ⁺	[M – Cp' + MeO] ⁺	[M – Cp'] ⁺	[M – 2Cp' + MeO] ⁺	[M – 2Cp' + OCH ₂] ⁺	[Cp'H] ⁺	[MeOCH ₂] ⁺
Cp' ₂ Sm	398 (5.92)	306 (1.18)	275 (0.93)	183 (5.68)	182 (11.00)	124 (100)	45 (58.20)
Cp' ₂ Yb	420 (5.77)	328 (1.43)	297 (1.89)	205 (0.77)	204 (0.48)	124 (56.00)	45 (100)

^a Recorded at EI, *T* 50–300°C, EM = 1.3 kV, based on the largest abundance of isotopes.

TABLE 2. Positional parameters and estimated standard deviations

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Yb	0.000	0.15752(4)	0.250	2.687(7)
O(1)	0.5016(4)	0.2659(6)	0.5804(4)	5.4(1)
O(2)	0.000	0.3955(6)	0.250	4.4(2)
C(1)	0.6695(5)	0.3986(8)	0.6907(6)	4.6(2)
C(2)	0.7061(5)	0.3409(8)	0.7828(7)	5.0(2)
C(3)	0.6874(6)	0.4259(9)	0.8539(6)	5.2(2)
C(4)	0.6402(2)	0.5348(8)	0.8069(7)	5.2(2)
C(5)	0.6292(5)	0.5185(8)	0.7060(6)	5.1(2)
C(6)	0.6730(7)	0.338(1)	0.5957(7)	9.2(3)
C(7)	0.5781(7)	0.301(1)	0.5342(6)	7.5(3)
C(8)	0.4166(7)	0.200(1)	0.5207(7)	6.6(2)
C(9)	–0.0840(6)	0.4751(8)	0.2646(8)	7.0(2)
C(10)	–0.0564(6)	0.6091(9)	0.244(1)	8.3(3)

3.2. Spectral analysis

The results of XPS for complex 1 are similar to those of bis(2-methoxyethylcyclopentadienyl) lanthanide chlorides and reveal that the oxygen atoms are coordinated with the central metal [14]. In addition the binding energy of samarium in 1 is 1081.9 eV, which is between Sm⁰*E*_b (1081.4 eV) and Sm^{III}*E*_b (1082.5 eV). It also shows the samarium is divalent in 1. The susceptibility and magnetic moment of complex 1 were determined by NMR. They are χ_M (293 K) (6039 × 10⁻⁶ cgs) and μ_{eff} (3.76 μ_B), respectively which show no difference from those of the Sm^{II} in the literature [15]. The ¹H NMR data for 3 are listed in Table 3, and indicated intramolecular oxygen coordination of that oxygen and ytterbium, because all proton resonances were shifted to lower field compared with MeOCH₂–CH₂C₅H₄Na and lay between 0.2–0.3 ppm.

TABLE 5. Bond distances (Å)

Yb-O(1)	2.564(3)	C(1)-C(2)	1.427(6)
Yb-O(2)	2.496(4)	C(1)-C(5)	1.409(6)
Yb-C(1)	2.707(4)	C(1)-C(6)	1.515(7)
Yb-C(2)	2.728(4)	C(2)-C(3)	1.423(7)
Yb-C(3)	2.746(4)	C(3)-C(4)	1.400(7)
Yb-C(4)	2.759(4)	C(4)-C(5)	1.428(7)
Yb-C(5)	2.725(4)	C(6)-C(7)	1.427(7)
O(1)-C(7)	1.411(6)	C(9)-C(10)	1.502(6)
O(1)-C(8)	1.437(5)	C(10)-C(10*)	1.504(9)
O(2)-C(9)	1.469(4)	Yb-Cp1	2.440(4)

The mass spectral data for the two divalent organolanthanide complexes are listed in Table 4.

The two complexes all revealed a parent molecular ion $[M]^+$ and related fragments including $[M-Cp' + MeO]^+$ and $[M-Cp']^+$; no fragment greater than $[M]^+$ or equal to 72 or 71 was detected. The data indicate that the two complexes are solvent-free monomeric, and that Ln-Cp' bond is the first cleared giving very high relative intensity peaks of $[Cp'H]^+$.

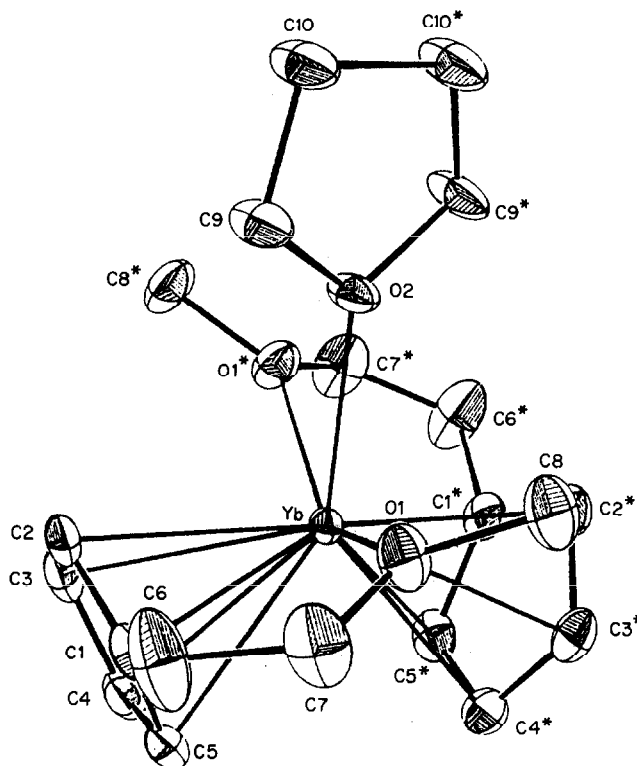


Fig. 1. Molecular structure of the complex $(MeOCH_2CH_2C_5H_4)_2Yb \cdot THF$ (3).

TABLE 6. Bond angles (°)

O(1)-Yb-O(1*)	143.5(2)	C(2)-Yb-C(4*)	131.5(1)
O(1)-Yb-O(2)	71.75(8)	C(2)-Yb-C(5)	49.5(1)
O(1)-Yb-C(1)	64.4(1)	C(2)-Yb-C(5*)	131.2(1)
O(1)-Yb-C(1*)	124.7(1)	C(3)-Yb-C(3*)	143.1(2)
O(1)-Yb-C(2)	85.2(1)	C(3)-Yb-C(4)	29.4(1)
O(1)-Yb-C(2*)	94.6(1)	C(3)-Yb-C(4*)	114.1(1)
O(1)-Yb-C(3)	113.1(1)	C(3)-Yb-C(5)	49.3(1)
O(1)-Yb-C(3*)	79.0(1)	C(3)-Yb-C(5*)	102.9(1)
O(1)-Yb-C(4)	110.2(1)	C(4)-Yb-C(4*)	86.1(3)
O(1)-Yb-C(4*)	96.5(1)	C(4)-Yb-C(5)	30.2(1)
O(1)-Yb-C(5)	80.7(1)	C(4)-Yb-C(5*)	82.8(1)
O(1)-Yb-C(5*)	125.8(1)	C(5)-Yb-C(5*)	94.7(2)
O(2)-Yb-C(1)	102.6(2)	C(7)-O(1)-C(8)	115.1(4)
O(2)-Yb-C(2)	89.6(2)	C(9)-O(2)-C(9*)	110.8(4)
O(2)-Yb-C(3)	108.5(1)	C(2)-C(1)-C(5)	107.3(4)
O(2)-Yb-C(4)	137.0(2)	C(2)-C(1)-C(6)	124.9(5)
O(2)-Yb-C(5)	132.6(2)	C(5)-C(1)-C(6)	127.8(5)
C(1)-Yb-C(1*)	154.9(3)	C(1)-C(2)-C(3)	108.3(4)
C(1)-Yb-C(2)	30.4(1)	C(2)-C(3)-C(4)	107.9(4)
C(1)-Yb-C(2*)	149.9(1)	C(3)-C(4)-C(5)	108.2(4)
C(1)-Yb-C(3)	50.0(1)	C(1)-C(5)-C(4)	108.3(4)
C(1)-Yb-C(3*)	120.4(1)	C(1)-C(6)-C(7)	116.5(4)
C(1)-Yb-C(4)	49.8(1)	O(1)-C(7)-C(6)	116.2(4)
C(1)-Yb-C(4*)	109.2(1)	O(2)-C(9)-C(10)	105.3(3)
C(1)-Yb-C(5)	30.1(1)	C(9)-C(10)-C(10*)	106.0(4)
C(1)-Yb-C(5*)	124.0(2)	O(1)-Yb-Cp1	97.6(1)
C(2)-Yb-C(2*)	179.3(3)	O(1)-Yb-Cp1*	98.0(1)
C(2)-Yb-C(3)	30.1(1)	O(2)-Yb-Cp1	115.8(2)
C(2)-Yb-C(3*)	150.4(1)	Cp1-Yb-Cp1*	128.4(2)
C(2)-Yb-C(4)	49.2(1)		

3.3. Molecular structure of $(MeOCH_2CH_2C_5H_4)_2Yb \cdot THF$ (3)

Figure 1 depicts the structure of the complex. The coordination geometry around the ytterbium ion can be described as an approximate trigonal bipyramid with two centroids of the 2-methoxyethylcyclopentadienyl rings. The two oxygen atoms of 2-methoxyethyl substitutes and the oxygen of THF form the apices of the trigonal bipyramid. The molecule shows C_2 symmetry about the Yb-O(2) axis. It means O(1), O(2) and O(1*) as well as O(2), cen(1) and cen(1*) are on the same plane. Complex 3 therefore has very high symmetry which is most unusual in low valent organolanthanide complexes. Selected bond lengths and angles are listed in Tables 5 and 6.

Angles are as follows: $cent(1)-Yb-cent(1)^* = 128.4^\circ$, $O(2)-Yb-cent(1) = O(2)-Yb-cent(1)^* = 115.8^\circ$, $O(1)-Yb-cent(1) = O(1)-Yb-cent(1)^* = 98.0^\circ$, $O(1)^*-Yb-cent(1) = O(1)^*-Yb-cent(1)^* = 97.6^\circ$, $O(1)-Yb-O(1)^* = 143.5(1)^\circ$. The $cent(1)-Yb-cent(1)^*$ angle is smaller than that of nonbridged low valent ytterbium complexes, such as $(C_5H_5)_2Yb(DME)$ (131°) [16], $[Me_3Si(C_5H_4)]_2Yb(THF)_2$ (133°) [17], $[t-C_4H_9-(C_5H_4)]_2Yb(THF)_2$ (134°) [5], $(C_5Me_5)_2Yb(NH_3)(THF)$ (135.1°) [18], $(C_5Me_5)_2Yb(py)_2$ (136.3°) [19], $(C_5Me_5)_2Yb(THF)$ (143.5°) [20], $(C_5Me_5)_2Yb$ (158°) [21] and

(t-C₄H₉C₅H₄)₂Sm(THF) (132.5°) [3]. It is obvious that the intramolecular coordination bonding of the oxygens of the ligands to the centre metal, with solvation, make the cyclopentadienyl rings closer to each other although steric repulsion is increased a little. However, the CpYbCp angle in **3** is closer to that in (C₅H₄CH₂CH₂CH₂C₅H₄)₂Yb · (THF) (127°) [4]. This is because the two cyclopentadienyl rings connected by the trimethylene bridged chain also increase the rigidity of complex **1**.

The ytterbium–carbon distances range from 2.707(4) to 2.764(4) Å and average 2.737 Å, which is comparable with those in (t-BuC₅H₄)₂Yb(THF)₂ (2.723 Å) [5], (C₅H₅)₂Yb(DME) (2.72 Å; 2.658 Å) [16,22], (C₅Me₅)₂-Yb(py)₂ (2.742 Å) [24] and [Me₃Si(C₅H₄)₂Yb(THF)₂ (2.75 Å) [24]. The Yb–O(THF) distance, 2.496(4) Å, is longer than that of all similar complexes, such as (t-BuC₅H₄)₂Yb(THF)₂ (2.430 Å) [5], (Me₃SiC₅H₄)₂-Yb(THF)₂ (2.410 Å) [25], (C₅Me₅)₂Yb(THF) (2.41 Å) [19], (C₅H₄CH₂CH₂CH₂C₅H₄)Yb(THF)₂ (2.42 Å) [4], (C₅Me₅)₂Yb(NH₃)(THF) (2.46 Å) [18] and (C₅H₅)₂-Yb(DME) [2.466(9) Å] [22]. This demonstrates that the Yb–O(THF) bond in complex **3** is weaker than that in the above complexes. That is why the THF in **3** is easy to remove in vacuum at room temperature.

Acknowledgment

The authors thank the National Science Foundation of China and Academia Sinica for financial support.

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