Organometallic Chemistry

Stereoselective formation of *ansa*-metallocenes in reactions of radical-anionic salts of acenaphthylene with lanthanide and calcium halides

I. L. Fedushkin,[a]★ Yu. A. Kurskii,[a] V. I. Nevodchikov,[a] M. N. Bochkarev,[a] S. Müchle,[b] and H. Schumann[b]

[a]G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences,
49 ul. Tropinina, 603600 Nizhny Novgorod, Russian Federation.
Fax: +7 (831 2) 66 1497. E-mail: igorfed@imoc.sinn.ru
[b]Institute of Inorganic and Analytical Chemistry, Technical University of Berlin,
135 Strasse des 17 Juni, D-10623 Berlin, Germany.*
Fax: (30) 31422168. E-mail: schumann@chem.tu-berlin.de

ansa-Metallocenes (η^5:η^5-$C_{24}H_{16}$)M(THF)$_2$ (M = Sm (**1**), Yb (**2**), Ca (**3**)) and (η^5:η^5-$C_{24}H_{16}$)MI(THF) (M = Dy (**8**), Er (**9**), Tm (**10**), Lu (**11**)) were prepared in 50—90% yields by the *in situ* reactions of two equivalents of potassium acenaphthylenide $K^+C_{12}H_8^-$ with MI_2 or MI_3, respectively. Complexes **2** and **3** were also obtained by direct reduction of acenaphthylene with ytterbium and calcium naphthalenides, respectively. An ESR signal of the acenaphthylene radical anion, which was observed upon dissolution of compound **2** in THF, indicates that the $[C_{24}H_{16}]^{2-}$ *ansa*-ligand dissociated into two $[C_{12}H_8]^{\bullet-}$ radical anions. Hydrolysis of complex **2** in benzene afforded 1,1´,3,3´-tetrahydro-3,3´-biacenaphthylene (**4**) and 3,3´,4,4´-tetrahydro-3,3´-biacenaphthylene (**5**). The reaction of complex **2** with $ZrCl_4$ and the reaction of compound **3** with Me_3SiCl proceeded with the cleavage of the C—C bond between two acenaphthylene fragments of the $[C_{24}H_{16}]^{2-}$ *ansa*-ligand to produce (η^2-$C_{12}H_8$)$ZrCl_2$(THF)$_3$ (**6**) and bis(trimethylsilyl)acenaphthene $(Me_3Si)_2C_{12}H_8$ (**7**), respectively. Compounds **1—3**, **6**, **7**, and **11** were characterized by ^{1}H and ^{13}C NMR spectroscopy. The temperature dependence of the ^{1}H NMR spectrum of compound **11** in tetrahydrofuran is indicative of the dynamic exchange of the solvent molecules in the coordination sphere of the Lu atom. After cooling of the solution to 210 K, the dynamic process was terminated as evidenced by the nonequivalence of the ^{1}H signals of two acenaphthylene fragments. According to the X-ray diffraction data for complex **11**, dimerization of two acenaphthylene radical anions at the Lu atom gave rise to the *rac*-*ansa*-metallocene structure. In compound **11**, the Lu atom is η^5-coordinated by two five-membered rings of the acenaphthylene ligands and also by the I atom and the THF molecule. The coordination environment about the Lu atom is a distorted tetrahedron. The average distance between the lutetium atom and the carbon atoms of the five-membered rings is 2.623 Å.

Key words: lanthanides, calcium, acenaphthylene, radical anions, recombination, *ansa*-metallocenes.

In recent years, metallocenes have been studied extensively because these compounds show promise as catalysts of the industrial polymer synthesis, and, particularly, of α-olefin polymerization.[1] In these processes, 14-electron metallocene alkyl cationic complexes of Group IV elements or isoelectronic neutral complexes of Group III metals and lanthanides act as catalytically active species. The processes with the use of achiral metallocenes gave

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* Institut für anorganische und analytische Chemie der technischen Universität Berlin, Straße des 17 Juni, 135, D-10623 Berlin, BRD.

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rise to atactic poly(α-olefins). In stereospecific polymerizations yielding isotactic polymers, C_2-symmetrical *ansa*-metallocenes are most advantageously employed. Previously,[2] the latter compounds have been synthesized by reductive coupling of various 6,6´-di- and 6-substituted fulvenes using lanthanide metals (Sm or Yb), Ca metal, or Ti and Zr dihalides. However, coupling of fulvenes in these reactions proceeded nonselectively to give both the *rac* and *meso* isomers of metallocenes. We expected that incorporation of fulvene into a fused aromatic system would provide the selectivity of coupling. Acenaphthylene is a nonalternant aromatic hydrocarbon whose resonance structures contain the fulvene fragment. Recently,[3] we have performed stereoselective coupling of acenaphthylene ($C_{12}H_8$) by reducing it with Sm or Yb metal to obtain C_2-symmetrical *ansa*-lanthanocenes (η^5:η^5-$C_{24}H_{16}$)M(THF)$_2$ (M = Yb or Sm).

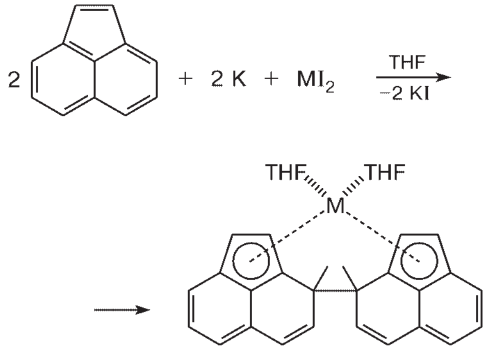
The aim of the present study was to examine the reactions of lanthanide triiodides with potassium acenaphthylenide giving rise to *ansa*-lanthanocenes (η^5:η^5-$C_{24}H_{16}$)MI(THF), to develop new procedures for the synthesis of (η^5:η^5-$C_{24}H_{16}$)M(THF)$_2$ (M = Yb, Sm, or Ca), and to reveal the factors responsible for the stereoselectivity of acenaphthylene coupling.

Results and Discussion

The radical anions of acenaphthylene, which are generated by its reduction with Sm or Yb metals, undergo selective coupling to give C_2-symmetrical *ansa*-lanthanocenes.[3] This coupling does not take place upon reduction of $C_{12}H_8$ with lithium, sodium, or potassium metals; instead, these reactions afford radical-anionic salts of these metals, which exist in solutions as solvent-separated ion pairs.[4] Reduction of naphthalene with alkali metals also gives rise to radical-anionic salts. However, the reactions of the latter with rare-earth halides yield exclusively lanthanide complexes with the naphthalene dianion.[5] To examine the possibility of the preparation of *ansa*-metallocenes (η^5:η^5-$C_{24}H_{16}$)M(THF)$_2$ by the exchange reactions, we studied the reactions of Sm, Yb, and Ca diiodides with potassium acenaphthylenide $K^+C_{12}H_8^-$ in tetrahydrofuran.

The *in situ* reactions of MI$_2$ (M = Sm, Yb, or Ca) with $K^+C_{12}H_8^-$ in THF afforded the target complexes (η^5:η^5-$C_{24}H_{16}$)M(THF)$_2$ (M = Sm (**1**), Yb (**2**), or Ca (**3**)) in 80—90% yields (Scheme 1).

Scheme 1

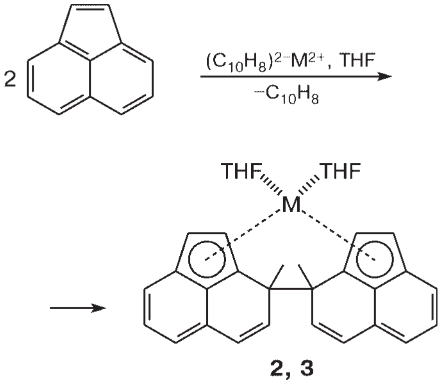


1—3

M = Sm (**1**), Yb (**2**), Ca (**3**)

According to the IR and NMR spectroscopic data, the Sm and Yb complexes thus obtained are identical with those prepared by direct reduction of $C_{12}H_8$ with Sm and Yb metals.[3] Compound **3** was synthesized for the first time and isolated as yellow crystals. Unfortunately, the poor quality of the crystals did not allow us to study compound **3** by X-ray diffraction analysis. The IR spectrum of complex **3** is identical with those of structurally characterized compounds **1** and **2**, which indicates that their molecular structures have close parameters. The ^{1}H NMR spectrum of compound **3** in THF-d$_8$ (Fig. 1, *a*), like that of its analog **2**, had eight signals for the protons of the $C_{24}H_{16}$ ligand, which were unambiguously assigned based on the ^{1}H—^{1}H NMR correlation experiments. The ^{1}H NMR spectrum remained virtually unchanged upon dissolution of complex **3** in benzene (C_6D_6). Compounds **2** and **3** were also obtained in high yields by reducing $C_{12}H_8$ with naphthalenides $(C_{10}H_8)^{2-}M^{2+}(THF)_2$ (M = Yb or Ca) (Scheme 2).

Scheme 2



2, 3

M = Yb (**2**), Ca (**3**)

Unlike the reactions of $C_{12}H_8$ with Yb and Ca metals, the reactions with their naphthalenides proceeded under substantially milder conditions due to high reductive ability of the naphthalene dianion.

When reduced with Sm, Yb, or Ca metals or their naphthalenides as well as under the conditions of the exchange reactions of MI$_2$ (M = Sm, Yb, or Ca) with

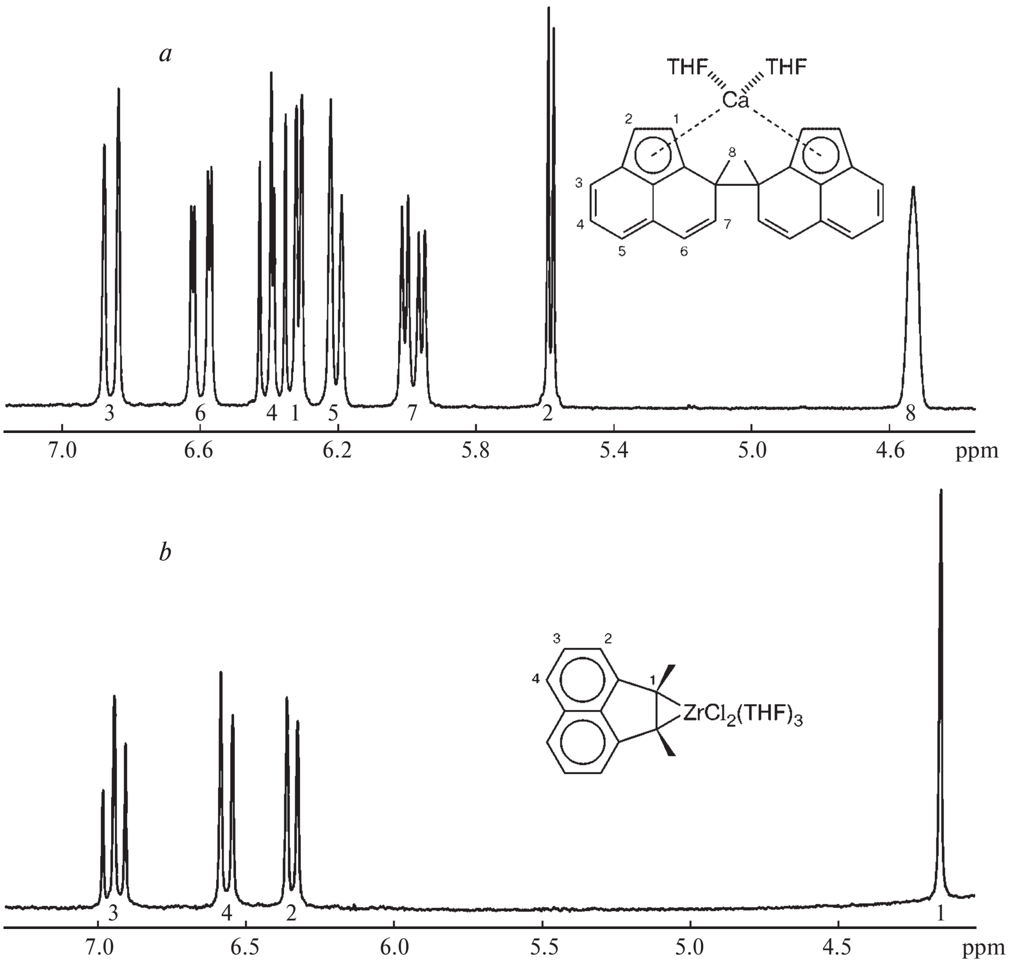
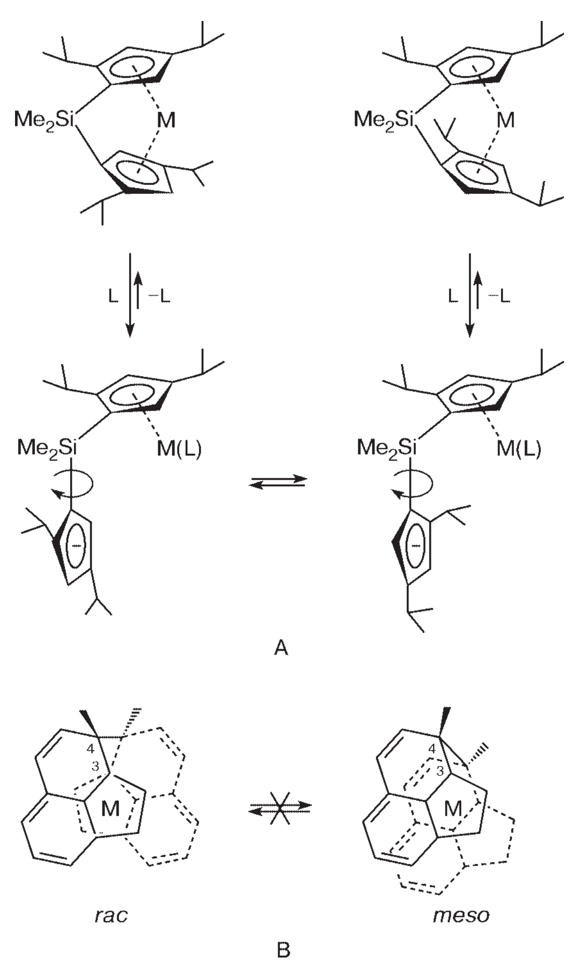


Fig. 1. ^{1}H NMR spectra of complexes **3** (*a*) and **6** (*b*) (200 MHz, THF-d_8, 295 K). The region of the signals of tetrahydrofuran is omitted.

$K^+C_{12}H_8^-$, acenaphthylene underwent strictly selective coupling to give C_2-symmetrical *rac*-*ansa*-metallocenes (η^5:η^5-$C_{24}H_{16}$)M(THF)$_2$. It has been demonstrated[6] that many *ansa*-lanthanocenes can undergo epimerization (*meso*-*rac* interconversion) to form thermodynamically more stable diastereomers. This process requires the cleavage of the metal—cyclopentadienyl bond and recoordination of the Cp ligand to the metal atom *via* its opposite side (Scheme 3, A). In the case of *ansa*-metallocenes **1—3**, this transformation does not occur because the rotation about the C(3)—C(4) bond is impossible (see Scheme 3, B).

The studies of the *meso*-*rac* interconversions, which take place in the exchange reactions used for the synthesis of *ansa*-lanthanocenes (for example, $Me_2Si[C_5H_2$-2,4-$(CHMe_2)_2]_2ScX$, where X = Cl or All) or occur upon dissolution of their pure diastereomers in various solvents, demonstrated[7] that epimerization is controlled by thermodynamical rather than by kinetic factors. Thus, dissolution of pure *rac*- or *meso*-*ansa*-lanthanocenes in various solvents (THF, toluene, Et_2O, *etc.*) was accompanied by interconversions, with the *rac*-forms of *ansa*-lanthanocenes always predominating, *i.e.*, the *rac*-forms are thermodynamically more stable than the *meso*-forms.[7] However, it should be noted that in the course of epimerization of the pure *rac* or *meso* diastereomers, the interconversions proceeded only to a small extent. We suggested that the coupling of the acenaphthylene radical anions at divalent metal cations proceeds stereoselectively because the $[C_{24}H_{16}]^{2-}$ *ansa*-ligand can dissociate in solutions to form two acenaphthylene radical anions, $[C_{12}H_8]^{\bullet-}$, which again recombine to give the thermodynamically more stable *rac* diastereomer. This suggestion was confirmed by the results of ESR studies of complexes **2** and **3** in solutions. The ESR spectrum of a solution of complex **2** in THF has a well-resolved signal of the acenaphthylene radical anion $C_{12}H_8^{\bullet-}$ (a_H = 0.06, 0.30, 0.54, and 0.64 mT; g = 2.0027) whose parameters are very close to those of lithium acenaphthylenide.[4] Apparently, dissociation proceeded in steps. At the first stage, the complex was ionized to form the solvated $[M(THF)_6]^{2+}$ cation and the $[C_{24}H_{16}]^{2-}$ dianion, which subsequently dissociated

Scheme 3

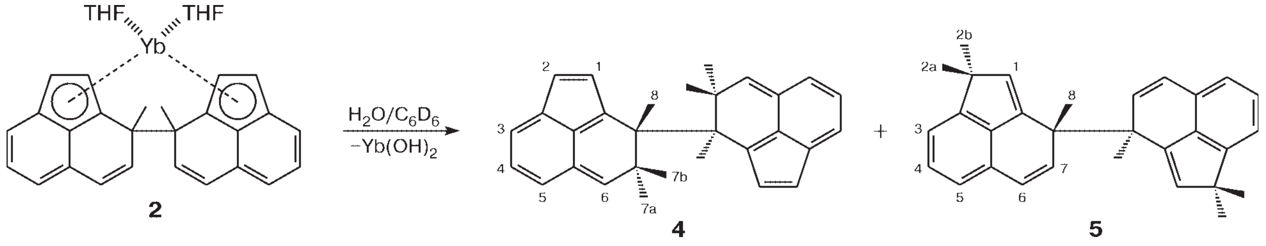


into two $[C_{12}H_8]^{\bullet-}$ radical anions. In the ^{1}H NMR spectra of complexes **2** and **3** in THF-d$_8$, neither paramagnetic shifts nor broadening of the signals for the protons of the ligands were observed. Hence, it can be stated that the degree of dissociation in THF is very low. In addition, the signals for the protons of the five-membered rings in the spectrum of **2** are split on the ^{171}Yb nucleus (I = 1/2, 14%), which indicates that the *ansa*-metallocene structure persists in the solution. The intensity of the ESR signal increases by a factor of several tens upon dissolution of complex **2** in Py. The presence of paramagnetic species in a pyridine solution of **2** is in evidence even in the ^{1}H NMR spectrum. This is manifested in substantial broadening of all signals. In a tetrahydrofuran solution of compound **3**, the acenaphthylene radical anion was not observed by the ESR method. However, this radical anion is easily observable in a solution in Py. Apparently, the degree of dissociation of the *ansa*-metallocene structure into the radical anions is determined by the energy of solvation of the cation by the solvent. Thus, the degree of dissociation in pyridine, which has a better solvating ability than THF, is much higher. In addition, although the ionic radius of Yb^{II} is very close to that of Ca^{II}, different atomic orbitals of these metal atoms are involved in the complex formation with the solvent resulting in the higher energy of solvation and, as a consequence, the higher degree of dissociation in the case of the Yb complex compared to the Ca complex. As the temperature was decreased to 200 K, the intensity of the ESR signal of complex **2** in THF increased by a factor of approximately 50. To our knowledge, reversible dissociation of the *ansa*-metallocene structure into radical anions was observed for the first time.

The results of the present study suggest that the chemical reactions of complexes **2** and **3** can proceed either with retention or with the cleavage of the C—C bond between two acenaphthylene fragments. We found that hydrolysis of complex **2** in benzene proceeded with retention of the C—C bond between the acenaphthylene fragments. The ^{1}H NMR spectroscopic data provide evidence that the latter reaction afforded two isomers of tetrahydrobiacenaphthylene **4** and **5** in a ratio of 3 : 1 (Scheme 4).

According to the data from ^{1}H NMR spectroscopy of the overall reaction mixture, the formation of the "mixed" isomer cannot be excluded (both the five- and six-membered rings are protonated). However, the amount of the latter was at most 3—4% of the total amount of complexes **4** and **5**. The fact that compound **4** was obtained as the major hydrolysis product was unexpected because we believed that the five-membered rings of the initial complex on which the negative charges are located would be protonated first. Conceivably, the observed ratio between **4** and **5** and the absence of noticeable amounts of other isomers are attributed to prototropic rearrangements occurring in the course of both hydrolysis and isolation of

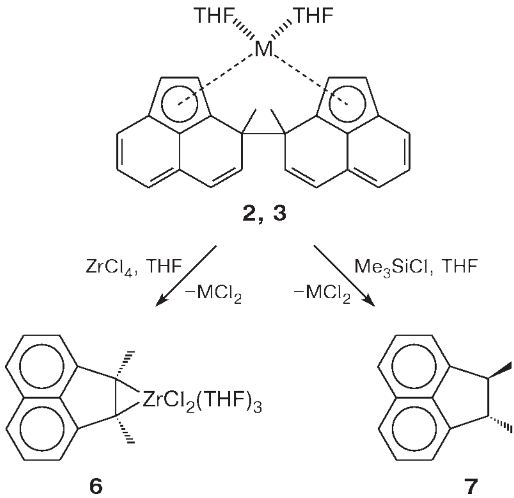
Scheme 4



products **4** and **5**. Recrystallization of the hydrolysis products from Et_2O allowed us to obtain compound **4** in the crystalline state. The ^1H NMR spectrum of the hydrolysis products in C_6D_6 has two complex multiplets at δ 4.39 and 4.16 belonging to the methine H(8) protons with the integral intensity ratio of 1 : 3. The $^1H—^1H$ NMR experiments demonstrated that the resonance signal at δ 4.16 correlates with two doublets of doublets at δ 2.75 (J = 17.8 and 2.6 Hz) and 2.47 (J = 17.8 and 5.8 Hz) corresponding to the H(7a) and H(7b) protons in compound **4**. The signal at δ 4.39 correlates with two doublets of doublets at δ 6.27 (J = 10.2 and 3.8 Hz) and 5.35 (J = 10.2 and 1.8 Hz) corresponding to the H(6) and H(7) protons in compound **5**. The signals observed in the latter case are close to those observed for complex **3** (δ 6.60, J = 9.6 and 2.0 Hz; δ 5.98, J = 9.6 and 3.4 Hz; a singlet at δ 4.54), but they are somewhat shifted downfield. The signals for the remaining protons at the double bonds fall within a narrow region (δ 7.30—7.00), which makes their unambiguous assignment difficult.

The reactions of compounds **2** and **3** with $ZrCl_4$ or Me_3SiCl proceeded with the cleavage of the C—C bond between two acenaphthylene fragments. The reaction of compound **2** with $ZrCl_4$ in THF afforded $(\eta^2\text{-}C_{12}H_8)ZrCl_2(THF)_3$ (**6**), which was isolated as dark-green crystals by crystallization from THF (Scheme 5).

Scheme 5



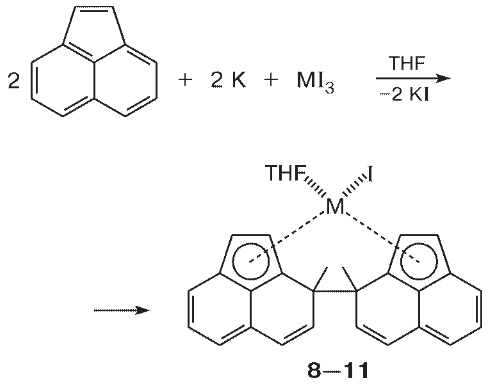
M = Yb (**2**), Ca (**3**)

Unlike the ^1H NMR spectrum of complex **2**, the spectrum of compound **6** has only four signals for the protons of the acenaphthylene ligand, *i.e.*, the *ansa*-metallocene structure underwent substantial transformations in the course of the reaction. The protons of the six-membered rings have standard chemical shifts, whereas the signals for the protons of the five-membered ring are substantially shifted upfield (see Fig. 1, *b*), which, apparently, indicates that the Zr atom in compound **6** is bound only to two C atoms. The reaction of compound **3** with two equivalents of Me_3SiCl in THF also readily proceeded to give 1,2-bis(trimetylsilyl)acenaphthene $(Me_3Si)_2C_{12}H_8$ (**7**) (see Scheme 5). After isolation of compounds **6** and **7**, sublimation of the residues always afforded free acenaphthylene in yields of higher than 90%.

Taking into account the selectivity of coupling of the acenaphthylene radical anions at divalent metal cations to form *ansa*-metallocenes, we examined the possibility of this process occurring at trivalent lanthanide cations. When we started our study, data on the transformations of this type (dimerization of the fulvene radical anions) occurring in the coordination spheres of trivalent lanthanides were lacking in the literature.

Neither activation with iodine nor the presence of the corresponding triiodides initiated the reactions of later lanthanide metals (Dy, Er, Tm, and Lu) with acenaphthylene. Under analogous conditions, La and Nd gave insoluble products, which we failed to unambiguously identify. However, we found that in the case of the end members of the lanthanide series, the target products were formed in the exchange reactions of the corresponding triiodides MI_3 with $K^+C_{12}H_8^-$. The *in situ* reactions of MI_3 with two equivalents of K metal and acenaphthylene in THF afforded *ansa*-lanthanocenes $(\eta^5{:}\eta^5\text{-}C_{24}H_{16})MI(THF)$ (M = Dy (**8**), Er (**9**), Tm (**10**), or Lu (**11**)) in 50—70% yields (Scheme 6).

Scheme 6



M = Dy (**8**), Er (**9**), Tm (**10**), Lu (**11**)

Compounds **8—11** have the identical IR spectra, which differ only slightly from the spectra of complexes **1—3**. The Dy, Er, and Tm cations possess high intrinsic magnetic moments due to which it is difficult to obtain informative NMR spectra for compounds **8—10**.

According to the results of X-ray diffraction analysis of complex **11**, dimerization of two acenaphthylene radical anions at the Lu atom gave rise to the *rac*-*ansa*-metallocene structure. Compound **11** crystallized from THF in the centrosymmetrical space group $P2_1/c$. The unit cell contains four enantiomeric pairs (a racemic mixture) of the molecules. Two crystallographically independent molecules belonging to an enantiomeric pair are shown in Fig. 2. The Lu atom is η^5-coordinated by two five-membered rings of the acenaphthylene ligands as well as by the I atom and the THF molecule, which slightly deviate from the bisector plane of the Cp_{centr}—Lu—Cp_{centr} angle (Cp_{centr} is the center of the five-membered ring). Therefore, the coordination environment about the Lu atom is a distorted tetrahedron. Taking into account the difference in the ionic radii of Yb^{II} (1.14 Å) and Lu^{III} (0.977 Å),[8] the average Lu—C(C(101)—C(105)) and Lu—C(C(113)—C(117)) distances (2.624 and 2.622 Å, respectively) are somewhat larger than that in the ytterbium(II) complex *rac*-(η^5:η^5-$C_{24}H_{16}$)Yb(THF)$_2$ (2.72 Å).[3] The Cp(1)—Lu—Cp(2) angle (123.8°) is substantially smaller than those in the lanthanide complexes with the noncoordinated cyclopentadienyl ligands ($Cp_2LnX(THF)$,[9] 130—140°) and in less strained *ansa*-bis(indenyl)lanthanocenes containing the —$(CH_2CH_2)_2O$ unit between two indenyl fragments, *viz.*, $[O(CH_2CH_2C_9H_6)_2]LnCl(THF)$ [10] (Ln = Nd, 131.4°; Gd, 132.6°; Ho, 132.6°), but is close to the corresponding values in the ethylene bisindenyl complexes (*meso*-[(η^5-C_9H_6)$_2$(CH_2)$_2$-1]YbN(SiMe$_3$)$_2$ [11] (122.0°) *rac*-[(η^5-C_9H_6)$_2$(CH_2)$_2$-1]Yb(THF)$_2$ (117.8°), and *rac*-[(η^5-$C_9H_4Me_2$-4,7)$_2$(CH_2)$_2$-1]Yb(THF)$_2$ [12] (118.8°) and in the acenaphthylene complex *rac*-(η^5:η^5-$C_{24}H_{16}$)Yb(THF)$_2$ [3] (119.2°). The C—C bond lengths in the five-membered ring are equalized, whereas alternation of the double and single C—C bonds is observed in the six-membered rings (see Fig. 2).

The ^1H NMR spectrum of complex **11** in tetrahydrofuran (THF-d_8) is analogous to the spectra of compounds **2** and **3** with the only difference that the signals for the protons of the five-membered ring of the acenaphthylene

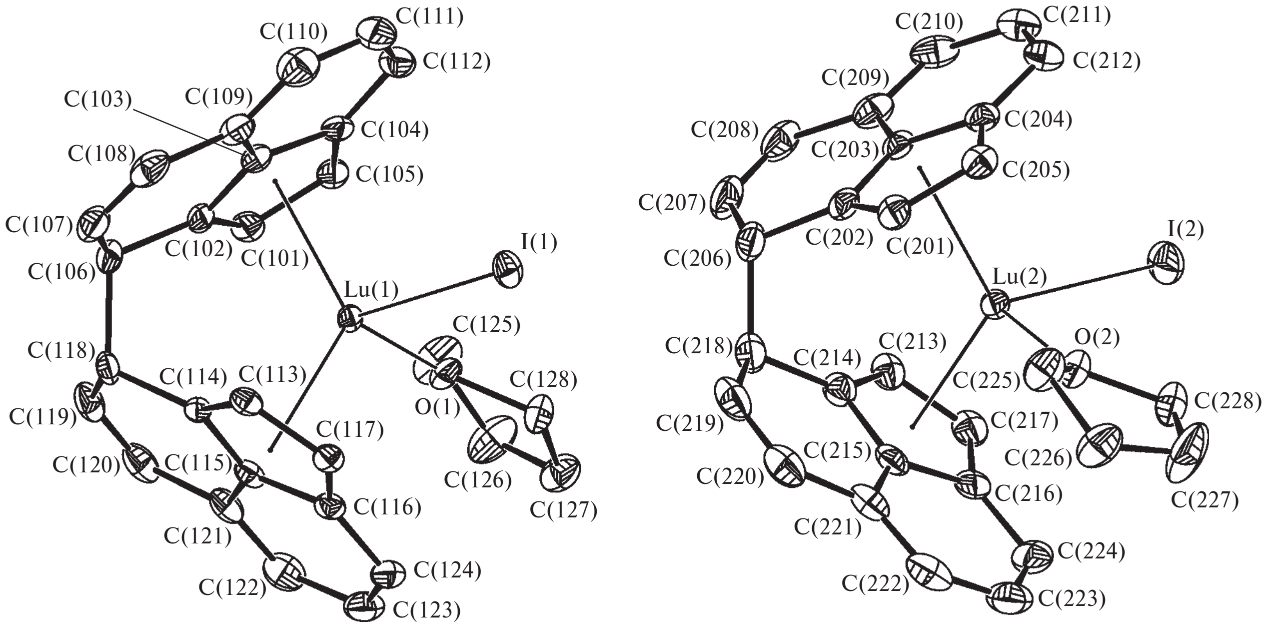


Fig. 2. Two crystallographically independent molecules of the complex (η^5:η^5-$C_{24}H_{16}$)LuI(THF) (**11**) (the thermal ellipsoids with the 50% probability). The hydrogen atoms are omitted.
Selected bond lengths (*d*) and bond angles (ω):

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Lu(1)—I(1)	2.9072(4)	Lu(1)—C(117)	2.634(5)	C(108)—C(109)	1.465(8)	Cp(3)—Lu(2)—Cp(4)	121.90(9)
Lu(1)—O(1)	2.272(4)	C(101)—C(102)	1.422(8)	C(109)—C(103)	1.413(8)	Cp(1)—Lu(1)—Cp(2)	123.81(9)
Lu(1)—C(101)	2.585(5)	C(102)—C(103)	1.428(7)	C(109)—C(110)	1.390(8)	I(2)—Lu(2)—Cp(3)	112.94(6)
Lu(1)—C(102)	2.591(5)	C(103)—C(104)	1.418(7)	C(110)—C(111)	1.418(9)	I(2)—Lu(2)—Cp(4)	110.18(6)
Lu(1)—C(103)	2.638(5)	C(104)—C(105)	1.415(8)	C(111)—C(112)	1.375(9)	O(2)—Lu(2)—Cp(3)	107.02(11)
Lu(1)—C(104)	2.686(5)	C(105)—C(101)	1.445(7)	C(112)—C(104)	1.437(8)	O(2)—Lu(2)—Cp(4)	106.75(12)
Lu(1)—C(105)	2.619(5)	C(102)—C(106)	1.525(7)	Lu(1)—Cp(1)	2.327(3)	I(1)—Lu(1)—Cp(1)	110.27(6)
Lu(1)—C(113)	2.577(5)	C(106)—C(118)	1.565(7)	Lu(1)—Cp(2)	2.324(2)	I(1)—Lu(1)—Cp(2)	110.10(6)
Lu(1)—C(114)	2.586(5)	C(106)—C(107)	1.515(8)	Lu(2)—Cp(3)	2.328(3)	O(1)—Lu(1)—Cp(1)	108.43(12)
Lu(1)—C(115)	2.618(5)	C(107)—C(108)	1.352(9)	Lu(2)—Cp(4)	2.323(3)	O(1)—Lu(1)—Cp(2)	106.11(11)
Lu(1)—C(116)	2.693(5)						

ligand are substantially broadened. The ^{1}H NMR spectrum of a solution of complex **11** in benzene (C_6D_6) is substantially different. Thus, this spectrum contains a double set of narrow signals (8+8) with equal integral intensities (Fig. 3). Apparently, the rapid (within the NMR time scale) exchange of the solvent molecules in the coordination sphere of the Lu atom occurs in a solution in tetrahydrofuran at ~20 °C, which leads to a change in the mutual arrangement of the iodine atom and the tetrahydrofuran molecule with respect to the C_2-symmetrical metallocene fragment (Scheme 7).

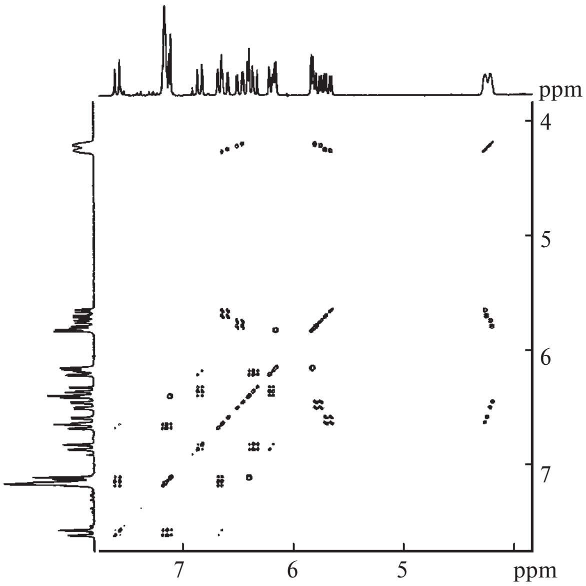
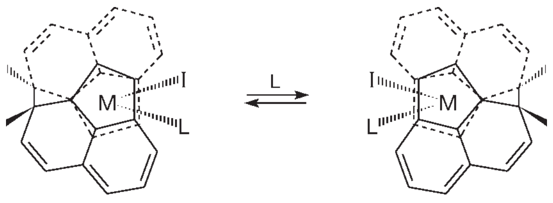


Fig. 3. ^{1}H—^{1}H NMR correlation spectrum (COSY) of complex **11** (200 MHz, C_6D_6, 295 K). The region of the signals of tetrahydrofuran is omitted.

Scheme 7



L = THF

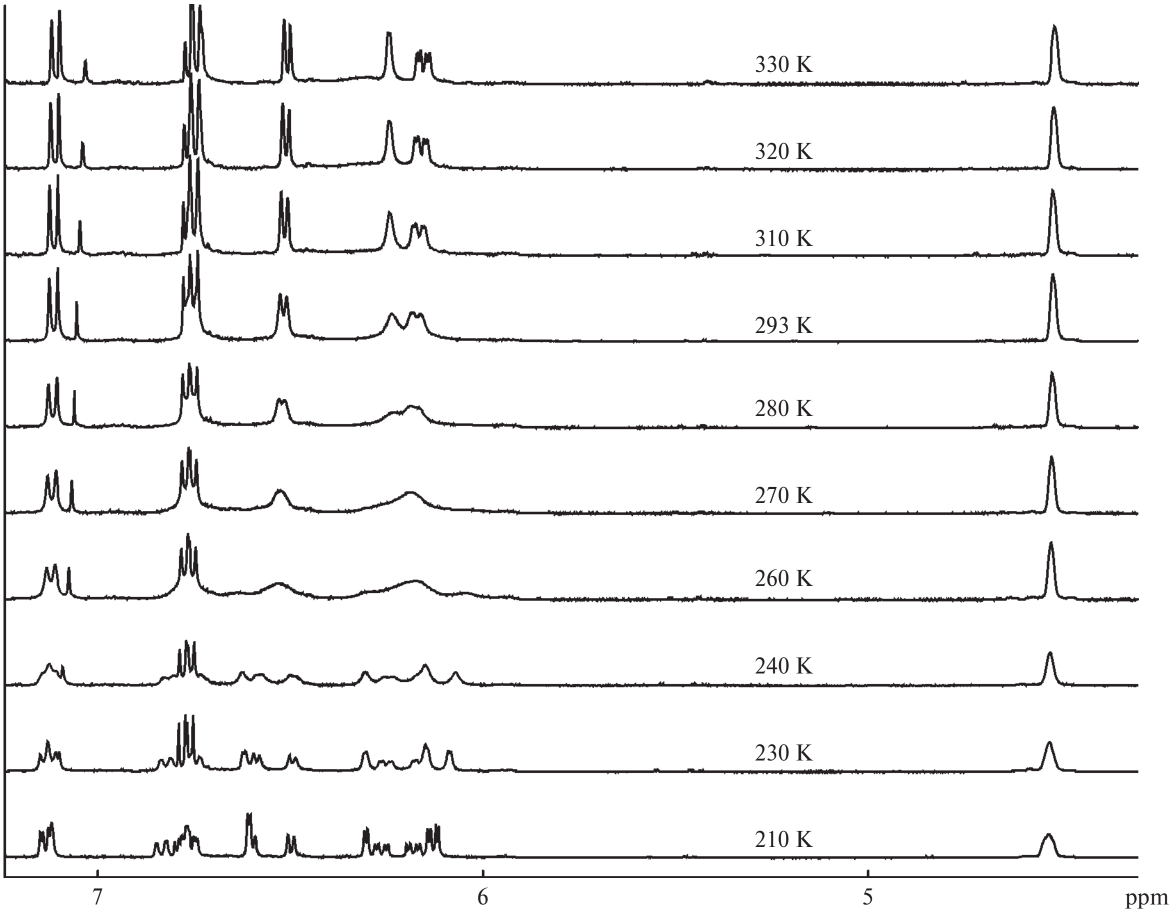


Fig. 4. Temperature dependence of the ^{1}H NMR spectrum of complex **11** (400 MHz, THF-d_8). The region of the signals of tetrahydrofuran is omitted.

Since the exchange of the solvent molecules occurs at the Lu atom, the broadened signals are only those belonging to the protons at the carbon atoms to which the metal atom is directly bound. In a solution in benzene, the iodine atom and the tetrahydrofuran molecule are stereochemically rigidly bound to the lutetium atom in both enantiomeric molecules of complex **11** resulting in the magnetic nonequivalence of the acenaphthylene fragments due to which the Lu atom is chiral. Assuming that the dynamic process in the coordination sphere of the lutetium atom in complex **11** can be slowed down or even terminated upon cooling, we examined the ^{1}H NMR spectra of complex **11** in THF-d_8 at lower temperatures. It can be seen from Fig. 4 that the number of the signals of the acenaphthylene ligands in the ^{1}H NMR spectrum of complex **11** in THF-d_8 is doubled at lower temperatures, which indicates that the exchange of the THF molecules is slowed down and, correspondingly, two $C_{12}H_8$ fragments of the *ansa*-metallocene structure are no longer magnetically degenerate.

In a solution, complex **11** does not give an ESR signal. Taking into account the above-considered data from ESR spectroscopy, the latter fact is evidence that the *ansa*-metallocene structure formed through coupling of the acenaphthylene radical anions becomes energetically more favorable compared to the ionic form on going from the monovalent alkali metal cations to the divalent ytterbium and calcium cations and then to the trivalent Ln^{3+} cations (Ln = Dy, Er, Tm, or Lu).

To summarize, we discovered coupling of the acenaphthylene radical anions at the lanthanide and calcium atoms occurring under the conditions of the exchange reactions of radical-anionic salts of acenaphthylene with halides of the corresponding metals. This coupling proceeds selectively to form *rac*-*ansa*-metallocenes $(\eta^5{:}\eta^5\text{-}C_{24}H_{16})M(THF)_2$. For these complexes, reversible dissociation of the *ansa*-metallocene structure into the radical anions was observed for the first time. In the reactions of *ansa*-metallocenes $(\eta^5{:}\eta^5\text{-}C_{24}H_{16})M(THF)_2$, the dimeric ligand core can either be retained or decompose into individual acenaphthylene fragments depending on the reaction conditions, primarily, on the nature of the solvent. In a solution in tetrahydrofuran at ~20 °C, the lutetium complex $(\eta^5{:}\eta^5\text{-}C_{24}H_{16})LuI(THF)$ undergoes rapid racemization due to the dynamic exchange of the solvent molecules in the coordination sphere of the metal atom. As the temperature decreases, the exchange is slowed down (and even is terminated) and the acenaphthylene fragments become magnetically nonequivalent.

Experimental

All operations were carried out either *in vacuo* or under an atmosphere of dry nitrogen using the Schlenk technique. Iodides $MI_2(THF)_2$ (M = Sm, Yb, or Ca) and $MI_3(THF)_3$ (M = Dy, Er, Tm, or Lu) were prepared by the reactions of the corresponding metals with iodine in THF. Tetrahydrofuran was dried and stored over sodium benzophenone ketyl and was taken for the reactions by condensing it *in vacuo* immediately before use. Sublimation (80 °C, 0.1 Torr) of acenaphthylene (75%, Aldrich) made it possible to remove some impurities and increase its purity to 85% (an impurity of acenaphthene was 10—15%). The amounts of acenaphthylene and the yields of the products given below were calculated with respect to pure acenaphthylene. The IR spectra were measured on a Specord M-80 spectrometer in Nujol mulls. The NMR spectra were recorded on Bruker DPX-200 and Bruker ARX-400 instruments; the chemical shifts were measured relative to the residual protons and ^{13}C isotopes of deuterated solvents. The ESR spectra were recorded on a Bruker ESR 200D-SRC spectrometer (9.35 GHz).

Biacenaphthylenyl[bis(tetrahydrofuran)]calcium $(\eta^5{:}\eta^5\text{-}C_{24}H_{16})Ca(THF)_2$ (3). A mixture of $CaI_2(THF)_2$ (3.7 g, 8.4 mmol), potassium (0.67 g, 17.1 mmol), and acenaphthylene (2.8 g, 18.4 mmol) in THF (30 mL) was stirred at ~20 °C until the potassium was completely dissolved. Then the solution was filtered off from the products that precipitated, and complex **3** was extracted with hot THF to separate it from KI. Complex **3** was obtained as yellow crystals in a yield of 3.0 g (73%), t.decomp. >140 °C. Found (%): C, 77.81; H, 6.38. $C_{32}H_{32}CaO_2$. Calculated (%): C, 78.65; H, 6.60. ^{1}H NMR (200 MHz, THF-d_8, 20 °C), δ: 6.86 (d, 2 H, H(3), J = 8.2 Hz); 6.60 (dd, 2 H, H(6), J_1 = 9.6 Hz, J_2 = 2.0 Hz); 6.39 (dd, 2 H, H(4), J_1 = 8.2 Hz, J_2 = 6.4 Hz); 6.31 (d, 2 H, H(1), J = 3.0 Hz); 6.21 (d, 2 H, H(5), J = 6.4 Hz); 5.98 (d, 2 H, H(7), J_1 = 9.6 Hz, J_2 = 3.4 Hz); 5.58 (d, 2 H, H(2), J = 3.0 Hz); 4.54 (s, 2 H, H(8)); 3.70 (m, 8 H, THF); 1.60 (m, 8 H, THF). ^{13}C NMR (50 MHz, THF-d_8, 20 °C), δ: 134.6, 127.6, 126.3, 124.8, 123.2, 119.7, 118.0, 112.5, 111.7, 111.2, 95.2, 49.0. IR, ν/cm^{-1}: 1180 w, 1030 s, 880 s, 720 w, 795 s, 745 s, 715 s.

Biacenaphthylenyl[bis(tetrahydrofuran)]samarium $(\eta^5{:}\eta^5\text{-}C_{24}H_{16})Sm(THF)_2$ (1) and biacenaphthylenyl[bis(tetrahydrofuran)]ytterbium $(\eta^5{:}\eta^5\text{-}C_{24}H_{16})Yb(THF)_2$ (2) were prepared according to analogous procedures. **Complex 1:** from $SmI_2(THF)_2$ (2.7 g, 4.9 mmol), potassium (0.4 g, 10.2 mmol), and acenaphthylene (1.65 g, 10.8 mmol). The yield was 2.62 g (89%). ^{1}H NMR (200 MHz, THF-d_8, 20 °C), δ: 17.67 (s, 2 H); 15.52 (s, 2 H); 12.84 (s, 2 H); 12.01 (s, 2 H); 6.89 (s, 2 H); 5.12 (s, 2 H); 3.6 (s, 8 H); 1.73 (s, 8 H); 0.72 (s, 2 H); −9.88 (s, 2 H). **Complex 2:** from $YbI_2(THF)_2$ (3.15 g, 5.5 mmol), potassium (0.44 g, 11.2 mmol), and acenaphthylene (1.8 g, 11.8 mmol). The yield was 3.12 g (91%). ^{1}H NMR (200 MHz, THF-d_8, 20 °C), δ: 6.87 (d, 2 H, J = 8.3 Hz); 6.65 (dd, 2 H, J_1 = 9.7 Hz, J_2 = 2.0 Hz); 6.45 (dd, 2 H, J_1 = 8.2 Hz, J_2 = 8.3 Hz); 6.29 (s, 2 H); 6.26 (d, 2 H, J = 4.5 Hz); 6.02 (dd, 2 H, J_1 = 9.7 Hz, J_2 = 3.6 Hz); 5.59 (d, 2 H, J = 3.1 Hz); 4.45 (s, 2 H); 3.71 (m, 8 H, THF); 1.59 (m, 8 H, THF). ^{13}C NMR (100 MHz, THF-d_8, 20 °C), δ: 132.6, 125.3, 124.5, 122.4, 121.1, 117.6, 116.0, 110.4 ($J_{^{13}C-^{171}Yb}$ = 5.7 Hz); 110.0, 108.8, 93.1 ($J_{^{13}C-^{173}Yb}$ = 5.7 Hz); 46.8.

Synthesis of $(\eta^5{:}\eta^5\text{-}C_{24}H_{16})Yb(THF)_2$ (2) from ytterbium naphthalenide. A mixture of $YbI_2(THF)_2$ (4.72 g, 8.26 mmol), lithium (0.11 g, 15.85 mmol), and naphthalene (1.62 g, 12.63 mmol) in THF (25 mL) was stirred at ~20 °C until the lithium was completely dissolved. The black powder of ytterbium naphthalenide that formed was filtered off and washed with THF (3×15 mL). Then a solution of acenaphthylene (3.2 g, 21.0 mmol) in THF (30 mL) was added with stirring. The crystals that formed were filtered off and washed with THF (15 mL). Complex **2** was obtained as dark-red crystals in a yield of 4.8 g,(93%). Complex **3** was prepared analogously from $CaI_2(THF)_2$ (3.3 g, 7.53 mmol), lithium (0.1 g, 14.4 mmol), naphthalene (1.41 g, 11.0 mmol), and acenaphthylene (2.8 g, 18.4 mmol) in a yield of 3.1 g (85%). The IR and NMR spectra of complexes **2** and **3** thus prepared are identical with those described above.

Hydrolysis of compound 2 in benzene. Water (0.13 g, 7.21 mmol) was added to a suspension of compound **2** (1.84 g, 2.96 mmol) in benzene (15 mL). The reaction mixture was stirred at ~20 °C until it became colorless. After centrifugation, the benzene solution was decanted from the precipitate and volatile products were removed *in vacuo*. The residue was recrystallized from Et_2O to obtain compound **4** as colorless crystals in a yield of 0.55 g (60%), m.p. 155 °C. ^{1}H NMR (200 MHz, CD_2Cl_2, 20 °C), δ: 7.67 and 7.54 (both d, 2 H each, H(5), H(6), J = 7.7 Hz); 7.61 (d, 2 H, H(3), J = 8.6 Hz); 7.50 (m, 2 H, H(6)); 7.40 (dd, 2 H, H(4), J_1 = 8.6 Hz, J_2 = 6.7 Hz); 7.09 (d, 2 H, H(5), J = 6.7 Hz); 4.56 (m, 2 H, H(8)); 3.16 (dd, 2 H, H(7a), J_1 = 17.8 Hz, J_2 = 5.8 Hz); 2.63 (dd, 2 H, H(7b), J_1 = 17.8 Hz, J_2 = 2.6 Hz). ^{13}C NMR (50 MHz, CD_2Cl_2, 20 °C), δ: 147.9, 144.8, 139.5, 131.4, 128.0, 127.9, 122.8, 122.2, 119.2, 118.8, 47.0, 32.6. IR, ν/cm^{-1}: 1600 w, 1495 m, 1155 s, 1015 m, 820 s, 785 v.s, 670 w, 640 w.

Acenaphthylene[tris(tetrahydrofuran)]zirconium dichloride (η^2-$C_{12}H_8$)$ZrCl_2(THF)_3$ (6). A mixture of complex **2** (1.65 g 2.65 mmol) and $ZrCl_4$ (0.63 g, 2.7 mmol) in THF (35 mL) was stirred at ~20 °C for several minutes. Then the solution was filtered and concentrated to 5 mL *in vacuo*. Complex **6** was obtained in a yield of 1.21 g (86%) as dark-green crystals, which decomposed upon heating above 110 °C. ^{1}H NMR (200 MHz, THF-d_8, 20 °C), δ: 6.95 (dd, 2 H, H(3), J_1 = 8.2 Hz, J_2 = 7.2 Hz); 6.57 (d, 2 H, H(4), J = 8.2 Hz); 6.34 (d, 2 H, H(2), J = 7.2 Hz); 4.15 (s, 2 H, H(1)); 3.72 (m, 12 H, THF); 1.61 (m, 12 H, THF). ^{13}C NMR (50 MHz, THF-d_8, 20 °C), δ: 147.3, 133.3, 127.4, 127.1, 115.3, 110.7, 87.5.

1,2-Bis(trimethylsilyl)acenaphthene $(Me_3Si)_2C_{12}H_8$ (7). A mixture of compound **3** (2.7 g, 5.52 mmol) and Me_3SiCl (1.3 g, 11.96 mmol) in THF (15 mL) was stirred at 20 °C for 30 min and then at 40 °C for 10 min. The solvent was removed *in vacuo* and the residue was extracted with hexane (2×15 mL). Crystallization from hexane afforded compound **7** in a yield of 1.52 g (93%) as large colorless crystals, m.p. 121 °C. Found (%): C, 72.25; H, 8.92. $C_{18}H_{26}Si_2$. Calculated (%): C, 72.41; H, 8.78. ^{1}H NMR (200 MHz, CD_2Cl_2, 20 °C), δ: 7.43 (d, 2 H, H(4), J = 7.8 Hz); 7.35 (dd, 2 H, H(3), J_1 = 7.8 Hz, J_2 = 6.6 Hz); 7.06 (d, 2 H, H(2), J = 6.6 Hz); 2.93 (s, 2 H, H(1)); –0.09 (s, 18 H, Me).

Biacenaphthylenyl(tetrahydrofuran)lutetium iodide (η^5:η^5-$C_{24}H_{16}$)LuI(THF) (11). A mixture of $LuI_3(THF)_3$ (2.37 g, 3.07 mmol), potassium (0.25 g, 6.4 mmol), and acenaphthylene (1.05 g, 6.9 mmol) in THF (25 mL) was stirred at ~20 °C until the potassium was completely dissolved. The solution was filtered off from the precipitate of KI that formed. Then the solution was concentrated to 10 mL by removing the solvent *in vacuo* to obtain complex **11** in a yield of 1.31 g (63%) as pale-yellow crystals, which decomposed upon heating above 160 °C. Found (%): Lu, 25.67. $C_{28}H_{24}ILuO$. Calculated (%): Lu, 25.79. ^{1}H NMR (200 MHz, THF-d_8, 20 °C), δ: 7.12 (d, 2 H, H(3), J = 8.4 Hz); 6.77 (dd, 2 H, H(4), J_1 = 8.4 Hz, J_2 = 6.4 Hz); 6.77 (dd, 2 H, H(6), J_1 = 9.8 Hz, J_2 = 1.8 Hz); 6.52 (d, 2 H, H(5), J = 6.4 Hz); 6.30 (br.s, 2 H, H(1)); 6.24 (s, 2 H, H(2)); 6.18 (dd, 2 H, H(7), J_1 = 9.8 Hz, J_2 = 3.6 Hz); 4.53 (s, 2 H, H(8)); 3.59 (s, 8 H, THF); 1.75 (s, 8 H, THF). ^{13}C NMR (50 MHz, THF-d_8, 20 °C), δ: 134.3 (br), 129.2, 128.5, 127.6, 127.1, 126.1, 124.6, 123.9, 123.1, 116.8 (br), 112.5, 48.9. ^{1}H NMR (400 MHz, C_6D_6, 20 °C), δ: 7.57 (d, 1 H, J = 8.6 Hz); 7.13 (the signal partially overlaps with the signal of benzene); 7.10 (d, 1 H, J = 3.4 Hz); 6.83 (d, 1 H, J = 8.6 Hz); 6.65 (d, 1 H, J = 6.4 Hz); 6.59 (dd, 1 H, J_1 = 9.8 Hz, J_2 = 2.1 Hz); 6.46 (dd, 1 H, J_1 = 9.8 Hz, J_2 = 2.1 Hz); 6.38 (d, 1 H, J = 3.0 Hz); 6.34 (dd, 1 H, J_1 = 8.6 Hz, J_2 = 6.8 Hz); 6.18 (d, 1 H, J = 6.8 Hz); 6.14 (d, 1 H, J = 3.0 Hz); 5.81 (d, 1 H, J = 3.0 Hz); 5.75 (dd, 1 H, J_1 = 9.4 Hz, J_2 = 3.8 Hz); 5.66 (dd, 1 H, J_1 = 9.8 Hz, J_2 = 3.8 Hz); 4.24 (s, 1 H); 4.19 (s, 1 H); 3.08 (m, 2 H, THF); 3.05 (m, 2 H, THF); 0.88 (m, 4 H, THF). IR, ν/cm^{-1}: 1300 w, 1190 m, 1165 m. sh, 1165 m, 1020 s, 855 s, 845 s, 800 v.s, 770 s, 750 s. The complexes (η^5:η^5-$C_{24}H_{16}$)MI(THF) (M = Dy (**8**), Er (**9**), and Tm (**10**)) were prepared from the corresponding triiodides analogously to complex **11**. Their IR spectra are identical. The results of analysis for the metal content in compounds **8—10** are in agreement with the calculated values.

X-ray diffraction study of the (η^5:η^5-$C_{24}H_{16}$)LuI(THF) complex (11). The X-ray diffraction data for complex **11** were collected on a Siemens SMART CCD diffractometer (ω scanning technique, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator) at 173 K. The absorption correction was applied using the SADABS program[13] (the maximum and minimum transmission coefficients were 0.8425 and 0.4698, respectively). The structure was solved by direct methods using the SHELXS97 program package[14] and refined by the full-matrix least-squares method based on F^2 using the SHELXL97 program package.[15] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were placed in idealized positions (U_{iso} = 0.08 Å^3). The geometric parameters of the crystal structure of complex **11** were analyzed using the PLATON program.[16] The crystal dimensions were 0.76×0.08×0.04 mm. The crystals of complex **11** are monoclinic, space group $P2_1/c$, a = 21.9128(1), b = 13.6755(2), c = 15.6181(2) Å, β = 107.786(1)°, V = 4456.55(9) Å^3, Z = 8, d_{calc} = 2.022 • 10^3 kg m^{-3}, μ = 5.834 mm^{-1}, F(000) = 2592, 1.78° ≤ θ ≤ 27.50°, $-28 \le h \le 23$, $-17 \le k \le 17$, $-17 \le l \le 20$, the total number of reflections was 33185, the number of independent reflections was 10226 [R_{int} = 0.0683], 10226 reflections were with $I > 2\sigma(I)$, 559 refinable parameters, GOF(F^2) = 1.012, the final R factors were as follows: R ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$) R_1 = 0.0365, wR_2 = 0.0615; the maximum and minimum residual electron densities were 0.995 and –1.274 e • Å^{-3}, respectively.

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