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First metal complex with the azulene dianion. Molecular structure of the $(2\eta^1:\eta^2\text{-Gaz})\text{Lu}(\eta^5\text{-Cp})(\text{DME})$ complex (Gaz is 7-isopropyl-1,4-dimethylazulene)

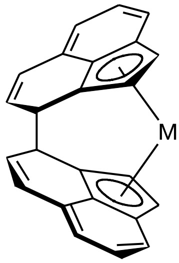
***I. L. Fedushkin,*[a]★ *M. N. Bochkarev,*[a] *S. Mühle,*[b] *and H. Schumann*[b]**

[a]*G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,*
49 ul. Tropinina, 603950 Nizhny Novgorod, Russian Federation.
Fax: +7 (831 2) 12 7497. E-mail: igorfed@imoc.sinn.ru
[b]*Institute of Chemistry, Technical University of Berlin,*
*135 Strasse des 17 Juni, D-10623 Berlin, Germany.**
Fax: +49 (30) 3142 2168

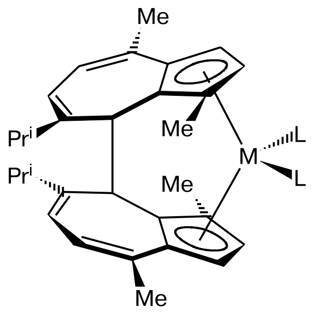
The metallocene derivative $(2\eta^1:\eta^2\text{-Gaz})\text{Lu}(\eta^5\text{-Cp})(\text{DME})$ (**1**) (Gaz is 7-isopropyl-1,4-dimethylazulene) was prepared by reduction of guaiazulene with the lutetium naphthalene complex $(\eta^5\text{-Cp})\text{Lu}(2\eta^1:\eta^2\text{-C}_{10}\text{H}_8)(\text{DME})$ in 1,2-dimethoxyethane (DME). Complex **1** crystallized from a solution as blue crystals. According to the results of X-ray diffraction analysis, molecule **1** has a skewed pseudo-sandwich structure in which the Lu atom is η^5-coordinated by the cyclopentadienyl ring and $2\eta^1:\eta^2$-coordinated by the seven-membered ring of the guaiazulene ligand. The coordination sphere of the metal atom in complex **1** is completed with the chelating DME molecule.

Key words: lutetium, metallocenes, guaiazulene, dianion.

Recently, we have found[1] that when coordinated to calcium or lanthanide cations, radical anions of nonalternant hydrocarbons, such as acenaphthylene and guaiazulene, undergo diastereoselective recombination to form *ansa*-metallocenes.



M = Sm, Yb, Ca;
L = THF



M = Yb, Ca;
L = THF, Py

Electrochemical studies demonstrated[2] that both these hydrocarbons can be reversibly reduced not only to radical anions but also to dianions. The first reduction potentials of these hydrocarbons have very similar values (these potentials relative to the standard calomel electrode in THF are −1.63 and −1.65 V for acenaphthylene and guaiazulene, respectively), whereas the second reduction potential of guaiazulene is much more negative (−2.45 V) than that of acenaphthylene (−1.85 V). These facts provide an explanation for the difference in the reactivity of acenaphthylene and guaiazulene derivatives of *ansa*-metallocenes. For example, the reactions with trimethylchlorosilane are accompanied by the cleavage of the bond between two cene fragments in acenaphthylene complexes, whereas this bond in guaiazulene complexes remains intact.[1d] Of azulene derivatives of metals, the following transition metal complexes have been synthesized: $(\mu_2\text{-}\eta^3:\eta^5\text{-Gaz})\text{Fe}_2(\text{CO})_5$,[3a] $(\mu_2\text{-}\eta^5:\eta^4\text{-Az})_2\text{Fe}_4(\text{CO})_{10}$,[3b] $(\eta^5\text{-Az})_2\text{Mn}_2(\text{CO})_6$,[3c] $(\eta^5\text{-Gaz})\text{Ru}(\text{CO})_2\text{Cl}$,[3d] and $(\eta^6\text{-Az})\text{Mo}(\eta^6\text{-C}_6\text{H}_6)$[3e] (Gaz is 7-isopropyl-1,4-dimethylazulene, Az is azulene). These complexes were generated by refluxing the corresponding metal carbonyls with azulene in heptane. The reactions of azulene with iron carbonyls[3a,b] or manganese carbonyls[3c] led to dimerization of azulene radical anions. In spite of the fact that various metal complexes with azulene have already been synthesized, data on the synthesis of metal complexes with its dianion are lacking in the literature.

Recently,[4] we have prepared and studied lithium and lanthanum complexes with the acenaphthylene dianion. In continuing our research, in the present study we synthesized the first metal complex with the guaiazulene

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* Institut für Chemie der Technischen Universität Berlin, Straβe des 17 Juni 135, D-10623 Berlin, Germany.

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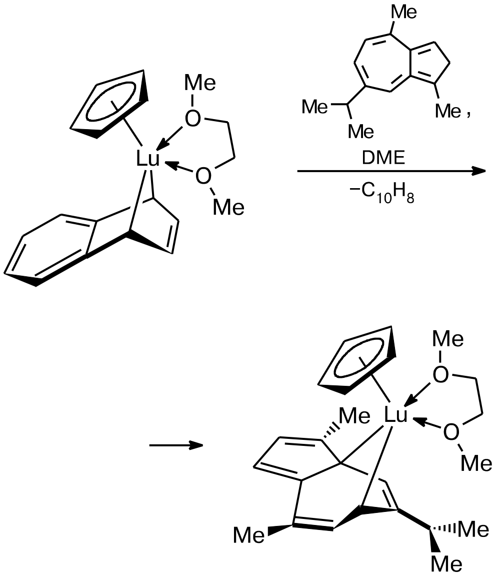
dianion and established its structure by X-ray diffraction analysis.

Results and Discussion

Synthesis of the lutetium complex with the guaiazulene dianion. A comparative estimate of the reduction potentials of the naphthalene and azulene dianions (−2.6 and −2.45 V, respectively) demonstrated that the former dianion possesses stronger reducing properties. Based on this fact, we developed a procedure for the synthesis of the complex with the guaiazulene dianion. We found that the reaction of equimolar amounts of the $(2\eta^1:\eta^2\text{-}C_{10}H_8)Lu(\eta^5\text{-}Cp)(DME)$ complex and guaiazulene in 1,2-dimethoxyethane (DME) afforded the target complex $(2\eta^1:\eta^2\text{-Gaz})Lu(\eta^5\text{-}Cp)(DME)$ (**1**) containing the guaiazulene dianion (Scheme 1).

Scheme 1



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The reaction proceeded at ~20 °C at a rate at which the reagents were mixed to give complex **1**, which precipitated from the reaction mixture as a finely crystalline powder in high yield. The electronic absorption spectrum of complex **1** in DME at ~20 °C has an absorption maximum (λ_{max} = 585 nm), which is slightly shifted with respect to that of free guaiazulene (λ_{max} = 602 nm). Since complex **1** is highly sensitive to atmospheric oxygen and moisture, its molar absorption coefficient cannot be determined with sufficient accuracy. However, a visual comparison of the color intensity of a solution of guaiazulene with that of the reaction mixture after completion of the reaction demonstrated that the molar extinction coefficient of the reaction product is, apparently, several orders of magnitude lower than that of the starting guaiazulene.

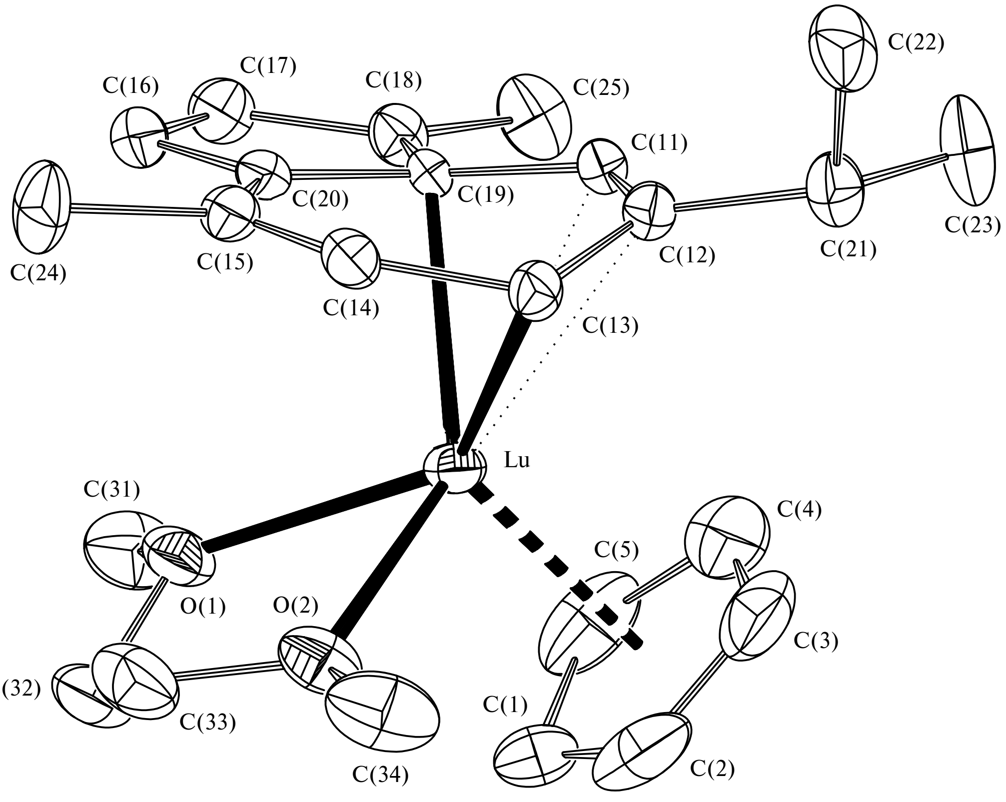

Fig. 1. Molecular structure of the $(2\eta^1:\eta^2\text{-Gaz})Lu(\eta^5\text{-}Cp)(DME)$ complex (**1**). The H atoms are omitted.

Molecular structure of complex 1. Crystallization of compound **1** from the reaction mixture afforded blue crystals suitable for X-ray diffraction analysis. According to the results of X-ray diffraction study, molecule **1** has a skewed pseudo-metallocene structure (Fig. 1) in which two carbocyclic ligands, *viz.*, cyclopentadienyl and guaiazulene, are coordinated to the Lu atom in the η^5 and $2\eta^1$:η^2 fashions, respectively. In the literature, the latter mode of binding is considered as either the 2σ interaction[5] or the η^4 interaction of the π type with the but-2-ene-1,4-diyl fragment.[6] The metal atom in compound **1** is coordinated also by the DME molecule. The selected bond lengths in complex **1** are given in Table 1. The fact that the lutetium cation is located in the vicinity of the seven-membered ring of the azulene ligand rather than in proximity to its five-membered ring suggests that the negative charge in the guaiazulene dianion of crystalline complex **1** is localized primarily on the seven-membered ring. This conclusion is consistent with the negative charge distributions in the radical anion and dianion of azulene calculated recently by the MNDO method.[7] According to these data, the total negative charges in the five- and seven-membered rings of the guaiazulene dianion are 0.86 and 1.28, respectively. The synthesis of the only rare-earth metal complex with the seven-membered anionic carbocycle has been described in the literature. Thus, the reaction of cycloheptatrienylpotassium with neodymium borate afforded the neodymium(III) complex with the cycloheptatriene trianion, $[(THF)(BH_4)_2Nd(\mu\text{-}\eta^7\text{:}\eta^7\text{-}C_7H_7)Nd(BH_4)(THF)_3]$, which was isolated and structurally characterized.[8] In the molecule of this complex, the Nd—C(carbocycle) bond lengths vary within a narrow range (2.63—2.67 Å), which is evidence for the regular η^7 coordination of the ligand to the Nd atoms. In complex **1**, the distances from the Lu atom to the C atoms of the cyclopentadienyl ligand (Lu—C(1), 2.617 Å; Lu—C(2), 2.636 Å; Lu—C(3), 2.621 Å; Lu—C(4), 2.616 Å; Lu—C(5), 2.606 Å) have very close values, which is indicative of the η^5 coordination of the cyclopentadienyl ligand. By contrast, the distances from the metal atom to the C atoms of the seven-membered ring vary within a broad range (2.400—2.844 Å). The distances from the Lu atom to the C atoms of the guaiazulene ligand and the C—C bond lengths in this ligand are presented in Figs. 2, *a* and *b*, respectively. It should be noted that the guaiazulene ligand in complex **1** is nonplanar, and its seven-membered ring is folded along the C(13)—C(19) line (see Fig. 1). The nonplanarity of this ligand is, apparently, associated with the fact that the negative charge is not uniformly distributed over all seven C atoms of the ring but is localized primarily on the C(13) and C(19) atoms (Fig. 2, *c*). This is responsible for the partial sp^3 character of the latter two atoms and, as a consequence, for a loss of planarity of the seven-membered ring. This fact is in good agreement with the observed alternation of the double and single C—C bonds in the seven-mem-

Table 1. Selected bond lengths (*d*) in complex **1**

Distance or bond	*d*/Å	Distance or bond	*d*/Å
Lu—O(1)	2.360(4)	Lu—O(2)	2.384(4)
Lu—C(1)	2.617(6)	Lu—C(2)	2.636(6)
Lu—C(3)	2.621(7)	Lu—C(4)	2.616(7)
Lu—C(5)	2.606(6)	Lu—C(11)	2.632(5)
Lu—C(12)	2.649(5)	Lu—C(13)	2.400(5)
Lu—C(14)	2.688(5)	Lu—C(19)	2.508(5)
O(1)—C(31)	1.449(7)	O(1)—C(32)	1.437(7)
O(2)—C(33)	1.444(8)	O(2)—C(34)	1.437(7)
C(1)—C(2)	1.401(11)	C(2)—C(3)	1.389(11)
C(3)—C(4)	1.374(11)	C(4)—C(5)	1.400(11)
C(1)—C(5)	1.393(11)	C(11)—C(12)	1.373(7)
C(12)—C(13)	1.460(7)	C(11)—C(19)	1.476(7)
C(12)—C(21)	1.527(7)	C(13)—C(14)	1.461(7)
C(14)—C(15)	1.353(8)	C(15)—C(20)	1.471(7)
C(15)—C(24)	1.516(8)	C(16)—C(17)	1.411(8)
C(16)—C(20)	1.405(7)	C(17)—C(18)	1.393(8)
C(18)—C(19)	1.428(7)	C(18)—C(25)	1.493(8)
C(19)—C(20)	1.455(7)	C(21)—C(22)	1.539(8)
C(21)—C(23)	1.523(8)	C(32)—C(33)	1.502(9)

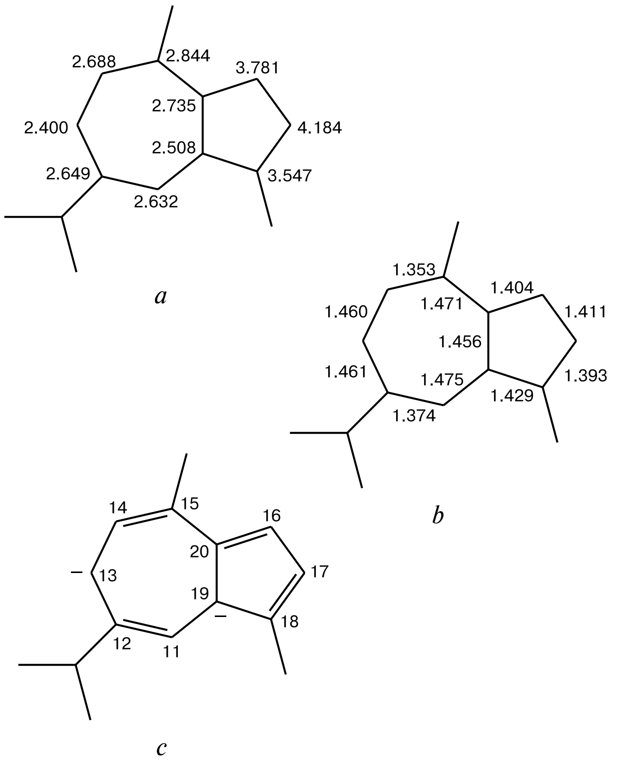

Fig. 2. Distances between the C atoms and the Lu atom (Å) (*a*), the distribution of the C—C bond lengths (Å) in the guaiazulene fragment of complex **1** (*b*), and localization of the negative charge and alternation of the bond lengths in the guaiazulene ligand (*c*).

bered ring (see Table 1). The mode of binding of the Lu atom to the anionic moiety of the ligand is analogous to that observed earlier in the lutetium complex $(2\eta^1:\eta^2\text{-}C_{10}H_8)Lu(\eta^5\text{-}Cp)(DME)$[9] in which the distances between the metal atom and the C(1) and C(4) atoms of the naphthalene fragment have close values (2.406 and 2.397 Å, respectively). In complex **1**, the C(13)—Lu and C(19)—Lu distances are 2.400 and 2.508 Å, respectively. Apparently, the C(11)—C(12) double bond (1.373 Å) in complex **1** is weakly coordinated to the Lu atom. Although the C(11)—Lu and C(12)—Lu distances (2.632 and 2.649 Å, respectively) are substantially larger than the C(13)—Lu and C(19)—Lu distances (2.400 and 2.508 Å, respectively), they are close to the Lu—C(Cp) distances (see Table 1).

Study of the composition and structure of complex 1 in solution by ^{1}H NMR spectroscopy. Compound **1** is virtually insoluble in benzene, which did not allow us to measure its ^{1}H NMR spectrum in this solvent. It appeared that complex **1** changed its color from blue to yellow upon dissolution in THF-d_8. Hence, we assumed that when passing from a DME solution to a THF solution, complex **1** undergoes substantial structural changes accompanied by a change in the electronic structure of the guaiazulene dianion. The aliphatic region of the ^{1}H NMR spectrum of complex **1** in THF-d_8 has two singlets of the methyl substituents at δ 1.89 (3 H) and 1.73 (3 H) and a doublet of the methyl groups of the isopropyl substituent (at δ 0.84 (6 H)), whose methine proton is observed at δ 1.82. Of the NMR signals for the ring protons of the guaiazulene ligand, only two signals at δ 5.31 (d, $J = 4$ Hz) and 4.93 (s) are pronounced. The remaining signals for the ring protons are observed in the narrow region (δ 5.6—5.8) and overlap with the singlet of the Cp ligand at δ 5.71 (5 H). It should be noted that a doublet of doublets ($J = 10$ Hz and $J = 2$ Hz) is observed at δ 1.54 (1 H) and the intensity of this signal is exactly equal to the intensities of the individual signals for the ring protons at δ 5.31 (1 H) and 4.93 (1 H). We hypothesized that the signal at δ 1.54 belongs to one of the ring protons. To obtain additional spectroscopic data for compound **1**, we dissolved it in THF, removed the solvent, dissolved the residue in C_6D_6, and recorded the ^{1}H NMR spectrum in this solution. By this means, we succeeded in measuring the well-resolved spectrum whose 2D ^{1}H—^{1}H correlation is shown in Fig. 3. The broad singlets at δ 3.44 and 1.23 are assigned to the THF molecules coordinated to the Lu atom. The integration of the intensities of these signals shows the presence of 1—1.5 mole of THF per mole of the complex. The doublet at δ 6.12 (1 H, $J = 10$ Hz) has a cross-peak with the doublet of doublets at δ 1.84 (1 H, $J = 10$ Hz, $J = 2$ Hz) and its upfield half is masked by the signal of the methyl group. This doublet of doublets belongs to the ring H(13) proton. Its strong upfield shift compared to the signals for other ring protons at δ 6.12 (d, 1 H, $J = 10$ Hz), 5.91 (d, 1 H, $J = 4$ Hz), 5.60 (d, 1 H, $J = 4$ Hz), and 5.46 (s, 1 H) provides evidence that the C(13) atom to which this proton is bound bears a substantial negative charge. The chemical shifts of the protons of the five-membered ring at δ 5.91 (d, 1 H, $J = 4$ Hz) and 5.60 (d, 1 H, $J = 4$ Hz) are in the region characteristic of the protons of the cyclopentadienyl anions. In our opinion, this indicates that compound **1** dissolved in THF exists in the form in which a portion of the negative charge in the guaiazulene dianion is delocalized over the five-membered ring and imparts the character of the cyclopentadienyl anion to this dianion, whereas another portion of the negative charge is localized on the C(13) atom, like in the crystalline state (see Fig. 3). Presumably, this form occurs as a dimer (see Fig. 3). The monomeric structure in which the Lu atom is simultaneously η^5-coordinated by the five-membered ring of the guaiazulene ligand and by the C(13) atom seems to be less probable because the metal atom is far removed from the C(13) atom. The driving force for the trasformation of the blue form of complex **1** into the yellow form is, apparently, the replacement of the coordinated DME molecules by THF. Taking into account that these two solvents are similar in solvating ability, we hypothesized that the transformation of one form of the complex into another form can be observed depending on the conditions, primarily, on the temperature. We found that a change in the temperature of a solution of complex **1** in DME from +80 to −100 °C did not lead to visible changes. However, it appeared that the color of the THF solution of complex **1** changed from yellow to dark-blue even upon slight cooling. The temperature dependence of the ^{1}H NMR spectrum of complex **1** in THF is shown in Fig. 4. It can be seen that a lowering of the temperature led to a synchronous decrease in the intensity of all signals in the spectrum of complex **1** along with the appearance of a set of signals corresponding to the blue form of the complex. The signals that appear at low temperature in the region of δ 5.5—3.5 cannot be assigned to the protons of the cyclopentadienyl ring and, apparently, belong to the protons at the double bonds of the five-membered ring. It should be noted that the spectrum recorded at low temperature has signals of the coordinated DME molecules (δ 3.61 and 3.58), which is indicative of the replacement of the THF molecules in the coordination sphere of the metal atom. It is this replacement that is responsible for the transformation of complex **1** observed at low temperature. A comparison of the integral intensities of both forms demonstrated that the yellow form ($\eta^1(\sigma):\eta^5(\pi\text{-Cp})$ coordination mode of the ligand) completely prevails at ~20 °C, whereas both forms are present in virtually equal amounts in a solution in THF at ~200 K.

In the present study, we proposed for the first time the procedure for the synthesis of metal complexes containing the azulene dianion. The lutetium complex prepared

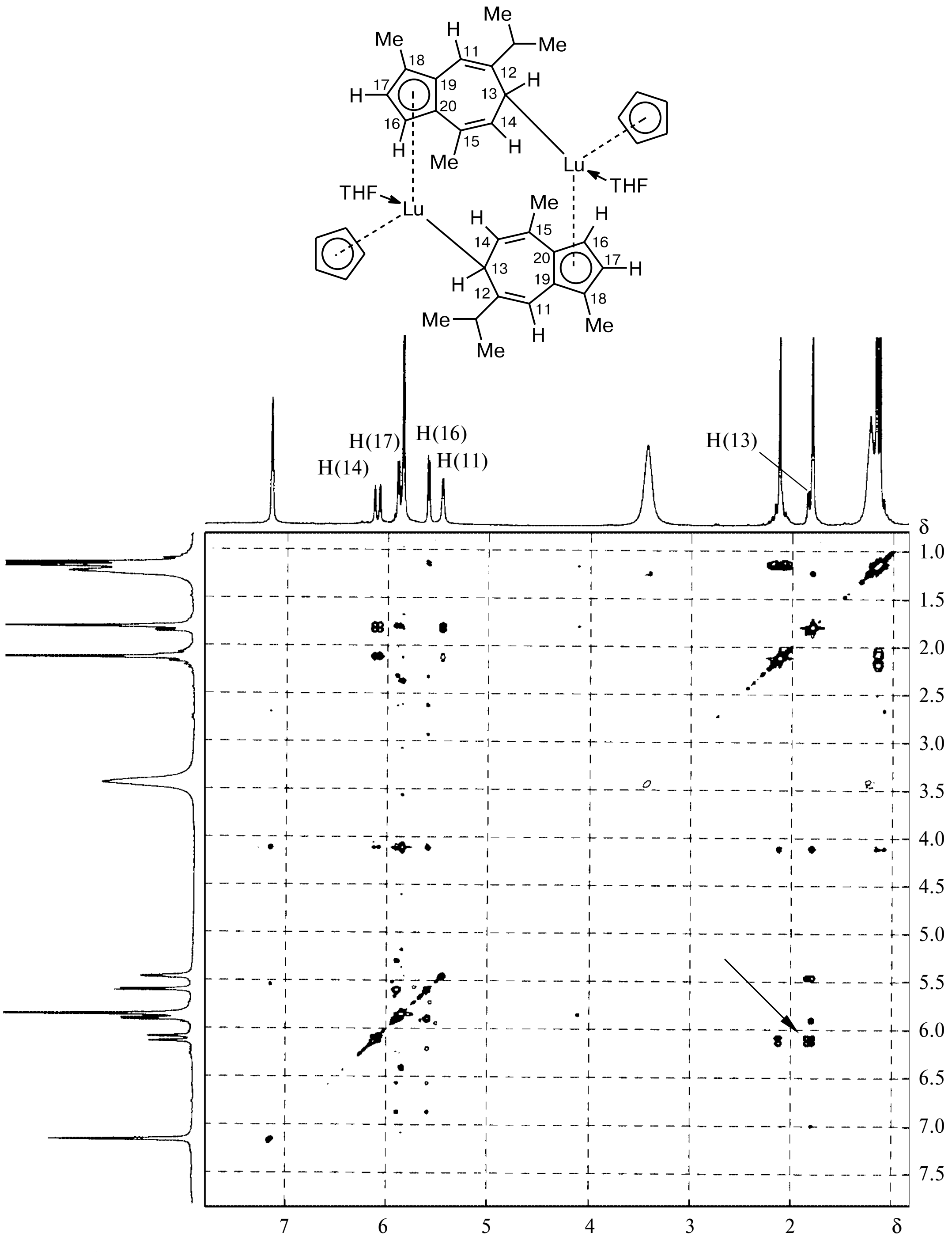

Fig. 3. Correlation ^1H—^1H NMR spectrum of complex **1** measured after dissolution of **1** in THF, removal of the solvent, and dissolution of the residue in C_6D_6 (200 MHz, 295 K). The cross-peak between the H(14) and H(13) protons is indicated by an arrow.

according to this procedure has a skewed metallocene structure with the $2\eta^1:\eta^2$-coordinated guaiazulene ligand.

Experimental

All operations were carried out *in vacuo* or under dry nitrogen using the Schlenk technique. The $(2\eta^1:\eta^2\text{-}C_{10}H_8)Lu(\eta^5\text{-}Cp)(DME)$ complex was prepared according to a known procedure.[9] Tetrahydrofuran and 1,2-dimethoxyethane were dried and stored over sodium benzophenone ketyl and condensed *in vacuo* immediately before use. Commercially available guaiazulene (Aldrich) was used. The IR spectrum was recorded on a Specord M80 spectrometer (Nujol mulls). The ^1H NMR spectra were measured on Bruker DPX-200 and Bruker ARX-400 instruments; the chemical shifts are given in the δ scale with respect to the

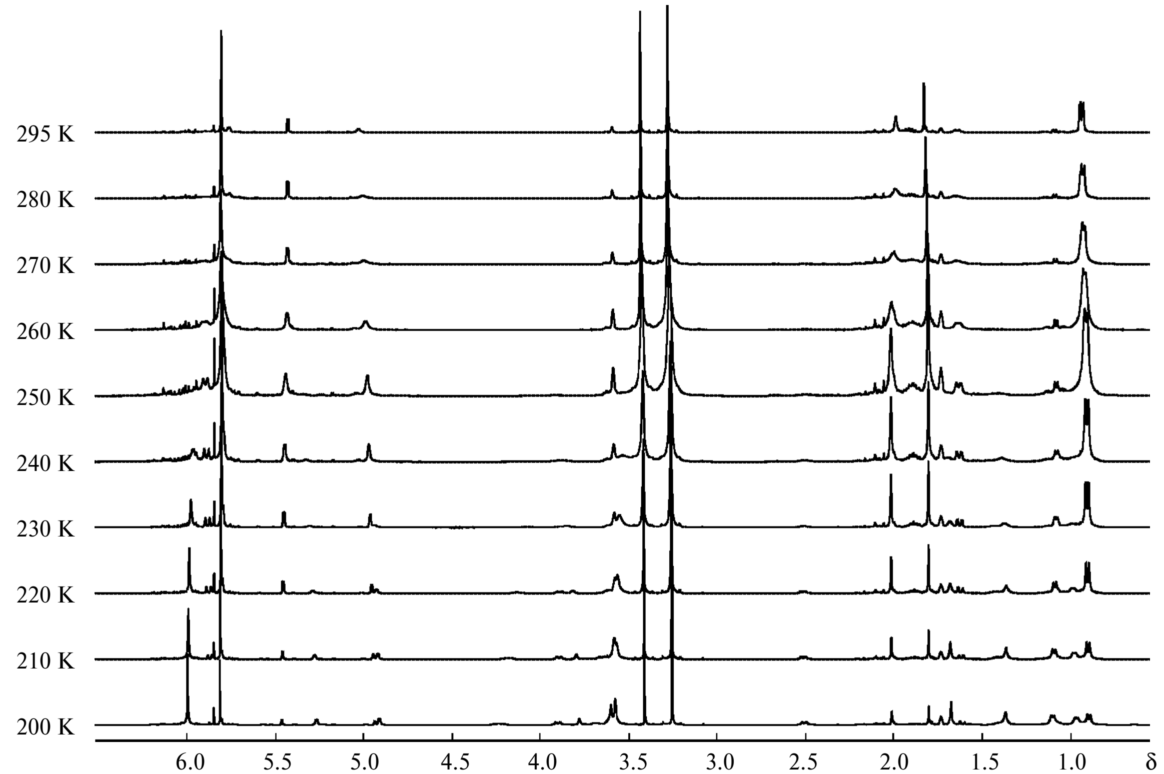

Fig. 4. Temperature dependence of the ^{1}H NMR spectrum of complex **1** (400 MHz, THF-d$_8$).

chemical shifts of the residual protons of deuterated solvents. The electronic absorption spectrum was recorded on a Specord M40 spectrometer in a 5-mm cell. The appearance of the absorption band in a solution of complex **1** is not associated with an impurity of free guaiazulene because the sample used for recording the spectrum was prepared in an all-sealed cell. Due to low solubility of complex **1** in DME at ~20 °C, crystals, which were placed at the bottom of the cell, were repeatedly washed with the solvent by condensation of the latter on the crystals in the spectroscopic cell from a tube sealed into the cell and decantation of the solution from this cell to the tube containing the solvent.

(7-Isopropyl-1,4-dimethylazulenyl)(cyclopentadienyl)lutetium 1,2-dimethoxyethanate (1). A solution of guaiazulene (0.29 g, 1.46 mmol) in DME (15 mL) was placed in a tube containing the $(C_{10}H_8)Lu(Cp)(DME)$ compound (0.66 g, 1.44 mmol) and DME (5 mL). The color intensity of the reaction mixture rapidly decreased and a finely crystalline powder precipitated during a few minutes. The solution was concentrated to 10 mL by removing the solvent *in vacuo*. The precipitate of complex **1** was dissolved at 80 °C and kept at ~20 °C for one day. The mother liquor was decanted from the crystals formed. Compound **1** was obtained in a yield of 0.59 g (78%) as blue crystals, m.p. 136—138 °C (decomp.). Found (%): Lu, 32.78. $C_{24}H_{33}LuO_2$. Calculated (%): Lu, 33.11. UV (DME), λ/nm: 585. ^{1}H NMR (200 MHz, THF-d$_8$, 20 °C), δ: 0.84 (d, 6 H, CH$\underline{\text{Me}}_2$); 1.54 (dd, 1 H, J = 10.0 Hz, J = 2.0 Hz); 1.73 (s, 6 H, Me); 1.82 (m, 1 H, C$\underline{\text{H}}$Me$_2$); 1.89 (s, 3 H, Me); 3.18 (s, 6 H, DME); 3.34 (s, 4 H, DME); 4.93 (s, 1 H); 5.33 (d, 1 H, J = 2.0 Hz); 5.50—6.00 (m, 9 H). IR (Nujol), ν/cm^{-1}: 1530 w, 1270 w, 1230 w, 1180 w, 1125 w, 1085 m, 1040 s, 1000 m, 855 s, 785 s, 755 s, 725 s.

X-ray diffraction study of complex 1. The X-ray diffraction data for complex **1** were collected on a Siemens SMART CCD diffractometer (ω scan technique, Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator) at 173 K. The absorption corrections were applied with the use of the SADABS program.[10] The structure was solved by direct methods with the use of the SHELXS97 program package[11] and refined by the full-matrix least-squares method based on F^2 with the use of the SHELXL97 program package.[12] All nonhydrogen atoms were refined anisotropically. The H atoms were placed in idealized positions (U_{iso} = 0.08 Å^3). The geometric parameters of the structure of complex **1** were analyzed using the PLATON program.[13] The crystallographic data, details of X-ray diffraction study, and characteristics of the refinement are as follows: crystal dimensions were 0.30×0.26×0.14 mm^3, orthorhombic crystal system, space group *Pbca*, a = 16.8103(2) Å, b = 15.08970(10) Å, c = 17.49300(10) Å, $\alpha = \beta = \gamma = 90°$, V = 4437.32(7) Å^3, Z = 8, d_{calc} = 1.582 • 10^3 kg m^{-3}, μ = 4.464 mm^{-1}, F(000) = 2112, $2.16° \le \theta \le 27.50°$, $-21 \le h \le 21$, $-15 \le k \le 19$, $-22 \le l \le 22$, a total of 31702 of reflections were measured, 5099 independent reflections (R_{int} = 0.0702), 5099 reflections with $I > 2\sigma(I)$, 250 parameters were refined, GOOF(F^2) = 1.052, the final R factors ($R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$) were R_1 = 0.0400, wR_2 = 0.0797, the ratio of the maximum to minimum residual density was 3.607/–1.155 e • Å^{-3}.

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