

# Reactions of cyclopentadienyl–naphthalene complexes of lutetium with C- and N-unsaturated compounds: molecular and crystal structure of $[\text{CpLu}(\text{DME})]_2[1,1-\mu-4,4-\mu-(\text{Ph})\text{C}-(\text{Ph})\text{C}=\text{C}(\text{Ph})-\text{C}(\text{Ph})]$ <sup>\*</sup>

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## Abstract

The naphthalene derivative of cyclopentadienyllutetium  $\text{CpLuC}_{10}\text{H}_8(\text{THF})_2$  (**1b**) (THF-tetrahydrofuran) easily reacts with azobenzene in THF solution to give a dimeric diphenylhydrazido complex  $[\text{CpLu}(\text{THF})]_2(\text{Ph}_2\text{N}_2)_2$  (**2**). Interaction of  $\text{CpLuC}_{10}\text{H}_8(\text{DME})$  (**1a**) (DME = 1,2-dimethoxyethane) with diphenylacetylene results in C–C coupling and formation of a new type of dinuclear complex with tetracharged bridging  $[\text{C}_4\text{Ph}_4]^{4-}$  ligand:  $[\text{CpLu}(\text{DME})]_2[1,1-\mu-4,4-\mu-(\text{Ph})\text{C}-(\text{Ph})\text{C}=\text{C}(\text{Ph})-\text{C}(\text{Ph})]$  (**3**). The structure of benzene solvate of **3** was determined by X-ray diffraction method (orthorhombic;  $a = 14.266(8)$ ,  $b = 15.625(7)$  and  $c = 21.612(10)$  Å, space group, *Pbcn*,  $Z = 4$ , 2266 reflections with  $F > 4\sigma(F)$ ,  $R = 0.039$ ). In the molecule of **3** there are two CpLu units joined by a  $\text{C}_4\text{Ph}_4$  ligand. The shortest Lu–C  $\mu_2$  distances 2.280(7) and 2.336(7) Å are observed between Lu atoms and end C atoms of  $\text{C}_4$  fragment. The crystal of **3** contains two enantiomeric forms of molecules connected by symmetry elements. The X-ray data together with the diammagnetism of **3** suggest in dialkylidene type of bridging ligand in this complex.

**Keywords:** Lutetium; Naphthalene derivative; Azobenzene; Diphenylacetylene; Dialkylidene ligand

## 1. Introduction

In continuation of our investigation of naphthalene–lanthanoid complexes [1,2] we have recently obtained mixed-ligand complexes of lutetium  $\text{CpLuC}_{10}\text{H}_8(\text{DME})$  (**1a**) and  $\text{CpLuC}_{10}\text{H}_8(\text{THF})_2$  (**1b**) containing a naphthalene dianion 1,4 bonded to a lutetium atom [3]. Preliminary investigations showed that reductive properties of **1a** towards organometallic compounds such as  $\text{Ph}_4\text{Sn}$  and  $\text{Cp}_2\text{V}$  are somewhat lower than that of  $\text{C}_{10}\text{H}_8\text{-Yb}(\text{THF})_3$  [4,5]. It has been shown that the later complexes easily reduces unsaturated organic substances with N=N [6,7] and C=N [8] double bonds. In order to gain more insight into reductive ability of naphthalene

dianion in **1a** and **1b**, we have studied their reactions with several unsaturated hydrocarbons. The present paper deals with reactions of cyclopentadienyl(naphthalene)lutetium with azobenzene and disubstituted acetylenes.

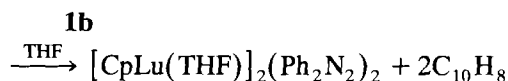
## 2. Results and discussion

Azobenzene was found to react with  $\text{C}_{10}\text{H}_8\text{Ln}(\text{THF})_3$  to give tetranuclear complexes  $[\text{Ln}(\mu_3\text{-}\eta^2\text{-Ph}_2\text{N}_2)_4(\mu_3\text{-PhN})_2(\text{THF})_x]$  (Ln = Yb;  $x = 4$ ) (Ln = Sm;  $x = 6$ ) [6,7]. Four  $\text{Ph}_2\text{N}_2$  molecules in them form diphenylhydrazido bridges but the fifth  $\text{Ph}_2\text{N}_2$  molecule is split into phenylimide units  $\text{PhN}^{2-}$  owing to four-electron reduction. Complex **1a** also readily reacts with azobenzene in DME solution but yields only resin-like products, from which we could not isolate individual compounds. A more definite result has been obtained when the THF analogue of **1a**,  $\text{CpLuC}_{10}\text{H}_8(\text{THF})_2$  (**1b**), has

<sup>\*</sup> We are pleased to dedicate this manuscript to Professor Herbert Schumann in recognition of his many important contributions to the field of organolanthanoid chemistry.

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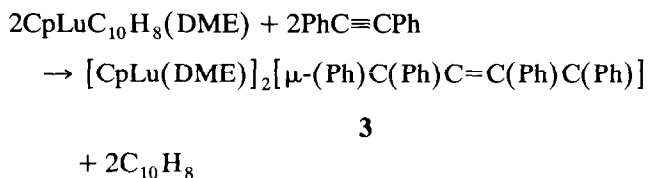
been used in the same reaction in THF medium. Mixing of these reagents at room temperature results in immediate colour change from dark red to pale brown. The Lu-containing product can be easily isolated from concentrated THF solution as colourless crystals. A composition of this product coincides (except metal and incorporated THF molecule) with that of ytterbium complex  $[\text{CpYb}(\text{THF})]_2(\text{Ph}_2\text{N}_2)_2$  obtained in the reaction of  $\text{Cp}_2\text{Yb}$  with  $\text{Ph}_2\text{N}_2$  [9]:



**2**

The IR spectra of **2** and its ytterbium analogue obtained by an independent method [10], are superimposable, and the melting points of both complexes are very close. These data suggest that the structures of **2** and the ytterbium analogue are the same. It should be noted that use of an excess of **1b** in this reaction did not lead to complete reduction of  $\text{Ph}_2\text{N}_2$  in contrast with that observed in the reactions of naphthaleneytterbium and naphthalenesamarium. This result confirms decreased reductive ability of lutetium complex comparing with naphthaleneytterbium.

The interaction of **1a** and **1b** with disubstituted acetylenes  $\text{Me}_3\text{SiC}\equiv\text{CSuMe}_3$ ,  $\text{Me}_3\text{SiC}\equiv\text{CPh}$  and  $\text{PhC}\equiv\text{CPh}$  depends on the character of substituents. The first of these ethynes does not react with **1a** nor with **1b** even on heating to  $60^\circ\text{C}$  (the decomposition temperature of **1b**). The second reacts at room temperature but gives an intractable mixture of products. The addition of diphenylacetylene to a suspension of **1a** in DME leads to dissolution of the initial lutetium complex and simultaneous formation of small dark-red glistening crystals of product **3**. Hydrolysis of this product gives CpH, DME and  $\text{Lu}(\text{OH})_3$  (1 : 1 : 1 molar ratio) and an organic compound, which has been identified as 1,2,3,4-tetra-phenylbut-1-ene on the basis of its analysis,  $^1\text{H}$  NMR and IR spectra. The ratio of hydrolysis products corresponds to the formula  $[\text{CpLu}(\text{DME})]_2(\text{Ph}_4\text{C}_4)$  (**3**), which was confirmed by the X-ray structure investigation. Upon hydrolysis of **3** migration of the double  $\text{C}=\text{C}$  bond from the 2 to the 1 position in the central butene ligand apparently takes place:



It can be supposed that the lutetium naphthalene complex **1a** causes reductive coupling of two diphenylacetylene molecules with the formation of the te-

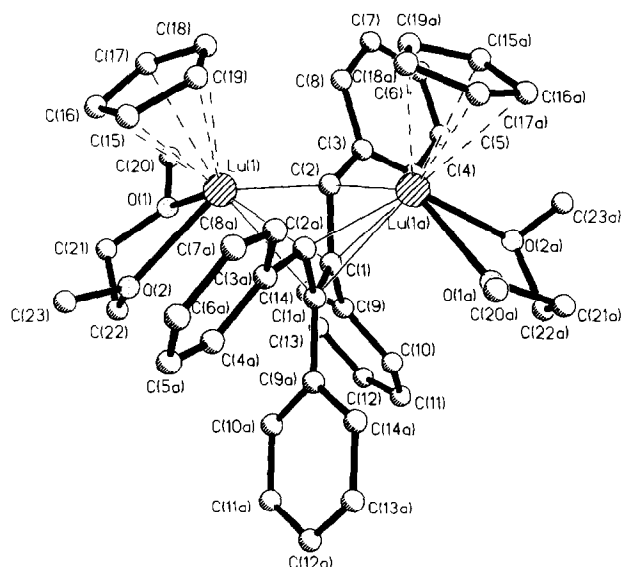


Fig. 1. The general view of **3** and atom labelling.

traphenylbuta-1,3-dien-1,4-diyl derivative of lutetium. Similar dimerization of  $\text{PhC}\equiv\text{CPh}$  was observed before in its reaction with metallocenes of Ti, Zr and Hf [11]. The addition of the second CpLu moiety into 1,4-positions of the conjugated unsaturated system of this intermediate, formed in the first step, gives **3** as the final reaction product.

The complex **3** is isolated as diamagnetic air-sensitive crystals sparingly soluble in DME and benzene. Recrystallization of **3** from a refluxing DME–benzene mixtures leads to the formation of the benzene-containing product,  $\mathbf{3} \cdot 2\text{C}_6\text{H}_6$  as dark-red crystals, which has been used for X-ray analysis.

The general view of **3** is shown in Fig. 1. The bond lengths and angles in the molecule of **3** are given in Tables 1 and 2, respectively. The  $\text{C}_4$  fragment of the central ligand is a bridge connecting two Lu atoms of  $\text{CpLu}(\text{DME})$  units. The symmetry of the molecule of **3** is  $\text{C}_2$ . The middle points of the  $\text{Lu}(1) \dots \text{Lu}(1a)$  line and the  $\text{C}(1) - \text{C}(1a)$  bond lie on the two-fold axis.

The central  $\text{C}(2)\text{C}(1)\text{C}(1a)\text{C}(2a)$  fragment is planar (within  $0.03 \text{ \AA}$ ). The average plane of this fragment is approximately perpendicular to the  $\text{Lu}(1) \dots \text{Lu}(1a)$  line. The four-membered  $\text{Lu}(1)\text{C}(2)\text{Lu}(1a)\text{C}(2a)$  cycle is bent on the  $\text{C}(2) \dots \text{C}(2a)$  line; the dihedral angle between the  $\text{Lu}(1)\text{C}(2)\text{C}(2a)$  and  $\text{Lu}(1a)\text{C}(2)\text{C}(2a)$  planes is  $147.8^\circ$ . The Lu(1) atom and geometrical centers of the Cp ligand (Xa), the  $\text{O}(1) \dots \text{O}(2)$  and  $\text{C}(2) \dots \text{C}(2a)$  lines (Xb and Xc respectively) are in one plane. The  $\text{XaLu}(1)\text{Xb}$ ,  $\text{XaLu}(1)\text{Xc}$  and  $\text{XbLu}(1)\text{Xc}$  angles are  $106.2^\circ$ ,  $129.0^\circ$  and  $124.7^\circ$  respectively, and the sum of these angles,  $359.9^\circ$ , is close to  $360^\circ$ . In contrast with the C(9) atom, approximately lying in the  $\text{C}(2)\text{C}(1)\text{C}(1a)\text{C}(2a)$  plane (the deviation is  $0.03 \text{ \AA}$ ), the C(3) atom is displaced out of this plane on  $0.40 \text{ \AA}$ .

Table 1  
Bond lengths *d*

Atoms	<i>d</i> (Å)	Atoms	<i>d</i> (Å)
Lu(1)–O(1)	2.419(6)	Lu(1)–O(2)	2.409(6)
Lu(1)–C(1)	2.629(7)	Lu(1)–C(2)	2.280(7)
Lu(1)–C(15)	2.60(1)	Lu(1)–C(16)	2.67(1)
Lu(1)–C(17)	2.65(1)	Lu(1)–C(18)	2.61(1)
Lu(1)–C(19)	2.56(1)	Lu(1)–Lu(1a)	3.502(2)
Lu(1)–C(1a)	2.608(7)	Lu(1)–C(2a)	2.336(7)
O(1)–C(20)	1.44(1)	O(1)–C(21)	1.43(1)
O(2)–C(22)	1.46(1)	O(2)–C(23)	1.42(1)
C(1)–C(2)	1.476(9)	C(1)–C(9)	1.52(1)
C(1)–Lu(1a)	2.608(7)	C(1)–C(1a)	1.45(1)
C(2)–C(3)	1.47(1)	C(2)–Lu(1a)	2.336(7)
C(3)–C(4)	1.41(1)	C(3)–C(8)	1.42(1)
C(4)–C(5)	1.39(1)	C(5)–C(6)	1.36(1)
C(6)–C(7)	1.39(1)	C(7)–C(8)	1.39(1)
C(9)–C(10)	1.41(1)	C(9)–C(14)	1.40(1)
C(10)–C(11)	1.39(1)	C(11)–C(12)	1.39(1)
C(12)–C(13)	1.36(1)	C(13)–C(14)	1.39(1)
C(15)–C(16)	1.42(2)	C(15)–C(19)	1.36(2)
C(16)–C(17)	1.37(2)	C(17)–C(18)	1.33(2)
C(18)–C(19)	1.32(2)	C(21)–C(22)	1.47(2)
C(24)–C(25)	1.38(1)	C(24)–C(29)	1.34(1)
C(25)–C(26)	1.35(1)	C(26)–C(27)	1.35(2)
C(27)–C(28)	1.38(2)	C(28)–C(29)	1.36(1)

Table 2  
Bond angles  $\omega$ 

Atoms	$\omega$ (°)	Atoms	$\omega$ (°)
O(1)–Lu(1)–O(2)	66.5(2)	O(1)–Lu(1)–C(1)	86.9(2)
O(2)–Lu(1)–C(1)	98.4(2)	O(1)–Lu(1)–C(2)	88.3(2)
O(2)–Lu(1)–C(2)	129.3(2)	Lu(1)–O(1)–C(21)	120.0(5)
O(2)–Lu(1)–C(1a)	84.3(2)	Lu(1)–O(2)–C(22)	113.3(6)
O(2)–Lu(1)–C(2a)	96.7(2)	C(22)–O(2)–C(23)	113.1(7)
C(2)–Lu(1)–C(2a)	75.7(3)	Lu(1)–C(1)–C(9)	136.8(5)
Lu(1)–O(1)–C(20)	123.6(5)	Lu(1)–C(1)–Lu(1a)	83.9(2)
C(20)–O(1)–C(21)	109.8(7)	C(9)–C(1)–Lu(1a)	137.9(5)
O(1)–C(21)–C(22)	103.6(8)	C(2)–C(1)–C(1a)	117.9(4)
O(2)–C(22)–C(21)	110.7(8)	Lu(1)–C(2)–C(3)	140.7(5)
Lu(1)–O(2)–C(23)	127.9(6)	Lu(1)–C(2)–Lu(1a)	98.7(2)
C(2)–C(1)–C(9)	121.8(6)	C(3)–C(2)–Lu(1a)	111.0(4)
C(9)–C(1)–C(1a)	120.2(4)	C(2)–C(3)–C(8)	117.7(6)
C(1)–C(2)–C(3)	121.6(6)	C(3)–C(4)–C(5)	122.8(7)
C(2)–C(3)–C(4)	128.7(6)	C(5)–C(6)–C(7)	118.8(7)
C(4)–C(3)–C(8)	113.5(7)	C(3)–C(8)–C(7)	123.9(7)
C(4)–C(5)–C(6)	121.7(7)	C(1)–C(9)–C(14)	119.1(7)
C(6)–C(7)–C(8)	119.3(7)	C(9)–C(10)–C(11)	121.0(8)
C(1)–C(9)–C(10)	123.2(7)	C(11)–C(12)–C(13)	118.7(8)
C(10)–C(9)–C(14)	117.7(7)	C(9)–C(14)–C(13)	119.9(7)
C(10)–C(11)–C(12)	120.2(8)	C(15)–C(16)–C(17)	104.1(10)
C(12)–C(13)–C(14)	122.4(8)	C(17)–C(18)–C(19)	108.1(9)
C(16)–C(15)–C(19)	107.0(10)	C(25)–C(24)–C(29)	118.1(9)
C(16)–C(17)–C(18)	110.9(10)	C(24)–C(25)–C(26)	120.3(9)
C(15)–C(19)–C(18)	109.9(10)	C(26)–C(27)–C(28)	119.8(9)
C(24)–C(29)–C(28)	122.7(9)	C(25)–C(26)–C(27)	120.8(9)
C(27)–C(28)–C(29)			

The Lu(1)–C(2) distance, 2.280(7) Å, is shorter than the Lu(1a)–C(2) distance, 2.336(7) Å, and the values of the Lu–C  $\sigma$ -bond lengths found in the monomeric compounds Cp<sub>2</sub>LuR(THF) (2.345 Å for R = *p*-C<sub>6</sub>H<sub>4</sub>Me [12], 2.376 Å for R = CH<sub>2</sub>SiMe<sub>3</sub> [12], and 2.47 Å for R = <sup>t</sup>Bu [13]) and the terminal Lu–C  $\sigma$  bond, 2.344 Å, in the dinuclear complex (Me<sub>5</sub>C<sub>5</sub>)<sub>2</sub>Lu(μ-CH<sub>3</sub>)Lu(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>CH<sub>3</sub> [14]. The Lu(1)–C(1) and Lu(1a)–C(1) distances (2.629(7) Å and 2.608(7) Å respectively) are significantly longer than the above-mentioned Lu–C  $\sigma$ -bond lengths and comparable with the average Lu–C(Cp)  $\eta^5$  distance, 2.62 Å, in **3**.

The C(1)–C(2) and C(1)–C(1a) distances in **3** (1.476(9) and 1.45(1) Å respectively) are in the range between the values of double C=C and single C–C bonds. Thus, in contrast with long–short–long distances

in the coordinated fragment of naphthalene in **1a**, some delocalization of electron density in the C<sub>4</sub> fragment of **3** evidently takes place. The C(2)–C(3) distance, 1.47(1) Å, is also shorter relative to the typical value of C(sp<sup>3</sup>)–C<sub>ar</sub> bond lengths, 1.513 Å [15], while the C(1)–C(9) distance, 1.52(1) Å, is close to this value. It may indicate that the C(3) and C(3a) atoms are also involved in the conjugated system. The similar distribution of the C–C bond distances in the  $\eta^4$ -coordinated fragment of diphenylbutadiene was found in the molecule [K(THF)<sub>2</sub>(μ-C<sub>4</sub>H<sub>4</sub>Ph<sub>2</sub>)<sub>2</sub>Lu(THF)<sub>2</sub>]<sub>n</sub> [16].

The Lu–O(1) and Lu–O(2) distances are 2.419(6)

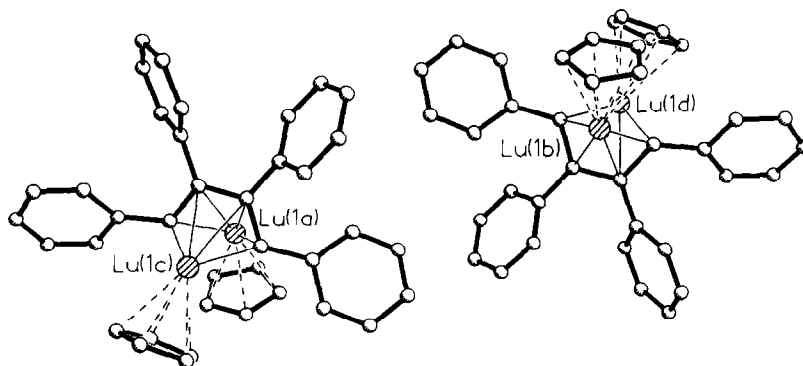
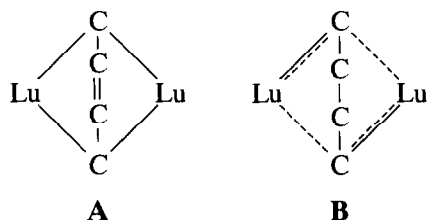


Fig. 2. Two enantiomeric molecules of **3** connected in the crystal structure by the center of symmetry (DME molecules were omitted for clarity).

and 2.409(6) Å respectively. The Me groups of DME molecules are significantly bent away from the C<sub>4</sub>Ph<sub>4</sub> fragment of **3** (Fig. 1) owing to the repulsion of Ph and Me groups. The deviations of the C(20) and C(23) atoms from the Lu(1)O(1)O(2) plane are 0.40 Å and 0.84 Å respectively.

It is interesting to note that all Ph rings are turned around C–C bonds connecting them with the central C<sub>4</sub> fragment in the same direction (clockwise for the molecule presented in Fig. 1). The rotation angles are 36.7° (around the C(2)–C(3) bond), and 48.9° (around the C(1)–C(9) bond). So, the C<sub>4</sub>Ph<sub>4</sub> ligand in **3** has an asymmetrical propeller-like structure, which provides chirality to the molecule of the complex on the whole. There are two enantiomeric forms of molecules in a crystal of **3**. The pair of these molecules connected by the centre of symmetry is shown in Fig. 2.

The formal 4 – charge of the bridging C<sub>4</sub>Ph<sub>4</sub> ligand together with the structural parameters suggest that Lu atoms in **3** are bonded by two carbon bridges of alkylidene type >C<sup>2–</sup>(C(2) and C(2a) atoms) connected by the ethene group. On the basis of valence bond consideration two formal description may represent the bonding in the LuC<sub>4</sub>Lu fragment:



Evidently structure **A** provides the main contribution to the complex structure. However, the observed difference in Lu(1)–C(2) and Lu(1)–C(2a) distances may be attributed to some contribution of structure **B**. The repulsion of the Ph rings and the CH<sub>3</sub> groups of DME ligand and asymmetric interposition of Ph rings may be responsible for this difference as well.

The formation of lanthanoid complexes of similar type were assumed before in the thermal decomposition of trialkyl derivatives R<sub>3</sub>Ln (Ln = Er or Lu, R = CH<sub>2</sub>SiMe<sub>3</sub> [17]) (Ln = Nd; R = CH<sub>2</sub>SiMe<sub>3</sub> or CH<sub>2</sub>Ph [18]) but the products were not isolated in the crystalline state. For one of them, [Li(TMED)] [Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(CHSiMe<sub>3</sub>)], a bridging type of alkylidene ligand was supposed on the basis of its IR spectrum [17]. The first structurally characterized lanthanoid carbene complexes (C<sub>5</sub>Me<sub>4</sub>Et)<sub>2</sub>YbL (L = :CN(R)C(Me)=C(Me)NR, R = Me or <sup>1</sup>Pr) have been obtained recently by Schumann et al. [19] by the reaction of (C<sub>5</sub>Me<sub>4</sub>Et)<sub>2</sub>Yb with stable carbenes–imidazol-2-ylidenes. The long Yb–C(carbene) distances (2.552 Å) and divalent state of Yb indicate that in these compounds carbene adds to metal as a coordinated π-donor ligand. The similar carbene com-

plexes of Sm, Eu and Yb have been obtained independently in the same way by DuPont Laboratory [20].

### 3. Experimental details

The instrumentation and general procedures employed for this study were identical with those given in a previous paper [1]. <sup>1</sup>H NMR spectra were recorded on a Tesla BS-487-C instrument. Organic reagents were recrystallized (Ph<sub>2</sub>C<sub>2</sub> and Ph<sub>2</sub>N<sub>2</sub>) or redistilled (PhC≡CSiMe<sub>3</sub> and Me<sub>3</sub>SiC≡CSiMe<sub>3</sub>) before use. Complex **1a** was obtained as described earlier [3].

#### 3.1. Synthesis of [CpLu(THF)]<sub>2</sub>(Ph<sub>2</sub>N<sub>2</sub>)<sub>2</sub> (**2**)

Sodium naphthalenide solution, obtained from 0.054 g (2.31 mmol) of Na metal and 0.350 g (2.70 mmol) of C<sub>10</sub>H<sub>8</sub> in 10 ml of THF, was added to a suspension of 0.608 g (1.15 mmol) of CpLuCl<sub>2</sub>(THF)<sub>3</sub> in 10 ml of THF. The reaction mixture was shaken until CpLuCl<sub>2</sub>(THF)<sub>3</sub> had dissolved; then NaCl precipitate was centrifuged off. To the dark-red solution of **1b** obtained, 0.218 g (1.20 mmol) of Ph<sub>2</sub>N<sub>2</sub> was added. The reaction mixture immediately turned light yellow. The solvent was evaporated in vacuum, and the residue was extracted with hexane (3 × 10 ml) to remove C<sub>10</sub>H<sub>8</sub> and excess Ph<sub>2</sub>N<sub>2</sub>. The solid obtained was dissolved in a minimum volume of THF and the solution was cooled to –15°C to give colourless crystals. After drying in vacuum at 50°C 0.325 g (54%) of **3** was obtained as a white powder melting point (m.p.) 203–205°C (decomposition).

Anal. Found: Lu, 35.1. C<sub>42</sub>H<sub>46</sub>N<sub>4</sub>O<sub>2</sub>Lu<sub>2</sub> calc.: Lu, 35.4%. IR data (Nujol): γ 1574, 1283, 1240, 1160, 1097, 1074, 1016, 985, 928, 887, 885, 805, 770, 750, 690, 510, 380, 345 cm<sup>–1</sup>.

#### 3.2. Synthesis of [CpLu(DME)]<sub>2</sub>(Ph<sub>4</sub>C<sub>4</sub>) (**3**)

To a suspension of 0.523 g (1.14 mmol) of **1a** in 15 ml of DME a solution of 0.203 g (1.14 mmol) of tolan in 5 ml of DME was added. After of vigorous shaking for 2 h, **1** dissolved completely and a crystalline precipitate was formed. The solution was decanted; the precipitate was washed twice with cold DME and dried in vacuum, yielding 0.273 g (50%) of **2** as dark-red glistening crystals (m.p. 173–175°C (decomposition)). From the mother solution after removal of DME in vacuum, naphthalene was separated by hexane extraction with a nearly quantitative yield (gas–ligand chromatography (GLC) analysis).

Anal. Found: Lu, 33.8. C<sub>46</sub>H<sub>50</sub>O<sub>4</sub>Lu<sub>2</sub> calc.: Lu, 34.4%. IR data (Nujol): 1560, 1522, 1318, 1275, 1240, 1174, 1137, 1088, 1040, 1020, 1008, 980, 856, 784, 737, 696, 576, 515, 439, 419, 373 cm<sup>–1</sup>.

### 3.3. Hydrolysis of 3

To a suspension of 0.272 g of **3** in 5 ml of benzene, 0.1 ml of degased water was added. A white precipitate of  $\text{Lu}(\text{OH})_3$  was centrifuged off and washed twice with small portions of benzene. In combined benzene solution CpH (0.034 g (97%)) and DME (0.029 g (60%)) were found by the GLC method. Removal of solvent and volatiles in vacuum yields 0.092 g (96%) of 1,2,3,4-tetraphenylbut-1-en with a m.p. at 146–148°C (after recrystallization from hexane).

Anal. Found: C, 93.22; H, 6.85. for  $\text{C}_{28}\text{H}_{24}$  calc.: C, 93.29; H, 6.71%. IR data (Nujol): 3065, 3040, 3010, 1586, 1480, 1065, 1022, 908, 860, 785, 760, 752, 747, 734, 696, 690, 675, 640, 584, 548, 530, 515, 500, 477  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.7–7.2 (m, 20H ( $\text{C}_6\text{H}_5$ )), 6.61 (s, 1H ( $\text{HC}(\text{Ph}=\text{)}}$ )), 4.02 (t, 1H ( $-\text{CH}(\text{Ph})-$ )), 3.22 (m, 2H ( $-\text{CH}_2\text{Ph}$ )) ppm.

### 3.4. X-ray analysis

An X-ray diffraction experiment was carried out with a Siemens P3/PC diffractometer. The crystal data, data collection and refinement are given in the Table 3. The structure was determined by a combination of the direct

Table 3  
Crystal data and details of the structure analysis of  $3 \cdot 2\text{C}_6\text{H}_6$

Empirical formula	$\text{C}_{46}\text{H}_{50}\text{O}_4\text{Lu}_2 \cdot 2\text{C}_6\text{H}_6$
Crystal size (mm)	$0.40 \times 0.35 \times 0.30$
Crystal system	Orthorhombic
Space group	<i>Pbcn</i>
Unit cell dimensions	
<i>a</i> (Å)	14.266(8)
<i>b</i> (Å)	15.625(7)
<i>c</i> (Å)	21.612(10)
Volume (Å <sup>3</sup> )	4817(4)
Z	4
Formula weight	1173.0
Density (calculated) ( $\text{Mg m}^{-3}$ )	1.617
Absorption coefficient ( $\text{mm}^{-1}$ )	4.127
<i>F</i> (000)	2336
Radiation	$\text{Mo K}\alpha$ ( $\lambda = 0.71073$ Å)
Temperature (K)	193
Range (°)	2.0–56.0
Scan type	$2\theta - \theta$
Index ranges	$0 \leq h \leq 15,$ $0 \leq k \leq 18,$ $0 \leq l \leq 25$
reflections collected	4680
observed reflections	2266 ( $F > 4.0\sigma(F)$ )
Weighting scheme	$w^{-1} = \sigma^2(F)$
Final <i>R</i> indices (observed data)	
<i>R</i>	0.0393
<i>wR</i>	0.0234
Goodness of fit	1.63
$(\Delta/\sigma)_{\text{av}}$ in the final cycle	0.048
Data-to-parameter ratio	7.8 to 1

Table 4. Atom coordinates and temperature factors

Atom	<i>x</i> ( $\times 10^4$ )	<i>y</i> ( $\times 10^{-4}$ )	<i>z</i> ( $\times 10^{-4}$ )	$U_{\text{eq}}$ ( $\times 10^{-3}$ Å <sup>2</sup> )
Lu(1)	1076(1)	1722(1)	2110(1)	24(1)
O(2)	2537(4)	1057(4)	2413(3)	43(2)
O(2)	1713(4)	782(4)	1333(3)	50(2)
C(1)	234(5)	565(4)	2797(3)	20(2)
C(2)	500(5)	1399(4)	3066(3)	20(2)
C(3)	736(5)	1488(4)	3726(4)	24(2)
C(4)	494(6)	948(5)	4222(3)	28(3)
C(5)	706(6)	1140(5)	4832(4)	36(3)
C(6)	1176(6)	1866(5)	4989(3)	40(3)
C(7)	1445(5)	2427(6)	4524(4)	36(3)
C(8)	1227(6)	2233(5)	3911(3)	32(3)
C(9)	497(5)	−276(5)	3105(3)	24(3)
C(10)	−147(6)	−946(5)	3204(4)	35(3)
C(11)	121(6)	−1694(6)	3507(4)	45(3)
C(12)	1035(7)	−1792(6)	3718(3)	45(3)
C(13)	1658(6)	−1144(5)	3621(4)	43(3)
C(14)	1412(5)	−390(5)	3319(3)	27(3)
C(15)	1323(10)	2967(6)	1331(5)	75(5)
C(16)	2238(8)	2820(6)	1560(6)	68(5)
C(17)	2194(7)	3078(6)	2163(5)	61(4)
C(18)	1336(9)	3356(7)	2304(4)	61(4)
C(19)	808(6)	3284(7)	1808(6)	60(4)
C(20)	3130(7)	1379(7)	2899(5)	75(4)
C(21)	3095(7)	618(6)	1962(5)	60(4)
C(22)	2399(7)	177(7)	1577(5)	79(5)
C(23)	1829(7)	948(8)	689(4)	87(5)
C(24)	4949(7)	166(6)	4130(4)	54(4)
C(25)	4040(7)	−137(6)	4139(4)	55(4)
C(26)	3354(7)	317(7)	4423(4)	55(4)
C(27)	3546(7)	1067(7)	4705(5)	56(4)
C(28)	4451(7)	1385(6)	4698(4)	54(4)
C(29)	5125(7)	922(6)	4405(4)	50(4)

method with calculations of difference Fourier maps. Besides the main molecule of **3** the crystal structure contains solvating benzene molecules. The structure of **3** was refined with anisotropic thermal factors for all non-hydrogen atoms. The H atoms were placed geometrically and refined in the riding model with fixed isotropic thermal factors ( $B_{\text{iso}} = 8$  Å<sup>2</sup>). Absorption was taken into account by the DIFABS program [21]. The final discrepancy factors are:  $R = 0.0393$ ,  $R_w = 0.0234$  and  $S = 1.63$  for observed reflections. The next weighting scheme  $w^{-1} = \sigma^2(F)$  was used for refinement structure. The average  $\Delta/\sigma$  value in the final cycle is 0.048. All calculations were performed using the SHELXTL-Plus package [22]. The final atomic coordinates are given in the Table 4.

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## References

- [1] M.N. Bochkarev, A.A. Trifonov, E.A. Fedorova, N.S. Emelyanov, T.A. Basalgina, G.S. Kalinina and G.A. Razuvaev, *J. Organomet. Chem.*, **372** (1989) 217.
- [2] M.N. Bochkarev, I.M. Penyagina, L.N. Zakharov, Yu.F. Rad'kov, E.A. Fedorova, S.Ya. Khorshev and Yu.T. Struchkov, *J. Organomet. Chem.*, **378** (1989) 363.
- [3] A.V. Protchenko, L.N. Zakharov, M.N. Bochkarev and Yu.T. Struchkov, *J. Organomet. Chem.*, **447** (1993) 209.
- [4] M.N. Bochkarev, V.V. Khramenkov, Yu.F. Rad'kov, L.N. Zakharov and Yu.T. Struchkov, *J. Organomet. Chem.*, **421** (1991) 29.
- [5] M.N. Bochkarev, I.L. Fedyushkin, V.K. Cherkasov, V.I. Nevodchikov, H. Schumann and F.H. Gorlitz, *Inorg. Chim. Acta*, **201** (1992) 69.
- [6] A.A. Trifonov, M.N. Bochkarev, H. Schumann and J. Loebel, *Angew. Chem. Int. Ed. Engl.*, **30** (1991) 1149.
- [7] N.S. Emelyanova, M.N. Bochkarev, H. Schumann, J. Loebel and L. Esser, *Koord. Khim.*, **20** (1994) 789.
- [8] M.N. Bochkarev, A.A. Trifonov, F.G.N. Cloke, C.I. Dalby, P.T. Matsunaga, R.A. Andersen, H. Schumann, J. Loebel and H. Hemling, *J. Organomet. Chem.*, **486** (1995) 177.
- [9] W.J. Evans, D.K. Drummond, L.R. Chamberian, R.J. Doedens, S.G. Bott, H. Zhang and J.L. Atwood, *J. Am. Chem. Soc.*, **110** (1988) 4983.
- [10] I.L. Fedyushkin and M.N. Bochkarev, *Russ. Chem. Bull.*, **42** (1993) 1408.
- [11] D.J. Sikora and M.D. Rausch, *J. Organomet. Chem.*, **276** (1984) 21.
- [12] H. Schumann, W. Genthe, N. Bruncks and J. Pickardt, *Organometallics*, **1** (1982) 1194.
- [13] W.J. Evans, A.L. Wayda, W.E. Hunter and J.L. Atwood, *J. Chem. Soc., Chem. Commun.*, (1981) 292.
- [14] P.L. Watson and G.W. Parshall G.W., *Account Chem. Res.*, **18** (1985) 51.
- [15] F.A. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. II*, (1987) S1.
- [16] N.S. Emelyanova, A.A. Trifonov, L.N. Zakharov, M.N. Bochkarev, A.F. Shestakov and Yu. T. Struchkov, *Metalloorgan. Khim.*, **6** (1993) 363.
- [17] H. Schumann, J. Muller, *J. Organomet. Chem.*, **169** (1979) C1.
- [18] B.A. Dolgoplosk, E.A. Tinyakova, I. Sh. Guzman, E.L. Vollerstein, N.N. Chigir, G.N. Bondarenko, O.K. Sharaev and V.A. Yakovlev, *J. Organomet. Chem.*, **201** (1980) 249.
- [19] H. Schumann, M. Glanz, J. Winterfeld, H. Helming, N. Kuhn and T. Kratz, *Angew. Chem., Int. Ed. Engl.*, **33** (1994) 1733.
- [20] A.J. Arduengo, III, M. Tamm, S.J. McLain, J.C. Calabrese, F. Davidson, and W. J. Marshall, *J. Am. Chem. Soc.*, **116** (1994) 7927.
- [21] N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, **39** (1983) 158.
- [22] G. M. Sheldrick, *Structure Determination Software Program Package (PC version)*. Siemens Analytical X-ray Instruments, Madison, WI, 1989.