Dimerization of cyclopentadienyl ligands in the synthesis of transition metal complexes. 1,4,5,6,7,10,11,12-Octamethyltricyclo[7.3.0.$0^{3,7}$]-dodeca-3,5,9,11-tetraene and the complex of 1,1′,3,3′-tetrakis-(*tert*-butyl)-1,1′-dihydrofulvalene with I_3^-

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1,4,5,6,7,10,11,12-Octamethyltricyclo[7.3.0.$0^{3,7}$]dodeca-3,5,9,11-tetraene was obtained as a by-product in the synthesis of $(C_5Me_5)_2CeCl$ from $CeCl_3$ and NaC_5Me_5. The complex of 1,1′,3,3′-tetrakis(*tert*-butyl)-1,1′-dihydrofulvalene with I_3^- was obtained as the major product in the reaction of YbI_3 with 1,3-$Bu^t_2C_5H_3Na$. The structures of the title compounds were established by X-ray diffraction analysis.

Key words: metallocenes, ytterbium, cerium, iodine, dimerization, cyclopentadiene, complexes, structure.

Generally, the synthesis of transition metal complexes with the composition L_mMX_n (L is cyclopentadienyl, indenyl, or fluorenyl; $m = 1$ or 2; X = H or Cl; $n = 1-3$) is accompanied by side reactions associated with condensation of the ligand L to form oligomeric or polymeric products with uncertain compositions and structures.[1,2] It was suggested that the process of coupling of the cyclopentadienyl ligands begins with their dimerization, as is the case, for example, with complexes containing fluorenyl ligands.[3,4]

An increase or a decrease in the rate of side reactions and in the yields of by-products are commonly related to the Lewis acidity of the transition metal halide, the reducing ability of the metal, the oxidizing ability of the ligand, the reaction temperature, and the nature of the solvent. However, these reasons are rather general and are not necessarily manifested as expected. Thus, for example, no problems associated with the preparation of sandwich complexes based on $LnCl_3$ or LnI_2, which are rather strong Lewis acids, even in tetrahydrofuran and at room temperature, were mentioned in the literature.[5,6]

The best known examples of reactions affording large amounts of by-products are those associated with the use of metal salts which can readily reduce, for example, titanium tetrahalides or tantalum pentachloride, in syntheses of metallocenes. These reactions are always accompanied by side processes of oxidation of the ligand anions to radicals followed by their condensation. Moreover, it was noted that stable titanium monofluorenylchlorides cannot be prepared from alkali metal fluorenides[4,7] or Me_3Si-substituted macroligands.[7,8] The first representative of zirconium chloride monofluorenides has been prepared quite recently, apparently, only owing to additional stabilization through coordination of the metal atom by the alkoxy group bound to the fluorenyl ligand.[9]

It should be noted that the major aim of most of the cited studies was to prepare metallocenes and to develop procedures which would preclude or, wherever possible, diminish side reactions. However, certain by-products may be of interest by themselves. The present work is devoted to the synthesis and study of the structures of 1,4,5,6,7,10,11,12-octamethyltricyclo[7.3.0.$0^{3,7}$]dodeca-3,5,9,11-tetraene (**1**) and 1,1′,3,3′-tetrakis(*tert*-butyl)-1,1′-dihydrofulvalene. The latter was isolated from a solution as an ionic complex with the I_3^- anion (**2**), which was formed in the course of preparation and/or decomposition of lanthanidocene complexes.

Results and Discussion

Synthesis and structure of 1,4,5,6,7,10,11,12-octamethyltricyclo[7.3.0.$0^{3,7}$]dodeca-3,5,9,11-tetraene. Recently,[10] the directed synthesis and the structure of 1,4,5,6,7,10,11,12-octamethyltricyclo[7.3.0.$0^{3,7}$]dodeca-

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3,5,9,11-tetraene (**1**) were described. Compound **1** was prepared by the reaction of Me_5C_5Br with Bu^tOK in the presence of 18-crown-6 followed by heating of the mixture *in vacuo* at 250 °C. We found that compound **1** was formed as a by-product in the synthesis of $(C_5Me_5)_2CeCl$, which was performed according to the equation

$$2\ Cp^*Na + CeCl_3 \rightarrow Cp^*_2CeCl + 2\ NaCl.$$

After distillation of the solvent, tetraene **1** was sublimed *in vacuo* as a pale-yellow powder containing cerocene chloride as an admixture. After recrystallization from toluene, compound **1** was isolated as colorless well-faceted crystals in ~8% yield.

The mechanism of formation of the "dimer" with composition $[Me_4C_5(\mu\text{-}CH_2)]_2$ in this reaction remains unclear and is, apparently, rather complex. Actually, the known cyclopentadienyl (and, particularly, pentamethylcyclopentadienyl) complexes of the last elements of the transition-metal series are rather resistant to heating and are not decomposed *in vacuo* at a temperature of up to 120—130 °C. In addition, the Ce atom in the complex under consideration exists in the lowest oxidation state. Consequently, the formation of compound **1** cannot result from simple decomposition of cerocene chloride Cp^*_2CeCl, as in the case, for example, of formation of complex **2** (see below).

According to the data of X-ray diffraction analysis of compound **1** (Fig. 1, Tables 1 and 2), two crystallographically independent centrosymmetrical molecules crystallize in the triclinic system with the space group $P\bar{1}$, unlike the known[10] form of **1**, in which two independent centrosymmetrical molecules crystallize in the monoclinic system with the space group $P2_1/n$. Note that the geometric characteristics of both modifications are virtually identical. The central six-membered ring adopts a "classical" chair conformation. There is a clear-cut distinction between the single and double bonds in the five-membered rings, which virtually do not adopt an envelope conformation: the C(2a)—C(5a) (C(2b)—C(5b)) atoms are in a single plane to within 0.01 Å, whereas the C(1a) and C(1b) atoms deviate from this plane by 0.09 Å.

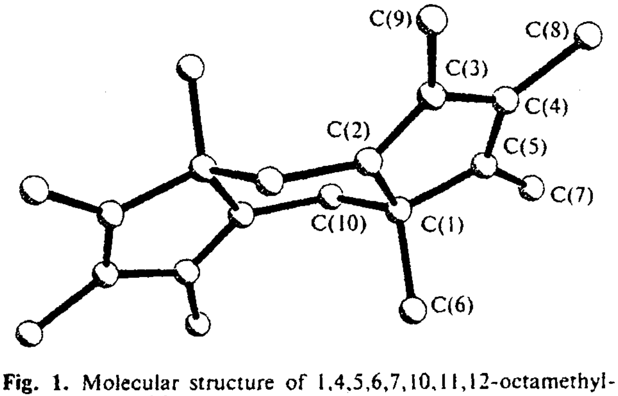

Fig. 1. Molecular structure of 1,4,5,6,7,10,11,12-octamethyltricyclo[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraene (**1**).

Table 1. Principal interatomic distances (*d*) in the structure of **1**

Bond	*d*/Å	Bond	*d*/Å
C(1a)—C(2a)	1.515(6)	C(1b)—C(2b)	1.508(7)
C(1a)—C(5a)	1.500(7)	C(1b)—C(5b)	1.513(6)
C(1a)—C(10a)	1.559(6)	C(1b)—C(10b)	1.548(7)
C(2a)—C(3a)	1.338(7)	C(2b)—C(3b)	1.330(7)
C(2a)—C(10′)	1.502(5)	C(2b)—C(10′b)	1.493(6)
C(3a)—C(4a)	1.484(6)	C(3b)—C(4b)	1.482(6)
C(4a)—C(5a)	1.344(7)	C(4b)—C(5b)	1.344(9)

Table 2. Principal angles (ω) in the structure of **1**

Angle	ω/deg
C(2a)—C(1a)—C(5a)	102.3(4)
C(2a)—C(1a)—C(10a)	108.2(3)
C(5a)—C(1a)—C(10a)	113.2(4)
C(1a)—C(2a)—C(3a)	109.8(3)
C(1a)—C(2a)—C(10′a)	118.5(3)
C(3a)—C(2a)—C(10′a)	131.3(4)
C(2a)—C(3a)—C(4a)	109.0(4)
C(3a)—C(4a)—C(5a)	108.6(4)
C(1a)—C(5a)—C(4a)	110.2(4)
C(1a)—C(10a)—C(2′a)	109.9(4)
C(2b)—C(1b)—C(5b)	102.8(4)
C(2b)—C(1b)—C(10b)	109.4(4)
C(5b)—C(1b)—C(10b)	112.6(4)
C(1b)—C(2b)—C(3b)	110.0(4)
C(1b)—C(2b)—C(10′b)	118.8(4)
C(3b)—C(2b)—C(10′b)	130.8(4)
C(2b)—C(3b)—C(4b)	108.9(4)
C(3b)—C(4b)—C(5b)	109.4(4)
C(1b)—C(5b)—C(4b)	108.8(4)
C(1b)—C(10b)—C(2′b)	110.0(4)

Synthesis and structure of 1,1′,3,3′-tetrakis(*tert*-butyl)-1,1′-dihydrofulvalene (2). The synthesis of the tautomeric forms of 1,1′,3,3′-tetrakis(*tert*-butyl)dihydrofulvalene by oxidative dimerization of lithium 1,3-di-*tert*-butylcyclopentadienide in the presence of iodine in tetrahydrofuran has been developed previously.[11] In attempting to synthesize $(1,3\text{-}Bu^t_2Cp)YbI_2$ by the reaction of YbI_3 with one equivalent of $Bu^t_2C_5H_3Na$ in THF, we obtained 1,1′,3,3′-tetrakis(*tert*-butyl)-1,1′-dihydrofulvalene in rather good yield instead of the expected monocyclopentadienyl complex. The reaction product was isolated from a toluene solution as an ionic complex with the $[I_3]^-$ anion (**2**). The composition of the cation was unidentified.

The formation of dihydrofulvalene in this reaction can be explained by two possible mechanisms. The first mechanism involves direct oxidation of the cyclopentadienyl anion under the action of YbI_3 to the radical followed by its dimerization. The second mechanism consists in rapid decomposition of unstable $(Bu^t_2C_5H_3)YbI_2$ to give the $Bu^t_2C_5H_3$ radical and YbI_2. However, it should be mentioned that the reducing function of the cyclopentadienyl ligand and the possibility of reduction of the Yb^{3+} ion with this ligand are not evident. This possibility, as applied to ytterbocene(III) chlorides, has not been considered previously[5] although it was implicitly mentioned[2] in a comparative study of procedures for the synthesis of Cp_2TaH_3. In view of this fact and taking into account the published data[7,8] on thermal instability of monofluorenyl titanium complexes and the lower stability of metallocene iodides, we believe that the latter mechanism is more adequate.

According to the X-ray diffraction data, there are no valent or van der Waals contacts between the I_3^- ion and the fulvalene fragment in complex **2** (Fig. 2, Tables 3 and 4). However, a rather short distance between the anions (4.204 Å) is indicative of either a weak direct interaction between these anions or, what is more probable, of an electrostatic interaction, for example, through the H^+ cation. Although we failed to reveal the position of the proton by X-ray diffraction analysis, its presence in the compound can be assumed based on the neutrality of the fulvalene molecule because the positions of all substituents at the C atoms, including the protons at the C(2), C(4), C(5), C(7), C(9), and C(10) atoms (Fig. 3), were determined from the experimental data (without refinement of their positions). The I_3^- anion in compound **2** is nonlinear, unlike the structures of ferrocenium triiodide (and a number of other inorganic triiodides), in which the bond angle in this fragment is 180° provided the I—I bond lengths are identical.[12] However, in the structure of dimethylferrocenium[13] and in some other triiodides, the anions are strongly polarized (the reasons for this phenomenon were not discussed in the published works), resulting in differences in the I—I bond lengths from a hundredth to a tenth of an Å and, as a consequence, in the distortion of the linear structure. The nonlinear structure of the I_3^- anion in complex **2** with virtually equal I_c—I(1) and I_c—I(2) bond lengths, where I_c is the central atom (Δ = 0.007 Å, which is several orders of magnitude lower than the values reported previously[13]), can be attributed, for example, to the presence of the $I_3^-...H^+...I_3^-...H^+...$ cation-anionic chain. One of the protons of the cyclopen-

Table 3. Principal interatomic distances (*d*) in the structure of **2**

Bond	*d*/Å	Bond	*d*/Å
I_c*—I(1)	2.899(3)	C(5)—C(15)	1.56(3)
I_c*—I(2)	2.906(3)	C(6)—C(7)	1.38(3)
C(1)—C(2)	1.37(3)	C(6)—C(10)	1.52(3)
C(1)—C(6)	1.42(3)	C(7)—C(8)	1.37(3)
C(1)—C(5)	1.52(3)	C(8)—C(9)	1.41(3)
C(2)—C(3)	1.38(3)	C(8)—C(19)	1.49(3)
C(3)—C(4)	1.41(3)	C(9)—C(10)	1.53(3)
C(3)—C(11)	1.52(3)	C(10)—C(23)	1.55(3)
C(4)—C(5)	1.51(5)		

* The central I atom.

Table 4. Pricipal angles (ω) in the structure of **2**

Angle	ω/deg	Angle	ω/deg
I(1)—I_c*—I(2)	176.6(9)	C(7)—C(6)—C(1)	125(2)
C(2)—C(1)—C(6)	125(2)	C(7)—C(6)—C(10)	110(2)
C(2)—C(1)—C(5)	108(2)	C(1)—C(6)—C(10)	125(2)
C(6)—C(1)—C(5)	126(2)	C(8)—C(7)—C(6)	112(2)
C(1)—C(2)—C(3)	113(2)	C(7)—C(8)—C(9)	108(2)
C(2)—C(3)—C(4)	108(2)	C(7)—C(8)—C(19)	128(2)
C(2)—C(3)—C(11)	127(2)	C(9)—C(8)—C(19)	124(2)
C(4)—C(3)—C(11)	125(2)	C(8)—C(9)—C(10)	111(2)
C(3)—C(4)—C(5)	110(2)	C(6)—C(10)—C(9)	99(2)
C(4)—C(5)—C(1)	101(2)	C(6)—C(10)—C(23)	118(2)
C(4)—C(5)—C(15)	113(2)	C(9)—C(10)—C(23)	112(2)
C(1)—C(5)—C(15)	116(2)		

* The central I atom.

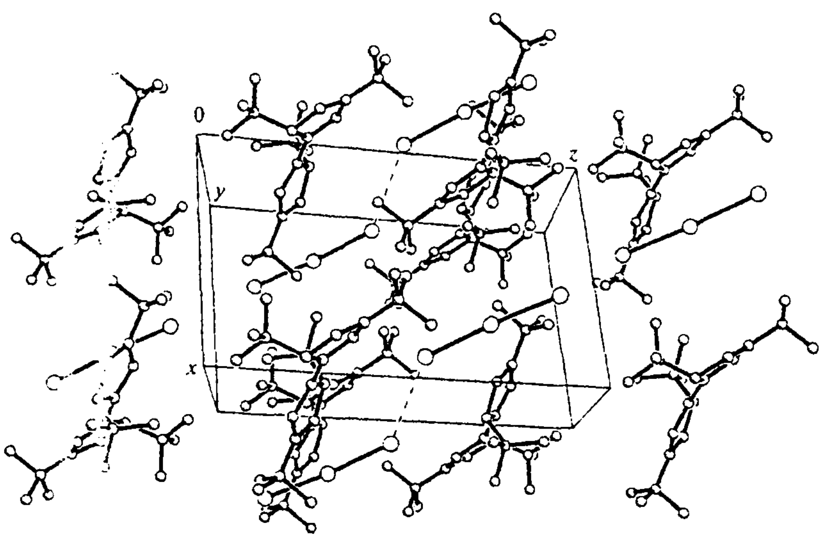

Fig. 2. Unit cell of the complex of 1,1′,3,3′-tetrakis(*tert*-butyl)-1,1′-dihydrofulvalene with I_3^- (**2**).

tadienyl rings, which are liberated upon condensation, can serve as a source of a proton in this chain. If this assumption is valid, the chemical formula of the compound under consideration should be written as follows: $\{[Q + I_3]^-H^+\}$, where Q is the neutral 1,1′,3,3′-tetrakis(*tert*-butyl)-1,1′-dihydrofulvalene molecule.

In the organic fragment of complex 2 (see Fig. 3), two Cp″ rings, which adopt an envelope conformation, are linked to each other through the sp^2-hybridized C atoms (C(1) and C(6)) and are inclined to one another (the angle between the planes is 146.4°), which is apparently associated with steric contacts between the *tert*-butyl groups at the quaternary C(5) and C(10) atoms, which are rotated in the same direction (the distance between the nearest C(17) and C(25) atoms is 3.98 Å, *i.e.*, these atoms are separated by a minimum allowed distance determined by the van der Waals radii of the methyl groups (~2 Å)). The double bonds in each five-membered ring are delocalized over the C(1)—C(4) atoms (the C(1)—C(2), C(2)—C(3), and C(3)—C(4) interatomic distances are 1.37, 1.38, and 1.41 Å, respectively) and over the C(6)—C(9) atoms (the C(6)—C(7), C(7)—C(8), and C(8)—C(9) distances are 1.38, 1.37, and 1.41 Å, respectively).

Hence, the possible mechanism of polymerization processes suggested previously is experimentally confirmed by the fact that the products formed in the initial stage of ligand condensation and consisting of two monomeric units were isolated in individual form in the course of the synthesis of metallocenes. In this case, the structures of the polymers depend on the number and the geometry of the alkyl substituents in the ring. In the course of the synthesis of metallocenes, polymers (rings without substituents), oligomers, or dimers can be formed as by-products, as in the case under consideration or in the case of substituted fluorenyl ligands.[7] This instability of monocyclopentadienyl, monofluorenyl, and, apparently, monoindenyl complexes of transition metals would be expected to be use in the future for the development of a general method r the synthesis of organic compounds of the above- nsidered type.

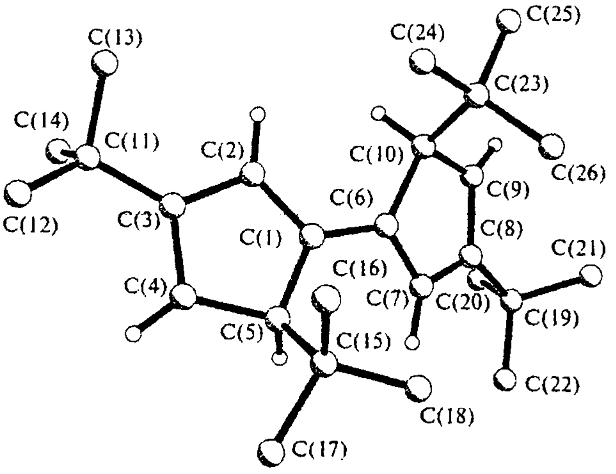

Fig. 3. Molecular structure of 1,1′,3,3′-tetrakis(*tert*-butyl)-1,1′-dihydrofulvalene.

xperimental

All operations assoc ted with the synthesis were carried out *in vacuo* or unde argon using the standard Schlenk technique. Diethyl ethe was distilled over $LiAlH_4$. Toluene was washed with H_2SO_4 nd distilled water, dried with $CaCl_2$, refluxed over $LiAlH_4$ f 3 h, and distilled. Tetrahydrofuran was refluxed over KOH or 2 h, distilled, and then distilled once again over $LiAlH_4$ r a Na/K alloy before use. Sodium di-*tert*-butylcyclopentadi ide was prepared according to known procedures.[14,15]

1,4,5,6,7,10,11,12- tamethyltricyclo[7.3.0.0^{3,7}]dodeca-3,5,9,11-tetraene (1). entamethylcyclopentadienylcerium chloride was prepared a cording to a known procedure (see, for example, Ref. 16) m $(C_5Me_5)_2Na$ (20 mL of 0.5 *M* solution in THF) and a hydrous $CeCl_3$ (1.22 g, 5 mmol, in 100 mL of THF). The lvent was removed *in vacuo* (10—15 Torr). The solid residue as dried at 50 °C and 1—2 Torr for 3 h. In the course of ying, a pale-yellow compound sublimed. After recrystalliz on of the resulting compound from toluene (50 mL, −30), transparent crystals of **1** were obtained in a yield of 2 g (8.3%). Found (%): C, 89.07; H, 10.85. $C_{20}H_{28}$. Calc ated (%): C, 89.49; H, 10.51. The sublimation of the m or product, *viz.*, $(C_5Me_5)_2CeCl$, occurred under higher acuum (10^{-2} Torr) starting from 150—180 °C.

1,1′,3,3′-Tetrakis(*ter* butyl)-1,1′-dihydrofulvalene (2). The synthesis of YbI_3, whi was used in the preparation of complex **2**, was carried t by the direct reaction of the metal with iodine taken in a r io of 3 : 1 (2% excess of iodine) in THF over one week. A er completion of the reaction, the solvent was removed *in* *acuo*, the residue was washed with benzene and dried at 25 (1—2 Torr). Then $1,3\text{-}Bu^t{}_2C_5H_3Na$ (1.83 g, 9.14 mmol) wa slowly added to a suspension of the resulting compound (9. g, 9.15 mmol) in THF (200 mL). The reaction mixture w stirred for 48 h, the solvent was removed *in vacuo*, and e orange residue was twice washed with hexane, dried *in v* *o* at 40 °C (2 h), and treated with toluene (200 mL). Th yellow precipitate consisting of a mixture of NaI and Yb $(THF)_x$ was filtered off and twice washed on a filter with luene. The slightly red filtrate was combined with the initi red toluene solution and the combined solution was conc trated at 10 Torr to 200 mL. Red crystals of **2**, which prec itated within 2 days after storage of the solution at ~20 °C, w e separated from the mother liquor, washed with pentane, ar dried *in vacuo* at 40 °C. A single-crystalline compound wa btained in a yield of 0.35 g. Repeat dissolution in toluene le o decomposition of the compound accompanied by eliminat n of iodine into the solution, which made it impossible to rec d a high-quality NMR spectrum.

X-ray diffraction ana sis of compounds 1 and 2. X-ray diffraction data were co cted from single crystals of compounds **1** (0.25×0.29×0. mm) and **2** (0.25×0.20×0.15 mm) on automated Nicolet and Syntex $P\bar{1}$ diffractometers, respectively (Mo-Kα radi ion, Nb filter, θ/2θ scanning technique). Crystals of **1** b ong to the triclinic system, a = 8.412(2) Å, b = 9.030(3) , c = 12.132(3) Å, α = 99.13(2)°, β = 100.62(2)°, γ = 68.5)°, V = 838.6(6) Å^3, Z = 2, space group $P\bar{1}$, d_{calc} = 1.060 cm^{-3}. Crystals of **2** belong to the triclinic system, a = 10 51(2) Å, b = 10.928(2) Å, c =

15.377(4) Å, α = 73.31(3)°, β = 92.31(3)°, γ = 110.93(3)°, V = 1507.4(6) Å^3, Z = 2, space group $P\bar{1}$, d_{calc} = 1.695 g cm^{-3}. The structures were solved by the direct method and refined using the SHELXTL-81[17] and SHELXL-93[18] program packages, respectively (for **1**, absorption (μ = 0.03 mm^{-1}) was ignored; and for **2**, the numerical absorption correction (μ = 5.16 mm^{-1}) was applied). Calculations were performed using 804 (for **1**) and 2286 (for **2**) independent reflections with $I > 2\sigma(I)$. The final values of the R factor were 0.037 and 0.0693 for complexes **1** and **2**, respectively.

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