Bis(di-*tert*-butylcyclopentadienyl)ytterbium(II). Synthesis and catalytic properties

S. Ya. Knjazhanski,[a,b] *A. I. Sizov,*[a] *A. V. Khvostov,*[a] *and B. M. Bulychev*[a]*

[a]*M. V. Lomonosov Moscow State University, Chemistry Department,*
Vorob'evy Gory, 119899 Moscow, Russian Federation.
Fax: 007 (095) 932 88 46. E-mail: highp@mch.chem.msu.su
[b]*Center of Investigations on Applied Chemistry**
Blvd. Enrique Reina Hermosillo 140,
Saltillo, Coah., México 25100.
E-mail: polimex@ciqa.mx

Polymeric $(Cp_2Yb \cdot THF)_n$ (**1**), ionic *ate*-complex Cp_3YbNa (**2**), and mono-adduct $(Bu^t_2C_5H_3)_2Yb \cdot THF$ (**3**) were prepared through a reaction of Cp″Na (Cp″ = C_5H_5 or $C_5H_3Bu^t_2$) with YbI_2 in THF. Cooling complex (**3**) in THF at −100 °C gives a bis-adduct, which reversibly dissociates to give the mono-adduct. The $(Bu^t_2C_5H_3)_2Yb \cdot THF$ complex shows catalytic activity in the homogeneous hydrogenation of hex-1-ene and in the polymerization of styrene.

Key words: ytterbium, metallocene, catalysis, hydrogenation, polymerization.

The bis-cyclopentadienyl compounds of lanthanides in the +2 oxidation state with composition Cp_2M (M = Sm, Eu, Yb) are strong Lewis acids. Because of their electronic structure, their metal atoms can have up to three vacant molecular orbitals.[1] For this reason, syntheses of metallocenes with sterically non-hindered cyclopentadienyl ligands (Cp = C_5H_5, C_5H_4R) in electron-donating solvents or in liquid ammonia give low-stable di- and trisolvates,[2,3] which rather readily lose the coordinated solvent molecules to give almost insoluble polymers[2,4–8] or react with cyclopentadienides of alkali metals to yield ionic *ate*-complexes.[9,10] If alkyl substituents, particularly bulky ones, are introduced into the Cp-rings, the solubility of bis-cyclopentadienyllanthanides increases. In this case the tendency toward polymerization and the stability of the *ate*-complexes decreases, and mononuclear monomeric compounds solvated by one or two weakly bound electron-donating molecules (usually, solvent molecules) are obtained from solution.[2,3,6,11–14] These molecules can be removed from the coordination sphere of the metal atom by heating *in vacuo*.[14–16] These compounds have rather similar structures,[17] which differ only in the interatomic distances M—C, the dihedral angles between the cyclopentadienyl rings, and the conformation of the latter. However, in crystalline complexes of composition $(Cp''_2Yb)_n$ and $(Cp''_2Eu)_n$, where Cp″ = $C_5H_3(SiMe_3)_2$[14] not only have intra- and intermolecular aghostic bonds between methyl group protons and atoms of f-elements been found, but also changes in the type of coordination of some Cp-ligands.

In the present work we studied the properties of and methods for synthesizing ytterbium(II) complexes, including a complex with two bulky *tert*-butyl substituents in the cyclopentadienyl rings that is a close analog of the complex with silicon-containing substituents.

Results and Discussion

The reaction of YbI_2 with two equiv. of C_5H_5Na in tetrahydrofuran yields a bright-yellow pyrophoric compound, whose elemental analysis identified it as $Cp_2Yb \cdot THF$ (**1**) (Cp = C_5H_5). On the other hand, it is known[18] that reduction of Cp_2YbCl with potassium naphthalide in THF gives red-purple monomeric disolvate crystals of the composition $Cp_2Yb \cdot 2THF$. The complete change in the color of the compound depending on the number of coordinated electron-donating molecules as well as the polymerization of simple bis-cyclopentadienyllanthanides occurring during partial or total desolvation are well known in the chemistry of these compounds. There is no doubt that compound **1** is also a polymer, since the bright-yellow precipitate is insoluble in organic solvents even after prolonged boiling.

As expected, the reaction between YbI_2 and three equivalents of CpNa results in a homoleptic *ate*-complex of the composition Cp_3YbNa (**2**). This compound is rather easily soluble in THF and even in a benzene—THF mixture (3 : 1); however, like compound **1**, it is com-

---

* Centro de Investigación en Química Aplicada (CIQA) Blvd. Enrique Reina Hermosillo 140, Saltillo, Coah., México 25100.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1833—1837, July, 1996.

1066-5285/96/4507-1745 $15.00

pletely inert in the homogeneous hydrogenation of hex-1-ene. Unlike bis-cyclopentadienylsamarium(II),[19—21] the oxidation state of the metal atom in complex **2** does not change in reactions with aluminum hydride derivatives and aluminumalkyls. One of the resulting compounds has the composition $[AlH_2 \cdot 4THF][Cp_3Yb(Na)YbCp_3]$ and has been described in Ref. 22.

Bis(di-*tert*-cyclopentadienyl)ytterbium(II) (**3**), like the similar complex of samarium[9] and its analog containing $SiMe_3$ groups at the Cp-rings,[14] is isolated through crystallization from mixed solvents such as THF—toluene and THF—pentane (−50 to 30 °C) as a monosolvate of the composition $(C_5H_3Bu^t{}_2)_2Yb \cdot THF$ (the solvation is only based on ^1H NMR and mass spectra (see below), since the accuracy of elemental analysis does not allow unambiguous conclusions concerning the composition of this compound). The introduction of alkyl groups into the cyclopentadienyl rings dramatically increases the solubility of lanthanide metallocenes both in electron-donating solvents and in aromatic and aliphatic hydrocarbons. The mononuclear ytterbocene synthesized in this work is not an exception. This compound is very easily soluble not only in appropriate organic solvents but also even in liquid argon at the temperature of liquid nitrogen. This property can be explained by the weak polarity of the compound and the high degree of shielding of the metal atom by bulky $C_5H_3Bu^t{}_2$ ligands, which hinder polymerization of the compound and coordination of more than one THF molecule under ordinary conditions. The high degree of shielding of the Yb atom is also proved by the fact that chelating ligands, which usually readily replace THF in its complexes, either do not react with complex **3** at all, like *e.g.* tetramethylethylenediamine, or are readily displaced by the more compact THF molecule from the coordination environment of the metal atom. For example, the violet solution of $Cp_2''Yb \cdot DME$ formed upon dissolution of crystalline compound **3** in dimethoxyethane quickly turns green (the color of $(C_5H_3Bu^t{}_2)_2Yb \cdot THF$) after the addition of one to two equiv. of THF. It should also be noted that, unlike $(C_5H_3(SiMe_3))_2Ln \cdot THF$,[14] heating complex **3** to 130 °C in a $5 \cdot 10^{-3}$ Torr vacuum, according to ^1H NMR data, does not cause its desolvation but results in its sublimation with no change in composition. However, this does not rule out the possibility of dissociation of the compound during thermal treatment with subsequent recombination on a cooled surface.

Taking into account that two of the three frontier molecular orbitals of the Yb atom in complex **3** remain vacant, one could expect that certain specific interactions would occur in this compound, *e.g.*, the formation of intramolecular aghostic bonds between methyl group protons and the metal atom, $C-H \rightarrow Yb$, which were found in its silicon-based non-solvated analog.[14] Unfortunately, although $(C_5H_3Bu^t{}_2)_2Yb \cdot THF$ can be obtained under certain conditions as hexahedral planes with distinct facets, all attempts to determine the structure of the compound by X-ray diffraction analysis proved unsuccessful because the crystals were completely X-ray amorphous.

The ^1H NMR spectra of complex **3** in C_6D_6 and $C_6D_5CD_3$ (Fig. 1,*a*) contain, in addition to bands corresponding to the protons of aliphatic substituents (δ ~1.44) and those of cyclopentadienyl rings (δ 5.67 and 6.25), a broadened peak at δ 3.55 (in benzene) and δ 3.75 (in toluene), whose position and shape almost do not change in the temperature range from −50 to 90 °C. The assignment of this signal to the molecule of coordinated THF was not obvious because of the unusual width of its profile and the absence of a second signal near δ 1.7 at temperatures from −50 to 25 °C (δ 3.67 and 1.72 for pure THF). These facts served as the basis for the assumption that an aghostic bond exists between a hydrogen atom of one of the methyl groups and the ytterbium atom and for assigning the signal at δ 3.55 to this interaction. However, when the temperature of a solution of compound **3** in toluene is increased to 70—90 °C, the band of protons in the *tert*-butyl group narrows; simultaneously, the $Yb \leftarrow O$ bond probably weakens, and a signal at δ 1.7 appears in the spectrum (Fig. 1, *b*). Cooling the solution to room temperature completely restores the original spectrum. We made the final confirmation that complex **3** contains coordinated THF by recording the ^1H NMR spectrum of a solution obtained by solvolysis of the complex by methanol-d_4 and by studying the mass spectrum of the gas phase obtained through thermolysis. In both cases, the spectra contained signals and masses from pure THF. Thus, the composition of the complex obtained does not differ from those of the samarium compound reported previously[9] and of the solvated silicon-containing europium and ytterbium analogs,[14,23] although its unusual proton spectrum, the X-ray amorphism of the crystals, and the higher stability against the elimination of the THF molecule upon heating imply that the structure of compound **3** differs somewhat from those of similar compounds.

Another feature of the behavior of complex **3** found by us is that the color of its THF-containing solutions changes from dark-green to yellow-brown, more typical of Yb^{III} compounds, when it is cooled to −100 °C. The original dark-green color of the solution is recovered by heating, and hence the color transition cannot be attributed to the oxidation of the compound during the experiments. On the other hand, prolonged cooling of a solid sample of compound **3** at the temperature of liquid nitrogen or of solutions of **3** in aromatic or aliphatic hydrocarbons does not result in noticeable color changes. This behavior unambiguously suggests that a second THF molecule is coordinated to the ytterbium atom. Thus, although steric hindrance exists, complex **3** still maintains the ability to coordinate an additional ligand to its vacant MOs. However, its bond with the metal atom is considerably weaker than those in other known bis-adducts[13,14,23] with bulky cyclopentadienyl groups, which are generally purple.

The high acidity of $(Bu^t{}_2C_5H_3)_2Yb \cdot THF$ and its ability to coordinate electron-donating molecules made it possible to assume that this compound, despite its solvated state, should have catalytic properties in trans-

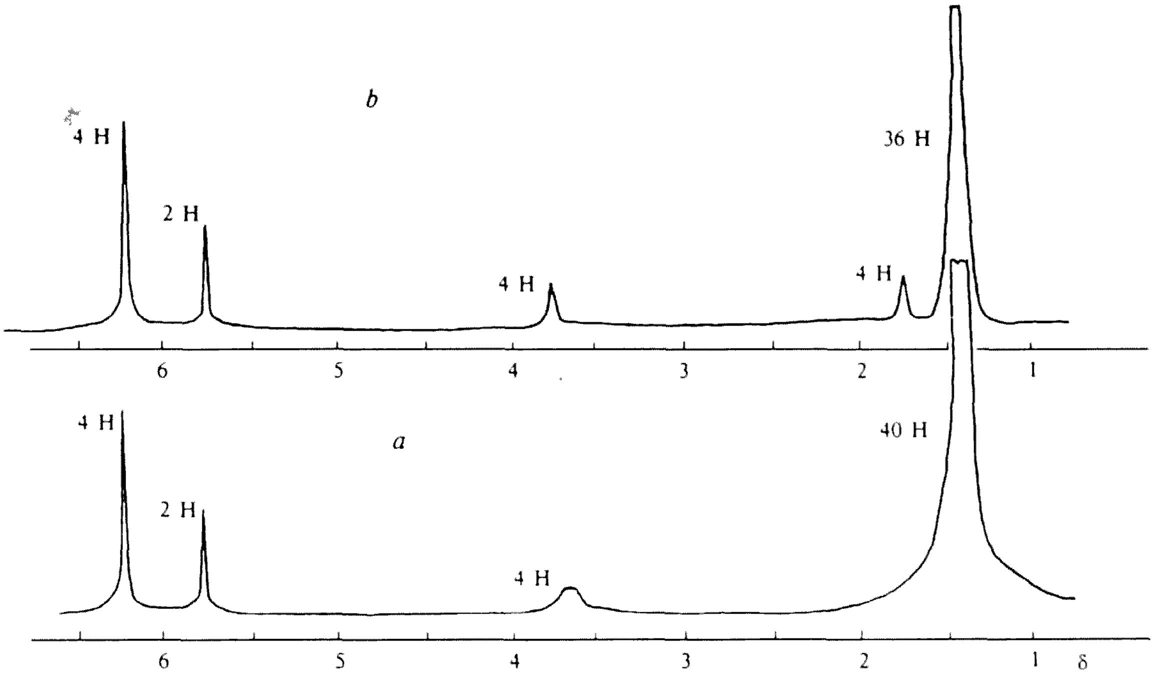

Fig. 1. ^{1}H NMR spectrum of $(Bu^t_2C_5H_3)_2Yb$ in deuterobenzene at –20 °C (*a*) and 90 °C (*b*).

formations of olefins. In fact, complex **3** possesses weak but measurable activity in the hydrogenation of hex-1-ene and in the polymerization of styrene. Both reactions are preceded by a prolonged induction period (30 to 40 min) and further occur at rates of 5 mol H_2/(g-at Yb min) (hydrogenation) and 2 mol styrene/(mol catalyst h) (polymerization). The rate of hydrogenation in the presence of complex **3** is one order of magnitude lower than that found in the same reaction catalyzed by $[(Bu^t_2C_5H_3)_2LuH]_2$ (40 mol H_2/(g-at Lu min))[24] and $[(Bu^t_2C_5H_3)_2SmH]_2$ (30 mol H_2/(g-at Sm min)).[25] It is difficult to explain the catalytic activity of complex **3** in this reaction by the formation in solution of "classic" ytterbocene(III) hydride, which may occur through activation and oxidative addition of molecular hydrogen (as was assumed, for example, in Refs. 26—28), since even keeping a toluene solution of compound **3** in hydrogen for 4—5 h at 70 °C does not result in a reaction between the components. Of course, one can assume that this compound is formed when both hydrogen and the olefin are present simultaneously.[26—28] It can only be noted that if a stoichiometric hydride of the composition $[(Bu^t_2C_5H_3)_2YbH]_2$ were formed in solution from complex **3**, the observed rate of hydrogenation would not differ by almost an order of magnitude from those found for the lutetium and samarium complexes. For these reasons, we think there is an equal probability that the catalytic processes of hydrogenation and polymerization of olefins on lanthanidocenes(II) involve intermediates whose compositions and structures differ from those of classic lanthanidocene hydrides. However, because of the redistribution of electron density, *e.g.*, due to the formation of intra- or intermolecular aghostic bonds or aghostic bonds between the substrate protons and the metallic center, the formal oxidation state of the metal atom in them is closer to +3 than to +2. The mechanism of olefin catalysis, which involves the formation of an aghostic substrate—metal bond, has been considered previously in several publications (see, *e.g.*, Refs. 28 and 29). However, in our case we should probably consider a somewhat different type of catalytic action. Despite the low effectiveness of compound **3** in hydrogenation and polymerization, the very fact of catalysis by this compound expands our concepts of both the potentialities of metallocene complexes of d- and f-elements in catalytic reactions and the possible types of mechanisms of homogeneous catalysis.

Experimental

All synthetic procedures and the preparation of compounds for physicochemical studies were carried out in a dry inert gas atmosphere or *in vacuo*.

Prior to use, the solvents were dehydrated by refluxing and distillation with $LiAlH_4$.

Ytterbium diiodide was synthesized through a reaction of metallic ytterbium (a twofold excess with respect to the stoichiometric amount) with iodine in THF. The suspension was stirred for two days until the color changed from orange to grayish-green. The solution was filtered, the solvent was concentrated, and the yellow bis-tetrahydrofuranate of ytterbium iodide was dried *in vacuo* with mild heating (yield 95 % with respect to iodine).

Styrene was freed from an inhibitor, washed with 10 % KOH, dried with Na_2SO_4 and activated molecular sieves 3A, and distilled with metallic sodium.

1,3-Di-*tert*-butylcyclopentadiene was obtained according to the procedure in Ref. 30 using a Grignard reagent. The monomer yield was 46 %. ^{1}H NMR (60 MHz, C_6D_6), δ, HMDS: 1.07 (s, 18 H, Bu^t), 2.73 (m, 2 H, $-CH_2-$), 5.63 (q), 5.83 (t), 6.08 (q, 2 H, $=CH-$).

Sodium 1,3-di-*tert*-butylcyclopentadienide was obtained according to the procedure in Ref. 31 in dry ammonia. The yield of the dry compound was 95 %.

Sodium cyclopentadienide was obtained by the standard procedure in THF and was used as a solution.

Synthesis of bis(η^5-cyclopentadienyl)ytterbium mono-tetrahydrofuranate (1). YbI_2 (0.009 mol) was added in small portions to a solution of C_5H_5Na (0.018 mol) in THF. The resulting cherry-colored solution was stirred for 2 h, the solvent was distilled off, and the brick-colored precipitate containing embedded white NaI was treated with dry benzene (150 mL). The orange solution was filtered off from the precipitate and concentrated to dryness to give 2.02 g (yield 60 %) of a yellow powder of $Cp_2Yb \cdot THF$. Found (%): Yb, 46.0. $C_{14}H_{18}YbO$. Calculated (%): Yb, 46.1. The complex dried *in vacuo* is insoluble in THF and benzene.

Synthesis of sodium tris(η^5-cyclopentadienyl)ytterbate(II) (2). YbI_2 (0.006 mol) was added in small portions to a solution of C_5H_5Na (0.018 mol) in THF (150 mL). The solution was stirred for 2 h and concentrated to a syrupy state, and then 150 mL of a benzene—THF mixture (3 : 1) was added. The resulting white precipitate of NaI was filtered off, and the solution was evaporated to dryness to give 1.76 g (yield 75 %) of a yellow powder of complex **2**. Found (%): Yb, 44.3; Na, 6.0. $C_{15}H_{15}YbNa$. Calculated (%): Yb, 44.2; Na, 5.9.

Synthesis of bis(1,3-di-*tert*-butylcyclopentadienyl)ytterbium-mono-tetrahydrofuranate (3). $C_5H_3Bu^t{}_2Na$ (0.064 mol) was added in small portions to a solution of YbI_2 in THF (0.031 mol). The dark-green solution was stirred for 2 h, the THF was distilled off, and toluene (150 mL) was added to the mixture of green and white precipitates. The white precipitate of NaI was filtered off, the solution was evaporated to dryness, and the emerald-green powder was dried by heating at 70 °C *in vacuo*; the yield of compound **3** was 90 %. Found (%): Yb, 30.8. $C_{30}H_{50}OYb$. Calculated (%): Yb, 28.9. ^{1}H NMR (300 MHz, 20 °C, benzene-d$_6$), δ: 1.44 (br.s, 4 OH), 3.55 (br.s, 4 H), 5.67 (t, 2 H, J_{H-H} = 2.5 Hz), 6.3 (d, 4 H, J_{H-H} = 2.6 Hz).

The catalytic activity of the complexes in the homogeneous hydrogenation of hex-1-ene was measured by the standard procedure at 20 °C and 1 atm in a two-compartment "duck" connected to a system of burettes for measuring the volume of hydrogen absorbed. The concentration of ytterbium in toluene solutions was varied from 0.01 to 0.03 mol L^{-1}, while the substrate (hex-1-ene)/ytterbium ratio was varied from 100 to 200. A cylinder filled with the $LaNi_5H_n$ hydride phase was used as the source of hydrogen. The catalyst activity was estimated from the starting rate of hydrogen absorption.

The polymerization of styrene was carried out in toluene at 25 °C in a standard reactor equipped with a stirrer and a system for sample withdrawal. The catalyst concentration was varied from 0.005 to 0.008 mol L^{-1}, while the styrene/catalyst ratio was varied from 500 to 1000. The samples of polystyrene were analyzed by gel-permeation chromatography in a THF solution with subsequent assignment of the results to monodisperse standard samples.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09-539).

References

1. J. V. Ortiz and R. Hoffmann, *Inorg. Chem.*, 1985, **24**, 2095.
2. W. J. Evans, *Adv. Organometallic Chem.*, 1985, **24**, 131.
3. W. J. Evans, *Polyhedron*, 1987, **5**, 803.
4. H. A. Zinnen, J. J. Pluth, and W. J. Evans, *J. Chem. Soc., Chem. Commun.*, 1980, 810.
5. G. W. Watt and E. W. Gillow, *J. Am. Chem. Soc.*, 1969, **91**, 775.
6. E. O. Fisher and H. Fisher, *J. Organomet. Chem.*, 1965, **3**, 181.
7. R. G. Hayes and J. L. Thomas, *Inorg. Chem.*, 1969, **8**, 2521.
8. F. Galderazzo, R. Pappaiardo, and S. Losi, *J. Inorg. Nucl. Chem.*, 1966, **28**, 987.
9. V. K. Bel'sky, Yu. K. Gunko, B. M. Bulychev, A. I. Sizov, and G. L. Soloveichik, *J. Organomet. Chem.*, 1990, **390**, 35.
10. G. B. Deacon, G. N. Pain, and T. D. Tuong, *Polyhedron*, 1985, **4**, 1149.
11. T. D. Tilley, R. A. Anderson, B. Spenser, H. Ruben, A. Zalkin, and D. H. Tompleton, *Inorg. Chem.*, 1980, **19**, 2999.
12. T. D. Tilley, R. A. Anderson, B. Spenser, and A. Zalkin, *Inorg. Chem.*, 1982, **21**, 2647.
13. W. J. Evans and T. A. Ulibarri, *Polyhedron*, 1989, **8**, 1007.
14. P. B. Hichcock, J. A. K. Howard, M. F. Lappert, and B. Prashar, *J. Organomet. Chem.*, 1992, **437**, 177.
15. W. J. Evans, L. A. Hughes, and T. P. Hanusa, *J. Am. Chem. Soc.*, 1984, **106**, 4270.
16. W. J. Evans, L. A. Hughe, and T. P. Hanusa, *Organometallics*, 1986, **5**, 1285.
17. W. J. Evans and S. E. Foster, *J. Organomet. Chem.*, 1992, **433**, 79.
18. J.-S. Xia, G.-C. Wei, Z.-S. Jin, W.-Q. Chen, and W.-C. Xue, *J. Rare Earths/Chin. Soc. Rare Earths*, 1992, **10**, 88.
19. W. J. Evans, L. R. Chamberlain, and J. W. Ziller, *J. Am. Chem. Soc.*, 1987, **109**, 7209.
20. W. J. Evans, L. R. Chamberlain, T. A. Ulibarri, and J. W. Ziller, *J. Am. Chem. Soc.*, 1988, **110**, 6423.
21. Yu. K. Gun'ko, B. M. Bulychev, A. I. Sizov, V. K. Belsky, and G. L. Soloveichik, *J. Organomet. Chem.*, 1990, **390**, 153.
22. S. Ya. Knyazhansky, I. Yu. Nomerotsky, B. M. Bulychev, V. K. Belsky, and G. L. Soloveichik, *Organometallics*, 1994, **13**, 2075.
23. P. B. Hitchkock, M. F. Lappert, and S. Prashar, *J. Organomet. Chem.*, 1991, **413**, 79.
24. S. Ya. Knjazhanski, E. B. Lobkovsky, B. M. Bulychev, V. K. Belsky, and G. L. Soloveichik, *J. Organomet. Chem.*, 1991, **419**, 311.
25. Yu. K. Gun'ko, Ph.D. Thesis (Chemistry), Moscow, Moscow State University, 1991 (in Russian).
26. M. R. Gagne, S. Nolan, and T. J. Marks, *Organometallics*, 1990, **9**, 1716.
27. W. J. Evans, D. M. DeCoster, and J. Greaves, *Macromolecules*, 1995, **28**, 7929.
28. W. E. Piers and J. E. Bercaw, *J. Am. Chem. Soc.*, 1990, **112**, 9406.
29. L. Clawson, J. Soto, S. L. Buchwald, M. L. Steigwald, and R. H. Grubbs, *J. Am. Chem. Sos.*, 1985, **107**, 3377.
30. T. Leith, *J. Chem. Soc., Chem.Commun.*, 1964, 3294.
31. J. E. Bercaw, R. H. Marvich, and L. G. Bell, *J. Am. Chem. Soc.*, 1972, **94**, 1219.

Received November 17, 1995;
in revised form February 23, 1996