Organometallic Chemistry

Reaction of a naphthalene complex $C_{10}H_8Yb(THF)_2$ with cyclopentadienyl-substituted alcohols and amines as a convenient synthetic route to the half-sandwich complexes of divalent ytterbium

*A. A. Trifonov, E. N. Kirillov, Yu. A. Kurskii, and M. N. Bochkarev**

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603600 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 66 1497. E-mail: mboch@imoc.sinn.ru

The reactions of ytterbium naphthalene complex $C_{10}H_8Yb(THF)_2$ with 2-cyclopentadienylethanol, 1-cyclopentadienylpropan-2-ol, 3-cyclopentadienyl-1-butoxypropan-2-ol, and cyclopentadienyldimethylsilyl-*tert*-butylamine were studied. The bivalent ytterbium complexes with chelate bifunctional cyclopentadienyl ligands $[(\eta^5\text{-}C_5H_5)CH_2CH_2(\eta^1\text{-}O)]Yb(THF)$, $[(\eta^5\text{-}C_5H_5)CH_2CH_2(\eta^1\text{-}O)]Yb(DME)$, $[(\eta^5\text{-}C_5H_5)CH_2CH(Me)(\eta^1\text{-}O)]Yb(THF)$, $[(\eta^5\text{-}C_5H_5)CH_2CH(CH_2OC_4H_9)(\eta^1\text{-}O)]Yb(THF)$, and $[(\eta^5\text{-}C_5H_5)SiMe_2(\eta^1\text{-}N(Bu^t))]Yb(THF)$ were obtained and characterized.

Key words: ytterbium(II), ytterbium(II) complexes, complex formation.

Complexes with strained geometry which are generated upon coordination of heterobifunctional cyclopentadienyl ligands with a transition metal atom are of considerable interest from the standpoint of their stabilities, structures, and catalytic potentialities. The use of cyclopentadienyl ligands containing functionalized substituents and capable of coordinating both according to the η^5-type via the Cp-ring and via the functional group of the side chain through the formation of the Ln—E covalent bond has notable advantages over biscyclopentadienyl and *ansa*-biscyclopentadienyl compounds in capabilities of creation of the coordination sphere of the metallocomplex and modification of its catalytic properties.

The range of compounds of rare-earth elements with heterobifunctional ligands reported thus far is rather narrow and is basically restricted to the cyclopentadienyl derivatives of trivalent Sc, Y, and Lu.[1–5] Complexes of trivalent La and Sm with the asymmetric cyclopentadienylalkoxy ligand $[(2S)\text{-}C_5H_4CH_2CH(Me)O]LnI(THF)_n$ (Ln = La, $n = 2$; Ln = Sm, $n = 1$)[6] have also been obtained and characterized. Similar compounds of bivalent lanthanides are not known.

Herein we report the synthesis of half-sandwich compounds of bivalent ytterbium with bifunctional cyclopentadienyl ligands.

Results and Discussion

Earlier,[7–10] we have found that samarium, europium, and ytterbium naphthalene complexes $C_{10}H_8Ln(THF)_x$ possess high reactivities with respect to many reagents, which served as the basis for their use as convenient starting materials for the preparation of various organolanthanide derivatives. They react most readily with compounds containing the active hydrogen atom (R—H). In all cases, the substitution of two R residues for the naphthalene dianion was observed. This route turned out to be convenient for the synthesis of half-

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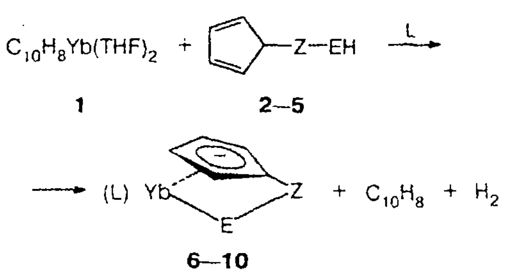
sandwich derivatives of bivalent ytterbium. The protolytic substitution of cyclopentadienyl-substituted alcohols and amines for the naphthalene ligand in complex $C_{10}H_8Yb(THF)_2$ (**1**) permitted us to obtain the target compounds in high yields.

Complex **1** was found to react readily with compounds **2—5** in THF or DME at room temperature (see Scheme 1). The reactions occur with the dissolution of complex **1** and resulted in the liberation of naphthalene and hydrogen and the formation of the corresponding cyclopentadienylalkoxy(amido) complexes of bivalent ytterbium (**6—10**).

Scheme 1



	Z	E
2, **6**, **7**	CH_2CH_2	O
3, **8**	$CH_2CH(Me)$	O
4, **9**	$CH_2CH(CH_2OBu)$	O
5, **10**	$SiMe_2$	Bu^tN

L = THF (**6**, **8—10**); DME (**7**)

Complexes **6—10** are fine-crystalline compounds extremely sensitive to atmospheric oxygen and moisture. All the compounds are soluble in THF and DME, but insoluble in aromatic and aliphatic hydrocarbons. The products obtained were characterized by IR and ^1H NMR spectroscopy and data from magnetochemistry and microanalysis.

The IR spectra of cyclopentadienylalkoxy derivatives **6—9** contain bands at 3030 and 760 cm^{-1}, which are characteristic of C—H oscillations of the aromatic cyclopentadienyl anion, and also sets of absorption bands in the ranges of 850—880 and 1050—1090 cm^{-1} corresponding to the C—O absorption both of the alkoxy groups of the ligand side chain and of the solvent molecules bound by coordination. The IR spectrum of complex **10** contains the absorption bands corresponding to the side chain groups, *viz.*, C—N (1200 cm^{-1}), Si—Me (1250 and 870 cm^{-1}), and Si—N (980 cm^{-1}), along with the absorption bands of the cyclopentadienyl ligand and THF. The intense bands of O—H and N—H oscillations observed in the spectra of the starting ligands **2—5** are absent in the spectra of the products **6—10**. All the compounds are diamagnetic, which confirms the bivalent state of the ytterbium atom.[11] It should be noted that the signals for the protons of monosubstituted cyclopentadienyl ligands in the ^1H NMR spectra of complexes **6—10** have the chemical shift values characteristic of the Cp-anion coordinated to the metal atom. In the ^1H NMR spectra of complexes **6—8** and **10**, these protons appear as three groups of signals with a 2 : 1 : 1 ratio of intensities, whereas in the spectrum of compound **9** they are represented as four signals.

The data of spectroscopic (IR and ^1H NMR) studies mentioned above permit one to conclude that the bidentate cyclopentadienyl ligands in complexes **6—10** are bound to the bivalent ytterbium atom through η^5-interaction of the Cp-ring and, at the same time, to side functional group through the Yb—O or Yb—N σ-bond.

Recently, we have obtained and characterized a complex of bivalent ytterbium $[(\eta^5\text{-}C_5Me_4)SiMe_2OSiMe_2(\eta^1\text{-}O)Yb(THF)]_2$ (**11**)[12] using a similar synthetic route. The X-ray diffraction study showed compound **11** to be a metallacycle with the bidentate ligand coordinated to the ytterbium atom involving both groups, *viz.*, the η^5-type through the tetramethylcyclopentadienyl ring and the η^1-type through the oxygen atom of the silyloxy group. In addition, the complex is a dimer in the crystalline state due to coordination of the ytterbium and oxygen atoms of the Si—O—Yb fragment of one molecule to the oxygen and ytterbium atoms of the same fragment of another molecule. Unfortunately, we failed to obtain monocrystalline samples for products **6—10** suitable for X-ray diffraction study. However, we suppose that cyclopentadienylalkoxy derivatives **6—9** form dimeric associates in the solid phase analogously to complex **11**.

Complexes **6—10** exhibit no catalytic activity in the polymerization of propylene in a toluene solution under ordinary conditions.

Experimental

IR spectra were recorded on a Specord M-80 instrument with KBr plates. The samples were prepared as suspensions in Nujol. ^1H NMR spectra were registered on a Gemini-300 spectrometer. Chemical shifts (ppm) are given relative to the known shifts of the residual protons of deuterated solvents. Analysis of organic products was carried out on a Milikhrom-1A microcolumn liquid chromatograph [UV-detector with a variable wavelength (λ = 250 nm), steel column (64×2 mm), Separon S6X (15 μm) as the adsorbent, elution with hexane—THF (200 : 1, v/v), elution rate = 200 μL min^{-1}].

The synthesis was performed under conditions excluding contact with atmospheric oxygen and moisture using the standard Schlenk technique. THF, DME, hexane, and toluene were dried over sodium benzophenone ketyl, degassed thoroughly, and condensed *in vacuo* to the reaction tube immediately before use. The starting ytterbium naphthalene complex was obtained as described earlier.[8] Cyclopentadienyl-substituted alcohols (**2—4**) used as the starting compounds were synthesized by nucleophilic opening of the corresponding oxiranes by the cyclopentadienyl anion according to the reported procedures.[13] Cyclopentadienyl-substituted amine **5** was prepared by the method[1] suggested for the preparation of tetramethylcyclopentadienyl-substituted analog $C_5Me_4SiMe_2NHBu^t$.

All compounds were synthesized according to the standard procedure.

(2-Cyclopentadienylethoxy)ytterbium tetrahydrofuranate (6). A solution of 0.57 g (5.18 mmol) of compound **2** in 10 mL of THF was added to a suspension of 2.30 g (5.17 mmol) of compound **1** in 40 mL of THF with stirring. The reaction was accompanied by slow dissolution of the precipitate and liberation of hydrogen. The reaction mixture turned brown. The mixture was stirred for 24 h and filtered. The solvent was removed *in vacuo*. The residue was extracted with hexane to remove naphthalene that was liberated. The hexane extract contained 0.21 g (86%) of $C_{10}H_8$. Slow diffusion of 15 mL of hexane to a solution of the product in 30 mL of THF *in vacuo* at −20 °C resulted in the formation of a reddish brown oily precipitate, which converted into an orange-pink fine crystalline product after storage at 0 °C for 1 month. Yield 0.81 g (44.5%). Found (%): C, 36.90; H, 4.11; Yb, 49.09. $C_{11}H_{16}O_2Yb$. Calculated (%): C, 37.41, H, 4.53, Yb, 48.99. IR, ν/cm^{-1}: 3030, 1305, 1200, 1175, 1160, 1125, 1080, 1050, 920, 900, 860, 760, and 720. ^1H NMR (pyridine-d_5, δ): 1.56 (m, 2 H, CH_2); 1.63 (m, 4 H, CH_2, THF); 3.49 (m, 2 H, CH_2); 3.67 (m, 4 H, CH_2O, THF); 6.41 (s, 2 H, Cp); and 7.33 and 7.70 (both s, 1 H each, Cp).

(2-Cyclopentadienylethoxy)ytterbium dimethoxyethanate (7). The reaction of 5.69 g (12.8 mmol) of compound **1** with 1.41 g (12.8 mmol) of compound **2** in 50 mL of DME was performed as described above. The hexane extracts were found to contain 1.51 g (92%) of $C_{10}H_8$. Diffusion of 15 mL of hexane to a solution of the product in 30 mL of DME yielded 2.89 g (61%) of a reddish brown fine crystalline compound. Found (%): C, 35.11; H, 4.41; Yb, 46.41. $C_{11}H_{18}O_3Yb$. Calculated (%): C, 36.60; H, 4.85; Yb, 46.41. IR, ν/cm^{-1}: 3030, 1250, 1190, 1130, 1090, 1060, 1040, 970, 860, 840, 810, 760, 730, 675, and 530. ^1H NMR (pyridine-d_5, δ): 1.51 (m, 2 H, CH_2); 3.13 (m, 6 H, Me, DME); 3.35 (m, 4 H, CH_2, DME); 3.57 (m, 2 H, CH_2); 6.53 (s, 2 H, Cp); and 7.34 and 7.73 (both s, 1 H each, Cp).

(1-Cyclopentadienylpropan-2-yloxy)ytterbium tetrahydrofuranate (8). The yellowish brown fine crystalline compound (0.47 g, 67%) and 0.21 g (86%) of $C_{10}H_8$ were obtained analogously from 0.86 g (1.93 mmol) of compound **1** and 0.24 g (1.93 mmol) of compound **3** in 30 mL of THF. Found (%): C, 39.56; H, 4.94; Yb, 47.00. $C_{12}H_{18}O_2Yb$. Calculated (%): C, 31.25; H, 4.90; Yb, 47.12. IR, ν/cm^{-1}: 3030, 1190, 1130, 1050, 950, 930, 900, 820, and 710. ^1H NMR (pyridine-d_5, δ): 0.78 (br. d, 3 H, Me, J = 5.77 Hz); 1.14 (s, 2 H, CH_2); 1.57 (m, 4 H, CH_2, THF); 3.22 (m, 1 H, CH); 3.59 (m, 4 H, CH_2O, THF); 6.88 (s, 2 H, Cp); and 7.39 and 7.79 (both s, 1 H each, Cp).

(1-*tert*-Butoxy-3-cyclopentadienylpropan-2-yloxy)ytterbium tetrahydrofuranate (9). The reaction of 0.60 g (1.35 mmol) of compound **1** with 0.26 g (1.35 mmol) of compound **4** in 25 mL of THF was performed analogously. The hexane extracts were found to contain 0.16 g (95%) of $C_{10}H_8$. Diffusion of 10 mL of hexane to a solution of the product in 20 mL of THF yielded 0.11 g (19%) of complex **9**. Found (%): C, 43.50; H, 6.05; Yb, 39.75. $C_{16}H_{26}O_3Yb$. Calculated (%): C, 43.74; H, 5.96; Yb, 39.38. IR, ν/cm^{-1}: 1325, 1260, 1180, 1170, 1120, 1075, 1040, 1025, 1010, 985, 950, 925, 890, 860, 840, 800, 730, 660, 640, 540, and 475. ^1H NMR (THF-d_8, δ): 1.10 (m, 3 H, Me); 1.53, 2.33 (both m, 2 H each, CH_2, C_4H_9); 2.73 (m, 2 H, CH_2); 3.30 (m, 2 H, CH_2, C_4H_9); 3.46 (m, 2 H, CH_2); 4.15 (m, 1 H, CH); and 5.52, 5.68, 5.74, and 5.79 (all m, 1 H each, Cp).

(Cyclopentadienyldimethylsilyl-*tert*-butylamido)ytterbium tetrahydrofuranate (10). The fine crystalline orange product was obtained analogously from a solution of 1.57 g (3.52 mmol) of compound **1** in 35 mL of THF and a solution of 0.69 g (3.53 mmol) of compound **5** in 10 mL of THF. Found (%): C, 40.61; H, 6.71; Yb, 39.27. $C_{15}H_{27}NOSiYb$. Calculated (%): C, 41.10; H, 6.16; Yb, 39.47. IR, ν/cm^{-1}: 3030, 2720, 1300, 1250, 1200, 1180, 1050, 980, 960, 850, 825, 810, 770, 740, and 650. ^1H NMR (pyridine-d_5, δ): 0.72 (m, 6 H, $SiMe_3$); 1.73 (m, 4 H, CH_2, THF); 2.34 (s, 9 H, Me_3C); 3.78 (m, 4 H, CH_2O, THF); 6.36 and 6.55 (both m, 1 H each, Cp); and 6.71 (m, 2 H, Cp).

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References

1. P. J. Shapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger, and J. E. Bercaw, *J. Am. Chem. Soc.*, 1994, **116**, 4623.
2. P. J. Shapiro, E. Bunnel, W. P. Schaefer, and J. E. Bercaw, *Organometallics*, 1990, **9**, 867.
3. Y. Mu, W. E. Piers, D. C. MacQuarrie, M. J. Zaworotko, and V. G. Young, *Organometallics*, 1996, **15**, 2720.
4. K. C. Hultzsch, T. P. Spaniol, and J. Okuda, *Organometallics*, 1997, **16**, 4845.
5. K. C. Hultzsch, T. P. Spaniol, and J. Okuda, *Organometallics*, 1998, **17**, 485.
6. A. A. Trifonov, F. Ferri, and J. Collin, *J. Organomet. Chem.*, 1999, **582**, 211.
7. M. N. Bochkarev, A. A. Trifonov, E. A. Fedorova, N. S. Emelyanova, T. A. Basalgina, G. S. Kalinina, and G. A. Razuvaev, *J. Organomet. Chem.*, 1989, **372**, 217.
8. M. N. Bochkarev, V. V. Khramenkov, Yu. F. Rad'kov, L. N. Zakharov, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1991, **408**, 329.
9. M. N. Bochkarev, I. M. Penyagina, L. N. Zakharov, Yu. F. Radkov, E. A. Fedorova, S. Ya. Khorshev, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1989, **378**, 363.
10. N. S. Emelyanova, A. V. Protchenko, E. A. Fedorova, O. A. Vasina, and M. N. Bochkarev, *Metalloorg. Khim.*, 1991, **4**, 895 [*Organomet. Chem. USSR*, 1991, 4 (Engl. Transl.)].
11. W. J. Evans and M. A. Hozbor, *J. Organomet. Chem.*, 1987, **326**, 299.
12. A. A. Trifonov, E. N. Kirillov, A. Fischer, F. T. Edelmann, and M. N. Bochkarev, *J. Chem. Soc., Chem. Commun.*, 2000, in press.
13. H. Ohta, T. Kobori, and T. Fujisawa, *J. Org. Chem.*, 1977, **42**, 1231.

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