Synthesis, properties, and reactivity of the stilbene complex of ytterbium (PhCH=CHPh)Yb(THF)$_2$. Crystal structure of (2,4,6-Bu$^t_3$C$_6$H$_2$O)$_2$Yb(THF)$_3$

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The stilbene complex of ytterbium (PhCH=CHPh)Yb(THF)$_2$ (**1**) was prepared by the reaction of YbI$_2$(THF)$_2$ with a twofold excess of (PhCH=CHPh)$^{\cdot-}$Li$^+$. Based on the data of IR and ESR spectroscopy and on the results of magnetic measurements, compound **1** was characterized as a complex of divalent ytterbium with the stilbene dianion. The reactivity of complex **1** toward different types of reagents was studied. The structure of the product of the reaction of **1** with 2,4,6-tri(*tert*-butyl)phenol (2,4,6-Bu$^t_3$C$_6$H$_2$O)$_2$Yb(THF)$_3$ was established by X-ray diffraction analysis.

Key words: ytterbium, stilbene, structure, reactivity.

In spite of the general intense progress in the chemistry of organolanthanides, a number of classes of these compounds remain virtually unknown. Derivatives of lanthanides containing π-coordinated olefin, diene, and polyene ligands are among the least known compounds[1] although the data on the synthetic pathways, the stability, and the reactivity of this type of compounds are of obvious interest in the search for efficient catalysts of polymerization of olefins and dienes.

The synthesis of the olefin heterobimetallic complex of lanthanide, (Me$_5$C$_5$)$_2$Yb(μ-C$_2$H$_4$)Pt(PPh$_3$)$_2$, containing the bridging μ-η^2-η^2-bonded ethylene ligand between the *d*- and *f*-block transition metal atoms was reported for the first time in Ref. 2. Complexation of (Me$_5$C$_5$)$_2$Eu with ethylene was detected by ^{1}H NMR spectroscopy.[3] However, the product was neither isolated nor characterized. The existence of the olefin—lanthanide π-interaction was suggested[4] based on the spectral characteristics (the IR spectrum and the UV-visible region) of products of cocondensation of ethylene and europium. The compound containing the bridging μ-η^2:η^2-ethylene fragment, [{(η^5-C$_5$Me$_4$)SiMe$_2$(η^1-NCMe$_3$)}(PMe$_3$)Sc]$_2$(μ-η^2:η^2-C$_2$H$_4$), was isolated in the reaction of hydride [{(η^5-C$_5$Me$_4$)SiMe$_2$(η^1-NCMe$_3$)}(PMe$_3$)Sc(μ^2-H)]$_2$ with ethylene.[5] The synthesis and the properties of complexes of decamethylsamarocene with mono- and diaryl-substituted alkenes were reported in Ref. 6. It was demonstrated[6] that (C$_5$Me$_5$)$_2$Sm reversibly reacted with stilbene and styrene to form the binuclear derivatives [(C$_5$Me$_5$)$_2$Sm]$_2$(μ-η^2:η^4-PhCH=CHPh) and [(C$_5$Me$_5$)$_2$Sm]$_2$(μ-η^2:η^4-CH$_2$=CHPh), respectively.

Data on homoleptic olefin complexes of lanthanides are unavailable in the literature. The aim of this work is to synthesize and study the reactivity of ytterbium derivatives containing the stilbene ligand.

Results and Discussion

We found that when a solution of stilbene in THF was added to a solution of metallic ytterbium in liquid ammonia at −60 °C, the color of the reaction mixture changed from blue to brown. In this case, the single line of the solvated electron in the ESR spectrum of the solution disappeared. At −100 °C, a broadened multicomponent signal is observed with the value g_i that corresponds to the published data for the stilbene radical anion.[7] Tetrahydrofuran solutions of the ammine stilbene complex of ytterbium (PhCH=CHPh)Yb(NH$_3$)$_n$ were prepared by evaporation of ammonia at −40 °C *in vacuo*. However, attempts to isolate this complex led to ammonolysis of the product to form Yb(NH$_2$)$_2$ and dibenzyl.

We succeeded in preparing the stilbene complex of ytterbium by the reaction of YbI$_2$(THF)$_2$ with two equivalents of stilbene-lithium in a THF solution. The reaction was accompanied by the disappearance of the signal of the stilbene radical anion in the ESR spectrum of the reaction mixture.

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$$YbI_2(THF)_2 + 2\ (PhCHCHPh^{\cdot-})Li^+ \xrightarrow{THF} \longrightarrow (PhCHCHPh)Yb(THF)_2 + 2LiI + PhCH{=}CHPh$$
1

Complex **1** was isolated in 84% yield as a black finely crystalline product insoluble in organic solvents.

The IR spectrum of compound **1** has bands at 700 and 760 cm^{-1}, which correspond to the deformation C—H vibrations of the aromatic rings, along with bands of coordinated THF molecules (at 1050 and 860 cm^{-1}). The substantial increase in the intensity of the band at 1600 cm^{-1}, which corresponds to C—C vibrations of the benzene ring, compared to that of the initial ligand indicates that the latter is substantially activated as a result of bonding with the ytterbium atom. The ESR spectra of solid samples of **1** have no signals either at room temperature or at 160 K. Complex **1** is diamagnetic at 20 °C, which corresponds to the zerovalent or divalent state of ytterbium.[1] By analogy with the naphthalene derivatives of lanthanides, which have been prepared previously[8–12] and which exhibit similar physicochemical properties, it can be suggested that compound **1** is a complex of divalent ytterbium with the stilbene dianion. The fact that complex **1** is insoluble in organic solvents indicates that it is apparently a coordination polymer, which is analogous to the polymer whose formation has been observed previously for the related diphenylbutadiene complex of lutetium $[K(THF)_2(PhCH{=}CHCH{=}CHPh)_2Lu(THF)_2]_n$.[13]

With the aim of studying the chemical properties and the character of the metal—ligand bond in the resulting compound, we performed the reactions of complex **1** with reagents of different nature. Thus, mild oxidation of **1** with atmospheric oxygen in a toluene medium afforded Yb_2O_3, *trans*-stilbene, and THF in quantitative yields. It should be noted that a contact of solid samples of **1** with pure oxygen resulted in an explosion. Hydrolysis of **1** in toluene afforded $Yb(OH)_3$, H_2, THF, and dibenzyl.

The synthesis of derivatives of divalent ytterbium and ease of isolation of the target product of the reaction of complex **1** with various C—H- and E—H-acids (E is an element) are of interest and show promise from the viewpoint of preparative possibilities. It was found that compound **1** in a THF medium readily reacted with cyclopentadiene, 1,2,3,4,5-pentamethylcyclopentadiene, diphenylamine, and 2,4,6-tri(*tert*-butyl)phenol at room temperature to form the corresponding derivatives of divalent ytterbium in high yields. In these reactions, stilbene or dibenzyl was eliminated and hydrogen was evolved. The data on the reactivity of compound **1** are given in Table 1.

When complex **1** was used as the initial compound, the new ytterbium complex $(Ph_2N)_2Yb(THF)_2$ (**2**) was first isolated and characterized. Complex **2** is a red-orange crystalline diamagnetic compound.

The reaction of complex **1** with two equivalents of 2,4,6-$Bu^t_3C_6H_2OH$ gave the $(Bu^t_3C_6H_2O)_2Yb(THF)_3$ complex (**3**) as yellow diamagnetic crystals. Crystals of **3** were studied by X-ray diffraction analysis (see below). Owing to shielding of the ytterbium atom by the bulky *tert*-butyl groups at the *ortho* positions of the phenyl ring, complex **3** is stable to oxidation and carboxylation, which is untypical of compounds of divalent ytterbium. Solutions of **3** in toluene and THF are stable in air and under a CO_2 atmosphere for up to 30 min and 2 h, respectively. It was demonstrated that oxidation of **3** was accompanied by the formation of phenoxy radicals, whose presence in the reaction mixture was detected by ESR spectroscopy. When a solution of **3** in toluene was concentrated *in vacuo* at 80—100 °C, its color changed from yellow to red. Cooling of this solution to ~20 °C gave dark-red diamagnetic crystals of the product, namely, the THF-free complex $[(2,4,6\text{-}Bu^t_3C_6H_2O)_2Yb]_2$ (**4**), in 67% yield.

The ^1H NMR spectrum of compound **4** has two singlets with chemical shifts (δ) 1.44 and 1.63 and two signals at δ 1.32 and 1.34 (the ratio of intensities of the signals of the first and second groups is 2 : 1). These signals correspond to the protons of the *tert*-butyl groups at the *ortho* and *para* positions of the benzene rings. The aromatic protons are manifested in the ^1H NMR spectrum as two signals at δ 7.33 and 7.36. The ^1H NMR spectrum is indicative of the nonequivalence of the phe-

Table 1. Reactions of complex **1** with various reagents

Reagent	Solvent	Duration /h	Products (yield (%))
H_2O	Toluene	0.5	$Yb(OH)_3$ (96.6), $PhCH_2CH_2Ph$ (95.2), THF (97.7), H_2
O_2	Toluene	1	Yb_2O_3 (95.9), PhCH=CHPh (93.4), THF (90.2)
CpH	THF	18	$Cp_2Yb(THF)_2$ (95.4), $PhCH_2CH_2Ph$ (100), H_2
Cp*H	THF	18	$Cp^*_2Yb(THF)_2$ (32), $PhCH_2CH_2Ph$ (83), H_2
Ph_2NH	THF	18	$(Ph_2N)_2Yb(THF)_2$ (80), $PhCH_2CH_2Ph$ (10), PhCH=CHPh (84), H_2
2,4,6-$Bu^t_3C_6H_2OH$	THF	6	$(2,4,6\text{-}Bu^t_3C_6H_2O)_2Yb(THF)_3$ (66), $PhCH_2CH_2Ph$ (5), PhCH=CHPh (93), H_2
DAD	THF	4	$Yb(DAD)_3$ (77), PhCH=CHPh (81)
MeI	THF	1	$YbI_2(THF)_2$ (89), [Me][a], PhCH=CHPh (92)
Me_3SiCl	THF	6	$YbCl_2(THF)_2$ (50), $Me_3SiSiMe_3$ (86), PhCH=CHPh (96)
Cp_3Yb	THF	24	$Cp_2Yb(THF)_2$ (73), $PhCH_2CH_2Ph$ (88)
Styrene[b]	—	8	Polystyrene (100)
Piperylene[b]	—	24	Polypiperylene (100)

[a] In this run, gaseous products were not studied.
[b] Polymerization was carried out in the absence of a solvent; the concentration of the catalyst was 5 mol.%.

noxy ligands, which is attributable to the dimeric structure of the complex containing two bridging and two terminal phenoxide groups (the coordination number of the ytterbium atom is equal to 3). An analogous structure has been established previously for the complex $[(2,6\text{-}Bu^t_2\text{-}4\text{-}Me\text{-}C_6H_2O)(\mu\text{-}2,6\text{-}Bu^t\text{-}4\text{-}Me\text{-}C_6H_2O)Yb]_2$ (**5**).[14]

X-ray diffraction study of single crystals of **3** demonstrated that the complex is monomeric. The coordination number of the ytterbium atom is 5. The ytterbium atom is surrounded by two phenoxide ligands and three coordinated THF molecules. Unlike the complex $(2,4,6\text{-}Bu^t_3C_6H_2O)_2Yb(THF)_3(THF)$ (**6**) described in Ref. 15, the crystals of **3** do not contain THF molecules of crystallization. The structure of molecule **3** is shown in Fig. 1. The atomic coordinates are given in Table 2. The principal bond lengths and bond angles are listed in Tables 2 and 3, respectively. The coordination environment about the ytterbium atom can be represented as a distorted square pyramid. The base of the pyramid is formed by four oxygen atoms, which belong to two transoid phenoxide fragments (O(1) and O(2)) and two THF molecules (O(3) and O(5)). The O(4) atom of the third THF molecule occupies the apical position. All angles between the adjacent oxygen atoms in the base are close to 90°. It should be noted that the bond lengths and bond angles in complex **3** are close to the corresponding parameters of complex **6**. However, the unit-cell volumes are substantially different. Thus, it is reasonable to suggest a larger unit-cell volume in the case of complex **6** containing one additional THF molecule. However, the experimental value for **3** (5788 Å^3) is actually larger than that for **6** (5374 Å).[3] The lengths of the bonds between the ytterbium atom and the oxygen atoms of the phenoxide ligands and of the THF molecules agree well with the corresponding distances observed previously in the related compounds.[14,15] The O(1)—Yb—O(2) angle (149.2(4)°) is close to the corresponding angle in **6** (149.0(6)°). The presence of short intramolecular contacts between the Yb atoms and the carbon atoms of the Bu^t groups in molecule **3** (Yb—C(108) (3.970 Å) and Yb—C(209) (3.949 Å), whose values are close to the sum of the van der Waals radii, and Yb—C(208) (3.905 Å), which is even shorter that this sum) are worthy of note. Apparently, this peculiarity of the molecular structure is indicative of weak nonbonded interactions between the above-mentioned atoms.

Interestingly, the reactions of complex **1** with water, CpH, and Cp*H were accompanied by hydrogenation of stilbene to dibenzyl, while the reactions with Ph_2NH and $2,4,6\text{-}Bu^t_3C_6H_2OH$ gave stilbene as the major product (93%). The reaction of **1** with iodomethane and Me_3SiCl taken in a molar ratio of 1 : 2 in THF at room temperature afforded the corresponding halides of divalent ytterbium. In this case, alkylation of stilbene was not observed. The reaction of **1** with a threefold molar excess of Bu^t—N=CHCH=N—Bu^t (DAD) gave the known complex $Yb(DAD)_3$ in high yield.[16] Interestingly, in no case was the conversion of *trans*-stilbene to its *cis* form observed. Complex **1** catalyzes polymerization of styrene and piperylene at room temperature. Attempts to synthesize a mixed cyclopentadienylstilbene complex of ytterbium failed. Thus, the reaction of disproportionation of $(PhCH{=}CHPh)Yb(THF)_2$ and Cp_3Yb resulted in reduction of the latter to Cp_2Yb and elimination of stilbene.

$$2\ Cp_3Yb + (PhCH{=}CHPh)Yb(THF)_2 \longrightarrow$$
$$\longrightarrow 3\ Cp_2Yb(THF)_2 + PhCH{=}CHPh.$$

The reaction of $(PhCH{=}CHPh)Yb(THF)_2$ with Cp_2Yb in THF or toluene, as well as the reaction of

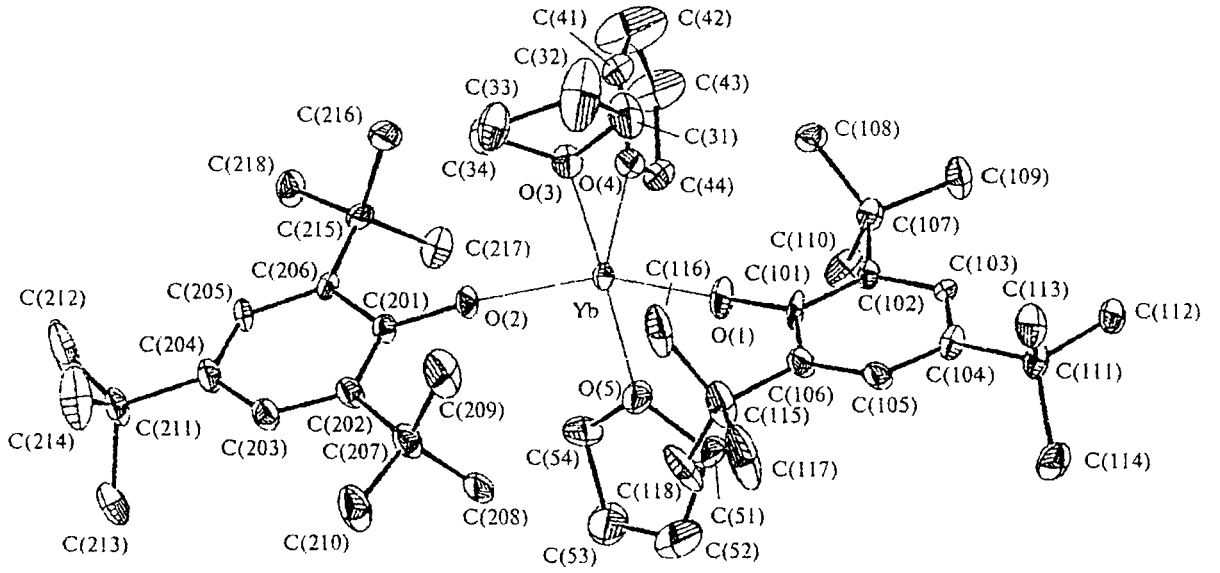

Fig. 1. Molecular structure of the complex $(2,4,6\text{-}Bu^t_3C_6H_2O)_2Yb(THF)_3$.

Table 2. Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic thermal parameters* ($\times 10^{-3}/Å^2$) in molecule 3

Atom	x	y	z	U_{eq}*
Yb	790(1)	6680(1)	9441(1)	29(1)
O(1)	2031(9)	6684(3)	10639(5)	49(3)
O(2)	−523(9)	6374(3)	8518(5)	37(2)
O(3)	−1195(9)	6806(3)	10214(6)	42(2)
O(4)	665(9)	7316(2)	8972(5)	37(2)
O(5)	2773(9)	6519(3)	8690(6)	54(3)
C(101)	2794(12)	6695(4)	11348(7)	39(4)
C(102)	3499(12)	7003(4)	11604(8)	30(3)
O(103)	4314(12)	7001(4)	12354(8)	29(3)
C(104)	4481(13)	6700(4)	12838(8)	39(3)
C(105)	3745(15)	6400(4)	12593(9)	43(4)
C(106)	2908(15)	6379(4)	11880(9)	43(4)
C(107)	3426(14)	7368(4)	11083(8)	39(3)
C(108)	1982(14)	7501(4)	10948(9)	42(4)
C(109)	4249(16)	7689(4)	11497(10)	54(4)
C(110)	4004(15)	7294(5)	10235(9)	55(4)
C(111)	5341(14)	6687(4)	13654(8)	42(3)
C(112)	6091(15)	7059(4)	13827(9)	45(4)
C(113)	4474(16)	6615(5)	14405(8)	55(4)
C(114)	6393(16)	6374(5)	13619(10)	57(4)
C(115)	2116(20)	6017(4)	11671(10)	65(5)
C(116)	553(19)	6091(5)	11660(12)	78(6)
C(117)	2390(26)	5718(5)	12350(12)	113(10)
C(118)	2557(24)	5861(5)	10845(11)	91(8)
C(201)	−1209(13)	6157(4)	7969(8)	30(3)
C(202)	−1334(15)	5774(4)	8095(8)	38(3)
C(203)	−2118(14)	5563(4)	7534(8)	41(4)
C(204)	−2782(14)	5713(4)	6822(8)	41(4)
C(205)	−2638(12)	6080(4)	6704(8)	32(3)
C(206)	−1907(12)	6322(4)	7245(8)	32(3)
C(207)	−624(18)	5579(4)	8854(9)	54(4)
C(208)	865(18)	5636(4)	8816(12)	73(6)
C(209)	−1158(21)	5737(5)	9658(9)	77(6)
C(210)	−921(21)	5161(4)	8856(11)	76(6)
C(211)	−3588(16)	5454(4)	6210(9)	50(4)
C(212)	−4429(27)	5659(5)	5571(15)	133(12)
C(213)	−2701(24)	5156(6)	5887(16)	126(11)
C(214)	−4638(23)	5235(7)	6672(14)	108(8)
C(215)	−4638(23)	6737(4)	7063(8)	37(3)
C(216)	−2523(15)	6952(4)	7734(9)	48(4)
C(217)	−361(14)	6869(5)	7002(9)	52(4)
C(218)	−2525(16)	6840(4)	6203(9)	49(4)
C(31)	−1188(17)	6962(6)	11034(10)	68(5)
C(32)	−2343(22)	6791(9)	11438(12)	118(10)
C(33)	−3046(17)	6549(6)	10823(11)	66(5)
C(34)	−2557(15)	6695(5)	10010(9)	53(4)
C(41)	−374(14)	7580(4)	9167(9)	45(4)
C(42)	−100(25)	7900(7)	8656(21)	144(13)
C(43)	1038(21)	7861(5)	8236(14)	93(8)
C(44)	1603(14)	7502(4)	8429(9)	43(4)
C(51)	4117(17)	6467(6)	9022(12)	81(7)
C(52)	4612(23)	6163(7)	8541(16)	111(9)
C(53)	3957(21)	6202(8)	7691(17)	132(12)
C(54)	2767(16)	6434(5)	7827(11)	62(5)

* U_{eq} was determined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths (d) in complex 3

Bond	d/Å	Bond	d/Å
Yb—O(1)	2.232(8)	O(1)—C(101)	1.34(2)
Yb—O(2)	2.219(8)	O(2)—C(201)	1.34(2)
Yb—O(3)	2.440(9)	C(102)—C(107)	1.56(2)
Yb—O(4)	2.418(9)	C(104)—C(111)	1.53(2)
Yb—O(5)	2.445(9)	C(106)—C(115)	1.56(2)
		C(107)—C(108)	1.52(2)

Table 4. Selected bond angles (ω) in complex 3

Angle	ω/deg
O(1)—Yb—O(2)	149.2(4)
O(1)—Yb—O(3)	89.2(3)
O(1)—Yb—O(4)	106.3(3)
O(1)—Yb—O(5)	90.2(3)
O(2)—Yb—O(3)	88.2(3)
O(2)—Yb—O(4)	104.2(3)
O(2)—Yb—O(5)	90.9(3)
O(3)—Yb—O(4)	87.3(3)
O(3)—Yb—O(5)	176.9(4)
O(4)—Yb—O(5)	95.8(3)
C(101)—O(1)—Yb	178.2(9)
C(201)—O(2)—Yb	173.2(8)
O(1)—C(101)—C(102)	122.7(3)
C(101)—C(102)—C(107)	121.1(11)

Cp_2Yb with PhCH=CHPh, did not occur even at high temperature. The reaction of Cp_2YbCl with stilbene-sodium afforded $Cp_2Yb(THF)_2$, while the reaction of $CpYbCl_2$ with $(PhCH{=}CHPh)Na_2$ gave a mixture of $Cp_2Yb(THF)_2$ and $(PhCH{=}CHPh)Yb(THF)_2$.

$$2\ CpYbCl_2 + 2\ (PhCH{=}CHPh)Na_2 \xrightarrow[-NaCl]{THF} Cp_2Yb(THF)_2 + (PhCH{=}CHPh)Yb(THF)_2 + PhCH{=}CHPh$$

Experimental

The compounds were synthesized *in vacuo* under conditions precluding exposure to oxygen and moisture using the standard Schlenk technique. THF, ether, hexane, and toluene were dried over sodium benzophenone ketyl. Styrene and piperylene were dried over molecular sieves (4A grade) and distilled into a reaction tube immediately before use. The IR spectra were recorded on a Specord M80 instrument; the samples were prepared as Nujol mulls. The ESR spectra were obtained on a Brucker-ER 200D-1SRC instrument. The ^1H NMR spectra were analyzed on a Gemini-300 instrument. The GLC analysis was performed on a Tsvet-530 chromatograph (katharometer as the detector; steel 2 m × 3 mm-column packed with 5% SE-30 on Chromaton N-AW; helium as the carrier gas). Stilbene and dibenzyl were analyzed on a Milikhrom-1A microcolumn liquid chromatograph (UV detector with the variable wavelength (λ = 250 nm), steel 64×2-mm column, Separon S6X 15 mm as the adsorbent, a hexane–THF mixture as the eluent, 200 : 1 (V/V), rate of the eluent

200 mm min^{-1}). The ytterbium content in the products was determined chelatometrically. The magnetic measurements were carried out according to a known procedure.[17]

Synthesis of (PhCH=CHPh)Yb(THF)$_2$ (1). $YbI_2(THF)_2$ (1.92 g, 3.36 mmol) was added with intense stirring and cooling to a solution of stilbene-lithium, which was prepared from *trans*-stilbene (1.21 g, 6.72 mmol) and Li (0.047 g, 6.72 mmol), in THF (60 mL). The reaction mixture was warmed to ~20 °C, stirred for 16 h, and centrifuged. The black precipitate that formed was twice washed with THF (50 mL) and dried at ~20 °C *in vacuo* for 0.5 h. The yield of $(PhCH=CHPh)Yb(THF)_2$ was 1.40 g (84%). Found (%): C, 53.47; H, 6.10; Yb, 34.56. $C_{22}H_{28}O_2Yb$. Calculated (%): C, 53.14; H, 5.63; Yb, 34.79. IR (Nujol mulls), ν/cm^{-1}: 1600 s, 1290 w, 1160 m, 1050 m, 1030 m, 970 s, 860 m, 760 s, 700 s.

Oxidation of 1. Dry oxygen was added carefully portionwise (2 mL) to a suspension of complex **1** (0.88 g, 1.77 mmol) in toluene (25 mL) at 20 °C until the precipitate turned white. The solution was separated from the precipitate (Yb_2O_3, 0.335 g, 95.9%). The precipitate was twice extracted with toluene (5 mL). Stilbene and THF were found in the toluene extract in yields of 0.29 g (93.4%) and 0.23 g (90.2%), respectively.

Hydrolysis of 1. Water (5 mL) was added to a suspension of complex **1** (0.46 g) in toluene (20 mL). A gas evolved, and the precipitate was decolorized. The solution was separated and the residue was twice extracted with toluene (10 ml). The precipitate of $Yb(OH)_3$ was obtained in a yield of 0.2 g (96.6%). Dibenzyl and THF were found in the toluene extract in yields of 0.16 g (95.2%) and 0.13 g (97.7%), respectively.

Reaction of 1 with cyclopentadiene. Cyclopentadiene (0.5 mL, 6.09 mmol) was added to a suspension of complex **1** (0.97 g, 1.95 mmol) in THF (25 mL). The reaction mixture was stirred for 18 h. The precipitate was dissolved, and a gas evolved. The reaction mixture turned violet. THF was removed *in vacuo*. The solid residue was extracted with toluene (10 mL) three times. Dibenzyl was detected in the toluene extract in a yield of 0.35 g (100%). Recrystallization of the solid residue from a THF—hexane mixture gave $Cp_2Yb(THF)_2$ in a yield of 0.83 g (95.4%).

Reaction of 1 with 1,2,3,4,5-pentamethylcyclopentadiene. C_5Me_5H (0.2 mL, 1.21 mmol) was added to a solution of complex **1** (0.71 g, 1.42 mmol) in THF (20 mL). The reaction mixture was stirred for 18 h. The precipitate was dissolved. The reaction mixture turned dark-cherry, and a gas evolved. After removal of THF, the residue was heated at 60—80 °C *in vacuo*. Dibenzyl that sublimated (0.22 g, 83%) was separated, and the stillage residue was recrystallized from pentane. The complex $(C_5Me_5)_2Yb(THF)_2$ was isolated in a yield of 0.26 g (32%).

Reaction of 1 with diphenylamine. *N,N'*-Diphenylamine (1.05 g, 6.23 mmol) was added to a suspension of compound **1** (1.55 g, 3.12 mmol) in THF (20 mL). The reaction mixture was stirred for 18 h. After removal of THF *in vacuo*, stilbene and dibenzyl were sublimated *in vacuo* at 80 °C. The residue was recrystallized from a THF—hexane mixture to obtain the product $[Ph_2N]_2Yb(THF)_2$ in a yield of 1.62 g (80%). Found (%): C, 58.78; H, 5.12; Yb, 26.89. $C_{32}H_{36}N_2O_2Yb$. Calculated (%): C, 58.79; H, 5.55; Yb, 26.47. IR (Nujol mulls), ν/cm^{-1}: 1610 m, 1320 m, 1175 m, 1160 m, 1080 w, 975 w, 750 s, 730 v.s, 695 w.

Reaction of 1 with 2,4,6-tri(*tert*-butyl)phenol. 2,4,6-Tri(*tert*-butyl)phenol (1.08 g, 4.1 mmol) was added to a suspension of compound **1** (1.02 g, 2.05 mmol) in THF (25 mL). The reaction mixture was stirred at ~20 °C for 6 h. The residue was dissolved and the reaction mixture turned bright-yellow. After removal of THF *in vacuo*, stilbene was sublimated upon heating at 80 °C (0.34 g, 93%). The residue was recrystallized from toluene and compound **3** was obtained in a yield of 1.24 g (66%). Found (%): C, 62.54; H, 8.98; Yb, 18.80. $C_{48}H_{82}O_5Yb$. Calculated (%): C, 63.20; H, 9.05; Yb, 18.97. IR (Nujol mulls), ν/cm^{-1}: 1610 w, 1305 m, 1265 m, 1250 m, 1170 m, 1140 w, 1090 m, 1040 m, 970 m, 930 m, 905 m, 890 m, 840 w, 730 v.s. ^1H NMR (hexamethyldisiloxane), δ: 1.35 (s, 18 H, *p*-Bu^t); 1.46 (s, 36 H, *o*-Bu^t); 1.64 (s, 12 H, THF); 3.79 (s, 12 H, THF); 7.09 (s, 4 H, aromatic).

Synthesis of complex 4. A solution of **3** (0.26 g, 0.28 mmol) in toluene (10 mL) was heated at 80—100 °C for 0.5 h. Then toluene was removed *in vacuo*. The red solid residue was dissolved in toluene (15 mL) and kept at this temperature for 6 h. Then the solution was concentrated to 1/2 of the initial volume and cooled to ~20 °C. The red crystals that formed were washed with toluene and dried at ~20 °C *in vacuo* for 40 min. Compound **4** was obtained in a yield of 0.17 g (0.24 mmol, 85.8%). Found (%): C, 62.54; H, 8.03; Yb, 24.38. $C_{36}H_{58}O_2Yb$. Calculated (%):C, 62.17; H, 8.34; Yb, 24.87. ^1H NMR (hexamethyldisiloxane), δ: 1.32 (s, 18 H, *p*-Bu^t); 1.34 (s, 18 H, *p*-Bu^t); 1.44 (s, 36 H, *o*-Bu^t); 1.63 (s, 36 H, *o*-Bu^t); 7.33 (s, 4 H, aromatic), 7.36 (s, 4 H, aromatic).

Reaction of 1 with DAD. DAD (0.74 g, 4.4 mmol) was added to a suspension of compound **1** (0.75 g, 1.5 mmol) in THF (20 mL). The reaction mixture was stirred at ~20 °C for 4 h. After removal of THF, stilbene was separated by sublimation *in vacuo* upon heating to 80 °C in a yield of 0.22 g (81%). The residue was recrystallized from hexane and $Yb(DAD)_3$ was obtained in a yield of 0.78 g (77%).

Reaction of 1 with Cp_3Yb. A solution of Cp_3Yb (0.37 g, 1 mmol) in THF was added to a suspension of compound **1** (0.25 g, 0.5 mmol) in THF (15 mL). The reaction mixture was stirred for 24 h. The precipitate was dissolved and the color of the solution changed from green to dark-violet. After removal of THF and heating of the residue at 80 °C *in vacuo*, stilbene was isolated by sublimation in a yield of 0.88 g (88%). Recrystallization of the residue from a THF—hexane mixture gave $Cp_2Yb(THF)_2$ in a yield of 0.53 g (73%).

Reaction of $Cp_2YbCl(THF)$ with $(PhCH=CHPh^{\cdot-})Na^+$. A solution of $(PhCH=CHPh^{\cdot-})Na^+$, which was prepared from stilbene (0.42 g, 2.7 mmol) and Na (0.052 g, 2.25 mmol), was added to a solution of $Cp_2YbCl(THF)$ (0.92 g, 2.25 mmol) in THF (20 mL). The reaction mixture was stirred for 4 h. The color of the mixture changed from orange to violet. THF was removed and the residue was extracted with toluene. Stilbene was found in the extract in a yield of 0.38 g (93%). Recrystallization of the residue from a THF—hexane mixture gave $Cp_2Yb(THF)_2$ in a yield of 0.76 g (76%).

Reaction of $CpYbCl_2(THF)_2$ with $(PhCH=CHPh)Na_2$. A solution of $(PhCH=CHPh)Na_2$, which was prepared from stilbene (0.48 g, 2.66 mmol) and Na (0.12 g, 5.22 mmol), was added to a solution of $CpYbCl_2(THF)_2$ (1.19 g, 2.63 mmol) in THF (25 mL). The solution was separated from the precipitate of NaCl by decantation and concentrated *in vacuo* to 1/2 of the initial volume. The insoluble black precipitate of $(PhCH=CHPh)Yb(THF)_2$ was obtained in a yield of 0.58 g (89%). When a small amount of hexane was added to the mother liquor, dark-violet crystals of $Cp_2Yb(THF)_2$ were obtained in a yield of 0.41 g (70.6%). The mother liquor contained stilbene (0.18 g, 78%).

X-ray diffraction analysis of compound 3 was carried out on a four-circle Enraf-Nonius CAD 4 diffractometer. The unit cell parameters and intensities of 8014 independent reflections were measured at 193(2) K (λ(Mo-Kα) = 0.71069 Å; the scanning range was $2° \le 2\theta \le 45°$). The crystals of the complex

are monoclinic, a = 0.076(3) Å, b = 36.121(6) Å, c = 16.086(3) Å, V = 5788(2) Å^3, ρ_{calc} = 1.047 g cm^{-3}, Z = 4; space group $P2_1/c$. The structure was solved by direct methods, which were alternated with calculations of difference electron density syntheses (the SHELXS 86[18] and SHELXL 93 program packages[19]), and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The hydrogen atoms were placed in calculated positions (C—H, 0.96 Å; U_{iso} = 0.08 Å^2). The maximum peaks of the residual positive and negative electron density were 1.546 and −1.228 e · Å^{-3}, respectively. The refinement with the use of 5143 independent reflections with $I > 2\sigma(I)$ converged to R = 0.0620, R_w = 0.1855, GOF = 1.060.

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