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Diazabutadiene derivatives of ytterbocenes. Syntheses, properties, and crystal structures of the $(C_5Me_5)_2Yb(Bu^tNCHCHNBu^t)$ and $[CpYb(\mu^2\text{-}OC_{13}H_8—C_{13}H_8O)(THF)]_2$ complexes*

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Oxidation of $(C_5Me_5)_2Yb(THF)_2$ with diazabutadiene $Bu^tN{=}CHCH{=}NBu^t$ (DAD) afforded the $(C_5Me_5)_2Yb(Bu^tNCHCHNBu^t)$ complex (**1**). The magnetic measurements and X-ray diffraction study confirmed the trivalent state of the ytterbium atom and the radical nature of the DAD ligand in complex **1**. The oxidation state of ytterbium in the $(C_5Me_5)_2$YbDAD—solvent system depends on the coordinating properties of the solvent, whereas the ytterbium atom in the Cp_2YbDAD complex (**2**) remains trivalent regardless of the solvent nature. In complex **2**, the redox replacement of $DAD^{\bullet -}$ with 9-fluorenone accompanied by the pinacol dimerization of 9-fluorenone and detachment of one Cp ligand from the ytterbium atom gave rise to the dimeric $[CpYb(\mu^2\text{-}OC_{13}H_8\text{-}C_{13}H_8O)(THF)]_2$ complex (**3**). The structure of complex **3** was established by X-ray diffraction analysis.

Key words: lanthanides, complexes, diazabutadiene, electron transfer, redox isomerism, synthesis, structure.

Possessing diversified coordination and redox properties, disubstituted diazabutadienes are of considerable interest as ligands for transition metal complexes. However, studies of their lanthanide derivatives are still in their infancy.**[1]** The $Bu^tN{=}CHCH{=}NBu^t$ molecule (DAD) can both act as a neutral donor ligand and readily oxidize electropositive metals by accepting one or two electrons to form the radical anion or dianion, respectively.**[2]** Ytterbium is characterized by a low potential of the Yb^{II}/Yb^{III} transformation,**[3]** and its complexes with diazabutadiene are convenient objects for investigating intramolecular metal—ligand electron transfer. Earlier,**[1b]** we have synthesized and characterized the homoligand complex DAD_3Yb. The investigation of its magnetic properties provided evidence that two redox isomers exist at low temperatures. As part of our continuing studies on intramolecular redox processes in ytterbium complexes with redox-active ligands, we attempted to synthesize new mixed-ligand diazabutadiene derivatives of ytterbium. In the present study, we report on the synthesis, structures, and magnetic properties of diazabutadiene derivatives of bis(pentamethylcyclopentadienyl)ytterbium(III) and bis(cyclopentadienyl)ytterbium(III) as well as the reaction of the latter with 9-fluorenone.

Results and Discussion

The reaction of the $Cp^*{}_2Yb(THF)_2$ complex ($Cp^* = C_5Me_5$) with a twofold molar excess of DAD was carried out in THF at room temperature (Scheme 1). After the removal of the solvent *in vacuo* and recrystallization of the residue from a concentrated solution in hexane, the $Cp^*{}_2Yb(Bu^tNCHCHNBu^t)$ complex (**1**) was isolated as dark-claret crystals in 72% yield.

Complex **1** is very sensitive to atmospheric oxygen and moisture and is readily soluble in aliphatic and aromatic hydrocarbons. The magnetic susceptibility measurement of **1** in the crystalline state**[4]** demonstrated that its magnetic moment (μ_{eff}) at room temperature is 4.1 μ_B. The same value of μ_{eff} was obtained by the magnetic measurement of complex **1** in a solution in benzene at 293 K according to the Evans method.**[5]** This magnetic moment corresponds to the ytterbium(III) ion with the $4f^{13}$ configuration, which indicates that the ytterbium atom is oxi-

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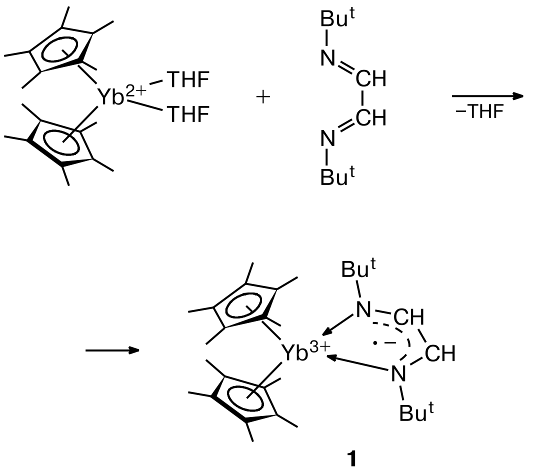
Scheme 1



dized to the trivalent state in the course of the reaction. Consequently, the DAD molecule accepts an electron to form the radical anion. However, it should be noted that the experimental magnetic moment μ_{eff} is somewhat smaller than the value calculated at this temperature for the ytterbium(III) complex coordinated by one radical-anionic ligand (4.8 μ_B).[6] This may be accounted for by two reasons, *i.e.*, either by the presence of an impurity of the diamagnetic ytterbium(II) complex $Cp^*{}_2Yb^{II}DAD^0$ or by antiferromagnetic interaction between the cation and radical anion. The IR spectrum of complex **1** corresponds to the reduced form of the diazabutadiene ligand. The absence of the absorption band of the C=N double bond at 1620 cm^{-1} characteristic of free DAD indicates that the order of the nitrogen—carbon bond is reduced due to electron delocalization in the radical-anionic diazabutadiene fragment.

The results of X-ray diffraction study are consistent with the radical-anionic character of the diazabutadiene ligand (Fig. 1, Tables 1 and 2).

In complex **1**, the C—N bonds in the imine groups of DAD (1.339(4) and 1.326(5) Å) are much longer than the analogous distances in the starting ligand (1.267 Å).[7] The C—C bond in the diimine fragment of complex **1** (1.398(5) Å) is substantially shorter than that in the free ligand (1.467(2) Å),[7] which is indicative of partially double bonding due to the delocalization of the negative charge over the N—C—C—N fragment. As a whole, the geometry of the DAD fragment is similar to that found in the Cp_2YbDAD (**2**) complex studied by us earlier,[1d] although the C—N bonds in complex **2** are slightly shorter, whereas the C—C bond is longer than the corresponding bonds in

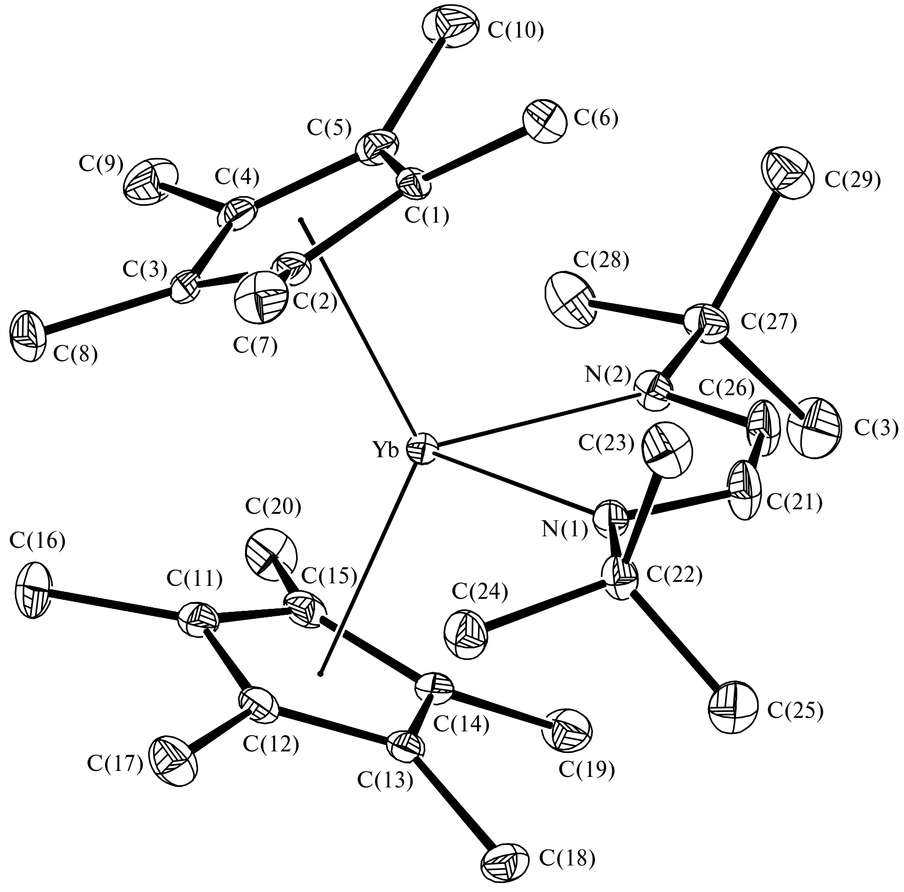


Fig. 1. Structure of complex **1**.

Table 1. Principal bond lengths (*d*) and bond angles (ω) in complex **1**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Yb—Cnt(Cp^{*1})	2.414(2)	Yb—C(11)	2.716(4)	Cnt(Cp^{*1})—Yb—Cnt(Cp^{*2})	130.27(6)
Yb—Cnt(Cp^{*2})	2.4009(18)	Yb—C(12)	2.701(4)	Cnt(Cp^{*1})—Yb—N(1)	109.85(9)
Yb—N(1)	2.385(3)	Yb—C(13)	2.656(3)	Cnt(Cp^{*1})—Yb—N(2)	110.47(8)
Yb—N(2)	2.394(3)	Yb—C(14)	2.662(3)	Cnt(Cp^{*2})—Yb—N(1)	108.87(8)
Yb—C(1)	2.694(5)	Yb—C(15)	2.698(4)	Cnt(Cp^{*2})—Yb—N(2)	109.01(8)
Yb—C(2)	2.715(6)	N(1)—C(21)	1.339(4)	N(1)—Yb—N(2)	74.53(10)
Yb—C(3)	2.703(4)	N(2)—C(26)	1.326(5)		
Yb—C(4)	2.682(3)	C(21)—C(26)	1.398(5)		
Yb—C(5)	2.696(5)				

Note. Cnt are the centers of the Cp* rings.

complex **1** (1.31(2), 1.30(2), and 1.40(2) Å, respectively). The geometric parameters of the Cp$^*{}_2$Yb fragment confirm the trivalent state of the ytterbium atom. The average Yb—C(Cp*) bond length in **1** (2.69 Å) is shorter than the corresponding value (2.74 Å) in the divalent ytterbium complex Cp$^*{}_2$Yb(py)$_2$, which has the identical coordination environment,[8] but is somewhat longer than the corresponding distances in trivalent decamethylytterbocene derivatives.[9] Oxidation of Yb^{II} derivatives to Yb^{III} derivatives should lead to a shortening of the Yb—C bond length by 0.16 Å due to a decrease in the effective ionic radius of the ytterbium atom,[10] whereas these changes in the bond length in complexes **1** and Cp$^*{}_2$Yb(py)$_2$ are much smaller. Presumably, the observed geometric parameters can be attributed to steric strains in the coordination sphere of the ytterbium atom caused by repulsions between the bulky Cp* and DAD ligands, which is also reflected in a noticeable decrease in the Cp*—Yb—Cp* angle in complex **1** (130.27(6)°) compared to that in Cp$^*{}_2$Yb(py)$_2$ (136.3(3)°).[8] The Yb—C distances in compound **1** are in the range observed in the trivalent ytterbium derivatives synthesized recently,[11] *viz.*, Cp$'_2$Yb(L) (Cp$'$ = C$_5$Me$_5$, 1,3-(Me$_3$C)$_2$C$_5$H$_3$, or 1,3-(Me$_3$Si)$_2$C$_5$H$_3$; L is 2,2-bipyridyl, 4,4′-dimethyl-2,2′-bipyridyl, or 1,10-phenanthroline). The Yb—N distances in complex **1** (2.385(3) and 2.394(5) Å) are substantially longer than those in complex **2** (2.306(9) and 2.309(9) Å).[1d] Apparently, such an increase in the metal—nitrogen distances is also associated with repulsions between the bulky *tert*-butyl groups of the diazabutadiene ligand and pentamethylcyclopentadienyl rings. The signal of the DAD radical anion was not detected in the ESR spectra of compound **1** in the crystalline state and in a toluene solution measured in the temperature range of 173—300 K.

Table 2. Principal bond lengths (*d*) and bond angles (ω) in complex **3**

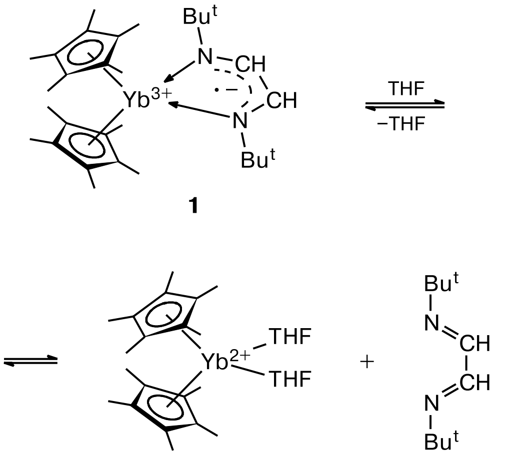
Bond	*d*/Å	Angle	ω/deg
Yb—Cnt(Cp)	2.365(6)	O(2)—Yb—O(1)	135.7(3)
Yb—O(1)	2.331(7)	O(2)—Yb—O(3)	87.7(7)
Yb—O(1)′	2.216(7)	O(1)—Yb—O(3)	102.5(3)
Yb—O(2)	2.108(8)	O(2)—Yb—O(1)$^{\#}$	72.2(3)
Yb—O(3)	2.346(7)	O(1)—Yb—O(1)$^{\#}$	67.8(3)
Yb—C(401)	2.631(14)	O(2)—C(201)—C(101)	107.4(8)
Yb—C(402)	2.636(14)	O(1)—C(101)—C(201)	113.3(8)
Yb—C(403)	2.668(12)		
Yb—C(404)	2.622(13)		
Yb—C(405)	2.643(14)		
C(101)—C(201)	1.561(15)		

Note. The equivalent atoms are generated from the basis atoms by the symmetry operation: $^{\#}$ $1 - x, y, 3/2 - z$.

In accordance with the paramagnetic nature of complex **1**, its ^{1}H NMR spectrum in C$_6$D$_6$ has a set a broadened signals, which are substantially shifted with respect to those characteristic of diamagnetic complexes. The protons of the Me groups of the Cp* ligand give a singlet at δ 0.05, the protons of the diimine group N=CH give a broad singlet at δ –22.64, whereas the protons of the *tert*-butyl groups of the DAD ligand are observed as four singlets (δ –6.67, 12.22, 19.16, and 24.22) with different intensities, whose overall intensity corresponds to 18 protons. The three-dimensional model of complex **1** provides an explanation for the observed nonequivalence of the protons of the *tert*-butyl groups. One of the Me groups is located in the space between the bulky Cp* ligands, which substantially hinders the rotation of the *tert*-butyl groups and results in the nonequivalence of their protons. The ^{1}H NMR spectrum of complex **1** in THF-d$_8$ corresponds to a diamagnetic compound and has signals with characteristic chemical shifts. Unlike the spectrum in benzene-d$_6$, the spectrum in THF-d$_8$ has the only singlet for the protons of the *tert*-butyl group (δ 1.21) and a singlet at δ 7.84 assigned to the protons of the imine groups, which corresponds to the spectrum of the free DAD ligand. The protons of the Cp* ring give a singlet at δ 1.90, which is also characteristic of the chemical shifts observed for pentamethylcyclopentadienyl derivatives of ytterbium(II).[12]

The results of the present study demonstrated that compound **1** both in the crystalline state and solutions of noncoordinating solvents has the structure of an ytterbium(III) complex with the diazabutadiene radical anion. In a solvating solvent (THF), the DAD ligands are displaced from the coordination sphere of the Yb atom, which is accompanied by electron transfer from the diazabutadiene radical anion to the metal cation and reduction of the latter to the divalent state (Scheme 2). Such a process can take place only when the energy of the Coulomb interaction between the $Cp^*_2Yb^+$ cation involving trivalent ytterbium and the $DAD^{\bullet -}$ radical anion is close to the energy of two Yb—O coordination bonds formed in the divalent ytterbium complex $Cp^*_2Yb(THF)_2$. In this case, the energy consumed for reduction of the ytterbium cation is compensated by the formation of ytterbium—oxygen coordination bonds. Earlier, an analogous behavior in coordinating solvents was observed for complexes of decamethylsamarocene with styrene[13a] and aromatic condensed polycyclic ligands.[13b] However, complex **1**, unlike samarium compounds, can be regenerated by removing THF and recrystallizing the residue from a noncoordinating solvent.

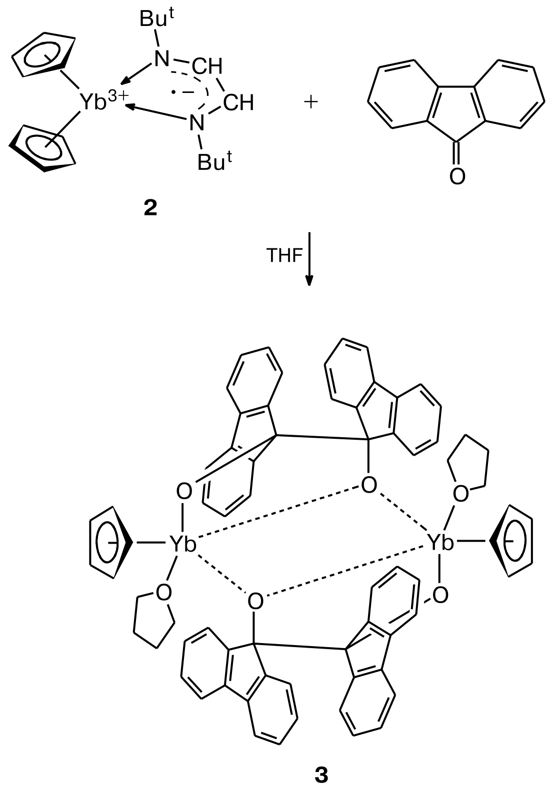
Scheme 2



Unlike the ^1H NMR spectra of complex **1**, the spectra of its nonmethylated analog **2** both in benzene-d_6, and THF-d_8 are identical and correspond to its paramagnetic form. The protons of the Cp ring exhibit a singlet at δ −23.32, the protons of the *tert*-butyl group are observed as a singlet at δ 45.22, and the proton of the imine group is observed as a broad singlet at δ 49.3. It is evident that in complex **2** dissolved in THF, $DAD^{\bullet -}$ in the coordination sphere of ytterbium is not replaced and the metal atom remains trivalent. This difference in the behavior of complexes **1** and **2** is consistent with their structural features, *viz.*, with the difference in the Yb—N bond lengths. Apparently, due to the closer contact between the Cp_2Yb^+ cation and the $DAD^{\bullet -}$ radical anion in molecule **2**, the energy of their Coulomb interaction is higher than the energy of the bond in complex **1**, and the formation of the Yb^{II}—O coordination bonds does not compensate for the energy consumed for the back electron transfer from the radical anion to the ytterbium atom and the replacement of the DAD molecule in its coordination sphere.

Earlier, only several lanthanide complexes with radical-anionic ligands have been described, and their reactivity remained virtually unknown.[12] The reactivity of mixed-ligand diazabutadiene complexes of ytterbium was studied using the redox replacement of the diazabutadiene ligand in complex **2** with 9-fluorenone as an example. It was expected that 9-fluorenone, being a stronger oxidizing agent than diazabutadiene (E_o is −1.35 [12] and −1.822 [2] V, respectively), would oxidize the radical anion of the latter and replace it in the coordination sphere of the ytterbium atom. The reaction of complex **2** with 9-fluorenone (taken in molar ratio of 1 : 1) was carried out in THF at room temperature (Scheme 3). Complex **3** was isolated as yellow paramagnetic (μ_{eff} = 4.3 μ_B) crystals in 78% yield by slow concentration of the reaction mixture. The IR spectrum of complex **3** has no absorption bands of the carbonyl groups of the starting 9-fluorenone (1720 cm^{-1}) but shows bands characteristic of vibrations of the aromatic C—H groups of the Cp ring (760 and 780 cm^{-1}) and the fluorenyl fragment (740 cm^{-1}) as well as C—O vibrations of the THF molecule (860 and 1050 cm^{-1}) and the fluorenyloxy ligand (1000 cm^{-1}).

Scheme 3



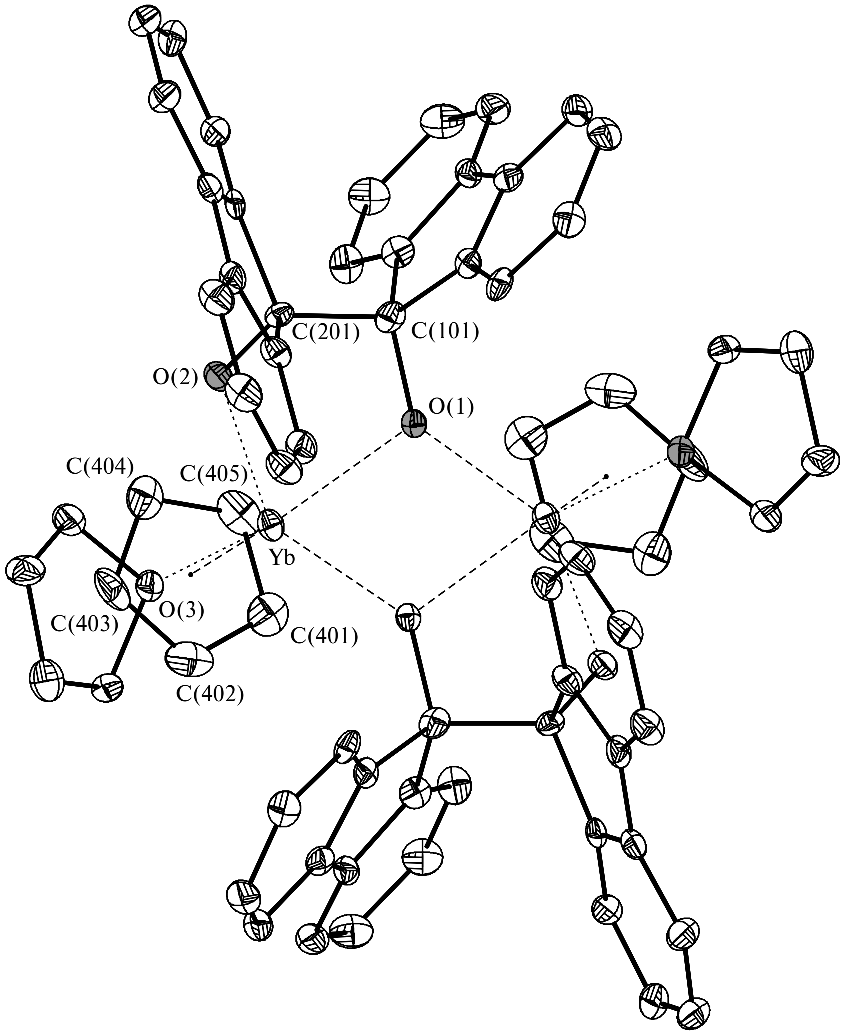


Fig. 2. Structure of complex **3**.

X-ray diffraction study of complex **3** (Fig. 2, Table 2) demonstrated that this compound occurs as a dimer consisting of two CpYb(THF) fragments linked through two 9,9-difluorenyl dioxide fragments. One of the oxygen atoms of these groups serves as a bridge between two ytterbium atoms, whereas another oxygen atom is coordinated to only one metal atom. Hence, the reaction of complex **2** with 9-fluorenone does not end in oxidation of the DAD radical anion and its replacement in the coordination sphere of ytterbium, but continues with the resulting pinacol condensation of 9-fluorenone and detachment of one of the Cp rings.

Experimental

Syntheses were carried out under conditions precluding exposure to atmospheric oxygen and moisture with the use of the standard Schlenk technique. The solvents (THF, hexane, and toluene) were dried with sodium benzophenone ketyl, thoroughly degassed, and condensed into a reaction tube under vacuum immediately before use. The IR spectra were recorded on a Specord M80 instrument. Samples were prepared as Nujol mulls. The ^1H and ^{13}C NMR spectra were recorded on Bruker DPX 200 and Bruker DPX 400 instruments. The chemical shifts are given in the δ scale relative to the known shifts of the residual protons of deuterated solvents. Magnetic measurements were carried out according to known procedures.[4,5]

Bis-pentamethylcyclopentadienyldi(*tert*-butyl)diazabutadiene-ytterbium, $Cp^*_2Yb(Bu^tNCHCHNBu^t)$ (1). A solution of DAD (0.844 g, 5.02 mmol) in THF (5 mL) was added to a solution of $Cp^*_2Yb(THF)_2$ (1.475 g, 2.51 mmol) in THF (15 mL). The reaction mixture was stirred for 1 h, and then the solvent was removed *in vacuo*. The dark-claret residue was dissolved in toluene (5 mL), the toluene was evaporated *in vacuo* at ~20 °C, and the procedure was repeated. The residue was extracted with hexane (2×10 mL). The solution was concentrated *in vacuo* to 5 mL and cooled at –20 °C for 18 h. The dark-claret crystals were separated from the mother liquor by decantation, washed with cold hexane, and dried *in vacuo*. Compound **1** was obtained in a yield of 1.105 g (72%). Found (%): C, 58.48; H, 8.61;

Table 3. Crystallographic parameters of complexes **1** and **3**

Parameter	Complex **1**	Complex **3**
Molecular formula	$C_{30}H_{50}N_2Yb$	$C_{35}H_{29}O_3Yb$
Molecular weight	611.76	670.62
Space group	*Pna*2$_1$	*Pbcn*
a/Å	13.7169(1)	15.5385(5)
b/Å	15.5660(2)	18.1485(6)
c/Å	13.3681(2)	18.8291(6)
$\alpha = \beta = \gamma$/deg	90	90
V/Å^3	2854.32(6)	5309.8(3)
Z	4	8
ρ_{calc}/g cm^{-3}	1.424	1.678
μ/mm^{-1}	3.295	3.558
Scan range θ/ω	1.98—27.49	1.73—25.00
Number of measured reflections	21159	28061
Number of reflections with $I > 2\sigma$	6400 (R_{int} = 0.0396)	4632 (R_{int} = 0.0868)
Number of refinable parameters	314	352
R_1 ($I > 2\sigma(I)$)	0.0222	0.0792
wR_2 ($I > 2\sigma(I)$)	0.0434	0.1453

Yb, 28.17. $C_{30}H_{50}N_2Yb$. Calculated (%): C, 58.90; H, 8.17; Yb, 28.27. IR (Nujol mulls), ν/cm^{-1}: 1210 (C—N), 1250 (Bu^t). ^{1}H NMR (20 °C, benzene-d$_6$), δ: −22.64 (s, 2 H, N=C$\underline{H}$); 0.05 (s, 30 H, Cp*); −6.67, 12.22, 19.16, and 24.22 (all s, 18 H, Bu^t); THF-d$_8$: 1.21 (s, 18 H, Bu^t); 1.90 (s, 30 H, Cp*); 7.84 (s, 2 H, N=C$\underline{H}$).

Reaction of the $Cp_2Yb(Bu^tNCHCHNBu^t)$ complex (2) with 9-fluorenone. A solution of 9-fluorenone (0.324 g, 1.80 mmol) in THF (5 mL) was added to a solution of bis-cyclopentadienyldi(*tert*-butyl)diazabutadieneytterbium (**2**) (0.851 g, 1.80 mmol) in THF (15 mL) at ~20 °C. The reaction solution was stirred for 10 min and kept at ~20 °C for 8 h. The yellow crystals that precipitated were separated from the mother liquor, washed with cold THF, and dried *in vacuo*. Complex **3** was obtained in a yield of 0.438 g (72%). Found (%): C, 62.29; H, 3.99; Yb, 25.50. $C_{70}H_{58}O_6Yb_2$. Calculated (%): C, 62.68; H, 4.32; Yb, 25.79. IR (Nujol mulls), ν/cm^{-1}: 740 (Flu); 760, 780 (Cp); 860 (C—O, THF); 1000 (C—O, Flu—O); 1050 (C—O, THF).

X-ray diffraction study. The X-ray diffraction data for complexes **1** and **3** were collected on a Siemens-SMART CCD diffractometer (λ(Mo-K$_\alpha$), graphite monochromator, 173 K, ω scanning mode). The crystallographic data and principal details of the refinement of compounds **1** and **3** are given in Table 3. The structures were solved by direct methods using the SHELXS-86 program package[15] and refined anisotropically by the least-squares method with the use of the SHELXL-93 program package.[16] The hydrogen atoms were placed in geometrically calculated positions and refined using the riding model.

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