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Reactions of ytterbium(II) bis(indenyl) complex $(C_9H_7)_2Yb(thf)_2$ with 2,2´-bipyridine and 1,4-bis(2,6-diisopropylphenyl)-1,4-diazabuta-1,3-diene. Structures and properties of $(C_9H_7)_2Yb(bipy)$ and $(C_9H_7)_2Yb(2,6\text{-}Pr^i{}_2C_6H_3NCHCHNC_6H_3Pr^i{}_2\text{-}2,6)$ complexes

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The reaction of the ytterbium(II) bis(indenyl) complex $(C_9H_7)_2Yb(thf)_2$ (**1**) with 2,2´-bipyridine afforded the diamagnetic $(C_9H_7)_2Yb(bipy)$ compound (**2**), whose structure was established by X-ray diffraction analysis. Under similar conditions, the reaction of complex **1** with 1,4-bis(2,6-diisopropylphenyl)-1,4-diazabuta-1,3-diene (DAD) led to oxidation of ytterbium giving rise to the paramagnetic $(C_9H_7)_2Yb(DAD)$ complex (**3**). Magnetic measurements, X-ray diffraction study, and ^1H NMR spectroscopy in benzene confirmed the trivalent state of the ytterbium atom and the radical-anionic nature of the diazadiene ligand in complex **3**. In the complex **3**—solvent system, the oxidation state of metal depends on the coordination ability of the solvent. In benzene, complex **3** exists as $(C_9H_7)_2Yb^{III}(DAD^{\bullet-})$, whereas $(C_9H_7)_2Yb^{II}(thf)_2$ and DAD^0 are present in THF.

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

1,4-Disubstituted diazabutadienes have found wide application as ligands in transition metal chemistry due to diversity of their coordination and redox properties.[1] Owing to the presence of lone electron pairs of the nitrogen atoms and the π electrons of the nitrogen—carbon double bonds, the diazadiene molecule can act as both the n- and π-donor when coordinated to a metal atom as the neutral ligand.[2] At the same time, diazadienes possess pronounced electron affinity[3] and can oxidize electropositive metals taking one or two electrons on the π* orbital to give the radical anion[4] or dianion,[5] respectively. The discovery of high catalytic activity of their compounds with Group 10 metals in olefin polymerization,[6] as well as redox isomerism in mixed-ligand copper complexes containing these ligands,[7] have inspired a renewed interest in diazadienes.

In lanthanide chemistry, the diazadiene ligands have found use rather recently, and the range of these compounds is limited primarily to 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene derivatives.[8] Study of the magnetic properties of the homoleptic trivalent ytterbium complex $(Bu^tNCHCHNBu^t)_3Yb$, which we have synthesized earlier, suggested the temperature-induced redox isomerism for this compound.[8c] As part of our continuing studies of intramolecular redox processes in ytterbium complexes with redox-active ligands, we extended the range of diimine ligands and attempted to synthesize new mixed-ligand derivatives of this metal. In the present study, we report the synthesis of the $(C_9H_7)_2Yb(bipy)$ and $(C_9H_7)_2Yb(2,6\text{-}Pr^i{}_2C_6H_3NCHCHNC_6H_3Pr^i{}_2\text{-}2,6)$ complexes, their structures, magnetic properties, and an unusual behavior in solutions.

Results and Discussion

As has been demonstrated earlier,[8h] 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene (DAB) readily oxidizes ytterbium bis(cyclopentadienides) $Cp_2Yb(thf)_2$ ($Cp = C_5H_5$, C_5Me_5)

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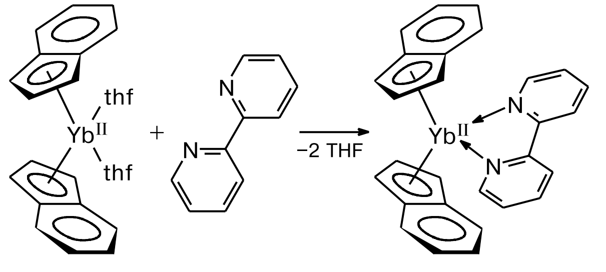
to the corresponding ytterbium(III) complexes $Cp_2Yb^{III}(DAB^{\bullet -})$ containing the diazadiene radical anion. It was of interest to study the reactions of the bis(indenyl) analog $(C_9H_7)_2Yb(thf)_2$ with diazadienes, which differ in the electron-withdrawing and steric properties.

2,2´-Bipyridine (bipy), which has a virtually planar structure, can be considered as a ligand containing the diimine fragment. Due to a lower reduction potential of bipy (−2.18 V)[9a] compared to that of 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene (−1.822 V),[9b] bipyridine derivatives of ytterbium have promise from the standpoint of possible redox tautomeric transformations. It is known that bipy oxidizes decamethylsamarocene giving rise to the radical-anionic complex $(C_5Me_5)_2Sm(bipy)$,[10] whereas the cyclopentadienyl derivatives of ytterbium(II) $Cp_2Yb(Et_2O)$ (Cp = C_5Me_5, $(1,3\text{-}Me_3C)_2C_5H_3$, $(1,3\text{-}Me_3Si)_2C_5H_3$), whose divalent state is more stable,[11] can react with bipy in different fashions to form complexes with both the neutral and reduced ligand depending on the nature of the substituents in the Cp ring.[12]

We found that $(C_9H_7)_2Yb(thf_2)$ (**1**) reacts with bipy in THF at room temperature to yield the ytterbium(II) complex $(C_9H_7)_2Yb(bipy)$ (**2**) (Scheme 1). The reaction is accompanied by an instantaneous change in the color of the reaction mixture from dark-red to dark-brown. Complex **2** was isolated by crystallization from a THF—toluene mixture as dark-brown crystals in 68% yield. Complex **2** is extremely sensitive to atmospheric oxygen and moisture, readily soluble in THF, moderately soluble in toluene, and insoluble in hexane.

Scheme 1



1 **2**

The ^1H NMR spectra of complex **2** in benzene-d_6 and THF-d_8 show a set of narrow signals at δ 0—10, which indicates that this complex is diamagnetic. The fact that the ^1H NMR spectrum of compound **2** in THF-d_8 at room temperature has signals of both coordinated and free THF and bipy molecules provides evidence for slow exchange between the thf and bipy ligands in the coordination sphere of the Yb atom. Magnetochemical measurements confirmed diamagnetism of complex **2** and the divalent state of the Yb atom.[13]

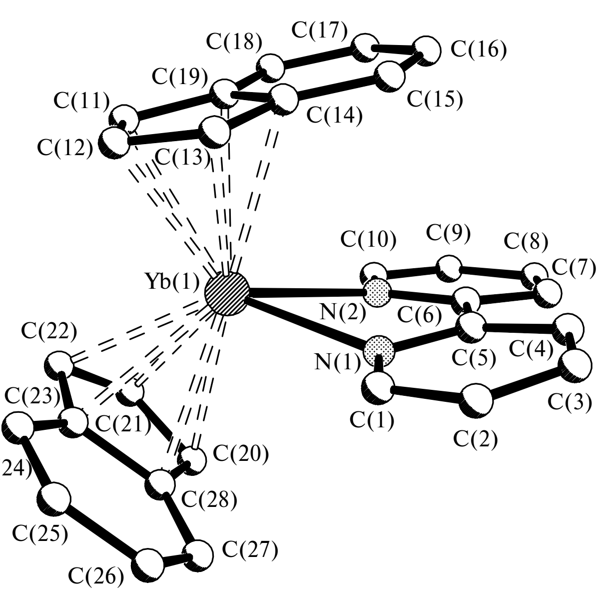


Fig. 1. Structure of the $(C_9H_7)_2Yb(bipy)$ complex (**2**). One of two crystallographically independent molecules is shown.

Therefore, the reaction of complex **1** with bipy, unlike that of $(C_5Me_5)_2Yb(Et_2O)$,[12] proceeds with retention of the oxidation state of the metal atom, which is attributable to the lower electron-donating ability of the indenyl ligand compared to the pentamethylcyclopentadienyl ligand and the lower reducing ability of complex **1**.

The structure of complex **2** was established by X-ray diffraction analysis (Fig. 1). The crystals of complex **2** contain two crystallographically independent molecules. The selected bond lengths and bond angles are listed in Table 1. The details of X-ray diffraction study are given in Table 2. Analysis of the Yb—C bond lengths confirms the divalent state of the ytterbium atom. The average Yb—C bond lengths in two molecules **2** are 2.701(3) and 2.691(3) Å, which are only slightly smaller than the corresponding distance in the starting ytterbocene **1** (2.73 Å, Table 3),[14] whereas oxidation of Yb^{II} to Yb^{III} should lead to more substantial shortening of the Yb—C bonds due to a decrease in the ionic radius of ytterbium from 1.14 to 0.985 Å.[15] The metal—nitrogen bonds in complex **2** (2.456(2), 2.433(2), 2.456(2), and 2.434(2) Å) are somewhat shorter than the corresponding distances in the ytterbium(II) pyridyl complex $(C_5Me_5)_2Yb(py_2)$ (2.586(7) and 2.544(6) Å)[16] but are comparable to the analogous bonds in the related bipyridine compound $(C_9H_6SiMe_2NHBu^t)_2Yb(bipy)$ (2.454(3) and 2.476(4) Å).[17]

The Cp_c—Yb—Cp_c angles in compound **2** (132.0 and 132.4°) are noticeably larger than that in the starting complex **1** (128.6°)[14] but they are virtually equal to the angle found[17] in $(C_9H_6SiMe_2NHBu^t)_2Yb(bipy)$ (132.1(3)°). Apparently, this is attributable to larger steric crowding of the coordination sphere of the metal

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **2** (for two crystallographically independent molecules)

I		II	
Bond*	*d*/Å	Bond	*d*/Å
Yb(1)—Cp$_c$(1)	2.424(3)	Yb(2)—Cp$_c$(1)	2.410(3)
Yb(1)—Cp$_c$(2)	2.408(3)	Yb(2)—Cp$_c$(2)	2.402(3)
Yb(1)—N(1)	2.456(2)	Yb(2)—N(3)	2.433(2)
Yb(1)—N(2)	2.434(2)	Yb(2)—N(4)	2.456(2)
Yb(1)—C(11)	2.699(3)	Yb(2)—C(39)	2.665(3)
Yb(1)—C(12)	2.687(3)	Yb(2)—C(50)	2.669(3)
Yb(1)—C(13)	2.702(3)	Yb(2)—C(49)	2.672(3)
Yb(1)—C(14)	2.732(3)	Yb(2)—C(48)	2.682(3)
Yb(1)—C(19)	2.722(3)	Yb(2)—C(40)	2.684(3)
Yb(1)—C(20)	2.717(3)	Yb(2)—C(47)	2.688(3)
Yb(1)—C(21)	2.712(3)	Yb(2)—C(51)	2.695(3)
Yb(1)—C(22)	2.672(3)	Yb(2)—C(41)	2.708(3)
Yb(1)—C(23)	2.668(3)	Yb(2)—C(56)	2.723(3)
Yb(1)—C(15)	2.698(4)	Yb(2)—C(42)	2.726(3)
C(5)—C(6)	1.494(3)	C(33)—C(34)	1.493(3)
N(2)—C(6)	1.346(3)	N(4)—C(34)	1.349(3)
N(2)—C(10)	1.339(3)	N(4)—C(38)	1.349(3)
C(10)—C(9)	1.384(4)	C(38)—C(37)	1.378(4)
C(9)—C(8)	1.371(4)	C(37)—C(36)	1.380(4)
C(7)—C(8)	1.388(4)	C(35)—C(36)	1.383(4)
C(6)—C(7)	1.389(4)	C(34)—C(35)	1.388(4)
C(5)—C(4)	1.391(4)	C(33)—C(32)	1.391(4)
C(3)—C(4)	1.382(4)	C(32)—C(31)	1.386(4)
C(2)—C(3)	1.379(4)	C(30)—C(31)	1.375(5)
C(1)—C(2)	1.382(4)	C(29)—C(30)	1.382(4)
N(1)—C(5)	1.348(3)	N(3)—C(29)	1.343(3)
N(1)—C(1)	1.348(4)	N(3)—C(33)	1.350(3)
Angle*	ω/deg	Angle	ω/deg
Cp$_c$(1)—Yb(1)—Cp$_c$(2)	132.4(7)	Cp$_c$(1)—Yb(2)—Cp$_c$(2)	132.0(7)
N(1)—Yb(1)—N(2)	66.48(7)	N(3)—Yb—N(4)	66.37(7)

* Cp$_c$ is the center of the cyclopentadienyl ring.

Table 2. Crystallographic parameters of complexes **2** and **3**

Parameter	2	3
Molecular formula	$C_{28}H_{22}N_2Yb$	$C_{44}H_{50}N_2Yb$
Molecular weight	559.52	779.90
Space group	$P\bar{1}$	*Pbcn*
a/Å	9.2355(6)	22.5088(3)
b/Å	15.9164(10)	17.1532(2)
c/Å	16.2554(11)	9.48840(10)
α/deg	63.170(10)	90
β/deg	89.9280(10)	90
γ/deg	88.2250(10)	90
V/Å^3	2131.1(2)	3663.45(8)
Z	4	4
ρ_{calc}/g cm^{-3}	1.744	1.414
μ/mm^{-1}	4.406	2.585
θ/ω Scan range	2.21—29.03	1.49—27.50
Number of measured reflections	15537	25698
Number of reflections with $I > 2.0\sigma$	10920 (R_{int} = 0.0177)	4213 (R_{int} = 0.0693)
Number of parameters in refinement	735	217
R_1 ($I > 2\sigma(I)$)	0.0324	0.0341
wR_2 ($I > 2\sigma(I)$)	0.0897	0.0600

Table 3. Geometric parameters of the $(C_9H_7)_2Yb(thf)_2$ (**1**), $(C_9H_7)_2Yb(bipy)$ (**2**), and $(C_9H_7)_2Yb(DAD)$ (**3**) complexes

Parameter	1[a]	2		3
		I[b]	II[c]	
Average bond length/Å				
M—C$_{ring}$	2.73	2.701	2.691	2.663
M—Cp	2.45	2.416	2.406	2.376
M—N	—	2.445	2.444	2.381
Cp—M—Cp angle/deg	128.6	132.4	132.0	124.9

[a] See Ref. 14.

[b] The first crystallographically independent molecule.

[c] The second crystallographically independent molecule.

atom in complex **1** compared to compound **2** and $(C_9H_6SiMe_2NHBu^t)_2Yb(bipy)$ due to the differences in the geometry of the thf and bipy ligands. The structures of two crystallographically independent molecules **2** differ most essentially in the dihedral angles between the planes of the pyridine rings N(2)C(10)C(9)C(8)C(7)C(6)—N(1)C(1)C(2)C(3)C(4)C(5) and N(4)C(38)C(37)C(36)C(35)C(34)—N(3)C(33)C(32)C(31)C(30)C(29) (11.2(8) and 4.8(8)°, respectively). The torsion angle between the planes of the pyridine rings serves as an indicator of the electronic state of the bipy ligand in the complex. If this angle in the free bipy and complexes with the neutral bipy ligand is rather large (10—17°),[12,18] the electron transfer to the highest occupied molecular orbital of the bipy molecule leads to a change in its geometry, including its flattening due to partial double bonding between two C atoms at positions 2 and 2′. Hence, the presence of two crystallographically independent molecules, which differ in the geometric parameters of the bipy ligand, could be considered as evidence for the existence of redox isomers **2**. However, the Yb—C bond lengths and the geometry of the bipy ligands in both molecules **2** are virtually identical, which rules out the existence of the redox isomers $(C_9H_7)_2Yb^{II}(bipy^0)$ and $(C_9H_7)_2Yb^{III}(bipy^{\bullet -})$. Apparently, the difference in the dihedral angles of the bipy ligands in two crystallographically independent molecules **2** is associated not with the electronic state but with steric restrictions caused by the mutual arrangement of the indenyl and bipy ligands. The torsion angle between the centers of the five- and six-membered fragments in the indenyl ligands is 127.3(3) and −50.8(3)° in the molecules, in which the dihedral angle between the pyridine

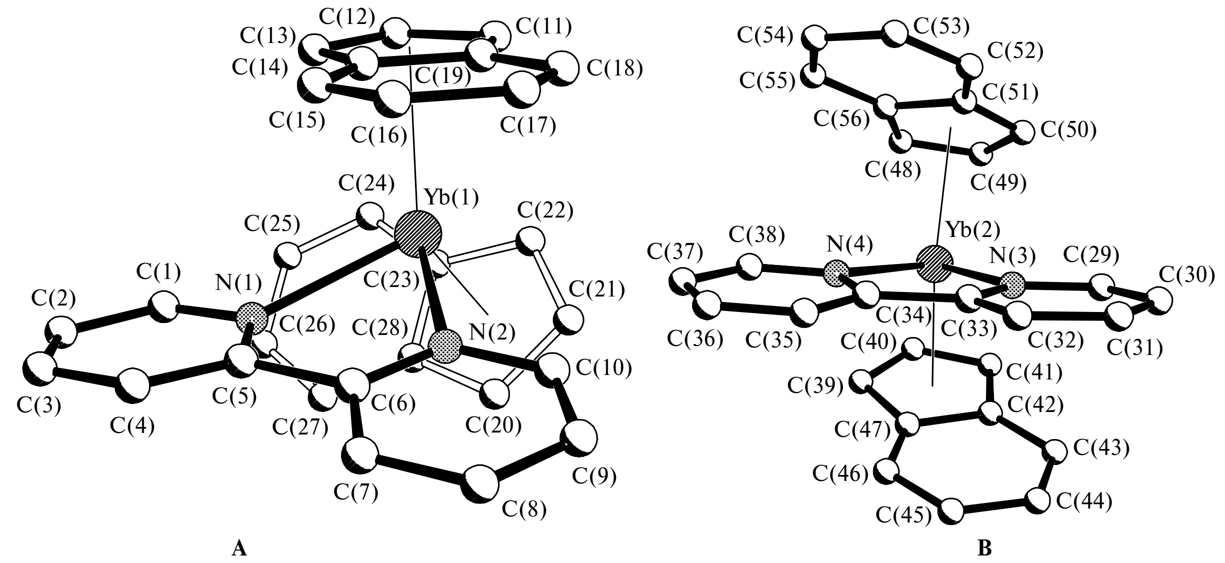


Fig. 2. Arrangement of the indenyl ligands with respect to the bipy ligand in two independent molecules of complex **2**.

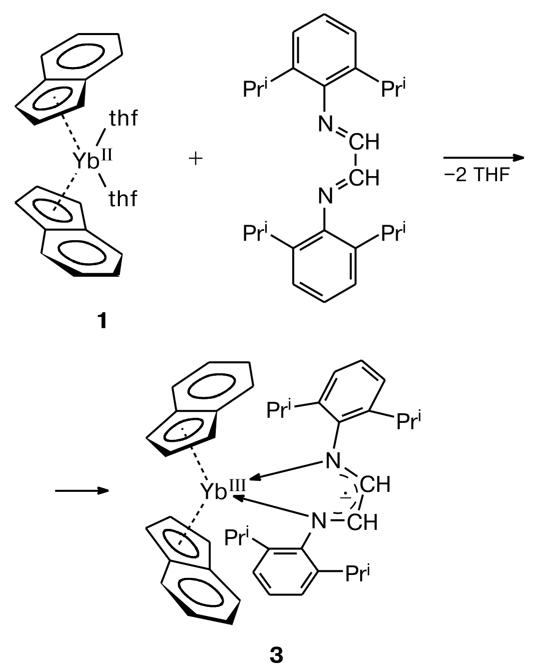
fragments of the bipy ligand is 11.2(3)° (molecule **A**) and 4.8(3)° (molecule **B**), respectively. As can be seen from Fig. 2, only one six-membered fragment C(14)—C(19) of the indenyl ligand in the molecule **A** of complex **2** is located above the N(2)C(6)—C(10) fragment of the bipy ligand. This mutual arrangement of the indenyl and bipy ligands in the coordination sphere of the Yb(1) atom allows the pyridine fragments of the bipy ligand to twist relative to one another by an angle characteristic of the neutral bipy molecule. It should be noted that the shortest distance between the C(14)—C(19) and N(2)C(6)—C(10) fragments is 3.393(3) Å, and the shortest distance between the C(23)—C(28) and N(1)C(1)—C(5) fragments is 4.120(3) Å. Contrastingly, the six-membered fragments of the indenyl groups are located above each pyridine fragment of the bipyridine ligand in the molecule **B** of complex **2**. The shortest distances between the N(4)C(34)—C(38) and C(51)—C(56) fragments and between the N(3)C(29)—C(33) and C(42)—C(47) fragments are 3.471(3) and 3.383(3) Å, respectively. Therefore, an increase in the dihedral angle between the pyridine fragments of the bipy ligand in the molecule **B** of complex **2** should lead to a sharp increase in the energy of nonbonded repulsions. As a consequence, the neutral bipy ligand in the molecule **B** of complex **2** has a flattened structure typical of the radical anion.

The neutrality of the bipy ligand in complex **2** is also confirmed by IR spectroscopic data. The IR spectra of both neutral and reduced 2,2´-bipy have been studied in detail[19] and can serve as a reliable source of information on the electronic state of this molecule. For example, strong absorption bands at 900—1000 and 1470—1575 cm^{-1}, which are indicative of the radical-anionic nature of the bipy ligand in complexes,[19] are absent in the spectrum of compound **2**, thus providing evidence for its neutral state.

Earlier,[12] it has been demonstrated that the metal—ligand electron transfer in the Cp$_2$Yb(bipy) compounds (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$_3$) is determined by both the electronic and steric properties of the carbocyclic ligands coordinated to the ytterbium atom. It was also of interest to study the influence of the electronic and steric properties of the diazadiene ligands on electron transfer in the reactions of complex **1** with various diazadienes. Unlike bipy, the 1,4-bis(2,6-diisopropylphenyl)-1,4-diazabuta-1,3-diene (DAD) molecule contains bulky substituents at the N atoms. The reduction potential of DAD is unknown. However, it is reasonable to assume that this compound is an even stronger electron acceptor than DAB.[9b] The reaction of complex **1** with DAD was carried out in a THF solution at room temperature. Recrystallization of the reaction product from hot hexane afforded black crystals of (C$_9$H$_7$)$_2$Yb(2,6-Pr$^i_2$C$_6$H$_3$NCHCHNC$_6$H$_3$Pr$^i_2$-2,6) (**3**) in 71% yield (Scheme 2).

Compound **3** is moderately soluble in toluene and hexane and is extremely sensitive to atmospheric oxygen and moisture. Single crystals of **3** suitable for X-ray diffraction study were prepared by slow cooling of a solution in hexane. The molecular structure of complex **3** is shown in Fig. 3. The principal bond lengths and bond angles are listed in Table 4. The details of X-ray diffraction study are given in Table 2. The geometric parameters of molecule **3** indicate that the Yb atom has an oxidation state of 3+. The average Yb—C$_{\text{ring}}$ bond length in molecule **3** is 2.663 Å, which is substantially smaller than the corresponding bond length (2.73 Å) in the starting ytterbium(II) complex (C$_9$H$_7$)$_2$Yb(thf)$_2$ (see Table 3)[14] but is somewhat

Scheme 2



larger than that in the ytterbium(III) ansa-bis(indenyl) complex (1-CH$_2$—C$_9$H$_6$)$_2$YbN(SiMe$_3$)$_2$ (2.623 Å).[20] Oxidation of Yb^{II} derivatives to Yb^{III} should lead to a shortening of the Yb—C bond by ~0.16 Å due to a decrease in the effective ionic radius.[15] However, this change in complexes **1** and **3** is significantly smaller. The observed situation is probably attributable to the fact that repulsions between the bulky indenyl and diazadiene ligands cause steric strains in the coordination sphere of the Yb atom, which is also reflected in a noticeable decrease in the Cp—Yb—Cp angle in complex **3** (124.9°) compared to that in complex **1** (128.6°).[14] The Yb—N distances in complex **3** are 2.381(3) Å, which is slightly shorter than those in the Cp*$_2$YbDAB complex (2.385(3) and 2.394(3) Å)[8h] but is substantially longer than those in the nonmethylated analog Cp$_2$YbDAB (2.306(9) and 2.309(9) Å).[8g] This situation is consistent with the fact that the volume of the indenyl ligand is intermediate between the volumes of the cyclopentadienyl and pentamethylcyclopentadienyl rings. Analysis of the geometry of the diazadiene fragment suggests its radical-anionic state. The C—N bond lengths in the imine groups of DAD in complex **3** are 1.330(4) Å, which is substantially longer than the analogous distances in the starting ligand (1.266(3) Å).[21] A comparison of the C—C bond length in the diimine fragment of complex **3** (1.412(7) Å) with that in the free ligand (1.467(5) Å)[7] shows that coordination leads to a noticeable shortening of this bond, which is indicative of partial double bonding with delocalization of the negative charge over the N—C—C—N fragment. On the whole, the geometry of the DAD fragment is similar to that observed earlier[8g,h] for the Cp$_2$YbDAB complexes (Cp = C$_5$H$_5$, C$_5$Me$_5$). Therefore, X-ray diffraction data demonstrated that complex **3** is an ytterbium(III) derivative, in which the metal atom is coordinated by the diazadiene radical anion.

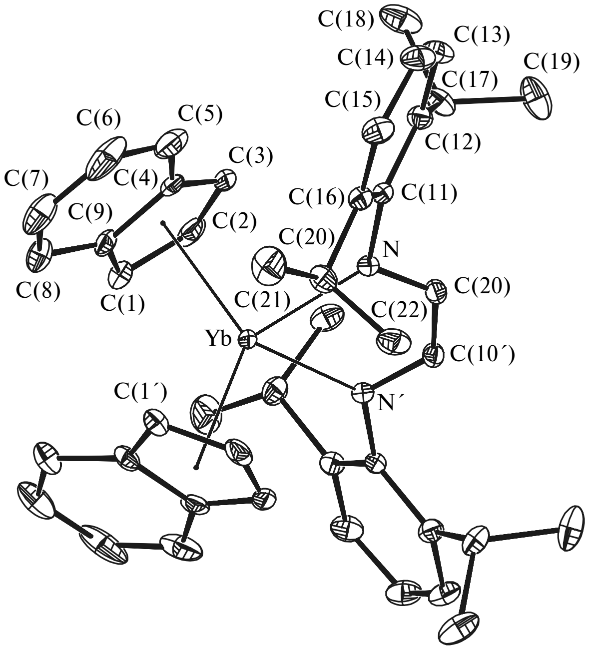


Fig. 3. Structure of the (C$_9$H$_7$)$_2$Yb(2,6-Pr$^i_2$C$_6$H$_3$NCHCHNC$_6$H$_3$Pr$^i_2$-2,6) complex (**3**).

Table 4. Selected bond lengths (*d*) and bond angles (ω) in complex **3***

Bond	*d*/Å	Angle	ω/deg
Yb—Cp$_c$	2.3760(18)	Cp$_c$—Yb—Cp$_c$**	124.93(6)
Yb—N	2.381(3)	Cp$_c$—Yb—N	100.45(8)
Yb—N**	2.381(3)	Cp$_c$—Yb—N**	123.94(8)
Yb—C(1)	2.603(4)	N**—Yb—N	73.70(14)
Yb—C(2)	2.611(4)		
Yb—C(3)	2.674(4)		
Yb—C(4)	2.731(4)		
Yb—C(9)	2.727(3)		
N—C(10)	1.330(4)		
N—C(11)	1.434(4)		
C(10)—C(10)**	1.412(7)		

* Cp$_c$ is the center of the cyclopentadienyl ring.

** The equivalent atoms are generated by the symmetry operation $-x + 1, y, -z + 3/2$.

In the crystalline state, complex **3** is paramagnetic. Investigation of its magnetic properties in a broad temperature range showed that the magnetic moment increases from 1.54 μ_B at 2 K to 3.40 μ_B at 300 K (Fig. 4). For complexes containing noninteracting spins, their con-

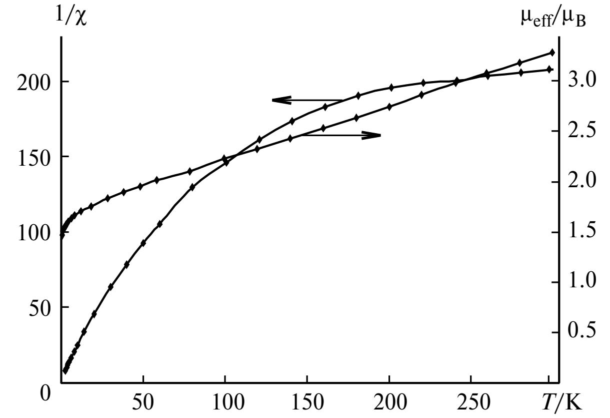


Fig. 4. Temperature dependences of μ_{eff} and $1/\chi$ for complex **3** in magnetic field of 5 kOe.

tribution to the molar magnetic susceptibility is additive and the magnetic moment can be calculated as the square root of the sum of the squares of the individual magnetic moments $\mu = (\mu_1{}^2 + \mu_2{}^2)^{1/2}$. For organic ytterbium(III) derivatives, in which the paramagnetic metal cation is coordinated by an organic radical anion, the magnetic moment should be 4.2 and 4.8 μ_B in temperatures ranges of 5—30 and 90—300 K, respectively.[22] As can be seen from Fig. 4, the experimental effective magnetic moment of compound **3** is substantially smaller. In the study[23] of the magnetic properties of the lanthanide phthalocyanine complexes assuming the presence of antiferromagnetic coupling, the authors proposed a model according to which the magnetic moment of an ytterbium derivative at room temperatures should be 3.4 μ_B. Analysis of the plots of μ_{eff} *vs* T and $1/\chi$ *vs* T, as well as the fact that the experimental magnetic moment of complex **3** at room temperature is in agreement with the calculated[23] value, suggest that the small value of μ_{eff} is attributable to antiferromagnetic coupling in molecule **3**.

Compound **3** is paramagnetic also in solutions of aromatic and aliphatic hydrocarbons. The ^{1}H NMR spectrum of a solution of complex **3** in benzene-d$_6$ at room temperature shows a set of broadened signals, which are substantially shifted relative to their diamagnetic positions (δ from 80 to −60; Fig. 5). The assignment of the signals in the spectrum was made using 2D ^{1}H—^{1}H correlation spectra (COSY). The ^{1}H NMR spectrum of complex **3** in a THF solution is radically different. In this solution, the complex is diamagnetic, and its ^{1}H NMR spectrum is a superposition of the spectra of **1** and free DAD (Fig. 6), whose signals are observed at δ 0—8.

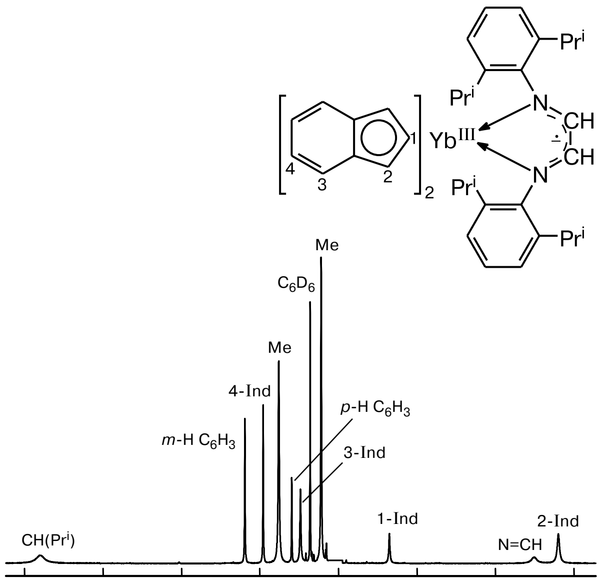


Fig. 5. ^{1}H NMR spectrum of complex **3** in benzene-d$_6$.

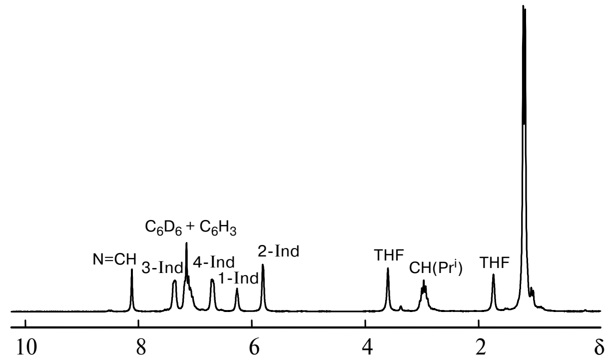


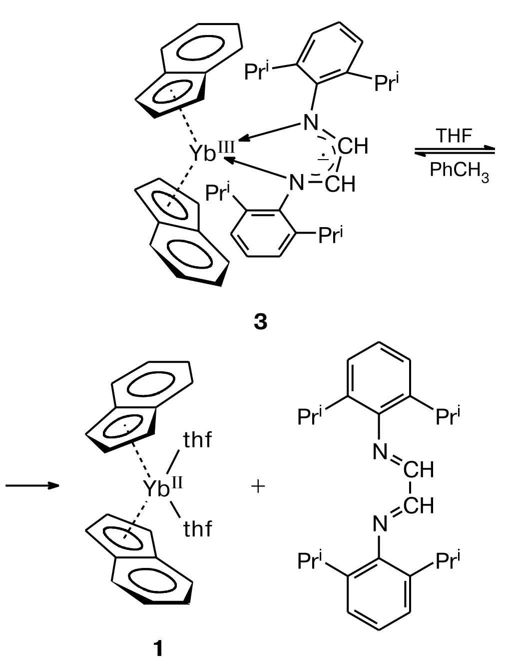
Fig. 6. ^{1}H NMR spectrum of complex **3** in THF-d$_8$.

Treatment of complex **3** with tetrahydrofuran followed by recrystallization from a THF—hexane mixture led to regeneration of the starting ytterbocene **1** in high yield (83%), and free DAD was found in the mother liquor. Apparently, compound **3** is an ytterbium(III) complex with the diazabutadiene radical anion both in the crystalline state and solutions in noncoordinating solvents. Upon dissolution of complex **3** in a coordinating solvent (THF), the DAD molecule is replaced from the coordination sphere of the Yb atom with the thf ligands accompanied by the electron transfer from the DAD radical anion to the metal cation and reduction of the latter to Yb^{II} (Scheme 3).

The reaction of ytterbocene with DAD is reversible. Thus, a mixture of complex **1** and DAD was found in a THF solution, whereas the use of a noncoordinating solvent gave rise to compound **3**.

The reaction of complex **1** with 2,2′-bipy afforded the diamagnetic ytterbium(II) derivative $(C_9H_7)_2Yb(bipy)_2$, whereas the reaction with a stronger electron acceptor, *viz.*, DAD, was accompanied by oxidation of Yb^{II} to Yb^{III} to give the $(C_9H_7)_2Yb^{III}(DAD^{\bullet -})$ complex. In the complex **3**—solvent system, the oxidation state of ytterbium depends on the coordination ability of the solvent. In

Scheme 3



benzene, complex **3** exists as $(C_9H_7)_2Yb^{III}(DAD^{\bullet -})$, whereas $(C_9H_7)_2Yb^{II}(thf)_2$ and DAD^0 are formed in THF.

Experimental

All operations associated with the synthesis, isolation, and study of the properties of Yb complexes were carried out under conditions precluding exposure to atmospheric oxygen and moisture with the use of the standard Schlenk technique. Tetrahydrofuran, 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 ^{1}H 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 the deuterated solvents. Volatile organic products were analyzed on a Tsvet-530 instrument equipped with a katharometer as the detector and a 2 m×3-mm steel column (5% SE-30 Chromaton N-AW); helium was used as the carrier gas. The magnetic properties of complex **3** were measured on a SQUID Quantum Design magnetometer in a temperature range of 2—300 K in magnetic field of 5 kOe. The paramagnetic component of the magnetic susceptibility of the complex χ was calculated taking into account the diamagnetic contribution of the ions according to the Pascal scheme ($438 \cdot 10^{-6}$ cm^3 mol^{-1}). The temperature dependence of the effective magnetic moment was calculated by the equation

$$\mu_{\text{eff}} = (3k/N\beta^2 \cdot \chi T)^{0.5} \approx (8\chi T)^{0.5},$$

where N is Avogadro's number, k is the Boltzmann constant, and β is the Bohr magneton.

Bis(indenyl)-2,2′-bipyridylytterbium $(C_9H_7)_2Yb(bipy)$ (2). A solution of bipy (0.209 g, 1.34 mmol) in THF (10 mL) was added to a solution of $(C_9H_7)_2Yb(thf)_2$ (0.367 g, 0.67 mmol) in THF (15 mL), which was accompanied by a change in the color of the reaction mixture from red to dark-brown. The reaction mixture was stirred for 0.5 h, after which the solvent was removed *in vacuo*. The dark-brown solution was extracted with hexane (15 mL) to remove unconsumed bipy. Toluene (5 mL) was added to the solid residue and then THF was gradually added until the precipitate was completely dissolved (~15 mL). The solution was slowly concentrated at room temperature to afford dark-brown crystals. The mother liquor was decanted from the crystals, and the crystals were washed with cold hexane and dried *in vacuo* at room temperature. Complex **2** was isolated in a yield of 0.255 g (68%). Found (%): C, 59.78; H, 4.26; Yb, 31.12. $C_{28}H_{22}N_2Yb$. Calculated (%): C, 60.12; H, 3.93; Yb, 30.93. IR, ν/cm^{-1}: 3020, 1580, 1310, 1200, 1010, 760, 740, 720, 710. ^{1}H NMR (20 °C, THF-d$_8$), δ: 5.69 (s, 4 H, Ind); 6.33 (s, 6 H, Ind); 6.92 (s, 4 H, Ind); 7.19 (m, 2 H, bipy); 7.95, 8.11, and 8.38 (all s, 2 H each, bipy). ^{13}C NMR (20 °C, THF-d$_8$), δ: 94.7, 116.4, 117.4, and 120.7 (all s, Ind); 124.2 (s, bipy); 126.9 (s, Ind); 132.7, 139.0, 145.6, and 155.3 (all s, bipy).

Bis(indenyl)-1,4-bis(2,6-diisopropylphenyl)-1,4-diazabuta-1,3-dienylytterbium $(C_9H_7)_2Yb(2,6-Pr^i{}_2C_6H_3NCHCHNC_6H_3Pr^i{}_2-2,6)$ (3). A solution of DAD (0.852 g, 2.26 mmol) in THF (10 mL) was added to a solution of $(C_9H_7)_2Yb(thf)_2$ (0.620 g, 1.13 mmol) in THF (20 mL). The color of the reaction mixture remained virtually unchanged. The reaction mixture was stirred for 0.5 h, after which the solvent was removed *in vacuo*. Then toluene (25 mL) was added to the solid residue and the solution was heated at 60 °C for 2 h. The resulting black solution was filtered and the solvent was removed *in vacuo*. Then toluene (20 mL) was added again and the mixture was kept at 60 °C for 1 h. The toluene was removed *in vacuo* and the solid residue was recrystallized from hot hexane. The mother liquor was decanted from the black crystals. The crystals were washed with cold hexane and dried *in vacuo* at room temperature to prepare compound **3** in a yield of 0.627 g (71%). Found (%): C, 67.17; H, 6.13; Yb, 22.67. $C_{44}H_{50}N_2Yb$. Calculated (%): C, 67.79; H, 6.41; Yb, 22.18. IR, ν/cm^{-1}: 3020, 1430, 1370, 1339, 1270, 1245, 1100, 1040, 820, 800, 775, 740, 720. ^{1}H NMR (20 °C, benzene-d$_6$), δ: −56.08 (s, 4 H, 2-Ind); −49.96 (s, 2 H, N=CH); −13.03 (s, 2 H, 1-Ind); 4.35 (s, 12 H, Me); 9.63 (s, 4 H, 3-Ind); 11.85 (s, 2 H, *p*-H, C_6H_3); 15.16 (s, 12 H, Me); 19.13 (s, 4 H, 4-Ind); 23.79 (s, 4 H, *m*-H, C_6H_3); 75.88 (s, 4 H, CH).

Reaction of $(C_9H_7)_2Yb(2,6-Pr^i{}_2C_6H_3NCHCHNC_6H_3Pr^i{}_2-2,6)$ (3) with THF. Hexane was slowly condensed into a red solution of compound **3** (0.140 g, 0.179 mmol) in THF (2 mL). Once crystallization started, the solution was cooled to −20 °C and allowed to stand for ~14 h. The mother liquor was decanted from the crystals, and the crystals were washed with cold hexane and dried *in vacuo*. Complex **1** was isolated in a yield of 0.082 g (83%) as red crystals. ^{1}H NMR (20 °C, pyridine-d$_5$), δ: 1.73 and 3.60 (both s, 8 H each, THF); 5.73 (d, 4 H, Ind, J = 3.2 Hz); 6.20 (m, 2 H, Ind); 6.65 and 7.32 (both m, 4 H each, Ind). In the mother liquor, DAD was found by GLC in a yield of 0.060 g (89%).

X-ray diffraction study. The experimental data sets were collected on an automated Smart APEX diffractometer. The main crystallographic data, characteristics of X-ray data collection, and details of the structure refinement are given in Table 2. The atomic coordinates were deposited with the Cambridge Structural Database. Both structures were solved by direct methods and refined by the least-squares method against F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms in complex **2** were revealed from the difference Fourier synthesis and refined isotropically. The H atoms in complex **3** were placed in geometrically calculated positions and refined using the riding model. All calculations were carried out with the use of the SHELXTL v. 6.10 program package.[24] The absorption correction was applied using the SADABS program.[25]

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