Inorganic Chemistry

Article

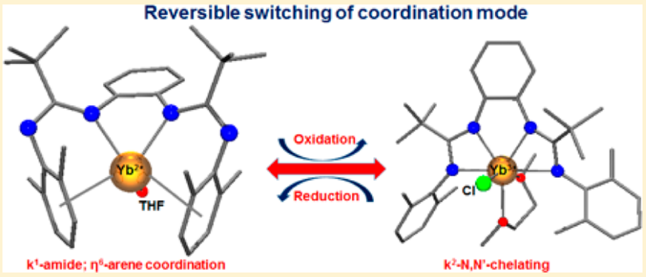
pubs.acs.org/IC

Reversible Switching of Coordination Mode of ansa bis(Amidinate) Ligand in Ytterbium Complexes Driven by Oxidation State of the Metal Atom

Aleksei O. Tolpygin, Anton V. Cherkasov, Georgii K. Fukin, and Alexander A. Trifonov*

G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinina 49, GSP-445, 603950 Nizhny Novgorod, Russia

Supporting Information



ABSTRACT: Reaction of bisamidine C_6H_4-1,2-{NC(*t*-Bu)-NH(2,6-$Me_2C_6H_3$)}$_2$ (**1**) and [$(Me_3Si)_2N$]$_2$Yb(THF)$_2$ (THF = tetrahydrofuran) (toluene; room temperature) in a 1:1 molar ratio afforded a bis(amidinate) Yb^{II} complex [C_6H_4-1,2-{NC(*t*-Bu)N(2,6-$Me_2C_6H_3$)}$_2$]Yb(THF) (**2**) in 65% yield. Complex **2** features unusual κ^1amide, η^6-arene coordination of both amidinate fragments to the ytterbium ion, resulting in the formation of a bent bis(arene) structure. Oxidation of **2** by Ph_3SnCl (1:1 molar ratio) or $(PhCH_2S)_2$ (1:0.5) leads to the Yb^{III} species [C_6H_4-1,2-{NC(*t*-Bu)N(2,6-$Me_2C_6H_3$)}$_2$]YbCl(1,2-dimethoxyethane) (**3**) and {[C_6H_4-1,2-{NC(*t*-Bu)N(2,6-$Me_2C_6H_3$)}$_2$]Yb(μ-SCH_2Ph)}$_2$ (**4**), performing "classic" κ^2N,N′-chelating coordination mode of ansa bis(amidinate) ligand. By the reduction of **3** with equimolar amount of sodium naphthalide [$C_{10}H_8^{\bullet -}$][Na^+] in THF, complex **2** can be recovered and restored to a bent bis(arene) structure. Complex **3** was also synthesized by the salt metathesis reaction of equimolar amounts of $YbCl_3$ and the dilithium derivative of **1** in THF.

INTRODUCTION

Organic derivatives of lanthanides containing neutral π-bonded arene ligands are of considerable interest as promising objects for investigation of the nature of f-metal−ligand bonding.[1] By virtue of the electropositivity of lanthanides,[2] the metal−ligand bonding in their organic derivatives is assumed to have predominantly ionic character, and ligands capable of forming stable anions were traditionally used in this field of chemistry.[3] On the other hand an insignificant contribution of the covalent component to lanthanide−ligand interactions removes restrictions associated with the compatibility of the orbitals in symmetry, and this can give rise to novel types of compounds whose reactivity differs from that of d-element derivatives. Diversity of types of metal−ligand bonding and ability of arene ligands to stabilize unusual oxidation states enhance the fundamental significance of lanthanide complexes containing π-bonded neutral aromatic ligands.[4] Two types of Ln^{II} and Ln^{III} complexes coordinated by π-bonded neutral aromatic ligands are known to date. The arene-halogenoaluminates (η^6-arene)-Ln[$(\mu\text{-}X)_2(AlX_2)$]$_3$ (X = Cl, Br, I) and (η^6-arene)Eu$(AlCl_4)_2$ constitute the first type, which appeared in the mid-1980s.[4a] The second type is presented by σ-bonded aryloxides, thiolates, and terphenyl derivatives featuring π-bonding between Ln ions and pendant aryl groups. The bonding mode of arene fragments to lanthanide ion can vary from η^2 to η^6.[4a]

Recently we reported on unusual κ^1N, η^6-arene coordination of bulky amidinate ligand in Yb^{II} hydride, which can be assigned to the second group of lanthanide arene complexes. This coordination mode was proved to be characteristic only for divalent ytterbium species, while in the Yb^{III} complexes the same ligand adopts κ^2N,N′-chelating coordination mode.[5] To get deeper insight into the factors determining the realization of κ^1N, η^6-arene or κ^2N,N′-coordination type, a complex of divalent ytterbium coordinated by ansa bis(amidinate) ligand was synthesized, and its redox chemistry was investigated.

RESULTS AND DISCUSSION

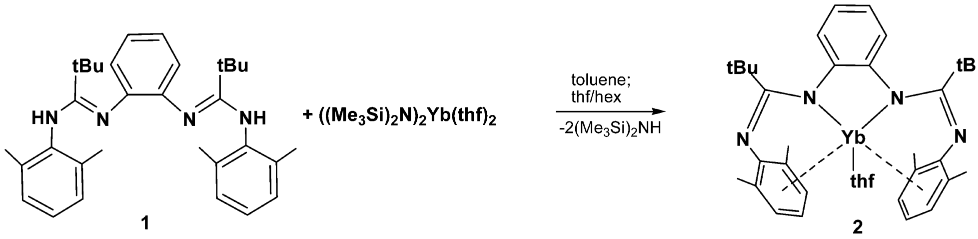
An amine elimination reaction of equimolar amounts of C_6H_4-1,2-{NC(*t*-Bu)NH(2,6-$Me_2C_6H_3$)}$_2$ (**1**)[6] and [$(Me_3Si)_2N$]$_2$Yb-(THF)$_2$[7] (THF = tetrahydrofuran) was carried out in toluene at ambient temperature (12 h). Evaporation of the volatiles and subsequent recrystallization of the solid residue from a THF−hexane mixture (~1:1) allowed for the isolation of red-brown crystals of complex **2** (Scheme 1) in 65% yield.

Complex **2** is highly air- and moisture-sensitive; it is well-soluble in THF, toluene, and hexane. ^{1}H NMR monitoring of the reaction indicated the quantitative formation of **2** and $(Me_3Si)_2NH$. Lowering of the isolated yield obviously is associated with high solubility of **2** in organic solvents. Monocrystalline samples of **2** suitable for X-ray analysis were obtained by slow concentration of a THF−hexane solution at ambient temperature. The molecular structure of **2** is depicted in Figure 1; the crystal and structural refinement data are summarized in Table 1. Complex **2** has four crystallographically

Received: October 7, 2013
Published: January 21, 2014

dx.doi.org/10.1021/ic402530w | *Inorg. Chem.* 2014, 53, 1537−1543

Scheme 1



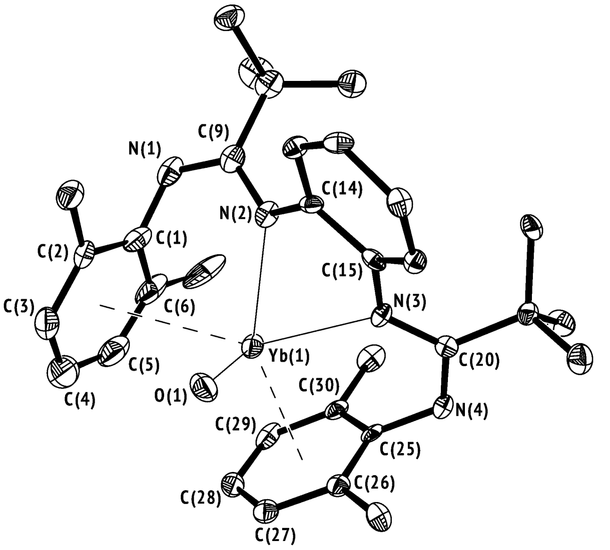


Figure 1. Molecular structure of complex [C_6H_4-1,2-{NC(*t*-Bu)N(2,6-$Me_2C_6H_3$)}$_2$]Yb(THF) (**2**). Thermal ellipsoids drawn at the 30% probability level. C atoms of THF molecule and all hydrogen atoms are omitted for clarity. Bond lengths, Å: Yb(1)−N(2) 2.373(7), Yb(1)−N(3) 2.406(6), Yb(1)−O(1) 2.383(6), N(1)−C(9) 1.30(1), N(2)−C(9) 1.39(1), N(3)−C(20) 1.358(9), N(4)−C(20) 1.321(9); bond angles, deg: N(2)−Yb(1)−N(3) 69.0(2), N(1)−C(9)−N(2) 120.1(8), N(4)−C(20)−N(3) 119.9(7).

independent molecules in an asymmetric unit. However since all of them have similar geometric parameters, only one molecule will be discussed. The X-ray study revealed that, unlike previously reported Ln^{III} complexes[6,8] featuring "classic" κ^2N,N′-chelating coordination mode of ansa bis(amidinate) ligand, in **2**, both amidinate groups chelate the Yb^{II} ion by κ^1amide and η^6-arene interactions. The most interesting feature of **2** is the formation of bent bis(arene) structure due to η^6-coordination of two 2,6-$Me_2C_6H_3$-units to the Yb^{II} center. The κ^1N, η^6-arene chelating coordination mode is rather rare and was previously documented for the Yb^{II} complexes with the bulky guanidinate and amidinate ligands.[5,9] Besides two nitrogen atoms and two η^6-coordinated 2,6-$Me_2C_6H_3$ rings, the ytterbium ion in **2** is coordinated by one oxygen atom of THF molecule, giving a formal coordination number of nine. The Yb−N bonds in **2** (2.406(6) and 2.373(7) Å) are somewhat longer compared to those in the Yb^{II} amidinate-hydrido complex [{*t*-BuC(NC$_6$H$_3$-2,6-*i*-Pr$_2$)$_2$}Yb(μ-H)]$_2$ (2.329(3) Å)[5a] and guanidinate-iodido [{[Cy$_2$NC(NC$_6$H$_3$-2,6-*i*-Pr$_2$)$_2$]Yb(μ-I)}$_2$] (2.360(3) Å) complexes[9] performing the same type of coordination of the NCN ligands. This fact can originate from higher coordination number of Yb^{II} in **2.** Two other nitrogen atoms are remote from the ytterbium atom (3.647(6) and 3.667(6) Å) and are not involved in the metal—ligand bonding since the Yb−N distances exceed the sum of covalent radii of these elements (R(Yb) = 1.70, R(N) = 0.75 Å).[10] The Yb−C distances fall into a rather large region (2.820(6)−3.657(6) Å) wherein one phenyl ring is located closer to the ytterbium ion than the second one (Yb−C$_{\text{average}}$: 2.91(1) and 3.30(1) Å; Yb-Ph$_{\text{centroid}}$: 2.55(1) and 3.01(1) Å). Bent bis(arene) structures resembling that of complex **2** were described for Yb^{II} ionic complexes containing BPh_4^- anion [Yb(*t*-Bu$_2$pz)(THF)BPh$_4$], [Yb{N(SiMe$_3$)$_2$}BPh$_4$],[11] and [Cp*YbBPh$_4$].[12] However despite the similar coordination numbers of the central atoms in **2** and [Yb(*t*-Bu$_2$pz)(THF)-BPh$_4$], [Cp*YbBPh$_4$] displays noticeably longer Yb−C distances (compare, [Yb(*t*-Bu$_2$pz)(THF)BPh$_4$]: Yb−C = 2.799(2)−2.945(2), Yb−C$_{\text{average}}$ = 2.88(1); Yb−C = 2.860(2)−3.050(2), Yb−C$_{\text{average}}$ = 2.95(1);[11] [Cp*YbBPh$_4$]: Yb−C = 2.884(5)−3.128(5), Yb−C$_{\text{average}}$ = 2.970(4) Å).[12] The average Yb−C bond lengths (2.96(1), 2.98(1) Å) in eight-coordinated Yb^{II} thiolate complex [Yb{SC$_6$H$_3$-2-(η^6-C$_6$H$_2$*i*-Pr$_3$)-6-(C$_6$H$_2$*i*-Pr$_3$)}$_2$] featuring additional Yb-η^6-arene interactions with coplanar orientation of C$_6$H$_2$*i*-Pr$_3$ rings are also shorter than those in **2.**[13] Apparently elongation of the Yb−C bonds in **2** as compared with the above-mentioned related Yb^{II} —arene complexes is due to connectivity of amidinate moieties with rigid ortho-phenylene linker. The value of the dihedral angle between the planes of two phenyl rings is 63.9(1)°. The N−C bonds within the NCN fragments are nonequivalent. One pair of bonds (N(1)−C(9) 1.30(1), N(4)−C(20) 1.321(9) Å) is somewhat shorter compared to the second one (N(2)−C(9) 1.39(1), N(3)−C(20) 1.358(9) Å).

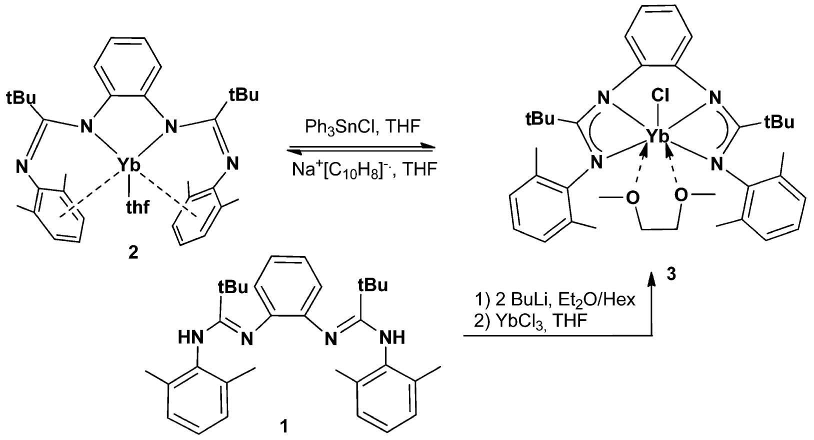
In the ^{1}H NMR spectrum of diamagnetic complex **2** (C_6D_6, 20 °C) the bis(amidinate) ligand gives a single set of signals: a sharp singlet at 1.78 ppm due to the *t*-Bu protons, the Me protons of $Me_2C_6H_3$ groups appear as two singlets at 2.00 and 2.22 ppm, while the aromatic protons of $Me_2C_6H_3$ and o-C_6H_4 fragments give rise to a multiplet in the low-field region (6.28−6.65 ppm). Two broadened singlets (at 1.03 and 2.53 ppm) correspond to the methylene protons of a coordinated THF molecule. The variable temperature (−60−50 °C) ^{1}H and ^{13}C NMR spectra of complex **2** in C_7D_8 and THF-d_8 were recorded, however did not give prove for retention of η^6-arene coordination in solution.

It is worth noting that despite its apparent similarity with lanthanide arene-haloaluminates, σ,π-bonded alyloxides and thiolates, complex **2** features stronger Ln−η^6 interaction. Thus arene-haloaluminates dissociate to the starting materials LnX$_3$ and AlX$_3$ when treated with THF. π-Bonded ligands in alyloxides and thiolates easily undergo displacement from the metal coordination sphere by coordinating donor solvents (THF, 1,2-dimethoxyethane (DME), and NH$_3$) upon dissolution, while the bent bis(arene) structure of **2** remains after crystallization from THF−hexane mixture.

Table 1. Crystallographic Data and Structure Refinement Details for Complexes 2−4

	2	3	4
formula	$C_{36}H_{48}N_4OYb$	$C_{39.5}H_{56.5}ClN_4O_{2.5}Yb$	$C_{78}H_{94}N_8S_2Yb_2$
M_r	725.82	835.88	1553.81
crystal size, mm	0.27 × 0.23 × 0.09	0.16 × 0.10 × 0.08	0.17 × 0.13 × 0.10
crystal system	orthorhombic	triclinic	triclinic
space group	$P2(1)2(1)2(1)$	$P\bar{1}$	$P\bar{1}$
a, Å	15.4041(4)	12.3731(7)	12.0273(5)
b, Å	26.9046(7)	15.9925(9)	12.6115(6)
c, Å	32.7428(8)	19.727(1)	13.6486(6)
α, deg	90	86.857(1)	110.180(1)
β, deg	90	78.881(1)	108.300(1)
γ, deg	90	82.954(1)	94.120(1)
cell volume, Å	13570.0(6)	3799.3(4)	1806.8(1)
Z	16	4	1
d_{calc}, g/cm^3	1.421	1.461	1.428
μ, mm^{-1}	2.789	2.572	2.677
F_{000}	5920	1714	790
2θ range, deg	52	52	52
index ranges	$-18 \leq h \leq 19$ $-33 \leq k \leq 33$ $-40 \leq l \leq 39$	$-15 \leq h \leq 14$ $-19 \leq k \leq 15$ $-24 \leq l \leq 24$	$-14 \leq h \leq 14$ $-15 \leq k \leq 15$ $-16 \leq l \leq 16$
reflns collected	117 198	23 019	15 786
independent reflns	26 604	14 838	7082
R_{int}	0.0733	0.0292	0.0112
completeness to θ	99.8	99.2	99.6
data/restraints/parameters	26 604/20/1547	14 838/54/890	7082/0/416
GOF	1.021	0.968	1.063
R_1 ($I > 2\sigma(I)$)	0.0460	0.0374	0.0159
wR_2 (all data)	0.0990	0.0873	0.0409
max. and min. transmission	0.7874/0.5197	0.8207/0.6837	0.7756/0.6589
largest diff. peak and hole, e/Å^3	1.782/−0.727	1.707/−1.019	1.287/−0.616

Scheme 2



Recently, with the example of Yb(II) hydrido complex [{*t*-BuC(NC_6H_3-2,6-*i*-Pr_2)2}Yb(μ-H)]$_2$, we have demonstrated that the κ^1N, η^6-arene chelating coordination of bulky amidinate ligand is realized only in Yb^{II} complexes, while oxidation of the ytterbium center to Yb^{III} results in a change of coordination fashion to a κ^2N,N′-chelating one.[5b] To get a deeper insight into the nature of bonding between ytterbium ion and ansa bis(amidinate) ligand and to explore the factors that govern the type of coordination, a series of oxidation reactions of **2** by mild one-electron oxidants was performed. The possibility of retention of a bent bis(arene) structure by Yb^{III} species was the focus of our interest.

The reaction of **2** with Ph_3SnCl in THF in 1:1 molar ratio was carried out at ambient temperature (12 h) and afforded Yb(III) bis(amidinate) chloro complex and $Ph_3Sn{-}SnPh_3$ (Scheme 2). Recrystallization of the reaction product from DME−THF−hexane mixture allowed for isolation of orange crystals of **3** in 75% yield. Magnetic mesurements indicated trivalent state of ytterbium in **3** (μ_{eff} = 4.7 μB, T = 293 K).[14] Complex **3** was also synthesized by the salt metathesis reaction of equimolar amounts of $YbCl_3$ and the dilithium derivative of **1** in THF (Scheme 2). This synthetic approach afforded 3 in 81% yield.

The molecular structure of complex **3** was established by X-ray analysis and is depicted in Figure 2; the crystal and structural refinement data are summarized in Table 1. Complex **3** crystallizes with two crystallographically independent molecules in the asymmetric unit. It crystallizes as a solvate **3**·$(THF)_{0.5}(C_6H_{14})_{0.25}$. The X-ray study revealed that in complex **3** unlike **2** the ansa bis(amidinate) ligand is coordinated to ytterbium in κ^2N,N′-chelating fashion. Similarly to the previously described lutetium derivative $[C_6H_4$-1,2-$\{NC(t\text{-Bu})N(2,6\text{-}Me_2C_6H_3)\}_2]LuCl(THF)_2$,[6] complex **3** adopts a monomeric structure. The ytterbium atom is coordinated by four nitrogen atoms of the bis(amidinate) ligand, terminal chloro ligand, and two oxygen atoms of DME molecule, thus resulting in coordination number of seven. The coordination environment of the metal atoms in **3** adopts geometry of distorted pentagonal bipyramid. Four nitrogen atoms, the metal atom, and one oxygen atom are disposed in the equatorial plane (maximum deviation of atoms from plane is 0.14(2) Å), while the chloro ligand and the second oxygen occupy the apical positions. The dihedral angle between two NMN planes in complex **3** has the value of 170.7(1)° and is slightly narrower compared to that in the lutetium analogue (176.3(1)°).[6] The MNCN fragments have different geometries: one is close to being planar (the value of dihedral angle between MNN and NCN planes is 179.7(2)°), while the second one is noticeably curved (the dihedral angle between the planes MNM and NCN is 148.6(2)°). The average Yb−N bond length in **3** (2.33(1) Å) is similar to the related values reported for the seven-coordinated ytterbium complexes coordinated by ansa bis(amidinate) ligands ($[\{(CH_2)_3\{NCN(SiMe_3)i\text{-}PrN(i\text{-}Pr)\}_2\}Yb(\mu\text{-}Cl)(THF)]_2$ (2.34(1) Å), $[(CH_2)_3\{NCN(SiMe_3)i\text{-}PrN(i\text{-}Pr)\}_2]YbCl(DME)$ (2.34(1) Å),[15] $[\{(CH_2)_3\{NC(Ph)NSiMe_3\}_2]Yb(\mu\text{-}Cl)(THF)_2$ (2.34(1) Å)[16]). The distances from Yb to "internal" nitrogens are significantly shorter (Yb(1)−N(2) 2.257(3), Yb(1)−N(3) 2.278(3) Å) than those to "external" nitrogens (Yb(1)−N(1) 2.382(2), Yb(1)−N(4) 2.390(3) Å). The lengths of amidinate N−C bonds in complex **3** have similar values, indicating the negative charge delocalization within the NCN fragments (1.317(4)−1.357(4) Å). The Yb−Cl bond length in **3** (2.544(1) Å) has a value close to that in $[(CH_2)_3\{NCN(SiMe_3)i\text{-}PrN(i\text{-}Pr)\}_2]YbCl(DME)$ (2.559(4) Å).[15]

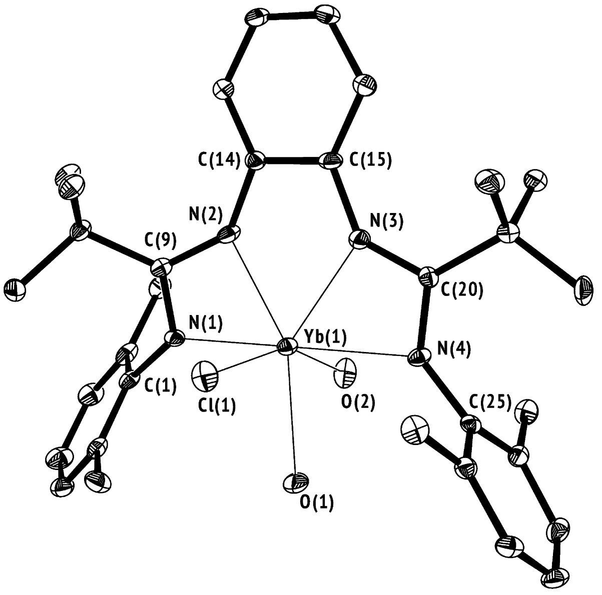
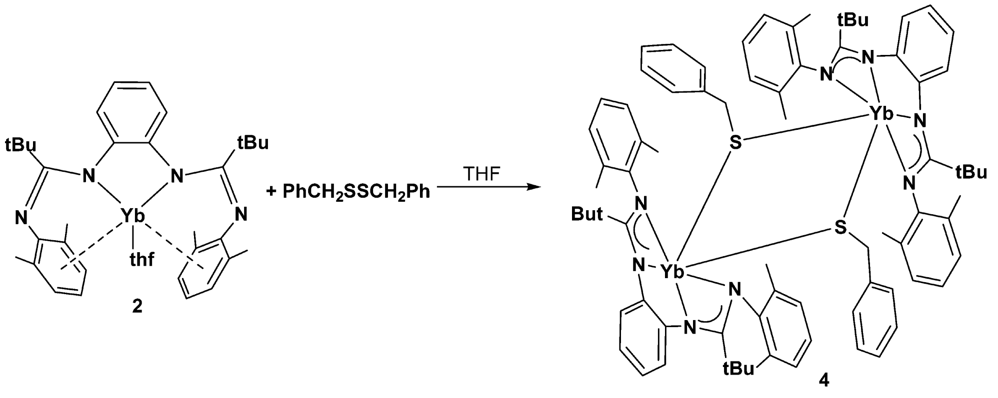


Figure 2. Molecular structure of complex $[C_6H_4$-1,2-$\{NC(t\text{-Bu})N(2,6\text{-}Me_2C_6H_3)\}_2]YbCl(DME)$ (**3**). Thermal ellipsoids drawn at the 30% probability level. C-atoms of DME molecule and all hydrogen atoms are omitted for clarity. Bond lengths, Å: Yb(1)−N(1) 2.382(2), Yb(1)−N(2) 2.257(3), Yb(1)−N(3) 2.278(3), Yb(1)−N(4) 2.390(3), Yb(1)−Cl(1) 2.544(1), Yb(1)−O(1) 2.373(2), Yb(1)−O(2) 2.378(3), N(1)−C(9) 1.317(4), N(2)−C(9) 1.356(4), N(4)−C(20) 1.332(4), N(3)−C(20) 1.357(4); bond angles, deg: N(1)−Yb(1)−N(4) 170.9(1), N(2)−Yb(1)−N(3) 68.9(1), N(1)−C(9)−N(2) 109.4(3), N(4)−C(20)−N(3) 109.5(3).

One-electron oxidation of complex **2** by $(PhCH_2S)_2$ in 1:0.5 molar ratio was carried out in THF at 20 °C (6 h). The reaction resulted in the formation of Yb^{III} bis(amidinate) sulfido complex **4** (Scheme 3), which was isolated after recrystallization from a THF−hexane mixture in 63% yield.

Single-crystal samples of **4** suitable for X-ray analysis were obtained by slow concentration of a solution in THF−hexane mixture at room temperature. The molecular structure of **4** is depicted in Figure 3; the crystal and structural refinement data are listed in Table 1. The X-ray study revealed that **4** adopts a dimeric structure where two $[C_6H_4$-1,2-$\{NC(t\text{-Bu})N(2,6\text{-}Me_2C_6H_3)\}_2]Yb$ units are connected by two μ^2-bridging benzylsulfide groups. The most important structural feature of **4** is the coordination mode of the amidinate ligand. In contrast to the κ^1N, η^6-arene coordination mode detected in the parent complex **2**, oxidation of the ytterbium center to the trivalent state led to switching to the classical κ^1,κ^1N,N-chelating fashion that is characteristic for Ln^{III} amidinates.[6] The

Scheme 3



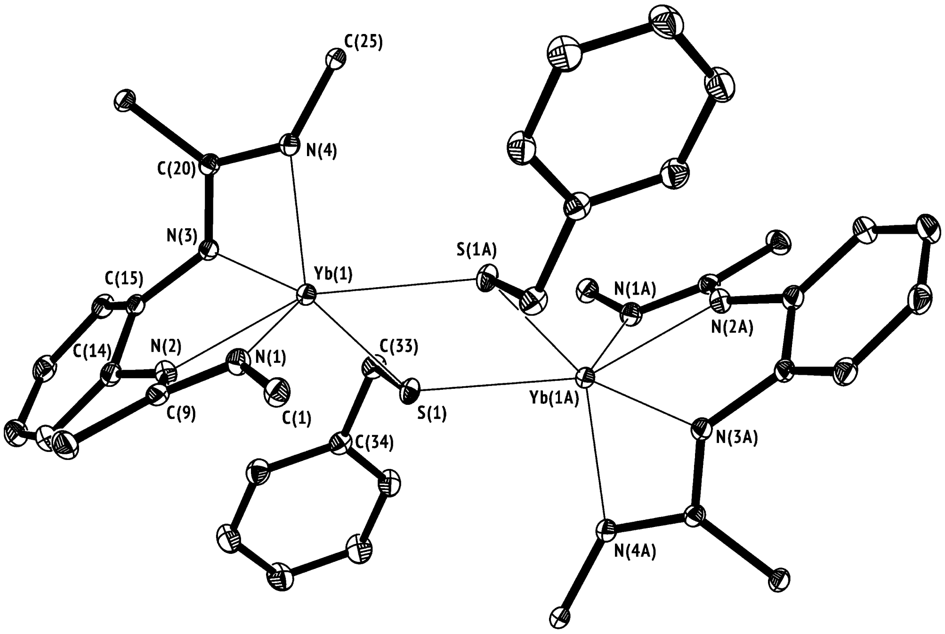


Figure 3. Molecular structure of complex {[C_6H_4-1,2-{NC(*t*-Bu)N(2,6-$Me_2C_6H_3$)}$_2$]Yb(μ-SCH_2Ph)}$_2$ (**4**). Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms, *t*-Bu−, and 2,6-*i*-$Pr_2C_6H_3$− fragments are omitted for clarity. Bond lengths, Å: Yb(1)−Yb(1A) 4.2834(2), Yb(1)−S(1) 2.6604(5), Yb(1)−S(1A) 2.7484(5), Yb(1)−N(1) 2.337(2), Yb(1)−N(2) 2.296(2), Yb(1)−N(3) 2.329(2), Yb(1)−N(4) 2.281(2); bond angles, deg: N(4)−Yb(1)−N(1) 123.98(5), N(2)−Yb(1)−N(3) 67.26(5), Yb(1)−S(1)−Yb(1A) 104.72(2), S(1)−Yb(1)−S(1A) 75.28(2).

Yb−N (Yb(1)−N(1) 2.337(2), Yb(1)−N(2) 2.296(2), Yb(1)−N(3) 2.329(2), Yb(1)−N(4) 2.281(2) Å) and C−N (N(1)−C(9) 1.339(2), N(2)−C(9) 1.340(2), N(3)−C(20) 1.328(2), N(4)−C(20) 1.358(2) Å) bonds within the YbNCN fragment are equivalent, indicating a symmetric coordination to the metal ion with delocalization of a negative charge within the conjugated amidinate ligand. The Yb−N distances in **4** (Yb−$N_{average}$ = 2.311(2) Å) are similar to the related values measured for six-coordinated amidinate Yb^{III} compounds (2.290(4)−2.385(4) Å).[17] In complex **4** the four-membered Yb_2S_2 core is absolutely planar, with the values of bond angles of YbSYb and SYbS of 104.72(2) and 75.28(2)°, respectively. The distance Yb(1)−Yb(1A) is 4.2834(2) Å. The Yb−S bond lengths in **4** are slightly different (2.6604(5) and 2.7484(5) Å), and their values are noticeably shorter, compared to those measured in the related amidinate bis(sulfide) complex of six-coordinated ytterbium ([{*t*-BuC(NC_6H_3-2,6-*i*-Pr_2)$_2$}Yb(μ-SCH_2Ph)$_2$]$_2$) (Yb−$S_{average}$ = 2.7548(9) Å).[5b] The MNCN fragments have slightly different geometries. The N(1)C(9)N(2)Yb(1) unit is nearly planar (the value of dihedral angle between the N(1)C(9)N(2) and N(1)Yb(1)N(2) planes is 177.4(1)°), while the N(3)C(20)N(4)Yb(1) fragment is noticeably distorted (the value of dihedral angle between the N(3)C(20)-N(4) and N(3)Yb(1)N(4) is 146.2(1)°).

Thereby it was proved that oxidation of ytterbium center results in transformation of coordination mode of the amidinate fragments from κ^1N, η^6-arene to κ^1,κ^1N,N.

To explore reversibility of change of coordination mode of the linked bis(amidinate) ligand system in the course of redox reactions, reduction of complex **3** by [$C_{10}H_8^{\bullet-}$][Na^+] (1:1 molar ratio) was carried out in THF at ambient temperature (Scheme 2). The reaction occurs with NaCl precipitation, reduction of Yb^{III} to Yb^{II}, and results in the formation of complex **2** in 71% yield. Complex **2** was authenticated by the X-ray analysis, ^{1}H and ^{13}C NMR-spectroscopy, and microanalysis. The X-ray study proved κ^1N, η^6-arene type of coordination of ansa bis(amidinate) ligand to ytterbium in the isolated complex.

■ CONCLUSIONS

The results of oxidation of **2** and reduction of **3** unambiguously prove that the coordination fashion of [C_6H_4-1,2-{NC(*t*-Bu)N(2,6-$Me_2C_6H_3$)}$_2$]$^{2-}$ ligand to ytterbium ion can be reversibly switched from κ^1N, η^6-arene to κ^2N,N′ by changing the oxidation state and consequently the ionic radius of the ytterbium ion. Reversible reconstruction of the bent bis(arene) structure of the Yb^{II} complex is the most exciting issue in this redox chemistry. To be able to distinguish which factor, electronic (electronic structure of the metal atom) or steric (ion size), plays the predominant role in the realization of either κ^1N, η^6-arene or κ^2N,N′ coordination, currently we are working on the synthesis and structural characterization of La^{III} and Ca^{II} complexes coordinated by {NC(*t*-Bu)N(2,6-$Me_2C_6H_3$)}$_2$]$^{2-}$ ligand.

■ EXPERIMENTAL SECTION

All experiments were performed in evacuated tubes by using standard Schlenk techniques, with rigorous exclusion of traces of moisture and air. After being dried over KOH, THF and DME were purified by distillation from sodium/benzophenone ketyl; hexane and toluene were dried by distillation from sodium/triglyme and benzophenone ketyl prior to use. C_6D_6 was dried with sodium and condensed in vacuo into NMR tubes prior to use. Ph_3SnCl, $(PhCH_2S)_2$, and *n*-BuLi were purchased from Acros. Anhydrous $YbCl_3$,[18] Yb[N($SiMe_3$)$_2$]$_2$-(THF)$_2$,[7] and [C_6H_4-1,2-{NC(*t*-Bu)NH(2,6-$Me_2C_6H_3$)}$_2$][8] were prepared according to literature procedures. NMR spectra were recorded with Bruker Avance DRX-400 and Bruker DRX-200 spectrometers in C_6D_6 at 25 °C, unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced internally to the residual solvent resonances and are reported relative to TMS. Infrared (IR) spectra were recorded as Nujol mulls with a Bruker-Vertex 70 instrument. Lanthanide metal analyses were carried out by complexometric titration.[19] The C, H, and N elemental analyses were performed in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry.

Synthesis of $[C_6H_4\text{-}1,2\text{-}\{NC(t\text{-}Bu)N(2,6\text{-}Me_2C_6H_3)\}_2]Yb(THF)$ (2). *Method A.* A solution of compound **1** (0.45 g, 0.93 mmol) in 30 mL of toluene was added to a solution of $Yb(NSiMe_3)_2(THF)_2$ (0.59 g, 0.93 mmol) in toluene (30 mL), and the reaction mixture was stirred overnight. Evaporation of the volatiles under vacuum and recrystallization of the resulting solid from THF/hexane (1:1) mixture afforded **2** as red-brownish crystals in 65% yield (0.44 g). ^{1}H NMR: (400 MHz, C_6D_6, 25 °C, TMS) δ 1.03 (br. s, 4H, β-THF), 1.78 (s, 18H, $C(CH_3)_3$), 2.00, 2.22 (s, 6H, $(C_6H_3(CH_3)_2)$), 2.53 (br. s, 4H, α-THF), 6.28 (t, $^3J_{H,H}$ = 7.01 Hz, 2H, 2,6-$Me_2C_6H_3$), 6.51 (d, $^3J_{H,H}$ = 7.01 Hz, 2H, 2,6-$Me_2C_6H_3$), 6.65 (m, 2H, C_6H_4), 6.84 (m, 4H, 2,6-$Me_2C_6H_3$, C_6H_4); $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C, TMS) δ 17.6, 18.5 ($C_6H_3(CH_3)_2$), 24.7 (β-THF), 32.3 ($C(CH_3)_3$), 40.3 ($C(CH_3)_3$), 68.8 (α-THF), 118.2, 118.3, 123.1, 128.8, 129.1, 130.0, 130.7, 142.3, 159.4 (2,6-$Me_2C_6H_3$, C_6H_4), 172.5 (NCN); IR (Nujol, KBr; υ (cm^{-1})) 493 (s), 502 (m), 548 (s), 561 (s), 632 (m), 647 (s), 694 (s), 742 (s), 777 (s), 792 (s), 809 (s), 875 (s), 920 (s), 962 (w), 982 (m), 1022 (s), 1039 (s), 1089 (s), 1217 (m), 1238 (s), 1256 (m), 1274 (s), 1360 (s), 1389 (s), 1511 (s), 1550 (s), 1581 (s), 1654 (s) cm^{-1}; Anal. Calcd for $C_{36}H_{48}N_4OYb$ (725.85): C, 59.57; H, 6.67; N, 7.72; Yb, 23.84; Found: C, 59.89; H, 6.93; N, 7.59; Yb, 23.75%.

Method B. A solution of $[C_{10}H_8^{\bullet-}][Na^+]$ in situ obtained from $C_{10}H_8$ (0.0845 g, 0.66 mmol) and Na (0.0152 g, 0.66 mmol) in THF (10 mL) was added to a solution of **3** (0.55 g, 0.66 mmol) in 20 mL of THF. The resulting dark-red solution was stirred for 12 h at room temperature. After NaCl was separated by filtration and THF was removed under vacuum, the solid residue was extracted with toluene (30 mL). Toluene was removed, and the remaining solid was recrystallized from THF/Hexane mixture. Red-brownish crystals of **2** were isolated in 71% yield (0.34 g). ^{1}H NMR: (400 MHz, C_6D_6, 25 °C, TMS) δ 1.03 (br. s, 4H, β-THF), 1.78 (s, 18H, $C(CH_3)_3$), 2.00, 2.22 (s, 6H, $(C_6H_3(CH_3)_2)$), 2.53 (br. s, 4H, α-THF), 6.28 (t, $^3J_{H,H}$ = 7.01 Hz, 2H, 2,6-$Me_2C_6H_3$), 6.51 (d, $^3J_{H,H}$ = 7.01 Hz, 2H, 2,6-$Me_2C_6H_3$), 6.65 (m, 2H, C_6H_4), 6.84 (m, 4H, 2,6-$Me_2C_6H_3$, C_6H_4).

Synthesis of $[C_6H_4\text{-}1,2\text{-}\{NC(t\text{-}Bu)N(2,6\text{-}Me_2C_6H_3)\}_2]YbCl(DME)$ (3). *Method A.* To a solution of compound **1** (0.48 g, 0.99 mmol) in Et_2O (10 mL) (Et = ethyl) a solution of *n*-BuLi (0.96 M, 2.1 mL, 2.00 mmol) in hexane was added at 0 °C, and the reaction mixture was stirred for 1 h. The volatiles were removed under vacuum, and the resulting solid residue was dissolved in 10 mL of THF. The solution formed was added to a suspension of $YbCl_3$ (0.28 g, 1.00 mmol) in THF (20 mL), and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was filtered, and the solvent was removed under vacuum. The remaining solid was extracted with toluene (50 mL), and the toluene extracts were filtered. The solvent was removed under vacuum, and the solid residue was recrystallized from DME/hexane mixture. Orange crystals of **3** were isolated in 81% yield (0.63 g). IR (Nujol, KBr; $\tilde{\nu}$ (cm^{-1})) 494 (s), 554 (s), 566 (w), 602 (s), 674 (m), 695 (s), 745 (s), 765 (s), 821 (s), 861 (s), 919 (s), 940 (m), 962 (s), 988 (s), 1004 (s), 1045 (s), 1095 (s), 1102 (s), 1162 (s), 1210 (s), 1249 (s), 1276 (s), 1361 (s), 1369 (s), 1415 (s), 1571 (s), 1589 (s), 1643 (s), 1774 (m), 1847 (m), 1907 (s) cm^{-1}; Anal. Calcd for $C_{36}H_{50}ClN_4O_2Yb$ (779.31): C, 55.48; H, 6.47; N, 7.19; Yb, 22.21; Found: C, 55.03; H, 6.12; N, 7.00; Yb 22.28%.

Method B. A solution of Ph_3SnCl (0.15 g, 0.39 mmol) in THF (10 mL) was added to a solution of **2** (0.29 g, 0.39 mmol) in THF (20 mL), and the reaction mixture was stirred for 12 h. The solvent was removed in vacuo, and the remaining solid was extracted with toluene (50 mL). After filtration of the toluene extracts the solvent was removed, and the solid residue was recrystallized from THF/DME/hexane mixture. Orange crystals of **3** were obtained in 75% yield (0.23 g). $Ph_3Sn{-}SnPh_3$ was isolated from the mother liquor as colorless crystals in 100% yield (0.13 g).

Synthesis of $\{[C_6H_4\text{-}1,2\text{-}\{NC(t\text{-}Bu)N(2,6\text{-}Me_2C_6H_3)\}_2]Yb(\mu\text{-}SCH_2Ph)\}_2$ (4). A solution of $(PhCH_2S)_2$ (0.086 g, 0.35 mmol) in THF (20 mL) was added to a solution of **2** (0.34 g, 0.70 mmol) in THF (20 mL), and the reaction mixture was stirred for 6 h. The solvent was evaporated in vacuo, and the solid residue was recrystallized from THF/hexane mixture. Complex **4** was obtained in 63% yield (0.34 g). IR (Nujol, KBr; υ (cm^{-1})) 491 (s), 501 (s), 551 (s), 601 (s), 640 (m), 675 (s), 698 (m), 707 (w), 745 (s), 766 (s), 797 (w), 818 (m), 827 (w), 840 (w), 864 (w), 916 (w), 946 (s), 955 (s), 978 (s), 1029 (s), 1041 (m), 1092 (s), 1139 (s), 1167 (s), 1195 (m), 1209 (s), 1253 (w), 1273 (s), 1299 (s), 1402 (s), 1424 (s), 1445 (s), 1512 (s), 1578 (s), 1594 (s), 1656 (s), 1776 (m), 1849 (m), 1915 (m) cm^{-1}; Anal. Calcd for $C_{78}H_{94}N_8S_2Yb_2$ (1553.87): C, 60.29; H, 6.10; N, 7.21; Yb, 22.27. Found C, 60.13; H, 6.17; N, 7.28; Yb, 22.31%.

X-ray Crystallography. The X-ray data for **2**–**4** were collected on a Smart Apex diffractometer (graphite-monochromated, Mo Kα radiation, ω-scan technique, λ = 0.71073 Å, T = 100(2) K). The structures were solved by direct methods and were refined on F^2, using *SHELXTL* package.[20] All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. All hydrogen atoms were placed in calculated positions and were refined in the riding model. The *SADABS*[21] program was used to perform area-detector scaling and absorption corrections. Compound **2** is a racemic twin with Flack parameter of x = 0.51(1). The details of crystallographic, collection, and refinement data are shown in Table 1, and corresponding cif files are available in the Supporting Information. CCDC-963778 (2), 963779 (3), 963780 (4) contain the supplementary crystallographic data for this Paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via ccdc.cam.ac.uk/products/csd/request.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving NMR and IR spectra; CIF files giving crystallographic data for the structures determined in this Paper. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC-963778 (2), 963779 (3), 963780 (4) contain the supplementary crystallographic data for this Paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via ccdc.cam.ac.uk/products/csd/request.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: trif@iomc.ras.ru. Fax: (+7)8314621497.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work was supported by the Russian Foundation for Basic Research (Grant 12-03-3300113; 12-03-31865), the Ministry of Education and Science of Russian Federation (Project No. 8445), Program of the Presidium of the Russian Academy of Science (RAS), and RAS Chemistry and Material Science Division.

■ REFERENCES

(1) Bochkarev, M. N.; Zakharov, L. N.; Kalinina, G. S. *Organoderivatives of Rare Earth Elements;* Kluwer: Dordrecht, 1995.

(2) Morss, L. R. *Chem. Rev.* **1976**, *76*, 827–841.

(3) For Cp-derivatives see: (a) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865–986. (b) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953–1976. For non-Cp derivatives: (c) Edelmann, F. T.; Freckmann, D. M.; Schumann, H. *Chem. Rev.* **2002**, *102*, 1851–1896. (d) Piers, W. E.; Emslie, D. J. H. *Coord. Chem. Rev.* **2002**, *233–234*, 131–155. (e) Trifonov, A. A. *Rus. Chem. Rev.* **2007**, *76*, 1051–1072. (f) Nief, F. *Eur. J. Inorg. Chem.* **2001**, 891–904.

(4) (a) Bochkarev, M. N. *Chem. Rev.* **2002**, *102*, 2089–2117. and references therein. (b) Deacon, G. B.; Shen, Q. *J. Organomet. Chem.* **1996**, *511*, 1–17. For recent publications see: (c) Hamidi, S.; Jende, L. N.; Dietrich, H. M.; Maichle-Mössmer, C.; Törnroos, K. W.;

Deacon, G. B.; Junk, P. C.; Anwander, R. *Organometallics* **2013**, 1209–1223. (d) Lee, H. S.; Niemeyer, M. *Inorg. Chem.* **2010**, *49*, 730–735.

(5) (a) Basalov, I. V.; Lyubov, D. M.; Fukin, G. K.; Shavyrin, A. V.; Trifonov, A. A. *Angew. Chem., Int. Ed.* **2012**, *52*, 3444–3447. (b) Basalov, I. V.; Lyubov, D. M.; Fukin, G. K.; Cherkasov, A. V.; Trifonov, A. A. *Organometallics* **2013**, *32*, 1507–1516.

(6) Tolpygin, A. O.; Shavyrin, A. S.; Cherkasov, A. V.; Fukin, G. K.; Trifonov, A. A. *Organometallics* **2012**, *31*, 5405–5413.

(7) Don Tilley, T.; Andersen, R. A.; Zalkin, A. *J. Am. Chem. Soc.* **1982**, *104*, 3725–3727.

(8) Tolpygin, A. O.; Skvortsov, G. G.; Cherkasov, A. V.; Fukin, G. K.; Glukhova, T. A.; Trifonov, A. A. *Eur. J. Inorg. Chem.* **2013**, 6009–6018.

(9) Heitmann, D.; Jones, C.; Junk, P. C.; Lippert, K.-A.; Stasch, A. *Dalton Trans.* **2007**, 187–189.

(10) Pyykko, P.; Atsumi, M. *Chem.—Eur. J.* **2009**, *15*, 186–197.

(11) Deacon, G. B.; Forsyth, C. M.; Junk, P. C. *Eur. J. Inorg. Chem.* **2005**, 817–821.

(12) Evans, W. J.; Champagne, T. M.; Ziller, J. W. *Organometallics* **2007**, *26*, 1204–1211.

(13) Niemeyer, M. *Eur. J. Inorg. Chem.* **2001**, 1969–1981.

(14) Evans, W. J.; Hozbor, M. A. *J. Organomet. Chem.* **1987**, *326*, 299–306.

(15) Zhang, X.; Wang, C.; Xue, M.; Zhang, Y.; Yao, Y.; Shen, Q. *J. Organomet. Chem.* **2012**, *713*, 182–188.

(16) Wang, J.; Yao, Y.; Cheng, J.; Pang, X.; Zhang, Y.; Shen, Q. *J. Mol. Struct.* **2005**, *743*, 229–235.

(17) (a) Yao, S.; Chan, H.-S.; Lam, C.-K.; Lee, H. K. *Inorg. Chem.* **2009**, *48*, 9936–9946. (b) Wang, J.; Yao, Y.; Zhang, Y.; Shen, Q. *Inorg. Chem.* **2009**, *48*, 744–751. (c) Luo, Y.; Yao, Y.; Shen, Q.; Sun, J.; Weng, L. *J. Organomet. Chem.* **2002**, *662*, 144–149.

(18) Taylor, M. D.; Carter, C. P. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387–392.

(19) Lyle, S. J.; Rahman, M. M. *Talanta* **1963**, *10*, 1177–1182.

(20) Sheldrick, G. M.; *SHELXTL v.6.12;* Structure Determination Software Suite, Bruker AXS: Madison, Wisconsin, 2000.

(21) Sheldrick, G. M. ; *SADABS v.2.01;* Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS: Madison, Wisconsin, 1998.