

# Bridging $\mu\text{-}\eta^5\text{:}\eta^4$ -Coordination of an Indenyl Ligand and Reductive Coupling of Diazabutadienes in the Assembly of Di- and Tetranuclear Mixed-Valent Ytterbium Indenyldiazabutadiene Complexes

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**Abstract:** The redox reaction of [Yb(C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>(thf)<sub>2</sub>] with the diazabutadiene PhN=C(Me)–C(Me)=NPh (DAD) has been found to depend on the molar ratio of the reactants. Reaction in a 1:2 molar ratio affords the dinuclear mixed-valent complex [Yb<sub>2</sub>( $\mu\text{-}\eta^5\text{:}\eta^4$ -C<sub>9</sub>H<sub>7</sub>)( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>][ $\mu\text{-}\eta^4\text{:}\eta^4$ -PhNC(Me)=C-

(Me)NPh]] containing an indenyl ligand with an unusual  $\mu\text{-}\eta^5\text{:}\eta^4$  bridging coordination. Reaction of equimolar

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amounts of these compounds results in an organolanthanide-mediated reductive coupling of the DAD ligands and formation of the tetranuclear mixed-valent complex [Yb<sub>2</sub>( $\mu\text{-}\eta^5\text{:}\eta^4$ -C<sub>9</sub>H<sub>7</sub>)( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>][ $\mu\text{-}\eta^4\text{:}\eta^4$ -PhNC(CH<sub>2</sub>)=C(Me)-NPh]]<sub>2</sub> with a novel tetradentate tetraimine ligand.

## Introduction

“Redox-active” 1,4-disubstituted diazabutadiene ligands (DAD) are advantageous ligands for transition-metal chemistry. Due to the redox properties and the low energy of the  $\pi^*$ -orbital of DAD ligands,<sup>[1]</sup> their complexes with ytterbium, which has two stable oxidation states and is characterized by a low potential of the Yb<sup>II</sup>/Yb<sup>III</sup> transformation,<sup>[2]</sup> are of particular interest as promising systems for the investigation of intramolecular metal–ligand electron transfer.<sup>[3]</sup> The reactions of ytterbocenes with DAD<sup>[4]</sup> and other diimines<sup>[5]</sup> have been found to occur in different ways depending on the electronic and steric properties of the carbocyclic ligand coordinated to the ytterbium atom and the nature of the diimine. [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Yb<sup>II</sup>(OEt<sub>2</sub>)] reacts with 2,2'-dipyridyl, 1,10-phenanthroline,<sup>[5a,d]</sup> and some other nitrogen-containing heterocycles<sup>[5b,c]</sup> (L) with oxidation of the ytterbium to the trivalent state and formation of the complexes [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Yb<sup>III</sup>(L<sup>-</sup>)] or [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Yb<sup>III</sup>](L<sup>2-</sup>), in which the diimine ligand is reduced to the radical anion or the dianion,

respectively. Similar reactions of ytterbocenes derived from bulkier cyclopentadienyl (1,3-R<sub>2</sub>C<sub>5</sub>H<sub>3</sub>) (R = Me<sub>3</sub>C, Me<sub>3</sub>Si)<sup>[5a]</sup> or less electron-donating indenyl ligands<sup>[4c]</sup> result in retention of the oxidation state of the ytterbium atom and the formation of the neutral adducts [Cp<sub>2</sub>Yb<sup>II</sup>(L)] (Cp = 1,3-R<sub>2</sub>C<sub>5</sub>H<sub>3</sub>, C<sub>9</sub>H<sub>7</sub>). Ytterbocenes [Cp<sub>2</sub>Yb(thf)<sub>2</sub>] (Cp = C<sub>5</sub>H<sub>5</sub>,<sup>[4a]</sup> C<sub>5</sub>Me<sub>5</sub>,<sup>[4b]</sup> C<sub>9</sub>H<sub>7</sub><sup>[4d]</sup>) react with *t*BuN=CHCH=N*t*Bu with oxidation of the metal atom and formation of the radical anionic complexes [(Cp)<sub>2</sub>Yb<sup>III</sup>(DAD<sup>-</sup>)]. Recently, we described an example of the influence of the steric hindrance in the coordination sphere of the ytterbium atom on the reactivity of ytterbocenes towards bulky diazadienes. The bis(indenyl) derivative [Yb(C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>(thf)<sub>2</sub>] (**1**) is easily oxidized by the diazadiene 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-N=CH-CH=N-C<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6 (**2**) to give the trivalent ytterbium compound [Yb(C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>(L<sup>-</sup>)],<sup>[4c]</sup> while the reaction, under the same conditions, of [Yb(C<sub>13</sub>H<sub>9</sub>)<sub>2</sub>(thf)<sub>2</sub>] (**3**) containing bulkier fluorenyl ligands results in C–C bond formation and isolation of the Yb<sup>II</sup> complex [Yb{ $\eta^5$ -C<sub>13</sub>H<sub>8</sub>C(=NC<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6)CH<sub>2</sub>NH-C<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6}<sub>2</sub>(thf)}].<sup>[6]</sup>

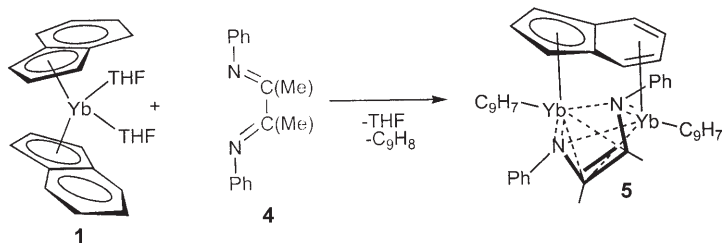
Replacement of the imino hydrogen atoms in the DAD molecule by two methyl groups to give 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-N=C(Me)–C(Me)=N-C<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6 dramatically influences the reaction pathway and leads, under the same conditions, to the formation of a different product, [Yb( $\eta^5$ -C<sub>13</sub>H<sub>9</sub>){2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-N=C(CH<sub>3</sub>)–C(CH<sub>2</sub>)=N-C<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6}(thf)}].<sup>[6]</sup> In order to gain insight into the sterically induced modification of the reductive reactivity of ytterbocenes towards DAD, we

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have investigated the reaction of complex **1** with the diaza-butadiene  $\text{PhN}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NPh}$  (**4**), which is less sterically demanding than **2**. Modification of the steric bulk of the DAD has been found to dramatically change the reaction pathway such that it results in partial Yb–indenyl bond cleavage and the assembly of di- and tetranuclear mixed-valent frameworks involving  $\mu-\eta^5:\eta^4$ -coordination of the indenyl units and an unusual coupling of the DAD ligands.

## Results and Discussion

The addition of a twofold molar excess of **4** in THF solution to a solution of **1** in the same solvent does not cause any change in the color of the reaction mixture. Evaporation of the solvent in vacuo leaves a deep red solid, which, on addition of toluene, dissolves with the formation of a brown solution. Heating of such a reaction mixture (60 °C, 72 h) and subsequent recrystallization from hot toluene affords the unexpected dinuclear complex  $[\text{Yb}_2(\mu-\eta^5:\eta^4-\text{C}_9\text{H}_7)(\eta^5-\text{C}_9\text{H}_7)_2\{\mu-\eta^4:\eta^4-\text{PhNC}(\text{Me})=\text{C}(\text{Me})\text{NPh}\}]$  (**5**) (60% yield) (Scheme 1).



Scheme 1. Reaction of **1** with **4** in a 1:2 molar ratio.

The reaction is accompanied by indene formation, which obviously arises as a product of hydrogen abstraction from a molecule of solvent or DAD by an indenyl radical. Yb–C bond cleavage and the formation of fluorene have been previously observed in the related reaction of **3** with 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>-N=C(Me)-C(Me)=N-C<sub>6</sub>H<sub>3</sub>*i*Pr<sub>2</sub>-2,6.<sup>[6]</sup> In this reaction, the DAD molecule was found to be the source of the hydrogen atom for abstraction.

Complex **5** is paramagnetic. The experimentally determined value of the effective magnetic moment for **5** ( $\mu_{\text{eff}} = 2.7 \mu\text{B}$  at 293 K) is intermediate between the average  $\mu_{\text{eff}}$  value reported for Yb<sup>III</sup> derivatives (4.3  $\mu\text{B}$ ) and that of diamagnetic Yb<sup>II</sup> compounds.<sup>[7]</sup> Thus, the magnetic measurements provide evidence of different oxidation states of the ytterbium atoms in **5**.

X-ray analysis has revealed **5** to be a dinuclear species, which is assembled as a result of unusual bridging  $\mu-\eta^5:\eta^4$ -coordination of one indenyl ligand and  $\mu-\eta^4:\eta^4$ -coordination of the DAD ligand (Figure 1, Table 1). The two ytterbium atoms in **5** are each coordinated by two indenyl ligands, but in different ways.

The Yb1 atom is  $\eta^5$ -bound by two cyclopentadienyl units of two indenyl ligands, while the Yb2 atom is coordinated by five- and six-membered rings in  $\eta^5$ - and  $\eta^4$ -fashion, re-

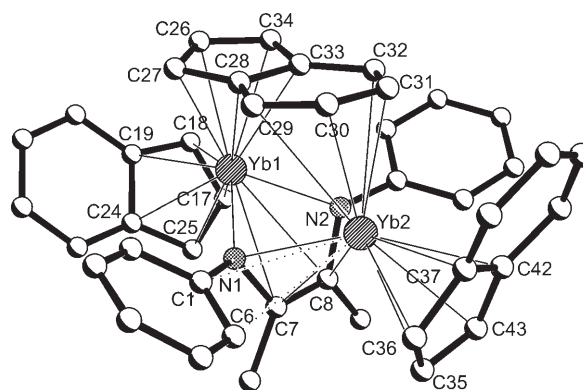


Figure 1. Molecular structure of complex **5**; hydrogen atoms have been omitted for the sake of clarity. Ring C35, C36, C37, C42, C43 is disordered over two positions. Selected bond lengths [Å] and angles [°]: Yb1–N1 2.238(6), Yb1–N2 2.249(7), Yb2–C7 2.713(7), Yb2–C8 2.743(8), Yb1–C26 2.565(7), Yb1–C27 2.641(8), Yb1–C28 2.791(8), Yb1–C33 2.771(8), Yb1–C34 2.635(8), Yb1–C25 2.577(8), Yb1–C17 2.604(9), Yb1–C24 2.614(7), Yb1–C18 2.652(8), Yb1–C19 2.676(7), Yb1–C7 2.858(7), Yb1–C8 2.842(8), N1–Yb2 2.522(7), Yb2–N2 2.553(8), Yb2–C36 2.878(16), Yb2–C36' 2.648(18), Yb2–C35 2.744(16), Yb2–C35' 2.753(18), Yb2–C37 2.788(15), Yb2–C37' 2.717(17), Yb2–C42 2.661(16), Yb2–C43 2.661(17), Yb2–C29 3.171(7), Yb2–C30 2.837(7), Yb2–C31 2.713(10), Yb2–C32 3.016(8), Yb2–C6 3.072, C1–Yb2 2.989(10), N1–C7 1.451(9), N2–C8 1.419(10), C7–C8 1.370(11); N1–Yb1–N2 74.4(2), N1–Yb2–N2 64.6(2), Yb2–C7–Yb1 80.75(2), Yb2–C8–Yb1 80.5(2), Centr. Cp1–Yb1–Centr. Cp2 128.5(2), Centr. C<sub>5</sub>–Yb2–Centr. Cp2 117.9(2).

Table 1. Selected Yb–N and Yb–C bond lengths [Å] for complexes **5** and **6**.

Bond	<b>5</b>	<b>6</b>
Yb1–N1	2.238(6)	2.246(3)
Yb1–N2	2.249(7)	2.225(4)
Yb1–C7	2.858(7)	2.972(5)
Yb1–C8 ( <b>5</b> ), Yb1–C9 ( <b>6</b> )	2.842(8)	2.961(5)
Yb1–C17	2.604(9)	2.604(5)
Yb1–C18	2.652(8)	2.592(5)
Yb1–C19	2.676(7)	2.618(5)
Yb1–C24 ( <b>5</b> ), Yb1–C20 ( <b>6</b> )	2.614(7)	2.687(5)
Yb1–C25	2.577(8)	2.661(5)
Yb1–C26	2.565(7)	2.598(4)
Yb1–C27	2.641(8)	2.638(4)
Yb1–C28	2.791(8)	2.756(4)
Yb1–C33	2.771(8)	2.752(4)
Yb1–C34	2.635(8)	2.613(4)
Yb2–N1	2.522(7)	2.577(4)
Yb2–N2	2.553(8)	2.551(4)
Yb2–C7	2.713(7)	2.654(4)
Yb2–C8 ( <b>5</b> ), Yb2–C9 ( <b>6</b> )	2.743(8)	2.664(4)
Yb2–C35 (35')	2.744(16) (2.753(18))	2.679(5)
Yb2–C36 (36')	2.878(16) (2.648(18))	2.740(4)
Yb2–C37 (37')	2.788(15) (2.717(17))	2.830(4)
Yb2–C42	2.661(16)	2.798(5)
Yb2–C43	2.661(17)	2.697(5)
Yb2–C29	3.171(7)	3.027(4)
Yb2–C30	2.837(7)	2.690(4)
Yb2–C31	2.713(10)	2.720(4)
Yb2–C32	3.016(8)	3.093(4)
Yb2–C1 ( <b>5</b> ), Yb2–C11 ( <b>6</b> )	2.989(10)	3.082(4)
Yb2–C6 ( <b>5</b> ), Yb2–C12 ( <b>6</b> )	3.072(10)	3.164(4)

spectively. The Yb2–C(C<sub>6</sub>-indenyl) bond lengths are in the range 2.713(10)–3.171(9) Å, and are somewhat longer than the Yb–C π-arene interactions reported for Yb<sup>III</sup> complexes of the type [(η<sup>6</sup>-CH<sub>3</sub>C<sub>6</sub>H<sub>5</sub>)Yb(AlCl<sub>4</sub>)<sub>3</sub>] (2.803–3.042 Å)<sup>[8]</sup> but comparable to those in the Yb<sup>II</sup> cationic part of [Yb<sub>2</sub>{μ-OC<sub>6</sub>H<sub>3</sub>(2,6-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}<sub>2</sub>]<sup>+</sup>[Yb{OC<sub>6</sub>H<sub>3</sub>(2,6-C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}<sub>4</sub>]<sup>-</sup>.<sup>[12c]</sup> Coordination of the six-membered ring leads to a noticeable distortion of its planarity. The twist angle along the C29...C32 axis in the bridging indenyl ligand is 7.7°, whereas the analogous values in the terminal ligands are about 2.0°. Such μ-bridging coordination of indenyl ligands is rather rare<sup>[9]</sup> and to the best of our knowledge has never been described for organolanthanides. The *ipso*- and *ortho*-carbon atoms of one of the phenyl rings of the DAD ligand are also involved in metal-ligand bonding through η<sup>2</sup>-coordination to the Yb2 atom (Yb2–C1 2.989(10), Yb2–C6 3.072(10) Å). These contacts are significantly shorter than those to the corresponding carbon atoms of the second phenyl ring (Yb2–C9 3.396(10), Yb2–C10 3.617(10) Å). Due to this interaction with the ytterbium atom, the displacement of *ipso*-carbon atom C1 from the plane of the NCCN fragment is 0.5948 Å, while for the *ipso*-carbon atom C9 not involved in coordination this value is 0.1982 Å. The average Yb–C(C<sub>5</sub>-indenyl) bond lengths in **5** are somewhat different for Yb1 (2.680(8) and 2.624(8) Å) and Yb2 (2.700(16) Å). They are shorter than those in the starting ytterbocene **1** (2.73 Å),<sup>[10a]</sup> but are remarkably longer than the corresponding distances in indenyl derivatives of trivalent ytterbium.<sup>[10b,c]</sup> The difference in the Yb–N bond lengths involving the two ytterbium atoms is even more pronounced. The Yb1–N1 (2.238(6) Å) and Yb1–N2 (2.249(7) Å) distances are very close to those of the covalent Yb<sup>III</sup>–N bonds in [(η<sup>5</sup>-MeC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>YbNPh<sub>2</sub>] (2.216(5) Å)<sup>[11a]</sup> and [(η<sup>5</sup>-MeC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>YbNPh<sub>2</sub>(thf)] (2.287(6) Å),<sup>[11a]</sup> and shorter than the Yb<sup>II</sup>–N bond length.<sup>[11b–d]</sup> The Yb–N distances at the second ytterbium atom Yb(2) (2.522(7) and 2.553(8) Å) are substantially longer and are comparable to the coordination Yb–N bond lengths in the Yb<sup>II</sup> complexes [(1,3-(Me<sub>3</sub>C)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>)<sub>2</sub>Yb(bipy)] and [(1,3-(Me<sub>3</sub>Si)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>)<sub>2</sub>Yb(phen)].<sup>[5a]</sup> Thus, the X-ray analysis data together with the value of the effective magnetic moment<sup>[7]</sup> indicate that complex **5** is a mixed-valent compound containing both Yb<sup>II</sup> and Yb<sup>III</sup> centers.<sup>[12]</sup> The Yb1...Yb2 interatomic distance in **5** is 3.610(3) Å, and therefore an interaction between the metal atoms is unlikely. The bond lengths within the NCCN fragment of **5** are consistent with the dianionic character of the DAD ligand<sup>[13]</sup> since the N–C bonds (1.459(9) and 1.419(10) Å) are substantially elongated compared to those in free diazabutadienes,<sup>[14]</sup> while the C–C bond length (1.370(11) Å) is shortened and is close to the values of aromatic C–C bonds.<sup>[15]</sup> The C7–C8 double bond of the doubly reduced ene-diamido moiety also

participates in dinuclear core formation, coordinating to both the Yb1 and Yb2 atoms in η<sup>2</sup>-fashion (Yb2–C7 2.713(7), Yb2–C8 2.743(8), Yb1–C7 2.858(7), Yb1–C8 2.842(8) Å).

The UV/Vis spectrum of **5** in THF shows a strong absorption at 284 nm, which corresponds well with the strong band of (DAD<sup>2-</sup>)(Li<sup>+</sup>)<sub>2</sub> in THF at 285 nm, thus providing further proof of the dianionic character of the DAD ligand (Figure 2).

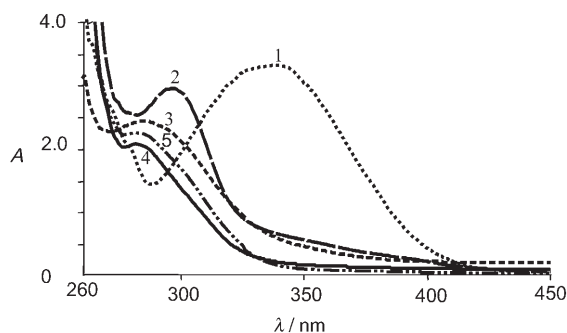
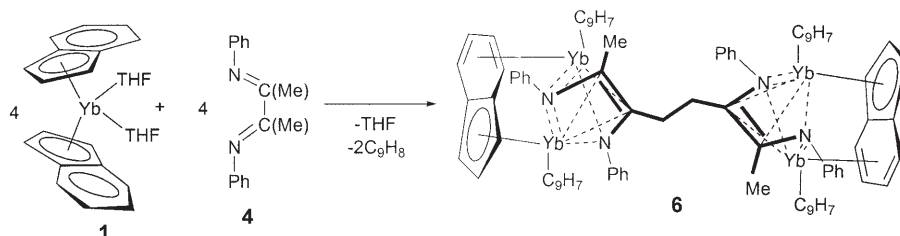


Figure 2. UV/Vis spectra: 1) PhN=C(Me)–C(Me)=NPh (**4**) in hexane; 2) [PhNC(Me)C(Me)NPh]<sup>-</sup> Na<sup>+</sup> in THF; 3) [PhNC(Me)C(Me)NPh]<sup>2-</sup>·2Li<sup>+</sup> in THF; 4) [Yb<sub>2</sub>(μ-η<sup>5</sup>:η<sup>4</sup>-C<sub>9</sub>H<sub>7</sub>)(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>{μ-η<sup>4</sup>:η<sup>4</sup>-PhNC(Me)=C(Me)NPh}] (**5**) in THF; 5) [Yb<sub>2</sub>(μ-η<sup>5</sup>:η<sup>4</sup>-C<sub>9</sub>H<sub>7</sub>)(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>{μ-η<sup>4</sup>:η<sup>4</sup>-PhNC(CH<sub>2</sub>)=C(Me)NPh}]<sub>2</sub> (**6**) in THF.

The reaction of complex **1** with an equimolar amount of the diazabutadiene **4** under similar conditions affords a different product, namely the tetranuclear complex [Yb<sub>2</sub>(μ-η<sup>5</sup>:η<sup>4</sup>-C<sub>9</sub>H<sub>7</sub>)(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>{μ-η<sup>4</sup>:η<sup>4</sup>-PhNC(CH<sub>2</sub>)=C(Me)NPh}]<sub>2</sub> (**6**) (53% yield) (Scheme 2). The formation of indene was again



Scheme 2. Reaction of complex **1** with an equimolar amount of diazabutadiene **4**.

detected in this reaction. Compound **6** is paramagnetic, with an effective magnetic moment of 2.6 μB at 293 K. X-ray analysis has shown that the molecule of **6** consists of two binuclear units [Yb<sub>2</sub>(μ-η<sup>5</sup>:η<sup>4</sup>-C<sub>9</sub>H<sub>7</sub>)(η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>{μ-η<sup>4</sup>:η<sup>4</sup>-PhNC(CH<sub>2</sub>)=C(Me)NPh}] (**5<sub>H</sub>**) arising from **5** as a result of hydrogen abstraction from one of the methyl groups on the imino unit. Coupling of two imino “ex-methyl” carbons of two **5<sub>H</sub>** units leads to the formation of the CH<sub>2</sub>–CH<sub>2</sub> bridge and assembly of the tetranuclear complex **6** (Figure 3).

Geometric parameters within the **5<sub>H</sub>** units are similar to those in **5**, although there are some distinctions. The average bond distances between the respective ytterbium atoms and the central carbon atoms of the ene-diamido fragment in **5**

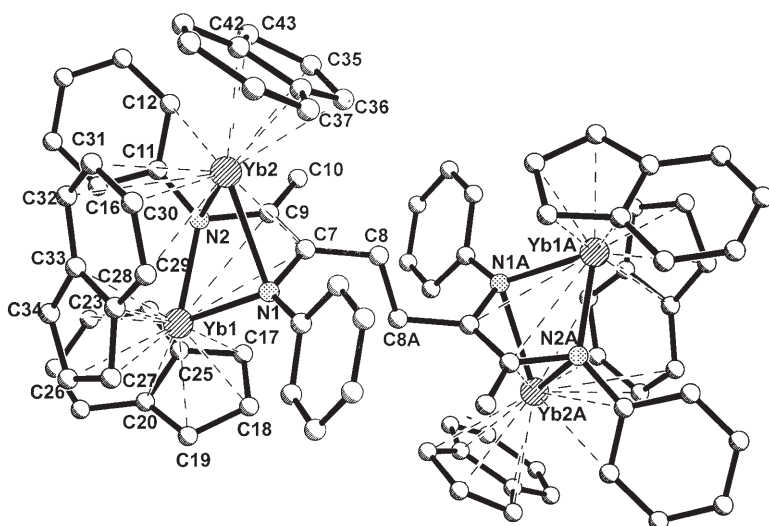


Figure 3. Molecular structure of complex **6**; hydrogen atoms have been omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Yb1–N2 2.225(4), Yb1–N1 2.246(3), Yb1–C7 2.972(5), Yb1–C9 2.961(5), Yb1–C17 2.604(5), Yb1–C18 2.592(5), Yb1–C19 2.618(5), Yb1–C20 2.687(5), Yb1–C25 2.661(5), Yb1–C26 2.598(4), Yb1–C27 2.638(4), Yb1–C28 2.756(4), Yb1–C33 2.752(4), Yb1–C34 2.613(4), Yb2–N2 2.551(4), Yb2–N1 2.577(4), Yb2–C7 2.654(4), Yb2–C9 2.664(4), Yb2–C35 2.679(5), Yb2–C36 2.740(4), Yb2–C37 2.830(4), Yb2–C42 2.798(5), Yb2–C43 2.697(5), Yb2–C29 3.027(4), Yb2–C30 2.690(4), Yb2–C31 2.720(4), Yb2–C32 3.093(4), N1–C7 1.427(5), N2–C9 1.413(5), C7–C9 1.370(6), C7–C8 1.492(6), C8–C8A 1.510(9); N2–Yb1–N1 71.95(13), N2–Yb2–N1 61.62(12), C7–Yb2–C9 29.87(13), Yb2–C7–Yb1 80.61(11), Yb2–C9–Yb1 80.65(10).

(2.789(7) Å) are noticeably shorter than the corresponding average distance in **6** (2.812(5) Å). The average value of the Yb2– $\eta^4$ -ring bond lengths in **6** (2.882 Å) is slightly shorter than that in **5** (2.938 Å). The length of the carbon–carbon bond formed in the reaction (C8–C8A 1.510(9) Å) is characteristic of a regular C–C  $\sigma$ -bond.<sup>[14]</sup>

## Conclusion

An unusual redox reactivity of ytterbocenes towards a DAD ligand has been identified, induced by steric constraints in the coordination sphere of the metal atom. Depending on the molar ratio of the reactants, the reactions lead either to the formation of a binuclear complex with a  $\mu$ - $\eta^5$ : $\eta^4$ -indenyl bridge or to the organolanthanide-mediated coupling of DAD ligands with the formation of a novel tetradentate imine ligand.

## Experimental Section

**General remarks:** All procedures were performed under vacuum using standard Schlenk techniques. After drying over KOH, THF was distilled from sodium benzophenone ketyl prior to use. Hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl or CaH<sub>2</sub>. Deuterated benzene was dried with sodium benzophenone ketyl and vacuum-transferred. [Yb(C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>(thf)<sub>2</sub>] was synthesized following a literature procedure.<sup>[44]</sup> All other commercially available chemicals were used after the appropriate purification. A Bruker DPX200 spectrometer was used to record the NMR spectra. Chemical shifts in the <sup>1</sup>H and <sup>13</sup>C

spectra were referenced internally according to the residual solvent resonances and are reported relative to tetramethylsilane. IR spectra were recorded on a Specord M80 instrument with samples as Nujol mulls. UV/Vis spectra were recorded from samples in evacuated quartz cuvettes on a Perkin-Elmer Lambda 25 spectrophotometer. GC analyses were performed using a Tzvet 530 gas chromatograph. Magnetic measurements were made using the Faraday method according to the published procedure.<sup>[16]</sup> Lanthanide metal analyses were carried out by complexometric titration. Elemental analyses were performed in the microanalytical laboratory of the Institute of Organometallic Chemistry of the Russian Academy of Sciences.

**Synthesis of [Yb<sub>2</sub>( $\mu$ - $\eta^5$ : $\eta^4$ -C<sub>9</sub>H<sub>7</sub>)( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>( $\mu$ - $\eta^4$ : $\eta^4$ -PhNC(Me)=C(Me)-NPh)] (5):** A solution of **4** (0.83 g, 3.50 mmol) in THF (15 mL) was added to a solution of **1** (0.96 g, 1.75 mmol) in THF (30 mL) at 18 °C. The reaction mixture was heated at 60 °C for 0.5 h. After removal of the THF in vacuo, toluene (40 mL) was added and the solution was heated at 60 °C for 72 h. The volatiles were then evaporated in vacuo and collected.

The solid residue was washed with hexane (2 × 10 mL) and the extracts were combined with the condensate. Indene (0.09 g, 84%) was found in the extracts by GC analysis. Recrystallization of the solid residue from hot toluene gave **5** as deep brown bipyrarnidal crystals (0.49 g, 60%). IR (Nujol, KBr):  $\bar{\nu}$  = 3050 (w), 1587 (m), 1328 (m), 1266 (m), 1250 (m), 1215 (w), 1146 (m), 1075 (w), 1037 (m), 941 (m), 856 (m), 789 (s), 775 (s), 750 (s), 734 (s), 696 (s), 662 (m), 584 (m), 550 (m), 438 cm<sup>-1</sup> (s); elemental analysis calcd (%) for C<sub>43</sub>H<sub>37</sub>N<sub>2</sub>Yb<sub>2</sub> (927.8): C 55.66, H 3.98, Yb 37.29; found: C 55.28, H 4.12, Yb 37.48.

**Synthesis of [Yb<sub>2</sub>( $\mu$ - $\eta^5$ : $\eta^4$ -C<sub>9</sub>H<sub>7</sub>)( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>)<sub>2</sub>( $\mu$ - $\eta^4$ : $\eta^4$ -PhNC(CH<sub>2</sub>)=C(Me)NPh)] (6):** A solution of **4** (0.58 g, 2.45 mmol) in THF (10 mL) was added to a solution of **1** (1.34 g, 2.45 mmol) in THF (40 mL) at 18 °C. The reaction mixture was heated at 60 °C for 0.5 h. After removal of the THF in vacuo, toluene (40 mL) was added and the solution was heated at 60 °C for 96 h. The volatiles were then evaporated in vacuo and collected. The solid residue was washed with hexane (2 × 10 mL) and the extracts were combined with the condensate. Indene (0.12 g, 90%) was found in the extracts by GC analysis. Recrystallization of the solid residue from hot toluene gave **6** as deep brown lamellate crystals (0.60 g, 53%). IR (Nujol, KBr):  $\bar{\nu}$  = 3050 (w), 1588 (m), 1327 (m), 1269 (s), 1252 (m), 1147 (m), 1030 (m), 940 (m), 791 (s), 764 (s), 752 (s), 735 (s), 696 (s), 583 (m), 550 (m), 436 cm<sup>-1</sup> (s); elemental analysis calcd (%) for C<sub>86</sub>H<sub>72</sub>N<sub>4</sub>Yb<sub>4</sub> (1853.6): C 55.72, H 3.88, Yb 37.33; found: C 55.36, H 3.50, Yb 37.66.

**X-ray diffraction study:** X-ray diffraction data were collected on a SMART APEX diffractometer (graphite-monochromated MoK $\alpha$  radiation,  $\phi$ - $\omega$ -scan technique,  $\lambda$  = 0.71073 Å). The intensity data were integrated by means of the SAINT program.<sup>[17]</sup> SADABS<sup>[18]</sup> was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against  $F^2$  using all reflections with the aid of the SHELXTL package.<sup>[19]</sup> All non-hydrogen atoms were refined anisotropically. The H atoms in **5** and **6** were placed in calculated positions and refined as a riding model. Crystallographic parameters for **5** and **6**, along with details of the data collection and refinement, are collected in Table 2. The terminal indenyl ligand at Yb2 in **5** was found to be disordered over two positions and was refined with a

Table 2. Crystallographic parameters, and details of the data collection and refinement, for **5** and **6**.

	<b>5</b>	<b>6</b>
formula	C <sub>43</sub> H <sub>37</sub> N <sub>2</sub> Yb <sub>2</sub>	C <sub>86</sub> H <sub>72</sub> N <sub>4</sub> Yb <sub>4</sub>
<i>M<sub>r</sub></i>	927.83	1853.64
<i>T</i> [K]	100	100
crystal system	tetragonal	monoclinic
space group	<i>P</i> 4(3)2(1)2	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> [Å]	10.0804(6)	16.8974(13)
<i>b</i> [Å]	10.0804(6)	10.8273(8)
<i>c</i> [Å]	64.982(5)	19.6113(15)
<i>α</i> [°]	90	90
<i>β</i> [°]	90	112.453(2)
<i>γ</i> [°]	90	90
volume, Å <sup>3</sup>	6603.1(8)	1282.0(3)
<i>Z</i>	8	2
<i>ρ</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]	1.867	1.856
<i>μ</i> [mm <sup>-1</sup> ]	5.665	5.640
<i>F</i> (000)	3592	1792
crystal size [mm]	0.10 × 0.08 × 0.08	0.16 × 0.10 × 0.03
<i>θ</i> <sub>max</sub> range [°]	23.00	25.00
index ranges	-11 ≤ <i>h</i> ≤ 11 -11 ≤ <i>k</i> ≤ 11 -71 ≤ <i>l</i> ≤ 71	-20 ≤ <i>h</i> ≤ 16 -12 ≤ <i>k</i> ≤ 12 -19 ≤ <i>l</i> ≤ 23
reflections collected	39547	17530
independent reflections	4594 [ <i>R</i> <sub>int</sub> = 0.046]	5830 [ <i>R</i> <sub>int</sub> = 0.0489]
absorption correction	SADABS	
max./min. transmission	0.6600/0.6012	0.8490/0.4656
refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>	
data/restraints/parameters	4594/136/500	5830/0/424
goodness-of-fit on <i>F</i> <sup>2</sup>	1.241	0.938
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]		
<i>R</i> <sub>1</sub>	0.0366	0.0376
<i>wR</i> <sub>2</sub>	0.0785	0.0574
<i>R</i> indices (all data)		
<i>R</i> <sub>1</sub>	0.0308	0.0502
<i>wR</i> <sub>2</sub>	0.0789	0.0614
largest diff. peak and hole [e Å <sup>-3</sup> ]	1.106/−1.889	1.163/−0.661

population in each position of 0.5. Salient bond lengths for **5** and **6** are collected in Table 1. CCDC-275862 (**5**) and CCDC-275863 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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