DOI: 10.1002/ejic.200601209

Reactions of Ytterbocenes with Diimines: Steric Manipulation of Reductive Reactivity

Alexander A. Trifonov*[a]

Dedicated to Prof. G. A. Abakumov on the occasion of his 70th birthday

Keywords: Lanthanides / Diimines / Reductive reactivity / N,N ligands / Redox tautomerism

This review is devoted to the investigation of reactions of ytterbocenes with diimines. These reactions are found to be strongly influenced by the steric crowding in the coordination sphere of the metal atom and the coordination capacities of π-aromatic ligands coordinated to the ytterbium. The reactions may occur with oxidation of the ytterbium atom as well as with retention of its oxidation state. C–C bond formation, C–H bond activation, C=N bond insertion, and oxidative Yb–C bond cleavage processes are documented for reactions of ytterbocenes with diimines. Steric overcrowding of the coordination sphere of the ytterbium atom can induce "extra" reducing ability of ytterbocenes and allow them to act not only as one- but also as two-electron reductants with respect to diimines.

1. Introduction

Diimino ligands appeared in transition-metal chemistry in the late 1960s and have turned out to be a promising coordination environment able to provide unusual structures and unique reactivity.[1] The high catalytic activity of the diimino complexes of late transition metals in olefin polymerization has demonstrated the high potential of this ligand system in catalysis.[2] The permanent attention for diimines is mainly roused by the diversity of their redox and coordination properties. The lone electron pair at nitrogen atoms and the π electrons of the C=N bonds allow the diimine molecule to act both as a N-donor and as a π-electron donor ligand in a variety of coordination modes. The redox-active diimine molecule can coordinate metal atoms in high oxidation states as a neutral ligand[3] (Scheme 1, A), but also, due to its pronounced electron affinity (for example, the reduction potential of *t*BuN=CH–CH=N*t*Bu is E^0_{SCE} = 1.822 V),[4] it can oxidize electropositive metals accepting one or two electrons, thus forming a radical anion (Scheme 1, B)[5] or dianion (Scheme 1, C).[6]

The diimine ligands were introduced into organolanthanide chemistry in the works of Cloke and Edelmann in the 1980s and allowed the synthesis of isolable lanthanide complexes.[7] The known compounds could be divided into two main groups based on the reduction state and the coordination mode of the diimino ligand. The first group is presented by homo- and hetero-ligated compounds containing the diimine radical anion coordinated to the lanthanide atom by two nitrogen atoms (Scheme 1, B).[7a–7f] The second group consists of complexes coordinated by the doubly reduced enediamido fragment 2σ:π-bonded to the central metal atom (Scheme 1, C).[7g,7h]

The redox-active character of diimines and the low energy of their π* orbitals[8] makes their complexes with lanthanide metals of two stable oxidation states promising ob-

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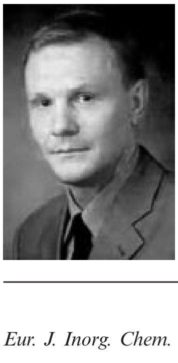
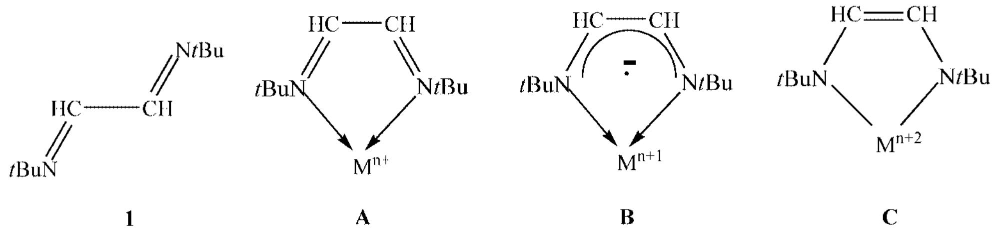
[a] G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences,
Tropinina 49, 603950, Nizhny Novgorod, GSP-445, Russia
Fax: +7-8312-621497
E-mail: trif@imoc.sinn.ru



Alexander Trifonov was born in Gorky (Nizhny Novgorod), Russia in 1962. In 1979–1984 he studied chemistry at the State University of Gorky and in 1984 received his diploma degree. During his PhD studies he worked at the Institute of Organometallic Chemistry of Russian Academy of Sciences (Nizhny Novgorod) under the supervision of Prof. M. N. Bochkarev and in 1989 received his PhD. He did postdoctoral studies at the Technical University of Berlin (Prof. H. Schumann, 1991), Université de Paris-Sud (Prof. H. Kagan, 1993–1995), and Mainz University (Prof. J. Okuda, 1999–2000). After returning to the Institute of Organometallic Chemistry, he defended the second thesis in 2003 and in 2004 became head of the Laboratory of Coordination Chemistry. Since 2005 he has been a professor of chemistry of Nizhny Novgorod State University. His research interests lie in the area of the synthesis of organometallic and coordination compounds of rare earth metals and their application in homogeneous catalysis and material chemistry.



Scheme 1.

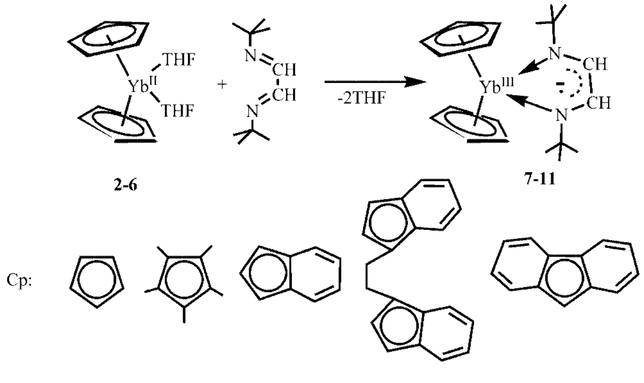
jects with respect to investigation of intramolecular metal–ligand electron transfers. Ytterbium seems to be the most advantageous candidate for this purpose due to a rather low $Yb^{II} \rightleftharpoons Yb^{III}$ transformation potential (for comparison, reduction potentials of M^{III}/M^{II} in aqueous solution vs. SHE: Eu, –0.35; Yb, –1.15; Sm, –1.55 V).[9] Diamagnetism of the divalent ytterbium (electron configuration Yb^{II} $4f^{14}$) complexes and moderate paramagnetism of its trivalent species (electron configuration Yb^{III} $4f^{13}$, μ = 3.29–4.45 μ_B)[10] makes NMR spectroscopy applicable for the investigation of ytterbium compounds in both oxidation states. On the other hand, noticeable differences in the magnetic properties of the Yb^{II} and Yb^{III} derivatives[10] allow easy estimation of the ytterbium atom oxidation state by means of magnetochemistry. Moreover, complexes of trivalent ytterbium emitting in the near-infrared region and containing conjugated diimino ligands which can act as sensitizers are of great interest because of potential applications in optoelectronic devices and medical diagnosis.[11] Compounds that undergo easy and reversible redox transformations by intramolecular electron transfer provoked by low-energy external excitations are of potential interest for the construction of molecular switches.

Complexes of trivalent ytterbium containing radical-anionic diimine ligands are promising models for investigation of metal–ligand bonding to provide a ground for a deeper understanding of the electronic structure of f-metal compounds and the contribution of f-electrons in a bonding interaction. The first tris(diazabutadiene) derivative of trivalent ytterbium (tBuNCHCHNtBu)$_3$Yb containing three radical-anionic diimine ligands has demonstrated a complex temperature-dependent magnetic behavior which allowed us to suggest the existence of redox tautomerism.[7f] In order to gain insight into the nature of bonding in diimino complexes of f-elements, we focused on the synthesis of mixed-ligand Yb^{III} compounds containing one paramagnetic ligand. The reactions of ytterbocenes with diimines were chosen as a synthetic approach to this class of compounds, and systematic investigation of these reactions has unexpectedly discovered a very rich and often unpredictable reactivity. The differences in reactivity as a function of steric crowding in the coordination sphere of the metal atom, coordination capacities of the π-aromatic ligands bound to ytterbium, and their tendency towards haptotropic rearrangements allow an expansion of ytterbocene reductive chemistry and the revelation of new types of reactions and complexes.

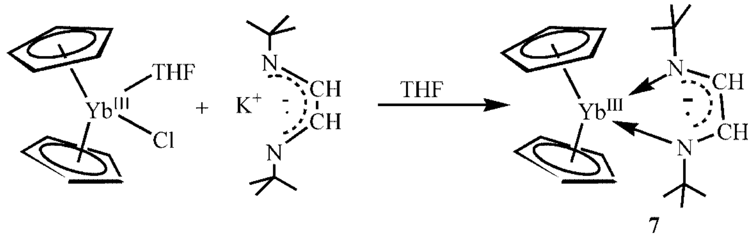
The review is mainly focused on the ytterbium derivatives since there is far less known about the diimine complexes of samarium and ytterbium. Work on this subject is being pursued at the moment.

2. Reactions Resulting in the Formation of Diimino Complexes $[Cp_2Yb^{III}(L^{-\cdot})]$ and $[Cp_2Yb^{II}(L^0)]$ (Cp = C_5H_5, C_5MeH_4, C_5Me_5, C_9H_7, $C_9H_6CH_2$, $C_{13}H_9$; L = RN=CH–CH=NR, bipy)

The N,N'-di-*tert*-butyl-1,4-diazabutadiene (**1**) was the first and remains the most widely employed diazabutadiene ligand in organolanthanide chemistry. Ytterbocenes $[Cp_2Yb(THF)_2]$ {Cp = C_5H_5 (**2**), C_5Me_5 (**3**), C_9H_7 (**4**), $C_9H_6CH_2$ (**5**), $C_{13}H_9$ (**6**)} reacted with **1** in a similar way, and the reactions afforded sandwich complexes of trivalent ytterbium containing the radical anion of diazabutadiene [Cp$_2$Yb(tBuNCHCHNtBu$^{-\cdot}$)] {Cp = C_5H_5 (**7**),[12] C_5Me_5 (**8**),[13] C_9H_7 (**9**),[14] $C_9H_6CH_2$ (**10**),[14] $C_{13}H_9$ (**11**)[15]} (Scheme 2). It is worthy to note that **1** oxidized complex **2** at room temperature in THF solution, while compounds **3**–**6** did not react with **1** in THF. This is proven by the ^{1}H NMR spectra of the reaction mixtures of **3**–**6** and **1** in [D$_8$]-thf which show superposition of the spectra of the diamagnetic Yb^{II} complexes and of free diazabutadiene. In contrast, ^{1}H NMR spectroscopy indicates paramagnetism of the product formed in the reaction of **2** and **1** in THF, thus giving evidence for the oxidation of the ytterbium atom to Yb^{III} oxidation state. The reactions of complexes **3**–**6** with **1** occurred only in toluene media at 60 °C and resulted in the formation of the complexes **8**–**11** (Scheme 2).



Scheme 2.



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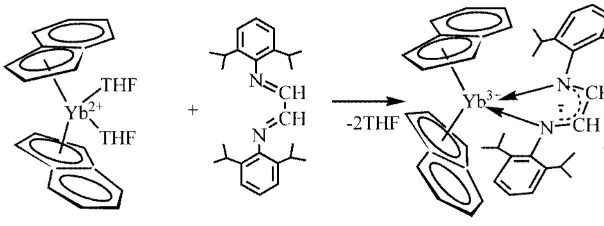
$$2(C_5H_5)_2YbCl(THF) + Na^+{}_2(tBuNCHCHNtBu^{2-}) \xrightarrow{THF}$$

$$\underset{\textbf{7}}{(C_5H_5)_2Yb(tBuNCHCHNtBu)} + (C_5H_5)_2Yb(THF)_2 + 2NaCl$$

Scheme 3.

Complex **7** was also obtained by the metathesis reaction of equimolar amounts of [$(C_5H_5)_2YbCl(THF)$] and ($tBuNCHCHNtBu^{-\cdot}$)K^+ (Scheme 3). An attempt to synthesize a dinuclear compound containing two [$(C_5H_5)_2Yb$] moieties linked by a μ-bridging enediamido fragment by the reaction of a twofold molar excess of [$(C_5H_5)_2YbCl(THF)$] with $Na^+{}_2(tBuNCHCHNtBu^{2-})$ afforded a mixture of complex **7** and [$(C_5H_5)_2Yb(THF)_2$] (Scheme 3).[12]

The bulkier 1,4-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (**12**) also reacted with ytterbocenes [$(C_9H_7)_2Yb(THF)_2$] and [$(C_5MeH_4)_2Yb(THF)_2$] in toluene, affording the derivatives of trivalent ytterbium coordinated by the radical anion of diazadiene [$(C_9H_7)_2Yb(iPr_2C_6H_3NCHCHNC_6H_3iPr_2)$] (**13**)[16] and [$(C_5MeH_4)_2Yb(iPr_2C_6H_3NCHCHNC_6H_3iPr_2)$] (**14**), respectively (Scheme 4).[17]



13

Scheme 4.

The structures of complexes **7**–**10**, **13**, **14** have been determined by X-ray diffraction studies which revealed that in all compounds, the ytterbium atom is η^5-coordinated by the two "cyclopentadienyl" units and the two nitrogen atoms of the radical-anionic diazabutadiene ligand, and it adopts the geometry of a distorted tetrahedron (Figures 1, 2, 3, 4, 5, and 6).

The Yb–$Cp_{Centr.}$ distances in complexes **7**–**10**, **13**, **14** (Table 1) are shorter than those in the starting Yb^{II} complexes.[18] The shortening of the Yb–$Cp_{Centr.}$ distances in complexes **7**–**10**, **13**, **14** compared with those in the starting ytterbocenes indicates the oxidation of the ytterbium atom from Yb^{II} to Yb^{III}.[19] However, in all cases the magnitude of the shortening is considerably less than that expected on the basis of the difference in the ionic radii of Yb^{II} and Yb^{III} (0.155 Å) and obviously results from reciprocal repul-

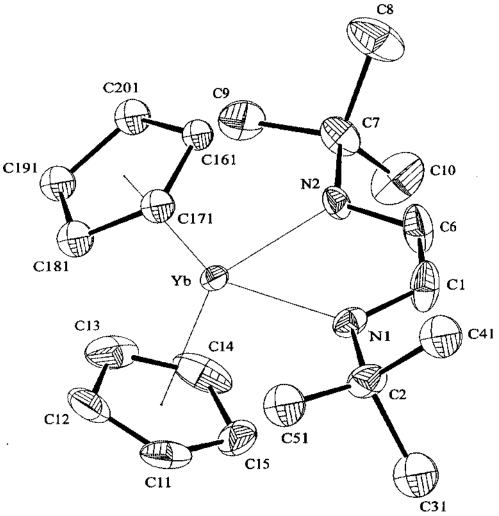


Figure 1. Molecular structure of complex [$(C_5H_5)_2Yb(tBuNCHCHNtBu)$] (**7**).

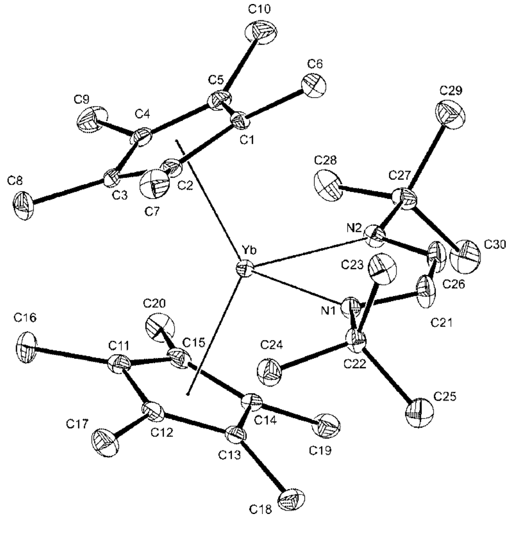


Figure 2. Molecular structure of complex [$(C_5Me_5)_2Yb(tBuNCHCHNtBu)$] (**8**).

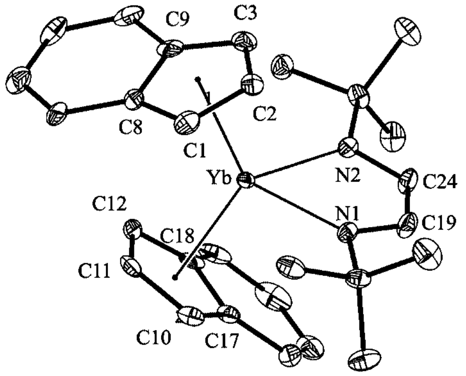


Figure 3. Molecular structure of complex [$(C_9H_7)_2$Yb(*t*BuNCH-CHN*t*Bu)] (**9**).

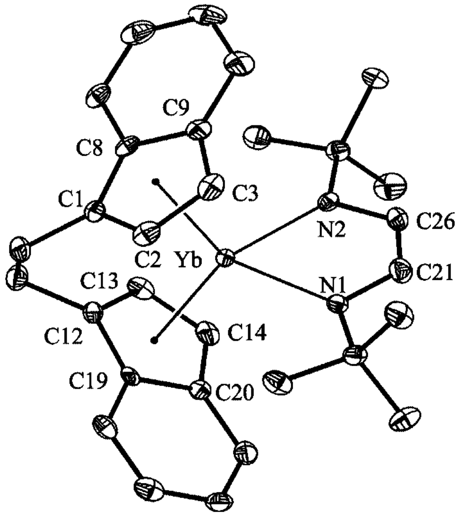


Figure 4. Molecular structure of complex [$(C_9H_6CH_2)_2$Yb(*t*Bu-NCHCHN*t*Bu)] (**10**).

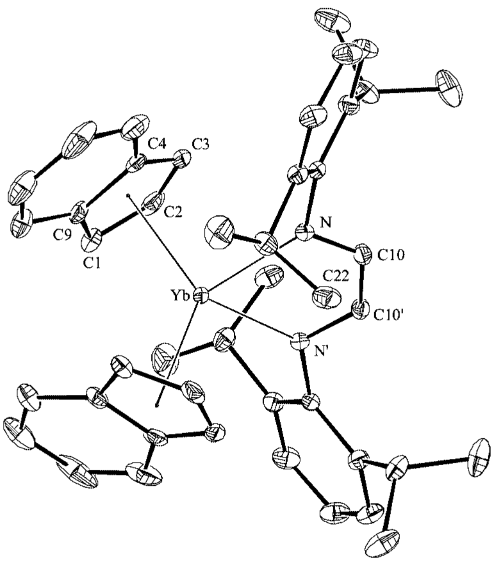


Figure 5. Molecular structure of complex [$(C_9H_7)_2$Yb(*i*Pr_2-C_6H_3NCHCHNC_6H_3*i*Pr_2)] (**13**).

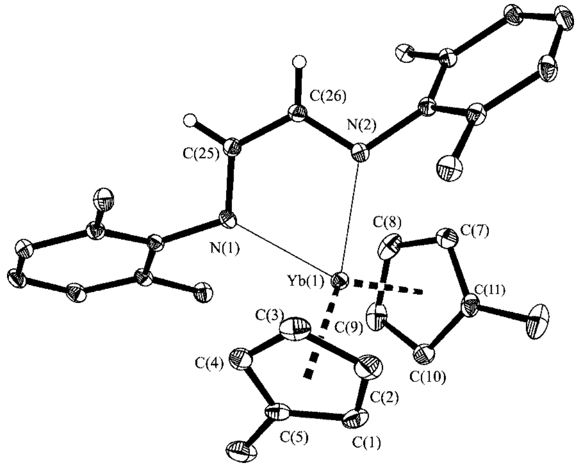


Figure 6. Molecular structure of complex [$(C_5MeH_4)_2$Yb(*i*Pr_2-C_6H_3NCHCHNC_6H_3*i*Pr_2)] (**14**). The methyl carbon atoms of the *i*Pr groups are omitted.

sion of the π-aromatic ligands coordinated to the ytterbium atom and the diazabutadiene ligand. The Yb–$Cp_{Centr.}$ bond lengths observed in the related complexes **7**–**10** increase as a function of the bulkiness of the η^5-coordinated ligand and become the maximum for the pentamethylcyclopentadienyl ligand, reflecting its highest steric demand in the series of synthesized compounds. The same tendency is also observed for Yb–N bond lengths in complexes **7**–**10** (Table 1). Comparison of the bonding situation in complexes **9** and **13**, containing the same indenyl ligands but different diazadienes, shows that the replacement of the *tert*-butyl radical by bulkier 2,6-diisopropylphenyl in the diazadiene molecule results in noticeable lengthening of the Yb–N bonds. The bond lengths within the diazabutadiene ligand of compounds **7**–**10**, **13**, **14** indicate its radical-anionic character. An electron transfer from the ytterbium atom to the LUMO of the ligand is expected to cause delocalization of the charge over the whole conjugated NCCN fragment which involves changes in the bond lengths. Compared with the N=C and C–C bond lengths in the parent free diazadiene molecules,[20,21] the N=C bonds in the diazadiene ligands of complexes **7**–**10**, **13**, **14** are substantially elongated, while the C–C bonds are shortened and close to the values of aromatic C–C bonds.[22] The structural parameters of complexes **7**–**10**, **13**, **14** are in agreement with the trivalent oxidation state of the ytterbium atom and the radical-anionic character of the diazadiene ligand. Unexpectedly, the complexes **7**–**11**, **13**, **14** in the solid state as well as in toluene solutions are ESR silent in the temperature range 173 to 300 K. This fact is attributable either to a substantial broadening of the signal of the diazadiene radical anion in the field of the paramagnetic Yb^{III} ion or to antiferromagnetic coupling of the spin carriers. The IR and UV/Vis spectra of complexes **7**–**11**, **13**, **14** identify the diazabutadiene ligand as a radical anion. The complexes **7**–**11**, **13**, **14** are paramagnetic with the values of the effective magnetic moments in the region 3.0–4.8 μ_B (300 K), giving evidence for the trivalent oxidation state of the ytterbium atom.[10]

Table 1. Values of effective magnetic moments (μ_{eff}, μ_B, 300 K), and selected bond lengths [Å] and bond angles [°] for complexes [$Cp_2Yb(t\text{BuNCHCHN}t\text{Bu}^{-\cdot})$].

Complex		Ref.	μ_{eff} [μ_B] 300 K	Bond lengths [Å] and bond angles [°] C–N[a]	C–C[a]	Yb–N	Yb–$Cp_{Centr.}$	$Cp_{Centr.}$–Yb–$Cp_{Centr.}$
[$(C_5H_5)_2Yb(t\text{BuNCHCHN}t\text{Bu})$]	**7**	[12]	4.80	1.31(2) 1.30(2)	1.40(2)	2.306(9) 2.309(9)	2.324(7) 2.334(4)	128.1(2)
[$(C_5Me_5)_2Yb(t\text{BuNCHCHN}t\text{Bu})$]	**8**	[13]	4.1	1.339(4) 1.326(5)	1.398(5)	2.385(3) 2.394(3)	2.414(2) 2.401(2)	130.27(6)
[$(C_9H_7)_2Yb(t\text{BuNCHCHN}t\text{Bu})$]	**9**	[14]	3.4	1.323(8) 1.309(8)	1.412(9)	2.318(5) 2.335(5)	2.383(3) 2.376(3)	125.44(11)
[$(C_9H_6CH_2)_2Yb(t\text{BuNCHCHN}t\text{Bu})$]	**10**	[14]	3.0	1.324(7) 1.331(6)	1.420(7)	2.321(4) 2.343(5)	2.371(2) 2.383(2)	120.05(8)
[$(C_{13}H_9)_2Yb(t\text{BuNCHCHN}t\text{Bu})$]	**11**	[15]	4.8	–	–	–	–	–
[$(C_9H_7)_2Yb(i\text{Pr}_2C_6H_3\text{NCHCHNC}_6H_3i\text{Pr}_2)$]	**13**	[16]	3.4	1.330(4)	1.412(7)	2.381(3)	2.376(2)	124.9(6)
[$(C_5MeH_4)_2Yb(i\text{Pr}_2C_6H_3\text{NCHCHNC}_6H_3i\text{Pr}_2)$]	**14**	[17]	4.06	1.338(2) 1.335(2)	1.395(2)	2.3577(14) 2.3926(13)	2.332(2) 2.331(2)	127.27(2)

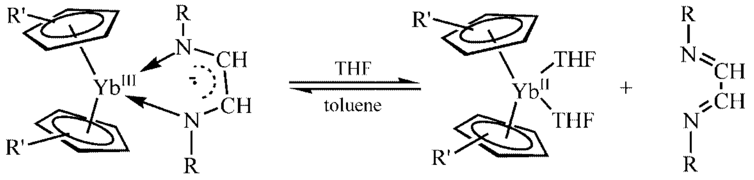
[a] C–N and C–C bond lengths within the NCCN fragment.

Magnetic measurements of crystalline samples of complexes **9**, **10**,[14] **13**,[16] **14**[17] in the temperature range 2–300 K show a similar shape of the plots of $1/\chi$ versus T and μ versus T with nonlinear dependence as a function of temperature. The effective magnetic moments of the complexes **9**, **10**, **13** increase from 1.50–1.60 μ_B at 2 K to 3.0–3.4 μ_B at 300 K. The values of the effective magnetic moments of **9**, **10**, **13** in benzene solution at 300 K, estimated according to the published procedure,[23] are in agreement with the data obtained for the crystalline samples by the SQUID method. Trivalent ytterbium is paramagnetic with an electron configuration of $4f^{13}$, and the expected magnetic moment of Yb^{III} complexes is 3.8 μ_B at 5–30 K and 4.5 μ_B at 90–300 K.[24] For complexes containing noninteracting spins, their contribution to the molar magnetic susceptibility is additive. A Yb^{III} complex additionally containing a radical anion, as is suggested for **9**, **10**, **13**, should show a magnetic moment of 4.2 μ_B in the temperature range of 5–30 K and 4.8 μ_B in the temperature range of 90–300 K, provided that the spins of the two unpaired electrons do not interact. However, the experimental values of the magnetic moments obtained for **9**, **10**, **13** are considerably lower than the expected values which can be caused either by redox tautomerism between paramagnetic [$(C_9H_7)_2Yb^{III}(L^{-\cdot})$] and diamagnetic [$(C_9H_7)_2Yb^{II}(L^0)$] molecules or by antiferromagnetic coupling of the two unpaired electrons in [$(C_9H_7)_2Yb^{III}(L^{-\cdot})$] (L = diazadiene). Antiferromagnetic coupling between trivalent rare earth ions and paramagnetic semiquinone ligands was found to be dominating for the series of complexes Ln(DTBSQ)$(HBPz_3)_2$ (Ln = Er, Tb, Dy, Yb; DTBSQ = 3,5-di-*tert*-butylsemiquinone; $HBPz_3$ = hydrotrispyrazolylborate).[25] Hatfield and co-workers have described a strong exchange coupling between the lanthanide ions and the phthalocyaninato ligand radical in bis(phthalocyaninato)lanthanide sandwich compounds $(Pc^{2-})Ln^{III}(Pc^{1-})$ (Ln = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). The value of the room-temperature magnetic moment for the trivalent ytterbium antiferromagnetically coupled with an organic radical anion was calculated as 3.46 μ_B.[26] The value of the magnetic moment (4.06 μ_B) observed at 300 K for complex **14** suggests that both ferro- and antiferromagnetic coupled states of Yb^{3+} and the radical anion are present at room temperature. The analysis of the plots $1/\chi$ versus T and μ versus T suggests that an antiferromagnetic spin interaction is a plausible reason for the low magnetic moments, however the available data do not allow definite exclusion of the existence of redox tautomers for **9**, **10**, **13**, **14**.

Complexes **8**–**10**, **13** have demonstrated uncommon solvent-mediated intramolecular redox transformations in solutions.[13,14,16] Complexes **8**–**10**, **13** in the crystalline state as well as in nonsolvating solvents (aromatic or aliphatic hydrocarbons) exist as paramagnetic derivatives of trivalent ytterbium coordinated by the diazadiene radical anion [$(R)_2Yb^{III}(L^{-\cdot})$] (R = C_5Me_5, C_9H_7, $-CH_2C_9H_6$; L = diazadiene), while in solvating solvents (THF) these compounds are diamagnetic. ^1H NMR, UV/Vis spectroscopy, and magnetic measurements proved the diamagnetism of complexes **8**–**10**, **13** in THF solutions and therefore the divalent oxidation state of the ytterbium atom. Moreover, recrystallization of complexes **8**–**10**, **13** from THF/hexane mixtures allowed the recovery of the parent ytterbocene in good yields. Dissolution of **8**–**10**, **13** in THF caused displacement of the radical-anionic diazadiene ligand by THF molecules. This process implies an electron transfer from the diazadiene radical anion to the ytterbium ion, resulting in the oxidation of the ligand to neutral diazadiene and reduction of Yb^{III} to Yb^{II} followed by substitution of the neutral diazadiene ligand by THF molecules (Scheme 5).[14,16]

One can suppose that steric repulsion of the bulky indenyl, pentamethylcyclopentadienyl, and diazadiene ligands is decisive for the examined reactions and the elongation and weakening of the Yb–N bonds in complexes **8**–**10**, **13**. Hence, the energy of the Coulomb interaction between the $[(R)_2Yb^{III}]^+$ cationic species and the radical anion of diazadiene is comparable with that of the coordination bonds between R_2Yb^{II} and THF molecules, and as a result the diazadiene ligand redox substitution becomes feasible.

Unlike complexes **8**–**10**, **13**, compound [$Cp_2Yb(t\text{BuNCHCHN}t\text{Bu})$] (**7**) did not undergo a reductive substitution process and remained paramagnetic in THF solutions.[12] Such a distinction in solution redox behavior is



8-10, 13

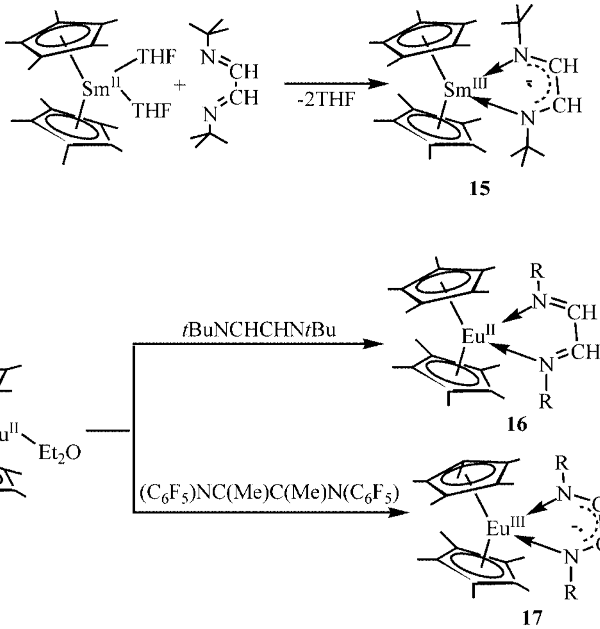
Scheme 5.

obviously caused by the structural difference of **7** and namely by the Yb–N bond lengths which are the shortest in the series of related compounds (Table 1). The shorter contact between cationic and anionic moieties in complex **7** should result in an increase in the energy of the Coulomb interaction, and the energy consumption for the reductive substitution of the diazadiene ligand can not be overcome by formation of coordination ytterbium–oxygen bonds. A similar behavior towards THF was described by Evans and co-workers for decamethylsamarocene complexes with aromatic polycyclic ligands.[27] However, unlike complexes **8**–**10**, **13**, the samarium derivatives can not be regenerated by removal of THF and addition of aromatic or aliphatic solvents.

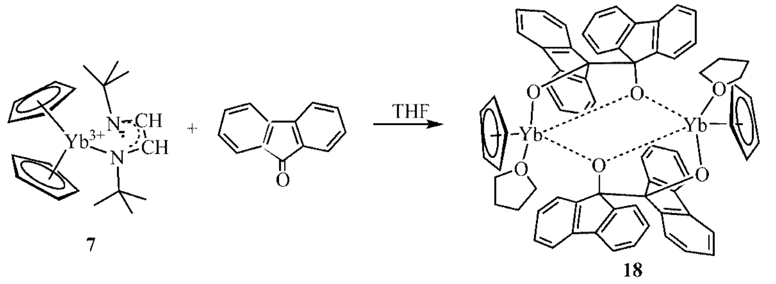
Distinctions in the reductive reactivity of metallocene derivatives of divalent samarium and europium toward diimines from that of ytterbium compounds are defined by the Ln^{II}/Ln^{III} transformation potentials characteristic for these elements. The reducing capacity of Ln^{II} compounds increases in the triad Eu < Yb < Sm (for comparison, reduction potentials M^{III}/M^{II} in aqueous solution vs. SHE: Eu, –0.35; Yb, –1.15; Sm, –1.55 V).[9a] Decamethylsamarocene easily reduced *N*,*N′*-di-*tert*-butyl-1,4-diazabutadiene, affording the derivative of trivalent samarium coordinated by the radical anion of diazadiene $(C_5Me_5)_2Sm^{III}$-(tBuNCHCHNtBu$^{-\cdot}$) (**15**),[7c] whereas the reaction of the europium analogue $(C_5Me_5)_2Eu(Et_2O)$ resulted in the formation of the adduct with the neutral diazadiene ligand $(C_5Me_5)_2Eu^{II}$(tBuNCHCHNtBu^0) (**16**).[28] On the other hand, the diazadiene $(C_6F_5)N{=}C(Me){-}C(Me){=}N(C_6F_5)$ possessing higher electron affinity oxidized $(C_5Me_5)_2Eu$-(Et_2O) in toluene solution at room temperature to the trivalent europium complex $(C_5Me_5)_2Eu^{III}\{C_6F_5NC(Me)C$-$(Me)NC_6F_5{}^{-\cdot}\}$ (**17**) (Scheme 6).[28] The difference in the oxidation state of the europium atom in complexes **16** and **17** is undoubtedly proven by the metric parameters and magnetic measurements of the compounds.

Solvent-mediated reversible intramolecular redox reaction, analogous to that previously described for ytterbium compounds,[13,14,16] was reported for complex **17**.

The reactivity of metallocene-type complexes of trivalent lanthanides containing the radical anion of diazadiene is poorly investigated. Complexes **7**–**11**, **13** are inactive in olefin polymerization. Reaction of complex **7** with 9-fluorenone in a 1:1 molar ratio in THF was found to occur with oxidation of the diazadiene radical anion, abstraction of



Scheme 6.



Scheme 7.

one cyclopentadienyl ring, pinakol condensation, and formation of the dimeric Yb^{III} complex $[CpYb(\mu^2\text{-}OC_{13}H_8\text{–}C_{13}H_8O)(THF)]_2$ (**18**) (Scheme 7).[13] An X-ray diffraction study of complex **18** has revealed that two [CpYb(THF)] moieties are linked by two 9,9-difluorenyldialcoxo ligands (Figure 7).

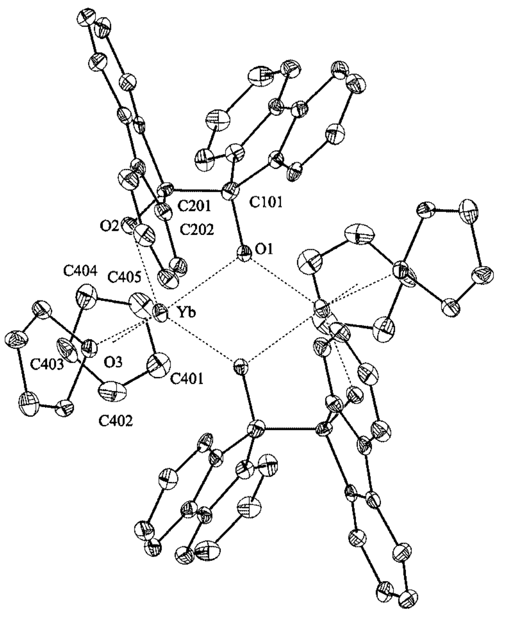
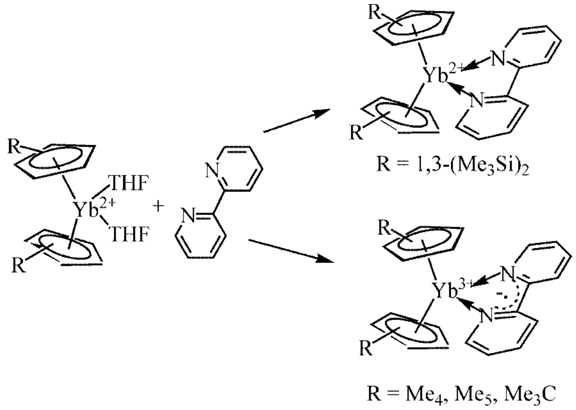


Figure 7. Molecular structure of complex $[CpYb(\mu^2\text{-}OC_{13}H_8\text{–}C_{13}H_8O)(THF)]_2$ (**18**).

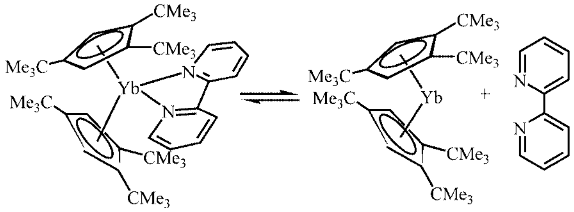
2,2′-Bipyridine (bipy), which has a virtually planar structure and contains a N=C–C=N fragment, can be considered as a diimine ligand. The reduction potential of bipy (–2.18 V)[29] is noticeably lower than that of 1,4-di-*tert*-butyl-1,4-diazabuta-1,3-diene (–1.822 V),[4] and bipyridine derivatives of ytterbium have promise from the standpoint of possible redox tautomeric transformations. Andersen and co-workers have investigated reactions of ytterbocenes bearing cyclopentadienyl ligands with different substituents $[Cp''_2Yb(Et_2O)]$ {Cp″ = C_5Me_5, C_5Me_4H, 1,3-$(Me_3C)_2$-C_5H_3, 1,3-$(Me_3Si)_2C_5H_3$} with 2,2′-bipyridine (bipy) and phenanthroline (phen), which afforded complexes $[Cp''_2Yb(L)]$ (L = bipy, phen).[30,31] The various ytterbocenes interacted differently with bipy and phenanthroline depending on the steric and electronic properties of the substituents on the cyclopentadienyl ligands, which also influence the extent of paramagnetism of the resultant compounds $[Cp''_2Yb(L)]$. The electron-withdrawing $SiMe_3$ groups make the metal more electropositive thus stabilizing the Yb^{II} oxidation state; the derived ytterbocene did not reduce bipy and phen, and the reactions afforded the adducts with neutral L $[Cp''_2Yb^{II}(L^0)]$. The ytterbocenes containing electron-donating alkyl groups (pentamethyl, tetramethyl, *t*Bu) on the cyclopentadienyl rings tend to reduce bipy and phen, affording paramagnetic Yb^{III} complexes containing a bipy radical anion $[Cp''_2Yb^{III}(L^{-\bullet})]$ (Scheme 8).



Scheme 8.

The measured magnetic moments of obtained complexes, which are less than those expected for complexes $[Cp''_2Yb^{III}(L^{-\bullet})]$ containing two noninteracting paramagnetic centers, are explained by electron exchange model for spin coupling between Yb^{III} and the single unpaired electron in the anion radical $L^{-\bullet}$. The extent of paramagnetism of paramagnetic complexes $[(C_5Me_5)_2Yb(bipy\text{-}X)]$ with 4,4′-disubstituted bipyridines (X = Me, Me_3C, OMe, Ph, CO_2Me, CO_2Et) was found to be dependent on the substituents on the bipyridine ligands. The values of χ and μ_{eff} at 400 K increase in the series OMe < H < CO_2R (R = Me, Et) $\leq$ Ph and correlate with the electron-withdrawing properties of the substituents.[32]

Unusual for substituted ytterbocene bipyridine adducts, rapid exchange (on the NMR time scale) between the complex $[\{1,2,4\text{-}(Me_3C)_3C_5H_2\}_2Yb(bipy)]$ and free 2,2′-bipyridine was observed in [D_8]toluene in a wide range of temperatures, thus indicating fluxional behavior in solution (Scheme 9).[31]



Scheme 9.

The electrochemical studies of complexes [$(C_5Me_5)_2$Yb(L)] (L = bipy, phen) have demonstrated that stabilization of their respective LUMOs of diimine ligands and destabilization of metal f-orbitals favors the spontaneous ground-state charge-transfer process. The spectroscopic data from the f-f transition region for [$(C_5Me_5)_2$Yb(L)] indicate that the f-orbital splitting in these compounds is not sensitive to the differences in the electronic structures of bipy and phen. The separation between the ligand-based oxidation wave ($L^{0/-}$) and the metal-based reduction wave ($Yb^{III/II}$) in the adducts [$(C_5Me_5)_2$Yb(L)] is 0.79 V for both bipy and phen derivatives. In the spectra of complexes [$(C_5Me_5)_2$Yb(L)] previously unreported, the near-IR bands have been assigned to ligand(π*)-to-metal(f-orbital) charge-transfer transitions. The Raman spectra give evidence of the radical-anionic nature of the diimine ligands in these complexes.[33]

The bis(indenyl) derivative [$(C_9H_7)_2Yb(THF)_2$] (**4**) reacted with bipy in THF at room temperature to yield the Yb^{II} complex [$(C_9H_7)_2Yb^{II}(bipy^0)$] (**19**). This is consistent with the lower electron-donating ability of the indenyl ligand compared with that of the pentamethylcyclopentadienyl ligand that results in lower reducing capacity of complex **4**. Surprisingly despite the higher electron affinity of diazadiene **1**, it did not react with complex **4** in THF media, while the reaction with bipy immediately afforded compound **19** in good yield. Obviously that can be attributed to the higher steric demand of the ligand **1**. Magnetic measurement, ^{1}H NMR, IR, and UV/Vis spectra of **19** indicate that the complex is a diamagnetic adduct with neutral bipy. The X-ray diffraction analysis of complex **19** has revealed that the crystals contain two crystallographically independent molecules. The Yb–C bond lengths indicate the divalent state of the ytterbium atom. The most essential difference of the two crystallographically independent molecules **19** are the dihedral angles between the planes of the pyridine rings: 11.2(8)° and 4.8(8)°.[16] 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. This angle in free bipy and in complexes with the neutral bipy ligand is in the region 10–17°;[29,30] 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 of **19**. However, the identity of the Yb–C bond lengths and the geometry of the bipy ligands in both molecules **19** rules out the existence of redox isomers. Apparently, the difference in the dihedral angles of the bipy ligands in two crystallographically independent molecules is associated not with the electronic state but with steric restrictions caused by the mutual arrangement of the indenyl and bipy ligands. Furthermore, in one of the molecules, the six-membered fragments of the indenyl ligands are located above each pyridine ring of the bipyridine ligand (Figure 8).

Therefore, an increase in the dihedral angle between the pyridine rings should result in close contacts between indenyl and bipy ligands and consequently in the increase in the energy of nonbonded repulsions.

3. Reactions Resulting in C–C Bond Formation

As mentioned earlier, the Yb–N bond lengths and the reversibility of the intramolecular metal–ligand electron transfer can be regulated by tuning the steric demand of the ligands coordinated to the ytterbium atom and the substituents at the nitrogen atoms of the diimine molecule. However, successive increase in the π-aromatic ligand size in the series C_5MeH_4, C_9H_7, $C_{13}H_9$ led (in the case of fluor-

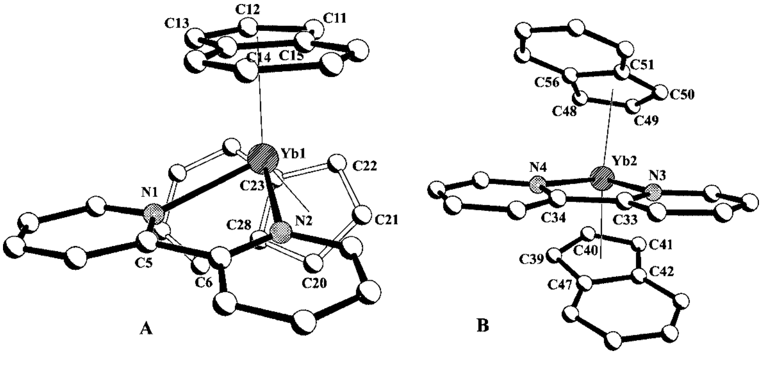
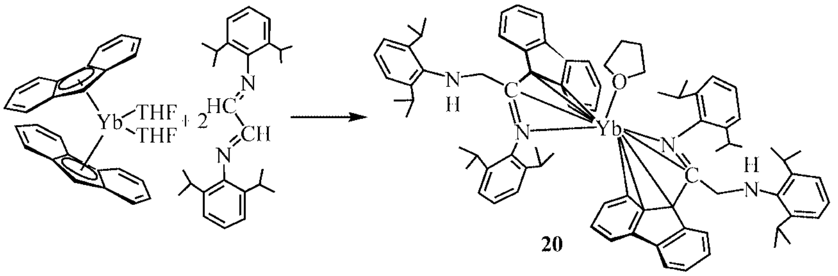


Figure 8. Two crystallographically independent molecules of complex [$(C_9H_7)_2Yb^{II}(bipy^0)$] (**19**).



Scheme 10.

enyl) to a dramatic change in the pathway of the reaction of 1,4-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (**12**) with a related ytterbocene. Unlike the previously mentioned reactions of ytterbocenes with diimines, the reaction of the bis(fluorenyl) complex $[(C_{13}H_9)_2Yb(THF)_2]$ with bulkier **12** under the same conditions did not occur with oxidation of the ytterbium atom but resulted in the formation of the unusual Yb^{II} derivative $[Yb\{\eta^5\text{-}C_{13}H_8C(=N\text{–}C_6H_3i\text{Pr}_2\text{-}2,6)CH_2NHC_6H_3i\text{Pr}_2\text{-}2,6\}_2(THF)]$ (**20**) which was isolated in 80% yield (Scheme 10).[34]

The Yb^{II} cation is η^5-coordinated by two novel monoanionic multifunctional ligands $\{C_{13}H_8C(=N\text{–}C_6H_3\text{-}i\text{Pr}_2\text{-}2,6)CH_2NHC_6H_3i\text{Pr}_2\text{-}2,6\}^-$ arising from unprecedented coupling of the allylic carbon atom of the fluorenyl ligand with the imino carbon atom of the diazadiene **12** (Figure 9).

The C–C bond formation in **20** also implies migration of the two H atoms initially bonded to the coupled carbon atoms and acquisition of these hydrogen atoms by the second imino group which results in the hydrogenated $–CH_2–NH–$ fragment. In the course of the reaction, the coordination mode of the fluorenyl ligand to the Yb atom changes from the η^5-type in the starting complex $[(C_{13}H_9)_2Yb(THF)_2]$,[15] to a rather unusual η^3-type by one carbon atom of the five-membered ring and two carbon atoms of the six-membered ring. The η^2-coordination of the imino group to the Yb atom results in formation of the planer η^5-bonded heteropentadienyl frame. The bonding situation gives evidence of a delocalized π system in the heteropentadienyl fragment. The arrangement around the ytterbium atom in **20** determines the geometry of the heteropentadienyl bent sandwich complex.

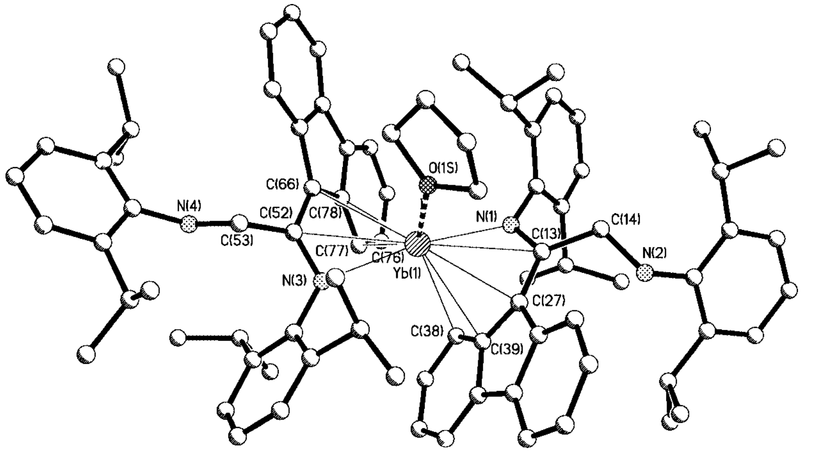
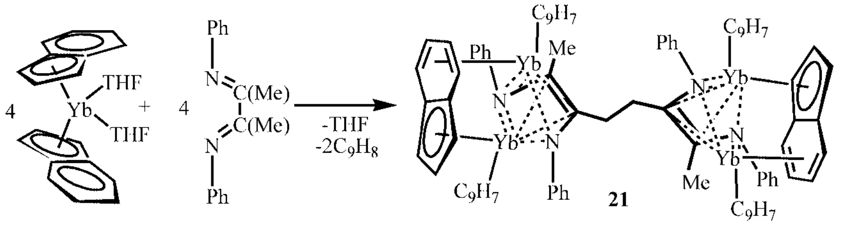


Figure 9. Molecular structure of complex $[Yb\{\eta^5\text{-}C_{13}H_8C(=N\text{–}C_6H_3i\text{Pr}_2\text{-}2,6)CH_2NHC_6H_3i\text{Pr}_2\text{-}2,6\}_2\ (THF)]$ (**20**).



Scheme 11.

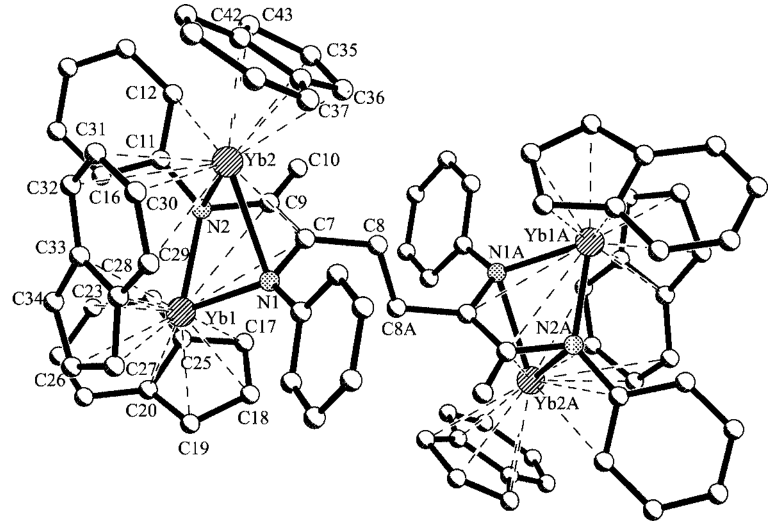
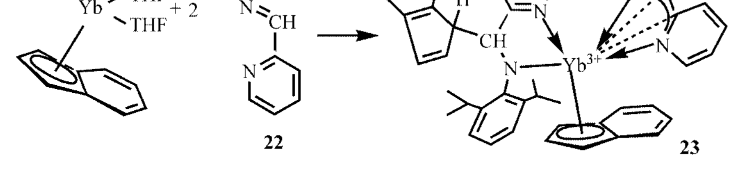


Figure 10. Molecular structure of complex $[Yb_2(\mu\text{-}\eta^5{:}\eta^4\text{-}C_9H_7)(\eta^5\text{-}C_9H_7)_2\{\mu\text{-}\eta^4{:}\eta^4\text{-}PhNC(CH_2){=}C(Me)NPh\}]_2$ (**21**).

Another example of C–C bond formation was documented for the reaction of bis(indenyl)ytterbium complex $[(C_9H_7)_2Yb(THF)_2]$ with an equimolar amount of the diazabutadiene PhN=C(Me)–C(Me)=NPh. The reaction occurred with reductive diimine coupling and afforded the tetranuclear complex $[Yb_2(\mu\text{-}\eta^5{:}\eta^4\text{-}C_9H_7)(\eta^5\text{-}C_9H_7)_2\{\mu\text{-}\eta^4{:}\eta^4\text{-}PhNC(CH_2){=}C(Me)NPh\}]_2$ (**21**) (Scheme 11).[35]

The reaction is accompanied by indene formation which obviously arises as a product of partial cleavage of Yb–indenyl bonds and hydrogen abstraction by the indenyl radical from a molecule of solvent or diimine. The molecule of **21** has a tetranuclear core which consists of two dinuclear units $[Yb_2(\mu\text{-}\eta^5{:}\eta^4\text{-}C_9H_7)(\eta^5\text{-}C_9H_7)_2\{\mu\text{-}\eta^4{:}\eta^4\text{-}PhNC(CH_2){=}C(Me)NPh\}]$ connected by the CH_2–CH_2 bridge, as a result of hydrogen abstraction from one of the methyl radicals at the imino group of the diazadiene ligand and coupling of these methylene carbon atoms (Figure 10).

The dinuclear fragments are assembled due to unusual bridging μ-η^5:η^4-coordination of the indenyl ligand and μ-η^4:η^4-coordination of the diimine ligand. Each ytterbium atom in complex **20** is coordinated by two indenyl ligands but in different ways. One ytterbium atom of the dinuclear unit is η^5-bound with two cyclopentadienyl fragments of two indenyl ligands, while the second ytterbium atom is coordinated by the five- and six-membered rings in η^5- and η^4-fashion, respectively. Coordination of the six-membered ring leads to noticeable distortion of its planarity. Such μ-bridging coordination of indenyl ligands is rather rare[36] 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 diimine ligand are also involved in metal–ligand bonding through η^2-coordination to the ytterbium atom. The average Yb–C(C_5-indenyl) and Yb–N bond lengths in **21** are somewhat different for the ytterbium atoms within a dinuclear unit. Complex **21** is paramagnetic with the experimental value of the effective magnetic moment 2.6 μ_B (293 K), which is intermediate between the average μ_{eff} value reported for Yb^{III} derivatives and that of diamagnetic Yb^{II} compounds.[10] Thus both the X-ray analysis data and magnetic measurements provide evidence that complex **21** is a mixed-valent compound containing both Yb^{II} and Yb^{III} atoms. The bonding situation within the NCCN fragment of **21** is consistent with a dianionic character of the diimino ligand. The double C–C bond of a doubly reduced enediamido moiety also participates in a dinuclear core formation, coordinating to both ytterbium atoms in η^2-fashion. The length of the carbon–carbon bond formed in the reaction is characteristic for ordinary C–C σ bonds.[22]



Scheme 12.

Iminopyridines containing a conjugated NCCN fragment might be considered as diimino ligands. Formation of a C–C bond resulted from N=C bond insertion into the Yb–(η^5-C_9H_7) bond which was observed in the reaction of bis(indenyl) derivative [$(C_9H_7)_2Yb(THF)_2$] with a twofold molar excess of *N*-2,6-diisopropylphenylimino-2-pyridine (**22**) (THF, 20 °C), which led to formation of the Yb^{III} complex [Yb(η^5-C_9H_7){N(2,6-$i$$Pr_2C_6H_3$)CH($C_9H_7$)($C_5H_5N$)}{$\eta^4$-2,6-$i$$Pr_2C_6H_3$NCH($C_5H_5N$)}] (**23**) (Scheme 12).[37]

Paramagnetism of complex **23** (μ_{eff} = 4.3 μ_B, 293 K) indicates the trivalent oxidation state of the ytterbium atom.[10] Compound **23** is a half-sandwich complex in which the coordination sphere of the Yb atom is set up by an η^5-coordinated C_9H_7 anion, two nitrogen atoms of an amido-pyridinato ligand, and two nitrogen atoms of an iminopyridine radical anion (Figure 11).

The chelating amido-pyridinato ligand arises from insertion of the N=C bond of iminopyridine **22** into the Yb–(η^5-C_9H_7) bond. This insertion results in Yb–C_9H_7 bond cleavage and formation of Yb–N and C–C bonds. To the best of our knowledge this is the sole example of such an insertion. The amido-pyridinato ligand is bound to the Yb atom by one covalent and one coordination bond. The bond angles about the methyne carbon atom of the amido-pyridinato ligand prove that, unlike the related carbon in the parent **22**, it adopts sp^3 hybridization. The geometric parameters within the planar NCCN fragment of the iminopyridine ligand in **22** give evidence of its reduced radical-anionic character. Formation of the amido-pyridinato ligand in complex **22** obviously implies rearrangement of the coordination fashion of one of the indenyl ligands in the $(C_9H_7)_2Yb$ fragment from η^5 to η^1 and subsequent insertion of the N=C bond of the iminopyridine molecule coordinated to the ytterbium atom into the Yb–C_9H_7 bond (Scheme 13).

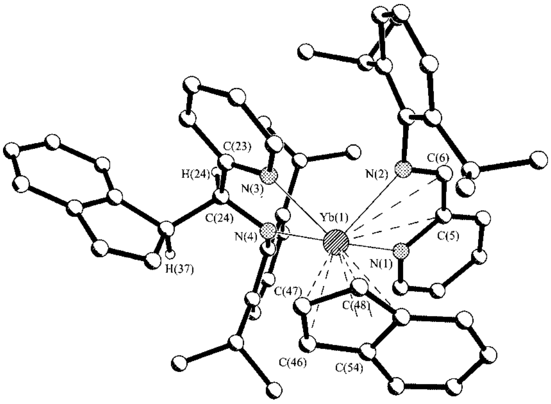


Figure 11. Molecular structure of complex [Yb(η^5-C_9H_7){N(2,6-$i$$Pr_2C_6H_3$)CH($C_9H_7$)($C_5H_5N$)}{$\eta^4$-2,6-$i$$Pr_2C_6H_3$NCH($C_5H_5N$)}] (**23**).

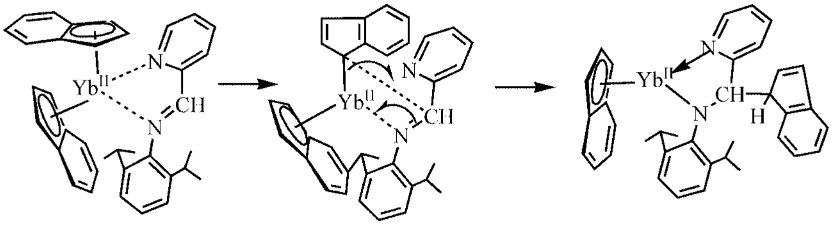
4. Reactions Resulting in C–H Bond Activation

In order to evaluate the influence of the steric and electronic properties of the diimine on the pathway of its reaction with ytterbocenes, the bis(fluorenyl) compound [$(C_{13}H_9)_2Yb(THF)_2$] was treated with the bulky diimine $i$$Pr_2C_6H_3N$=C(Me)C(Me)=$NC_6H_3$$i$$Pr_2$ (**23**) bearing two methyl substituents at the imino carbon atoms (in contrast to diimine **12**). It was found that replacement of the imino hydrogen atoms by two methyl radicals dramatically influenced the reaction pathway and led to formation of the novel half-sandwich Yb^{II} derivative [Yb(η^5-$C_{13}H_9$){2,6-$i$$Pr_2C_6H_3$–N=C($CH_3$)–C($CH_2$)=N–$C_6H_3$$i$$Pr_2$-2,6}(THF)] (**24**) (Scheme 14).[34]

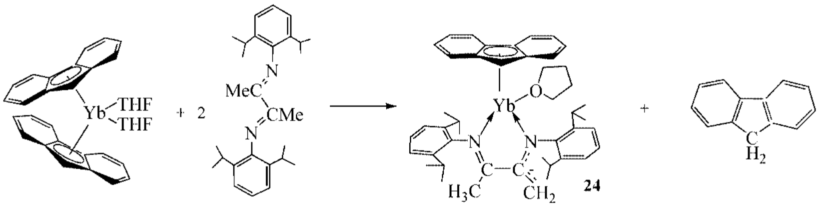
The compound is diamagnetic, corresponding to the Yb^{II} oxidation state. The coordination sphere of the ytterbium atom in **24** is set up by one fluorenyl ligand coordinated in η^5-fashion, two nitrogen atoms of the novel monoanionic ligand $\{2,6\text{-}i\text{Pr}_2C_6H_3\text{–N=C(CH}_3\text{)–C(CH}_2\text{)=N–}C_6H_3 i\text{Pr}_2\text{-2,6}\}^-$ (resulting from proton abstraction from the methyl radical at the imino group of the parent diimine), and one THF molecule (Figure 12).

Unlike the geometry of the diimine radical anions in Yb^{III} complexes exhibiting redistribution of the bond lengths characteristic of the delocalized NCCN π system, the geometry of the monoanionic ligand in **24** indicates a partial double bonding and delocalization of the negative charge only in the NCC fragment (Scheme 15).[34] Flat geometry of the methylene carbon atom (the sum of the bond angles is 359.8°) in this fragment and the C–C bond length give evidence for sp^2 hybridization of this carbon atom.

Concentration of the negative charge on the N atom of the $NCCH_2$ fragment results in shortening of the respective Yb–N bond and nonequivalence of the Yb–N bonds. Partial double C–C bonding in the $NCCH_2$ fragment becomes evident also from NMR spectra of **24** which indicate that the two methylene protons become diastereotopic. The geometry of the $NCCH_2$ fragment may be formally presented as the result of the existence and interconversion of two resonance forms of complex **24** (Scheme 15). Isolation of fluorene from the reaction in nearly quantitative yield



Scheme 13.



Scheme 14.

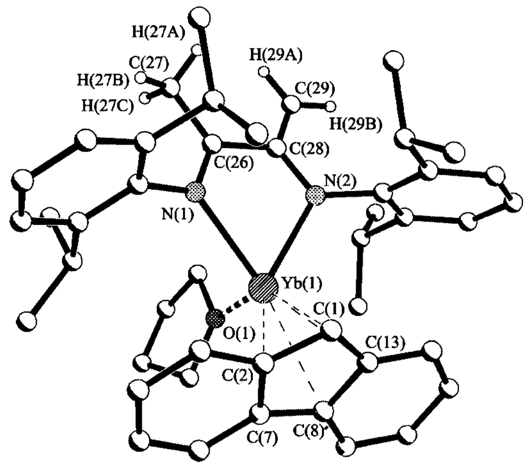
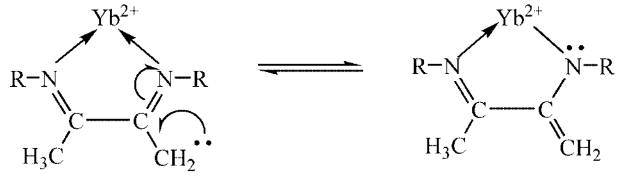


Figure 12. Molecular structure of complex [Yb(η^5-$C_{13}H_9$){2,6-$i$$Pr_2C_6H_3$–N=C($CH_3$)–C($CH_2$)=N–$C_6H_3$$i$$Pr_2$-2,6}(THF)] (**24**).



Scheme 15.

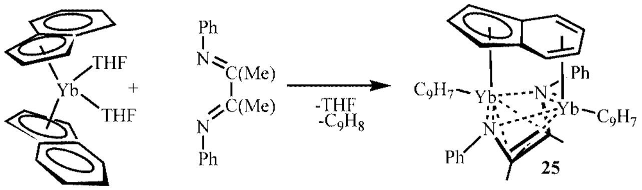
proves that the fluorenyl anion (or radical) is responsible for the proton abstraction from **23** and formation of the monoanionic diimino ligand.

The previously mentioned reaction of the formation of complex **21** (Scheme 11) also implies the stage of C–H bond activation. It is noteworthy that the substituents at the imino carbon atoms of the diimine molecule strongly influence their reactions with ytterbocenes. Thus the diimine $i$$Pr_2C_6H_3$N=CHCH=N$C_6H_3$$i$$Pr_2$ (**12**) easily oxidized complex [($C_{13}H_9$)$_2$Yb(THF)$_2$], and the reaction afforded complex [(C_9H_7)$_2$Yb^{III}($i$$Pr_2C_6H_3$NCHCHN$C_6H_3$$i$$Pr_2$$^{-\cdot}$)] (**13**),[16] while the analogue bearing two methyl groups at the imino carbon atoms $i$$Pr_2C_6H_3$N=C(Me)C(Me)=N$C_6H_3$$i$$Pr_2$ (**23**) did not react with the same ytterbocene even after continuous heating in toluene at 60 °C.[38]

5. Reactions Resulting in Yb–C Bond Cleavage

Yb–C bond cleavage was observed in several reactions of ytterbocenes with diazadienes and iminopyridines and was always accompanied by oxidation of the ytterbium atom to the trivalent state. This type of reactivity has never been documented for the reactions with bipy or phen.

The reaction of [(C_9H_7)$_2$Yb(THF)$_2$] with diimine PhN=C(Me)–C(Me)=NPh in equimolar amounts was mentioned to afford a tetranuclear mixed-valent ytterbium complex [Yb$_2$(μ-η^5:η^4-C_9H_7)(η^5-C_9H_7)$_2${μ-η^4:η^4-PhNC(CH_2)=C(Me)NPh}]$_2$ (**21**) that resulted from reductive diimine coupling. The same reaction in 1:2 molar ratio resulted in formation of the dinuclear mixed-valent complex [Yb$_2$(μ-η^5:η^4-C_9H_7)(η^5-C_9H_7)$_2${μ-η^4:η^4-PhNC(Me)=C(Me)NPh}] (**25**) (Scheme 16).[35] The reaction occurred with partial cleavage of the Yb–C bonds and was accompanied by indene formation.



Scheme 16.

Complex **25** is paramagnetic. The effective magnetic moment found for **25** (μ_{eff} = 2.7 μ_B at 293 K) is intermediate between the average μ_{eff} value reported for Yb^{III} derivatives (4.3 μ_B) and that of diamagnetic Yb^{II} compounds[10] and provides evidence of different oxidation states of ytterbium atoms. Assembling of the dinuclear species of **25** becomes possible due to the unusual bridging μ-η^5:η^4-coordination of the indenyl ligand and μ-η^4:η^4-coordination of the doubly reduced diimine ligand (Figure 13).

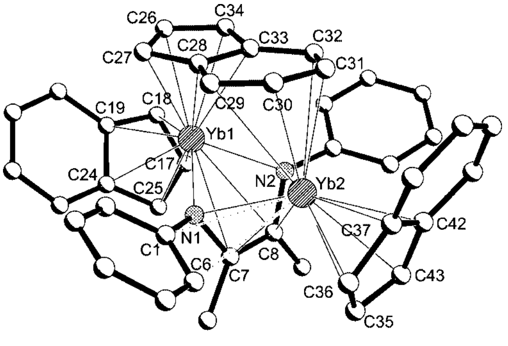
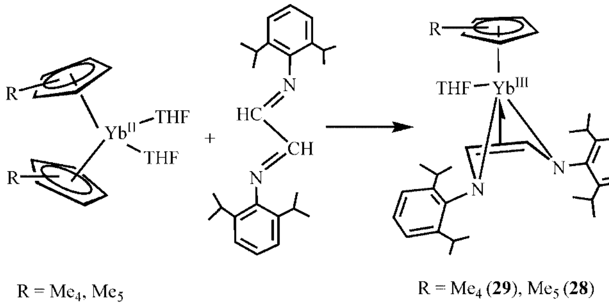


Figure 13. Molecular structure of complex [Yb$_2$(μ-η^5:η^4-C_9H_7)(η^5-C_9H_7)$_2${μ-η^4:η^4-PhNC(Me)=C(Me)NPh}] (**25**).

Cleavage of the Yb–C bonds occurred in the reactions of ytterbocenes containing bulky cyclopentadienyl ligands $[Cp^*_2Yb(THF)_2]$ {Cp* = C_5Me_5 (**26**), C_5Me_4H (**27**)} with 1,4-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene (**12**). The reductive reactivity of ytterbocenes in their reactions with **12** has been found to be strongly dependent on steric crowding in the coordination sphere of the ytterbium atom. Unlike the previously described reaction of complex $[(C_5MeH_4)_2Yb(THF)_2]$ which resulted in formation of the Yb^{III} derivative with the radical anion of diimine $[(C_5MeH_4)_2Yb(iPr_2C_6H_3NCHCHNC_6H_3iPr_2)]$ (**14**), interactions of ytterbocenes **26** and **27** containing bulkier polymethylated cyclopentadienyl ligands with **12** under similar conditions resulted in elimination of one Cp* ring, oxidation of the ytterbium atom, and formation of the mono(cyclopentadienyl) Yb^{III} complex $[(Cp^*)Yb^{III}(iPr_2C_6H_3NCH{=}CHNC_6H_3iPr_2{}^{2-})(THF)]$ {Cp* = C_5Me_5 (**28**), C_5Me_4H (**29**)} (Scheme 17).[17]



Scheme 17.

Consequently, depending on the steric crowding in the coordination sphere of the metal atom, ytterbocenes can act as both one- and two-electron reductants in their reactions with diimines. Obviously, complexes $[Cp^*_2Yb(THF)_2]$ demonstrate sterically induced reductive reactivity,[39] and double reduction of **12** becomes possible due to oxidation of the Yb^{II} to Yb^{III} and oxidation of one Cp* anion.

In complexes **28** and **29** the coordination sphere of the Yb^{III} is set up by a η^5-coordinated Cp* ligand, the dianion of diazabutadiene which is bonded in η^4-fashion, and one THF molecule (Figures 14 and 15).

The geometry of the planar NCCN fragment in **28** and **29** is consistent with a dianionic character of the diimino ligand. The bonding situation within the diimino ligand and its coordination mode in **28** and **29** is different from those observed for the radical-anionic ligand in **14**. The C=C bond of a doubly reduced enediamido moiety NCCN also participates in metal–ligand bonding and is coordinated to the ytterbium atom in η^2-fashion. The Yb–N bond lengths in **28** and **29** are remarkably shorter than those in compound **14**, thus indicating a different type of metal–ligand bonding which may be considered in these complexes as 2σ:π.

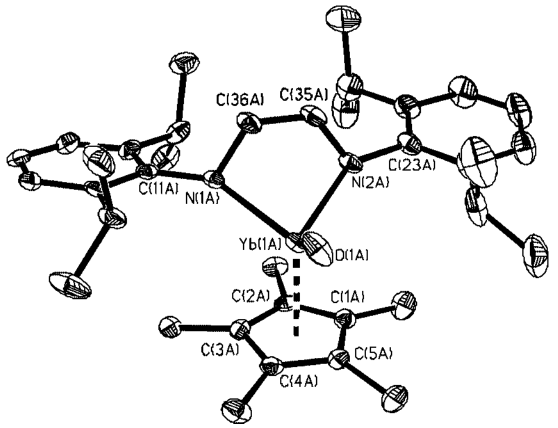


Figure 14. Molecular structure of complex $[(C_5Me_5)Yb^{III}(iPr_2C_6H_3NCH{=}CHNC_6H_3iPr_2{}^{2-})(THF)]$ (**28**). The methylene groups of the THF molecule are omitted.

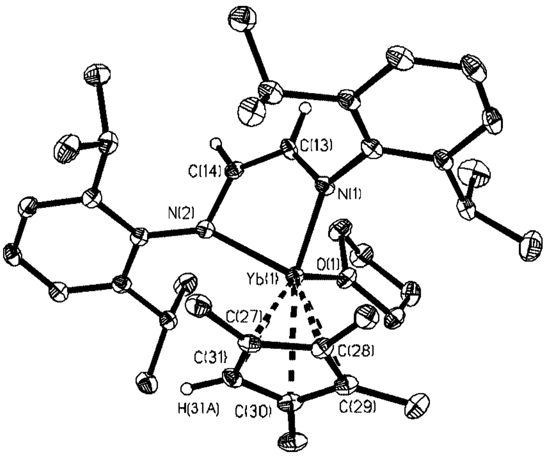
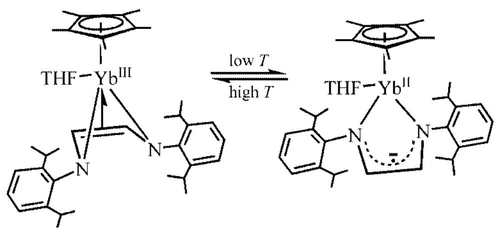


Figure 15. Molecular structure of complex $[(C_5Me_4H)Yb^{III}(iPr_2C_6H_3NCH{=}CHNC_6H_3iPr_2{}^{2-})(THF)]$ (**29**).

The investigation of the magnetic properties of **28** has been performed in a wide range of temperatures. Complex **28** is a very attractive object for investigation of redox tautomeric transformations since both forms {$[(C_5Me_5)Yb^{III}(DAD^{2-})(THF)]$ and $[(C_5Me_5)Yb^{II}(DAD^{\cdot-})(THF)]$} (DAD = $iPr_2C_6H_3NCH{=}CHNC_6H_3iPr_2$) contain a single paramagnetic center, and spin antiferromagnetic coupling can be excluded. The magnetic moment of **28** at 300 K is 4.41 μ_B which is close to the calculated free Yb^{III} ion value for a $^2F_{7/2}$ multiplet.[24c] The magnetic moment of **28** at 2 K of 2.03 μ_B is too low for Yb^{III} and is more compatible with the magnetic moments observed for organic radical anions with $S = ½$ (1.73 μ_B). The field dependence of the magnetization performed at 2 K for sample **28** was satisfactory fitted with the Brilloun function with $S = ½$. However, the value of the saturation magnetization at 50 kOe of 1.21 μ_B is slightly higher than the expected value for a free radical with $S = ½$ and $g = 2.0023$. Such magnetic behavior may be attributed to temperature-induced redox tautomeric transformations of two forms of complex **28** (Scheme 18).



Scheme 18.

To the best of our knowledge, complexes **28** and **29** are the first examples of a terminal η^4-coordination mode of the diimine dianion to a lanthanide atom. In the organolanthanide complexes previously reported, dianionic diimino ligands adopted a μ-bridging coordination mode bonding two homo- or heterometallic centers (Scheme 19) in **30**, **31**,[7a,7g] **32**,[40] **33**.[41]

Replacement of the indenyl ligand by a bulkier fluorenyl analogue in a ytterbocene molecule switched the pathway of the reaction with *N*-(2,6-diisopropylphenyl)imino-2-pyridine (**22**) from C–C bond formation to Yb–C bond cleavage.[37] The reaction of the complex $[(C_{13}H_9)_2Yb(THF)_2]$ with **22** under similar conditions resulted in cleavage of all η^5-Yb–$C_{13}H_9$ bonds, oxidation of the Yb atom to the trivalent state, and formation of the tris(iminopyridine) compound $[\{2,6\text{-}i\text{Pr}_2C_6H_5NCH(C_5H_5N)^{-\bullet}\}_3Yb^{III}]$ (**34**) (Scheme 20).

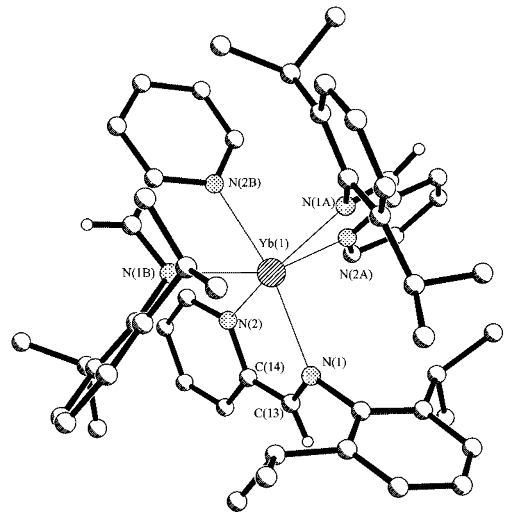
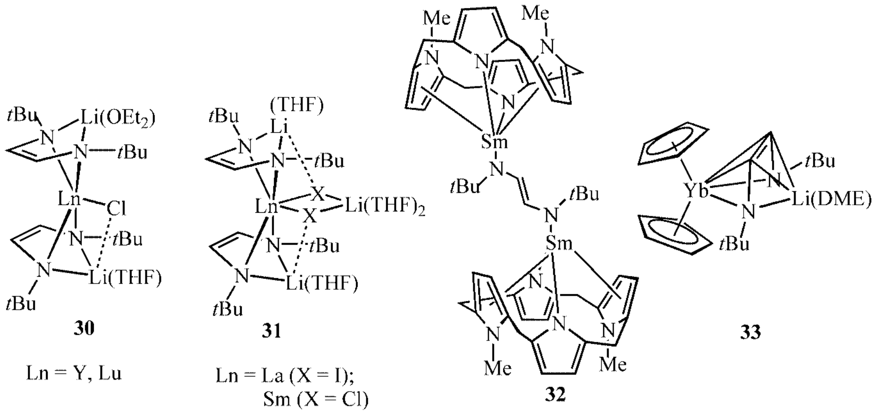
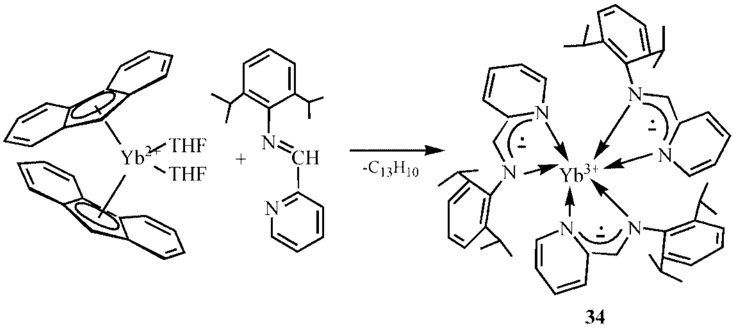


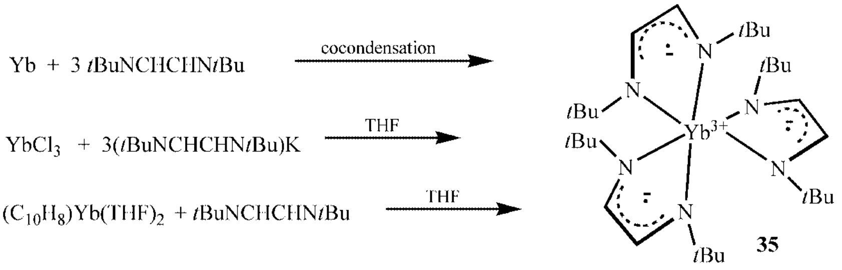
Figure 16. Molecular structure of complex $[\{2,6\text{-}i\text{Pr}_2C_6H_5\text{-}NCH(C_5H_5N)^{-\bullet}\}_3Yb^{III}]$ (**34**).



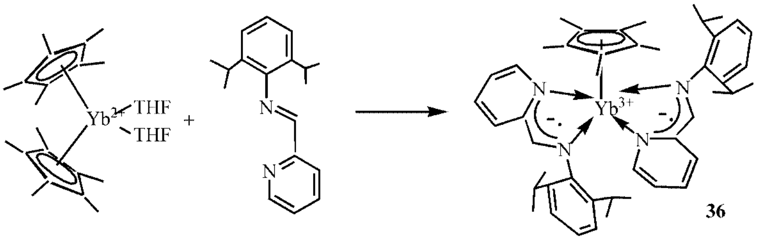
Scheme 19.



Scheme 20.



Scheme 21.



Scheme 22.

The magnetic moment of complex **34** (3.74 μ_B, 293 K) gives evidence of the trivalent oxidation state of the ytterbium atom. The Yb^{III} atom in **34** is coordinated by three chelating iminopyridine ligands bound by two nitrogen atoms (Figure 16).

The Yb–N bond lengths in **34** are comparable to the appropriate distances in Yb^{III} complexes with radical-anionic diimine ligands. The bonding situation within the planar diimino fragment is consistent with the radical-anionic form of the iminopyridine ligand. Previously we synthesized a related tris(diazabutadiene) complex of trivalent ytterbium [(*t*BuNCHCHN*t*Bu)$_3$Yb] (**35**) in which the Yb^{III} atom is coordinated by three radical anions of diazabutadiene (Scheme 21).[7f]

The nature as well as the coordination environment of the ytterbium atom in both complexes **34** and **35** is very similar; nevertheless, the value of the magnetic moment of **35** (5.78 μ_B, 293 K) is much higher than that of **34** (3.74 μ_B, 293 K). The low-temperature magnetic investigation of complex **35** suggested the existence of temperature-induced redox tautomeric transformations for this compound.[7f]

'Complex [(C$_5$Me$_5$)$_2$Yb(THF)$_2$] containing the pentamethylcyclopentadienyl ligand, which has the highest steric demand in the series of the studied compounds, reacted with *N*-2,6-diisopropylphenylimino-2-pyridine (**22**) in a different way. The reaction of [(C$_5$Me$_5$)$_2$Yb(THF)$_2$] with a twofold molar excess of **22** under similar conditions occurred with abstraction of one Cp* ring, oxidation of the ytterbium atom, and afforded a novel half-sandwich complex of trivalent ytterbium [(C$_5$Me$_5$)Yb^{III}{2,6-*i*Pr$_2$C$_6$H$_3$NCH(C$_5$H$_5$N)$^{-\cdot}$}$_2$] (**36**) (Scheme 22).[37] The value of the magnetic moment of complex **36** (3.71 μ_B, 293 K) is consistent with the trivalent oxidation state of the ytterbium atom.[10] In complex **36** the ytterbium atom is coordinated by one C$_5$Me$_5$ ligand in η^5-fashion and two iminopyridine radical anions. Both chelating iminopyridine radical anions in **36** are bound to the ytterbium atom through two coordination Yb–N bonds (Figure 17). Complex **36** is the first example of a half-sandwich lanthanide compound containing two radical-anionic ligands.

6. Conclusions

The pathway of reactions of ytterbocenes with diimines is strongly influenced by the steric crowding in the coordination sphere of the metal atom created by both π-aromatic ligands and substituents at the nitrogen atoms of the diimine molecule. Moreover, coordination capacities and a tendency of π-aromatic ligands coordinated to the ytterbium atom for haptotropic rearrangements (η^5–η^3–η^1) play a crucial role in the modification of the reactivity of ytterbocenes toward diimines. These reactions may occur with oxidation of the ytterbium atom as well as with retention of its oxidation state. C–C bond formation, C–H bond activation, C=N bond insertion, and oxidative Yb–C bond cleavage processes were documented for reactions of ytterbocenes with diimines. Steric overcrowding of the coordination sphere of the ytterbium atom can induce “extra” reducing ability of ytterbocenes and allow them to act not only as one- but also as two-electron reductants with respect to diimines. Fine tuning of the Yb–N bond length in complexes [Cp$_2$Yb^{III}(L$^{-\cdot}$)] (L = diimine) by means of regulation of both steric and electronic properties of Cp and L ligands provides control of intramolecular metal–ligand electron transfer. Complexes [Cp$_2$Yb^{III}(L$^{-\cdot}$)] and [CpYb^{III}(L^{2-})(THF)] are promising objects for the investigation of spin coupling and temperature-induced redox tautomerism which provide a ground for exploring bonding models and electronic structure of compounds of f-transition metals.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Grant No. 05-03-32390), Program of the Presidium of the Russian Academy of Science (RAS), and RAS Chemistry and Material Science Division. A. T. thanks the Russian Foundation for science support.

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Received: December 19, 2006