Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 691 (2006) 3383–3390

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Bis-aryloxo-functionalized NHC complexes of ytterbium(III): Syntheses and structures of $\mathrm{Yb[O\text{-}4,6\text{-}{}^{t}Bu_2\text{-}C_6H_2\text{-}2\text{-}CH_2\{C(RNCHCHN)\}]_2N({}^{i}Pr)_2}$ (R = ^{i}Pr, Me)

Zhi-Guo Wang [a], Hong-Mei Sun [a], Hai-Sheng Yao [a], Ying-Ming Yao [a], Qi Shen [a,b,*], Yong Zhang [a]

[a] College of Chemistry and Chemical Engineering, Suzhou University, Hengyi Road, Suzhou industrial Park, Suzhou 215123, PR China
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, Shanghai 200433, PR China

Received 15 March 2006; received in revised form 10 April 2006; accepted 20 April 2006
Available online 29 April 2006

Abstract

The transamination of anionic homoleptic amido ytterbium complex, $\mathrm{LiYb[N(\mathit{i}\text{-}Pr)_2]_4}$ with aryloxo-functionalized N-heterocyclic carbene (NHC) precursor, $\mathrm{HO\text{-}4,6\text{-}di\text{-}{}^{t}Bu\text{-}C_6H_2\text{-}2\text{-}CH_2\{CH[\mathit{i}\text{-}Pr\text{-}NCHCHN]\}Cl}$ ($\mathrm{H_2LCl}$) **1** and $\mathrm{HO\text{-}4,6\text{-}di\text{-}{}^{t}Bu\text{-}C_6H_2\text{-}2\text{-}CH_2\{CH[Me\text{-}NCHCHN]\}Cl}$ ($\mathrm{H_2L'Cl}$) **2**, and BuLi in 1:2:1 molar ratio in THF at 0 °C afforded the first bisaryloxo- NHC monoamido ytterbium complexes, $\mathrm{L_2Yb[N(\mathit{i}\text{-}Pr)_2]}$ **3** and $\mathrm{L'_2Yb[N(\mathit{i}\text{-}Pr)_2]}$ **4**, respectively. The same reactions in the molar ratio of 1:1 without BuLi yields also the complex **3** and **4,** not the bis-amido mono aryloxo-NHC complex $\mathrm{\{LYb[N(\mathit{i}\text{-}Pr)_2]_2\}}$ and $\mathrm{\{L'Yb[N(\mathit{i}\text{-}Pr)_2]_2\}}$. The in situ low-temperature reaction of **2** with two equivalents of BuLi, followed by addition of one equivalent of $\mathrm{YbCl_3}$ in THF does not afford the expected $\mathrm{LYbCl_2}$, instead, $\mathrm{[Li(DME)_3][YbCl_4(DME)]}$ **5** and a dimeric imidazole-aryloxo lithium $\mathrm{\{[O\text{-}4,6\text{-}di\text{-}{}^{t}Bu\text{-}C_6H_2\text{-}2\text{-}CH_2\{CH(MeNCHCHNH)\}]Li(THF)\}_2}$ **6** which results from the 1,2-benzyl migration in N-heterocyclic carbene, are obtained. Complexes **3**, **4**, **5** and **6** have been characterized by elemental analysis and X-ray crystallography, and by NMR spectroscopy for **6**.

Keywords: Bis-aryloxo-functionalized; NHC complexes; Ytterbium(III)

1. Introduction

The application of N-heterocyclic carbenes (NHCs) as ligands in organometallic chemistry has attracted increasing attention, as their strong σ-donating properties and easy to tune their steric and electronic features by the substituents on the nitrogen atoms [1]. The vast majority of NHC complexes of late transition metals have been reported [1a,2], while the chemistry of NHC systems of lanthanides elements is considerably less developed. Only the lanthanide NHC complexes in which the NHC coordinates as a dative donor solvent molecule were synthesized until 2001 [3]. The reason for it may be attributed to the lack of NHC derivatives suitable for these f-block metals, as the neutral ligands in these metals complexes are prone to dissociation. Recently, a chelate NHC ligand that links an anionic functionalized group has been developed and shows the potential in the synthesis of lanthanide-NHC complexes. The first amido-functionalized NHC complexes of trivalent samarium(III), yttrium(III) [4a], cerium(III) [4b] and neodymium [4c] were synthesized.

Aryloxo (alkoxo) groups, as alternatives to cyclopentadienyl anions, have widely been used in organometallic complexes of transition metals and lanthanides metals. The aryloxo (alkoxo)-functionalized NHCs have been found their applications in the complexes of copper [5a], silver [5b], titanium [5c] and palladium [5d]. Recently, we designed and synthesized two novel aryloxo-tethered

---

[*] Corresponding author. Tel.: +86 512 65880306; fax: +86 512 65880305.
E-mail address: qshen@suda.edu.cn (Q. Shen).

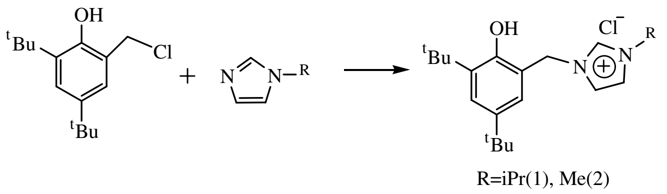
0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.04.029

NHC precursors, (4,6-di-*tert*-butyl-2-hydroxybenzyl)*N*-isopropylimidazolium chloride (H_2LCl) and 4,6-di-*tert*-butyl-2-hydroxybenzyl)*N*-methylimidazolium chloride ($H_2L'Cl$), and successfully synthesized the corresponding NHC complexes of Ni(II) [6a] and Fe(II) [6b]. However, no lanthanide complex with aryloxo (alkoxo)-functionalized NHC ligand was found in the literature up to date. Moreover, aryloxo lanthanides derivatives have shown good catalytic activities in homogeneous catalysis including ethylene polymerization [7a], ring-opening polymerization of caprolactones [7b], and organic synthesis as well [7c,7d]. Studying on the synthesis and chemical behavior of the analogue complexes of aryloxo-lanthanides with NHC should be helpful for further understanding the effects of NHC in homogeneous reactions catalyzed by organolanthanide complexes. Accordingly, we put our attention to the chemistry of lanthanide complexes with aryloxo-functionalized NHC systems. In this paper we report the synthesis of the first bis-aryloxo-tethered NHC complex of ytterbium, $L_2Yb[N(i\text{-}Pr)_2]$ and $L'_2Yb[N(i\text{-}Pr)_2]$, by the transamination reaction of $LiYb[N(i\text{-}Pr)_2]_4$ with NHC precursors, H_2LCl and $H_2L'Cl$, and LiBu and the 1,2-benzyl migration in aromatic carbene.

2. Results and discussion

2.1. Syntheses of $L_2Yb[N(i\text{-}Pr)_2]$ 3 and $L'_2Yb[N(i\text{-}Pr)_2]$ 4

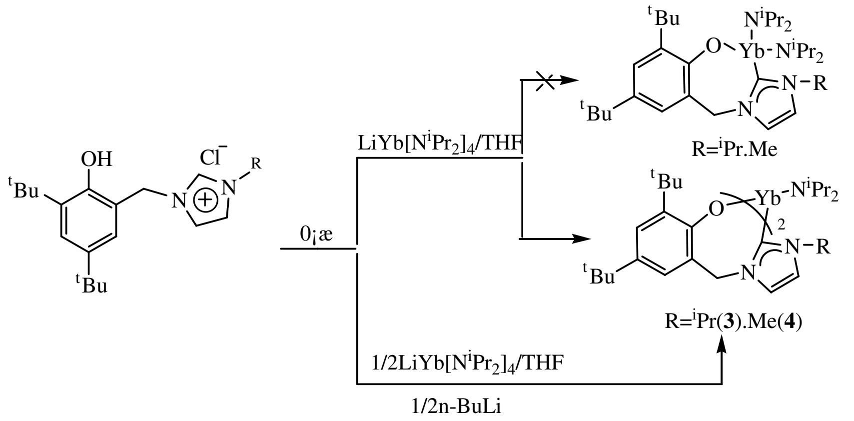
The chelate NHC precursors, [HO-4,6-di-^{t}Bu-C_6H_2-2-CH_2{CH(RNCHCHN)}Cl] (R = *i*-Pr, **1**, H_2LCl; Me, **2**, $H_2L'Cl$), are synthesized easily via nucleophilic attack of a 1-alkylimidazole on an alkyl halide. Thus, 2-chloromethyl-4,6-di-*tert*-butylphenol reacted with *N*-isopropylimidazole and *N*-methylimidazole, respectively, in THF at room temperature for 0.5 h afforded the corresponding **1** and **2** in the yield of 84% and 98% (Scheme 1).



Scheme 1.

The transamination reaction was used here for the synthesis of target complex to avoid the isolation of free NHC. A neutral triamide complex of lanthanide $Ln[(NSiMe_3)_2]_3$ has already shown to be the desired reagent [4]. However, the synthesis of a neutral lanthanide triamides with other amido groups, especially with less bulky amido groups, is difficult because of the demand of high coordination number of lanthanide metals and an anionic complex $[MLn(NR_2)_4]$ (M = Li, Na) is often obtained instead. Considering the fact that the part of MNR_2 in $[MLn(NR_2)_4]$ may be used as a reagent for the deprotonation of imidazolium salt, an anionic amide complex was tried to use as a starting material instead of a neutral one here. Thus, anionic complex of ytterbium $LiYb[N(i\text{-}Pr)_2]_4$ was synthesized by the reaction of $YbCl_3$ with four equivalents of $LiN(i\text{-}Pr)_2$ [8], and used in sequential reaction. Based on the lack of bis(NHC) complex of lanthanide in the literature, the synthesis of bis-NHC complex of Yb was first tried. The reaction of $LiYb[N(i\text{-}Pr)_2]_4$ with **1** and BuLi in the molar ratio of 1:2:1 works cleanly in THF at 0 °C for 4 h, then at room temperature for 36 h. After workup, the yellow crystals are isolated in 70% yield, which are fully characterized to be the bis-phenoxo-NHC complex of Yb **3**. The same reaction with **2** affords the analogue complex **4** in 78% yield (Scheme 2). What we should emphasize is that even the reaction proceeds at 0 °C, the desired NHC complexes of Yb can still be prepared.

An attempt to synthesize mono-carbene complexes of Yb by the reaction of $LiYb(Ni\text{-}Pr_2)_4$ with **1** and **2**, respectively, in a 1:1 molar ratio without BuLi in THF at 0 °C failed and the same bis-NHC complexes of **3** and **4** were isolated in reasonable lower yield (27% for **3** and 32%, for **4**). It seems that the mono-NHC complex is not stable enough in the present case, and prone to react further with the second molecule of **1**(**2**). The situation is different from those for the reaction of $Ln[(NSiMe_3)_2]_3$ with amido-functionalized NHC published, where mono-NHC complex of



Scheme 2.

lanthanide was obtained in high yield [4]. The reason for the difference observed between this system and those reported in Ref. [4] may be due to difference in steric hindrance of the ligand systems. The ligand combination in Ref. [4] is apparently more sterically demanding, thus preventing ligand redistribution.

Complexes **3** and **4** are very sensitive to air and moisture. The paramagnetism of the complexes precludes ^{13}C NMR spectroscopic identification of the carbene carbon. Yb–$C_{carbene}$ bond in solution is inferred from strongly shifted CH backbone resonances of the heterocycle. The same situation is also observed in the case of amido-functionalized NHC complex of Sm [4a,4c]. The further confirmation of the syntheses of **3** and **4** was made by X-ray crystal structure analysis.

The single crystals of **3** and **4** suitable for structural analysis were obtained by recrystallization from toluene at 0 °C. The details crystallographic data were collected in Table 1. The molecular structures were shown in Figs. 1 and 2, respectively, and the selected bond lengths and angles are listed in Table 2.

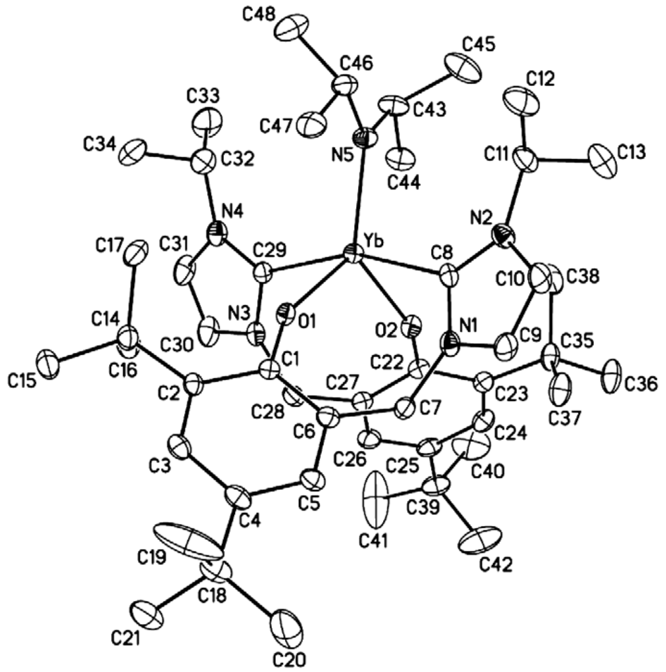


Fig. 1. ORTEP diagram of complex **3** showing atom numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Complexes **3** and **4** are isostructural. The central metal is coordinated to two O anions and two $C_{carbene}$ atoms (O(1, 2), C(8, 29) for **3** and O(1, 2), C(8, 27) for **4**) of two phenoxo-NHC ligands and N(5) atom of N(*i*-Pr)$_2$ group, adopting a distorted trigonal-bipyramidal geometry in which O(1), O(2) and N(5) occupy the equatorial sites, while, two C atoms (C(8), C (29) for **3** and C(8), C(27) for **4**) axial. The equatorial angles of O(1)–Yb(1)–O(2), O(1)–Yb(1)–N(5), and O(2)–Yb(1)–N(5) are 106.1(2)°, 130.1(2)°, and 123.8(2)° for **3**, and 109.2(1)°, 124.6(1)°, and 126.2(1)° for **4**, respectively, which deviate from the ideal angle of 120°. The axial angle C(8)–Yb(1)–C(29) in complex **3** and C(8)–Yb(1)–C(27) in complex **4** is 162.3(2)° and 159.6(1)°, respectively, which is distinctly non-linear. For both of **3** and **4**, the two carbene ligands bind to Yb asymmetrically, which distorted by the Yb–C–N chelate angles 118.5(2)° and 138.1(5)° for one NHC

Table 1
Details of the crystallographic data and refinements for complexes **3**, **4**, **5**, and **6**

	3 · toluene	**4** · 1.5toluene · 0.5THF	**5**	**6** · 4THF
Empirical formula	$C_{55}H_{84}N_5O_2Yb$	$C_{56.50}H_{84}N_5O_{2.50}Yb$	$C_{16}H_{40}Cl_4LiO_8Yb$	$C_{58}H_{94}Li_2N_4O_6$
F_w	1020.3	1046.33	682.26	957.25
Temperature	193(2)	193(2)	193(2)	173(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	*Pbca*	C_2/c	$P2_1/n$	$P\bar{1}$
a (Å)	8.652(2)	1 26.371(2)	15.027(4)	9.28(4)
b (Å)	22.730(3)	21.438(2)	13.867(3)	10.286(3)
c (Å)	25.989(4)	21.432(2)	14.870(4)	15.532(5)
α (°)	90	90	90	76.15(2)
β (°)	90	111.418(2)	113.161(7)	84.74(3)
γ (°)	90	90	90	86.45(3)
V (Å^3)	11018(3)	11279.4(17)	2848.9(12)	1425.8(9)
Z	8	8	4	1
Density (Mg/m^3)	1.230	1.232	1.591	1.115
Absorption coefficient (mm^{-1})	1.7391	1.701	0.898	0.070
F(000)	4280	4384	1364	524
Reflections collected	36474	55105	26677	13629
Observed reflections	7311	9253	4064	2700
Unique reflections	10004	10305	5196	5174
Parameters refined	566	595	280	325
R [$I > 2\sigma(I)$]	0.0664	0.0382	0.0718	0.0757
R_w	0.1135	0.0947	0.1331	0.1945
GOF on F^2	1.144	1.090	1.151	0.959

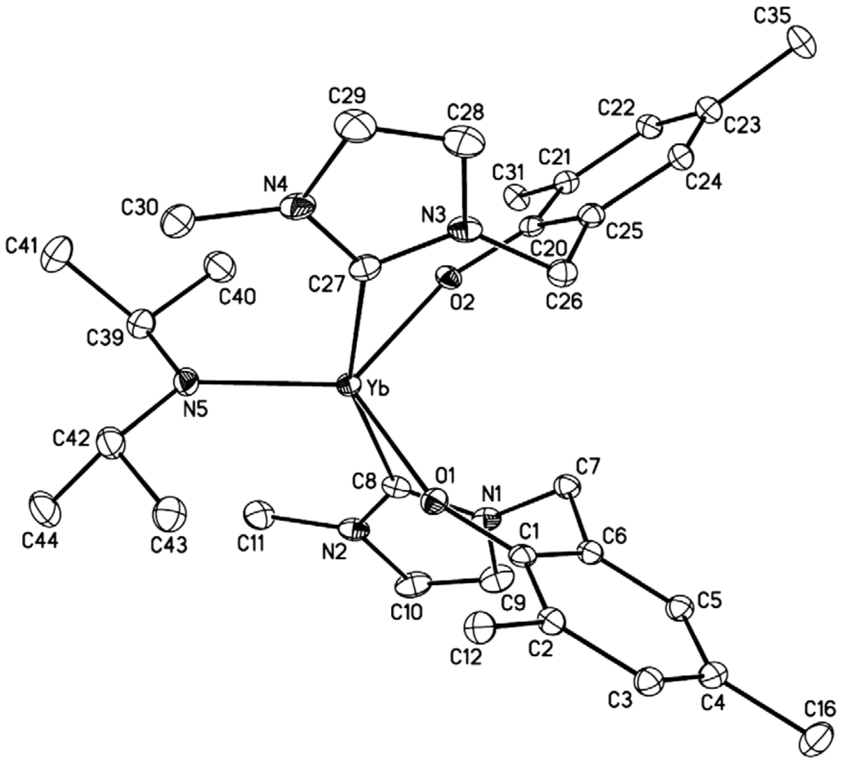


Fig. 2. ORTEP diagram of complex **4** showing atom numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen and butyl carbon atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) for **3** and **4**

Complex 3			
Yb–O(2)	2.094(4)	Yb–O(1)	2.116(4)
Yb–N(5)	2.198(6)	Yb–C(29)	2.526(7)
Yb–C(8)	2.543(7)	O(1)–C(1)	1.324(7)
O(2)–C(22)	1.333(7)	N(1)–C(8)	1.357(9)
N(1)–C(9)	1.394(8)	N(1)–C(7)	1.477(8)
N(2)–C(8)	1.352(8)	N(2)–C(10)	1.373(9)
O(2)–Yb–O(1)	106.10(18)	O(2)–Yb–N(5)	123.8(2)
O(1)–Yb–N(5)	130.1(2)	O(2)–Yb–C(29)	84.5(2)
O(1)–Yb–C(29)	87.26(19)	N(5)–Yb–C(29)	97.8(2)
O(2)–Yb–C(8)	85.4(2)	O(1)–Yb–C(8)	81.51(19)
N(5)–Yb–C(8)	100.0(2)	C(29)–Yb–C(8)	162.3(2)
N(1)–C(8)–Yb	118.5(5)	N(2)–C(8)–Yb	138.1(5)
Complex 4			
Yb–O(2)	2.146(3)	Yb–O(1)	2.147(3)
Yb–N(5)	2.206(3)	Yb–C(8)	2.483(4)
Yb–C(27)	2.491(4)	O(1)–C(1)	1.333(5)
O(2)–C(20)	1.331(5)	N(1)–C(8)	1.355(5)
N(1)–C(9)	1.382(5)	N(1)–C(7)	1.467(5)
N(2)–C(8)	1.361(5)	N(2)–C(10)	1.375(6)
O(2)–Yb–O(1)	109.22(10)	O(2)–Yb–N(5)	124.63(12)
O(1)–Yb–N(5)	126.15(12)	O(2)–Yb–C(8)	87.15(11)
O(1)–Yb–C(8)	80.60(12)	N(5)–Yb–C(8)	99.73(14)
O(2)–Yb–C(27)	80.44(12)	O(1)–Yb–C(27)	88.23(11)
N(5)–Yb–C(27)	100.65(13)	C(8)–Yb–C(27)	159.59(14)
N(1)–C(8)–Yb	117.5(3)	N(2)–C(8)–Yb	138.0(3)

ligand and 120.9(5)° and 136.2(5)° for the other NHC ligand in **3**, and 117.3(3)°, 137.4(3)° and 117.5(3)°, 138.0(3)° in **4**. The Yb–$C_{carbene}$ distances of 2.483(4) Å and 2.491(4) Å (average Yb–$C_{carbene}$ distance of 2.487 Å) in **4** are shorter than 2.526(7) Å and 2.543(7) Å (average Yb–$C_{carbene}$ distance of 2.535 Å) found in **3**. This may contribute to the more bulky isopropyl group than methyl group. The average Yb–$C_{carbene}$ distance of 2.487 Å is shorter than the monodentate Yb–$C_{carbene}$ distance of 2.552(4) Å [3b]. The values can compared with 2.501(5) Å, 2.588(2) Å, 2.699(2) Å [4,5], and 2.656(5) [4c] for the complexes of Y, Sm, Ce(III), and Nd, respectively, when the differences in ionic radii between Yb and each of these metals are considered. The Yb–$N_{isopropyl}$ bond distance of 2.198(6) Å in **3** is almost consistent with 2.206(3) Å in **4**. These values are comparable with the average value of 2.208 Å, in anionic homoleptic ytterbium complex of $LiYb[N(i\text{-}Pr)_2]_4$ [8]. The Yb–O bond lengths of 2.116(4) Å (Yb–O(1)) and 2.094(4) Å (Yb–O(2)), the average value of 2.105 Å, in**3** is somewhat shorter than 2.146(3) and 2.147(3) Å, average distance of 2.146 Å in **4**. The Yb–O bond length of 2.105 Å for **3** is comparable with 2.08 Å found in five-coordinated complex of $Yb(OC_6H_3Ph_2\text{-}2,6)_3(THF)_2$ [9], while 2.146(3) Å for **4** is somewhat larger.

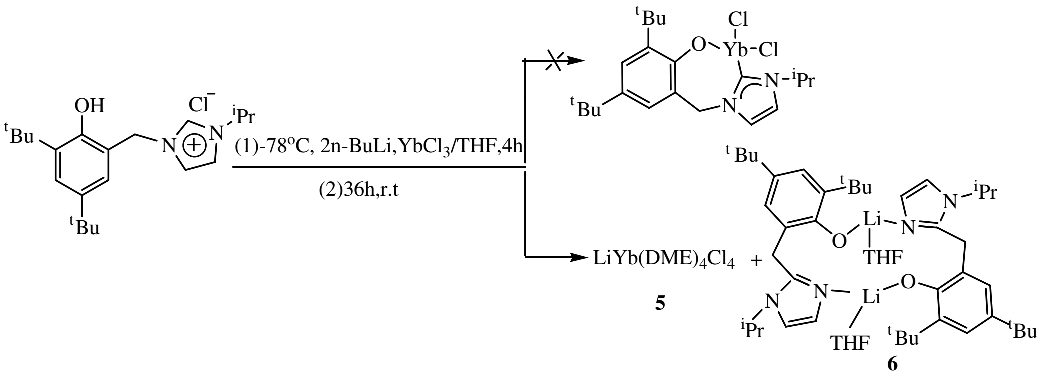
*2.2. Metalation reaction of $YbCl_3$ with the reaction solution of **2** and BuLi*

NHC lanthanide halides are the useful precursors for the further transformations and metalation reaction of transition metal halides with the corresponding alkali metal salt is the common synthetic pathway for theses complexes. So, the synthesis of $LYbCl_2$ is tried by the reaction of $YbCl_3$

with in situ generated LLi. Thus, the in situ reaction of **2** with two equivalents of BuLi at −78 °C, followed by addition to one equivalent of $YbCl_3$ in THF was carried out. After workup, a red solution was obtained which yielded the first crop of red crystals by crystallization from the mixture of toluene/DME. The mother liquor was evaporated to dry and the residue was extracted by THF. The THF solution was crystallized at −10 °C to afford the second crop of colorless crystals. The red crystals were characterized by X-ray crystal structure analysis to be an ion pair complex of $[YbCl_4(DME)]^-[Li(DME)_3]^+$ **5**, while the colorless crystals to be unexpected dimeric THF-solvated imidazole-phenoxo lithium, $\{[O\text{-}4,6\text{-di-}^tBu\text{-}C_6H_2\text{-}2\text{-}CH_2\text{-}\{CH(i\text{-}PrNCHCHNH)\}]Li(THF)\}_2$ **6** (Scheme 3). The further study indicates that the reaction of BuLi with **2** without $YbCl_3$ under the same conditions also yields **6**.

The molecular structures of **5** and **6** are shown in Figs. 3 and 4. The selected bond lengths and angles are listed in Table 3.

The central metal Yb in complex **5** coordinates to four Cl atoms and two oxygen atoms from solvated DME molecule to form a six-coordinated distorted octahedron geometry. Such a stable structure of **5** may prevent it from further reaction. In complex **6** two molecules of $[O\text{-}4,6\text{-di-}^tBu\text{-}C_6H_2\text{-}2\text{-}CH_2\{CH(MeNCHCHNH)\}]Li(THF)$ connected asymmetrically by two bridged O atoms. Each Li ion coordinates to two O atoms and one N atom from phenoxo-tethered imidazole and one O atom from a free THF to form a tetrahedral geometry. The Li–O bond lengths of 1.879(5) and 1.913(5) Å, respectively, are comparable with $[(Ph_2P(O)N(CH_2Ph)CH_3)LiOC_6H_2\text{-}2,6\text{-}\{C(CH_3)_3\}2\text{-}4\text{-}CH_3]_2$ [10]. The bond lengths of Li–N bonds are 2.048(6) Å (Table 3), which lay in the range of dative Li–N bond lengths. It is obvious that complex **6** results from the 1,2-migration of the benzyl group from nitrogen to the carbene center of the transient derivative. The 1,2-silyl migration from nitrogen to carbene center has already been reported [11]. Very recently, the 1,2-benzyl migration was also mentioned in the synthesis of titanium NHC complexes incorporating an imidazolium-linked bis(phenol) [5c], however, the details has not been presented. The failure in the synthesis of NHC ytterbium chloride directly by the metalation reaction might be supposed that the competition between two reactions, reactions of $YbCl_3$ with LiCl and with the transient lithium carbene, exists, and the former reaction should be much favorable under the conditions used. The



Scheme 3.

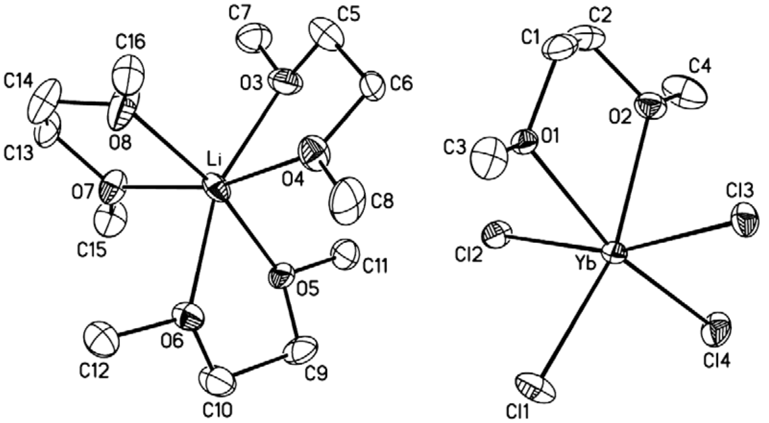


Fig. 3. ORTEP diagram of complex **5** showing atom numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

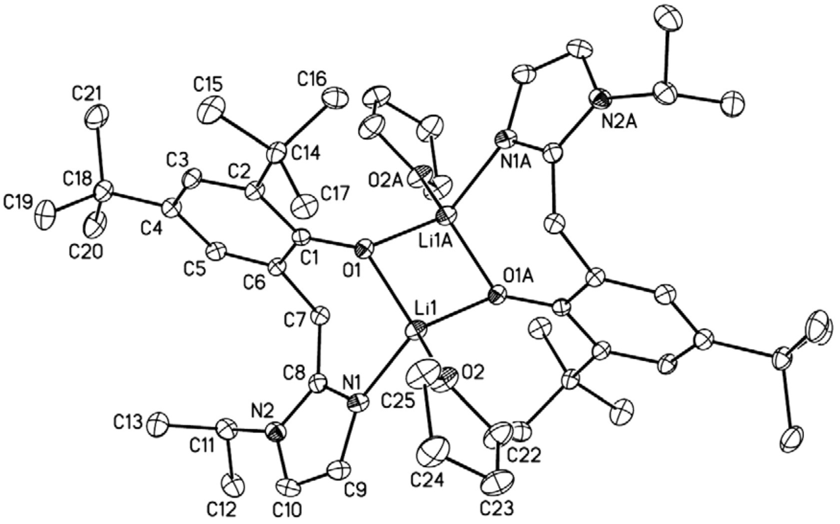


Fig. 4. ORTEP diagram of complex **6** showing atom numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) for **5** and **6**

Complex **5**			
Yb–O(2)	2.364(7)	Yb–O(1)	2.374(7)
Yb–Cl(1)	2.511(3)	Yb–Cl(2)	2.554(3)
Yb–Cl(3)	2.564(3)	Yb–Cl(4)	2.515(3)
O(3)–Li	2.29(2)	O(4)–C(6)	1.416(15)
C(5)–C(6)	1.477(18)		
O(2)–Yb–O(1)	70.4(3)	O(2)–Yb–Cl(1)	160.9(2)
O(1)–Yb–Cl(1)	90.56(19)	O(2)–Yb–Cl(4)	96.2(2)
O(1)–Yb–Cl(4)	166.57(19)	Cl(1)–Yb–Cl(4)	102.86(12)
O(2)–Yb–Cl(2)	82.1(2)	O(1)–Yb–Cl(2)	85.50(18)
Cl(1)–Yb–Cl(2)	95.74(11)	Cl(4)–Yb–Cl(2)	92.80(11)
O(4)–Li–O(7)	164.0(12)	O(4)–Li–O(3)	76.1(7)
Complex **6**			
O(1)–C(1)	1.310(3)	O(1)–Li(1)	1.879(5)
N(1)–Li(1)	2.048(6)	N(1)–C(8)	1.328(4)
C(7)–C(8)	1.500(4)	C(6)–C(7)	1.521(4)
O(2)–Li(1)	2.028(5)	C(1)–C(6)	1.416(4)
C(1)–O(1)–Li(1)	133.5(2)	C(1)–O(1)–Li(1A)	128.7(2)
Li(1)–O(1)–Li(1A)	83.8(2)	O(1)-Li(1)–O(1A)	96.2(2)
O(1)–Li(1)–O(2)	126.1(3)	C(8)–N(1)–Li(1)	119.2(2)
O(1A)–Li(1)–O(2)	107.4(2)		

isolation of **6** demonstrated unambiguously that the transient lithium carbene LLi is thermolabile, readily decomposing at even low temperature to the 2-alkylated imidazole lithium derivative via 1,2-benzyl migration as shown in Scheme 4.

The unsuccessfulness in the synthesis of NHC ytterbium chlorides is not special. The similar situation is also observed for cerium complex, in that case the reaction of the amine NHC *t*-BuNHCH$_2$CH$_2$[C{*t*-BuN(CHCH)N}]-(HL*), KMe, and 1/2 equivalent of [CeI$_3$THF$_4$] does also not afford [(L*)$_2$CeI], but [CeI$_3$THF$_4$] and H$_2$L* I [4b]. These results indicated that the synthesis of NHC lanthanide halides is much more difficult than that of the corresponding amide complexes. The further study on the synthesis of this kind of complex is proceeding.

3. Conclusions

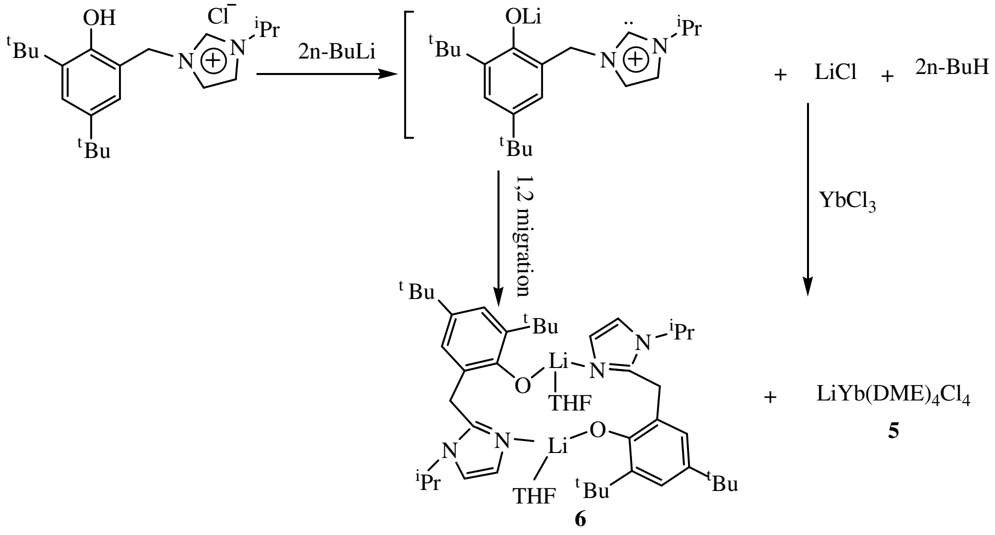
The first bis-aryloxo-functionalized NHC complexes of monoamido ytterbium, L$_2$YbN(*i*-Pr)$_2$ **3** and L$'_2$YbN-(*i*-Pr)$_2$ **4** were prepared by the transamination of anionic homoleptic lanthanide amides, LiYb[N(*i*-Pr)$_2$]$_4$, with the corresponding H$_2$LCl and H$_2$L$'$Cl and LiBu. The success in the use of anionic lanthanide amide as a precursor may provide a convenient way for the synthesis of a series of amides complexes with Ln–NHC fragment. Attempt to synthesize bis-amido ytterbium aryloxo-NHC complex resulted in isolation of bis-aryloxo-NHC complexes of **3** and **4**. The in situ low-temperature reaction of **2** with two equivalents of BuLi followed with one equivalent of YbCl$_3$ in THF affords [Li(DME)$_3$][YbCl$_4$(DME)] **5** and a dimeric imidazole-aryloxo lithium {[O-4,6-di-^{t}Bu-C$_6$H$_2$-2-CH$_2${CH(MeNC-HCHNH)}]Li(THF)}$_2$ **6**, instead of the expected LYbCl$_2$. The isolation of **6** demonstrates 1,2-benzyl migration from nitrogen to carbene center is easily occurred.

The study on the synthesis of aryloxo-NHC derivatives of ytterbium and other lanthanide metals and the reactivity of these complexes is proceeding in our laboratory.

4. Experimental section

4.1. General considerations

All of the manipulations were performed in a purified argon atmosphere using standard Schlenk techniques. Toluene, THF and DME were degassed and distilled from sodium benzophenone ketyl under argon prior to use. The compounds **1** and **2** were synthesized according to the literature [6]. LiN(*i*-Pr)$_2$ was synthesized by the reaction of HN(*i*-Pr)$_2$ with BuLi in hexane. Lanthanide analyses were carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA 1110 instrument. ^{1}H



Scheme 4.

NMR spectrum was recorded on a Varian-400 spectrometer. The uncorrected melting points were determined in sealed Ar-filled capillary tubes.

*4.2. Synthesis of $L_2YbN(i\text{-}Pr)_2$ **3***

A solution of $LiYb[N(i\text{-}Pr)_2]_4$ (12.5 ml, 4 mmol) in THF was added dropwise to the suspension of **1** (3.48 g, 8 mmol) under stirring, and then BuLi (3.8 ml, 1.4 mmol) was introduced at 0 °C for 4 h, then for 36 h at room temperature. The solvent was removed in vacuum, and the residue was exacted with toluene and centrifuged to remove precipitation. The obtained solution was crystallized at room temperature for a few days to afford light yellow crystals of **3** (2.85 g, 70%); m.p. 193–194 °C (dec.). Anal. Calc. for $C_{55}H_{84}N_5O_2Yb$: C, 65.86; H, 8.23; N, 6.84; Yb, 14.06. Found: C, 65.54; H, 8.34; N, 6.76: Yb, 14.26.

*4.3. Synthesis of $L'_2YbN(i\text{-}Pr)_2$ **4***

Complex **4** was prepared by an analogous procedure described as above, except **2** (3.37 g, 10 mmol) was used instead of **1**. Light yellow crystals obtained from toluene/THF at −15 °C for a few days (4.08 g, 78%); m.p. 176–177 °C (dec.). Anal. Calc. for $C_{56.50}H_{84}N_5O_2Yb$: C, 64.79; H, 8.02; N, 6.69; Yb, 16.53. Found: C, 64.54; H, 8.12; N, 6.42; Yb, 16.48.

4.4. Metathesis of $YbCl_3$ with 2 and BuLi

BuLi (3.42 ml, 4 mmol) was slowly added to a cold (−78 °C) slurry of **2** (0.729 g, 2 mmol) in THF and stirred for 4 h, during which time the color of solution changed from yellow to red. The solution was then added to a slurry of $YbCl_3$ (0.2795 g, 2 mmol) in THF to give a yellow solution. The mixture was stirred for 4 h at −78 °C and then for another 24 h at room temperature. After evaporation of the solvent, the solid residue was extracted by toluene. For crystallization a small amount of DME was added. The first crop of red crystals suitable for X-ray diffraction study **5** was isolated (0.736 g, 54%). From the mother liquor at 10 °C, the second crop of colorless crystals suitable for X-ray diffraction study, **6** was obtained (0.622 g, 65%). Anal. Calc. for $C_{16}H_{40}C_{14}LiO_8Yb$: C, 52.76; H, 5.86; Yb, 25.35. Found: C, 52.64; H, 5.83; Yb, 25.31. Anal. Calc. for $C_{58}H_{94}Li_2N_4O_6$: C, 72.70; H, 9.82; N, 5.85. Found: C, 72.54; H, 9.67; N, 5.69. ^1H NMR ($CDCl_3$, δ, ppm): 1.51 (s, 18H), 1.80 (s, 18H), 1.43 (d, 12H), 3.65 (m, 4H), 4.17 (brs, 2H), 6.19 (brs, 2H), 6.80 (d, brs, 2H), 6.99 (d, 2H).

4.5. X-ray crystallography

Suitable single crystals of complexes **3**, **4**, **5** and **6** were sealed in a thin-walled glass capillary. Intensity data were collected on a Rigaku Mercury CCD area detector in ω scan mode using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Cell parameters were refined from the observed positions of all strong reflections in each data set. The diffracted intensities were corrected for Lorentz-polarization effects and empirical absorption corrections. The structures were solved by heavy-atom and direct methods and were refined by least-squares methods on all unique $|F|^2$ values. With anisotropic displacement parameters, programs used were SHELXS-97 and SHELXL-97 for structure solution, refinement, and molecular graphics. Details of the intensity data collection and crystallographic data for **3**, **4**, **5** and **6** are given in Table 1, and further details of the structure determinations are given in the Supporting Information.

Acknowledgement

We are grateful to National Natural Science Foundation of China and PhD Foundation from Education Ministry of China for the financial support.

Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited with Cambridge Crystallographic Data Centre, CCDC. Nos. 601689, 269256, 601701, 601702 for **3**, **4**, **5** and **6**. Copies of this information may be free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.04.029.

References

[1] (a) For recent reviews, see D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, Chem. Rev. 100 (2000) 39;
(b) T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18;
(c) I.E. Marko, S. Sterin, O. Buisine, R. Mignani, P. Branlard, B. Tinant, J.P. Declercq, Science 298 (2002) 204;
(d) W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1290;
(e) M. Muehlhofer, T. Strassner, W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1745;
(f) R.H. Crabtree, Pure Appl. Chem. 75 (2003) 435.

[2] (a) K.J. Cavell, D.S. McGuinness, Coord. Chem. Rev. 248 (2004) 671, and references therein;
(b) R.E. Douthwaite, J. Houghton, B. Kariuki, Chem. Commun. (2004) 698;
(c) X.L. Hu, I. Castro-Rodriguez, K. Meyer, Chem. Commun. (2004) 2164;
(d) X. Wang, S. Liu, G.X. Jin, Organometallics 23 (2004) 6002;
(e) D.S. McGuinness, V.C. Gibson, J.W. Steed, Organometallics 23 (2004) 6288.

[3] (a) A.J. Arduengo III, M. Tamm, S.J. McLain, J.C. Calabrese, F. Davidson, W.J. Marshall, J. Am. Chem. Soc. 116 (1994) 7927;
(b) H. Shumann, M. Glanz, J. Winterfeld, H. Hemling, N. Kuhn, T. Kratz, Angew. Chem. Int. Ed. 33 (1994) 1733;
(c) W.J. Oldham Jr., S.M. Oldham, B.L. Scott, K.D. Abney, W.H. Smith, D.A. Costa, Chem. Commun. (2001) 1348;
(d) W.A. Herrmann, F.C. Munck, G.R.J. Artus, O. Runte, R. Anwander, Organometallics 16 (1997) 682;
(e) R.D. Fischer, Angew. Chem., Int. Ed. Engl. 33 (1994) 2165;
(f) H. Schumann, M. Glanz, J. Winterfeld, H. Hemling, N. Kuhn, T. Kratz, Chem. Ber. 127 (1994) 2369.

[4] (a) P.L. Arnold, S.A. Mungur, A.J. Blake, C. Wilson, Angew. Chem. Int. Ed. 42 (2003) 5981;
(b) S.T. Liddle, P.L. Arnold, Organometallics 24 (2005) 2597;
(c) P.L. Arnold, S.T. Liddle, Chem. Commun. (2005) 5638.

[5] (a) P.L. Arnold, A.C. Scarisbrick, A.J. Blake, C. Wilson, Chem. Commun. (2001) 2340;
(b) P.L. Arnold, M. Rodden, K.M. Davis, A.C. Scarisbrick, A.J. Blake, C. Wilson, Chem. Commun. (2004) 1612;
(c) Hidenori Aihara, Tsukasa Matsuo, Hiroyuki kawaguchi, Chem. Commun. (2003) 2204;
(d) A.W. Waltman, R.H. Grubbs, Organometallics 23 (2004) 3105.

[6] (a) W.F. Li, H.M. Sun, Z.G. Wang, M.Z. Chen, Q. Shen, Y.J. Zhang, Organomet. Chem. 690 (2005) 6227;
(b) M.Z. Chen, H.M. Sun, W.F. Li, Z.G. Wang, Q. Shen, Y. Zhang, J. Organomet. Chem. 11 (2006) 2489.

[7] (a) J.E. Bercaw, J. Am. Chem. Soc. 96 (1974) 5087;
(b) S.T.N. Mclain, E. Drysdale, US patent 1991, 028(5), 667.;
(c) P. Sun, C. Qian, L. Wang, R. Chen, Syn. Commun. (2002) 2937;
(d) C. Qian, F. Cao, R. Chen, Tetrahedron Lett. (2001) 4673.

[8] M.Q. Xue, Y.M. Yao, L.S. Mao, Q. Shen, Chin. J. Struct. Chem. 22 (2003) 147.

[9] G.B. Deacon, S. Nickel, P. MacKinnon, E.R.T. Tiekink, Aust. J. Chem. 43 (1990) 1245.

[10] F. Ignacio, D.P. Richard, D.B. Philip, F.M. Mary, G.D. Matthew, L.O. Fernando, J. Organomet. Chem. 689 (2004) 1890.

[11] S. Solé, H. Gornitzka, O. Gertand, J. Am. Chem. Soc. 120 (1998) 9100.