

Synthesis and crystal structure of $\text{Li}[(O-4,6\text{-di-}^t\text{Bu-C}_6\text{H}_2)_2(\text{CH}_2)_2]_2\text{Y}[\text{MeIm}]_2(\text{THF})_2$ (MeIm = *N*-Methylimidazole)^o

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ABSTRACT

The title complex $\text{Li}[(O-4,6\text{-di-}^t\text{Bu-C}_6\text{H}_2)_2(\text{CH}_2)_2]_2\text{Y}[\text{MeIm}]_2(\text{THF})_2$ has been synthesized by the reaction of $\text{LiY}[\text{N}(^i\text{Pr})_2]_4$ with H_2LCl ($\text{L} = O-4,6\text{-di-}^t\text{Bu-C}_6\text{H}_2-2\text{-CH}_2\text{-[C\{N(CHCH)NMe\}]}$) and LiBu in a 1:3:2 molar ratio at the room temperature in THF, and characterized by single-crystal X-ray diffraction. It crystallizes in monoclinic, space group $C2/c$ with $a = 2.7424(4)$, $b = 2.18819(18)$, $c = 1.7540(2)$ nm, $\beta = 129.259(2)^\circ$, $V = 8149.9(17)\text{\AA}^3$, $M_r = 1393.73$, $Z = 4$, $D_c = 1.136$ Mg/m³, μ (MoK α) = 0.77 mm⁻¹ and $F(000) = 3016$. The structure was refined to $R = 0.077$ and $wR = 0.1820$ for 7393 observed reflections with $I > 2\sigma(I)$. The Y ion is coordinated to four phenoxo groups and N atoms of *N*-Methylimidazole from the cleavage of NHC to form a distorted octahedral geometry. Both of the temperature and the substitution group effect on the reaction lead to the cleavage of NHC ligand to form the title complex. © 2013 Trade Science Inc. - INDIA

KEYWORDS

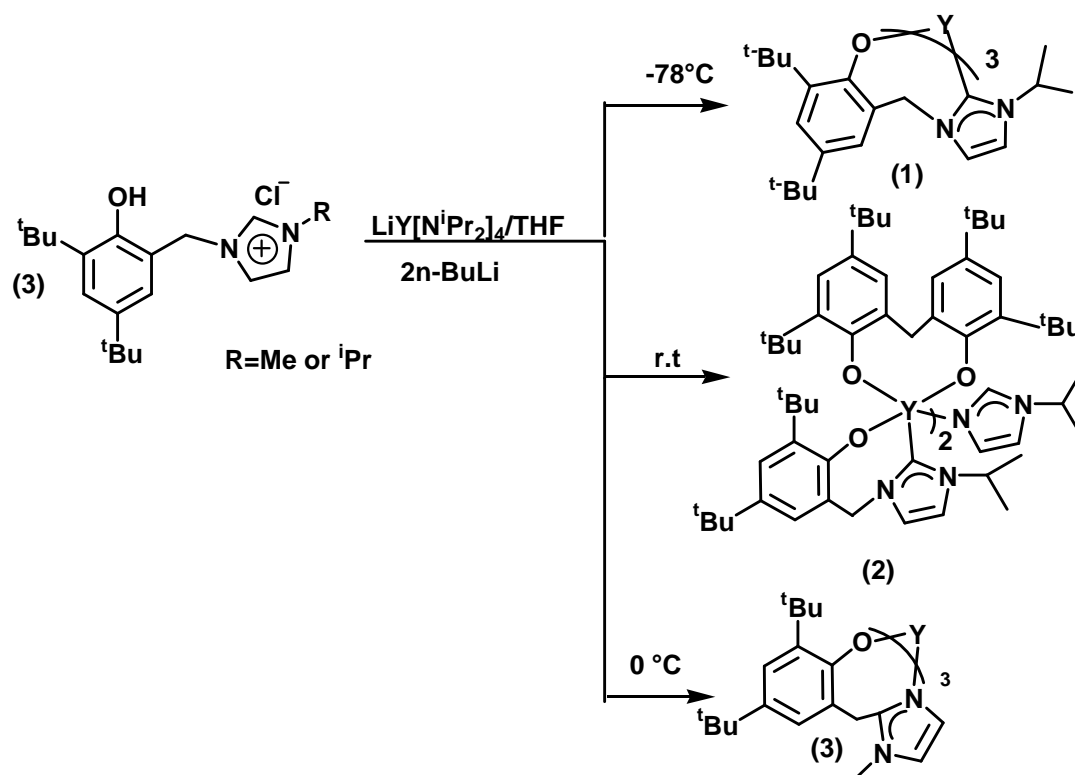
Organolanthanide;
N-aryloxo imidazolium;
Crystal structure;
Cleavage;
Yttrium.

INTRODUCTION

Recently, the application of anionic functionalized *N*-heterocyclic carbenes (NHCs), such as amido- or aryloxo (alkoxo)-functionalized NHCs as the ligands, have attracted much more attention in organolanthanide chemistry^[1-4]. We have successfully synthesized heteroleptic ytterbium complexes $\text{L}_2\text{YbN}^i\text{Pr}_2$ and $\text{L}'_2\text{YbN}^i\text{Pr}_2$ ($\text{L} = O-4,6\text{-di-}^t\text{Bu-C}_6\text{H}_2-2\text{-CH}_2\text{-[C\{N(CHCH)NMe\}]}$, $\text{L}' = O-4,6\text{-di-}^t\text{Bu-C}_6\text{H}_2-2\text{-CH}_2\text{-[C\{N(CHCH)N}^i\text{Pr}]}$) and tris-phenoxo-NHC yttrium complex, $\text{L}'_3\text{Y}$ (**1**) by the reaction of $\text{LiLn}[\text{N}^i\text{Pr}_2]_4$ with $\text{H}_2\text{L}'\text{Cl}$ and BuLi , respectively^[5], while by the reaction of $\text{LiLn}[\text{N}^i\text{Pr}_2]_4$ with $\text{H}_2\text{L}'\text{Cl}$ and BuLi at room temperature, a monophenoxo-NHC complex co-supported

by a bridged bisphenoxo group, $\text{L}'\text{Y}[(O-4,6\text{-di-}^t\text{Bu-C}_6\text{H}_2)_2(\text{CH}_2)_2][^i\text{PrIm}]_2$ (*i*PrIm *N*-isopropylimidazole) (**2**), is obtained from the cleavage of NHC^[6] and the reaction of $\text{LiY}[\text{N}(^i\text{Pr})_2]_4$ with H_2LCl and LiBu in a 1:3:2 molar ratio at 0 °C, a tris-phenoxo-imidazole yttrium complex, L_3Y (**3**), was obtained from the 1,2-benzyl migration of NHC ligands^[7]. (Scheme 1).

During our further study on the transamination of $\text{LiY}[\text{N}(^i\text{Pr})_2]_4$ with H_2LCl and LiBu in a 1:3:2 molar ratio at the room temperature was not obtained $\text{LY}[(O-4,6\text{-di-}^t\text{Bu-C}_6\text{H}_2)_2(\text{CH}_2)_2][\text{MeIm}]_2$ instead of a heterobimetallic complex supported by a bridged bisphenoxo group, $\text{Li}[(O-4,6\text{-di-}^t\text{Bu-C}_6\text{H}_2)_2(\text{CH}_2)_2]_2\text{Y}[\text{MeIm}]_2(\text{THF})_2$, from the cleavage of NHC. Here we report the preliminary results



Scheme 1

EXPERIMENTAL

General procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture by using standard Schlenk techniques. THF was degassed and distilled from sodium benzophenone ketyl under argon prior to use. N-aryloxo imidazolium chloride H_2LCl was prepared according to the literature^[8]. The melting point was determined in a sealed argon filled capillary tube and uncorrected. The elemental analyses of C, H and N were performed by the direct combustion on a Carlo-Erba EA-1110 instrument, and the lanthanide metal analysis was carried out by complexometric titration. ^1H NMR spectra were obtained in CDCl_3 (400MHz).

Synthesis of $\text{Li}[(O\text{-}4,6\text{-di-}^t\text{Bu-C}_6\text{H}_2)_2(\text{CH}_2)_2]_2\text{Y}[\text{MeIm}]_2(\text{THF})_2$

A solution of $\text{LiY}[\text{N}(\text{iPr})_2]_4$ (15.2 mL, 4 mmol) in THF was added dropwise to the suspension of (H_2LCl) (3.48 g, 8 mmol) under stirring. After that BuLi (7.6 mL, 8 mmol) was introduced at room temperature for 10 h, and then the mixture was stood at room tempera-

ture for 24 h. The solvent was removed in vacuum, and the residue was extracted 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 the title complex (1.78 g, 32%). m.p.: 194°C (dec.). Anal. Calcd. (%) for $\text{C}_{82}\text{H}_{128}\text{LiN}_4\text{O}_8\text{Y}$: C, 70.60; H, 9.18; N, 4.01; Y, 6.37. Found: C, 70.12; H, 9.24; N, 3.95; Y, 6.56. ^1H NMR (CDCl_3 , 400MHz): 1.44(s, 36H), 1.77(s, 36H), 1.82 (s, 8H), 3.43 (m, 4H), 3.78 (s, 8H), 3.88 (s, 6H), 6.88 (s, 2H), 6.95 (s, 4H), 6.98 (s, 2H), 7.06 (s, 2H), 7.2 (s, 2H), 7.42 (s, 2H).

Structure determination

A colorless crystal with dimensions of $0.30\text{mm} \times 0.29\text{mm} \times 0.25\text{mm}$ was sealed in a thin-walled glass capillary filled with argon for X-ray diffraction studies. Intensity data were collected on a Rigaku Mercury CCD area detector equipped with a graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The diffracted intensities were corrected for Lorentz-polarization effects and empirical absorption corrections. A total of 40396 reflections were collected in the range of $3.0 \leq \theta \leq 25.3$ by using an φ - ω scan mode at

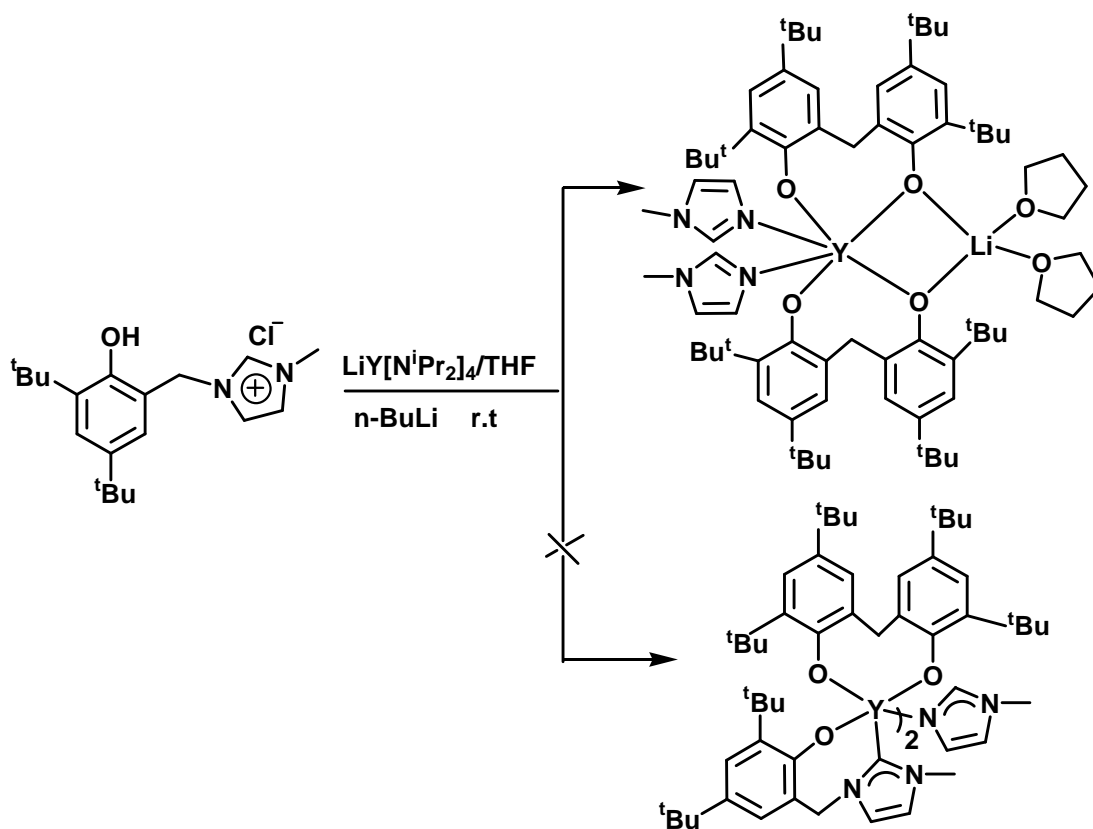
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193 (2) K, of which 7393 ($R_{\text{int}} = 0.084$) were independent. 5883 observed reflections with $I > 2\sigma(I)$ were used in the structure refinement. The structure was solved by direct methods. Non-hydrogen atoms were determined with successive difference Fourier syntheses. The hydrogen atoms were located at the calculated positions. The anisotropic thermal parameters for the non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2 . The final refinement converged to $R = 0.077$ and $wR = 0.1820$ ($w = 1/[\sigma^2(F_o^2) + (0.0984P)^2 + 10.7641P]$, where $P = (F_o^2 + 2F_c^2)/3$), $(\Delta/\sigma)_{\text{max}} < 0.001$, $S = 1.07$, $(\Delta\rho)_{\text{max}} = 1.35$ and $(\Delta\rho)_{\text{min}} = -0.42 \text{ e}/\text{\AA}^3$. The programs for structure solution and

refinement are SHELXS-97^[9] and SHELXL-97^[10], respectively.

RESULTS AND DISCUSSION

Reaction of $\text{LiY}[\text{N}(\text{i-Pr})_2]_4$ with 3 equiv of $[\text{HO}-4,6\text{-di-}^t\text{Bu-C}_6\text{H}_2-2\text{-CH}_2\{\text{CH}(\text{iPrNCHCHN})\}]\text{Cl}$ and 2 equiv of BuLi in THF at room temperature gave a colorless solution. After workup, the title complex was isolated as light blue crystals in 32% yield (Scheme 2). The composition of the title complex was confirmed by elemental analysis and $^1\text{H NMR}$, and its definitive structure was determined by X-ray diffraction.



Scheme 2

The molecular structure of the title complex is shown in Figure 1. The details crystallographic data were collected in TABLE 1, the selected bond lengths and bond angles are given in TABLE 2.

As shown in Figure 1, the title complex is a heterobimetallic complex supported by a carbon bridged bisphenoxo group, in which Y ion is coordinated to four phenoxo groups and two N atoms of imidazole ring from the cleavage of NHC to form a distorted octahedral ge-

ometry and the O (1), O (2), O (1ⁱ), O (2ⁱ) occupy the equatorial sites, while N (1) and N (1ⁱ) sit on the axis. The axial angle of 144.65(15)° (N (1)–Y–N (1ⁱ)) is distinctly non-linear. The lithium ion is coordinated to four O atoms from two THF molecules and two bridged bisphenoxo group to form a tetrahedral geometry.

The Y–O (1), Y–O (2), Y–O (1ⁱ) and Y–O (2ⁱ) bond distances are 0.2453 (3), 0.2149 (2), 0.2453 (3) and 0.2149 (2) nm, respectively and The Y–O (1), Y–

O (1ⁱ) bond distances are longer than Y–O (2) and Y–O (2ⁱ), which is due to the effect of lithium ion coordinated by O (2) and O (2ⁱ) atoms on the bond distance. The averaged Y–O distance of 0.2301 nm is longer

than 0.2168(2)nm found in the six-coordinated [O-4,6-di-^tBu-C₆H₂-2-CH₂-[C{N(CHCH)NⁱPr}]₃Y^[5] and 0.2149 (2) nm reported in the complex L₃Y^[7] from the 1,2-benzyl migration of NHC ligand.

TABLE 1 : Crystallographic data and structure refinement parameters for complex 1

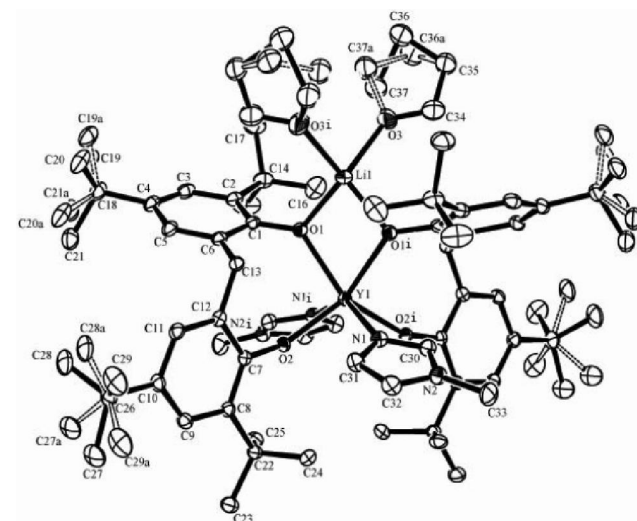
Empirical formula	C ₇₄ H ₁₁₂ Li N ₄ O ₆ Y	F(000)	3016
Formula weight	1393.73	Calculated density/ (g·cm ⁻³)	1.136
Temperature/K	193(2)	Absorption coefficient/mm ⁻¹	0.769
Wavelength/nm	0.071073	Θ range for data collection/(°)	3.02-25.35°
Crystal system	monoclinic	Limiting indices	-32<=h<=33, -25<=k<=26, -19<=l<=21
Space group	C 2/c	Observed reflections(I>2σ(I))	6041
a/nm	27.424(4)	Reflections collected/unique	40396 / 7393
b/nm	21.8819(18)	Refinement method	Full-matrix least-squares on F ²
c/nm	17.540(2)	Data/restraints/parameters	7393 / 0 / 434
β/(°)	129.259(2)	Goodness-of-fit on F ²	1.069
Volume/nm ³	8149.8(16)	Final R indices	R1=0.0774, wR2=0.1820
Z	4	R indices (all data)	R1=0.981, wR2=0.1938

TABLE 2 : Selected bond lengths (nm) and bond angles (°)

Bond	Dist.	Bond	Dist.
Y(1)-O(2 ⁱ)	0.2149(2)	Y(1)-O(2)	0.2149(2)
Y(1)-O(1)	0.2453(3)	Y(1)-O(1 ⁱ)	0.2453(3)
Y(1)-N(1)	0.2484(3)	Y(1)-N(1 ⁱ)	0.2484(3)
O(3)-Li(1)	0.2102(8)	O(1)-C(1)	0.1345(4)
O(1)-Li(1)	0.1948(7)	O(2)-C(7)	0.1334(4)
Angle	(°)	Angle	(°)
O(2 ⁱ)-Y(1)-O(2)	118.53(13)	O(2 ⁱ)-Y(1)-O(1)	140.66(9)
O(2)-Y(1)-O(1)	93.18(9)	O(2 ⁱ)-Y(1)-O(1 ⁱ)	93.18(9)
O(2)-Y(1)-O(1 ⁱ)	140.66(9)	O(1)-Y(1)-O(1 ⁱ)	71.66(13)
O(2 ⁱ)-Y(1)-N(1)	82.07(11)	O(2)-Y(1)-N(1)	80.06(13)
O(1)-Y(1)-N(1)	128.94(10)	O(1 ⁱ)-Y(1)-N(1)	82.18(10)
O(2 ⁱ)-Y(1)-N(1 ⁱ)	80.07(11)	O(2)-Y(1)-N(1 ⁱ)	82.07(10)
O(1)-Y(1)-N(1 ⁱ)	82.18(10)	N(1)-Y(1)-N(1 ⁱ)	144.65(15)

The Y–N bond distances are 0.2484(3) nm which is longer than 0.2465(3) nm in L₃Y complex but shorter than 0.2556(7) nm in the [ClY{*i*-OC₆H₄(CH₂NMe₂)-2}₃Y{OC₆H₄(CH₂NMe₂)-2}₃Na]^[11] complex. The Li–O (3) and Li–O (3A) bond distances (0.1948 nm) coordinated the carbon bridged bisphenoxo group is shorter than Li–O (1) and Li–O (1ⁱ)(0.2102nm) coordinated THF molecules, reflecting the conjugated effect between the benzene ring and oxygen atom.

The reaction outcomes have been greatly affected



Symmetric codes: *i* -x+1,y,-z+3/2; Displacement ellipsoids at the 30% probability level

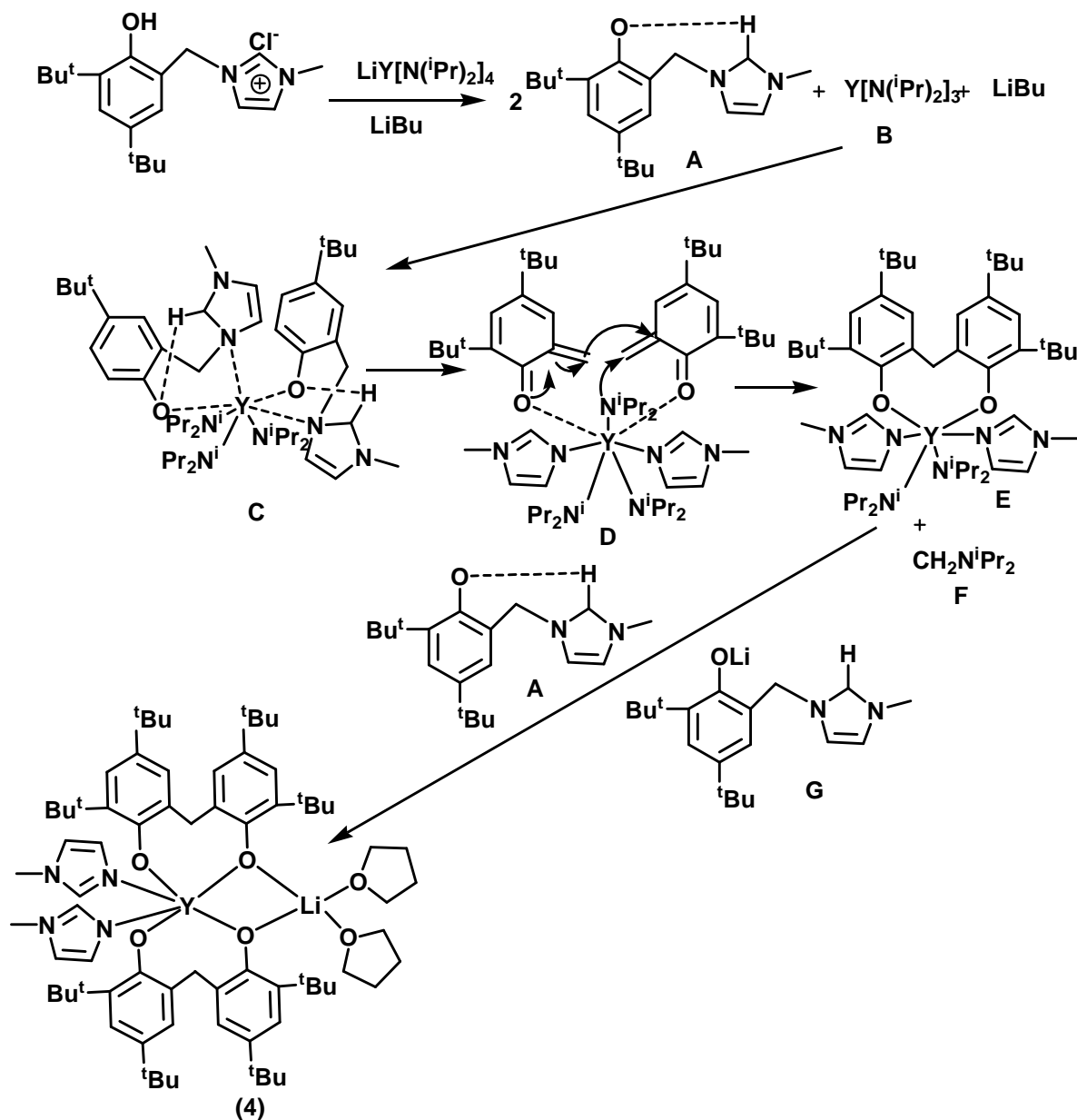
Figure 1 : View of t of title complex

by the reaction temperature and substitution group in the nitrogen atoms of imidazole ring, the reaction of the reaction of LiY[N(iPr)₂]₄ with H₂L'Cl and LiBu in a 1:3:2 molar ratio at the room temperature gives a monophenoxo-NHC complex co-supported by a bridged bisphenoxo group, L'Y[(O-4,6-di-^tBu-C₆H₂)₂(CH₂)][ⁱPrIm]₂(ⁱPrIm) N-isopropylimidazole), while the reaction of LiY[N(iPr)₂]₄ with H₂LCI and LiBu at the same condition gives the hetero-bimetallic complex supported by a bridged bisphenoxo group,

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$\text{Li}[(O-4,6\text{-di-}^t\text{Bu-C}_6\text{H}_2)_2(\text{CH}_2)_2\text{Y}[\text{MeIm}]_2(\text{THF})_2]$. The formation of the title complex indicates that the cleavage of NHC from ligand L occurs concomitantly during the transamination reaction proceeding. The cleavage

of NHC is not surprising, as three examples have already been reported^[12,13,6]. The mechanism for the formation of title complex is not clear so far, and supposed mechanism is shown in Scheme 3.



Scheme 3

The reaction of $\text{LiY}[\text{N}^i\text{Pr}_2]_4$ with one equiv of H_2LCl , and H_2LCl with BuLi could give (A) and (B), respectively^[6]. The coordination of N and phenoxo from phenol-NHC to metal could afford (C). The isomerization of benzene ring and cleavage of NHC would yield (D). Intramolecular addition of carbon of phenyl to methylene and two NPr₂ groups to methylene should afford (E) and release amine. The reaction of (E) with

(A) and (G) could yield the title complex. Further confirmation of the mechanism is proceeding.

In conclusion, the structure of NHC ligand and the reaction condition have great effect on the reaction outcome. A hetero-bimetallic complex supported by a bridged bisphenoxo group has been obtained from the cleavage of NHC ligand. Further study on the mechanism for the formation of title complex and the influence

of metal, NHC, and reaction condition on reaction is currently in progress.

ACKNOWLEDGEMENT

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SUPPORTING INFORMATION AVAILABLE

Crystallographic data, in CIF format, for the structure analysis of 3, and a figure of the crystal structure of complex 4. This material is available free of charge via the Internet at <http://www.tradescienceinc.com>.

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