Mono- and Tris-Phenoxo-Tethered N-Heterocyclic Carbene Yttrium Complexes: Syntheses and Molecular Structures

Zhi-Guo Wang,[†] Hong-Mei Sun,[†] Hai-Sheng Yao,[†] Qi Shen,*[,†,‡] and Yong Zhang[†]

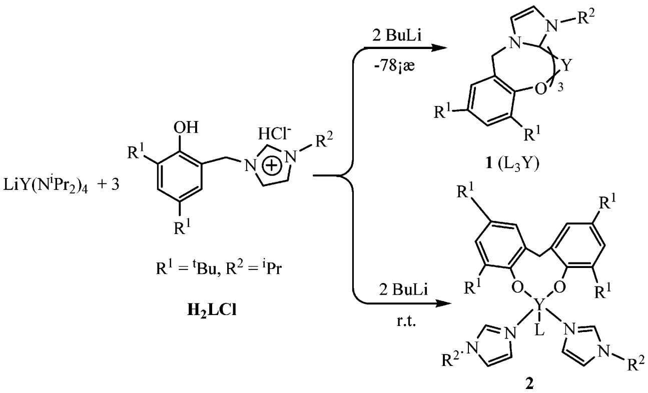
College of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, People's Republic of China, and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, Shanghai 200433, People's Republic of China

Received June 6, 2006

Summary: The reaction of $LiY[N^iPr_2]_4$ *with* H_2LCl *(L = O-4,6-di-*^{t}*Bu-*C_6H_2*-2-*CH_2*-[C{N(CHCH)N*^{i}*Pr}]) and BuLi in the molar ratio of 1:3:2 at −78 °C affords a yttrium complex supported by three anionic NHC ligands,* L_3Y *(**1**). Reaction temperature has a great effect on the reaction outcome. The same reaction at room temperature yields a monoanionic NHC yttrium complex co-supported by a bridged bisphenoxo group,* $LY[(O\text{-}4,6\text{-di-}^tBu\text{-}C_6H_2)_2(CH_2)][^iPrIm]_2$ *(*^{i}*PrIm = N-isopropylimidazole) (**2**) formed from the cleavage of NHC.*

The application of N-heterocyclic carbene (NHC) in organometallic chemistry of transition metals, especially late transition metals, has attracted increasing attention.[1] Exploration of anionic-functionalized NHC, in which a chelating anionic group incorporates into the N-alkyl sidearm leading to enhanced binding of NHC to electropositive metals, provides the opportunity to isolate stabilizing NHC complexes of electropositive lanthanides. To date, a variety of amino-functionalized NHC complexes of lanthanides have been reported,[2] and yttrium complexes have recently been found to exploit the hemilabile reactivity of the NHC, affording an extremely highly active catalyst for ring-opening polymerization of lactide.[3] Our interest in this area is to understand the chemistry of lanthanide complexes with phenoxo-functionalized NHCs, as lanthanide complexes supported by phenoxo groups have widely been used in homogeneous catalysis.[4] In this context we have designed and synthesized phenoxo-functionalized imidazolium chlorides and synthesized heteroleptic ytterbium complexes $L'_2YbN^iPr_2$ ($L' = O$-4,6-di-^{t}Bu-C_6H_2-2-CH_2-[C{N(CHCH)NR}], R = ^{i}Pr and Me) by the reaction of $LiYb[N^iPr_2]_4$ with $H_2L'Cl$ and BuLi, respectively.[5] During our further study on the similar reaction with $LiY[N^iPr_2]_4$ in the molar ratio of 1:3:2, it was found that the reaction temperature has a great effect on the reaction outcome. The reaction at −78 °C yields a tris-phenoxo-NHC yttrium complex, L_3Y (L = *O*-4,6-di-^{t}Bu-C_6H_2-2-CH_2-[C{N(CHCH)N^{i}Pr}]) (**1**), while at room temperature a monophenoxo-NHC complex co-supported by a bridged bisphenoxo group, $LY[(O\text{-}4,6\text{-di-}^tBu\text{-}C_6H_2)_2(CH_2)][^iPrIm]_2$ (^{i}PrIm = *N*-isopropylimidazole) (**2**), is obtained from the cleavage of NHC (Scheme 1). Here we report the preliminary results.

Scheme 1



The treatment of $LiY[N^iPr_2]_4$[6] with 2 equiv of BuLi and 3 equiv of H_2LCl in THF at −78 °C for 10 h, then at room temperature for 24 h, afforded a light yellow solution. After workup, light yellow crystals were obtained in 58% yield and were characterized by elemental analysis, ^1H NMR, and ^{13}C NMR to be **1**.[7] Further confirmation was obtained by X-ray diffraction.

The ^{13}C NMR spectroscopy of **1** showed the $C_{carbene}$ resonates at δ 199.9 ppm, which is very close to the values found in known NHC Y complexes, i.e., 186.0, 190.3, and 194.0 ppm for $(^tBuNCH_2CH_2[C\{N(CHCH)N^tBu\}])Y[N(SiMe_3)_2]_2$,[2a] $Y[N(SiHMe_2)_2]_3[C\{MeN(CHCH)NMe\}]$, and $Y[N(SiHMe_2)_2]_3[C\{MeN(CHCH)NMe\}]_2$,[8] respectively. Single crystals of **1**

---

* Corresponding author. Fax: (86)512-65880305. Tel: (86)512-65880306. E-mail: qshen@suda.edu.cn.

[†] Suzhou University.

[‡] Shanghai Institute of Organic Chemistry.

(1) For recent reviews, see: (a) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand. G. *Chem. Rev.* **2000**, *100*, 39. (b) Cavell, K. J.; McGuinness, D. S., *Coord. Chem. Rev.* **2004**, *248*, 671, and references therein.

(2) (a) Arnold, P. L.; Mungur, S. A.; Blake, A. J.; Wilson, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 5981. (b) Liddle, S. T.; Arnold, P. L. *Organometallics* **2005**, *24*, 2597. (c) Arnold, P. L.; Liddle, S. T. *Chem. Commun.* **2005**, 5638. (d) Arnold, P. L.; Liddle, S. T. *Organometallics* **2006**, *25*, 1485.

(3) Dipti, P.; Liddle, S. T.; Mungur, S. A.; Rodden, M.; Blake, A. J.; Arnold, P. L. *Chem. Commun.* **2006**, 1124.

(4) (a) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087. (b) McLain, S. T. N.; Drysdale. E. U.S. Patent 5,028,667, 1991. (c) Sun, P.; Qian, C.; Wang, L.; Chen, R. *Synth. Commun.* **2002**, 2937. (d) Qian, C.; Cao, F.; Chen, R. *Tetrahedron Lett.* **2001**, 4673.

(5) Wang, Z. G.; Sun, H. M.; Yao, H. S.; Yao, Y. M.; Shen, Q.; Zhang, Y. *J. Organomet. Chem.* **2006**, *691*, 3383.

(6) Aspinall, C. H.; Tillotson, M. R. *Polyhedron* **1994**, *13*, 3229.

(7) Synthesis of **1**: To the suspension of H_2LCl (2.2 g, 6.0 mmol) in THF were added dropwise a solution of $LiY[N^iPr_2]_4$ (10.5 mL, 2.0 mmol) in THF and then a hexane solution of BuLi (4.8 mL, 4.0 mmol) under stirring at −78 °C. The mixture was stirred at −78 °C for 10 h. Then the yellow solution was gradually warmed to room temperature and stirred for an additional 24 h at room temperature. The solvent was removed in a vacuum, and the residue was extracted with hexane and centrifuged to remove the precipitate. The obtained solution was concentrated and crystallized at room temperature for a few days to afford light yellow crystals of **1** (1.2 g, 58%). Mp: 165 °C (dec). Anal. Calcd for $C_{63}H_{93}N_6O_3Y$: C, 70.56; H, 8.68; N, 7.84; Y, 8.29. Found: C, 70.44; H, 8.49; N, 7.64: Y, 8.22. ^1H NMR (C_6D_6, 400 MHz): 1.38 (s, 27H), 1.69(s, 27H), 2.8(d, 18H), 3.62(m, 3H), 4.56(s, 6H), 5.52(s, 3H), 5.94(m, 3H), 7.02(brs, 3H), 7.28(brs, 3H). $^{13}C\{^1H\}$ NMR(C_6D_6) 30.8 (CH_3), 31.7(CH_3), 34.5, 35.8, 54.1 (CH_2), 63.4 (CH_2), 119.7(CH), 120.1(CH), 124.7(CH), 125.4(CH), 199.9 (NCN).

10.1021/om060496e CCC: $33.50

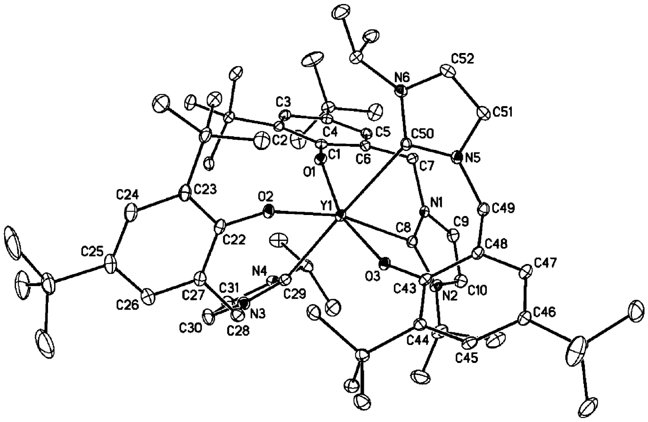


Figure 1. Crystal structure of **1** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y(1)−O(2) = 2.150(2), Y(1)−O(1) = 2.184(2), Y(1)−O(3) = 2.170(2), Y(1)−C(50) = 2.606(3), Y(1)−C(8) = 2.615(3), Y(1)−C(29) = 2.641(3), O(3)−Y(1)−C(50) = 78.74(9), O(2)−Y(1)−C(8) = 165.56(9), C(50)−Y(1)−C(29) = 169.93(10)

suitable for structural analysis were grown by recrystallization from hexane. The molecular structure is shown in Figure 1.

The Y ion is coordinated to three phenoxo groups and three NHC ligands to form a distorted octahedral geometry in which O(1), O(3), C(29), and C(50) occupy the equatorial sites, while O(2) and C(8) occupy axial sites. The axial angle of 165.56(9)° (O(2)−Y(1)−C(8)) is distinctly nonlinear. The $\mathrm{Y{-}C_{carbene}}$ lengths range from 2.606(3) to 2.641(3) Å, and the average $\mathrm{Y{-}C_{carbene}}$ of 2.621(3) Å is shorter than 2.660 Å found in five-coordinated $\mathrm{Y[N(SiHMe_2)_2]_3[C\{MeN(CHCH)NMe\}]_2}$[8] and comparable to 2.551 Å for four-coordinated $\mathrm{Y[N(SiHMe_2)_2]_3[C\{MeN(CHCH)NMe\}]}$[8] and longer than 2.501(5) Å in $\mathrm{YL\{N(SiMe_3)_2\}_2}$ [L = $\mathrm{{}^tBuNHCH_2CH_2[C\{{}^tBuN(CHCH)N\}]}$.[2a] The Y−O lengths are 2.150(2), 2.170(2), and 2.184(2) Å, respectively, and the average length is 2.168(2) Å, which is considerably elongated in comparison with the average value of 2.119 Å in (Danip)Y[*O*-2,6-di-^{i}Pr-$\mathrm{C_6H_3}$]]$_2$(THF) [Danip = $\mathrm{C_6H_3}$-2,6-di-(2′-MeO-$\mathrm{C_6H_4}$)],[9] reflecting the enhanced steric and electronic saturation of the metal center.

To our best knowledge, this is the first lanthanide complex with three anionic NHC ligands and the first structure of a tris-NHC complex of lanthanide, although the tris-NHC complex of $\mathrm{ErCl_3(NHC)_3}$ was reported in 1997, but no structure was presented.[7]

When the same reaction was conducted at room temperature, a mono-NHC complex supported by a bridged biphenoxo ligand LY[(*O*-4,6-di-^{t}Bu-$\mathrm{C_6H_2}$)$_2$($\mathrm{CH_2}$)][^{i}PrIm]$_2$ (**2**)[10] was isolated in 42% yield. The resonance for the carbene carbon in **2** is at *δ* 198.4 ppm, which falls within the range of reported values for Y−NHC complexes, i.e., 190.3 ppm for $\mathrm{Y[N(SiHMe_2)_2]_3[C\{MeN(CHCH)NMe\}]}$[8] and 194.0 ppm for $\mathrm{Y[N(SiHMe_2)_2]_3[C\{MeN(CHCH)NMe\}]_2}$[8] and comparable to 199.9 ppm in **1**. The molecular structure of **2** was further determined by single-crystal X-ray crystallography (Figure 2).

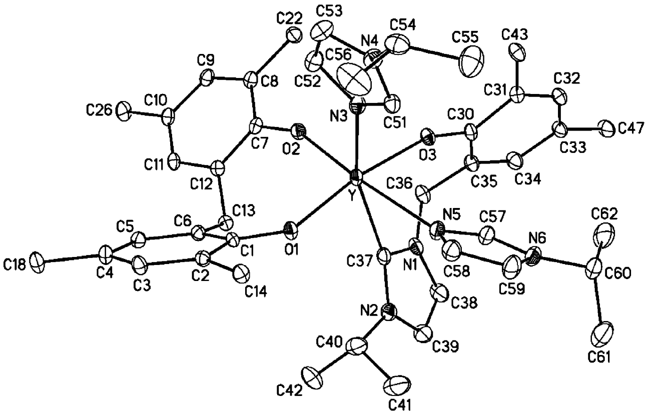
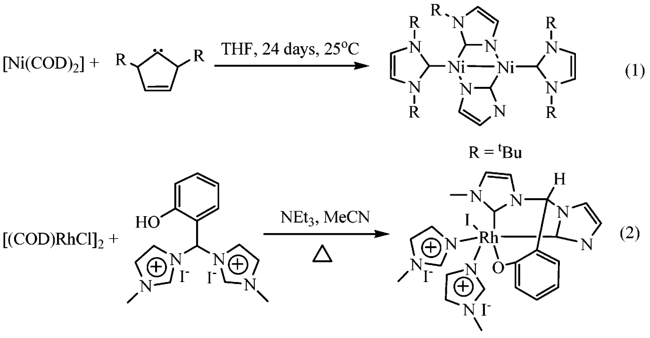


Figure 2. Crystal structure of **2** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Y−O(2) = 2.118(3), Y−O(3) = 2.161(3), Y−O(1) = 2.162(3), Y−N(3) = 2.472(4), Y−N(5) = 2.527(4), Y−C(37) = 2.576(5); O(3)−Y−C(37) = 81.93(14), O(2)−Y−O(1) = 95.52(12), O(2)−Y−C(37) = 102.13(16), O(1)−Y−C(37) = 92.92(14), N(3)−Y−C(37) = 161.65(16), N(5)−Y−C(37) = 77.38(16).

Scheme 2



A bridged bisphenoxo group, two ^{i}PrIm from the cleavage of ligand L, and one L are bound to the central metal Y, forming a pseudo-octahedral geometry. One of the bridging phenoxo oxygen atoms (O(1)), one nitrogen atom (N(3)) from ^{i}PrIm, one oxygen atom (O(3)), and one $\mathrm{C_{carbene}}$ from L occupy equatorial positions, while the other oxygen atom from bridged bisphenoxo groups (O(2)) and one nitrogen atom (N(5)) of ^{i}PrIm occupy axial positions. The corresponding bond angle of O(2)−Y−N(5) is distorted away from the idealized 180° to 174.95(13)°. The bond length of 2.161(3) Å for Y−O(3) is consistent with 2.168(2) Å in **1**. The average bond length of Y−O (bridged O) is 2.140(3) Å, which is comparable to the value of 2.119 Å found in [(MBMP)Yb(O^{i}Pr$_2$)(THF)$_2$]$_2$[MBMP = [(*O*-2-Me-6-^{t}Bu-$\mathrm{C_6H_2}$)$_2$($\mathrm{CH_2}$)],[11] when differences in ionic radii are considered. The value of 2.576(5) Å for $\mathrm{Y{-}C_{carbene}}$ can compare with those for all the NHC yttrium complexes published and is almost consistent with 2.621(3) Å in **1**. The Y−N bond lengths, 2.472(4) and 2.527(4) Å, fall in the range of dative bond lengths from 2.47 to 2.63 Å[11] and are comparable to the values in complex $\mathrm{(C_{12}H_8N)_2Sm(N\text{-}MeIm)_4}$,[12] when the difference in ionic radii was considered.

---

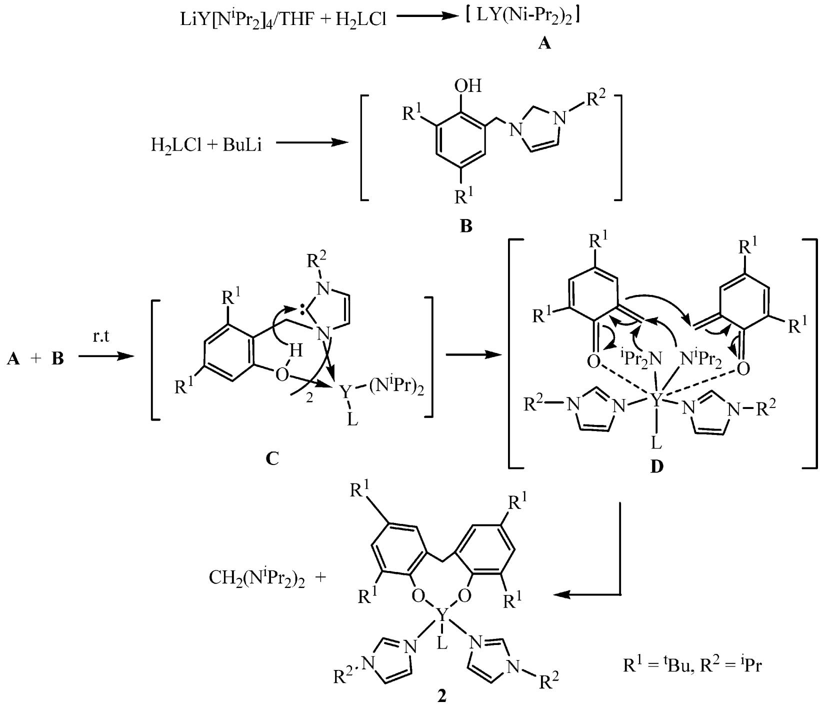
(8) Wolfgang, A. H.; Florian, C. M.; Georg, R. J. A.; Oliver, R.; Reiner, A. *Organometallic* **1997**, *16*, 682.

(9) Rabe, G. W.; Mei, Z. P.; Riederer, F. A.; Yap, G. P. A. *Inorg. Chem.* **2003**, *42*, 3527.

(10) Synthesis of **2**: Complex **2** was prepared by a procedure analogous to that described above. A solution of LiY[N^{i}Pr$_2$]$_4$ (10.5 mL, 2.0 mmol) in THF was added dropwise to the suspension of $\mathrm{H_2LCl}$ (2.19 g, 6.0 mmol) under stirring, and then BuLi (4.8 mL, 4.0 mmol) was introduced at room temperature. The mixture was stirred at room temperature for 34 h. Light yellow crystals were obtained from toluene/THF at −15 °C for a few days (0.89 g, 42%). Mp: 178 °C (dec). Anal. Calcd for $\mathrm{C_{62}H_{93}N_6O_3Y}$: C, 70.23; H, 8.78; N, 7.92; Y, 8.39. Found: C, 70.12; H, 8.65; N, 7.90; Y, 8.36. ^{1}H NMR ($\mathrm{C_6D_6}$, 400 MHz): 0.56(d, 18H), 1.38(s, 9H), 1.25(s, 9H), 1.40 (s, 18H), 1.51(s, 18H), 2.59(s, 2H), 3.68(s, 3H), 4.58(s, 3H), 5.25(s, 3H), 5.76(brs, 3H), 7.05 (brs, 2H), 7.07(brs, 2H), 7.15(brs, H), 7.54(brs, 1H), 7.90(brs, 1H). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): 30.8 ($\mathrm{CH_3}$), 32.5($\mathrm{CH_3}$), 31.7($\mathrm{CH_3}$), 34.5, 35.8, 54.1($\mathrm{CH_2}$), 60.6(C($\mathrm{C_2}$)), 120.2(CH), 128.2(CH), 128.5(CH), 128.7(CH), 198.4(NCN).

(11) Yao, Y. M.; Xu, X. P.; Liu, B.; Zhang, Y.; Shen, Q.; Wang, W. T. *Inorg. Chem.* **2005**, *44*, 5133.

Scheme 3



The formation of **2** indicates that the cleavage of NHC from the ligand L occurs concomitantly during the reaction. The cleavage of NHC is not surprising, as two examples have already been reported: one is the cleavage of NHC from 1,3-bis-*tert*-butylimidazol-2-ylidene (Scheme 2, eq 1);[13] the other is from a bis-NHC precursor (Scheme 2, eq 2).[14] To our surprise, the cleavage of NHC leads to the formation of a methene-bridged [(*O*-4,6-di-^{t}Bu$_2$-C$_6$H$_2$)$_2$(CH$_2$)], not an ethylene-bridged ligand [(*O*-4,6-di-^{t}Bu-C$_6$H$_2$)$_2$(CH$_2$)$_2$]. The mechanism for the formation of **2** is not clear so far, and the supposed mechanism is shown in Scheme 3. The reaction of LiY[N^{i}Pr$_2$]$_4$ with 1 equiv of H$_2$LCl, and H$_2$LCl with BuLi, could give **A** and **B**, respectively.[15] The reaction of **A** with **B** would afford the intermediate **C** first, then **D** would form via a hydrogen transfer from phenol to carbene carbon and the coordination of ^{i}PrTm to Y. Intramolecular additions of carbon of phenyl to methylene and two N^{i}Pr$_2$ groups to methylene should afford **2** and release amine. Further confirmation of the mechanism is proceeding.

In conclusion, a tris-phenoxo-NHC complex of yttrium **1** has been synthesized by the reaction of LiY[N^{i}Pr$_2$]$_4$ with H$_2$LCl and BuLi at −78 °C. The same reaction conducted at room temperature results in the cleavage of NHC and a mono-phenoxo-NHC ytterium complex **2**. Further study on the mechanism for the formation of **2** and the influence of the metal, NHC, and reaction conditions on the reaction and the chemistry behavior of the lanthanide complex obtained is currently in progress.

Acknowledgment. We are grateful to National Natural Science Foundation of China, Ph.D. Foundation from Education Ministry of China, and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, for the financial support.

Supporting Information Available: X-ray crystallographic information for **1** and **2**. This material is available free of charge via the Internet at http://pus.acs.org.

OM060496E

---

[12] Evans, W. J.; Hanusa, T. P.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1987**, *6*, 295.

[13] Evans, W. J.; Rabe, G. W.; Ziller, J. W. *Organometallics* **1994**, *13*, 1641.

[14] Caddick, S.; Cloke, F. G. N.; Hitchcock, P. B.; Lewis, A. K. de K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5824.

[15] Mas-Marazá, E.; Poyatos, M.; Sanaú, M.; Peris, E. *Organometallics* **2004**, *23*, 323.

[16] Arnold, P. L.; Rodden, M.; Wilson, C. *Chem. Commun.* **2005**, 1743.