Unique Formation of a Pentanuclear Lanthanum(III) Thiolate Oxide Cluster via Control of Hydrolysis

Hong-Xi Li,[†] Mei-Ling Cheng,[†] Zhi-Gang Ren,[†] Wen-Hua Zhang,[†] Jian-Ping Lang,*,[†,‡] and Qi Shen[†]

Key Laboratory of Organic Synthesis of Jiangsu Province, School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, Jiangsu, China, and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

Received December 3, 2005

The reaction of [(TMS)$_2$N]$_3$La(μ-Cl)Li(THF)$_3$ (**1**) and HSPh produced a bimetallic complex [{(TMS)$_2$N}$_2$La(THF)]$_2$(μ-SPh)(μ-Cl)] (**2**). Compound [{(TMS)$_2$N}$_2$La$_5$O(SPh)$_{10}$LiCl$_2$(THF)$_6$] (**3**) was prepared by control of the hydrolysis of **2** and LiCl or **1** and HSPh with the proper amount of water. **1** was treated first with $^1/_6$ equiv of H$_2$O and then with equimolar HSPh; a polymeric complex [{(TMS)$_2$N}$_2$-(μ-SPh)La(μ-SPh)Li(THF)$_2$]$_\infty$ (**4**) was isolated. **3** contains a central [(μ-SPh)$_4$(μ_3-SPh)$_2${La(THF)}$_4$(μ_3-O)]$^{4+}$ tetrahedral fragment in which two La atoms are linked by a pair of μ-SPh$^-$ and μ_3-Cl$^-$ ligands to a [{(TMS)$_2$N}$_2$La]$^+$ fragment, while the other two are bridged by two μ-SPh$^-$ ligands to a [Li(THF)$_2$]$^+$ fragment, forming a bee-shaped structure.

Organolanthanide compounds are usually prepared under an inert gas using conventional Schlenk techniques with dried solvents. However, some unexpected organolanthanide−oxo complexes[1] are incidentally isolated in varied yields even when the reactions are carried out in a glovebox under an inert gas where contamination by O$_2$ and H$_2$O is maintained to be less than 1 ppm. Elucidation of the origin of the O atom in these compounds proved difficult because of their poor yield, solubility, or reproducibility. Therefore, the introduction of the O atom in many cases is always ascribed to the hydrolysis of lanthanide ions with the adventitious water,[2] even though cleavage of the C−O bond of tetrahydrofuran (THF) or ether,[3] decomposition of grease,[4] and

oxygen-containing reagents such as O$_2$,[5] SeO$_2$,[6] and alkoxides[7] were reported to be the oxygen sources in some cases. Because the adventitious water in many reactions could not be avoided, deliberate initialization of hydrolysis in these reactions via the addition of a quantitative amount of water was considered to be a useful way of obtaining organolanthanide−oxo derivatives. In this regard, several groups have reported some interesting examples that are mainly related to organolanthanide oxides supported by cyclopentadienyl, alkoxide, amine, Schiff base, and carborane ligands.[8] However, few attempts have been made on oxolanthanide chalcogenolate complexes.[9]

On the other hand, we have recently been involved in the preparation and determination of the structures and catalytic properties of new aminolanthanide thiolate complexes.[10] The adventitious water was also observed to work in some of our reactions, which made them quite messy. On the basis of the considerations (i) that, in the presence of water, these thiolate complexes tend to be hydrolyzed because of their weak Ln−S bonds and the oxophilicity of the lanthanide-(III) ion and (ii) that if such a hydrolysis is maintained to a small scale, the resulting hydrolyzed species in solution may interact with the remaining precursor to form new soluble

* To whom correspondence should be addressed. E-mail: jplang@suda.edu.cn.
† Suzhou University.
‡ Chinese Academy of Sciences.

(1) (a) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865−986. (b) Giljie, J. W.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 895−910. (c) Edelmann, F. T.; Freckmann, D. M. M.; Schumann, H. *Chem. Rev.* **2002**, *102*, 1851−1896.
(2) (a) Schuetz, S. A.; Silvernail, C. M.; Incarvito, C. D.; Rheingold, A. L.; Clark, J. L.; Day, V. W.; Belot, J. A. *Inorg. Chem.* **2004**, *43*, 6203−6214. (b) Hitchcock, P. B.; Lappert, M. F.; Prashar, S. *J. Organomet. Chem.* **1991**, *413*, 79−90. (c) Anwander, R.; Munck, F. C.; Priermeier, T.; Scherer, W.; Runte, O.; Herrmann, W. A. *Inorg. Chem.* **1997**, *36*, 3545−3552. (d) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5084−5092. (e) Guan, J.; Shen, Q.; Hu, J.; Lin, Y. *J. Struct. Chem. (China)* **1990**, *9*, 184−187.

(3) (a) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1291−1296. (b) Aspinall, H. C.; Tillotson, M. R. *Inorg. Chem.* **1996**, *35*, 2163−2164. (c) Dubé, T.; Conoci, S.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2000**, *19*, 1182−1185. (d) Deelman, B.-J.; Booij, M.; Meetsma, A.; Teuben, J. H.; Kooijman, H.; Spekt, A. L. *Organometallics* **1995**, *14*, 2306−2317.
(4) Kraut, S.; Magull, J.; Schaller, U.; Karl, M.; Harms, K.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1193−1201.
(5) (a) Zhang, X.; Loppnow, G. R.; McDonald, R.; Takats, J. *J. Am. Chem. Soc.* **1995**, *117*, 7828−7829. (b) Dubé, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **1998**, *17*, 3967−3973. (c) Geissinger, M.; Magull, J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 2043−2048. (d) Moustiakimov, M.; Kritikos, M.; Westin, G. *Inorg. Chem.* **2005**, *44*, 1499−1504.
(6) Banerjee, S.; Huebner, L.; Romanelli, M. D.; Kumar, G. A.; Riman, R. E.; Emge, T. J.; Brennan, J. G. *J. Am. Chem. Soc.* **2005**, *127*, 14008−14014.
(7) (a) Evans, W. J.; Sollberger, M. S.; Shreeve, J. L.; Olofson, J. M.; Hain, J. H., Jr.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 2492−2501. (b) Yunlu, K.; Gradeff, P. S.; Edelstein, N.; Kot, W.; Shalimoff, G.; Streib, W. E.; Vaartstra, B. A.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 2317−2321.

lanthanide thiolate and/or oxide complexes, we explored some hydrolysis reactions of preformed organolanthanide thiolate complexes with water. In this paper, we report an interesting example where an unprecedented pentanulcear lanthanum thiolate oxide complex was incidentally isolated because of the adventitious water but was regenerated in an acceptable yield via control of hydrolysis. This represents a new route to oxolanthanide thiolate compounds and may be applicable to other related systems.

We previously reported the preparation of lanthanide thiolate complexes from protonolysis of some preformed lanthanide(III) bis(trimethylsilyl)amino chloride complexes with HSPh.[10] When we ran an analogous reaction of $[(TMS)_2N]_3La-(\mu-Cl)Li(THF)_3$ (**1**) (TMS = trimethylsilyl) in THF with equimolar HSPh in *n*-hexane at ambient temperature, colorless plates of the binuclear complex $[\{((TMS)_2N)_2La(THF)\}_2(\mu-SPh)(\mu-Cl)]\cdot C_7H_8$ (**2**·C_7H_8)[11] in 56% yield coupled with several colorless prisms of a pentanuclear lanthanum thiolate oxide cluster $[\{(TMS)_2N\}_2La_5O(SPh)_{10}LiCl_2(THF)_6]\cdot C_7H_8$ (**3**·C_7H_8) were isolated. Where did the O atom in **3** originate? When we bubbled dry O_2 into a THF solution of **2** and equimolar LiCl for 1−30 min, it always resulted in an insoluble white material, which ruled out the role of the adventitious O_2 in the formation of **3**. Then we assumed that it might be the water that worked in this reaction. The addition of $^1/_6$ equiv of water to a THF solution of **2** and equimolar LiCl initiated an evident hydrolysis, which led to the formation

of an amount of insoluble solids. Subsequent filtration followed by a standard workup did produce **3** in 5% yield and a thiolate-free compound $[\{(TMS)_2N\}_3La]$ in 17% yield.[12] A change of the **2**/H_2O molar ratios from 10:1 to 3:1 did not increase the yield of **3**. Interestingly, **3** could be obtained in 19% yield from the direct addition of $^1/_{10}$ equiv of water to a mixture of **1** and equimolar HSPh.[13] However, if a THF solution of **1** was treated first with $^1/_6$ equiv of water and then with equimolar HSPh, only a polymeric complex $[\{(TMS)_2N\}_2(\mu-SPh)La(\mu-SPh)Li(THF)_2]_\infty$ (**4**) was isolated in 22% yield.[14] When the molar ratio of **1**/H_2O/HSPh was changed to 1:0.1:1, a similar reaction afforded a mixture of **4** (15% yield) and **3** (0.5% yield). Therefore, these results revealed that control of the proper amount of water in hydrolysis and even the addition sequence between water and other reagents are critical to the formation of **3**. Complexes **2**−**4** were sensitive to air and moisture and readily soluble in THF and toluene, and their identities were confirmed by elemental analysis, ¹H NMR, IR, and X-ray analysis.

An X-ray analysis[15a] revealed that **2** contains two $\{((TMS)_2N)_2La(THF)\}^+$ fragments that are interconnected by one μ-Cl⁻ and one μ-SPh⁻, forming a dimeric structure with a crystallographic C_2 axis running along the Cl1···S1···C13···C16 line (Figure 1). La1 and La1A adopt a distorted square-pyramidal geometry, coordinated by one μ-Cl, one μ-S (SPh), one O (THF), and two N $\{(TMS)_2N\}$ atoms.

Compound **3** consists of a central $[(\mu-SPh)_4(\mu_3-SPh)_2\{La(THF)\}_4(\mu_4-O)]^{4+}$ tetrahedral fragment in which La1 and La1A are bridged by a pair of μ-SPh⁻ ligands to a $[Li(THF)_2]^+$ fragment while La2 and La2A are connected by two pairs of μ_3-Cl⁻ and μ-SPh⁻ ligands to a $[\{(TMS)_2N\}_2La]^+$

(8) (a) Bradley, D. C. *Chem. Rev.* **1989**, *89*, 1317−1322. (b) Mehrotra, R. C.; Singh, A.; Tripathi, U. M. *Chem. Rev.* **1991**, *91*, 1287−1303. (c) Zhou, X.; Ma, H.; Wu, Z.; You, X.; Xu, Z.; Huang, X. *J. Organomet. Chem.* **1995**, *503*, 11−13. (d) Mehrotra, R. C.; Singh, A. *Chem. Soc. Rev.* **1996**, 1−13. (e) Wang, R.; Zheng, Z.; Jin, T.; Staples, R. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1813−1815. (f) Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 5410−5411. (g) Bürgstein, M. R.; Roesky, P. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3549−551. (h) Evans, W. J.; Greci, M. A.; Ziller, J. W. *Inorg. Chem.* **2000**, *39*, 3213−3220. (i) Daniele, S.; Hubert-Pfalzgraf, L. G.; Hitchcock, P. B.; Lappert, M. F. *Inorg. Chem. Commun.* **2000**, *3*, 218−220. (j) Evans, W. J.; Allen, N. T.; Greci, M. A.; Ziller, J. W. *Organometallics* **2001**, *20*, 2936−2937. (k) Westin, G.; Moustiakimov, M.; Kritikos, M. *Inorg. Chem.* **2002**, *41*, 3249−3258. (l) Tasiopoulos, A. J.; O'Brien, T. A.; Abboud, K. A.; Christou, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 345−349. (m) Hosmane, N. S.; Maguire, J. A. *Organometallics* **2005**, *24*, 1356−1389. (n) Natrajan, L.; Pécaut, J.; Mazzanti, M.; LeBrun, C. *Inorg. Chem.* **2005**, *44*, 4756−4765. (o) Schuetz, S. A.; Day, V. W.; Clark, J. L.; Belot, J. A. *Inorg. Chem. Commun.* **2002**, *5*, 706−710. (p) Xu, Q.; Wang, Z. M.; He, Z.; Lu, Z.; Liao, C. S.; Yan, C. H. *Inorg. Chem.* **2002**, *41*, 6802−6807. (q) Roesky, P. W.; Canseco-Melchor, G.; Zulys, A. *Chem. Commun.* **2004**, 738−739.

(9) Pernin, C. G.; Ibers, J. A. *Inorg. Chem.* **1997**, *36*, 3802−3803.

(10) (a) Li, H. X.; Ren, Z. G.; Zhang, Y.; Zhang, W. H.; Lang, J. P.; Shen, Q. *J. Am. Chem. Soc.* **2005**, *127*, 1122−1123. (b) Li, H. X.; Zhang, Y.; Ren, Z. G.; Cheng, M. L.; Wang, J.; Lang, J. P. *Chin. J. Chem.* **2005**, *23*, 1499−1502.

(11) To a THF (30 mL) solution of **1** (1.13 g, 1.28 mmol) was slowly added a hexane (10 mL) solution of HSPh (0.131 mL, 1.28 mmol; *d* = 1.073 g/mL, 99%). The clear colorless solution was stirred overnight at ambient temperature and then was concentrated to dryness in vacuo. The residue was extracted with toluene (10 mL × 2), and the solution was combined and concentrated to ca. 10 mL. The solution was cooled to −18 °C for several days to form colorless plates of **2**·C_7H_8, which were isolated by filtration, washed with hexane, and dried in vacuo. Yield: 0.43 g (56%). Anal. Calcd for $C_{38}H_{93}ClLa_2N_4O_2SSi_8$: C, 37.78; H, 7.76; N, 4.64. Found: C, 37.26; H, 7.81; N, 4.33. Mp: 111−114 °C. ¹H NMR (400 MHz, THF-d_8): δ 0.54 (s, 72H, Si(CH₃)₃), 1.74 (br, THF), 3.61 (br, THF), 7.01−7.45 (m, 5H, Ph). IR (KBr disk): 3047 (w), 2955 (w), 2883 (w), 1576 (s), 1472 (s), 1433 (s), 1249 (s), 1085 (s), 1066 (m), 1023 (s), 842 (s), 738 (s), 694 (s), 576 (w), 418 (s) cm⁻¹.

(12) To a THF (30 mL) solution of **2** (0.926 g, 0.766 mmol) and anhydrous LiCl (0.033 g, 0.766 mol) was slowly added a THF solution (2 mL) of H_2O (2.29 μL, 0.127 mmol). An amount of white precipitate was observed to form quickly. The resulting mixture was stirred overnight at room temperature and was concentrated to dryness in vacuo, leaving a colorless oily residue. Hexane (10 mL) was added to the residue, which was then stirred for another 15 min. After removal of the hexane by vacuum evaporation, a dry free-flowing powder was left. The white solid was washed thoroughly with hexane (4 × 5 mL). The resulting solid was extracted with hot hexane (15 mL) and toluene (10 mL) (about 35 °C). The combined extract was concentrated to ca. 10 mL and cooled to 2 °C for several days to form colorless prisms of **3**·C_7H_8, which were isolated by filtration, washed with hexane, and dried in vacuo. Yield: 0.040 g (5%). Anal. Calcd for $C_{96}H_{134}Cl_2La_5LiN_2O_7S_{10}Si_4$: C, 43.78; H, 5.13; N, 1.06. Found: C, 43.41; H, 5.58; N, 1.65. Mp: 136−138 °C. ¹H NMR (400 MHz, THF-d_8): δ 0.35 (s, 36H, Si(CH₃)₃), 1.73 (br, THF), 3.59 (br, THF), 6.81−7.73 (m, 50H, Ph). IR (KBr disk): 3051 (w), 3001 (w), 2887 (w), 1598 (s), 1477 (s), 1441 (s), 1285 (s), 1252 (m), 1161 (m), 1068 (m), 1031 (s), 851 (s), 743 (s), 701 (m), 588 (s), 480 (w), 420 (s) cm⁻¹. The solution collected from hexane washing was concentrated to about 10 mL. Compound $[\{(TMS)_2N\}_3La]$ (**5**) was formed by cooling the solution to −18 °C for several days. Yield: 0.16 g (17%). Anal. Calcd for $C_{18}H_{54}LaN_3Si_6$: C, 34.87; H, 8.78; N, 6.78. Found: C, 34.53; H, 8.43; N, 7.07. ¹H NMR (400 MHz, THF-d_8): δ 0.37 (s, Si(CH₃)₃). IR (KBr disk): 2959 (s), 1466 (s), 1370 (w), 1355 (m), 1261 (m), 1175 (m), 1054 (s), 951 (s), 705 (w), 618 (w), 406 (w) cm⁻¹.

(13) To a THF (30 mL) solution of **1** (1.287 g, 1.46 mmol) was slowly added a hexane (5 mL) solution of HSPh (0.150 mL, 1.46 mmol). The solution was stirred overnight and then treated with a THF solution (2 mL) of H_2O (2.63 μL, 0.146 mmol). The clear colorless solution went opaque and gradually developed some white precipitate. The resulting mixture was again stirred overnight at room temperature. A workup similar to that used in method 1 gave rise to colorless crystals of **3**·C_7H_8. Yield: 0.14 g (19%).
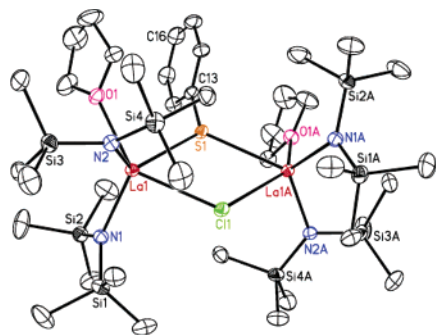
Figure 1. Molecular structure of **2** with 30% probability. All H atoms are omitted for clarity.
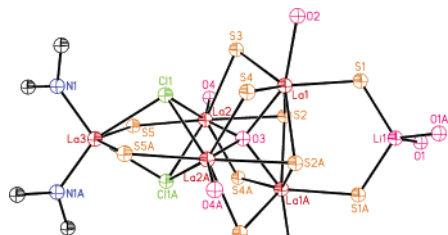
Figure 2. Molecular structure of **3** with 30% probability. All C and H atoms are omitted for clarity.

fragment, thereby forming a bee-shaped structure (Figure 2).[15b] The whole molecule possesses a C_2 axis running along the La3···O3···Li1 line. The μ_4-O atom lies at the center of the La$_4$ tetrahedron and interacts with four La atoms, with La–O lengths ranging from 2.383(3) to 2.555(4) Å. The four edges of the La$_4$ tetrahedron are bridged by four μ-SPh$^-$ ligands, while its two faces are capped with two μ_3-SPh$^-$ ligands. The mean Ln–S bond distance is 2.9766 Å. Each La atom in this La$_4$ tetrahedron is saturated by a THF molecule, while La3 binds to two (TMS)$_2$N$^-$ anions. Thus,

La1/La1A, La2/La2A, and La3 display a distorted square-capped trigonal-prismatic coordination geometry, a distorted bisquare-capped trigonal-prismatic coordination geometry, and a distorted octahedral coordination geometry, respectively (see the Supporting Information). The tetrahedral coordination sphere of Li1 is completed by two μ-S and two O atoms from THF molecules.

The structure of **4**,[15c] similar to that of its praseodymium analogue,[10] contains a 1D wavelike chain structure in which the two [{(TMS)$_2$N}$_2$La]$^+$ and [Li(THF)$_2$]$^+$ fragments are alternatively bridged by μ-SPh$^-$ ligands along the crystallographic *a* axis (see the Supporting Information).

Compounds **2**−**4** were found to initiate the polymerization of ϵ-caprolactone at ambient temperature in a few minutes to give poly(ϵ-caprolactone) with low polydispersity ($M_w/M_n = 1.42-1.63$). Compared with **1** and their mono- or disubstituted (silylamino)lanthanide complexes,[16] **2**−**4** initiated faster polymerization and produced poly(ϵ-caprolactone) with narrower molecular weight distribution. This result may be ascribed to the weak Ln–S bonds in **2**−**4**.[17] The catalytic activities in the polymerization of ϵ-caprolactone decreased in the order of **3** > **2** > **4** (see the Supporting Information) mainly because of the different clusterings.

In summary, the present work demonstrated that a unique pentanuclear lanthanum benzenethiolate oxide compound **3**, once incidentally isolated, could be reproduced via control of the hydrolysis of **2** and LiCl or **1** and HSPh with the proper amount of water. This synthetic strategy may be applied to the preparation of other new oxolanthanide thiolate complexes with better catalytic performances. Studies in this respect are ongoing in our laboratory.

(14) To a THF (30 mL) solution of **1** (0.924 g, 1.07 mmol) was slowly added a THF (2 mL) solution of H$_2$O (3.22 μL, 0.179 mmol). Some precipitate was observed to form within seconds. The mixture was stirred overnight at room temperature and treated with a hexane (5 mL) solution of HSPh (0.110 mL, 1.07 mmol). After the resulting mixture was stirred for one more night, the volatile species were evaporated in vacuo, leaving an oily residue. Hexane (10 mL) was added to the residue, which was stirred for another 15 min. After removal of the hexane by vacuum evaporation, the solid was again extracted with hot hexane (15 mL) and toluene (5 mL) (about 40 °C) and filtered. Colorless crystals of **4** were formed by cooling the filtrate to 2 °C for several days. Yield: 0.195 g (22%). Anal. Calcd for C$_{32}$H$_{62}$-LiN$_2$O$_2$LaS$_2$Si$_4$: C, 46.35; H, 7.54; N, 3.38. Found: C, 46.53; H, 7.89; N, 3.17. Mp: 145−147 °C. ^{1}H NMR (400 MHz, THF-d_8): δ 0.49 (s, 36H, Si(CH$_3$)$_3$), 1.71 (br, THF), 3.62 (br, THF), 6.99−7.61 (m, 10H, Ph). IR (KBr, disk): 3058 (w), 2960 (m), 2880 (w), 1581 (s), 1450 (s), 1443 (m), 1256 (w), 1179 (m), 1090 (s), 1051 (m), 1027 (s), 890 (w), 743 (s), 696 (m), 660 (w), 481 (m), 416 (w) cm^{-1}.

(15) (a) Crystal data for **2**: monoclinic, space group $C2/c$, a = 20.7862-(15) Å, b = 11.4386(7) Å, c = 30.107(2) Å, β = 106.665(2)°, V = 6857.8(8) Å^3, Z = 4, ρ_{calcd} = 1.258 g/cm^3, μ(Mo Kα) = 1.471 cm^{-1}, R1 = 0.0422, wR2 = 0.0972, GOF = 1.120. (b) Crystal data for **3**: monoclinic, space group $C2/c$, a = 26.247(4) Å, b = 20.784(2) Å, c = 25.361(3) Å, β = 114.473(3)°, V = 12592(3) Å^3, Z = 4, ρ_{calcd} = 1.438 g/cm^3, μ(Mo Kα) = 1.952 cm^{-1}, R1 = 0.0599, wR2 = 0.1365, GOF = 1.114. (c) Crystal data for **4**: triclinic, space group $P\bar{1}$, a = 8.718(3) Å, b = 11.384(4) Å, c = 22.573(8) Å, α = 103.077(11)°, β = 96.329(12)°, γ = 90.864(7)°, V = 2167.1(12) Å^3, Z = 2, ρ_{calcd} = 1.271 g/cm^3, μ(Mo Kα) = 1.220 cm^{-1}, R1 = 0.0695, wR2 = 0.1708, GOF = 1.037.

(16) (a) Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 2330−2332. Agarwal, S.; Karl, M.; Anfang, S.; Dehnicke, K.; Greiner, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 361−362. (b) Hou, Z.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1−22. (c) Li, H. X.; Xu, Q. F.; Chen, J. X.; Cheng, M. L.; Zhang, Y.; Zhang, W. H.; Lang, J. P.; Shen, Q. *J. Organomet. Chem.* **2004**, *689*, 3438−3448.

(17) (a) Nakayama, Y.; Shibahara, T.; Fukumoto, H.; Nakamura, A. *Macromolecules* **1996**, *29*, 8014−8016. (b) Hou, Z.; Zhang, Y.; Tezuka, H.; Xie, P.; Tardif, O.; Koizumi, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2000**, *122*, 10533−10543. (c) Ma, H.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2003**, 4770−4780. (d) Kim, J. Y.; Livinghouse, T. *Org. Lett.* **2005**, *7*, 1737−1739. (e) Ma, H.; Okuda, J. *Macromolecules* **2005**, *38*, 2665−2673.