Synthesis and Structure of the First Tetranuclear Organolanthanide Cluster Containing a μ_4-Imido Group

Zuowei Xie,* Shaowu Wang, Qingchuan Yang, and Thomas C. W. Mak

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

Received December 8, 1998

*Summary: Reaction of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ with 4 equiv of $NaNH_2$ in dry THF, followed by treatment with 1 equiv of $LnCl_3$, gave unprecedented tetranuclear clusters of the general formula $[\{(\eta^5\text{-}\mu_2\text{-}C_9H_6SiMe_2NH)Ln\}_2(\mu_3\text{-}Cl)(THF)]_2(\mu_4\text{-}NH)\cdot THF$ (Ln = Gd (**1**), Er (**2**)) in moderate yield. Their molecular structures have been confirmed by single-crystal X-ray analyses, which represent the first organometallic clusters containing a central μ_4-imido group.*

Imido−transition-metal complexes play an important role both in biological processes such as nitrogen fixation and in a series of industrial processes.[1] Cycloadditions, C−H bond activations, and ring-opening polymerizations can all be catalyzed by various imido complexes.[1−3] Numerous imido−metal complexes have been reported;[1−4] however, syntheses of organometallic clusters containing a central μ_4-imido group have thus far remained elusive. We report here unprecedented reactions between $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$[5] and $NaNH_2$, which led to the isolation and structural characterization of the first organolanthanide clusters containing a μ_4-NH^{2-} group after treatment with $LnCl_3$ in THF: $[\{(\eta^5\text{-}\mu_2\text{-}C_9H_6\text{-}SiMe_2NH)Ln\}_2(\mu_3\text{-}Cl)(THF)]_2(\mu_4\text{-}NH)\cdot THF$ (Ln = Gd (**1**), Er (**2**)).

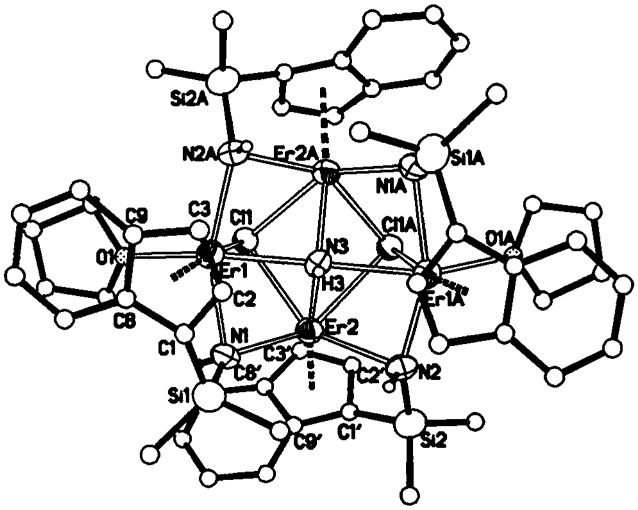

Figure 1. Molecular structure of cluster **2** (the solvated THF molecule is not shown). Selected bond distances (Å) and angles (deg): Er1−N1 = 2.431(4) [2.496(7)]; Er1−N2 = 2.330(4) [2.354(6)]; Er1−N3 = 2.425(1) [2.495(1)]; Er1−O1 = 2.337(4) [2.431(7)]; Er1−Cl1 = 2.762(1) [2.824(2)]; Er1−C1 = 2.635(5) [2.654(9)]; Er1−C2 = 2.684(7) [2.684(14)]; Er1−C3 = 2.825(7) [2.787(10)]; Er1−C8 = 2.753(6) [2.811(9)]; Er1−C9 = 2.881(6) [2.902(9)]; Er2−N1 = 2.345(4) [2.391(7)]; Er2−N2 = 2.473(4) [2.464(6)]; Er2−N3 = 2.386(4) [2.405(6)]; Er2−Cl1 = 2.741(1) [2.805(2)]; Er2−Cl1A = 2.866(1) [2.927(2)]; Er2−C1′ = 2.588(6) [2.639(10)]; Er2−C2′ = 2.608(6) [2.668(10)]; Er2−C3′ = 2.700(7) [2.787(11)]; Er2−C8′ = 2.705(7) [2.724(9)]; Er2−C9′ = 2.664(6) [2.853(10)]; Er1−N3−Er1A = 176.3(3) [174.9(5)]; Er2−N3−Er2A = 105.1(3) [107.1(4)]; Er2−N3−Er1A = 91.5(1) [91.5(1)]; Er2−N3−Er1 = 90.8(1) [91.6(1)]; Er1−N1−Er2 = 91.7(1) [91.8(2)]; Er1−N2−Er2A = 91.6(1) [93.6(2)]; Er1−Cl1−Er2 = 77.0(1) [75.3(1)]; Er1−Cl1−Er2A = 75.5(1) [77.1(1)]; Er2−Cl1−Er2A = 85.0(1) [84.9(1)]. Distances and angles in brackets are those of cluster **1**.

Treatment of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ with 4 equiv of $NaNH_2$ in dry THF at room temperature, followed by reaction with 1 equiv of $LnCl_3$, after workup gave **1** as colorless crystals and **2** as light pink crystals in 51% and 44% yields, respectively.[6] Both **1** and **2** are soluble in THF and pyridine, sparely soluble in toluene, and insoluble in hexane. IR spectra exhibit the N−H absorption at about 3268 cm^{-1}. No characteristic B−H absorption at about 2600 cm^{-1} was observed in the IR spectra, indicating that these clusters do not contain any carboranyl groups.[7] Due to the strong paramagnetism

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* To whom correspondence should be addressed. Fax: (852)-26035057. Tel: (852)26096269. E-mail: zxie@cuhk.edu.hk.

(1) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

(2) Gibson, V. C. *Adv. Mater.* **1994**, *6*, 37.

(3) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

(4) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 2, p 162.

(5) Xie, Z.; Wang, S.; Yang, Q.; Mak, T. C. W. *Organometallics*, submitted for publication.

(6) Preparation of **1**: To a suspension of $NaNH_2$ (0.16 g, 4.1 mmol) in THF (10 mL) was added a THF solution (5 mL) of $Me_2Si(C_9H_7)(C_2B_{10}H_{11})$ (0.32 g, 1.0 mmol), and the mixture was stirred at room temperature for 20 h. The resulting purple solution was filtered into a stirred suspension of $GdCl_3$ (0.26 g, 1.0 mmol) in THF (8 mL) at room temperature, and this reaction mixture was then stirred overnight. After filtration, the clear purple solution was concentrated to about 8 mL; hexane vapor diffusion resulted in **1** as colorless crystals over days (0.21 g, 51%). IR (KBr, cm^{-1}): ν 3267 (w), 3057 (w), 2954 (s), 2884 (s), 1406 (m), 1329 (m), 1243 (s), 1007 (vs), 870 (m), 839 (s), 777 (vs), 712 (m), 665 (m). ^1H NMR (pyridine-d_5): many broad, unresolved resonances. Anal. Calcd for $C_{50}H_{65}Cl_2Gd_4N_5O_{1.5}Si_4$ (**1**−1.5THF): C, 38.19; H, 4.17; N, 4.45. Found: C, 37.82; H, 4.30; N, 4.25. Preparation of **2**: **2** was prepared in 44% yield as light pink crystals in a manner analogous to that used for **1**. IR (KBr, cm^{-1}): ν 3268 (m), 3065 (m), 2955 (s), 2892 (m), 1328 (s), 1246 (s), 1143 (m), 1024 (m), 838 (vs), 813 (vs), 775 (vs), 747 (s), 662 (m). ^1H NMR (300 MHz, pyridine-d_5, relative to pyridine-d_5, 25 °C): δ 7.23 ($\nu_{1/2} = 15$ Hz, arene C_9H_6), 7.05 ($\nu_{1/2} = 15$ Hz, arene C_9H_6), 6.67 ($\nu_{1/2} = 17$ Hz, arene C_9H_6), 6.23 ($\nu_{1/2} = 17$ Hz, arene C_9H_6), 3.04 ($\nu_{1/2} = 30$ Hz, η^5-C_9H_6), 1.96 ($\nu_{1/2} = 30$ Hz, η^5-C_9H_6), 3.41 ($\nu_{1/2} = 10$ Hz, THF), 1.35 ($\nu_{1/2} = 10$ Hz, THF), 0.89 ($\nu_{1/2} = 15$ Hz, Me_2Si), 0.54 ($\nu_{1/2} = 15$ Hz, Me_2Si). Anal. Calcd for $C_{56}H_{77}Cl_2Er_4N_5O_3Si_4$: C, 39.09; H, 4.51; N, 4.07. Found: C, 38.76; H, 4.92; N, 3.96.

(7) (a) Xie, Z.; Wang, S.; Zhou, Z.; Xue, F.; Mak, T. C. W. *Organometallics* **1998**, *17*, 489. (b) Xie, Z.; Wang, S.; Zhou, Z.; Mak, T. C. W. *Organometallics* **1998**, *17*, 1907.

10.1021/om981002j CCC: $18.00

of Gd^{3+} ($\mu_{\text{eff}} = 8.0\ \mu_{\text{B}}$) and Er^{3+} ($\mu_{\text{eff}} = 9.5\ \mu_{\text{B}}$),[8] ^{1}H NMR spectra are not very informative. Both **1** and **2** were thus characterized by single-crystal X-ray analyses and elemental analyses.

X-ray diffraction studies[9] reveal that both **1** and **2** are tetranuclear clusters and they are also isostructural and isomorphous. As shown in Figure 1, the structure contains a butterfly arrangement of four metals which are connected by four doubly bridging μ_2-NHSiMe$_2$-(indenyl) units over the edges, by two triply bridging μ_3-Cl atoms spanning Ln(1), Ln(2), and Ln(2A) and Ln(1A), Ln(2), and Ln(2A), respectively, and by a quadruply bridging μ_4-NH group located on the crystallographic 2-fold axis. The coordination sphere around each metal is completed by either bonding to one indenyl group in an η^5-fashion or bonding to both η^5-indenyl and one THF molecule (for Ln(1) and Ln(1A)). As a result, each metal has a distorted-octahedral geometry with a formal coordination number of 8.

The N atom of the μ_4-NH group adopts a distorted-trigonal-bipyramidal geometry with Ln(1) and Ln(1A) occupying the axial sites, the Ln(1)−N(3)−Ln(1A) and Ln(2)−N(3)−Ln(2A) angles being 174.9(5) and 107.1(4)° for **1** and 176.3(3) and 105.1(3)° for **2**, respectively. The average Gd−N(3) (μ_4-NH) distance of 2.450(6) Å is 0.045 Å longer than that of Er−N(3) in **2**, which is consistent with the 0.049 Å difference between Shannon's ionic radii[12] of Gd^{3+} and Er^{3+}. These measured values can be compared with the 2.350(2) Å Sm−N (μ_5-N$_2$) distance in [(THF)$_2$Li(OEPG)Sm]$_2$(μ_5-N$_2$Li$_4$) (OEPG = octaethylporphyrinogen),[13] the 2.500(9) Å Sm−N (μ_3-NHNH) distance in [(C$_5$Me$_5$)Sm]$_4$(μ_3-NHNH)$_2$(μ_2:μ-NHNH$_2$)$_4$(NH$_3$)$_2$,[14] and the 2.24(1) Å Yb−N (μ_3-NPh) distance in Yb$_4$(μ-η^2:η^2-N$_2$Ph$_2$)$_4$(μ_3-NPh)$_2$(THF)$_4$.[15] The average Gd−N and Er−N (μ_2-NHSiMe$_2$(indenyl)) distances are 2.426(7) and 2.395(4) Å, respectively, which are somewhat shorter than the relevant Ln−N(3) distances. The average Ln−C distances of 2.751(14) Å in **1** and 2.704(7) Å in **2** are comparable to those normally observed in indenyllanthanide compounds.[16] The average Gd−Cl distance of 2.852(2) Å is 0.062 Å longer than that of Er−Cl, which is comparable to those of Ln−Cl (μ_3−Cl) distances found in the lanthanide analogues.[17] As far as we are aware, **1** and **2** are the first organometallic clusters containing a central μ_4-NH group to be reported.

The reactions between Me$_2$Si(C$_9$H$_7$)(C$_2$B$_{10}$H$_{11}$) and excess NaNH$_2$ are very interesting. ^{11}B NMR results show that the Si−C(carborane) bond is completely broken after the reaction mixture is stirred in THF for 2 h, indicating that NaNH$_2$ serves as both base and nucleophile in the reactions.[18,19] It is therefore rational to propose that NH$_2^-$ anions attack both the acidic proton of the indenyl and the Si atom to generate [H$_2$NSiMe$_2$(C$_9$H$_6$)]$^-$, followed by reaction with another 1 mol of NH$_2^-$ to produce [HNSiMe$_2$(C$_9$H$_6$)]$^{2-}$, which may then react with NH$_2^-$, affording NH^{2-}. Self-assembly of LnCl$_3$, [HNSiMe$_2$(C$_9$H$_6$)]$^{2-}$, and NH^{2-} in THF gives the tetranuclear clusters **1** and **2**. The reactions of other silicon compounds with NaNH$_2$ are under investigation.

Acknowledgment. We thank the Hong Kong Research Grants Council (Earmarked Grant CUHK 4183/97P) for financial support.

Supporting Information Available: Tables of crystallographic data and data collection details, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and figures containing the atom-numbering schemes for clusters **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM981002J

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(8) Cotton, S. *Lanthanides and Actinides*; Oxford University Press: New York, 1991; p 11.

(9) Crystal data for **1** (C$_{56}$H$_{77}$Cl$_2$Gd$_4$N$_5$O$_3$Si$_4$; fw 1680.5): orthorhombic, space group *Aba*2, $a = 21.625(2)$ Å, $b = 19.226(2)$ Å, $c = 15.125(1)$ Å, $V = 6288.4(8)$ Å^3, $T = 293$ K, $Z = 4$, $d_{\text{calcd}} = 1.775$ g cm^{-3}, $2\theta_{\max} = 51°$, absorption corrections applied by using ABSCOR,[10] relative transmission factors in the range 0.837−1.24. A total of 10 116 reflections were collected and led to 3018 unique reflections, 3018 of which with $I > 2\sigma(I)$ were considered as observed; R1 = 0.0631, wR2(F^2) = 0.1583. Crystal data for **2** (C$_{56}$H$_{77}$Cl$_2$Er$_4$N$_5$O$_3$Si$_4$; fw 1720.5): orthorhombic, space group *Aba*2, $a = 21.528(1)$ Å, $b = 19.101(1)$ Å, $c = 15.104(1)$ Å, $V = 6210.9(6)$ Å^3, $T = 293$ K, $Z = 4$, $d_{\text{calcd}} = 1.840$ g cm^{-3}, $2\theta_{\max} = 51°$, absorption corrections applied by using ABSCOR,[10] relative transmission factors in the range 0.856−1.00. A total of 8935 reflections were collected and led to 2884 unique reflections, 2873 of which with $I > 2\sigma(I)$ were considered as observed; R1 = 0.0518, wR2(F^2) = 0.1124. Data were collected at 293 K on an MSC/Rigaku RAXIS-IIC imaging plate using Mo Kα radiation ($\lambda = 0.710\,73$ Å) from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. Both structures were solved by direct methods and refined by full-matrix least-squares calculations on F^2 using the Siemens SHELXTL/PC package of crystallographic software.[11] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were geometrically fixed by using the riding model.

(10) Higashi, T. ABSCOR−An Empirical Absorption Correction Based on Fourier Coefficient Fitting; Rigaku Corp., Tokyo, 1995.

(11) SHELXTL V 5.03 Program Package; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995.

(12) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(13) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1994**, *116*, 4477.

(14) Wang, K.-G.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1992**, *11*, 1011.

(15) Trifonov, A. A.; Bochkarev, M. N.; Schumann, H.; Loebel, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1149; *Angew. Chem.* **1991**, *103*, 1170.

(16) (a) Qian, C.; Zou, G.; Sun, J. *J. Chem. Soc., Dalton Trans.* **1998**, 1607. (b) Qian, C.; Zou, G.; Sun, J. *J. Organomet. Chem.* **1998**, *566*, 21. (c) Gao, F.; Wei, G.; Jin, Z.; Chen, W. *J. Organomet. Chem.* **1992**, *438*, 289.

(17) (a) Kretschmer, W. P.; Teuben, J. H.; Troyanov, S. I. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 88; *Angew. Chem.* **1998**, *110*, 92. (b) Evans, W. J.; Sollberger, M. S.; Hanusa, T. P. *J. Am. Chem. Soc.* **1988**, *110*, 1841. (c) Evans, W. J.; Sollberger, M. S. *Inorg. Chem.* **1988**, *27*, 4417.

(18) NaNH$_2$ was suggested to be an intermediate in the reaction of MeSiCl$_3$ with Na in liquid NH$_3$ leading to the formation of (MeSi)$_6$(NH)$_9$; see: Räke, B.; Roesky, H. W.; Usón, I.; Müller, P. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1432; *Angew. Chem.* **1998**, *110*, 1508.

(19) (a) Schumann, H.; Albrecht, I.; Loebel, J.; Hahn, E. F.; Hossain, M. B.; Van der Helm, D. *Organometallics* **1986**, *5*, 1296. (b) Schumann, H.; Rosenthal, E. C. E.; Kociok-Köhn, G.; Molander, G. A.; Winterfeld, J. *J. Organomet. Chem.* **1995**, *496*, 233.