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A New Versatile Ligand: Its Synthesis and Applications in Organolanthanide Chemistry

Zuowei Xie,* Shaowu Wang, Zhong-Yuan Zhou, Feng Xue, and Thomas C. W. Mak

Department of Chemistry, The Chinese University of Hong Kong, Shatin NT, Hong Kong, China

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Summary: Treatment of $Me_2Si(C_5H_5)Cl$ with $Li_2C_2B_{10}H_{10}$ followed by hydrolysis gave the new versatile ligand $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$ in 79% isolated yield, which can be converted into the monoanion, dianion, and trianion, respectively. It makes possible the synthesis of a wide range of organometallic complexes.

Olefin transformations are one kind of the most important reactions in the chemical industry. Many catalysts have been developed to make this process more smooth, efficient, and selective.[1] Of course, many factors will influence the performance of the catalysts. Among these, the ligand is probably one of the most important elements, since it controls the molecular geometry of the catalysts, which in turn affect the olefin transformations. From this point of view, the development of new ligands is very critical and is of great interest.[1] It has been known that the bridged ligands have some interesting properties which can afford complexes with advantageous solubility, crystallizability, thermal stability, and resistance to ligand redistribution, particularly for f-element organometallic complexes.[2] We report here the synthesis and applications of a new bridged ligand that incorporates both cyclopentadienyl and *o*-carboranyl groups.

The reaction of $Me_2Si(C_5H_5)Cl$[3] with $Li_2C_2B_{10}H_{10}$[4] proceeds according to eq 1 to give $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$ (**1**) in 79% isolated yield.

$$Me_2SiCl(C_5H_5) + Li_2C_2B_{10}H_{10} \xrightarrow[(2)\ H_3O^+]{(1)\ \text{toluene/ether}} \underset{\mathbf{1}}{Me_2Si(C_5H_5)(C_2B_{10}H_{11})} \quad (1)$$

1 is a versatile ligand which can be easily converted into the monoanion (**2**), dianion (**3**) and trianion (**4**), respectively (Scheme 1).

A wide range of organolanthanide complexes can be generated through the metathesis reaction of lanthanidechloride with various anions derived from this versatile ligand. For example, treatment of **2** with 1 equiv of $NdCl_3$ in THF gave $[Me_2Si(C_5H_4)(C_2B_{10}H_{11})]NdCl_2{\cdot}3THF$ (**5**) in 62% yield. A single-crystal X-ray diffraction study of this complex[5] (Figure 1a) reveals a monomeric structure with a pseudooctahedral coordina-

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

[1] For recent reviews, see: (a) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 144. (b) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3907. (c) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (d) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

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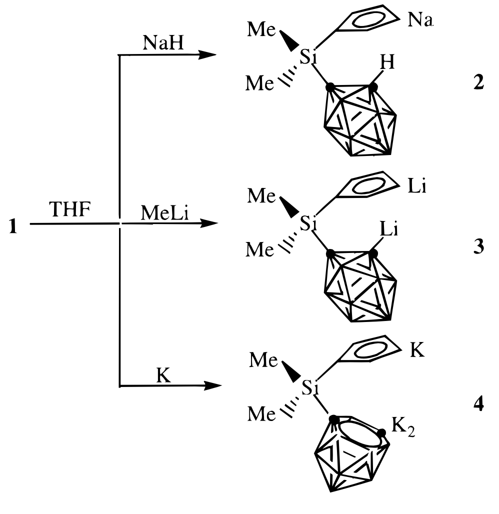
Scheme 1



tion geometry around the Nd metal typical of $(C_5H_5)LnCl_2 \cdot 3THF$ complexes.[6] There is no intramolecular interaction between B−H of the carborane cage and metal ion probably because a B−H bond is a weaker σ-donor than THF.

Reaction of **2** with 0.5 molar equiv of $NdCl_3$ in THF generated $[Me_2Si(C_5H_4)(C_2B_{10}H_{11})]_2NdCl \cdot 2THF$ (**6**) in 78% yield, which can also be generated by treatment of **5** with 1 equiv of **2**. The X-ray crystal structure of **6**[7] (Figure 1b) displays a distorted-trigonal-bipyramidal geometry that is not common for $(C_5H_5)_2LnCl$ types of complexes.[2,8]

Treatment of **3** with 1 molar equiv of $NdCl_3$ in THF did not produce the expected organoneodymium chloride complex $[Me_2Si(C_5H_4)(C_2B_{10}H_{10})]NdCl \cdot n THF$; instead, the ion-paired complex $[\{Me_2Si(C_5H_4)(C_2B_{10}H_{10})\}_2Nd][Li(THF)_4]$ (**7**) was isolated in 64% yield. This indicates that the chloride intermediate is extremely reactive. The crystal structure of complex **7**[9] consists of discrete anions and cations. The anion (Figure 1c) adopts a distorted-tetrahedral geometry around the Nd atom.

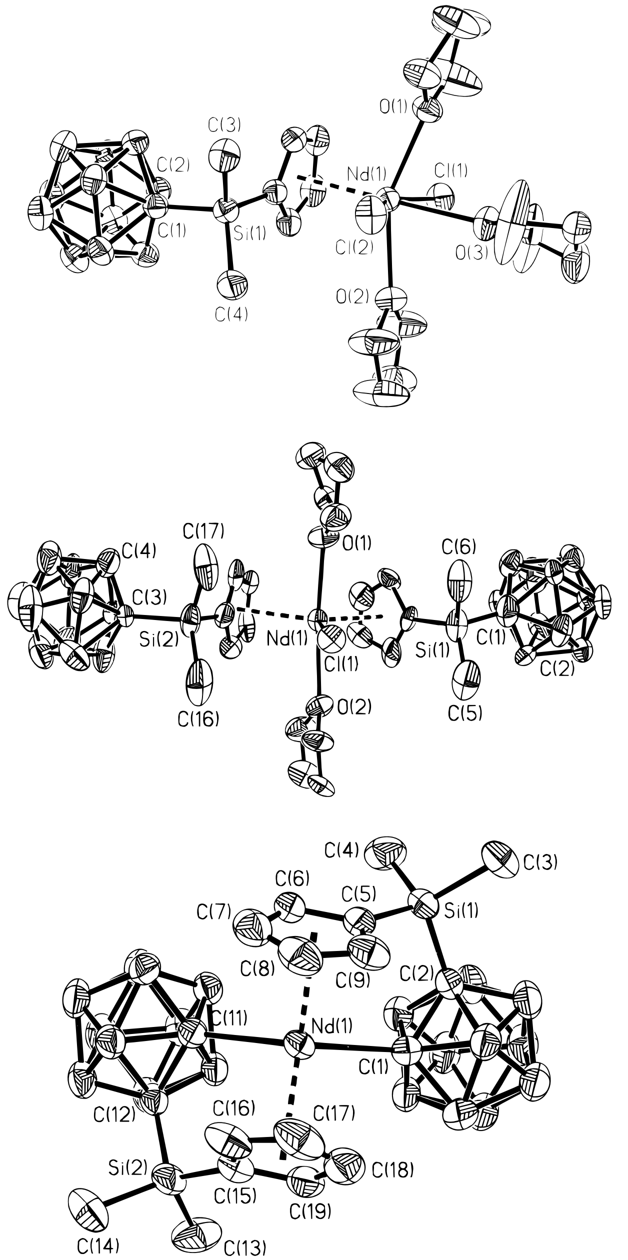


Figure 1. ORTEP illustrations, with thermal ellipsoids drawn at the 35% probability level, of compounds **5** (a, top) and **6** (b, middle) and the anion of **7** (c, bottom). All hydrogen atoms are omitted for clarity. Selected bond distances (Å): (a) average Nd(1)−C(C_5 ring) = 2.788(3), average Nd(1)−O = 2.510(2), Nd(1)−Cl(1) = 2.701(1), Nd(1)−Cl(2) = 2.675(1); (b) average Nd(1)−C(C_5 ring) = 2.775(3), average Nd(1)−O = 2.591(1), Nd(1)−Cl(1) = 2.670(1); (c) average Nd(1)−C(C_5 ring) = 2.728(1), Nd(1)−C(1) = 2.619(1), Nd(1)−C(11) = 2.583(1).

Two intramolecular Nd−C σ bonds (2.583(1), 2.619(1) Å) are significantly longer than those found in $L_2NdCH(SiMe_3)_2$ complexes[10] (L = C_5Me_5, 2.517(7) Å; L_2 = $Me_2Si(C_5Me_4)_2$, 2.506(7) Å), indicating steric and/or electronic effects. Complex **7** can also be prepared by treatment of **6** with 2 equiv of MeLi in THF.

Trianion **4** reacted with $NdCl_3$ in a molar ratio of 1:1 to yield a complex which has been formulated as {[Me$_2$-

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(5) Crystal data for **5** ($C_{21}H_{45}Cl_2B_{10}NdO_3Si$; fw 696.90): monoclinic, space group $P2_1/c$, a = 14.877(1) Å, b = 16.566(1) Å, c = 14.713(1) Å, β = 111.77(1)°, V = 3367.4(4) Å^3, d_{calcd} = 1.375 g/cm^3, Z = 4, R1 = 0.039 ($I > 2.0\sigma(I)$), wR2 = 0.100, data-to-parameter ratio 14.2. Data were collected at 294 K on a MSC/Rigaku RAXIS−IIC Image Plate using Mo Kα radiation (λ = 0.710 73 Å) from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA. The structure was solved by direct methods and refined on F^2 using the Siemens SHELXTL V 5.03 program package (PC version) (SHELXTL V5.03 program set; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995).

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(7) Crystal data for **6** ($C_{26}H_{58}ClB_{20}NdO_2Si_2$; fw 854.79): monoclinic, space group $P2_1$, a = 7.878(2) Å, b = 24.140(5) Å, c = 11.610(2) Å, β = 92.00(3)°, V = 2206.6(8) Å^3, d_{calcd} = 1.287 g/cm^3, Z = 2, R1 = 0.043 ($I > 2.0\sigma(I)$), wR2 = 0.106, data-to-parameter ratio 6.7.

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(9) Crystal data for **7** ($C_{34}H_{72}B_{20}LiNdO_4Si_2$; fw 968.48): monoclinic, space group $P2_1/n$, a = 14.700(3) Å, b = 22.574(5) Å, c = 15.965(3) Å, β = 92.76(3)°, V = 5292(2) Å^3, d_{calcd} = 1.216 g/cm^3, Z = 4, R1 = 0.049 ($I > 2.0\sigma(I)$), wR2 = 0.126, data-to-parameter ratio 12.1.

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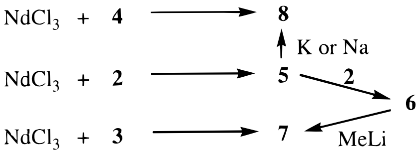
$Si(C_5H_4)(C_2B_{10}H_{11})]Nd(THF)_2\}_n$ (**8**; $n = 1$ or ∞) on the basis of spectroscopic and analytical studies.[11] The ^1H NMR spectrum of the hydrolysis products of this complex supported the ratio of two THF molecules per ligand. The solid-state IR spectrum exhibits both a characteristic B−H stretching mode at 2503 cm^{-1} and a medium band at 2361 cm^{-1} due to a Nd−H−B stretching mode.[12] It is anticipated that the solid-state structure of **8** may be polymeric[12] or monomeric.[13] Complex **8** can also be synthesized via the reaction of **5** with excess amounts of potassium or sodium metal in THF. All of these synthetic routes are summarized in Scheme 2.

Scheme 2



In conclusion, a new versatile bridged ligand incorporating both cyclopentadienyl and *o*-carboranyl groups has been synthesized. Its applications in organolanthanide chemistry imply that this ligand should have a rich chemistry with other transition metals. This bridged ligand also offers a possibility for the preparation of the mixed π-ligand complexes which are normally inaccessible by using nonbridging ligands.[12a]

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Supporting Information Available: Tables of crystallographic data collection information, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates and figures giving atom-numbering schemes for complexes **5**−**7** and text giving experimental procedures and compound characterization data (39 pages). Ordering information is given on any current masthead page.

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(11) $^{11}B\{^1H\}$ NMR (pyridine-d_5, chemical shifts relative to $BF_3 \cdot OEt_2$): δ −3.1 (2), −9.6 (2), −13.8 (4), −14.6 (2). IR (KBr pellet, cm^{-1}): ν 3066 (w), 2961 (m), 2502 (br vs), 2361 (m), 1260 (m), 1095 (s), 1042 (s), 797 (s). Complexometric Anal. Calcd for $C_{17}H_{37}B_{10}O_2NdSi$: Nd, 26.04. Found: Nd, 26.66.

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