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Cyclopentadienyl–Carboranyl Hybrid Compounds: A New Class of Versatile Ligands for Organometallic Chemistry

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ABSTRACT

A new class of organic–inorganic hybrid compounds bearing a cyclic π -ligand, an icosahedral carborane moiety, and a bridging group has been developed. These are very versatile ligands, featuring both an organic and an inorganic moiety as well as a bridging ligand. They can be readily converted into mono-, di-, tri- and pentaanionic species under suitable reaction conditions, leading to the generation of a new class of organometallic compounds in which the carboranyl unit can be cast in the role of a bulky substituent, a σ -, η^5 , η^6 , or η^7 π -ligand. This Account provides an overview of our recent work in this area.

Introduction

Ligands are an essential part of coordination/organometallic compounds. They impose a dominant control

Zuowei Xie was born in Zhejiang, China, in 1964. He received his B.S. and M.S. degrees from Hangzhou University and the Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences, in 1983 and 1986, respectively. In 1990, he completed his Ph.D. research at both the Shanghai Institute of Organic Chemistry and the Technische Universität Berlin under a collaborative program jointly supervised by Professors Changtao Qian, Yaozeng Huang, and Herbert Schumann. After serving for a year and half as a Research Associate at the Shanghai Institute of Organic Chemistry, he spent three and a half years as a postdoctoral fellow at the University of Southern California with Professor Christopher A. Reed. He then joined the Department of Chemistry at the Chinese University of Hong Kong in 1995, where he is now a Professor. He received from the State Commission on Science and Technology of China a National Natural Science Prize, a Young Scholar award, and an Outstanding Young Investigator award in 1997, 2000, and 2001, respectively, and is the holder of the K. C. Wong Education Foundation Lectureship of 2002. His research interests encompass the chemistry of boron clusters, carboranes and metallacarboranes, organometallic chemistry of f-block and early transition metal complexes, homogeneous catalysis and coordinative unsaturation, and the activation of small molecules and polymer synthesis.

over both the chemical and the physical properties of the resultant complexes. Therefore, it comes as no surprise that ligand design has become a central theme in the development of the chemistry of coordination/organometallic compounds, particularly in terms of their roles as catalysts for asymmetric synthesis¹ and olefin polymerization.²

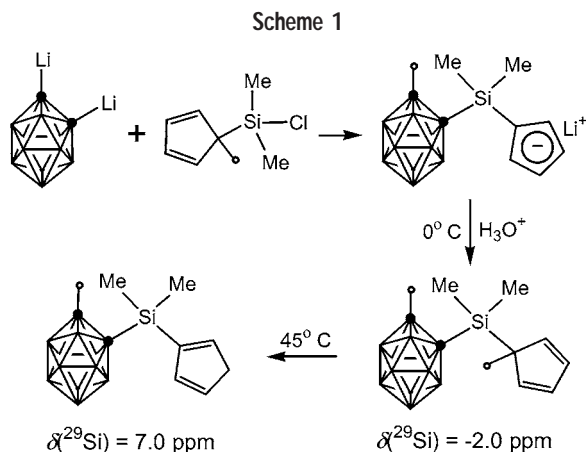
In recent decades, various types of ligands have been synthesized for different purposes, among which the cyclopentadienyl and carboranyl groups stand out. Cyclopentadienyl, a $6e^-$ π -ligand, has long been a ubiquitous component of metallocenes, and it is hard to imagine what organometallic chemistry would be without this ligand.³ In a parallel fashion—although coming to the scene at a somewhat later stage—the dicarbollide ion ($C_2B_9H_{11}^{2-}$), an isolobal inorganic analogue of cyclopentadienyl, has been the bedrock for metallacarborane chemistry.⁴ The merits of these two ligands, each in its individual form, had been scrutinized previously, and it was not until after our successful synthesis of a Me_2Si -bridged cyclopentadienyl–carboranyl compound, $Me_2Si(C_5H_5)(C_2B_{10}H_{11})$,⁵ that we were able to examine the synergistic effects derivable from systems wherein the two moieties are united. Subsequent variation of the nature of the bridging group and/or the structure of the cyclopentadienyl unit provided a plethora of this new type of organic–inorganic hybrid ligands, which are extremely useful for the production of organometallic complexes of extraordinary structures and/or with unique properties. This Account reviews our recent work on the design and synthesis of these hybrid ligands as well as their applications in organometallic chemistry.

Design and Synthesis of Ligands

Our initial idea was to link the cyclopentadienyl unit and the *nido*-carborane dianion together by a bridging group to prevent ligand redistribution in the formation of mixed sandwich complexes of the type $[(\eta^5-C_5Me_5)(\eta^6-C_2B_{10}H_{12})Ln]^-$ ($Ln =$ lanthanides),⁶ and to couple the cyclopentadienyl moiety and the dicarbollide ion together

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to enhance olefin polymerization efficiency by the catalysts $[(\eta^5\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})]\text{MR}$ (M = group 4 metals) through opening up the coordination sphere of the central metal ion.⁷ Since the *nido*-carborane dianion and dicarbollide ion are all prepared from *o*-carborane,⁴ a compound bearing both cyclopentadienyl and carboranyl moieties became our first target molecule. Coupling of these two groups can be readily achieved by treatment of $\text{Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ with $(\text{C}_5\text{H}_5)\text{SiMe}_2\text{Cl}$, as shown in Scheme 1.^{5,8,9}



A dilithium salt must be used, since one molar equivalent is consumed by the acidic proton of cyclopentadiene in $(\text{C}_5\text{H}_5)\text{SiMe}_2\text{Cl}$, and the remaining one is necessary to provide the nucleophile for reaction with the $\text{Si}-\text{Cl}$ bond to form the target molecule. This reaction can be closely monitored by ^{11}B NMR. Thus, following this motif, a new class of organic–inorganic hybrid ligands can be prepared^{10–23} via a nucleophilic substitution reaction of $\text{Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ with different electrophiles, in which both the nature of the electrophilic site and the structure of the cyclopentadienyl ring can be varied. Some examples are listed in Figure 1. This list can, of course, be extended to include systems with two or more bridging atoms, chiral substituents, and other cage systems.

It is noteworthy that, for the generation of neutral ligands, direct hydrolysis with a saturated NH_4Cl aqueous solution is used if the bridging atom is carbon or silicon (Scheme 1).⁵ However, in the case where the bridging atom is phosphorus or boron, nonaqueous workup must be employed (Scheme 2) to avoid decomposition of the phosphines or boranes.²⁴

Versatility of Ligands

The acidic protons in the cyclopentadienyl–carboranyl hybrid compounds in Figure 1 have typical $\text{p}K_{\text{a}}$ values of ~ 23 ,²⁵ ~ 16 ,²⁶ ~ 20 ,²⁶ and ~ 23 ²⁶ for *o*-carborane, cyclopentadiene, indene, and fluorene, respectively. Therefore, by using suitable bases, it is possible to generate the corresponding mono- or dianionic counterparts. On the other hand, the *o*-carborane can be reduced to the di- and tetraanion by group 1 metals^{27–29} or can be converted into dicarbollide ion via a deboration reaction under suitable reaction conditions.⁴ Scheme 3 illustrates the high versa-

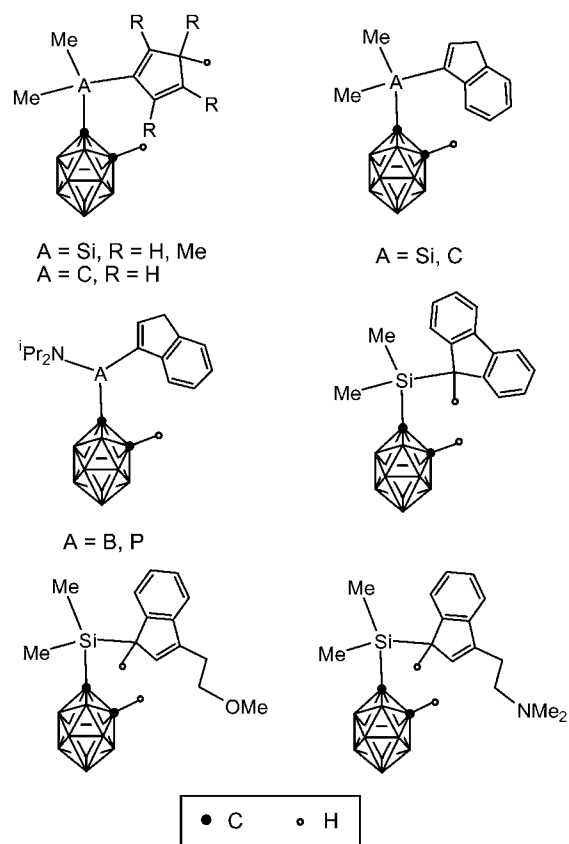
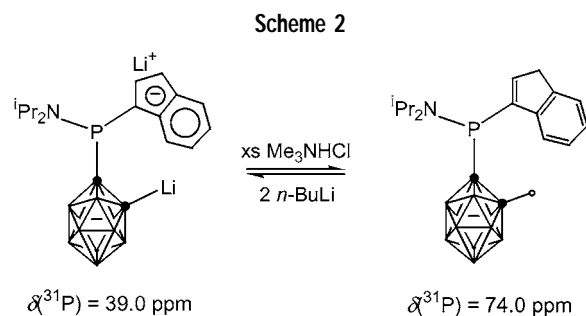


FIGURE 1. Some organic–inorganic hybrid compounds.



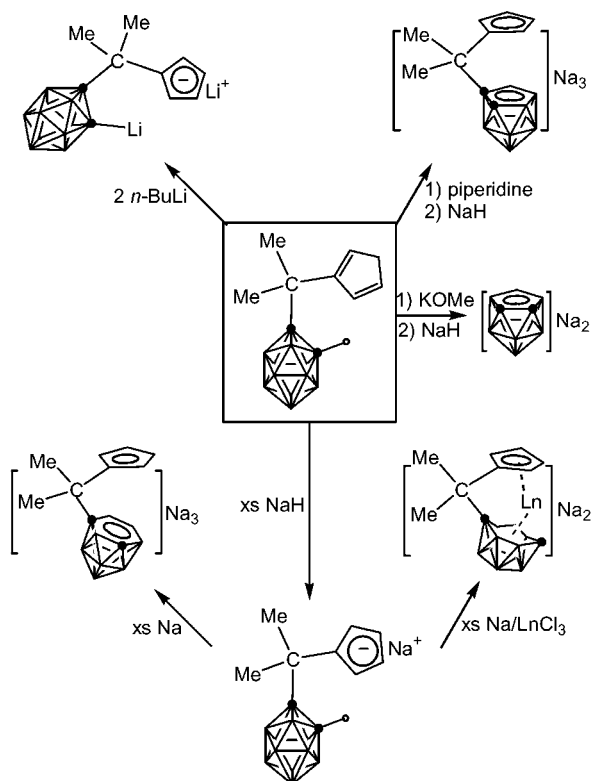
tility of this class of compounds in a typical example of $\text{Me}_2\text{C}(\text{C}_5\text{H}_5)(\text{C}_2\text{B}_{10}\text{H}_{11})$.¹¹

It is noted that the presence of a d^0 transition metal ion is necessary to convert this type of compounds into the pentaanionic species because the highly electro-positive metal ion can enhance the electron-accepting ability of the carborane cage.¹¹ The key to preparing the trianion $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_9\text{H}_{10})]^{3-}$ is to use a mild deboration reagent such as piperidine.³⁰ Otherwise, $\text{C}(\text{cage})-\text{C}(\text{bridging atom})$ bond cleavage is always observed, leading to the formation of dicarbollide ion $\text{C}_2\text{B}_9\text{H}_{11}^{2-}$.¹¹ Since the Me_2Si , RB , and RP linkages are susceptible to nucleophilic attack, their analogues of $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_9\text{H}_{10})]^{3-}$ are not accessible.

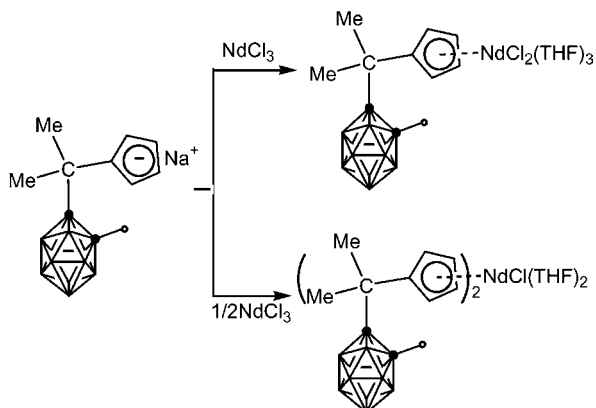
Applications in Organometallic Chemistry

Stabilization of Early Lanthanocene Chlorides. Early lanthanocene chlorides of the types $(\text{C}_5\text{H}_5)\text{LnCl}_2(\text{solvent})_x$ and $(\text{C}_5\text{H}_5)_2\text{LnCl}(\text{solvent})_x$ are usually unstable and un-

Scheme 3



Scheme 4

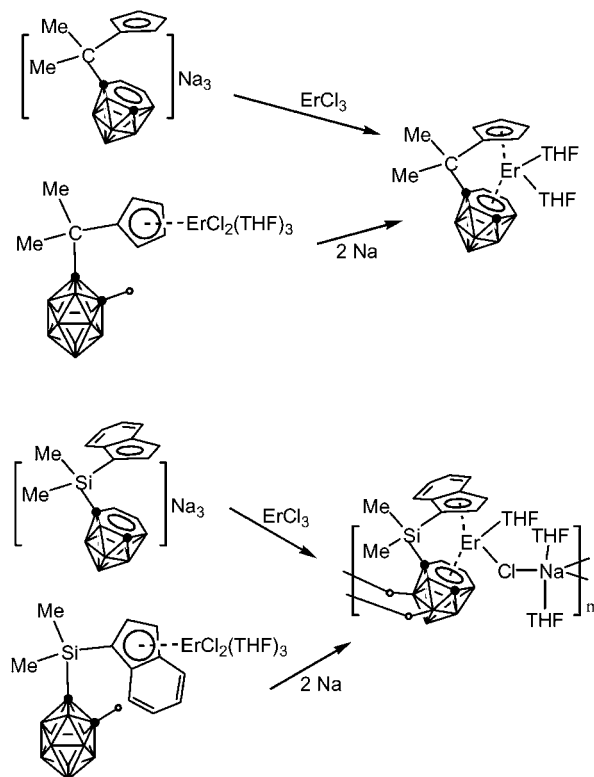


dergo ligand redistribution reactions to form thermodynamically stable complexes $(C_5H_5)_3Ln$.³¹ To prevent this reaction, a bulky or a bridged ligand is often employed. In the monoanionic salts of the above-mentioned hybrid ligands, the carboranyl moiety serves as a highly sterically demanding substituent of π -ligands, which can effectively prevent ligand redistribution reactions of early lanthanocene chlorides, resulting in the isolation and structural characterization of (carboranyl-Cp) $LnCl_2(THF)_3$ and (carboranyl-Cp) $_2LnCl(THF)_2$ types of complexes.^{9,11} Two examples are shown in Scheme 4, which furnished important starting materials for the preparation of complexes containing Ln–C, Ln–H, and Ln–heteroatom bonds.³¹

Stabilization of Mixed Sandwich Lanthanacarboranes.

Attempts to prepare the mixed sandwich lanthanacarborane $[(C_5Me_5)(C_2B_{10}H_{12})Eu(THF)_2]^{2-}$ failed due to the ligand redistribution resulting in the formation of

Scheme 5



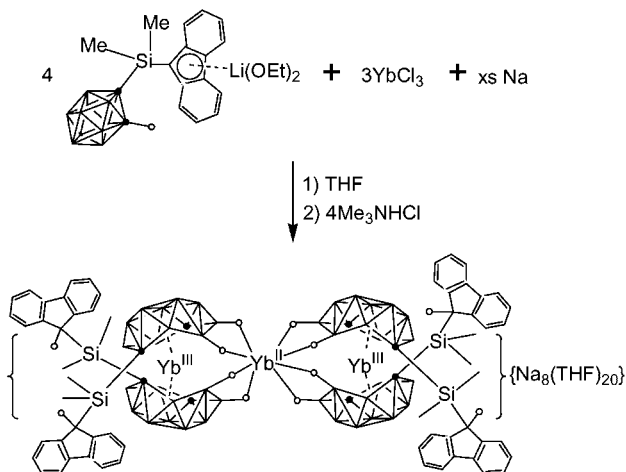
$(C_5Me_5)_2Eu(THF)_2$ and $[(C_2B_{10}H_{12})_2Eu(THF)_2]^{2-}$.⁶ Similar ligand redistribution reactions were also observed with other lanthanacarboranes in the C_2B_9 ³² and C_2B_4 ³³ systems. By bridging the two π -ligands via a Me_2C or Me_2Si linkage, the resultant mixed sandwich lanthanacarboranes can be effectively stabilized. There are two general methods to prepare this type of complex: salt metathesis between the trianion $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]^{3-}$ and $LnCl_3$, and reduction of $[Me_2C(C_5H_4)(C_2B_{10}H_{11})]LnCl_2(THF)_3$ with 2 equiv of group 1 metals. The structures of the products are dependent upon the ligand types.^{9,11} Scheme 5 shows typical examples.

Stabilization of High Oxidation State of the Metals.

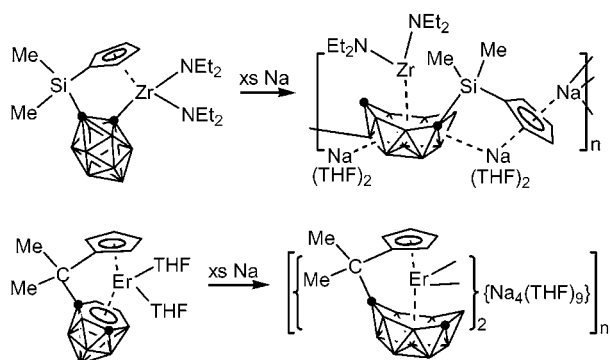
It is well-documented that organoytterbium(III) and organozirconium(IV) compounds can be readily reduced by Na metal to form the corresponding organoytterbium(II) and organozirconium(II) complexes.^{31,34} We have found that our ligands can effectively prevent metal ions from reduction, leading to the formation of metallacarboranes of Yb and Zr in their highest oxidation states, even in the presence of group 1 metals.^{22,35}

Interaction between $YbCl_3$, $[Me_2Si(C_{13}H_8)(C_2B_{10}H_{11})]Li(OEt)_2$, and excess finely cut Na metal in THF, followed by treatment with 1 equiv of dry Me_3NHCl , gave a novel full-sandwich, mixed-valent metallacarborane complex, $\{ \{ [\eta^7-Me_2Si(C_{13}H_8)(C_2B_{10}H_{11})]_2Yb^{III} \}_2 Yb^{II} \} \{ Na_8(THF)_{20} \}$ (Scheme 6).²² Direct reaction of $[\eta^5-\sigma-Me_2Si(C_5H_4)(C_2B_{10}H_{10})]Zr(NEt_2)_2$ with excess Na metal afforded a half-sandwich complex, $\{ \{ (\mu-\eta^5): \eta^7-Me_2Si(C_5H_4)(C_2B_{10}H_{11}) \} Zr(NEt_2)_2 \{ Na_3(THF)_4 \} \}_n$.³⁵ A mixed sandwich lanthanacarborane, $\{ \{ [\eta^5:\eta^7-Me_2C(C_5H_4)(C_2B_{10}H_{11})]Er \}_2 \{ Na_4(THF)_9 \} \}_n$,

Scheme 6



Scheme 7



was also prepared by treatment of $[\eta^5:\eta^6\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Er}(\text{THF})_2$ with excess Na metal (Scheme 7).¹¹

The most important structural feature in these complexes is the *arachno*-carborane tetraanion, which is η^7 -bound to the metal ion (Figure 2). This η^7 -carboranyl ligand is responsible for stabilizing the high oxidation state of the metals, as illustrated in $\{[\eta^7\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{Yb}^{\text{III}}\}_2\{\text{Na}_8(\text{THF})_{20}\}$, in which the capping Yb remains in its high oxidation state (+3) while the *exo* Yb is reduced

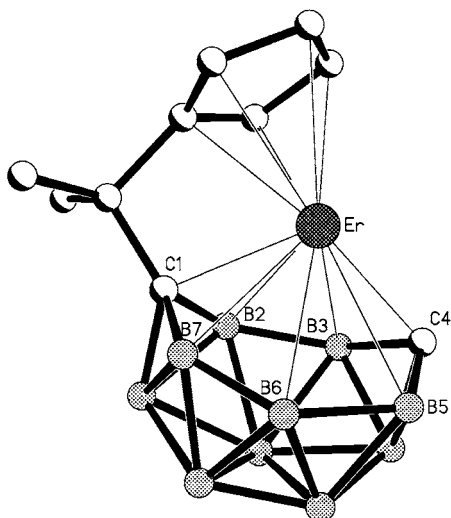
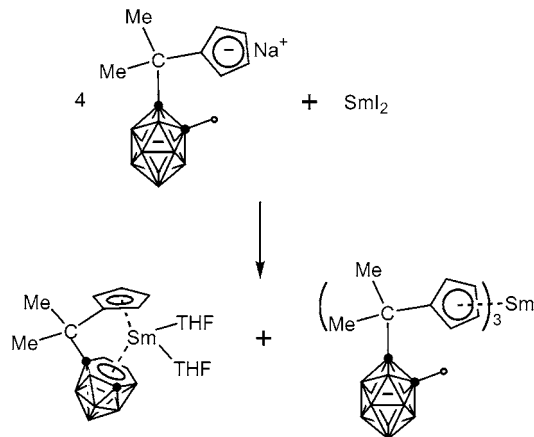


FIGURE 2. η^7 -Bonding mode.

Scheme 8



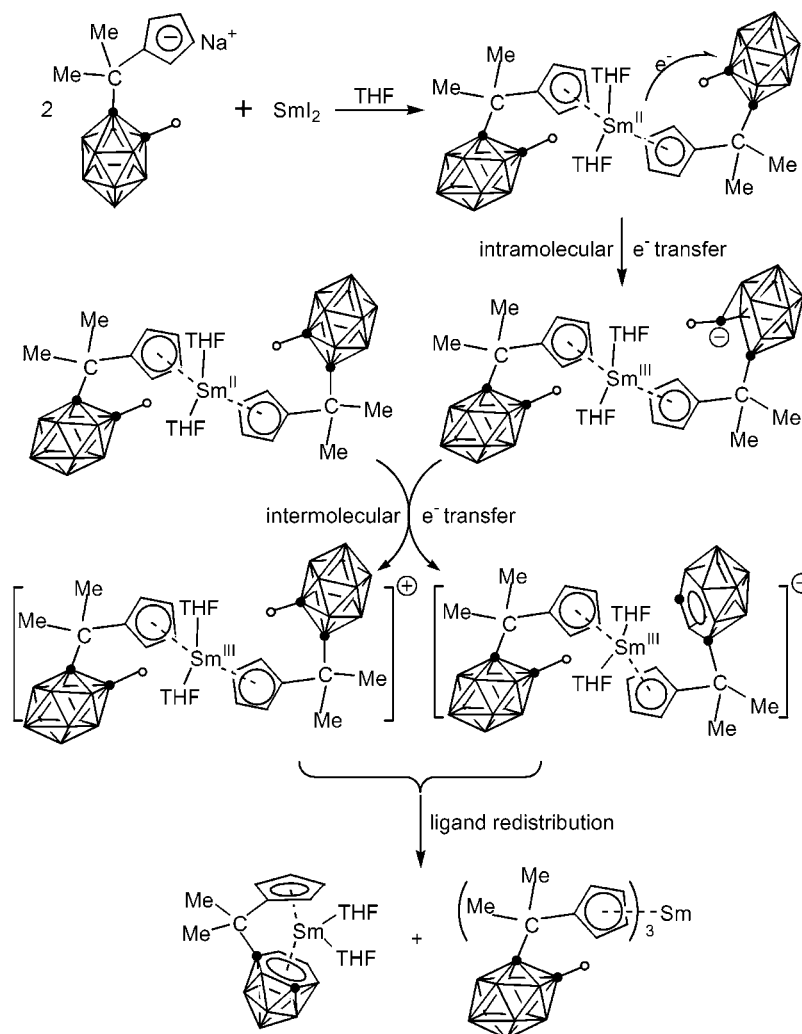
by Na to the low oxidation state (+2). The formation of $\{[\eta^5:\eta^7\text{-Me}_2\text{Si}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Zr}(\text{NEt}_2)_2\}_n\{\text{Na}_3(\text{THF})_4\}_n$ rather than the bent zirconocene is predictable by the 18-electron rule since *arachno*- $\text{C}_2\text{B}_{10}\text{H}_{12}^{4-}$ is a $10e^- \pi$ -ligand.³⁶ Lanthanides (4f elements) do not obey the 18-electron rule, so full-sandwich or mixed-sandwich lanthanacarboranes can be isolated.

Redox Reactions. It has been reported that high-oxidation-state metal ions such as Ln^{3+} ($\text{Ln} = \text{Eu},^6 \text{Sm},^9 \text{Yb}^9$) and M^{4+} ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$)³⁷ can oxidize *nido*- $\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{10}^{2-}$ dianionic species back to the *o*- $\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ neutral carboranes. Under certain reaction conditions, however, metallacarboranes bearing both oxidative and reductive components can be achieved via redox reactions using our ligand systems.

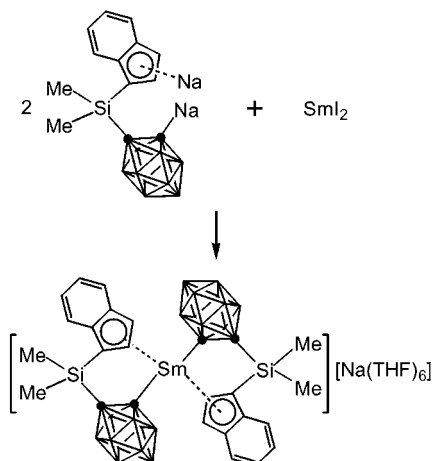
SmI_2 is a common reducing agent and is widely used in organic synthesis.³⁸ Although it is not able to reduce *o*- $\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{10}$, its organometallic counterpart $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Sm}(\text{THF})_2$ can readily reduce *o*- $\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ to *nido*- $\text{R}_2\text{C}_2\text{B}_{10}\text{H}_{10}^{2-}$.⁹ This property makes the synthesis of high-valent samaracarboranes possible. Treatment of $\text{SmI}_2(\text{THF})_x$ with $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Na}(\text{THF})$ resulted in the isolation of both mixed-sandwich samaracarborane $[\eta^5:\eta^6\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Sm}(\text{THF})_2$ and tris-ligated organosamarium compound $[\eta^5\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{11})]_3\text{Sm}$, shown in Scheme 8.¹¹ During the reaction, Sm^{2+} is apparently oxidized to Sm^{3+} ; meanwhile, the neutral carborane is reduced to the dianion. A plausible mechanism is shown in Scheme 9. Similarly, reaction of $\text{SmI}_2(\text{THF})_x$ with $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Na}$ afforded a redox product, $[\eta^5:\eta^6\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Sm}(\text{THF})_2$.¹⁷ This type of redox reaction is a useful general method for the preparation of such kinds of mixed-sandwich samaracarboranes.

Interaction between $\text{SmI}_2(\text{THF})_x$ and dianionic salts of the hybrid ligands offered different products. $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Na}_2$ reacted with $\text{SmI}_2(\text{THF})_x$, yielding a Sm(III) complex, $\{[\eta^5:\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]_2\text{Sm}\}[\text{Na}(\text{THF})_6]$, via an intermolecular electron-transfer reaction (Scheme 10). This complex was also prepared in a much higher yield from the reaction of $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Na}_2$ with $\text{SmI}_2(\text{THF})_x$, followed by treatment with $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{11})]\text{Na}$, through an intramolecular electron-transfer reaction.¹⁷

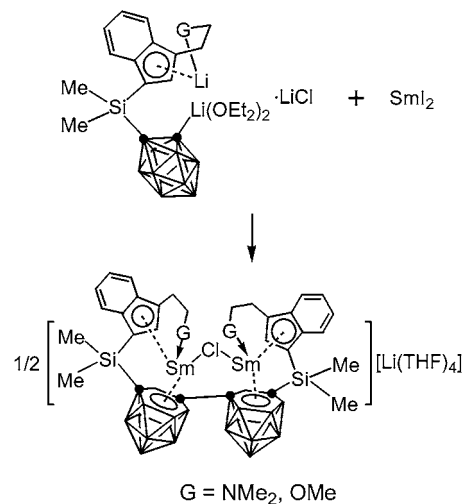
Scheme 9



Scheme 10



Scheme 11

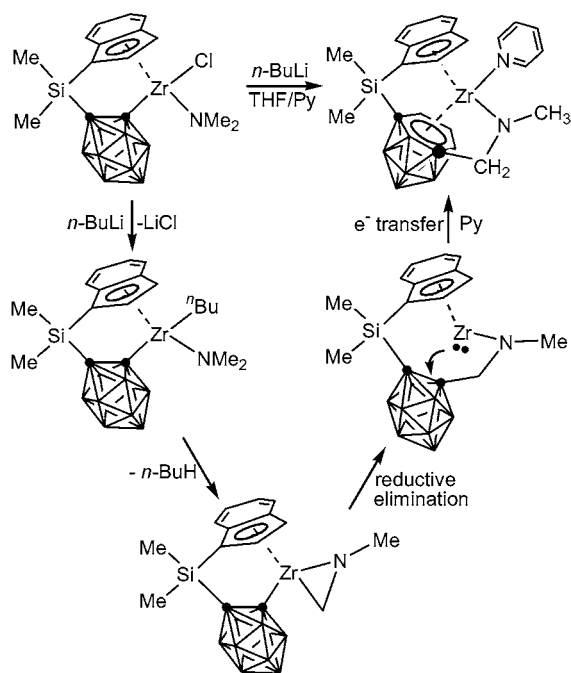


Substituents on the aromatic ring have a profound influence on the formation of the product. For example, reaction of [Me₂Si(C₉H₅CH₂CH₂G)(C₂B₁₀H₁₀)]Li₂(OEt₂)₂·LiCl with SmI₂(THF)_x gave novel samaracarboranes [$\{\eta^5\text{-}\eta^1\text{-}\eta^6\text{-Me}_2\text{Si}(\text{C}_9\text{H}_5\text{CH}_2\text{CH}_2\text{G})(\text{C}_2\text{B}_{10}\text{H}_{10})\text{Sm}\}_2(\mu\text{-Cl})\}[\text{Li}(\text{THF})_4]$ (G = NMe₂, OMe), in which the reduction and coupling of the

carborane cage occurred in a tandem manner (Scheme 11).²¹

An intramolecular redox reaction was also observed in zirconium complexes. Treatment of [$\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})\text{ZrCl}(\text{NMe}_2)$] with 1 equiv of *n*-BuLi in THF/pyridine gave [$\eta^5\text{-}\eta^6\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10}\text{CH}_2\text{NMe})\text{Zr-}$

Scheme 12

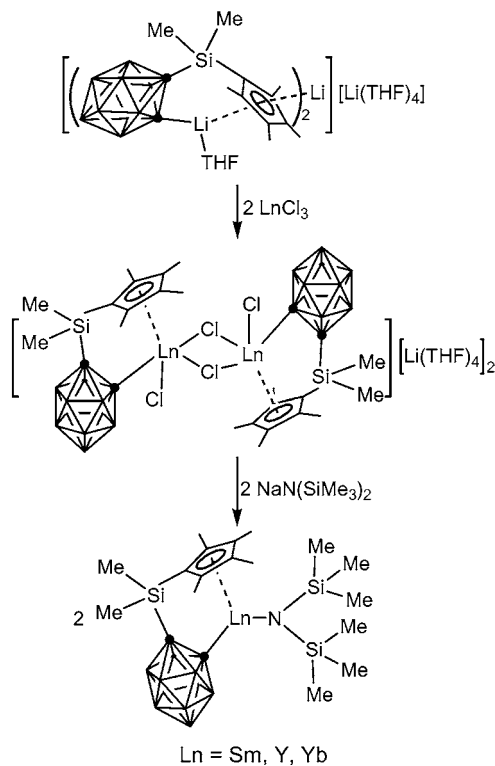


(NC₅H₅). Obviously, the formation of this complex involves sp³ C–H bond activation and cage reduction. The proposed mechanism is shown in Scheme 12.³⁵ Reaction with *n*-BuLi, followed by butane elimination, gives a metallacyclic complex. Reductive elimination affords a Zr(II) species. Intramolecular oxidative addition/electron-transfer reaction generates the final product. This is a new methodology for the preparation of high-valent group 4 metallocarboranes that cannot be prepared by the conventional metathesis.

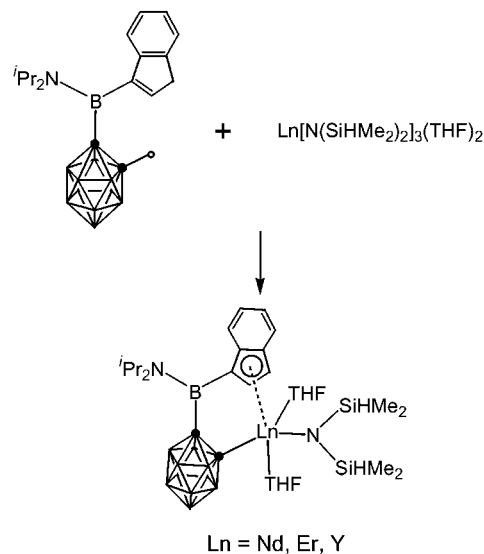
Catalysis. Recently developed constrained-geometry ligands containing both monocyclopentadienyl and σ -heteroatom (N, O, and P) components have attracted considerable attention.³⁹ The dianionic species of our organic–inorganic hybrid compounds are a novel class of constrained-geometry ligands bearing a carboanion functionality (see Scheme 3, for example). The resultant constrained-geometry transition metal complexes have some interesting catalytic properties in the polymerization of olefin and methyl methacrylate (MMA).

Both salt metathesis and amine elimination methods are useful in the preparation of the above-mentioned constrained-geometry metal complexes. The former often leads to double salt adducts. The latter is always recommended if feasible. Reaction of LnCl₃ with 0.5 equiv of [$\{\{\mu\text{-}\eta^5\}: \sigma\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\}\text{Li}(\text{THF})_2\}\text{Li}[\text{Li}(\text{THF})_4]$] gave organolanthanide complexes of the general formula [$\{\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\}\text{LnCl}(\mu\text{-Cl})_2[\text{Li}(\text{THF})_4]_2$] (Ln = Sm, Y, Yb). Substitution of the chloro groups by a bulky amido moiety yielded an unsolvated complex, [$\eta^5\text{-}\sigma\text{-Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})\}\text{YN}(\text{SiMe}_3)_2$] (Scheme 13).¹³ Amine elimination reaction of ^{*i*}Pr₂NB(C₉H₇)(C₂B₁₀H₁₁) with Ln[N(SiHMe₂)₂]₃(THF)₂ generated directly the metal amides [$\eta^5\text{-}\sigma\text{-}^i\text{Pr}_2\text{NB}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})\}\text{LnN}(\text{SiHMe}_2)_2(\text{THF})_2$] (Ln = Nd, Er, Y) (Scheme 14).²³ These amide complexes

Scheme 13



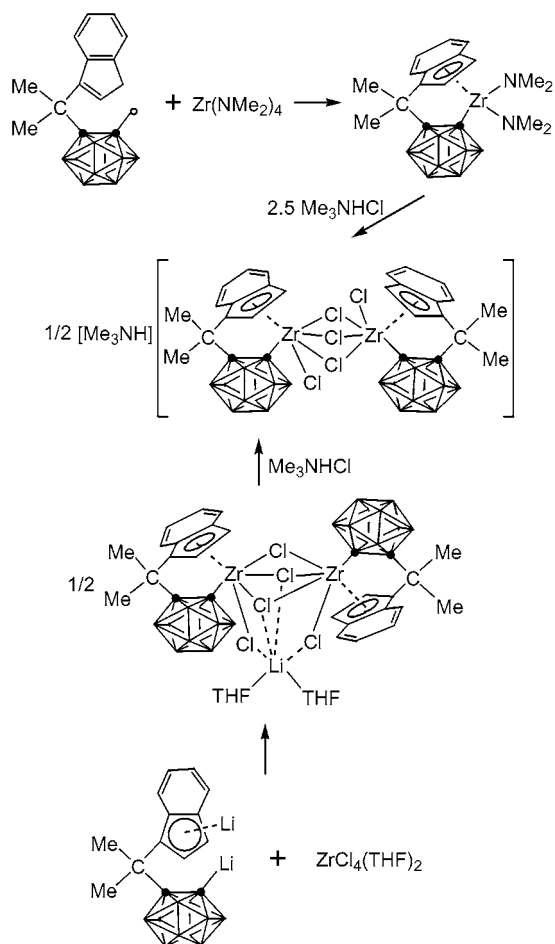
Scheme 14



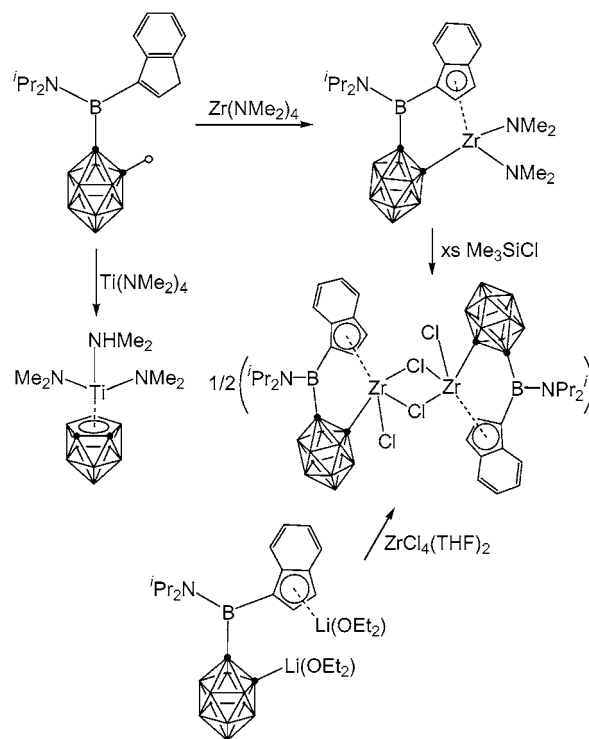
can initiate the polymerization of MMA, leading to syn-rich poly(MMA)s, but the activity is low.

Constrained-geometry group 4 metal complexes can generally be prepared by either of the above methods. Amine elimination between a neutral ligand and a M(NR₂)₄ gives a metal amide in which N(p_π) → M(d_π) interactions are observed (Scheme 15).¹⁶ The keys to the success of this type of reactions are the steric accessibility, p*K*_a values of the ligand, and susceptibility of the bridging atom to the nucleophilic attack. For example, there was no reaction between Ti(NEt₂)₄ and Me₂Si(C₉H₇)(C₂B₁₀H₁₁) or Me₂Si(C₅H₅)(C₂B₁₀H₁₁), although both Zr(NEt₂)₄ and Ti(NMe₂)₄ reacted readily with these neutral ligands to give

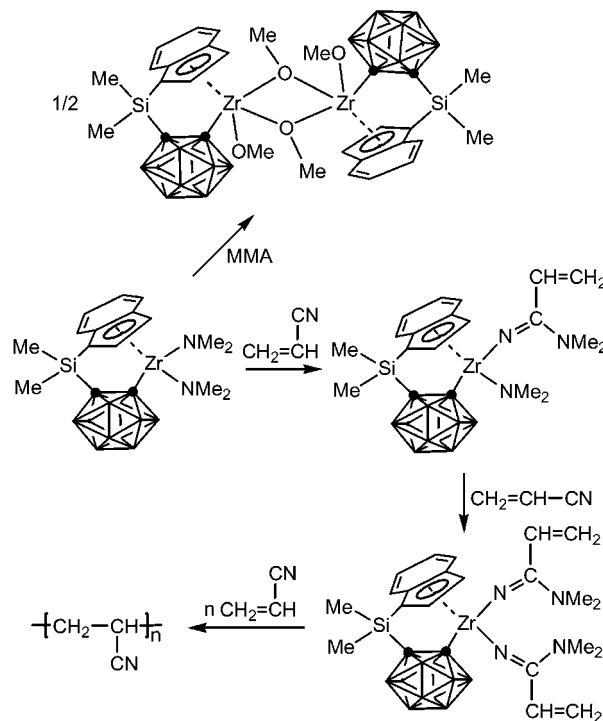
Scheme 15



Scheme 16



Scheme 17



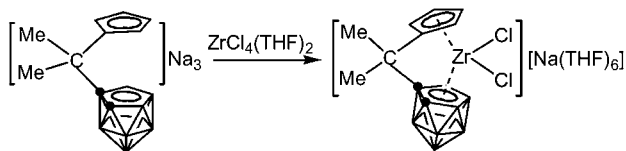
amide complexes in good yields. Interaction between ${}^i\text{Pr}_2\text{NB}(\text{C}_9\text{H}_7)(\text{C}_2\text{B}_{10}\text{H}_{11})$ and $\text{Ti}(\text{NMe}_2)_4$ did not lead to the isolation of the expected complex $[\eta^5\text{-}\sigma\text{-}{}^i\text{Pr}_2\text{NB}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Ti}(\text{NMe}_2)_2$; instead, the deborated product $(\eta^5\text{-}\text{C}_2\text{B}_9\text{H}_{11})\text{Ti}(\text{NMe}_2)_2(\text{HNMe}_2)$ was isolated (Scheme 16).⁴⁰ The group 4 metal amides can be converted into the corresponding chloro derivatives by reacting with Me_3SiCl or Me_3NHCl . The products are dependent upon the ligands and central metal ions. They can also be prepared by salt metathesis of MCl_4 and the corresponding di-anionic salts, as shown in Schemes 15 and 16, respectively.

These constrained-geometry group 4 metal amides and chlorides can all catalyze the polymerization of ethylene with moderate to very high activities upon activation with methylalumoxane (MAO). Both the central metal ion and the coligand affect the catalytic performance of the catalysts, and the following trends are observed: (1) $\text{Zr} > \text{Ti} > \text{Hf}$, and (2) $\text{Cl} > \text{Me} \approx \text{NMe}_2$. Among these precatalysts, $[\{\eta^5\text{-}\sigma\text{-}{}^i\text{Pr}_2\text{NB}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})\}\text{ZrCl}_2]_2$ exhibits the highest ethylene polymerization activity ($3.94 \times 10^6 \text{ g mol}^{-1} \text{ atm}^{-1} \text{ h}^{-1}$), which indicates that the B-linkage would have some intramolecular Lewis acid coactivations, increasing the electrophilicity of the central metal ion.⁴⁰

The electron-deficient metal amide complex $[\eta^5\text{-}\sigma\text{-}\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NMe}_2)_2$ is an active catalyst for the polymerization of acrylonitrile in the absence of any cocatalysts. The isolation and structural characterization

of single- and double-insertion products of $[\eta^5\text{-}\sigma\text{-}\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}[\text{NC}(\text{CHCH}_2)(\text{NMe}_2)](\text{NMe}_2)$ and $[\eta^5\text{-}\sigma\text{-}\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}[\text{NC}(\text{CHCH}_2)(\text{NMe}_2)]_2$ indicate that the Zr–N bonds are more reactive than the Zr–C(cage) bond (Scheme 17). This result is also supported by the isolation and structural characterization of $[\{\eta^5\text{-}\sigma\text{-}\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})\}\text{Zr}(\mu\text{-OMe})(\text{OMe})]_2$ from the reaction of $[\eta^5\text{-}\sigma\text{-}\text{Me}_2\text{Si}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NMe}_2)_2$ with MMA.⁴¹ No poly(MMA) was detected. Interestingly, the bis-ligated

Scheme 18



zirconium complex $[\eta^5\text{-}o\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_{10}\text{H}_{10})_2\text{Zr}]$ is reported to be able to catalyze the polymerization of MMA with low activity without any cocatalyst.¹²

The mixed-sandwich group 4 metallocarboranes $\{[\eta^5\text{-}\eta^5\text{-Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_9\text{H}_{10})\}\text{MCl}_2\}[\text{Na}(\text{THF})_6]$, prepared from the reaction of $[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_2\text{B}_9\text{H}_{10})]\text{Na}_3(\text{THF})_6$ with MCl_4 , are also highly active ethylene polymerization catalysts upon activation with MAO. Scheme 18 shows a typical example.³⁰ Studies on the synthesis and catalytic activity of its neutral alkyl derivatives are in progress.

Conclusions

By taking advantage of the unique carborane molecules and traditional cyclic π -ligands as well as bridging ligands, a new class of organic–inorganic hybrid ligands has been developed. They possess not only the common features of both moieties but also unique properties of their own, which meet challenges in organometallic chemistry.

These compounds are really very versatile ligands. They can be readily converted into the mono-, di-, tri-, and pentaanionic species under suitable reaction conditions, leading to the generation of a new class of organometallic compounds in which the carboranyl moiety serves as a bulky substituent, a σ -, η^5 , η^6 , or η^7 π -ligand, respectively.

These ligands are finding many applications in organometallic chemistry. They can prevent ligand redistribution reactions of early lanthanocene chlorides and mixed-sandwich lanthanacarboranes, and they can stabilize the high oxidation state of the central metals. They can offer organometallic complexes high catalytic activities in olefin polymerization upon activation with MAO, and low activity in the polymerization of MMA in the absence of any cocatalysts.

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References

- (1) (a) Knowles, W. S. Asymmetric Hydrogenations. *Angew. Chem., Int. Ed.* **2002**, *41*, 1998–2007. (b) Noyori, R. Asymmetric Catalysis: Science and Opportunities. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008–2022. (c) Sharpless, K. B. Searching for New Reactivity. *Angew. Chem., Int. Ed.* **2002**, *41*, 2024–2032.
- (2) Gladysz, J. A., Guest Editor. Special Issue on Frontiers in Metal-Catalyzed Polymerization. *Chem. Rev.* **2000**, *100* (4), 1167–1682.
- (3) Togni, A.; Halterman, R. L. *Metallocenes: Synthesis, Reactivity, Applications*; Wiley-VCH: New York, 1998; Vols. 1 and 2.
- (4) (a) Hawthorne, M. F.; Young, D. C.; Wegner, P. A. Carbametallic Boron Hydride Derivatives. I. Apparent Analogs of Ferrocene and Ferricinium Ion. *J. Am. Chem. Soc.* **1965**, *87*, 1818–1819. (b) Grimes, R. N. Transition Metal Metallocarboranes. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 1, pp 373–430. (c) Grimes, R. N. Metallocarboranes in the New Millennium. *Coord. Chem. Rev.* **2000**, *200/202*, 773–811. (d) Saxena, A. K.; Hosmane, N. S. Recent Advances in the Chemistry of Carborane Metal Complexes Incorporating d- and f-Block Elements. *Chem. Rev.* **1993**, *93*, 1081–1124. (e) Saxena, A. K.; Maguire, J. A.; Hosmane, N. S. Recent Advances in the Chemistry of Heterocarborane Complexes Incorporating s- and p-Block Elements. *Chem. Rev.* **1997**, *97*, 2421–2462. (f) Xie, Z. Advances in the Chemistry of Metallocarboranes of f-Block Elements. *Coord. Chem. Rev.* **2002**, *231*, 23–46.
- (5) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Xue, F.; Mak, T. C. W. A New Versatile Ligand: Its Synthesis and Applications in Organolanthanide Chemistry. *Organometallics* **1998**, *17*, 489–491.
- (6) Khattar, R.; Manning, M. J.; Knobler, C. B.; Johnson, S. E.; Hawthorne, M. F. Synthesis, Structure, and Characterization of Lanthanacarboranes. Molecular Structures of $[\text{closo-}1,1,1\text{-}(\text{MeCN})_3\text{-}1,2,4\text{-EuC}_2\text{B}_{10}\text{H}_{12}]_{\infty}$ and $[\text{1,1-(THF)}_2\text{-}o\text{-}1,1'\text{-Eu}(\text{1,2,4-EuC}_2\text{B}_{10}\text{H}_{12})_2]^{2-}$. *Inorg. Chem.* **1992**, *31*, 268–273.
- (7) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. Group 4 Metal Dicarbolide Chemistry. Synthesis, Structures, and Reactivity of Electrophilic Alkyl Complexes $(\text{Cp}^*)(\text{C}_2\text{B}_9\text{H}_{11})\text{M}(\text{R})$, M = Hf, Zr. *J. Am. Chem. Soc.* **1991**, *113*, 1455–1457.
- (8) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Mak, T. C. W. Synthesis and Structural Characterization of the First Mixed Lanthanacarborane Incorporating η^5 -Cyclopentadienyl and η^6 -Carboranyl Ligands. *Organometallics* **1998**, *17*, 1907–1909.
- (9) Xie, Z.; Wang, S.; Zhou, Z.-Y.; Mak, T. C. W. Synthesis, Reactivity, and Structural Characterization of Organolanthanide Compounds Incorporating both Cyclopentadienyl and Carboranyl Groups. *Organometallics* **1999**, *18*, 1641–1652.
- (10) Xie, Z.; Chui, K.; Yang, Q.; Mak, T. C. W. A New Class of Metallocarboranes: Synthesis and Molecular Structure of the First Example of an Organolanthanide Compound Bearing an η^7 -Carboranyl Ligand. *Organometallics* **1999**, *18*, 3947–3949.
- (11) Chui, K.; Yang, Q.; Mak, T. C. W.; Xie, Z. Synthesis, Structure, and Reactivity of Organolanthanide Carboranyl Compounds and Lanthanacarboranes Derived from a Versatile Ligand, $\text{Me}_2\text{C}(\text{C}_5\text{H}_5)(\text{C}_2\text{B}_{10}\text{H}_{11})$. *Organometallics* **2000**, *19*, 1391–1401.
- (12) Hong, E.; Kim, Y.; Do, Y. A Neutral Group 4 Poly(methyl methacrylate) Catalyst Derived from o-Carborane. *Organometallics* **1998**, *17*, 2933–2935.
- (13) Zi, G.; Yang, Q.; Mak, T. C. W.; Xie, Z. Tetramethylcyclopentadienyl vs Cyclopentadienyl Substituents. Synthesis and Structural Characterization of Organolanthanide Compounds Derived from the Versatile Ligand $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4\text{H})(\text{C}_2\text{B}_{10}\text{H}_{11})$. *Organometallics* **2001**, *20*, 2359–2366.
- (14) Lee, M.-H.; Hwang, J.-W.; Kim, Y.; Do, Y. Synthesis and Characterization of Group 4 Constrained Geometry Complexes Containing a Linked Cyclopentadienyl-o-Carboranyl Ligand. *Organometallics* **2000**, *19*, 5514–5517.
- (15) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. Carbon versus Silicon Bridges. Synthesis of a New Versatile Ligand and Its Applications in Organolanthanide Chemistry. *Organometallics* **2000**, *19*, 334–343.
- (16) Wang, H.; Wang, Y.; Li, H.-W.; Xie, Z. Synthesis, Structural Characterization, and Olefin Polymerization Behavior of Group 4 Metal Complexes with Constrained-Geometry Carborane Ligands. *Organometallics* **2001**, *20*, 5110–5118.
- (17) Xie, Z.; Wang, S.; Yang, Q.; Mak, T. C. W. Application of a New Versatile Ligand to Lanthanide(II) Chemistry: Synthesis, Reactivity, and Structure of a New Class of Organolanthanide Complexes. *Organometallics* **1999**, *18*, 2420–2427.
- (18) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. Cyclopentadienyl vs Indenyl Substituents. Organolanthanide Complexes and Biscarborane Compounds Derived from a Versatile Ligand, $\text{Me}_2\text{Si}(\text{C}_9\text{H}_7)(\text{C}_2\text{B}_{10}\text{H}_{11})$. *Organometallics* **1999**, *18*, 4478–4487.
- (19) Xie, Z.; Wang, S.; Yang, Q.; Mak, T. C. W. Synthesis and Structure of the First Tetranuclear Organolanthanide Cluster Containing a μ^4 -Imido Group. *Organometallics* **1999**, *18*, 1578–1579.
- (20) Wang, S.; Yang, Q.; Mak, T. C. W.; Xie, Z. Synthesis and Structural Characterization of Novel Organolanthanide Clusters Containing Amido and Imido Groups. *Organometallics* **1999**, *18*, 5511–5517.
- (21) Wang, S.; Li, H.-W.; Xie, Z. Samarium-Mediated Tandem Reactions of o-Carborane. Synthesis and Molecular Structure of $[\{\eta^5\text{-}\eta^1\text{-}\eta^6\text{-Me}_2\text{Si}(\text{C}_9\text{H}_5\text{CH}_2\text{CH}_2\text{G})(\text{C}_2\text{B}_{10}\text{H}_{10})\text{Sm}\}_2(\mu\text{-Cl})][\text{Li}(\text{THF})_4]$ (G = NMe_2 and OMe). *Organometallics* **2001**, *20*, 3624–3625.

- (22) Wang, S.; Li, H.-W.; Xie, Z. A Novel Full-Sandwich Lanthanocarborane Complex Bearing an η^7 -Carboranyl Ligand, $\{[\eta^7\text{-Me}_2\text{Si}(\text{C}_{13}\text{H}_9)(\text{C}_2\text{B}_{10}\text{H}_{11})]_2\text{Yb}^{\text{III}}\}_2\text{Yb}^{\text{III}}\}\{\text{Na}_8(\text{THF})_{20}\}$. *Organometallics* **2001**, *20*, 3842–3844.
- (23) Zi, G.; Li, H.-W.; Xie, Z. Synthesis, Structural Characterization, and Reactivity of Organolanthanide Complexes Derived from a New, Versatile Boron-Bridged Ligand, $^i\text{Pr}_2\text{NB}(\text{C}_9\text{H}_7)(\text{C}_2\text{B}_{10}\text{H}_{11})$. *Organometallics* **2002**, *21*, 1136–1145.
- (24) Wang, H.; Xie, Z. Synthesis, Structural Characterization, and Reactivity of Organolanthanide Complexes Derived from a New Phosphorus-Bridged Versatile Ligand, $^i\text{Pr}_2\text{NP}(\text{C}_9\text{H}_7)(\text{C}_2\text{B}_{10}\text{H}_{11})$. *Book of Abstracts*, 9th Symposium on Chemistry Postgraduate Research in Hong Kong, Hong Kong, China, March 2002; Abstract I-76.
- (25) Shatenshtein, A. I.; Zakharkin, L. I.; Petrov, E. S.; Yakoleva, E. A.; Yakushin, F. S.; Vukmirovich, Z.; Isaeva, G. G.; Kalinin, V. N. The Equilibrium and Kinetic Acidities of Isomeric Carborane Methines. *J. Organomet. Chem.* **1970**, *23*, 313–322.
- (26) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 251.
- (27) Chui, K.; Li, H.-W.; Xie, Z. Synthesis and Structural Characterization of *closo-exo*, *exo-nido*, and *pseudocloso* Group 1 Carborane Compounds of the C_2B_{10} System. *Organometallics* **2000**, *19*, 5447–5453.
- (28) Evans, W. J.; Hawthorne, M. F. Synthesis of Fourteen Vertex Metallocarboranes by Polyhedral Expansion. *J. Chem. Soc., Chem. Commun.* **1974**, 38–39.
- (29) Xie, Z.; Yan, C.; Yang, Q.; Mak, T. C. M. $\{[\{(\eta^7\text{-C}_2\text{B}_{10}\text{H}_{12})(\eta^6\text{-C}_2\text{B}_{10}\text{H}_{12})\text{U}\}[\text{K}_2(\text{THF})_5]_2]\}$: A Metallocarborane Containing the Novel $\eta^7\text{-C}_2\text{B}_{10}\text{H}_{12}^{4-}$ Ligand. *Angew. Chem., Int. Ed.* **1999**, *38*, 1761–1763.
- (30) Wang, Y.; Xie, Z. Unpublished results.
- (31) Schumann, H.; Messe-Markscheffel, J. A.; Esser, L. Synthesis, Structure, and Reactivity of Organometallic π -Complexes of the Rare Earths in the Oxidation State Ln^{3+} with Aromatic Ligands. *Chem. Rev.* **1995**, *95*, 865–986.
- (32) Xie, Z.; Liu, Z.; Chiu, K.-y.; Xue, F.; Mak, T. C. W. Synthesis and Structural Characterization of *closo*- and *exo-nido*-Lanthanocarboranes. *Organometallics* **1997**, *16*, 2460–2464.
- (33) Zhang, H.; Wang, Y.; Maguire, J. A.; Hosmane, N. S. A Dinuclear Holmium(III) ‘Carbons Apart’ Carborane Cluster, $[\text{C}_{34}\text{H}_{92}\text{B}_8\text{C}_{14}\text{Ho}_2\text{-Li}_2\text{N}_6\text{Si}_4]\cdot\text{C}_{10}\text{H}_8$. *Acta Crystallogr.* **1996**, *C52*, 8–11.
- (34) Binger, P.; Podubrin, S. Metallocene(II) Complexes of Zirconium and Hafnium. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 4, pp 439–463.
- (35) Wang, Y.; Wang, H.; Li, H.-W.; Xie, Z. Unexpected Intramolecular Oxidative Addition: Novel Synthetic Route to High-Valent Group 4 Metallocarboranes Bearing a η^6 - or η^7 -Carboranyl Ligand. *Organometallics* **2002**, *21*, 3311–3313.
- (36) Chui, K.; Yang, Q.; Mak, T. C. W.; Lam, W.-H.; Lin, Z.; Xie, Z. Synthesis, Structure, and Bonding of d^0/f^n Metallocarboranes Incorporating the η^7 -Carboranyl Ligand. *J. Am. Chem. Soc.* **2000**, *122*, 5758–5764.
- (37) Salentine, C. G.; Hawthorne, M. F. Studies of Metallocarboranes Incorporating the Early Transition Metals. *Inorg. Chem.* **1976**, *15*, 2872–2882.
- (38) Molander, G. A. Application of Lanthanide Reagents in Organic Synthesis. *Chem. Rev.* **1992**, *92*, 29–68.
- (39) Okuda, J.; Eberle, T. Half-Sandwich Complexes as Metallocene Analogs. In *Metallocenes: Synthesis, Reactivity, Applications*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: New York, 1998; Vol. 1, pp 415–453.
- (40) Zi, G.; Li, H.-W.; Xie, Z. Synthesis, Structural Characterization, and Catalytic Property of Group 4 Metal Carborane Compounds with a $^i\text{Pr}_2\text{NB}$ -Bridged Constrained-Geometry Ligand. *Organometallics* **2002**, *21*, 3850–3855.
- (41) Wang, H.; Li, H.-W.; Xie, Z. Multiple Insertion of Small Molecules into the Zr–N Bonds of $[\eta^5\text{-}\sigma\text{-Me}_2\text{A}(\text{C}_9\text{H}_6)(\text{C}_2\text{B}_{10}\text{H}_{10})]\text{Zr}(\text{NMe}_2)_2$ (A = C, Si). Submitted for publication.

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