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Review

# Group 4 metallocenes incorporating constrained-geometry carboranyl ligands

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## Contents



**Abstract**

Ligand modifications have played a crucial role in developing new catalyst precursors for optimizing polymerization activity as well as polymer properties. *o*-Carborane is a highly versatile molecule and can be converted into the *closo*-$C_2B_{10}H_{10}^{2-}$, *nido*-$C_2B_9H_{11}^{2-}$, *nido*-$C_2B_{10}H_{12}^{2-}$, and *arachno*-$C_2B_{10}H_{12}^{4-}$ ligands which are capable of being bonded to metal ions in σ-, $\eta^5$-, $\eta^6$-, and $\eta^7$-fashion, respectively. Such unique features make the replacement possible of either a cyclopentadienyl or an amido unit in the traditional CpSiN constrained-geometry ligands, by a carboranyl moiety. These modifications lead to a novel class of constrained-geometry ligands bearing a carboanion functionality and to a new version of constrained-geometry ligand frameworks incorporating a dicarbollyl moiety. These ligands provide interesting opportunities for the design of metallocenes with new metal/charge and π/σ component combinations and for the study of the role of carborane in catalysis. Achievements, problems and perspectives in this new and rapidly growing field are discussed in this article.


*Keywords:* Carborane; Catalyst; Cyclopentadienyl; Group 4 metal; Insertion; Metallacarborane; Metallocene; Olefin; Polymerization

## 1. Introduction

Ligand modifications have played a crucial role in developing new catalyst precursors for optimizing polymerization activity as well as polymer properties, such as stereoregularity, molecular weight, bulky and polar comonomer incorporation, and microstructure [1]. It has been documented that a ligand containing bifunctional groups often offers complexes with some additional advantage [2]. Recently developed constrained-geometry ligands containing both monocyclopentadienyl and σ-heteroatom components have attracted considerable attention [3]. Group 4 metallocenes derived from these ligands are very active catalysts (so called constrained-geometry catalyst (CGC)) for the copolymerization of ethylene with α-olefins due to the increased electron-deficiency and more open coordination environment of the central metal ions by displacing one $Cp^-$

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Table 1
Selected structural data of metallocenes with constrained-geometry carboranyl ligands

| Compound | M–X (length, Å) | | X–M–X′ (angle, °) | | Ref. |
|---|---|---|---|---|---|
| $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ | Ti–C (ring) | 2.369 (3) | Cent–Ti–C (cage) | 105.0 | [15] |
| | Ti–C (cage) | 2.209 (2) | N–Ti–N | 106.1 (2) | |
| | Ti–N | 1.894 (2) | C (ring)–C–C (cage) | 108.5 (2) | |
| $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]TiCl(NMe_2)$ | Ti–C (ring) | 2.341 (2) | Cent–Ti–C (cage) | 105.7 | [15] |
| | Ti–C (cage) | 2.179 (2) | C (ring)–C–C (cage) | 108.5 (2) | |
| | Ti–N | 1.862 (2) | Cl–Ti–N | 113.4 (1) | |
| | Ti–Cl | 2.277 (1) | | | |
| $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ | Zr–C (ring) | 2.510 (3) | Cent–Zr–C (cage) | 100.3 | [15] |
| | Zr–C (cage) | 2.343 (3) | N–Zr–N | 113.1 (2) | |
| | Zr–N | 2.024 (3) | C (ring)–C–C (cage) | 110.7 (2) | |
| $[\eta^5{:}\sigma\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ | Zr–C (ring) | 2.519 (5) | Cent–Zr–C (cage) | 108.4 | [15] |
| | Zr–C (cage) | 2.353 (4) | N–Zr–N | 110.6 (2) | |
| | Zr–N | 2.015 (4) | C (ring)–Si–C (cage) | 105.2 (2) | |
| $[\eta^5{:}\sigma\text{-}Me_2Si(C_5H_4)(C_2B_{10}H_{10})]Zr(NEt_2)_2$ | Zr–C (ring) | 2.543 (2) | Cent–Zr–C (cage) | 107.6 | [15] |
| | Zr–C (cage) | 2.384 (2) | N–Zr–N | 110.1 (1) | |
| | Zr–N | 2.031 (2) | C (ring)–Si–C (cage) | 104.7 (1) | |
| $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ | Ti–C (ring) | 2.391 (3) | Cent–Ti–C (cage) | 105.4 | [15] |
| | Ti–C (cage) | 2.196 (3) | N–Ti–N | 104.5 (2) | |
| | Ti–N | 1.896 (3) | C (ring)–C–C (cage) | 108.7 (2) | |
| $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ | Zr–C (ring) | 2.521 (8) | Cent–Zr–C (cage) | 101.6 | [15] |
| | Zr–C (cage) | 2.326 (7) | N–Zr–N | 108.0 (3) | |
| | Zr–N | 2.016 (8) | C (ring)–C–C (cage) | 109.4 (6) | |
| $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr(NEt_2)_2$ | Zr–C (ring) | 2.538 (2) | Cent–Zr–C (cage) | 100.6 | [15] |
| | Zr–C (cage) | 2.361 (2) | N–Zr–N | 106.6 (1) | |
| | Zr–N | 2.030 (2) | C (ring)–C–C (cage) | 110.5 (2) | |
| $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ | Zr–C (ring) | 2.541 (5) | Cent–Zr–C (cage) | 109.9 | [15] |
| | Zr–C (cage) | 2.348 (5) | N–Zr–N | 107.3 (2) | |
| | Zr–N | 2.019 (4) | C (ring)–Si–C (cage) | 104.8 (2) | |
| $[\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})]Zr(NEt_2)_2$ | Zr–C (ring) | 2.561 (4) | Cent–Zr–C (cage) | 107.5 | [15] |
| | Zr–C (cage) | 2.362 (4) | N–Zr–N | 107.6 (2) | |
| | Zr–N | 2.029 (4) | C (ring)–Si–C (cage) | 105.0 (2) | |
| $[Me_3NH][\{\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\mu\text{-}Cl)_{1.5}]_2$ | Zr–C (ring) | 2.539 (14) | Cent–Zr–C (cage) | 98.4 | [15] |
| | Zr–C (cage) | 2.367 (12) | C (ring)–C–C (cage) | 111.0 (14) | |
| | Zr–Cl(μ) | 2.634 (3) | | | |
| | Zr–Cl (terminal) | 2.449 (4) | | | |
| $\{Li(THF)_2\}\{[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]ZrCl(\mu\text{-}Cl)_{1.5}\}_2$ | Zr–C (ring) | 2.527 (9) | Cent–Zr–C (cage) | 99.5 | [15] |
| | Zr–C (cage) | 2.375 (9) | C (ring)–C–C (cage) | 109.6 (7) | |
| | Zr–Cl(μ) | 2.641 (3) | | | |
| | Zr–Cl (terminal) | 2.424 (3) | | | |
| $[Me_2NH_2][\{\eta^5{:}\sigma\text{-}Me_2Si(C_9H_6)(C_2B_{10}H_{10})\}ZrCl(\mu\text{-}Cl)_{1.5}]_2$ | Zr–C (ring) | 2.545 (12) | Cent–Zr–C (cage) | 105.4 | [15] |
| | Zr–C (cage) | 2.393 (10) | C (ring)–Si–C (cage) | 104.1 (4) | |
| | Zr–Cl (μ) | 2.622 (3) | | | |
| | Zr–Cl (terminal) | 2.401 (3) | | | |
| $[\eta^5{:}\sigma\text{-}{}^iPr_2NB(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ | Zr–C (ring) | 2.522 (2) | Cent–Zr–C (cage) | 103.0 | [23] |
| | Zr–C (cage) | 2.345 (2) | N–Zr–N | 106.4 (1) | |
| | Zr–N | 2.026 (2) | C (ring)-B-C (cage) | 114.0 (2) | |
| $[\eta^5{:}\sigma\text{-}{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ | Ti–C (ring) | 2.403 (3) | Cent–Ti–C (cage) | 110.0 | [30] |
| | Ti–C (cage) | 2.208 (3) | N–Ti–N | 103.9 (2) | |
| | Ti–N | 1.889 (3) | C (ring)–P–C (cage) | 97.7 (1) | |
| $[\eta^5{:}\sigma\text{-}{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ | Zr–C (ring) | 2.552 (8) | Cent–Zr–C (cage) | 106.6 | [30] |
| | Zr–C (cage) | 2.354 (8) | N–Zr–N | 110.0 (3) | |
| | Zr–N | 2.020 (7) | C (ring)–P–C (cage) | 98.7 (3) | |
| $[\eta^5{:}\sigma\text{-}{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})]Hf(NMe_2)_2$ | Hf–C (ring) | 2.551 (8) | Cent–Hf–C (cage) | 107.1 | [30] |
| | Hf–C (cage) | 2.354 (8) | N–Hf–N | 107.2 (6) | |
| | Hf–N | 2.020 (7) | C (ring)–P–C (cage) | 98.1 (6) | |