

### III.C.2 Boron–Carbon Polymers: Carboranes

An important group of heteroatom **boranes** are the *closo*-**carboranes** (or carbaboranes). *Closo*-carboranes are **oligomers** of **boron** that contain one or more carbon atoms in the polyhedral cage structure. These oligomers are generally unaffected by atmospheric oxygen and moisture. Some of the materials are thermally stable to 500 °C. A particularly important group of carboranes are the derivatives of *closo*-dodecaborane. These compounds are prepared from *nido*-decaborane and **acetylene** in the presence of ethyl **sulfide** (Fig. 27). The primary product of the reaction is *closo*-1,2- $C_2B_{10}H_{12}$  (*ortho* isomer). The *ortho* **isomer** undergoes rearrangement at 450 °C to *closo*-1,7- $C_2B_{10}H_{12}$  (*meta* isomer), and at 700 °C to *closo*-1,12- $C_2B_{10}H_{12}$  (*para* isomer). The H atoms attached to the electropositive carbons, like acetylene, are acidic. Thus the C—H bonds may be metallated with reagents like *n*-BuLi. The lithiated derivative reacts with **nucleophiles** to produce a wide variety of **organometallic** products. For example, the reaction of the *meta* isomer with a dichloro end-functional oligomeric **siloxane** will give a carborane–siloxane **copolymer** (Fig. 28). Some of these materials are co

example, the reaction of the *meta* isomer with a dichloro end-functional oligomeric siloxane will give a carborane–siloxane copolymer (Fig. 28). Some of these materials are commercially available (Dexil®) as rubbers and resins. They preserve their elasticity and mechanical properties at low temperatures, and are thermally stable to 600 °C.

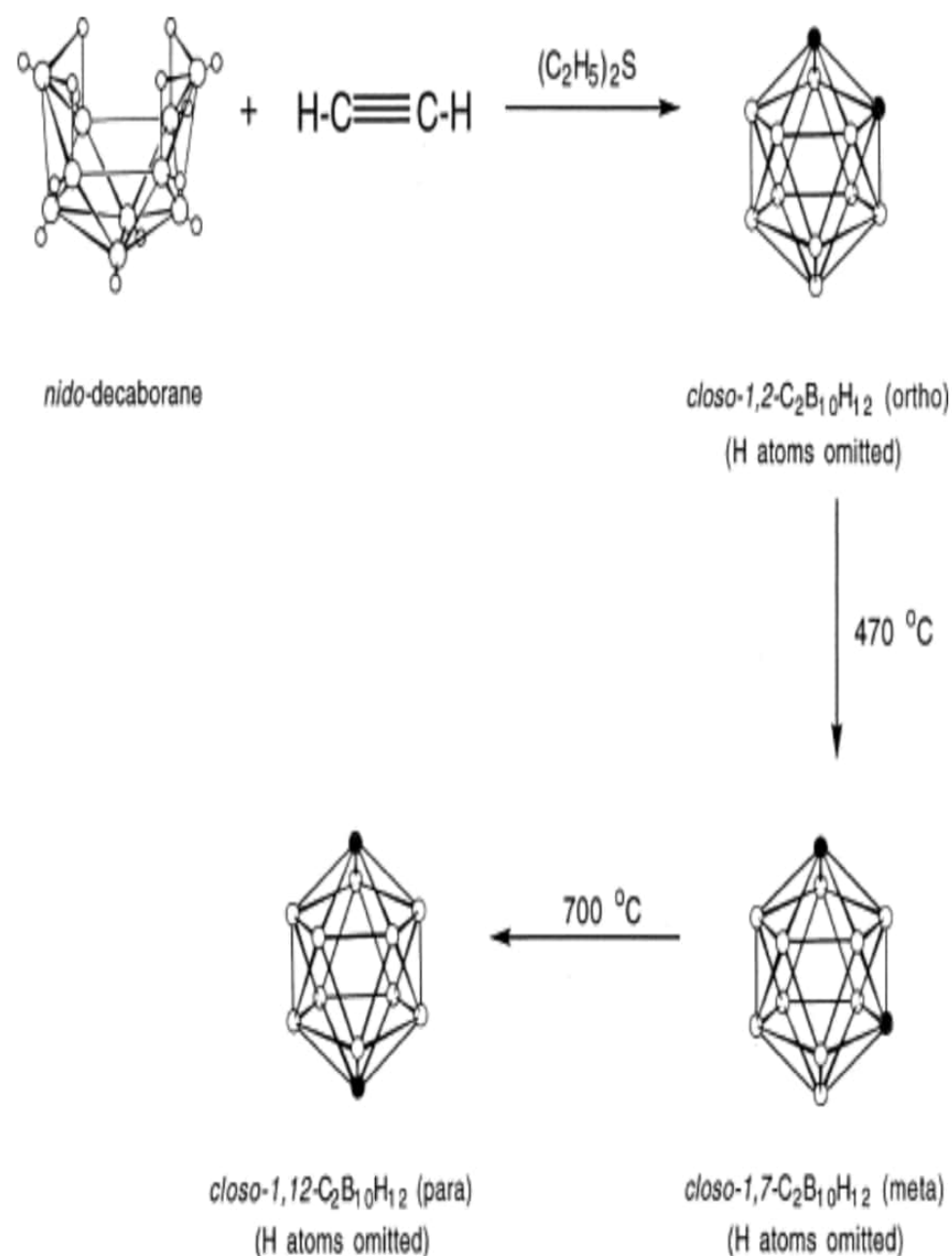
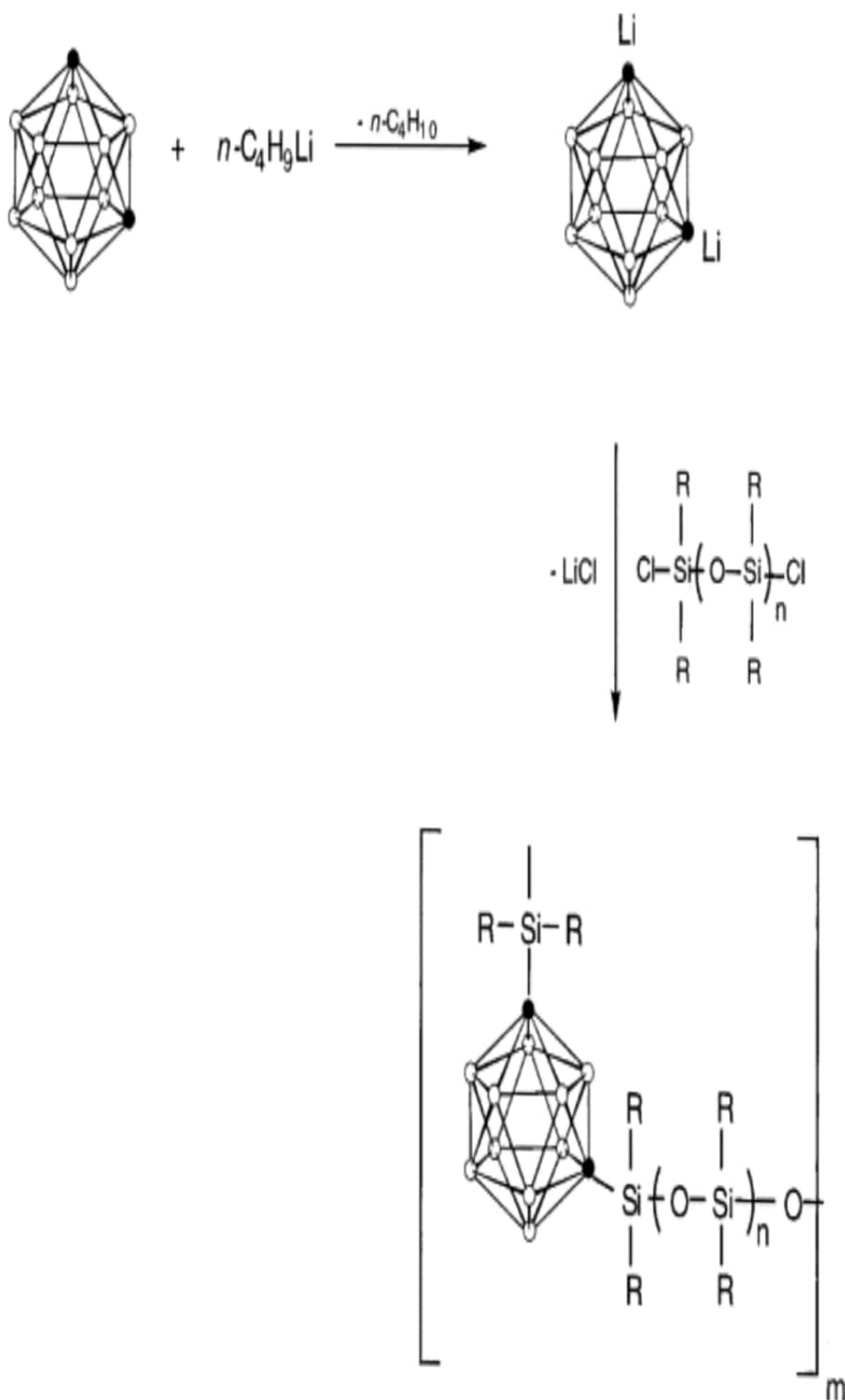


FIGURE 27. Synthesis of *closo*-dodecacarboranes.



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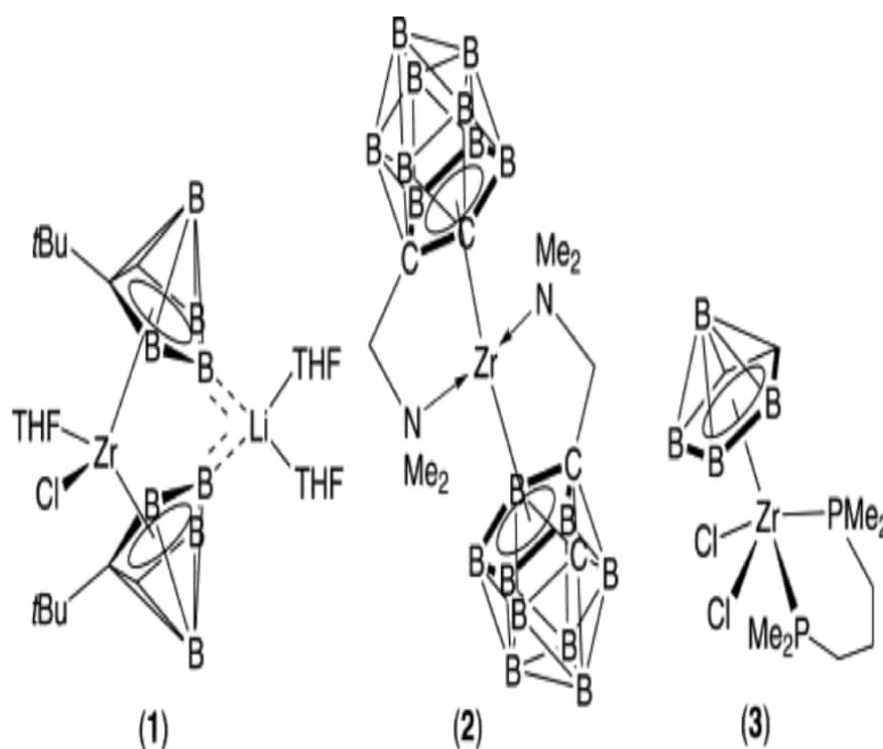
FIGURE 28. Synthesis of carborane–siloxane copolymer.

## Transition Metal Groups 3–6

E. Hollink, D.W. Stephan, in *Comprehensive Coordination Chemistry II*, 2003

### 4.3.2.1.1 Carborane ligand complexes

The zwitterionic complex  $[\text{Li}(\text{THF})_2][\text{ZrCl}\{\text{C}_2\text{B}_4\text{H}_4(\text{SiMe}_3)_2\}_2(\text{THF})]$  (**1**) was prepared and characterized crystallographically. The carborane ligands were bound in a  $\eta^5$ -fashion, thus resembling a metallocene.<sup>1</sup> A subsequent study expanded the chemistry to include related carborane derivatives, as well as Hf analogs.<sup>2</sup>



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Related Zr carborane complexes  $\text{Zr}(\text{nor})(\eta^5\text{-1,2-C}_2\text{B}_9\text{H}_{11})$  (por = TPP, octaethylp

FEEDBACK

Related Zr carborane complexes  $\text{Zr}(\text{por})(\eta^5\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11})$  (por = TPP, [octaethylporphyrin](#) (OEP)) that incorporate [porphyrin](#) ligands were readily synthesized from reaction of the  $\text{ZrCl}_2(\text{por})$  precursor with the Tl or Na salt of the dianionic carborane.<sup>3,4</sup> X-ray structural data for  $\text{Zr}(\text{OEP})(\eta^5\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11})$  confirmed the  $\eta^5$ -bonding mode of the carborane.

Using an alternative synthetic approach,  $\text{Zr}(\eta^5\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11})(\text{NEt}_2)_2(\text{NHet}_2)$  was derived from reaction of the neutral carborane ligand  $\text{C}_2\text{B}_9\text{H}_{13}$  with  $\text{Zr}(\text{NEt}_2)_4$ . The amine donor was readily exchanged with THF or 4-picoline.<sup>5</sup> Alternatively, the amido ligands were replaced by Cl atoms upon reaction with  $[\text{NH}_2\text{Et}_2]\text{Cl}$ , providing  $\text{ZrCl}_2(\eta^5\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11})(\text{NHet}_2)$ . Upon activation, the bis-amido species  $\text{Zr}(\eta^5\text{-}1,2\text{-C}_2\text{B}_9\text{H}_{11})(\text{NEt}_2)_2(\text{NHet}_2)$  exhibited good activity for the polymerization of  $\text{C}_2\text{H}_4$  and [copolymerization](#) of  $\text{C}_2\text{H}_4$ /norbornene.<sup>6,7</sup>

The complexes  $\text{M}(\eta^5\text{-}\eta^1\text{-RC}_2\text{B}_9\text{H}_9\text{-CH}_2\text{NMe}_2)_2$  (M = Zr (**2**), Hf) and *closo*-1- $\text{ZrCl}[(\text{NHCH}_2)\eta^5\text{-C}_2\text{B}_9\text{H}_{10}](\text{THF})$ <sup>8,9</sup> with chelating amino or amido groups were prepared. The former species were obtained by addition of the monoanionic ligand to  $\text{MCl}_4$ , v