

Chapter 2

Nickel-1,2-*o*-Carboryne Complexes

2.1 Introduction

1,2-*o*-Carboryne (1,2-dehydro-*o*-carborane), which was first reported as a reactive intermediate in 1990 [1], is very energetically comparable with its two-dimensional relative benzyne [2]. Reactivity studies also showed that they are quite similar in reactions with unsaturated molecules [3–9].

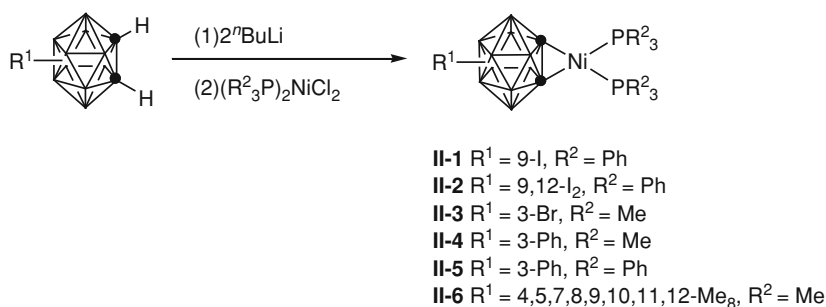
Like benzyne, carboryne can be trapped and stabilized by transition metals. The reaction of organozirconium dichloride with 1 equiv of $\text{Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ or treatment of $(\eta^2\text{-C}_2\text{B}_{10}\text{H}_{10}) \text{ZrCl}_2(\text{THF})_3$ with anionic ligands can give a class of zirconium-1,2-*o*-carboryne complexes [10]. Molecular orbital calculations suggested that the bonding interactions between Zr and 1,2-*o*-carboryne are best described as a resonance hybrid of both Zr–C σ and Zr–C π bonding forms which is similar to that observed in Zr-benzyne complex [11]. For late transition metals, salt metathesis is also a good method for the synthesis of metal-1,2-*o*-carboryne complexes by reaction of MCl_2 ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}, \text{Co}$) with $\text{Li}_2\text{C}_2\text{B}_{10}\text{H}_{10}$ [12–14]. A series of Ni-1,2-*o*-carboryne was recently prepared in our group by the reaction of phosphine ligated nickel halide. The C(cage)–C(cage) bonds in these complexes are much shorter than those in Zr-1,2-*o*-carboryne complexes [10]. The reactivity studies on $(\eta^2\text{-C}_2\text{B}_{10}\text{H}_{10})\text{Ni}(\text{PPh}_3)_2$ show that the coordinated PPh_3 molecules are labile, which can be substituted by other phosphines such as PCy_3 , $\text{P}(\text{OEt})\text{Ph}_2$, and $\text{P}(\text{OEt})_3$ to give $(\eta^2\text{-C}_2\text{B}_{10}\text{H}_{10})\text{Ni}(\text{PPh}_3)(\text{PCy}_3)$, $(\eta^2\text{-C}_2\text{B}_{10}\text{H}_{10})\text{Ni}[\text{P}(\text{OEt})\text{Ph}_2]_2$, and $(\eta^2\text{-C}_2\text{B}_{10}\text{H}_{10})\text{Ni}[\text{P}(\text{OEt})_3]_2$, respectively with quantitative conversion.

Our earlier investigation on the B-substituted carborane has revealed that the substituent on carborane plays an important role for the formation of these late transition metal complexes. The reactions of $\text{Li}_2\text{C}_2\text{B}_{10}\text{Me}_8\text{H}_2$ with $(\text{PPh}_3)_2\text{NiCl}_2$ or $(\text{dppe})\text{NiCl}_2$ gave redox reaction products $(\sigma\text{-C}_2\text{B}_{10}\text{Me}_8\text{H}_3)\text{Ni}(\text{PPh}_3)_2$ or $(\eta^2\text{-C}_2\text{B}_{10}\text{Me}_8\text{H}_2)\text{Ni}(\mu\text{-}\sigma\text{:}\sigma\text{:}\eta^2\text{-dppe})\text{Ni}(\text{dppe})$, whereas the complete redox reaction took place for the reactions with $(\text{PPh}_3)_2\text{PdCl}_2$ and $(\text{PPh}_3)_2\text{PtCl}_2$. In view of the very rich and exciting chemistry of nickel-benzyne complexes [15–19], we are interested in further exploring the nickel-1,2-*o*-carboryne complexes with

substituents on the cage boron. In this section we will describe the synthesis and structure of these B-substituted nickel-1,2-*o*-carboryne complexes.

2.2 Synthesis and Structure of B-Substituted Nickel-1,2-*o*-Carboryne Complexes

Treatment of 9-*I*-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ and 9,12-*I*₂-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ with 2 equiv of *n*-BuLi in THF at 0 °C, followed by reaction with 1 equiv of $(\text{PPh}_3)_2\text{NiCl}_2$ in THF at the temperatures -30 °C to room temperature gave $(\eta^2\text{-9-}I\text{-1,2-}\text{C}_2\text{B}_{10}\text{H}_9)\text{Ni}(\text{PPh}_3)_2$ (**II-1**) as a yellow solid or $(\eta^2\text{-9,12-}I_2\text{-1,2-}\text{C}_2\text{B}_{10}\text{H}_8)\text{Ni}(\text{PPh}_3)_2$ (**II-2**) as yellow crystals in 55 or 72% isolated yield, respectively (Scheme 2.1).



Scheme 2.1 Synthesis of B-substituted 1,2-*o*-Carboryne-Ni complexes

Under the same conditions, the product from the reaction of 3-bromo-1,2-dilithio-*o*-carborane with 1 equiv of $(\text{PPh}_3)_2\text{NiCl}_2$ was not stable and decomposed to generate 3-Br-1,2- $\text{C}_2\text{B}_{10}\text{H}_{11}$ and Ni(0) species. However, the less bulky and more electron-donating ligand of PMe_3 can stabilize this Ni-1,2-*o*-carboryne complex and $(\eta^2\text{-3-Br-1,2-}\text{C}_2\text{B}_{10}\text{H}_9)\text{Ni}(\text{PMe}_3)_2$ (**II-3**) can be synthesized as yellow crystals in 31% isolated yield from the interaction of 3-bromo-1,2-dilithio-*o*-carborane with 1 equiv of $(\text{Me}_3\text{P})_2\text{NiCl}_2$ in THF at the temperatures -30 °C to room temperature (Scheme 2.1).

Similarly, complexes $(\eta^2\text{-3-}\text{C}_6\text{H}_5\text{-1,2-}\text{C}_2\text{B}_{10}\text{H}_9)\text{Ni}(\text{PMe}_3)_2$ (**II-4**) and $(\eta^2\text{-3-}\text{C}_6\text{H}_5\text{-1,2-}\text{C}_2\text{B}_{10}\text{H}_9)\text{Ni}(\text{PPh}_3)_2$ (**II-5**) can be isolated as yellow or orange crystals in 42 or 76% isolated yields by the reaction of 3-phenyl-1,2-dilithio-*o*-carborane with 1 equiv of $(\text{Me}_3\text{P})_2\text{NiCl}_2$ or $(\text{Ph}_3\text{P})_2\text{NiCl}_2$ in THF, respectively.

In the case of 4,5,7,8,9,10,11,12-octamethyl-*o*-carborane, neither PPh_3 nor PMe_3 can efficiently stabilize the corresponding Ni-1,2-*o*-carboryne species, leading to a

mixture of products. A few brown X-ray-quality-crystals of (η^2 -4,5,7,8,9,10,11,12-Me₈-C₂B₁₀H₂)Ni(PMe₃)₂ (**II-6**) was obtained from toluene solution at room temperature during the recrystallization of the product.

Complexes **II-1–4** are sensitive to moisture and air whereas **II-5** is air- and moisture-stable, both in the solid-state and in solution. Interestingly, **II-5** is very thermally stable even in refluxing THF. However, heating the THF solution of **II-1–4** can lead to a decomposition, generating neutral carboranes and Ni(0) species. It's believed that both the interaction between phenyl ring and metal center and the sterically demanding PPh₃ ligand have contributed to the exceptional stability of this complex. Complexes **II-1–5** are slightly soluble in ether and toluene and highly soluble in THF. They were fully characterized by various spectrometric methods and elemental analyses.

The ¹H and ¹³C NMR spectra of **II-1–5**, which only display the signals of PPh₃ or PMe₃ ligand, do not give much information on the solution structures. The cage carbons were not observed for **II-1–5**. The ¹¹B{¹H} NMR spectra display a 3:6:1, 2:6:2, 1:1:2:2:2, 2:1:3:4, and 1:1:1:2:5 pattern for **II-1**, **II-2**, **II-3**, **II-4**, and **II-5** respectively. One singlet at ~22 ppm corresponding to BI vertex can be observed for **II-1** and **II-2**. The BBr signal of **II-3** is overlapped with other BH signals at -10 to -14 ppm. In the ¹¹B NMR spectra of **II-4** and **II-5**, the BPh signal can be observed as a singlet at -3 ppm. The ³¹P NMR spectra show one singlet at ~30 ppm for PPh₃ ligand in **II-1,2,5** or one singlet at ~-9 ppm for PMe₃ ligand in **II-3,4**.

The B-H...M interactions in late transition-metal complexes usually lead to a significantly reduced *J*_{BH} value, a very deshielded ¹¹B signal, and a very high-field ¹H resonance [20–24]. It is noted that there is no significant high-field ¹H signal and low-field ¹¹B signal observed in the ¹H and ¹¹B NMR spectra of **II-1–5**. The IR spectra (KBr) exhibited one very strong and broad stretching band ν_{B-H} at about 2570 cm⁻¹ for **II-1–3**, whereas that of **II-4** and **II-5** showed two ν_{B-H} bands at 2550 and 2530 cm⁻¹ (**II-4**)/2510 cm⁻¹ (**II-5**).

The solid-state structures of **II-2–6** were further confirmed by single-crystal X-ray analyses. As shown in Figs. 2.1, 2.2, 2.3, 2.4, 2.5, complexes **II-2–6** have similar coordination geometries, which contain a three-membered ring formed through two Ni-C(cage) bonds and the coordination plane about the nickel atom is essentially planar. There are two crystallographically independent molecules in the unit cell of **II-5**. Figure 2.4 shows its representative structure. Selected bond distances and angles around the metal centers are listed in Table 2.1 for comparison.

The C(cage)-C(cage) bond distances (1.55–1.57 Å) are close to each other for **II-2,3,4,6** and similar with those observed in the Ni-1,2-*o*-carboryne complexes [1.556(5) Å in (η^2 -C₂B₁₀H₁₀)Ni(PPh₃)₂, 1.576(6) Å in (η^2 -C₂B₁₀Me₈H₂)Ni(μ - σ : σ : η^2 -dppen)Ni(dppe), 1.551(4) Å in (η^2 -C₂B₁₀H₁₀)Ni(PPh₃)(PCy₃), 1.553(6) Å and 1.561(5) Å in (η^2 -C₂B₁₀H₁₀)Ni(dppe)], which is much shorter than that of 1.63 Å found in *o*-carborane. The large steric effect results in the shorter C(cage)-C(cage) bond distances of 1.523(3) Å in **II-5**. It is noteworthy that, since all B-H hydrogen atoms are in calculated positions, a detailed discussion of the B-H distances is not warranted.

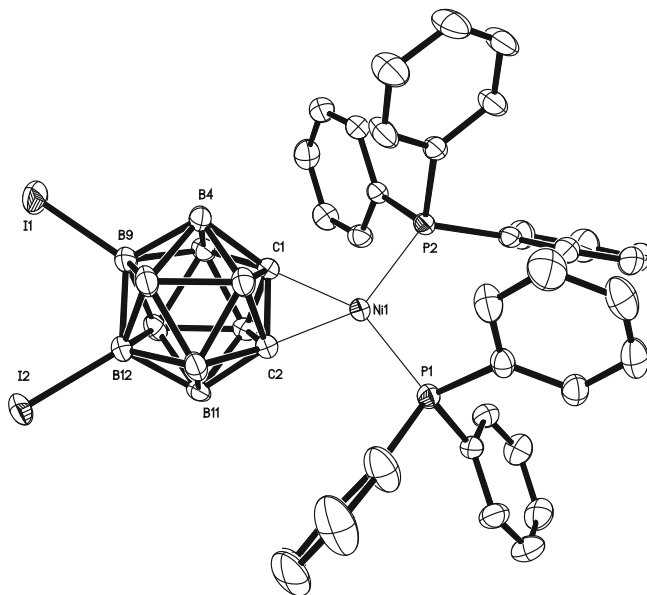


Fig. 2.1 Molecular structure of $(\eta^2\text{-}9,12\text{-I}_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_8)\text{Ni}(\text{PPh}_3)_2$ (**II-2**)

Fig. 2.2 Molecular structure of $(\eta^2\text{-}3\text{-Br-}1,2\text{-C}_2\text{B}_{10}\text{H}_9)\text{Ni}(\text{PPh}_3)_2$ (**II-3**)

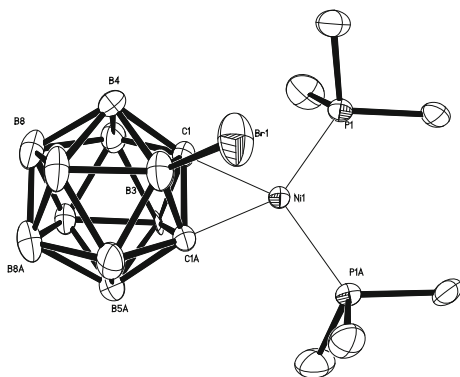


Fig. 2.3 Molecular structure of $(\eta^2\text{-}3\text{-C}_6\text{H}_5\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_9)\text{Ni}(\text{PMe}_3)_2$ (**II-4**)

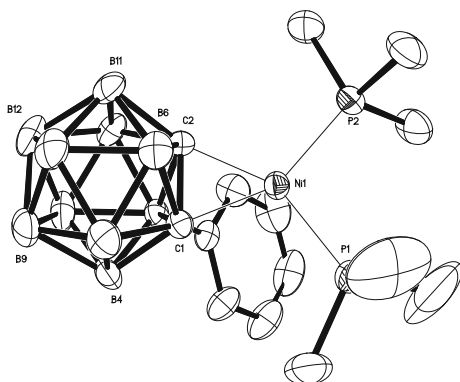


Fig. 2.4 Molecular structure of $(\eta^2\text{-}3\text{-C}_6\text{H}_5\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_9)$ $\text{Ni}(\text{PPh}_3)_2$ (**II-5**), showing one of two independent molecules in the unit cell

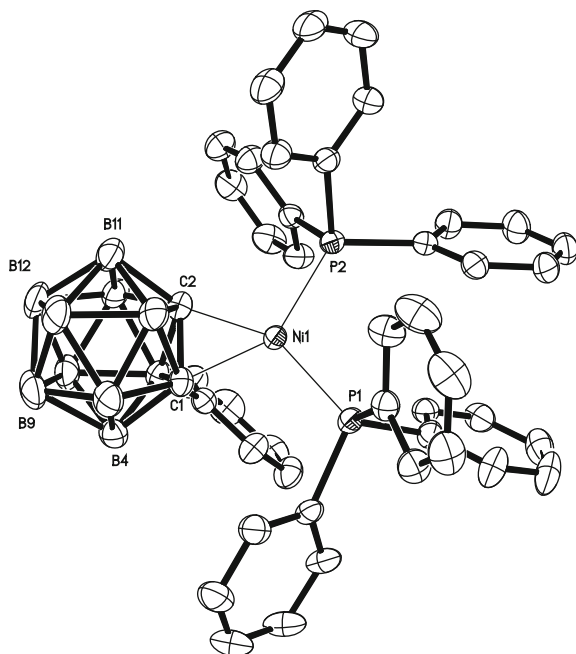


Table 2.1 Selected bond distances (Å) and angles (deg) for late transition metal-1,2-*o*-carboryne complexes

	II-2	II-3	II-4		II-5	II-6
C(1)-C(2)	1.550(6)	1.595(14)	1.565(5)	1.576(4)	1.523(3)	1.562(14)
Ni(1)-C(1)	1.926(4)	1.918(6)	1.917(3)	1.927(3)	1.950(2)	1.923(10)
Ni(1)-C(2)	1.917(4)	1.918(6)	1.929(3)	1.924(3)	1.924(2)	1.899(10)
Ni(1)···B(3)	2.647(6)					2.613(12)
Ni(1)···B(6)	2.626(6)	2.721(20)	2.631(4)	2.583(4)	2.581(3)	2.609(11)
Ni(1)-P(1)	2.190(1)	2.169(2)	2.166(1)	2.164(1)	2.215(1)	2.166(3)
Ni(1)-P(2)	2.214(1)	2.169(2)	2.169(1)	2.163(1)	2.221(1)	2.167(3)
Ni(1)-C(1)-C(2)	65.9(2)	65.4(2)	66.3(2)	65.7(2)	65.9(1)	65.1(5)
Ni(1)-C(2)-C(1)	66.5(2)	65.4(2)	65.6(2)	65.9(2)	67.7(1)	66.7(5)
C(1)-Ni(1)-C(2)	47.6(2)	49.1(4)	48.1(1)	48.3(1)	46.3(1)	48.2(4)

2.3 Summary

We have prepared several B-substituted nickel-1,2-*o*-carboryne complexes and fully characterized their structures. Our studies show that the reaction between phosphine ligated metal halide and Li₂C₂B₁₀H₁₀ is a good synthetic route for the preparation of these complexes. These late transition metal-1,2-*o*-carboryne complexes have similar structural features and the C(cage)–C(cage) bonds in these complexes are much shorter than those in Zr-1,2-*o*-carboryne complexes.

References

1. Gingrich HL, Ghosh T, Huang Q, M Jones Jr (1990) J Am Chem Soc 112:4082
2. Kiran B, Anoop A, Jemmis ED (2002) J Am Chem Soc 124:4402
3. Huang Q, Gingrich HL, Jones M Jr (1991) Inorg Chem 30:3254
4. Cunningham RT, Bian N, Jones M Jr (1994) Inorg Chem 33:4811
5. Ho DM, Cunningham RJ, Brewer JA, Bian N, Jones M Jr (1995) Inorg Chem 34:5274
6. Barnett-Thamattoor L, Zheng G, Ho DM, Jones M Jr, Jackson JE (1996) Inorg Chem 35:7311
7. Atkins JH, Ho DM, Jones M Jr (1996) Tetrahedron Lett 37:7217
8. Lee T, Jeon J, Song KH, Jung I, Baik C, Park KM, Lee SS, Kang SO, Ko J (2004) Dalton Trans, p 933
9. Jeon J, Kitamura T, Yoo B-W, Kang SO, Ko J (2001) Chem Commun, p 2110
10. Ren S, Deng L, Chan H-S, Xie Z (2009) Organometallics 28:5749
11. Wang H, Li H-W, Huang X, Lin Z, Xie Z (2003) Angew Chem Int Ed 42:4347
12. Saylor AA, Beall H, Sieckhaus JF (1973) J Am Chem Soc 95:5790
13. Zakharkin LI, Kovredov AI (1975) Izv Akad Nauk SSSR Ser Khim, p 2619
14. YuA Ol'dekop, Maier NA, Erdman AA, Prokopovich VP (1982) Zh Obshch Khim 52:2256
15. Buchwald SL, Nielsen RB (1988) Chem Rev 88:047
16. Bennett MA, Schwemlein HP (1989) Angew Chem Int Ed Engl 28:1296
17. Bennett MA, Wenger E (1997) Chem Ber 130:1029
18. Jones WM, Klosin J (1998) Adv Organomet Chem 42:147

19. Retbøll M, Edwards AJ, Rae AD, Willis AC, Bennett MA, Wenger E (2002) *J Am Chem Soc* 124:8348
20. Brew SA, Stone FGA (1993) *Adv Organomet Chem* 35:135
21. Franken A, McGrath TD, Stone FGA (2006) *J Am Chem Soc* 128:16169
22. McGrath TD, Du S, Hodson BE, Lu XL, Stone FGA (2006) *Organometallics* 25:4444
23. McGrath TD, Du S, Hodson BE, Stone FGA (2006) *Organometallics* 25:4452
24. Hodson BE, McGrath TD, Stone FGA (2005) *Organometallics* 24:3386

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