

# Synthesis and characterization of three nickel(ii) carborane complexes containing *nido*- or *closo*-carborane diphosphine ligand

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## Abstract

Three nickel(II) carborane complexes,  $[\text{Ni}_2(\mu\text{-Cl})_2\{7,8\text{-}(\text{PPh}_2)_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}_2]$  (**1**),  $[\text{Ni}\{7\text{-}(\text{OPPh}_2)\text{-}8\text{-}(\text{PPh}_2)\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}\{7,8\text{-}(\text{PPh}_2)_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}\}]$  (**2**) and  $[\text{NiBr}_2\{1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}\}] \cdot \text{CH}_2\text{Cl}_2$  (**3**), have been synthesized by the reactions of 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$  in ethanol under different conditions, respectively. For complex **1**, it could also be obtained under the solvothermal condition. All the three complexes were characterized by elemental analysis, FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and X-ray structure determination. Single crystal analysis shows that the molecular symmetry of complex **1** is centrosymmetric, containing two same structure units –  $\text{Ni}(7,8\text{-}(\text{PPh}_2)_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10})$  linked by two bridged-Cl atoms. The central square plane formed by the  $[\text{Ni}_2\text{Cl}_2]$  unit is almost parallel to the two side NiPP planes. For complex **2**, the coordination environment of the Ni atom is a seriously distorted square-planar, in which two positions come from the chelating diphosphine ligand  $[7,8\text{-}(\text{PPh}_2)_2\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$  degraded from the *closo* species, while the other two are occupied by an unsymmetrical chelating phosphine oxide ligand  $[7\text{-}(\text{OPPh}_2)\text{-}8\text{-}(\text{PPh}_2)\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{10}]^-$ . As for complex **3**, the geometry at the Ni atom is a slightly distorted square-planar. The *closo* carborane diphosphine ligand  $1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$  was coordinated bidentately to the metal ion through the two phosphorus atoms, and the two Br atoms are at *cis* position which can fulfill the four coordination mode of the metal.

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**Keywords:** Synthesis and characterization; Crystal structure; Nickel(II) carborane complexes; 1,2-Bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane(10); 7,8-Bis(diphenylphosphino)-7,8-dicarba-*nido*-undecaborane(10)

## 1. Introduction

Polyhedral heteroboranes have been the subject of intense research for over 40 years. A subset of this extensive class of compounds is dicarba-*closo*-dodecaboranes, commonly referred to as carboranes. An extensive field of carborane chemistry has developed, concerned with substitution of the C–H or B–H vertices of these clusters [1], and the products have potential applications in many diverse areas, including medicinal chemistry, esp. boron neutron capture treatment (BNCT) of tumor [2], special polymers [3], agents for the extraction of metal ions [4],

supramolecular chemistry [5] and as ligands for metals [6]. The *closo* carborane diphosphine derivative  $1,2\text{-}(\text{PPh}_2)_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}$  reported in 1963 for the first time [7] is a typical bidentate phosphine ligands. Because of its ability to form stable five-member chelating between the ligand and the metal atom, this diphosphine ligand has become the intensely studied carborane derivative in the coordination chemistry [8–13].

In the previous studies, the reactions about this ligand were always conventionally carried out under the protection of inert gases, which can make the reaction system avoid exposing to oxygen or air. However, if the reaction was purposively carried out under no protection of inert gases, and replaced it with an air atmosphere, what will the reaction result be? What influence the environment of the reaction will put on the structure of the ligand, the

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metal complex, and even the carborane skeleton? To compare the outcome obtained from different conditions and further understand the degradation of the *closo* diphosphine ligand 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, three reactions were investigated under two different environments. In addition, enlightened by the result reported by our group that the solvothermal method could be employed to synthesize metallaborane [14], we have also successfully introduced this method into the reaction of the carborane. These results will be discussed in this paper, together with description of the molecular structures of three different carborane Ni complexes obtained from the different reaction environments with the formula [Ni<sub>2</sub>(μ-Cl)<sub>2</sub>{7,8-(PPh<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}<sub>2</sub>] (1), [Ni{7-(OPPh<sub>2</sub>)-8-(PPh<sub>2</sub>)-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}]{7,8-(PPh<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}] (2) and [NiBr<sub>2</sub>{1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>}] · CH<sub>2</sub>Cl<sub>2</sub> (3).

## 2. Experimental

### 2.1. Materials and measurement

Solvents, which were employed to prepare complexes 1 and 3, were dried with appropriate drying agents and distilled under dinitrogen prior to use. 95% Ethanol and dichloromethane for preparation of complex 2 were directly used without further purification. [Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and 1,2-bis(diphenylphosphino)-1,2-dicarba-*closo*-dodecaborane were synthesized according to the literature procedures [7,15].

Infrared spectra were obtained from KBr pellets on a Nicolet-460 FT-IR spectrophotometer. Elemental analysis (C, H) was performed with a Perkin-0Elemer 2400 II elemental analyzer. The <sup>1</sup>H and <sup>13</sup>C NMR were recorded on a Varian Mercury 400 spectrometer in CDCl<sub>3</sub> solution with tetramethylsilane (TMS) as internal standard at 400.15 and 100.63 MHz, respectively. The <sup>13</sup>C spectra are broadband proton decoupled. The chemical shifts are reported in parts per million with respect to the references and are stated relative to external TMS for <sup>1</sup>H and <sup>13</sup>C NMR.

## 3. Synthetic procedure

### 3.1. Synthesis of [Ni<sub>2</sub>(μ-Cl)<sub>2</sub>{7,8-(PPh<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}<sub>2</sub>] (1)

Method A: NiCl<sub>2</sub> · 6H<sub>2</sub>O (23.8 mg, 0.10 mmol) was added to a suspension of 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (51.2 mg, 0.10 mmol) in ethanol (10 ml). The mixture was stirred for 6 h at room temperature under the protection of dry nitrogen. The red solid was filtered off, washed with ethanol and dried in vacuum (24.4 mg, 40.9%). m.p. 188–189 °C. The crystal suitable for X-ray diffraction was obtained from a dichloromethane solution after partial evaporation of the solvent. FT-IR ν<sub>KBr</sub> (cm<sup>-1</sup>): 3025m, 2560m, 1420m, 710m. <sup>1</sup>H NMR (400.15 MHz, CDCl<sub>3</sub>): δ7.24–7.48 ppm (m, 40H, Aryl-H); –2.21 ppm (br, 2H, B-H-B); <sup>13</sup>C NMR (100.63 MHz, CDCl<sub>3</sub>): 127.8–136.6 ppm

(s, 48C, Aryl-C); 77.9 ppm (m, 4C, Ccarborane). Anal. Calc. for C<sub>52</sub>H<sub>60</sub>B<sub>18</sub>Cl<sub>2</sub>Ni<sub>2</sub>P<sub>4</sub>: C, 52.40; H, 5.07; found: C, 52.31; H, 5.09%.

Method B: [Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (70.1 mg, 0.10 mmol), 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (51.2 mg, 0.10 mmol) and 10 ml of distilled ethanol were mixed in a Teflon-lined autoclave in a dry nitrogen atmosphere and then maintained at 140 °C for 120 h, followed slow cooling to room temperature. The solid was filtered off, washed with ethanol, and dried in vacuum (38.7 mg, 64.9%).

### 3.1.1. Synthesis of [Ni{7-(OPPh<sub>2</sub>)-8-(PPh<sub>2</sub>)-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}]{7,8-(PPh<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}] (2)

NiCl<sub>2</sub> · 6H<sub>2</sub>O (23.8 mg, 0.10 mmol) and 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (51.2 mg, 0.10 mmol) were mixed in 10 ml of 95% ethanol. The stirring process was continued for about 6 h at room temperature in the air, and then the yellow solid was filtered off, washed with ethanol, and dried in vacuum (27.5 mg, 51.0%). m.p. 207–208 °C. The single crystal for X-ray diffraction was grown from a dichloromethane-*n*-hexane solution. FT-IR ν<sub>KBr</sub>(cm<sup>-1</sup>): 3000m, 2545m, 1475m, 1250s, 730m. <sup>1</sup>H NMR (400.15 MHz, CDCl<sub>3</sub>): δ7.20–7.58 ppm (m, 40H, Aryl-H); –2.24 ppm (br, 2H, B-H-B); <sup>13</sup>C NMR (100.63 MHz, CDCl<sub>3</sub>): δ125.9–134.9 ppm (s, 48C, Aryl-C); 76.1 ppm (m, 4C, Ccarborane). Anal. Calc. for C<sub>52</sub>H<sub>60</sub>B<sub>18</sub>NiOP<sub>4</sub>: C, 57.92; H, 5.61; found: C, 57.85; H, 5.55%.

### 3.1.2. Synthesis of [NiBr<sub>2</sub>{1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>}] · CH<sub>2</sub>Cl<sub>2</sub> (3)

NiBr<sub>2</sub> · 6H<sub>2</sub>O (32.7 mg, 0.10 mmol) was added to the suspension of 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> (51.2 mg, 0.10 mmol) in ethanol (10 ml). The mixture was stirred 6 h under a dry nitrogen atmosphere, then the red solid was filtered, washed with ethanol, and dried in vacuum (33.3 mg, 45.5%). m.p. 216–217 °C. The crystal suitable for X-ray diffraction was obtained from a dichloromethane solution layered with *n*-hexane. FT-IR ν<sub>KBr</sub> (cm<sup>-1</sup>): 2980m, 2570m, 1455m, 725m. <sup>1</sup>H NMR (400.15 MHz, CDCl<sub>3</sub>): δ7.13–7.51 ppm (m, 20H, Aryl-H); <sup>13</sup>C NMR (100.63 MHz, CDCl<sub>3</sub>): 128.8–137.8 ppm (s, 24C, Aryl-C); 75.7 ppm (m, 2C, Ccarborane). Anal. Calc. for C<sub>27</sub>H<sub>32</sub>B<sub>10</sub>Cl<sub>2</sub>Br<sub>2</sub>NiP<sub>2</sub>: C, 39.74; H, 3.95; found: C, 39.68; H, 3.88%.

## 3.2. X-ray structure determination

The collections of crystallographic data for the complexes were carried out on a Bruker Smart-1000 CCD diffractometer, using graphite-monochromatized Mo Kα (λ = 0.71073 Å) at 298(2) K. The structures were solved by direct method and expanded using Fourier difference techniques with SHELXTL-97 program package [16]. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F<sup>2</sup>. All the H atoms were located in a difference Fourier map and thereafter refined isotropically, except the bridge H atoms of the com-

Table 1  
Details of the crystal parameters, data collection and refinement for complexes **1**, **2** and **3**

Cryst Crystal data	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>52</sub> H <sub>60</sub> B <sub>18</sub> Cl <sub>2</sub> Ni <sub>2</sub> P <sub>4</sub>	C <sub>52</sub> H <sub>60</sub> B <sub>18</sub> NiOP <sub>4</sub>	C <sub>27</sub> H <sub>32</sub> B <sub>10</sub> Br <sub>2</sub> Cl <sub>2</sub> NiP <sub>2</sub>
Formula weight	1191.78	1078.17	816.00
Temperature (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	P2(1)/n	P1
a (Å)	27.880(13)	13.652(2)	11.141(6)
b (Å)	16.766(8)	21.577(4)	12.364(7)
c (Å)	21.434(10)	21.860(4)	13.778(8)
α (°)	90	90	85.969(7)
β (°)	127.554(6)	103.134(3)	70.020(6)
γ (°)	90	90	79.975(7)
V (Å <sup>3</sup> )	7943(6)	6270.8(18)	1756.3(17)
Z	4	4	2
Absorption coefficient (mm <sup>-1</sup> )	0.649	0.446	3.091
D (Mg m <sup>-3</sup> )	0.997	1.142	1.543
F(000)	2448	2232	824
Crystal size (mm)	0.40 × 0.39 × 0.38	0.32 × 0.31 × 0.29	0.49 × 0.46 × 0.41
Θ range (°)	2.26–25.01	1.89–25.01	1.57–25.01
Limiting indices	−25 ≤ h ≤ 33, −19 ≤ k ≤ 19, −25 ≤ l ≤ 24	−14 ≤ h ≤ 16, −25 ≤ k ≤ 24, −26 ≤ l ≤ 15	−13 ≤ h ≤ 13, −8 ≤ k ≤ 14, −16 ≤ l ≤ 16
Independent reflection	6864	10696	6044
Maximum and minimum transmission	0.7905 and 0.7813	0.8815 and 0.8704	0.3638 and 0.3127
Goodness-of-fit on F <sup>2</sup>	1.015	1.007	1.011
R[I > 2σ(I)]	R <sub>1</sub> = 0.0734, wR <sub>2</sub> = 0.1864	R <sub>1</sub> = 0.0778, wR <sub>2</sub> = 0.1793	R <sub>1</sub> = 0.0699, wR <sub>2</sub> = 0.1826
R(all data)	R <sub>1</sub> = 0.1692, wR <sub>2</sub> = 0.2613	R <sub>1</sub> = 0.2010, wR <sub>2</sub> = 0.2566	R <sub>1</sub> = 0.1118, wR <sub>2</sub> = 0.2224
Largest difference in peak and hole (×10 <sup>2</sup> e Å <sup>-3</sup> )	0.958 and −0.429	1.146 and −0.676	1.538 and −1.369

plexes **1** and **2**. For these H atoms, they were refined isotropically with fixed U and for getting reasonable bond parameters for these H atoms, DFIX restraints were utilized for the correlative distances. Details of the crystal parameters, data collection and refinement are summarized in Table 1.

## 4. Results and discussion

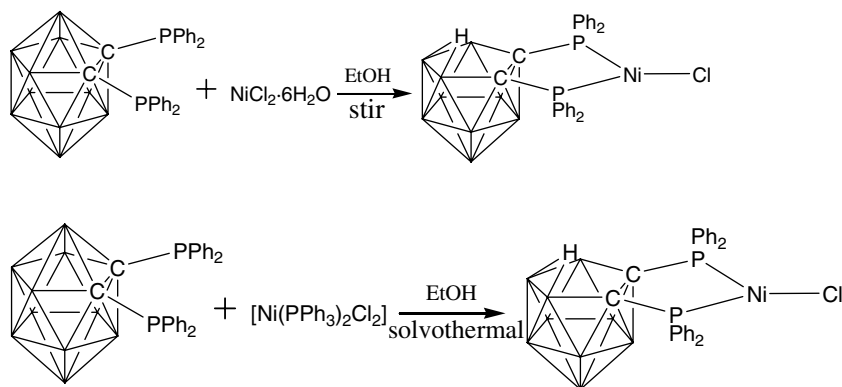
### 4.1. Synthesis and spectral characterization

The partial degradation of the *closo* diphosphine ligand 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> by metal driven has been disclosed [17–19]. Neutral complexes of the *nido*-[7,8-(PPh<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>−</sup> with the similar formula [M{7,8-(PPh<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}(PPh<sub>3</sub>)] (M = Cu, Ag, Au) have also been obtained by reactions of some d<sup>10</sup> metal complexes with the *closo* ligand in ethanol under the reflux conditions [17,20,21]. Very recently, our group have reported that group 10 metal complexes [M(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (M = Ni, Pd, Pt) could also make the carborane skeleton convert from *closo* to *nido* with the C–P bond retention in ethanol under the reflux condition [22]. With comparison to the *closo* ligand, the degradation species [7,8-(PPh<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>−</sup> has two particular features in forming stable metal complexes. The first one, it is an electronegative anion, and this can enhance its ligating ability to the metal ion. The second, it can make the B(3)–H coordination to the metal possible

when the ligand was coordinated to the metal atom through forming a stable five-membered chelating ring.

Treatment NiCl<sub>2</sub> · 6H<sub>2</sub>O and 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> with a molar ratio 1:1 in ethanol under the stirring condition with the protection of dry N<sub>2</sub> at room temperature, a Ni(II) complex containing the *nido* carborane diphosphine anion, with the formula [Ni<sub>2</sub>(μ-Cl)<sub>2</sub>{7,8-(PPh<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}]<sub>2</sub> was obtained. This is the first time that inorganic M(II) metal compound rather than its metal complexes was directly used to degrade the *closo* 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>. The result obtained from the reaction of anhydrous NiCl<sub>2</sub> with the *closo* diphosphine is same to the above reaction, indicating that the existing H<sub>2</sub>O has no influence on the reaction itself. As our group previously reported that solvothermal method can be employed to synthesize metallaborane [14]. Here we tentatively introduced this method into the reaction of carborane. By the reaction of [Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] with 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> in ethanol under the solvothermal condition, complex **1** could also be obtained with 64.9% yield, which is higher than that obtained by using the method A. This result showed that solvothermal method could also be used to degrade the *closo*carborane diphosphine ligand with the C–P bond retention. The reactions are shown in Scheme 1.

In order to study the environmental influence on the reaction, we carried out the reaction of NiCl<sub>2</sub> · 6H<sub>2</sub>O with the *closo* ligand in air. The experimental result showed that, except the degradation process of the *closo* carborane



Scheme 1. Preparation of complex **1** by treatment of the *closo* ligand with  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  or  $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$  in ethanol under different conditions.

skeleton has taken place; one phosphorus atom of the  $\text{PPh}_2$  groups was oxidized. Thereof an unsymmetrical ligand  $[\text{7}-(\text{OPPh}_2)\text{-8}-(\text{PPh}_2)\text{-7,8-}\text{C}_2\text{B}_9\text{H}_{10}]^-$  was formed. A new Ni(II) carborane complex  $[\text{Ni}\{\text{7}-(\text{OPPh}_2)\text{-8}-(\text{PPh}_2)\text{-7,8-}\text{C}_2\text{B}_9\text{H}_{10}\}\{\text{7,8-}(\text{PPh}_2)_2\text{-7,8-}\text{C}_2\text{B}_9\text{H}_{10}\}]$ , containing two different types of ligands, which structure is completely dissimilar from the complex **1**, was obtained. The result obtained from this experiment clearly showed that the environment of the reaction, especially the oxygen of the air, could play an important role in the reaction process.

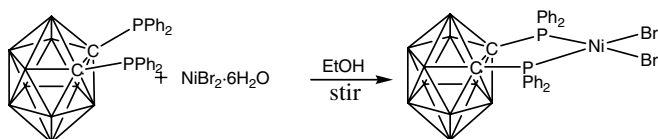
With similar compound  $\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$  to replace  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  to react with the *closo* ligand 1,2-( $\text{PPh}_2$ )<sub>2</sub>-1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$  under the same condition used for preparation complex **1** (Method A), we obtained a complex with the formula  $[\text{NiBr}_2\{1,2-(\text{PPh}_2)_2\text{-1,2-}\text{C}_2\text{B}_{10}\text{H}_{10}\}] \cdot \text{CH}_2\text{Cl}_2$  (**3**). The reaction is given in Scheme 2. This complex was composed of the unit cell  $[\text{NiBr}_2\{1,2-(\text{PPh}_2)_2\text{-1,2-}\text{C}_2\text{B}_{10}\text{H}_{10}\}]$  and one  $\text{CH}_2\text{Cl}_2$  solvent molecular. The structure of this complex is also dissimilar from the complex **1**. The first difference, also a substantial one, is the carborane skeleton of these two complexes. In complex **3** the carborane skeleton was retained its initial *closo* structure, while in complex **1** the carborane skeleton was degraded from *closo* to *nido*. The second one is the haloid atoms bonded to the Ni atom. In complex **3** the two bromine atoms were all retained. However in complex **1**, only one chlorine atom was preserved, and the other was substituted by a *nido* diposphine ligand  $[\text{7,8-}(\text{PPh}_2)_2\text{-7,8-}\text{C}_2\text{B}_9\text{H}_{10}]^-$ . The differences above indicated that the metal compound itself could also play a crucial role during the degradation process of the *closo* carborane skeleton.

All the complexes were characterized by FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Many similarities can be found by comparing the IR spectra of these complexes. The  $\nu_{\text{C-H}}$

stretching vibration of benzene rings is within a range 2980–3025  $\text{cm}^{-1}$ . The  $\nu(\text{B-H})$  resonances at about 2550  $\text{cm}^{-1}$  can dropped in the normal range of B–H vibration from 2625 to 2450  $\text{cm}^{-1}$  [23]. The peak at ca. 1420–1475  $\text{cm}^{-1}$  is the inplane deformation mode of the benzene ring. A strong absorption at about 1250  $\text{cm}^{-1}$  for complex **2** may be attributed to the P=O bond. The  $^1\text{H}$  NMR (400.15 MHz) showed a resonance at ca. –2.1 to –2.3 ppm which could be assigned to the bridge H atoms of B–H–B in complexes **1** and **2** [17]. The resonance at ca. 77 ppm in the  $^{13}\text{C}$  NMR spectra (100.63 MHz) for these three complexes should be assigned to the carbon atom of carborane cage [24].

#### 4.2. Crystal structure study

Crystal structures of the three complexes are shown in Figs. 1–3, respectively. Selected bond lengths and angles are given in Table 2. Complex **1** crystallizes in the monoclinic space group  $C2/c$ , containing four formula units in the unit cell. As demonstrated from Fig. 1, the molecular symmetry of complex **1** is centrosymmetric and the symmetry transformations used to generate equivalent atoms are  $-x + 3, -y + 3/2, -z + 1$ . Two same units  $[\text{Ni}\{7,8-(\text{PPh}_2)_2\text{-7,8-}\text{C}_2\text{B}_9\text{H}_{10}\}]$  are bridged by two Cl atoms. The distance between the two Ni atoms is 3.266 Å, which is obviously shorter than 3.397 Å in  $[\{\text{NiCl}(\text{t-Bu}_2\text{PCH}_2\text{CH}_2\text{t-Bu}_2\text{P})_2\}_2]$  [25]. This may be resulted from the steric influence of the larger t-Bu than that of Ph. The dihedral angle between the central plane formed by Ni(1), Cl(1), Ni(1)#1 and Cl(1)#1 (Ni(1)#1 and Cl(1)#1, the equivalent atoms generated by symmetry) and the P(1)Ni(1)P(2) plane is only 3.8°, indicating that these two planes are almost parallel to each other. The coordination sphere of the Ni atom can be described as a square-planar formed by two Cl atoms and two P atoms. The bond length of Ni(1)–Cl(1) is 2.226(2) Å, which is in agreement well with the average distance 2.200 Å in dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II) [26]. The average distance of P–Ni (2.168 Å) and the P–Ni–P angle (86.88(7)°) are also consistent with the corresponding values 2.154(4) Å and 87.3(2)° in the above complex. Within the



Scheme 2. Preparation of complex **3** by treatment of the *closo* ligand with  $\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$ .

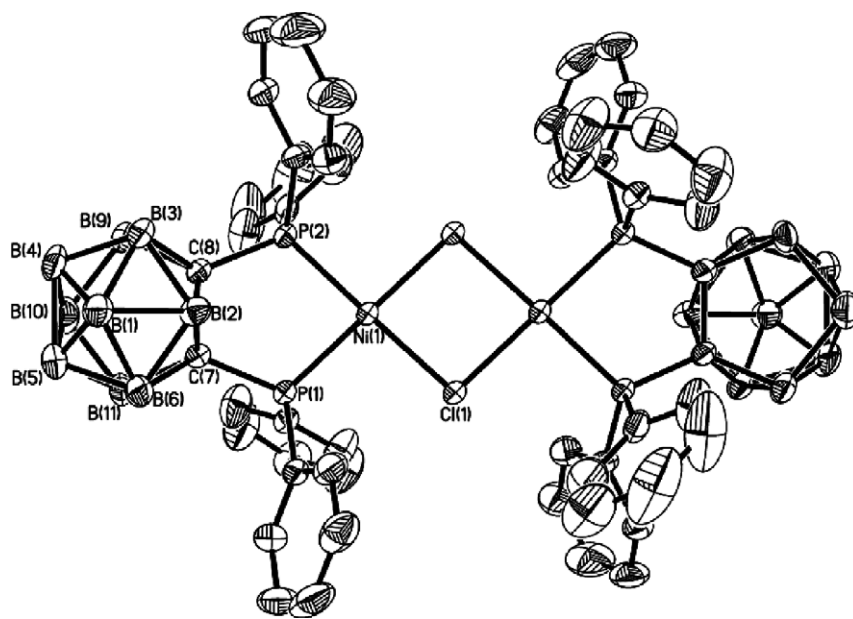


Fig. 1. The crystal structure of complex 1. The H atoms have been omitted for clarity.

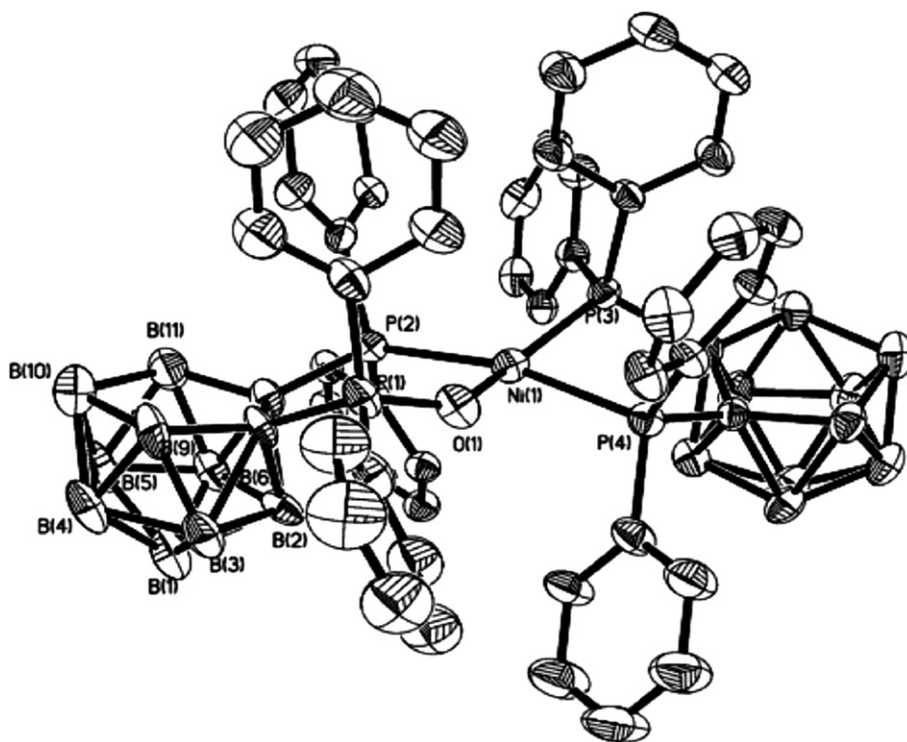


Fig. 2. The crystal structure of complex 2. The H atoms have been omitted for clarity.

Ni(1)P(1)C(7)C(8)P(2) five-membered chelating ring, due to the Ni atom out of the plane formed by the other four atoms  $0.55 \text{ \AA}$ , there form an envelope conformation between these five atoms. The distances of P–C<sub>c</sub> and C<sub>c</sub>–C<sub>c</sub> (the carbon of the carborane skeleton) listed in the Table 2 are slightly shorter than those in the free *clos*o ligand 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> [27].

In the case of the complex 2, it also contains four formula units in the unit cell, and crystallizes in the mono-

clinic space group  $P2(1)/n$ . The central nickel atom is tetracoordinated by three donor phosphorus atoms and one oxygen atom, which come from two different chelating ligands. An inspection of bond distances and angles involving the metal center shows that the coordination polyhedron has a clearly distorted square-planar geometry. The distortion from square planarity that will be described below is probably caused by the geometric requirement of the oxidation of the ligand as well as the steric repulsions

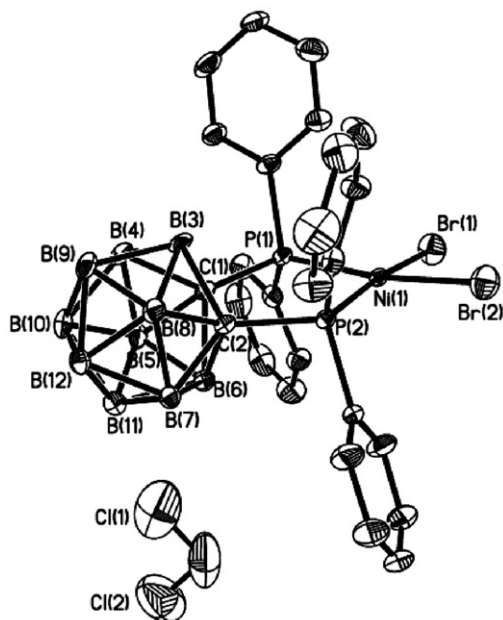


Fig. 3. The crystal structure of complex 3. The H atoms have been omitted for clarity.

of its terminal phenyl groups. The deviation of Ni(1) and O(1) from the plane P(2)P(3)P(4) are 0.2221 and 0.9267 Å, respectively, and there has obvious difference between the two opposite vertical angles, 83.64(7)° for P(4)–Ni(1)–P(3) and 93.33(15)° for O(1)–Ni(1)–P(2), respectively. The average P–Ni bond length is 2.2654 Å, which is obviously longer than the average value 2.168 Å in the complex 1. The Ni–O bond (1.853(5) Å) is slightly shorter than the corresponding distance 1.937(11) Å in the complex [NiOS(O)(CH<sub>3</sub>)(etp)][BPh<sub>4</sub>] (etp = PhP(CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>) [28]. The distance of P=O is also slightly shorter than that in H[7,8-(OPPh<sub>2</sub>)<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] with the value 1.483(5) cf. 1.528 Å [29]. The distance of P(1)–C(7)

(1.769(7) Å) is obviously shorter than P(2)–C(8) (1.867(7) Å), indicating that the oxidation of the P atom has influence on the P–Cc bond length. The dihedral angle between the planes Ni(1)O(1)P(1) and P(1)P(2)Ni(1) is 25.3°, showing that the envelope conformation presented in the complex 1 has been distorted in complex 2.

Complex 3 crystallizes in the triclinic space group  $P\bar{1}$  with two formula units in the unit cell. Fig. 3 depicts a perspective of structure unit of complex 3 showing the atom numbering. The environment of the Ni atom is four coordinates, in which two positions are occupied by the chelating *closo* diphosphine ligand 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>, and the other two come from the two bromine atoms at *cis* position. The mean deviation 0.0439 Å from the plane Br(1)Br(2)Ni(1)P(1)P(2) and the dihedral angle 11° between the two planes P(1)Ni(1)P(2) and Br(1)Ni(1)Br(2) show that the coordination sphere of the Ni atom is a slightly distorted square-planar, similar to that in the complex 1. The average distances of the Ni–Br (2.312 Å) and P–Ni (2.157 Å) are very close to the corresponding distances 2.328(2) and 2.148(5) Å in the complex dibromo[1,2-bis(diphenylphosphino)ethane]nickel(II) [30]. The angles of Br(1)–Ni(1)–Br(2) (94.10(6)°) and P(1)–Ni(1)–P(2) (93.62(8)°) are also comparable to the homologous values in the same complex, while they are all obviously bigger than the corresponding angles Cl(1)–Ni(1)–Cl(1)# (85.74(7)°) and P(1)–Ni(1)–P(2) (86.88(7)°) in the complex 1. This is maybe aroused by the larger volume of the Br atom than that of the Cl atom. The Ni–P bond lengths in complex 3 given in Table 2 are in agreement well with those in complex 1. As for other parameters in complex 3, such as the angles of P–Cc–Cc, and the distances of P–Cc, Cc–Cc, no noticeable differences have been found with comparison to those in the free ligand 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> [21], except for the P(1)–C(1)–C(2)–P(2) torsion angle. The P(1)–C(1)–C(2)–P(2) torsion angle is only 0.3(6)° in complex 3, while this angle in the free ligand is 10.6(3)°, indicat-

Table 2  
Selected bond lengths (Å) and angles (°) for complexes 1, 2 and 3

1		2		3	
Ni(1)–P(1)	2.172(2)	Ni(1)–O(1)	1.853(5)	Ni(1)–P(1)	2.152(2)
Ni(1)–P(2)	2.164(2)	Ni(1)–P(2)	2.2887(18)	Ni(1)–P(2)	2.162(2)
Ni(1)–Cl(1)	2.226(2)	Ni(1)–P(3)	2.268(2)	Ni(1)–Br(1)	2.3144(17)
Ni(1)–Cl(1)#1	2.230(2)	Ni(1)–P(4)	2.2396(19)	Ni(1)–Br(2)	2.3098(17)
Cl(1)–Ni(1)#1	2.230(2)	P(1)–O(1)	1.483(5)	P(1)–C(1)	1.879(8)
P(1)–C(7)	1.807(6)	P(1)–C(7)	1.769(7)	P(2)–C(2)	1.884(7)
P(2)–C(8)	1.800(6)	P(2)–C(8)	1.867(7)	C(1)–C(2)	1.682(10)
C(7)–C(8)	1.586(9)	P(3)–C(8')	1.814(6)	P(2)–Ni(1)–P(1)	93.62(8)
P(2)–Ni(1)–P(1)	86.88(7)	P(4)–C(7')	1.807(7)	P(2)–Ni(1)–Br(2)	86.05(7)
P(2)–Ni(1)–Cl(1)	178.38(8)	C(7)–C(8)	1.578(9)	P(1)–Ni(1)–Br(2)	170.81(7)
P(1)–Ni(1)–Cl(1)	94.29(7)	C(7')–C(8')	1.575(8)	P(2)–Ni(1)–Br(1)	173.22(7)
P(2)–Ni(1)–Cl(1)#1	93.02(7)	O(1)–Ni(1)–P(4)	83.77(16)	P(1)–Ni(1)–Br(1)	87.31(7)
P(1)–Ni(1)–Cl(1)#1	176.31(9)	O(1)–Ni(1)–P(3)	157.87(15)	Br(2)–Ni(1)–Br(1)	94.10(6)
Cl(1)–Ni(1)–Cl(1)#1	85.74(7)	P(4)–Ni(1)–P(3)	83.64(7)	C(1)–P(1)–Ni(1)	109.8(2)
Ni(1)–Cl(1)–Ni(1)#1	94.26(7)	O(1)–Ni(1)–P(2)	93.33(15)	C(2)–P(2)–Ni(1)	110.3(2)
C(7)–P(1)–Ni(1)	111.2(2)	P(4)–Ni(1)–P(2)	166.29(8)	C(2)–C(1)–P(1)	113.3(5)
C(8)–P(2)–Ni(1)	111.2(2)	P(3)–Ni(1)–P(2)	102.99(7)	C(1)–C(2)–P(2)	112.5(5)

The symmetry transformations used to generate equivalent atoms for complex 1:  $-x + 3/2, -y + 3/2, -z + 1$ .

ing that the symmetry of the ligand in complex **3** has obviously changed and approached  $C_{2v}$  very much.

## 5. Conclusion

In this work, for the first time, we studied the reactions of the *closo* carborane diphosphine 1,2-(PPh<sub>2</sub>)<sub>2</sub>-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> with some Ni(II) hydrates under the different conditions and obtained three Ni carborane complexes with different structures. With no protection of inert gases, the phosphorus atom of the carborane diphosphine ligand could be oxidized by the oxygen of the air, and the obtaining of the complex **2** implied that the two P atoms could not be oxidized at the same time. On the other hand, the structural differences of complexes **1** and **3** indicated that the metal compounds themselves have also affected the degradation process of the *closo* carborane diphosphine.

## 6. Supplementary material

CCDC 604942, 604941 and 609306 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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