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Synthesis and the structure of the triphenylphosphine complex of *o*-nickelacarborane, 3,3-$(PPh_3)_2$-3,1,2-$NiC_2B_9H_{11}$

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The reaction of bis(*o*-dicarbollyl)nickel(IV) with PPh_3 in EtOH gave rise to the complex 3,3-$(PPh_3)_2$-3,1,2-$NiC_2B_9H_{11}$ (**2**) whose structure was established by X-ray diffraction analysis.

Key words: metallocarboranes, X-ray diffraction analysis.

Previously,[1—4] it has been found that nickelacarborane complexes with coordinated nitrogen-containing ligands of the general formula $L_2NiC_2B_9H_{11}$, where L_2 is 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen), can be prepared in preparative yields by the reactions of salts of bis(*o*-dicarbollyl)nickel(III) or neutral bis(*o*-dicarbollyl)nickel(IV) (**1**) with the corresponding ligands in ethanol. The structures of the resulting complexes were established by X-ray diffraction analysis.[3]

In the present study, we synthesized the bis-triphenylphosphine complex of *o*-nickelacarborane, 3,3-$(PPh_3)_2$-3,1,2-$NiC_2B_9H_{11}$ (**2**), by the reaction of triphenylphosphine with complex **1** in ethanol. The highest yield of complex **2** (41%) was obtained using the reagent ratio PPh_3 : **1** = 3 : 1. An increase in the reagent ratio to 4 : 1 did not lead to an increase in the yield, whereas the reaction with the use of the stoichiometric ratio (2 : 1) afforded complex **2** in lower yield (28—29%). The reaction proceeded slowly even at room temperature. At the temperature of the boiling solvent, the reaction was completed in 2 h.

Complex **2** was obtained as an olive-green crystalline compound, which did not melt up to 250 °C. According to the X-ray diffraction data (Fig. 1, Tables 1 and 2), the Ni^{II} atom in complex **2** is coordinated by two phosphorus atoms of the triphenylphosphine ligands (Ni—P, 2.238(2) and 2.216(2) Å) and by the open face of the carbollyl fragment (Ni(1)—C(1), 2.096(7) Å; Ni(1)—C(2), 2.141(5) Å; C(1)—C(2), 1.620(8) Å; Ni(1)—B(1), 2.095(7) Å; Ni(1)—B(2), 2.176(7) Å; Ni(1)—B(3), 2.159(6) Å). All distances in the carbollyl dianion have values typical of compounds of this type (Table 2).

It should be noted that refluxing of structurally characterized complex **2** in benzene or ethanol did not afford red products, unlike the complex to which structure **2** has been assigned previously[5,6] and which has been prepared by the reaction of (triphenylphosphine)nickel chloride with thallium dicarbollide.[5,6]

Experimental

The IR spectra were recorded on a Nicolet Protegee-460 IR Fourier spectrophotometer (USA) in KBr pellets. The mass

Table 1. Crystallographic parameters of complex **2**

Parameter	Characteristic
Molecular formula	$C_{38}H_{41}B_9NiP_2$
Molecular weight	715.65
Space group	$P\bar{1}$
a/Å	10.836(2)
b/Å	11.571(2)
c/Å	16.620(3)
α/deg	84.652(4)
β/deg	76.016(4)
γ/deg	64.211(5)
V/Å^3	1820.6(5)
Z	2
ρ_{calc}/g cm^{-3}	1.305
μ/cm^{-1}	6.490
$\theta/2\theta$ Scan range	1.26—30.11
Number of measured reflections	12696
Number of reflections with $I > 2\sigma$	9544
Number of parameters in the refinement	615
R_1 ($I > 2\sigma(I)$)	0.0709
wR_2	0.1321

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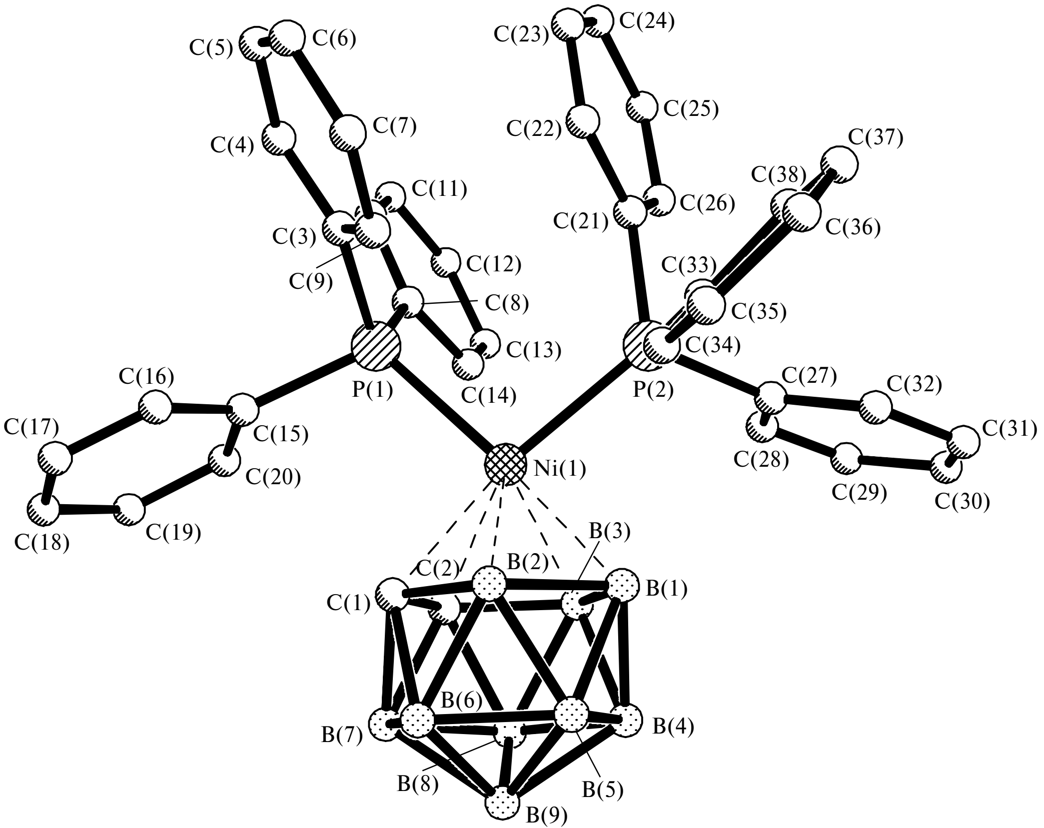

Fig. 1. Structure of complex **2**.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in complex **2**

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Ni(1)—C(1)	2.096(7)	C(1)—Ni(1)—B(1)	79.9(3)	C(1)—B(7)—B(8)	104.7(5)	B(5)—B(1)—Ni(1)	120.1(4)
Ni(1)—C(2)	2.141(5)	B(1)—Ni(1)—C(2)	80.7(2)	C(1)—B(7)—B(9)	103.8(5)	B(3)—B(1)—Ni(1)	66.3(3)
Ni(1)—B(2)	2.176(7)	B(1)—Ni(1)—B(3)	51.1(2)	C(2)—B(8)—B(9)	104.4(4)	C(1)—B(2)—B(6)	60.5(4)
Ni(1)—P(1)	2.238(2)	C(1)—Ni(1)—B(2)	45.3(3)	C(2)—B(8)—B(7)	58.7(4)	C(1)—B(2)—B(1)	102.5(5)
P(1)—C(15)	1.833(6)	C(2)—Ni(1)—B(2)	79.4(2)	C(2)—C(1)—B(6)	110.7(5)	B(5)—B(2)—Ni(1)	117.6(4)
P(2)—C(33)	1.809(6)	C(1)—Ni(1)—P(2)	161.9(2)	C(2)—C(1)—B(7)	61.5(4)	B(1)—B(2)—Ni(1)	62.8(3)
P(2)—C(21)	1.851(6)	C(2)—Ni(1)—P(2)	143.4(2)	B(6)—C(1)—B(7)	61.1(4)	C(2)—B(3)—B(8)	60.6(4)
B(1)—B(3)	1.836(9)	B(2)—Ni(1)—P(2)	116.6(2)	B(2)—C(1)—Ni(1)	69.9(3)	C(2)—B(3)—Ni(1)	67.1(3)
B(3)—C(2)	1.632(8)	B(1)—Ni(1)—P(1)	174.5(2)	B(7)—C(1)—Ni(1)	127.2(4)	B(8)—B(3)—Ni(1)	122.5(4)
B(7)—C(1)	1.725(9)	B(3)—Ni(1)—P(1)	131.3(2)	B(3)—C(2)—B(8)	64.2(4)	C(1)—B(6)—B(2)	56.1(4)
C(1)—C(2)	1.620(8)	P(2)—Ni(1)—P(1)	97.64(6)	B(3)—C(2)—B(7)	115.6(5)	B(2)—B(6)—B(5)	59.4(4)
Ni(1)—B(1)	2.095(7)	C(15)—P(1)—Ni(1)	113.4(2)	B(8)—C(2)—B(7)	61.6(4)	C(1)—B(6)—B(9)	104.4(5)
Ni(1)—B(3)	2.159(6)	C(33)—P(2)—Ni(1)	114.5(2)	C(1)—C(2)—Ni(1)	66.1(3)	C(2)—B(7)—B(6)	105.1(5)
Ni(1)—P(2)	2.216(2)	C(21)—P(2)—Ni(1)	119.7(2)	B(7)—C(2)—Ni(1)	125.2(4)	C(2)—B(7)—B(8)	59.7(4)
P(1)—C(3)	1.810(5)	B(4)—B(1)—Ni(1)	119.1(4)	C(1)—Ni(1)—C(2)	44.9(2)	C(2)—B(7)—B(9)	104.0(5)
P(1)—C(9)	1.824(6)	B(2)—B(1)—Ni(1)	67.5(3)	C(1)—Ni(1)—B(3)	78.3(2)	C(2)—B(8)—B(4)	100.7(4)
P(2)—C(27)	1.840(6)	C(1)—B(2)—B(5)	105.0(5)	C(2)—Ni(1)—B(3)	44.6(2)	C(2)—B(8)—B(3)	55.2(3)
B(1)—B(2)	1.798(9)	B(5)—B(2)—B(6)	59.8(4)	B(1)—Ni(1)—B(2)	49.8(2)	C(2)—C(1)—B(2)	115.1(5)
B(2)—C(1)	1.648(10)	C(1)—B(2)—Ni(1)	64.8(3)	B(3)—Ni(1)—B(2)	84.5(2)	B(2)—C(1)—B(6)	63.4(4)
B(7)—C(2)	1.713(9)	B(6)—B(2)—Ni(1)	120.3(4)	B(1)—Ni(1)—P(2)	86.1(2)	B(2)—C(1)—B(7)	115.8(5)
B(8)—C(2)	1.732(8)	C(2)—B(3)—B(4)	106.5(5)	B(3)—Ni(1)—P(2)	101.7(2)	C(2)—C(1)—Ni(1)	69.0(3)
		C(2)—B(3)—B(1)	104.3(4)	C(1)—Ni(1)—P(1)	95.7(2)	B(6)—C(1)—Ni(1)	127.5(5)
		B(4)—B(3)—Ni(1)	117.9(4)	C(2)—Ni(1)—P(1)	98.4(2)	B(3)—C(2)—C(1)	111.4(5)
		B(1)—B(3)—Ni(1)	62.6(3)	B(2)—Ni(1)—P(1)	124.8(2)	C(1)—C(2)—B(8)	110.9(4)
		C(1)—B(6)—B(5)	101.4(5)	C(3)—P(1)—Ni(1)	115.9(2)	C(1)—C(2)—B(7)	62.3(4)
		C(1)—B(6)—B(7)	59.4(4)	C(9)—P(1)—Ni(1)	111.2(2)	B(3)—C(2)—Ni(1)	68.3(3)
		C(2)—B(7)—C(1)	56.2(3)	C(27)—P(2)—Ni(1)	114.9(2)	B(8)—C(2)—Ni(1)	126.7(4)
		C(1)—B(7)—B(6)	59.5(4)	B(2)—B(1)—B(3)	106.6(5)		

spectra were obtained on a Varian MAT-311 spectrometer. The UV spectra were measured on a Specord UV VIS spectophotometer; the samples were prepared as 0.0001 *M* solutions in ethanol. Bis(*o*-dicarbollyl)nickel(IV) (**1**) was prepared according to a procedure described previously.[7] The reactions were carried out under an argon atmosphere.

Synthesis of 3,3′-bis(triphenylphosphino)-1,2-dicarba-3-nickela-*closo*-dodecaborane(II) (2). ***A.*** A solution of triphenylphosphine (0.78 g, 3 mmol) in a mixture of anhydrous ethanol (20 mL) and dichloromethane (5 mL) was added to a solution of bis(*o*-dicarbollyl)nickel(IV) (0.32 g, 1 mmol) in anhydrous ethanol (30 mL). The reaction mixture was refluxed for 2 h and then slowly cooled on an oil bath to 20 °C. The olive-green crystals that precipitated were separated from the solution by decantation, washed with ethanol and hexane, and dried *in vacuo* (0.1 Torr, 22 °C). Complex **2** was obtained in a yield of 0.30 g (41.9%). Found (%): C, 63.00; H, 6.19; Ni, 7.94. $C_{38}H_{41}B_9NiP_2$. Calculated (%): C, 63.77; H, 5.77; Ni, 8.20. IR, ν/cm^{-1}: 3060 s, 2560 s, 1590 w, 1575 w, 1313 w, 1190 m, 1165 m, 1128 m, 1091 m, 1030 w, 1000 w, 982 w, 750 m, 725 m, 700 s, 545 s, 525 m, 515 m. MS, *m/z*, ion: 395, $C_{20}H_{25}B_9P^+$; 262, PPh_3^+; 192, $C_2H_{11}B_9Ni^+$; 134, $C_2B_9H_{11}^+$; 77, $C_6H_5^+$; 58, Ni^+. UV, nm: 212, 226, 263.

B. In another experiment, the above-described reaction mixture was kept at ~20 °C for 24 h. The yield of **2** was 0.29 g (40.5%).

X-ray diffraction analysis of complex 2. X-ray diffraction analysis was performed in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences) on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λMo radiation, graphite monochromator, 110 K, ω scanning technique, the scan step was 0.3°, frames were exposed for 30 s, $2\theta_{max} = 60°$) according to a standard procedure.[8] The semiempirical correction for absorption was applied.[9] The structure was solved by the direct methods using the SHELXS 97 program package[10] and refined by the full-matrix least-squares method with anisotropic thermal parameters (the positions of the H atoms were fixed with $U_H = 0.08$ Å^2) using the SHELXL 97 program package.[11]

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