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# COMMUNICATION

# A structurally characterized *ortho*-cycloboronated *closo* twelve-vertex 1,2-dinickeladodecaborane

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**Abstract**—A novel *closo* twelve-vertex dinickelaborane [($\mu$-1,2-Cl)-3-Cl-6-($PPh_3$)-($\mu$-1,4-$Ph_2PC_6H_4$)-($\mu$-2,8-$Ph_2PC_6H_4$)-*closo*-1,2-$Ni_2B_{10}H_6$]·0.25($CH_2Cl_2$) (compound **1**) is synthesized and characterized by X-ray diffraction analysis. © 1997 Elsevier Science Ltd

*Keywords*: metalloborane; dinickelaborane; twelve-vertex cluster; ortho-cycloboronation; crystal structure; synthesis.

Although research on metallaboranes has been extremely fruitful over the past years, the reported nickelaboranes structurally characterized by X-ray diffraction analysis have so far been limited to a few compounds: $[Me_4N]_2[Ni(B_{10}H_{12})_2]$ [1], *closo* eight-vertex $[(C_5H_5)_4Ni_4B_4H_4]$ [2], *nido* nine-vertex $[(C_5H_5)_4Ni_4B_5H_5]$ [3] and *closo* ten-vertex $[(PhMe_2P)_2NiB_9H_7Cl_2]$ [4]. Hawthorne and co-workers reported the synthesis of *closo*-$[(C_5H_5)_2Ni_2B_{10}H_{10}]$ [5] which was characterized by NMR spectra. We now report a novel *ortho*-cycloboronated *closo* twelve-vertex dinickelaborane defined by single crystal X-ray diffraction analysis. It shows the cage not only to have *ortho*-cycloboronation but also to bind Cl atom and $PPh_3$ ligand. This is the first example in which all of them appear in one metallaborane cluster [3,4,6–8].

Reaction of $[NiCl_2(PPh_3)_2]$ with *closo*-$[B_{10}H_{10}]^{2-}$ and salicylic acid in refluxing $CH_2Cl_2$ for 120 h, followed by chromatographic separation, yielded the unexpected product, a black air-stable compound (**1**), as one of the chromatographically separable metallaborane products. The crystal structure is shown in Fig. 1.

The molecular structure is seen to be based upon the *closo* twelve-vertex cluster with two Ni atoms in adjacent positions. The Ni—Ni distance of 2.4008(12) Å is consistent with others [2,3]. There is a Cl-bridge between two Ni atoms and Ni(1)—Cl(1) and Ni(2)—Cl(1) distances are 2.239(2) and 2.243(2) Å respectively. One phenyl of each metal bonded phosphine ligand is *ortho*-cycloboronated to form five-membered rings Ni(1)—P(1)—C(111)—C(112)—B(4) and Ni(2)—P(2)—C(211)—C(212)—B(8), respectively. The Ni(1)—B(4) and Ni(2)—B(8) distances [Ni(1)—B(4) 2.068(6), Ni(2)—B(8) 2.074(6) Å] are shorter than other Ni—B distances in (**1**). This indicates that the *ortho*-cycloboronation can strengthen Ni—B bonding. In (**1**), one Cl atom and one $PPh_3$ ligand are bound to B(3) and B(6), respectively [Cl(2)—B(3) 1.799(6) Å, P(3)—B(6) 1.943(6) Å]. Furthermore, the plane formed by the atoms Cl(1), P(3), B(6), Cl(2), B(3), B(9) and B(11) divides almost equally the cluster and two five-membered rings.

*Crystal data and structure solution*

$Ni_2Cl_2P_3C_{54}B_{10}H_{49}\cdot 0.25CH_2Cl_2$, black crystal, $M = 1108.49$, monoclinic, space group $P2_1/c$,

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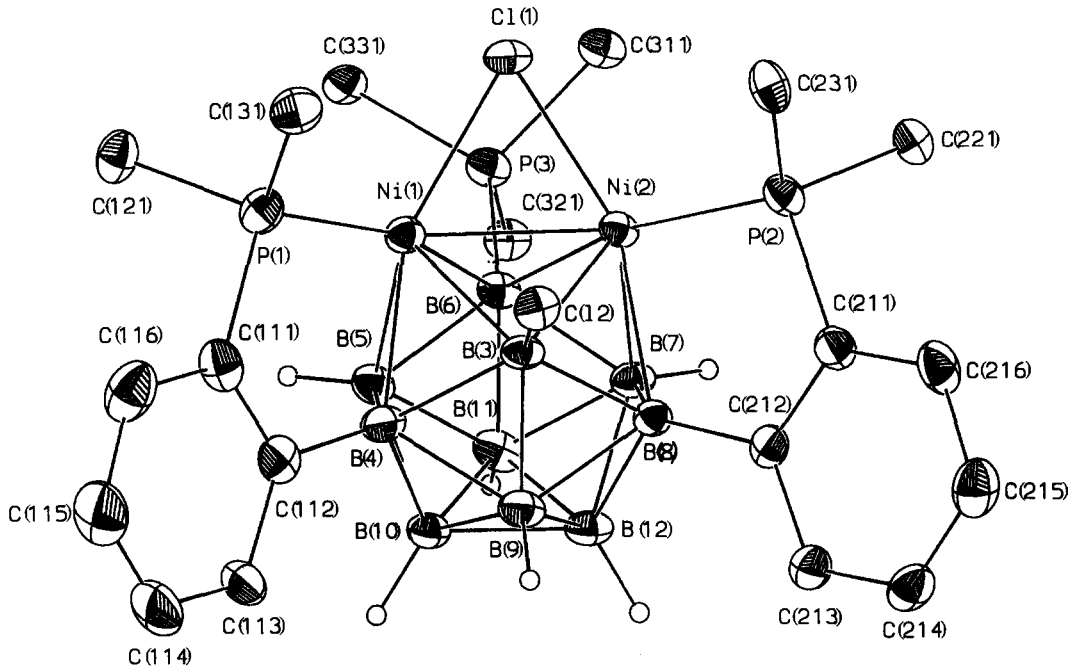


Fig. 1. ZORTEP drawing of the crystal and molecular structure of compound (**1**) (30% probability ellipsoids) and selected bond distances (Å) and angles (°): Ni(1)—B(3) 2.091(6), Ni(1)—B(5) 2.151(6), Ni(1)—B(6) 2.152(6), Ni(1)—P(1) 2.212(2), Ni(2)—B(3) 2.119(6), Ni(2)—B(6) 2.145(6), Ni(2)—B(7) 2.155(6), Ni(2)—P(2) 2.223(2); Ni(1)—Cl(1)—Ni(2) 64.78(5), Cl(1)—Ni(1)—Ni(2) 57.69(5), Cl(1)—Ni(2)—Ni(1) 57.73(5), Ni(1)—B(4)—C(112) 115.3(4), Ni(2)—B(8)—C(212) 115.2(4), Ni(1)—P(1)—C(111) 106.9(2), Ni(2)—P(2)—C(211) 106.1(2).

$a = 11.703(2)$, $b = 21.082(4)$, $c = 22.068(8)$ Å, $\beta = 99.98(2)°$, $V = 5362(2)$ Å$^3$, $Z = 4$, $D_c = 1.373$ g cm$^{-3}$, $\lambda$(Mo-$K_\alpha$) = 0.71073 Å, $\mu$(Mo-$K_\alpha$) = 0.954 mm$^{-1}$, $F(000) = 2274$. Crystal dimensions are $0.27 \times 0.12 \times 0.07$ mm. Data were collected at 294 K on an Enraf-Nonius CAD-4 diffractometer with $\omega$-$2\theta$ scan technique, using graphite-monochromated Mo-$K_\alpha$ radiation [9]. 7442 independent reflections were collected in the range $1.35 < \theta < 22.97°$. Data were corrected for Lorentz, polarization and empirical absorption effects using SDP-Plus program [10]. The structure was solved by direct and difference Fourier methods and refined by full-matrix least-squares calculations using the SHELXS [11] and SHELXL [12] programs to $R = 0.036$ and $Rw = 0.087$ ($F^2$) for 4045 observed reflections with $I > 2\sigma(I)$. Hydrogen atoms were treated as riding on their attached atoms and refined isotropically. The $CH_2Cl_2$ was disordered and was allowed for by 0.25 occupancy sites. Diagrams were prepared with the aid of the ZORTEP program [13].

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