Pergamon

PII: S0277–5387(97)00118–6

Polyhedron Vol. 16, No. 21, pp. 3873–3875, 1997

0277–5387/97 \$17.00+0.00

COMMUNICATION

Synthesis and crystal structure of the first metallaborane cluster containing three rings of *exo*-polyhedral cyclization

Jian-Min Dou,[a] Chun-Hua Hu,[a] Jie Sun,[b] Jing-De Wei[c] and Pei-Ju Zheng[a]*

[a] Research Center of Analysis and Measurement, Fudan University, Shanghai 200433, P.R. China

[b] Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P.R. China

[c] Department of Chemistry, Fudan University, Shanghai 200433, P.R. China

(Received 10 January 1997; accepted 25 March 1997)

Abstract—The novel *nido* 11-vertex nickelaborane [{μ-3,7-(PhCOS)}-{μ-7,8-(PhCOS)}-{μ-7,11-(PhCOS)}-10-PPh_3-*nido*-7-$NiB_{10}H_7$] (**1**) was synthesized and characterized by X-ray diffraction analysis. This is the first metallaborane cluster that has three rings of *exo*-polyhedral cyclization. © 1997 Elsevier Science Ltd

Keywords: synthesis; crystal structure; metallaborane; nickelaborane; *exo*-polyhedral cyclization; thiobenzoate.

Metallaborane chemistry has been expanded rapidly and several hundred polyhedral compounds have been synthesized and characterized [1–3]. It is interesting that some of them exist one or two five- or six-membered ring(s) of *exo*-polyhedral cyclization of metal ligand(s) to cluster. The groups of cyclization include *P*-phenyl ligand [4–8] and acetate [9]. Greenwood and co-workers reported exo-polyhedral cyclization of nido eleven-vertex platinaborane [μ-2,7-($SCSNEt_2$)-7-(PMe_2Ph)-*nido*-7-$PtB_{10}H_{11}$] *via* ligand-exchange reaction [10]. We have prepared and characterized two *closo* 11-vertex ruthenaborane clusters whose groups of cyclization are benzoates [11,12]. We now report the novel *nido* 11-vertex nickelaborane cluster that has three five-membered rings and the group of cyclization is thiobenzoate. This is the first cluster containing three rings of *exo*-polyhedral cyclization in metallaborane chemistry.

Reaction of [$NiCl_2(PPh_3)_2$] (0.6 mmol), with *closo*-$[B_{10}H_{10}]^{2-}$ (0.6 mmol) and thiobenzoic acid (1.2 mmol) in refluxing CH_2Cl_2 solution for 63 h in dry N_2, followed by chromatographic separation, yielded the blue air-stable crystalline compound (**1**) (Rf = 0.86, 1.3% yield) as one of the chromatographically separable products. It was characterized by single-crystal X-ray diffraction analysis.‡ The structure is shown in Fig. 1.

---

* Author to whom correspondence should be addressed. Tel: 86 21 65493848; Fax: 86 21 65490653; e-mail: jtwang-@fudan.ihep.ac.cn.

‡ Crystallographic data. A blue prismatic crystal of $NiS_3PO_3C_{39}B_{10}H_{37}$ having approximate dimensions 0.20 × 0.20 × 0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-K_α ($\lambda = 0.71069$ Å) radiation. Obtained from a least-squares refinement using 20 carefully centered reflections in the range $14.47 < 2\theta < 21.26°$, cell constants corresponded to a primitive monoclinic cell with dimensions: $a = 20.886(7)$, $b = 9.370(2)$, $c = 20.433(5)$ Å, $\beta = 104.46(2)°$, $V = 4251(2)$ Å^3. Space group is $P2_1/a$ and $Z = 4$. The data were collected at a temperature of 20 ± 1°C using the ω-2θ scan technique to a maximum 2θ value of 50.0°. In the index range $22 \geqslant h \geqslant 0$, $11 \geqslant k \geqslant 0$ and $25 \geqslant l \geqslant -26$, 6947 reflections were collected, of which 6715 were unique ($R_{int} = 0.032$). An empirical absorption correction was applied which resulted in transmission factors ranging from 0.89 to 1.00. The structure was solved by direct methods (SHELXS86). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 4711 observed reflections ($I > 3.00\sigma(I)$) and 514 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.038$ and $Rw = 0.049$.

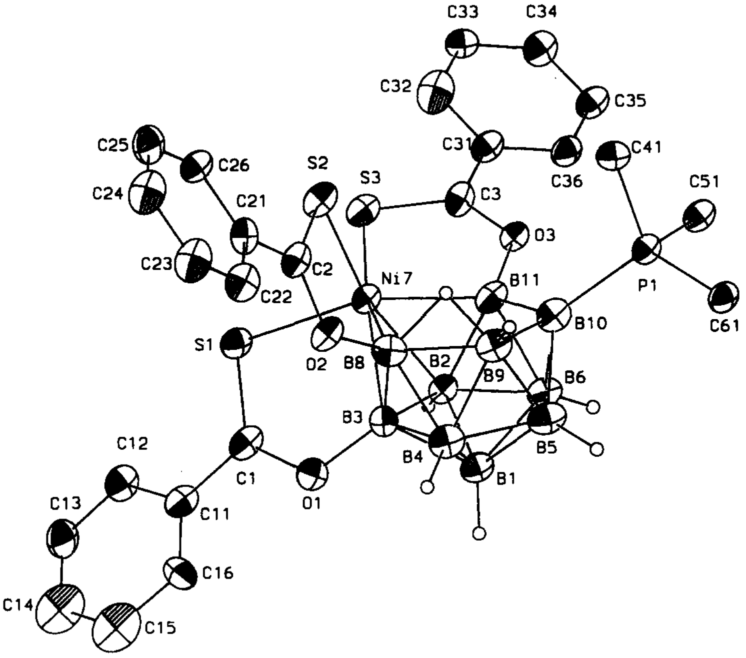

Fig. 1.

The cluster has the *nido* 11-vertex $\{NiB_{10}\}$ polyhedral skeleton and has three $\overline{\text{Ni-S-C-O-B}}$ five-membered rings of *exo*-polyhedral cyclization by thiobenzoates. The Ni atom is bound to three S atoms and four B atoms. Ni(7)–S(3) distance is 2.232(1) Å that is consistent with the Ni–S distances (average at 2.231 Å) in complex $[Ni(PhCOS)_2(Ph_2PCH_2CH_2PPh_2)]$ [13], but the distances of Ni(7) to S(1) and S(2) are 2.328(1) and 2.349(2) Å, respectively, which are significantly longer than Ni–S distances in literature [13]. This may be interpreted by steric effect of three $\overline{\text{Ni-S-C-O-B}}$ five-membered rings. Bond lengths of S(1)–C(1) [1.652(4) Å], S(2)–C(2) [1.673(4) Å] and S(3)–C(3) [1.670(4) Å] are significantly shorter than the usual single-bond distance (*ca* 1.8 Å), indicating a partial delocalization of electrons over the O–C–S moiety. Because of conjugation, B–O distances [B(3)–O(1) 1.482(5) Å, B(8)–O(2) 1.469(5) Å and B(11)–O(3) 1.490(4) Å] are longer than those of reported B–OR groups [2].

The bond length of Ni(7)–B(2) is 2.119(4) Å which is consistent with the corresponding Ni–B distance [2.11(1) Å] [14], but the distances of Ni(7) to B(3), B(8) and B(11) are 2.080(4), 2.109(4) and 2.118(4) Å, respectively, which are shorter than reported corresponding Ni–B distances [2.18(1), 2.24(1) and 2.22(1) Å, respectively] in the non-cyclized nickelaborane [14]. The fact that the distances of boron atoms participating in *exo*-polyhedral cyclizations to nickel atom are shorter shows that cyclization can strengthen the nickel-to-boron bonding.

In the cluster, the PPh_3 ligand connects with B(10) atom of the cage [P(1)–B(10) 1.898(4) Å]. The bond length of B(10)–B(11) [1.691(6) Å] and B(9)–B(10) [1.839(6) Å] are 0.149 and 0.131 Å shorter than the corresponding values in literature [14]. It may be attributed to the phosphine atom acting as a two-electron donor, thus eliminating the need for the bridging hydrogen atom between B(10) and B(11). The two-electron contribution to the B(10) strengthens the B(10)–B(11) and B(9)–B(10) bonding.

Acknowledgement—The authors acknowledge the support of the Chinese National Natural Science Foundation.

REFERENCES

1. Kennedy, J. D., *Prog. Inorg. Chem.*, 1984, **32**, 519.
2. Kennedy, J. D., *Prog. Inorg. Chem.*, 1986, **34**, 211.
3. Greenwood, N. N., *Pure & Appl. Chem.*, 1991, **63**, 317.
4. Crook, J. E., Greenwood, N. N., Kennedy, J. D. and McDonald, W. S., *J. Chem. Soc., Chem. Commun.*, 1982, 383.
5. Bould, J., Crook, J. E., Greenwood, N. N., Kennedy, J. D. and McDonald, W. S., *J. Chem. Soc., Chem. Commun.*, 1983, 949.
6. Bould, J., Greenwood, N. N., Kennedy, J. D. and McDonald, W. S., *J. Chem. Soc., Chem. Commun.*, 1982, 465.
7. Bould, J., Crook, J. E., Greenwood, N. N., Kennedy, J. D. and Thornton-Pett, M., *J. Chem. Soc., Dalton Trans.*, 1990, 1441.
8. Erlington, M., Greenwood, N. N., Kennedy, J.

D. and Thornton-Pett, M., *J. Chem. Soc. Dalton Trans.*, 1986, 2277.

9. Fontaine, X. L. R., Greenwood, N. N., Kennedy, J. D., Thornton-Pett, M. and Zheng, P.-J., *J. Chem. Soc., Chem. Commun.*, 1987, 1717.
10. Beckett, M. A., Greenwood, N. N., Kennedy, J. D. and Thornton-Pett, M., *Polyhedron*, 1985, **4**, 505.
11. Zheng, P.-J., unpublished results.
12. Yao, H.-J., Fu, J., Jin, R.-S., Wei, J.-D., Chen, J. and Zheng, P.-J., *Chin. J. Struct. Chem.*, 1995, **14**, 364.
13. Ramalingam, K., Aravamudam, G., Seshasayee, M. and Verghese, B., *Acta Cryst.*, 1987, **C43**, 471.
14. Guggenberger, L. J., *J. Am. Chem. Soc.*, 1972, **94**, 114.