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# Stability of nickel bis(dicarbollide) complexes

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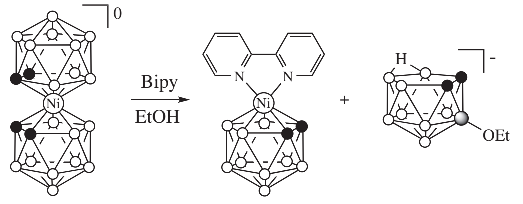
**Reactions of nickel(IV) bis(dicarbollide) with 2,2′-bipyridine or 1,10-phenanthroline in ethanol result in destruction of the metallacarborane cage with formation of the parent and 3-ethoxy substituted *nido*-carboranes.**



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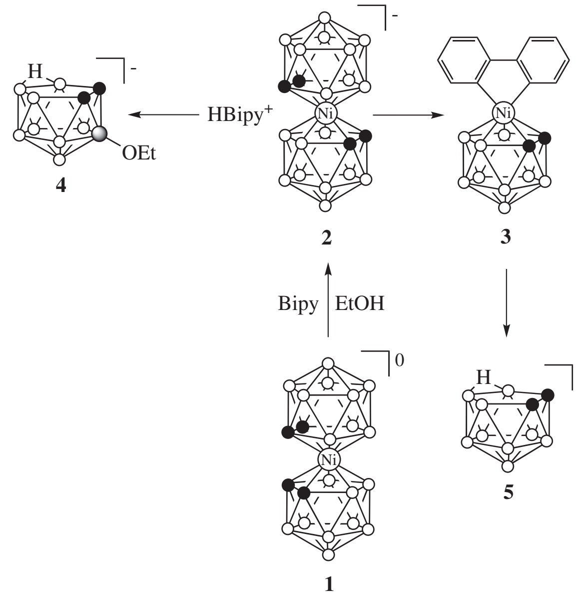
Despite the fact that nickel bis(dicarbollide) complexes are known over 50 years,[1,2] interest in them has significantly increased during the last decade due to their potential applications in materials science including molecular switches,[3–5] solar cells,[6] and conductive metal-organic frameworks.[7] Therefore, data on the stability of such complexes under different conditions is of great importance. Even though a number of nickel bis(dicarbollide) derivatives have been obtained to date,[2–6] the available information on the stability of the parent complexes is fragmentary and somewhat contradictory. In particular, the reduction of nickel(IV) bis(dicarbollide) to nickel(III) analogue with partial degradation in the presence of hard Lewis bases such as hydroxide ion or amines has been reported.[1(c)] Slow reduction-degradation reactions of nickel(IV) bis(dicarbollide) in alcohols and in polar solvents which may contain water, such as acetone, tetrahydrofuran and acetonitrile, was observed as well.[1(c)] The so-called ‘complex’ of nickel bis(dicarbollide) with 2,2′-bipyridine was reported to decompose in ethanolic solution to nickel(II) complex, 3-Bipy-3,1,2-Ni$C_2B_9H_{11}$,[8,9] whose structure was established by single crystal X-ray diffraction.[10] The reaction with 1,10-phenanthroline proceeds in a similar way.[11] It should be noted that neither the nature of the intermediate ‘complex’ nor the pathway of transformation of the second dicarbollide ligand in the bis(dicarbollide) anion are known. This prompted us to reexamine the reactions of nickel bis(dicarbollides) with 2,2′-bipyridine and 1,10-phenanthroline for better understanding their mechanism.

We found that the reaction of nickel(IV) bis(dicarbollide) **1** with 4 equiv. of 2,2′-bipyridine in ethanol at room temperature leads to its rather fast (within 3 h) reduction to nickel(III) bis(dicarbollide) **2** along with formation of some amount of known poorly soluble crimson nickelacarborane 3-Bipy-3,1,2-Ni$C_2B_9H_{11}$ **3** which was identified by NMR spectroscopy (Scheme 1).[†] The subsequent slower reaction (~ 7 days) results in complete degradation of the nickel bis(dicarbollide) complex with formation of a mixture of two *nido*-carboranes. These compounds are the symmetrically substituted *nido*-carborane [3-EtO-7,8-$C_2B_9H_{11}$]$^-$ **4** isolated by fractional crystallization from hot ethanol as the complex salt [Ni(Bipy)$_3$][3-EtO-7,8-$C_2B_9H_{11}$]$_2$ and identified by single crystal X-ray diffraction (Figures 1 and S1 of Online Supplementary Materials),[‡] and the parent *nido*-carborane [7,8-$C_2B_9H_{12}$]$^-$ **5** (see Scheme 1).



Scheme 1

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[†] *3-Bipy-3,1,2-Ni$C_2B_9H_{11}$* **3**. $^{11}B\{^1H\}$ NMR (acetone-$d_6$) $\delta$: –3.3 (1B), –10.1 (2B), –11.2 (1B), –16.0 (2B), –20.4 (2B), –21.6 (1B); $^1H$ NMR (acetone-$d_6$) $\delta$: 8.59 (d, 2H, *J* 8.0 Hz, Bipy), 8.28 (d, 2H, *J* 8.0 Hz, Bipy), 8.25 (t, 2H, *J* 7.4 Hz, Bipy), 7.65 (t, 2H, *J* 7.4 Hz, Bipy), 2.36 (s, 2H, $CH_{carb}$); $^{13}C$ NMR (acetone-$d_6$) $\delta$: 153.3 (Bipy), 138.1(Bipy), 125.7 (Bipy), 122.3 (Bipy), 23.6 ($C_{carb}$).

[‡] *Crystallographic data for [Ni(Bipy)$_3$][3-EtO-7,8-$C_2B_9H_{11}$]$_2$.* $C_{30}H_{24}N_6Ni^{2+}\cdot 2(C_4H_{16}B_9O)^-$ triclinic, space group $P\bar{1}$: $a$ = 10.0956(7), $b$ = 15.1974(11) and $c$ = 15.5660(11) Å, $\alpha$ = 74.8000(10)°, $\beta$ = = 79.8710(10)°, $\gamma$ = 85.221(2)°, $V$ = 2267.0(3) Å$^3$, $Z$ = 2, $M$ = 882.17, $d_{cryst}$ = 1.292 g cm$^{-3}$. Single crystal X-ray study was carried out with SMART APEX II CCD diffractometer [$\lambda$(Mo-K$\alpha$) = 0.71073 Å, graphite monochromator, $\omega$-scans] at 120 K. The structure was solved by the direct methods and refined by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms. $wR_2$ = 0.1117

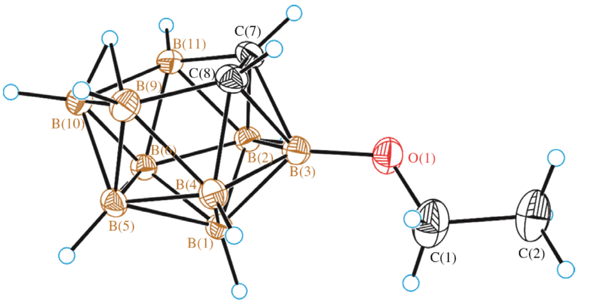

**Figure 1** General view of molecular structure of [3-EtO-7,8-$C_2B_9H_{11}$]$^-$ **4**. Displacement ellipsoids are drawn at the 50% probability level.

The ethoxy group in [3-EtO-7,8-$C_2B_9H_{11}$]$^-$ anion is attached to the 3-positioned boron atom adjacent to both cage carbons atoms. The length of the B–O bond [1.398(2) and 1.402(2) Å for two independent anions] is substantially shorter than those in other ethoxy derivatives of polyhedral boron hydrides $(Bu_4N)_2[B_{12}H_{11}OEt]$ [1.442(5)],[12] $[(C_5H_5N)_2CH_2][B_{12}H_{11}OEt]$ [1.436(3)].[13] One of the [3-EtO-7,8-$C_2B_9H_{11}$]$^-$ anions in asymmetric unit cell of $[Ni(Bipy)_3]$[3-EtO-7,8-$C_2B_9H_{11}$]$_2$ is totally ordered while in the other one, the Et group is disordered over two positions. Orientation of the ethoxy group relative to the carborane cage is somewhat different in symmetrically independent anions (see Online Supplementary Materials, Figure S1 and Table S1). The geometry of the $[Ni(Bipy)_3]^{2+}$ cation in $[Ni(Bipy)_3]$[3-EtO-7,8-$C_2B_9H_{11}$]$_2$ does not differ significantly from those found in other salts with polyhedral boron hydride anions.[14,15]

The $^{11}$B NMR spectrum of [3-EtO-7,8-$C_2B_9H_{11}$]$^-$ anion **4**[§] contains singlet at –1.4 ppm and five doublets at –12.5, –18.3, –23.4, –39.0 and –40.7 ppm with integrals in the 1 : 2 : 2 : 2 : 1 : 1 ratio, which is close to the spectrum of earlier reported 3-allyloxy derivative of *nido*-carborane.[16] In the $^1$H NMR spectrum, the signals of the ethoxy group at 3.64 and 1.08 ppm are in the range characteristic of other ethoxy derivatives of polyhedral boron hydrides;[13,17,18] the chemical shifts of the $CH_{carb}$ groups and the BHB hydrogen of the *nido*-carborane cage being 1.81 and –2.77 ppm, respectively.

The reaction is highly accelerated by refluxing in ethanol, reaching full completion within 5 hours. It should be noted that *nido*-carborane derivatives bearing 3-positioned substituents of the boron cage cannot be obtained by direct synthesis, but exclusively by deboronation of the corresponding 3-substituted *ortho*-carboranes, which in turn can be prepared by indirect methods.[19] For example, the corresponding 3-ethoxy-*ortho*-carborane can be obtained by the incorporation of {EtOB} fragment into open pentagonal face of the parent *nido*-carborane upon treatment with $EtOBCl_2$[20] or by nucleophilic substitution of the diazonium group in [3-$N_2$-*ortho*-$C_2B_{10}H_{11}$][$BF_4$] with sodium ethoxide.[21] Therefore, the substitution reaction should precede the destruction of the bis(dicarbollide) complex. The electrophilic and electrophile-induced nucleophilic substitution reactions in bis(dicarbollide) complexes are well known and usually proceed at positions 8 and 8′,[22] whereas reactions with nucleophiles are much less studied. The treatment of cobalt bis(dicarbollide) with 40% aqueous NaOH results in selective removal of the B(6)H vertex adjacent to both carborane cage carbons creating a $C_2B_3$ open pentagonal face into which metal ions can be inserted giving so-called dicarbacanastide complexes.[23] Thus, the attack of nucleophile in the dicarbollide complexes, as in the case of *ortho*-carborane, occurs at the vertex adjacent to both cage carbons.

Based on the aforesaid, we suggested the following reaction pathway which includes the initial reduction of the nickel(IV) complex **1** to the nickel(III) complex **2** followed by the attack of the latter by ethanol. This attack leads to 'knocking-out' of the metal atom from the polyhedron with the release of the substituted *nido*-carborane ligand [3-EtO-7,8-$C_2B_9H_{11}$]$^-$ **4**. Meanwhile, the metallacarborane fragment with 'naked' nickel is caught by 2,2″-bipyridine to form nickelacarborane 3-Bipy-3,1,2-$NiC_2B_9H_{11}$ **3**. This is then destroyed in the presence of an excess of 2,2′-bipyridine to form cationic nickel complex $[Ni(Bipy)_3]^{2+}$ and the parent *nido*-carborane [7,8-$C_2B_9H_{12}$]$^-$ **5** (see Scheme 1).

To validate the proposed route, we used the phenanthrolinium salt of nickel(III) bis(dicarbollide) $[H(Phen)_2][3,3'\text{-}Ni(1,2\text{-}C_2B_9H_{11})_2]$[24] as the starting material. Its boiling in ethanol for 5 h caused complete degradation with the formation of an equimolar mixture of the parent and 3-ethoxy substituted *nido*-carboranes identified by $^{11}$B and $^1$H NMR spectroscopy.

Going ahead, we studied stability of cesium salt of nickel(III) bis(dicarbollide) $Cs[3,3'\text{-}Ni(1,2\text{-}C_2B_9H_{11})_2]$ in boiling ethanol (thanks to anonymous referee for this proposal) and found that the destruction of nickel(III) bis(dicarbollide) into the parent and 3-ethoxy substituted *nido*-carboranes proceeded in the absence of the chelating ligand as well. Thus, the N-heterocyclic ligand does not directly participate in the nickel bis(dicarbollide) destruction and its role is limited by trapping nickel dicarbollide to form complex 3-L-3,1,2-$NiC_2B_9H_{11}$, which then would degrade to the parent *nido*-carborane. The easy degradation of nickel bis(dicarbollide) in ethanol raises the question of the possibility of its use for design of molecular switches and requires further study of its stability with respect to other nucleophilic reagents, including various solvents.

On the other hand, the obtained results suggest that 6,6′-disubstituted nickel bis(dicarbollides) (position 3 in the *nido*-carborane ligand) should be resistant to nucleophilic attack. Indeed, when compound $[6,6'\text{-}Ph_2\text{-}3,3'\text{-}Ni(1,2\text{-}C_2B_9H_{10})_2]$[25] was boiled in ethanol in the presence of 2,2′-bipyridine, only a reversible reduction $Ni^{IV} \rightarrow Ni^{III}$ was observed without destroying the metallacarborane structure. Thus, the introduction of additional substituents into positions 6 and 6′ of the nickel bis(dicarbollide) complexes [3(*b*),4] should contribute to increasing stability of molecular switches.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.09.019.

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calculated on $F^2_{hkl}$ for all 13830 independent reflections with $2\theta < 30.5°$, [GOF = 1.042, $R$ = 0.0421 calculated on $F_{hkl}$ for 10743 reflections with $I > 2\sigma(I)$].

CCDC 1907219 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

[§] *[3-EtO-7,8-$C_2B_9H_{11}$]$^-$ anion* **4**. $^{11}$B NMR (acetone-$d_6$) $\delta$: –1.4 (1B, s), –12.5 (d, 2B, $J$ 134 Hz), –18.3 (d, 2B, $J$ 129 Hz), –23.4 (d, 2B, $J$ 144 Hz), –39.0 (d, 1B, $J$ 158 Hz), –40.7 (d, 1B, $J$ ~ 120 Hz); $^1$H NMR (acetone-$d_6$) $\delta$: 3.64 (m, 2H, $OCH_2CH_3$), 1.81 (s, 2H, $CH_{carb}$), 1.08 (m, 3H, $OCH_2CH_3$), –2.77 (br. s, 1H, BHB).

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