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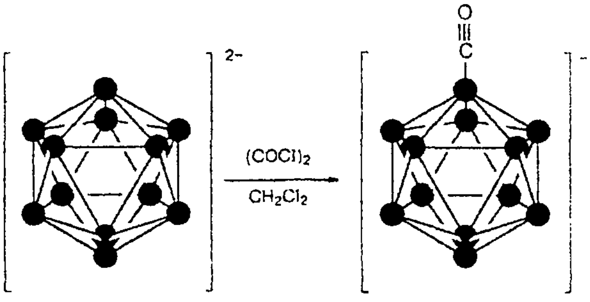
A mild synthesis of the $[B_{12}H_{11}CO]^-$ anion

I. B. Sivaev,[a*] *V. I. Bregadze,*[a] *and S. Sjöberg*[b]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: bre@ineos.ac.ru
[b]*Department of Organic Chemistry, Institute of Chemistry, Uppsala University,*
Thunbergsvägen 5, Box 531, S-751 21 Uppsala, Sweden.
Fax: 46 (18) 50 8542. E-mail: ssj@kemi.uu.se

Key derivatives in the chemistry of the dodecahydro-*closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ (**1**) are its carbonyl derivatives $[B_{12}H_{11}CO]^-$ (**2**), 1,7- and 1,12-$[B_{12}H_{10}(CO)_2]$, which possess high reactivity and can be used for the synthesis of a variety of anion $[B_{12}H_{12}]^{2-}$ derivatives (acids, ethers, esters, amides, alcohols, amines, isocyanates, *etc.*).[1] In connection with this, it seems to be promising to use monocarbonyl derivative **2** for the synthesis of biologically active boron-containing compounds, which could be used in boron neutron capture therapy of malignant tumors.[2] Chemical properties of anion **2** remain almost unstudied, because the only reported method for preparation of $[B_{12}H_{11}CO]^-$ is an inconvenient, for laboratory practice, synthesis from acid $(H_3O)_2[B_{12}H_{12}]\cdot nH_2O$ and CO at 1000 atm in the presence of $Co_2(CO)_8$ as the catalyst.[3] Only transformation of $[B_{12}H_{11}CO]^-$ to $[B_{12}H_{11}NCO]^{2-}$, when it reacts with sodium azide has been reported.[4] It is also known[5] that reaction of decahydro-*closo*-decaborate anion $[B_{10}H_{10}]^{2-}$ with oxalyl chloride results in formation of monocarbonyl derivative $[2\text{-}B_{10}H_9CO]^-$.

We found that reaction of tetrabutylammonium salt of $[B_{12}H_{12}]^{2-}$ with oxalyl chloride in CH_2Cl_2, carried out under mild conditions at 20 °C and atmospheric pressure, results in quantitative conversion of anion **1** to monocarbonyl derivative $[B_{12}H_{11}CO]^-$.



1 **2**

In the IR spectrum of product **2**, there are intensive absorption bands at 2507 and 2172 cm^{-1} that are assigned to the stretching vibrations of the B—H bonds of the boron skeleton (2480 cm^{-1} for $[B_{12}H_{12}]^{2-}$) and the $[-C{\equiv}O]^+$ group, respectively. The ^{11}B NMR spectrum of product **2** consists of three doublets at δ −3.0 (*J* = 142 Hz), −12.1 (*J* = 129 Hz), and −12.1 (*J* = 135 Hz) and a singlet at δ −33.5 (with the integral intensity ratio of 1 : 5 : 5 : 1).

Anion **2** is also formed when oxalyl chloride reacts either with triethylammonium salt $[B_{12}H_{12}]^{2-}$ in MeCN or with tetrabutylammonium salt $[B_{12}H_{12}]^{2-}$ in THF.

Carbonyl derivative **2** is readily hydrated to form the corresponding carboxy derivative $[B_{12}H_{11}COOH]^{2-}$ (**3**) as indicated by disappearance of the band at 2172 cm^{-1} and appearance of the absorption band of the carbonyl group at 1660 cm^{-1} in the IR spectrum. In this case, the

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band assigned to the stretching vibrations of B—H bonds is shifted to the long-wave region to 2478 cm^{-1}. The reaction is reversible: the carbonyl derivative **2** is formed as a result of passing a solution of carboxy derivative **3** through a column with a strong ion-exchanger in H$^+$-form and the subsequent concentration of the resulting eluate.

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