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Preliminary communication

DIRECT SYNTHESIS OF METALLOCARBORANE COMPLEXES VIA METAL ATOM OR ORGANOMETALLIC REAGENTS

George J. Zimmerman, Robert Wilczynski and Larry G. Sneddon*
Department of Chemistry and Laboratory for Research
on the Structure of Matter
University of Pennsylvania
Philadelphia, Pennsylvania 19104
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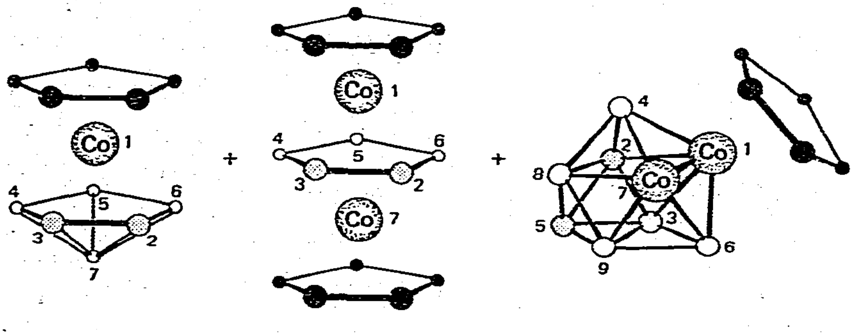
SUMMARY

Both metal atom and organometallic reagents have been used for the direct synthesis of various metallocarborane clusters without the prior synthesis of the carborane system. As examples, the reaction of cyclopentadiene, pentaborane(9) and 2-butyne with cobalt atoms and the reaction of 2-butyne and pentaborane(9) with $(\eta\text{-}C_5H_5)Co(CO)_2$ are reported.

In the past, the synthesis of a metallocarborane cluster has usually required the initial synthesis of the carborane cage which could then be reacted with an appropriate metal salt or organometallic reagent to form the complex. In only a few cases has a metallocarborane compound been obtained by direct formation of the carborane fragment at the metal site [1]. We now wish to report our preliminary results demonstrating that either metal atom or organometallic reagents can be used to effect the direct conversion of boron hydrides and alkynes into metallocarborane clusters without the prior synthesis of the carborane cage system. The use of these techniques may considerably broaden the scope of possible metallocarborane clusters and may eventually lead to the development of metal assisted syntheses of the carboranes themselves. As an illustration of these technuques, we report the following reactions:

In a typical reaction employing the metal atom technique, 25 ml of pentaborane(9), 25 ml of 2-butyne and 25 ml of cyclopentadiene were co-condensed with 0.25 g of cobalt vapor at -196°C. The metal atoms were generated by electrical heating (7.4 V 58 A) of cobalt powder in a Sylvania CS-1008 tungsten/alumina crucible mounted between two water cooled copper electrodes. After metal deposition was complete (1-2 hours) the mixture was allowed to warm to room temperature, the volatiles removed <u>in vacuo</u> and the residue in the reactor was extracted with methylene chloride. Separation by preparative thin layer chromatography of this extract gave the three metallocarborane complexes shown in the figure: 2,3-$(CH_3)_2$-1,2,3-$(\eta$-$C_5H_5)CoC_2B_4H_4$ (I), 14.5mg, 3.1%, 2,3-$(CH_3)_2$-1,7,2,3-$(\eta$-$C_5H_5)_2Co_2C_2B_3H_3$ (II), 5.2 mg, 1.3%, and 2,5-$(CH_3)_2$-1,7,2,5-$(\eta$-$C_5H_5)_2$ $Co_2C_2B_5H_5$ (III), 4.0 mg, 1.2%.* Both I and II were previously known and

$$B_5H_9 + C_5H_6 + CH_3C{\equiv}CCH_3 + Co\text{ (atoms)} \longrightarrow$$



I II III

Figure

Open circles represent BH units, shaded circles C-CH_3 units and dark circles C-H units. One cyclopentadienyl ring has been omitted on Compound III for clarity.

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[*] Yields are calculated based on metal vaporized and assumed only 50% of the metal reaches the reaction zone.

were identified by comparison of their mass spectra and ^{11}B and ^{1}H nmr spectra with literature values [2]. Compound III is a new isomer [3] of the $C_2B_5Co_2$ cage system and the structure shown in the figure was deduced from the following spectroscopic data. The 100 mHz pmr spectrum of III in CD_2Cl_2 shows two cyclopentadienyl resonances each of intensity five at 4.45 and 4.34 ppm, and two methyl resonances each of intensity three at 1.93 and 1.66 ppm. The 32.1 mHz ^{11}B nmr in CD_2Cl_2 consists of five doublets of equal intensity at 73.2 ppm (J=156Hz), 55.4 (164), 1.0 (133), -1.9 (129) and -13.4 (164)**. Thus, both the ^{11}B and ^{1}H nmr spectra indicate the absence of any plane of symmetry. Furthermore, the observance of two doublets at very low field in the ^{11}B nmr is consistent with the presence of the two different four coordinate boron atoms (positions B4 and B6 in the figure) attached to two metal atoms [3a,4]. Therefore, if the cobalt atoms are assumed to occupy five coordinate positions in the cage and the carbon atoms remain adjacent, then only the structure indicated is in agreement with the above data. It was also found that III could be quantitatively isomerized at 190°C to the previously known 5,6-$(CH_3)_2$-1,8,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5$ [3a], which provides further evidence for the proposed structure.

Also isolated from the above reaction were moderate amounts of hexamethyl benzene (~20 mg). This suggested that an important step in the metal atom reaction may be an initial formation of a cyclopentadienyl cobalt fragment, $(\eta\text{-}C_5H_5)Co$. Indeed work by Vollhardt and others [5] has shown that $(\eta\text{-}C_5H_5)Co(CO)_2$ is a useful oligomerizaiton catalyst for alkynes and may also involve the formation of such a fragment. We therefore also investigated the use of $(\eta\text{-}C_5H_5)Co(CO)_2$ as a reagent for metallocarborane synthesis.

Initial reactions were performed in sealed tubes to which equimolar amounts of $(\eta\text{-}C_5H_5Co(CO)_2$, pentaborane(9) and 2-butyne were added. After heating for 3 hours at 200°C, the volatiles were removed _in vacuo_ and the residue separated by thin layer chromatography to give the known compounds:

** Chemical shifts are referenced to boron trifluoride etherate, with positive values indicating a shift to lower field.

$5,6\text{-}(CH_3)_2\text{-}1,8,5,6\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_5$, and $1,7\text{-}(CH_3)_2\text{-}3,5,1,7\text{-}(\eta\text{-}C_5H_5)_2Co_2C_2B_4H_4$, [3] in 1% and 0.5% yields respectively, based on pentaborane(9) consumed. The production of only multimetal species in this reaction is probably the result of the high temperatures employed and we are currently exploring reactions with more moderate conditions in order to obtain monometal complexes.

Although the yields of clusters obtained by using either technique described above are low, we have clearly demonstrated the feasibility of utilizing either metal atom or organometallic reagents as aids for carborane construction. Further efforts will now be directed toward optimizing these conditions as well as attempts to incorporate other heteroatoms in the cage.

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