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FORMATION OF *p*-CARBORANE(12) FROM *mo*-CARBORANE(12) VIA THE COBALT COMPLEX $[(o\text{-}C_2B_{10}H_{12})_2Co^{III}]^-$

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SUMMARY

Oxidation of the cobalt complex obtained from $o\text{-}C_2B_{10}H_{12}{}^{2-}$ and $CoCl_2$ in anhydrous tetrahydrofuran (THF) leads to a mixture of *o*-, *p*- and *m*-carborane(12) isomers whose ratio depends on the temperature (within the range 25–150°) and the length of heating. Similar mixtures of isomers have been obtained from the oxidation of $p\text{-}C_2B_{10}H_{12}{}^{2-}$ and $m\text{-}C_2B_{10}H_{12}{}^{2-}$ respectively and $CoCl_2$ in anhydrous THF.

It is suggested that the presence of the cobalt atom in the complex reduces the activation energy required for the isomerization which is not observed with uncomplexed $C_2B_{10}H_{12}{}^{2-}$ anions even at temperatures as high as 150°.

A mechanism is proposed to explain the function of the cobalt atom in this process.

It has been shown previously that dianions obtained by the reduction of *o*-, *m*- and *p*-carboranes(12) with sodium metal in liquid ammonia undergo structural isomerization during the oxidation stage but that spontaneous isomerization of the dianions does not take place[1,2].

In order to substantiate this point of view we have studied the composition of the oxidation products of the cobalt complexes prepared from *o*-, *m*- and $p\text{-}C_2B_{10}H_{12}{}^{2-}$ and $CoCl_2$ in anhydrous tetrahydrofuran (THF). $[(o\text{-}C_2B_{10}H_{12})_2Co^{III}]^-$ was first prepared by Hawthorne and co-workers[3] who showed that the complexes $[(\pi\text{-}C_5H_5)Co^{III}(o\text{-}C_2B_{10}H_{12})]^0$ and $[(o\text{-}C_2B_{10}H_{12})_2Co^{III}]^-$ underwent isomerization in refluxing benzene or on melting to yield at least four isomers characterised by different positions of the carbon atoms in the polyhedral ligand.

We have found that the cobalt complex $(o\text{-}C_2B_{10}H_{12})_2Co^{III}]^-$ undergoes isomerization of the ligand cage at temperatures as low as 20°. On oxidation of the isomerized complex in anhydrous THF, as well as in aqueous media, with oxidants such as O_2, Cu^{2+}, CrO_3, $KMnO_4$ and others, *p*-carborane(12) was obtained together with *o*- and *m*-carboranes(12). The ratio of carborane isomers obtained in the reaction mixture after oxidation was found to depend on the length of storage of the complex with THF as well as on the temperature (see Table 1).

Isomerization of the sodium salt of $o\text{-}C_2B_{10}H_{12}{}^{2-}$ does not occur at room temperature, but heating the salt in an autoclave for 16–20 h at 150° results in partial isomerization of the polyhedral anion, and subsequent oxidation with benzo-

TABLE 1

INFLUENCE OF STORAGE TIME AND TEMPERATURE ON THE RATIO OF *o*-, *m*- AND *p*-CARBORANES(12) PRESENT IN THE REACTION MIXTURE AFTER OXIDATION[a] OF $[(o\text{-}C_2B_{10}H_{12})_2Co^{III}]^-$

No	*Isomerization conditions*		*Carborane*(12) *content*		(%)[b]
	h	*t*(°C)	*p*-	*m*-	*o*-
1	24	25	2.1	20.2	77.7
2	96	25	5.2	59.9	34.9
3	144	25	2.7	50.8	46.5
4	2	150	5.4	55.5	39.1

[a] Oxidation was carried out using an excess of $CuCl_2$ in aqueous CH_3COOH.
[b] The content of each isomer was determined as the average of three measurements using a GLPC method to an estimated error of ±4%.

TABLE 2

ISOMERIZATION OF COBALT COMPLEXES IN REFLUXING THF FOLLOWED BY OXIDATION WITH ANHYDROUS $CuCl_2$

Initial complex	*Yield* (%)	*Carborane*(12) *content* (%)		
		p-	*m*-	*o*-
$[(o\text{-}C_2B_{10}H_{12})_2Co]^-$	80–85	0.4	36.3	63.3[a]
$[(m\text{-}C_2B_{10}H_{12})_2Co]^-$	15–25	5.2	70.5	24.3
$[(p\text{-}C_2B_{10}H_{12})_2Co]^-$	25–30	7.7	84.4	7.9

[a] Zakharkin *et al.*[4] have mistakenly pointed out that under these conditions only *m*-carborane(12) is formed.

quinone yields a mixture of *o*- and *m*-carboranes(12) in a ratio of 95/5.

Similar Co^{III} complexes have been obtained from the dianions $m\text{-}C_2B_{10}H_{12}{}^{2-}$ and $p\text{-}C_2B_{10}H_{12}{}^{2-}$ and anhydrous $CoCl_2$ in THF.

$$4\,m(p)\text{-}C_2B_{10}H_{12}{}^{2-}+3CoCl_2 \xrightarrow{\text{THF}} 2\,[(m(p)\text{-}C_2B_{10}H_{12})_2Co^{III}]^-+Co^0$$

In a similar manner to $[(o\text{-}C_2B_{10}H_{12})_2Co^{III}]^-$, these complexes also undergo isomerization of the ligand cage at room temperature to yield on oxidation *o*-, *m*- and *p*-carboranes but with different ratios from those present with $[(o\text{-}C_2B_{10}H_{12})_2Co]^-$ and also from each other (see Table 2).

With $[(o\text{-}C_2B_{10}H_{12})_2Co]^-$, the total yield of carborane isomers obtained (80–85%) was found to be independent of the presence of an excess of oxidant. With the analogous *m*- and *p*- complexes, however, a large excess of oxidant was found to be necessary but even under these conditions the yield of carboranes never exceeded 30%.

These data suggest that under mild isomerization conditions each complex yields a large number of isomers which exhibit differing stabilities toward oxidizing agents and that after oxidation different products corresponding to partial or complete (boric acid) degradation of the polyhedron are formed together with *o*-, *m*- and *p*-carboranes(12). Spontaneous isomerization of *m*-$C_2B_{10}H_{12}^{2-}$ to *o*-$C_2B_{10}H_{12}^{2-}$ would have resulted in the formation of the same cobalt complexes both from *o*-$C_2B_{10}H_{12}^{2-}$ and *m*-$C_2B_{10}H_{12}^{2-}$ together with the same ratio of oxidation products.

We have shown earlier[1,2] that oxidation of the dianion *p*-$C_2B_{10}H_{12}^{2-}$ leads to the formation of *m*-carborane(12) only. The fact that all three carborane (12) isomers are formed on oxidation of each of the three cobalt complexes studied here suggests unequivocally that the presence of the transition metal markedly reduces the activation energy required for the structural isomerization of the polyhedral ligands and leads to the stabilization of the resulting isomeric structures which are not formed with uncomplexed $C_2B_{10}H_{12}^{2-}$ anions even at temperatures as high as 150°.

We believe that the oxidation of the cobalt complexes studied in this investigation proceeds by a different mechanism from that for the oxidation of uncomplexed $C_2B_{10}H_{12}^{2-}$ dianions, the main step being the oxidation of the Co^{III} atom in the complex to Co^{IV}:

$$[(C_2B_{10}H_{12})_2Co^{III}]^- \xrightarrow{-e} [(C_2B_{10}H_{12})_2Co^{IV}]^0$$

which then leads to the formation of two neutral molecules of carborane(12) and to metallic cobalt as a result of an intramolecular reduction–oxidation reaction:

$$[(C_2B_{10}H_{12})_2Co^{IV}]^0 \rightarrow 2\,C_2B_{10}H_{12} + Co^0$$

Further oxidation of the metallic cobalt could lead to the formation of the ion Co^{2+}.

The present results confirm that the dianions obtained by the reduction of *o*-, *m*- and *p*-carboranes in the presence of alkali metal should exhibit different structures[1,2].

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