

STABLE CARBENOIDS XLV ¹ - LIGAND EXCHANGE BETWEEN (CH₃)₃SiCBr₂Li AND HALOMETHYL-TRIMETHYLSILANES. EVIDENCE FOR TWO COMPETING MECHANISMS

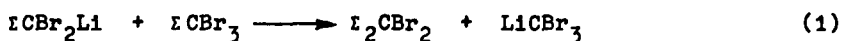
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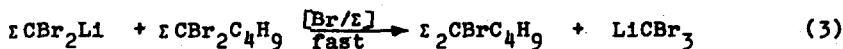
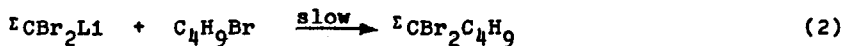
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Summary: Reaction of (CH₃)₃SiCBr₂Li with (CH₃)₃SiCBr₃, (CH₃)₃SiCCl₃, (CH₃)₃SiCBr₂C₄H₉, and (CH₃)₃SiCBr₂ produced carbosilanes and Li-carbenoids by either a [Li/(CH₃)₃Si]- or a [Br/(CH₃)₃Si]-exchange.

In the foregoing communication, ¹ a ligand exchange between $\epsilon\text{CBr}_2\text{Li}$ and ϵCBr_3 (ϵ stands for (CH₃)₃Si) was reported (eq. (1)). This paper describes ligand exchanges between $\epsilon\text{CBr}_2\text{Li}$ and other halomethyl-trimethylsilanes. It is shown that two different mechanisms are operative.



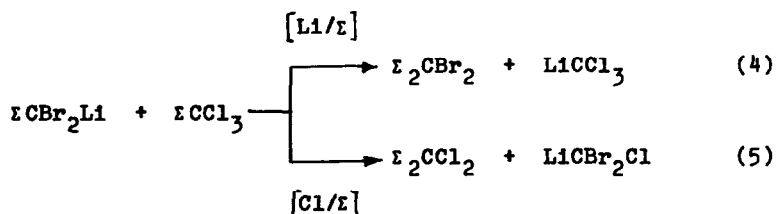
When $\epsilon\text{CBr}_2\text{Li}$ is treated with n-butyl bromide (or, if $\epsilon\text{CBr}_2\text{Li}$ is prepared from ϵCBr_3 and n-butyllithium instead of phenyllithium ¹), it undergoes coupling to give, surprisingly, a carbosilane ², identified as $\epsilon_2\text{CBrC}_4\text{H}_9$ (liquid, $n_D^{20} = 1.4855$), instead of the expected silane, $\epsilon\text{CBr}_2\text{C}_4\text{H}_9$. It thus appears, that the formation (eq. (2)) of $\epsilon\text{CBr}_2\text{C}_4\text{H}_9$ (which was not detected among the products) is followed by a fast ligand exchange with a second carbenoid molecule to give the carbosilane and LiCBr_3 (eq. (3)). The latter was successfully trapped with dry ice (as tribromo acetic acid) or ϵCl (as ϵCBr_3).



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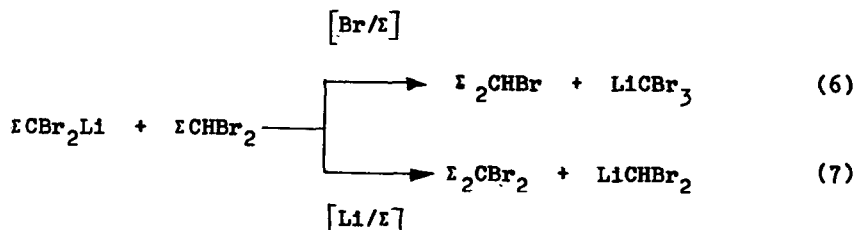
The coupling (eq. (2)) proved to be rather slow: good yields of $\epsilon_2\text{CBrC}_4\text{H}_9$ (about 75%, based on eq. (2) and (3)) were obtained only after 2 hours at -105° (starting from 0.17 M $\epsilon\text{CBr}_2\text{Li}$).

Eq. (3) undoubtedly describes an exchange between a bromo atom of $\epsilon\text{CBr}_2\text{C}_4\text{H}_9$ and the trimethylsilyl group of the carbenoid (symbolized: $[\text{Br}/\epsilon]$). This type of ligand exchange seems to have no precedent in the literature. The question arises, whether eq. (1) also entails a $[\text{Br}/\epsilon]$ -exchange or whether a $[\text{Li}/\epsilon]$ -exchange is involved, i.e.: the well-known displacement of halomethyl anions from silanes³. A substrate which should give different products from the two reactions is ϵCCl_3 ⁴ (prepared in 54% yield from LiCCl_3 ⁵ and ϵCl , m.p. $133\text{--}134^\circ$). ϵCCl_3 and $\epsilon\text{CBr}_2\text{Li}$ underwent a quantitative reaction in less than 1 hour at -110° to yield, exclusively, the products from a $[\text{Li}/\epsilon]$ -exchange (eq. (4)); no $[\text{Cl}/\epsilon]$ -exchange⁶ was observed (eq. (5)). Thus a $[\text{Li}/\epsilon]$ -exchange might also be involved in eq. (1).



However, we find that $[\text{Br}/\epsilon]$ -exchange is able to compete with the $[\text{Li}/\epsilon]$ -exchange. Thus, treatment of $\epsilon\text{CBr}_2\text{Li}$ with pure ϵCHBr_2 ⁷ (prepared in 70% yield from LiCHBr_2 ⁸ and ϵCl , $n_D^{20} = 1.4995$) as well as the methanolysis of pure $\epsilon\text{CBr}_2\text{Li}$ suspensions, leads to the products shown in eq. (6) and (7) ($\epsilon_2\text{CHBr}$ was identified with a sample obtained by methanolysis of $\epsilon_2\text{CBrLi}$ and isolated by preparative v.p.c. as a liquid of 97% purity, $n_D^{20} = 1.4693$; NMR (in CCl_4): τ 7,85 (1 H) and 9,84 (18H)).

The rate ratio $k_{(6)}:k_{(7)}$ (found between 0,6 and 3) depends upon the initial concentration of the substrates. Reaction (7), which is favoured in more dilute mixtures, is reasonably interpreted as the normal displacement, but a $[\text{H}/\epsilon]$ -exchange can not be excluded at present.



Our results clearly demonstrate two different exchange mechanisms, but it is uncertain which one is operating in reaction (1). Further research is in progress in an effort to solve this problem and to reveal the factors which control the two mechanisms. Steric requirements, the formation tendency of carboranes, and the basicities of the reacting and resulting carbenoids all appear to play an important role.

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References:

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