Tetrahedron Letters No.54, pp.4697-4699, 1970. Pergamon Press. Printed in Great Britain.

STABLE CARBENOIDS XLV [1] - LIGAND EXCHANGE BETWEEN $(CH_3)_3SiCBr_2Li$ AND HALOMETHYL-TRIMETHYLSILANES. EVIDENCE FOR TWO COMPETING MECHANISMS

Roland von Nagel and Gert Köbrich
Organisch-chemisches Institut, Universität Heidelberg, 69 Heidelberg, Germany+)

(Received in UK 10 October 1970; accepted for publication 21 October 1970)

Summary: Reaction of $(CH_3)_3SiCBr_2Li$ with $(CH_3)_3SiCBr_3$, $(CH_3)_3SiCCl_3$, $(CH_3)_3SiCBr_2C_4H_9$, and $(CH_3)_3SiCHBr_2$ produced carbosilanes and Li-carbenoids by either a $[Li/(CH_3)_3Si]$- or a $[Br/(CH_3)_3Si]$-exchange.

In the foregoing communication, [1] a ligand exchange between ΣCBr_2Li and ΣCBr_3 (Σ stands for $(CH_3)_3Si$) was reported (eq. (1)). This paper describes ligand exchanges between ΣCBr_2Li and other halomethyl-trimethylsilanes. It is shown that two different mechanisms are operative.

$$\Sigma CBr_2Li + \Sigma CBr_3 \longrightarrow \Sigma_2CBr_2 + LiCBr_3 \qquad (1)$$

When ΣCBr_2Li is treated with n-butyl bromide (or, if ΣCBr_2Li is prepared from ΣCBr_3 and n-butyllithium instead of phenyllithium [1]), it undergoes coupling to give, surprisingly, a carbosilane [2], identified as $\Sigma_2CBrC_4H_9$ (liquid, $n_D^{20} = 1.4855$), instead of the expected silane, $\Sigma CBr_2C_4H_9$. It thus appears, that the formation (eq. (2)) of $\Sigma CBr_2C_4H_9$ (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 ΣCl (as ΣCBr_3).

$$\Sigma CBr_2Li + C_4H_9Br \xrightarrow{slow} \Sigma CBr_2C_4H_9 \qquad (2)$$

$$\Sigma CBr_2Li + \Sigma CBr_2C_4H_9 \xrightarrow[fast]{[Br/\Sigma]} \Sigma_2CBrC_4H_9 + LiCBr_3 \qquad (3)$$

+) Present address: Organisch-chemisches Institut, Technische Universität Hannover, 3 Hannover, Germany.

The coupling (eq. (2)) proved to be rather slow: good yields of $\Sigma_2CBrC_4H_9$ (about 75%, based on eq. (2) and (3)) were obtained only after 2 hours at -105° (starting from 0.17 M ΣCBr_2Li).

Eq. (3) undoubtedly describes an exchange between a bromo atom of $\Sigma CBr_2C_4H_9$ and the trimethylsilyl group of the carbenoid (symbolized: $[Br/\Sigma]$). This type of ligand exchange seems to have no precedent in the literature. The question arises, whether eq. (1) also entails a $[Br/\Sigma]$-exchange or whether a $[Li/\Sigma]$-exchange is involved, i.e.: the well-known displacement of halomethyl anions from silanes [3]. A substrate which should give different products from the two reactions is ΣCCl_3 [4] (prepared in 54% yield from $LiCCl_3$ [5] and ΣCl, m.p. 133-134°). ΣCCl_3 and ΣCBr_2Li underwent a quantitative reaction in less than 1 hour at -110° to yield, exclusively, the products from a $[Li/\Sigma]$-exchange (eq. (4)); no $[Cl/\Sigma]$-exchange [6] was observed (eq. (5)). Thus a $[Li/\Sigma]$-exchange might also be involved in eq. (1).

$$\Sigma CBr_2Li + \Sigma CCl_3 \begin{cases} \xrightarrow{[Li/\Sigma]} \Sigma_2CBr_2 + LiCCl_3 & (4) \\ \xrightarrow[{[Cl/\Sigma]}]{} \Sigma_2CCl_2 + LiCBr_2Cl & (5) \end{cases}$$

However, we find that $[Br/\Sigma]$-exchange is able to compete with the $[Li/\Sigma]$-exchange. Thus, treatment of ΣCBr_2Li with pure $\Sigma CHBr_2$ [7] (prepared in 70% yield from $LiCHBr_2$ [8] and ΣCl, $n_D^{20} = 1.4995$) as well as the methanolysis of pure ΣCBr_2Li suspensions, leads to the products shown in eq. (6) and (7) (Σ_2CHBr was identified with a sample obtained by methanolysis of Σ_2CBrLi 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 $[H/\Sigma]$-exchange can not be excluded at present.

$$\Sigma CBr_2Li + \Sigma CHBr_2 \begin{cases} \xrightarrow{[Br/\Sigma]} \Sigma_2CHBr + LiCBr_3 & (6) \\ \xrightarrow[{[Li/\Sigma]}]{} \Sigma_2CBr_2 + LiCHBr_2 & (7) \end{cases}$$

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 carbosilanes, and the basicities of the reacting and resulting carbenoids all appear to play an important role.

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this work.

References:

1 Part XLIV: G. Köbrich and R.v.Nagel, Tetrahedron Lett., 1970, preceding paper.

2 Cf. G. Fritz, J. Grobe and D. Kummer, Adv. Inorg. Radiochem., 7, 349 (1965).

3 H. Gilman, A.G. Brook, and L.S. Miller, J. Amer. Chem. Soc., 75, 4531 (1953); G.E. Coates, M.L.H. Green, P. Powell, and K. Wade, Principles of Organometallic Chemistry, p. 133, Methuen & Co. London, 1968.

4 W.R. Bamford and B.C. Pant, J. Chem. Soc. (C), 1967, 1470.

5 G. Köbrich, K. Flory, and W. Drischel, Angew. Chem., 76, 536 (1964); G. Köbrich, K. Flory, and R.H. Fischer, Chem. Ber., 99, 1793 (1966).

6 Cf. G. Köbrich and R.H. Fischer, Chem. Ber., 101, 3219 (1968).

7 H. Normant and J. Villiéres, Compt. rend., 260, 4535 (1965); J. Villiéres, Bull. Soc. Chim. France, 1967, 1520.

8 G. Köbrich and R.H. Fischer, Chem. Ber., 101, 3208 (1968).