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STABLE CARBENOIDS XLIV [1] - PREPARATION, SILYLATION, AND LIGAND EXCHANGE REACTIONS OF $(CH_3)_3SiCBr_2Li$ AND $[(CH_3)_3Si]_2CBrLi$

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Summary: Compounds $[(CH_3)_3Si]_nCBr_{4-n}$ (n=1,2,3) have been prepared by silylation of the corresponding Li-carbenoids. $(CH_3)_3SiCBr_2Li$ and $(CH_3)_3Si$ $_2CBrLi$ are stable at -100°. Rapid ligand exchanges are reported between the former and $(CH_3)_3SiCBr_3$ and between the latter and $LiCBr_3$.

Previous papers in this series have shown that two reactions which were discovered in, and first published from, our laboratory, are of general utility: (1) the low-temperature metallation of halohydrocarbons in THF or Trapp mixture to form stable Li-carbenoids, [2,3] and (2) the metathesis between these carbenoids and metal halides to give new α-haloorganometallic compounds. [2c,3,4] A recent paper by Seyferth et al., [5] in which both procedures were used to prepare trimethylsilyl-dichloromethyllithium and bis(trimethylsilyl)-chloromethyllithium, prompts us to report some results of our work done since 1967 with trimethylsilyl-dibromomethyllithium and bis(trimethylsilyl)-bromomethyllithium.

Both of these carbenoids have been assumed as transient intermediates in a reaction sequence leading to tetrakis(trimethylsilyl)-methane from CBr_4 and Li-metal. [6] Their thermal stability at -100° was demonstrated by the finding of Merkle, [7] that a fourfold iteration of bromo-lithium exchange and silylation with trimethylchlorosilane ultimately also gave tetrakis-(trimethylsilyl)-methane in moderate yield (eq. (1) - (4); the symbol Σ stands

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$$CBr_4 \xrightarrow{RLi} LiCBr_3 \xrightarrow{\Sigma Cl} \Sigma CBr_3 \qquad (1)$$

$$\Sigma CBr_3 \xrightarrow{RLi} \Sigma CBr_2Li \xrightarrow{\Sigma Cl} \Sigma_2CBr_2 \qquad (2)$$

$$\Sigma_2CBr_2 \xrightarrow{RLi} \Sigma_2CBrLi \xrightarrow{\Sigma Cl} \Sigma_3CBr \qquad (3)$$

$$\Sigma_3CBr \xrightarrow{RLi} \Sigma_3CLi \xrightarrow{\Sigma Cl} \Sigma_4C \qquad (4)$$

We have examined each reaction step in detail. Pure ΣCBr_3 (m.p. 201-203°, previously available in only 8% yield [8]) was obtained in 71% yield from $LiCBr_3$ [9] and ΣCl (eq. (1)). ΣCBr_3 underwent very rapid Br/Li exchange with phenyllithium to give ΣCBr_2Li, silylation of which afforded Σ_2CBr_2 (eq. (2)). In the same way, Σ_3CBr (recently prepared in 35% yield from Σ_3CH and NBS [10]) was obtained in 79% yield, m.p. 197-198°, from Σ_2CBr_2 via Σ_2CBrLi (eq. (3)). Combination of procedures (2) - (4) gave 79% Σ_4C (based on ΣCBr_3; m.p. 408-410°, uncorr., from ethanol). All reactions were carried out in THF or Trapp mixture between -110° and -100°.

Although these reactions seem to be quite simple and straightforward, they are actually rather complex. Thus, a mixture of ΣCBr_2Li and ΣCBr_3 (as is present during the preparation of the former from the latter) will undergo extremely rapid ligand exchange (completed in less than 30 sec at -105°) to give Σ_2CBr_2 (yield, based on eq. (5), 70-81%; m.p. 70°, after sublimation; NMR (in CCl_4): τ 9,71) and $LiCBr_3$ (identified by carboxylation as tribromoacetic acid):

$$\Sigma CBr_2Li + \Sigma CBr_3 \longrightarrow \Sigma_2CBr_2 + LiCBr_3 \qquad (5)$$

An equally rapid symproportionation was noted between the carbenoids Σ_2CBrLi and $LiCBr_3$, to give ΣCBr_2Li (nicely evidenced, i.a., by mixing suspensions of the pure carbenoids at -110°):

$$\Sigma_2CBrLi + LiCBr_3 \longrightarrow 2\ \Sigma CBr_2Li \qquad (6)$$

Considering now, that Σ_2CBr_2 (from eq. (2)) is transformed into Σ_2CBrLi by phenyllithium under the conditions of the formation of ΣCBr_2Li from ΣCBr_3, we meet the curious and unique situation, that at least a large portion of the carbenoid ΣCBr_2Li, which is finally silylated, according to eq. (2), has actually arisen via the transformations shown in eq. (5) and (6).

Displacements of halomethyl anions from "neutral" silanes, as outlined in reaction (5), are quite common, and are known to occur readily under basic conditions.[11] On the other hand, ligand exchanges between different carbenoids, as shown in the symproportionation (6), are rare and have only recently been reported by Köbrich and Fischer,[12] e.g.:

$$LiCBr_3 + LiCCl_3 \longrightarrow LiCBr_2Cl + LiCBrCl_2.$$

A third type of ligand exchange is described in the following paper.

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