# 13C NMR study on magnesium carbenoids

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13C NMR chemical shifts suggest that α-iodoalkyl-magnesium compounds have a carbenoid character in between that of α-haloalkyllithium and the corresponding zinc compounds.

The term 'carbenoid' has been coined by Closs and Moss for α-haloalkyllithium compounds.[1] The term is associated with[2,3] the ability of these species to react directly with alkenes to give cyclopropanes, to undergo direct C–H-insertion reactions and to be subject to direct attack by nucleophiles. This electrophilic behaviour of lithium carbenoids implies a low lying LUMO, which manifests itself in a remarkable downfield shift of the 13C NMR signal of the carbenoid carbon.[4,5] Regarding other main group metal carbenoids, the zinc species have been well studied and characterized[6–9] in the context of the Simmons–Smith cyclopropanation reaction.[10] We report here a study of α-halo-alkylmagnesium compounds.[11]

α-Iodoalkylmagnesium compounds are accessible by an iodine/magnesium exchange reaction.[12–14] Treatment of the diiodo compound **1** with diisopropylmagnesium (**2**) at −78 °C
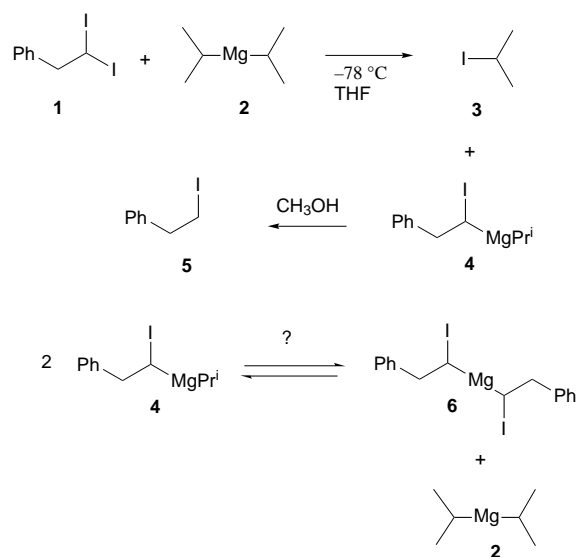
for two hours followed by protonation with CH₃OH gave 97% of the iodoalkane **5**. We had, however, no information about whether the magnesium carbenoid **4** is in a Schlenk equilibrium with diisopropylmagnesium (**2**) and the bis-α-iodoalkyl-magnesium **6**.

For this reason we initiated a low temperature 13C NMR study of the reaction. When incremental amounts of 0.5 equiv. of the diiodo compound **1** were added at −80 °C into a solution of **2** in THF a set of spectra were recorded which are schematically reproduced in Fig. 1.

Diisopropylmagnesium (**2**) shows two 13C NMR signals at δ 9.6 and 26.3. After addition of 1.0 equiv. of the diiodoalkane **1**, 2-iodopropane (**3**) (δ 23.1 and 31.0) and a new species
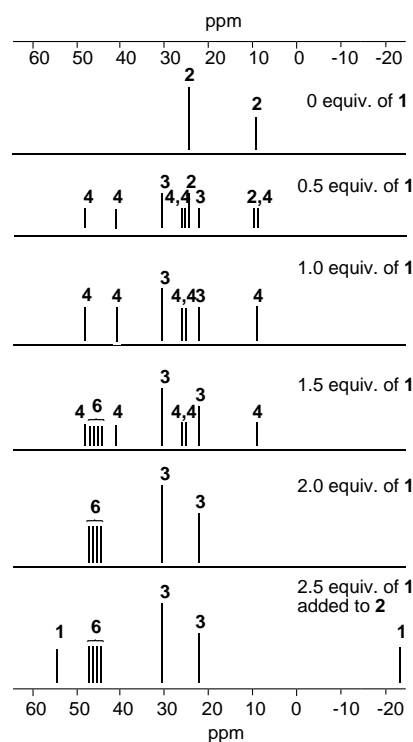
Fig. 1 13C NMR titration. Addition of 0.5 equiv. each of 1,1-diiodo-2-phenylethane (**1**) to diisopropylmagnesium (**2**) at −78 °C in THF.

were formed (δ 9.0, 26.5, 26.6, 41.4, 48.3). The latter was identified as the carbenoid **4** having two diastereotopic methyl groups due to the chirality of **4**. After addition of a further equivalent of the diiodoalkane **1** the carbenoid **4** was completely converted into a 1:1 mixture of the diastereomeric carbenoids **6** [*meso* and (±): δ 44.1, 46.7, 46.9, 47.3]. Only if more than the 2 equiv. of **1** were added was an excess of **1** detectable in solution (δ −23.1, 54).

This shows that the carbenoid **4** has no tendency to disproportionate into **6** and **2**. In a separate experiment it could be shown that the bis(iodoalkyl)magnesium **6** is not converted into **4** by addition of diisopropylmagnesium (**2**). This constitutional stability of the magnesium carbenoids **4** and **6** at −78 °C clearly contrasts with the behaviour of the analogous dialkylzinc reagents, which rapidly comproportionate and disproportionate at −78 °C in THF.[8] Likewise, the corresponding alkylzinc iodides are also subject to a rapid Schlenk equilibrium.[8]
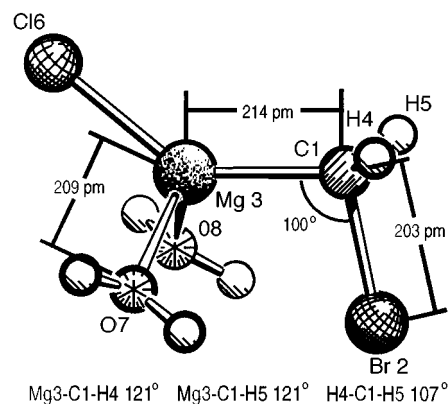
The 13C NMR chemical shift data for the carbenoid carbon in **4** and **6** showed a significant downfield shift Δδ[4] relative to the mono-iodo compound **5**. We similarly recorded the chemical shifts for the corresponding bromo- and chloro-magnesium carbenoids, *cf.* Table 1. As seen previously for the lithium carbenoids,[4] the Δδ values are halogen dependent. Finally, data for methyl iodide and bis(iodomethyl)zinc[7,8] have been included in the table.

Table 1 Carbenoid-specific downfield shifts of ^{13}C NMR signals

Structure	$\Delta\delta$ at C-1

(Values appearing with structures in Table 1)

- I–H bicyclic: −7.9 ; I–Li bicyclic: 83.2 — $\Delta\delta$ = 91
- Br–H bicyclic: 34.7 ; Br–Li bicyclic: 90.7 — $\Delta\delta$ = 56
- Ph–CH2–I: 139.8   5.5 ; with Mg (iPr) **4**: 146.3   41.4 ; dimer **6**: 146.5   44.1 / 146.7   46.7 — ≈ 36
- Ph–CH2–Br: 136.7   39.4 ; with Mg (iPr): 145.6   63.7 ; dimer **7**: 145.8   66.7 / 146.2   67.0 — ≈ 24
- butyl–CH–Cl: 44 ; with Mg (iPr): 68.8 ; dimer: 69.4 / 69.6 — ≈ 24
- I–CH2–I: −20.8 ; with Zn: −17 — ≈ 4

Fig. 2 Calculated and experimental structure data for α-bromoalkyl-magnesium compounds

The lengthening of the carbon–bromine bond is borne out by bromine EXAFS studies[24] on a mixture of the diastereomeric carbenoids **7**. These measurements indicated a carbon–bromine bond length of 200 pm and a bromine–magnesium distance of 305 pm. The significant lengthening of the carbon–bromine bond in **7** implies a high lying σ and a low lying σ* orbital. The latter should be the cause of the observed downfield shift of the carbenoid carbon signal. The LUMO in **4** and **6** appears not to be localized exclusively at the carbon–halogen bond. Unexpected and conspicuous downfield shifts have also been recorded (cf. Table 1) for the ipso-carbon of the phenyl group in **4**, **6** and **7**. For steric reasons, a conformation is preferred in which the halogen and the phenyl group are antiperiplanar with respect to the C1–C2 bond. This sets the stage for a $\sigma_{C\text{-}ipso\text{–}C2}$ to $\sigma^*_{C1\text{–}Hal}$ delocalization. The resulting LUMO should therefore also have coefficients at the ipso-carbon of the phenyl group due to σ-delocalization similar to, but smaller than, that seen in the adamantyl cation.[25]
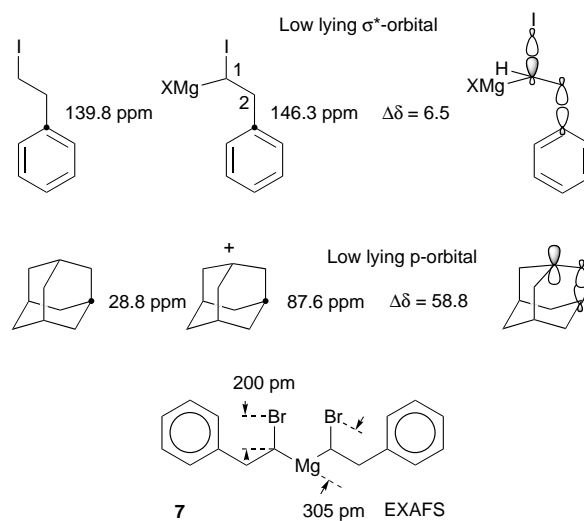
This study showed that the organomagnesium compounds **4** and **6** do not enter a Schlenk equilibrium at −80 °C. Their carbenoid character is reflected in a significant downfield shift $\Delta\delta$ of the ^{13}C NMR signal of the carbenoid carbon. This may be caused by substantial weakening of the carbon–halogen bond in the magnesium carbenoids, as suggested by ab initio calculations and EXAFS studies.

Acknowledgements

While the significance of the $\Delta\delta$ values is unknown, it is tempting to associate them qualitatively with the 'carbenoid' character of the organometallic compounds.[15] Therefore (keeping the halogen constant) the carbenoid character should decrease in the series Li > Mg > Zn.[16]

The downfield shifts of the ^{13}C NMR signals should be a consequence of structural peculiarities of the various carbenoids. So far, X-ray structure data are available for zinc carbenoids[6] and dichloromethyllithium.[22] In order to gain more insight into the structural aspects of magnesium carbenoids we turned to ab initio calculations using GAUSSIAN94 and geometry optimization at the MP2 level.[23] Calculations on BrCH2MgCl solvated by two water molecules revealed the following structural features (see Fig. 2). The carbon–bromine bond is, at 203 pm, more than 5 pm longer than the calculated value for CH_3Br (195 pm), cf. the standard bond length of 197 pm. The magnesium–carbon–bromine angle is, at 100°, significantly less than tetrahedral. This suggests partial sp²-hybridization at carbon (sum of bond angles H5–C–Mg, Mg–C–H4, and H5–C–H4 = 349°) and more p-character in the carbon–bromine bond.[2]

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