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Preliminary communication

Alkoxy–alkyl mixed bridged organomagnesium compounds

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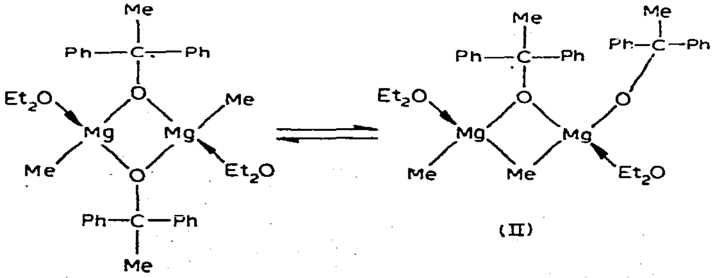
Recently, we reported the first observation of a stable alkoxy–alkyl mixed bridged organoaluminum compound in solution ($Me_2AlOCPh_2Me{\cdot}Me_3Al$)[1]. Since this time Wallbridge[2] and Mole[3] have made extensive contributions toward the understanding of the composition in solution of other organoaluminum mixed bridged systems. We would now like to report the first observation of a stable alkoxy–alkyl mixed bridged organomagnesium compound in solution. These studies involve variable temperature (+40 to –80°) 60 MHz NMR studies in diethyl ether in conjunction with ebullioscopic molecular association measurements in the same solvent. The systems studied were (1) $MeMgOCPh_2Me$ and (2) $MeMgOCPh_2Me{\cdot}MgMe_2$. The compound $MeMgOCPh_2Me$ (1) was prepared by treating Me_2Mg with $Ph_2C{=}O$ and $MeMgOCPh_2Me{\cdot}MgMe_2$ was prepared by adding (1) to Me_2Mg.

Association measurements on $MeMgOCPh_2Me$ in the concentration range at 0.0537–0.115 *M* show that this compound has an *i* value of 1.32 at the lower concentration range, increasing and leveling off at 2.01 at the higher concentrations indicating a dimer in solution. The molecular association data and low temperature NMR study of $MeMgOCPh_2Me$ in the higher concentration range suggest that Scheme 1 describes the composition of this compound in solution.



(II)

Scheme 1

(I)

The temperature dependence of the spectra of $(MeMgOCPh_2Me)_2$ is easily followed by examination of the +40° to −80° spectra (Fig. 1). At +40° one signal is observed at τ 11.46 which is in the region where methyl groups directly bonded to magnesium atoms absorb

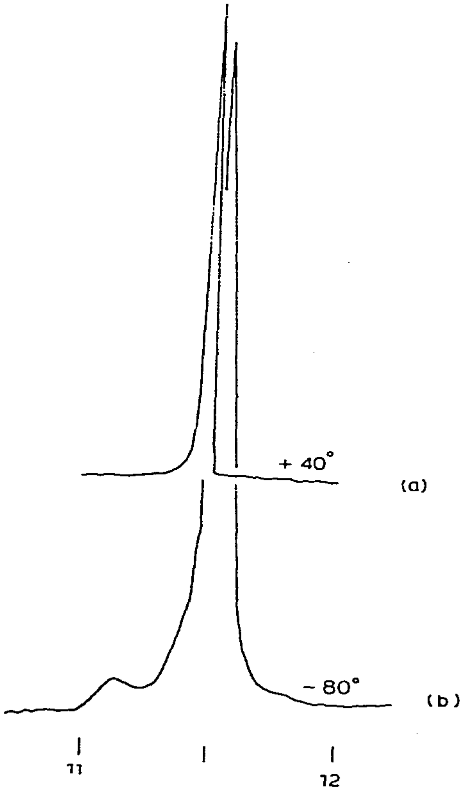
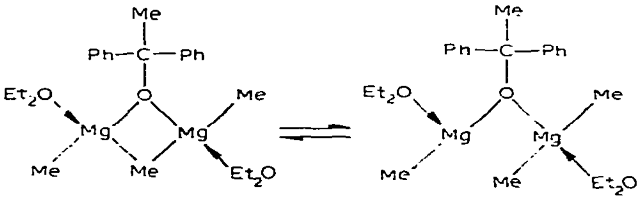


Fig. 1. NMR spectra for $MeMgOCPh_2Me$: (a) +40°; (b) −80°.

Observation of the methyl group attached to the alkoxide carbon atom was not possible due to its absorption in the same region as the spinning side bands and ^{13}C satellite peaks emanating from the solvent peaks. Preliminary work on other methylmagnesium alkoxides show an absorption for the methyl group attached to the alkoxide carbon at approximately τ8, and in a cases a single resonance was observed. Lowering of the temperature to −80° results in two peaks, a minor one at τ11.18 and a major one at τ11.51. Bridging methyl groups characteristically resonate downfield from terminal methyl groups due to the electron deficient bonding of the bridging methyl groups as compared to the normal electron pair bonding of the terminal methyl groups[4,5,6]. Therefore, the τ 11.18 signal represents a deshielded methyl environment and is assigned to the bridging methyl position in structure II. The τ 11.51 signal represents terminal methyl groups and accounts for approximately 95% of all the methyl groups indicatir that the structure of dimeric $MeMgOCPh_2Me$ may be represented almost entirely by I.

Stoichiometric addition of Me_2Mg to $MeMgOCPh_2Me$ forms the new chemical species $MeMgOCPh_2Me{\cdot}MgMe_2$. The association of this compound in diethyl ether in the concentration range of 0.0196–0.098 *M* is monomeric (i = 0.90–1.06) based on the empirical formula $MeMgOCPh_2Me{\cdot}MgMe_2$ suggesting that a new chemical species has indeed formed. The association data and low temperature NMR data (Fig. 2) are consistent with the following model.



(III) (IV)

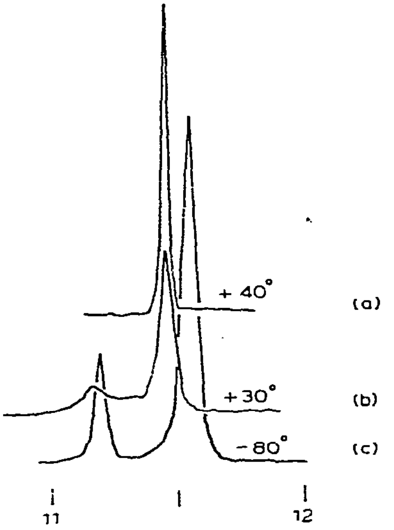
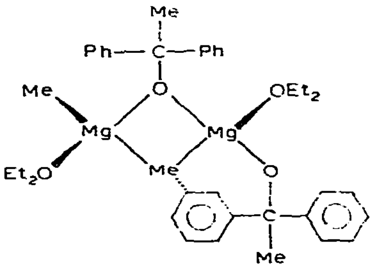


Fig. 2. NMR spectra for $MeMgOCPh_2{\cdot}Me_2Mg$: (a) +40°; (b) +30°; (c) −80°.

At +40° one signal is observed for the Me—Mg resonance at τ 11.48 and again observation of the alkoxide methyl was not possible. At +30° the τ 11.48 signal splits into two signals located at τ 11.16 and 11.48. Lowering of the temperature to −80° resulted in a shifting of the latter two signals to τ 11.24 and 11.56. The signals are assigned to the bridging and terminal methyl groups respectively and have an approximate relative area ratio of 1/4.9 indicating an equilibrium between structures III and IV.

The reason for the lower field absorption of the bridging methyl group in II relative to the bridging methyl group in III may be explained by a deshielding effect of the phenyl groups in the terminal position of structure II.



We also have preliminary evidence for the existence of other alkoxy, alkyl, dialkylamino–alkyl, and hydrido–alkyl mixed bridged organomagnesium compounds in solution.

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