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Chemistry of Metal–Diene Complexes: Identification of Magnesium Methylcuprates in the Reactions of $[(COD)CuBr]_2$ with Dimethylmagnesium and Methyl 'Grignard' Reagents

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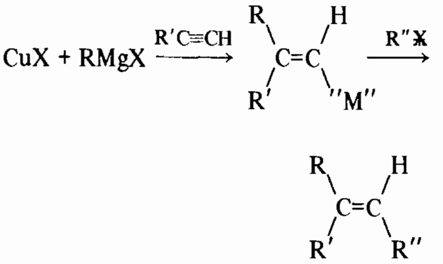
Lithium dialkylcuprates have proven to be very versatile reagents in organic synthesis [1, 2]. Recently, magnesium organocuprate reagents (Normant Reagents) derived from the reaction of Grignard reagents with cuprous halide, have attracted a great deal of interest and have been utilized very imaginatively in organic synthesis [2–6]. For example, a stoichiometric mixture of Grignard reagent and cuprous halide is a versatile reagent for the stereoselective synthesis of trisubstituted alkenes from terminal alkynes (eqn. 1).



$$\mathrm{CuX + RMgX} \xrightarrow{\mathrm{R'C{\equiv}CH}} \begin{matrix} R & & H \\ & C{=}C & \\ R' & & \text{"M"} \end{matrix} \xrightarrow{R''X} \begin{matrix} R & & H \\ & C{=}C & \\ R' & & R'' \end{matrix} \qquad (1)$$

Although the precise composition of this reagent or the identification of the reactive species present in the reaction mixture has not been determined, the Normant reagent has been represented by the formula $RCu{\cdot}MgX_2$.

More recently, in the reaction of $[(COD)CuBr]_2$ (COD = 1,5-cyclooctadiene) with Grignard reagents, formation of new organocuprates, $(COD)R_2CuMgX$, has been claimed, although no evidence for the existence of these complexes was presented [7]. Due to our continuing interest in the chemistry of organocuprates [8] and metal–diene complexes [9], we decided to perform a detailed investigation of the reaction of $[(COD)CuBr]_2$ with Grignard reagents, particularly with MeMgX (where X = Cl, Br and CH_3). Surprisingly, we observed the formation of THF soluble magnesium methylcuprate complexes which contained no halide or cyclooctadiene components, contrary to earlier suggestions. A brief account of our studies is presented here.

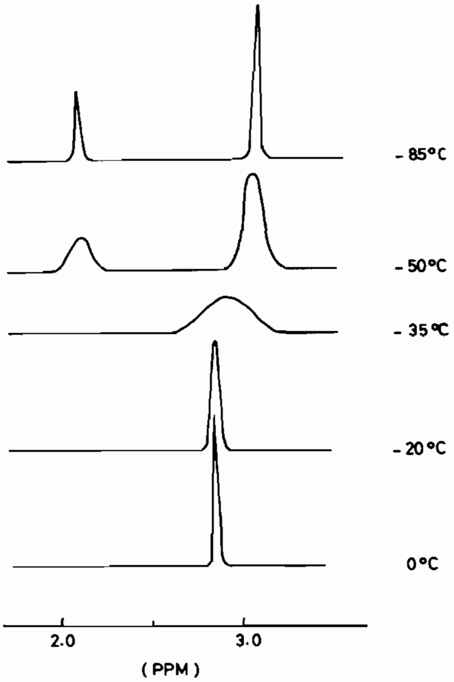


Fig. 1. Variable temperature ^1H NMR of $MgCu_2Me_4$ in THF obtained by reaction of $[(COD)CuBr]_2$, CuBr or MeCu with Me_2Mg or 'MeMgBr' in appropriate ratios. Signal positions are with respect to the THF multiplet.

$$[(COD)CuBr]_2 + 4MeMgBr \rightarrow MgCu_2Me_4 + C_8H_{12} + 3MgBr_2 \qquad (2)$$

When a THF solution of 'MeMgBr' was added to a slurry of $[(COD)CuBr]_2$ in THF in 4:1 molar ratio at dry ice acetone temperature and the reaction mixture allowed to warm to –20 °C with stirring for ≅10 minutes, a clear solution resulted. The ^1H NMR spectrum of this solution at –85 °C showed two singlets in 3:1 ratio upfield from the THF signal at δ 3.04 and 2.08 ppm (with respect to the THF multiplet). The solution was found to be stable at 0 °C for several hours and at –10 °C for at least two days. The solvent of this reaction was removed under reduced pressure at 0 °C and condensed into a separate flask. GlC analysis of the trapped material showed the presence of cyclooctadiene. The residual solid was redissolved in fresh THF and the ^1H NMR spectrum recorded. Interestingly, the spectrum was found to be identical to that of the earlier spectrum, thus further suggesting the non-involvement of cyclooctadiene in the complex. When $[(COD)CuBr]_2$ was treated with Me_2Mg in 1:2 molar ratio at –28 °C

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and the reaction mixture allowed to warm to −20 °C with stirring, again a clear solution resulted within 10 minutes. The ^{1}H NMR spectrum of this solution was found to be identical to that of the above reaction mixture, thus suggesting the formation of the same complex. The ^{1}H NMR spectrum of the reaction mixture (eqns. 2 and 3) were found to be similar to that of the spectrum

$$[(COD)CuBr]_2 + 2Me_2Mg \rightarrow MgCu_2Me_4 + C_8H_{12} + MgBr_2 \quad (3)$$

obtained from the reaction of MeCu with Me_2Mg in 2:1 ratio in THF which produced the THF soluble complex, $MgCu_2Me_4$ (eqn. 4). Variable temperature NMR studies (Fig. 1) showed that the two singlets

$$2MeCu + Me_2Mg \rightarrow MgCu_2Me_4 \quad (4)$$

which appeared at δ 3.04 and 2.08 ppm upfield from THF at −85 °C collapsed into a single peak at temperatures above −30 °C, thus suggesting a rapid exchange process. When $MgCu_2Me_4$ was prepared in dimethylether and the spectrum recorded at −120 °C, no further splitting of the two signals could be observed. Molecular association studies performed at reduced pressure in THF revealed that $MgCu_2Me_4$ is dimeric. This compound in the solid state was found to be thermally stable up to ≅80 °C as observed by vacuum DTA-TGA studies.

Similarly, when $[(COD)(CuBr]_2$ was treated with 'MeMgBR' or Me_2Mg in 1:6 and 1:3 molar ratio respectively in THF at −20 °C, a clear solution resulted in both cases. The ^{1}H NMR spectra recorded at −85 °C were found to be identical to the spectrum obtained for the product of the reaction of MeCu with Me_2Mg in 1:1 molar ratio (singlet upfield to THF at δ 3.34 ppm with respect to the THF multiplet). These results support the formation of a new magnesium–copper 'ate' complex, $MgCuMe_3$ in these three reactions. Molecular association studies suggest that $MgCuMe_3$ is monomeric in THF.

$$[(COD)CuBr]_2 + 6MeMgBr \rightarrow 2MgCuMe_3 + 2C_8H_{12} + 4MgBr_2$$

$$[(COD)CuBr]_2 + 3Me_2Mg \rightarrow 2MgCuMe_3 + 2C_8H_{12} + MgBr_2$$

$$MeCu + Me_2Mg \rightarrow MgCuMe_3$$

$MgCuMe_3$ was found to be stable in THF for over two days at room temperature, and at 0 °C for at least a week.

In conclusion, the above proton NMR results clearly demonstrate that THF soluble magnesium methylcuprate'ate' complexes: $MgCuMe_3$ and $MgCu_2Me_4$ were formed when $[(COD)CuBr]_2$ was allowed to react with Me_2Mg or 'MeMgBr' in an appropriate ratio. Cyclooctadiene and bromide played no detectable role in 'ate' complex formation; the same complexes were formed when freshly prepared CuBr, CuCl or MeCu were allowed to react with Me_2Mg or 'MeMgBr'. The difference in the reactivity of the reagents prepared from $[(COD)CuBr]_2$ and CuBr is probably due to the purity of the starting material. CuBr is known to oxidize rapidly in air whereas $[(COD)CuBr]_2$ is quite stable.

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