Journal of Organometallic Chemistry, 212 (1981) C47—C50
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

CONCERNING THE SOLUTION COMPOSITION OF THE NORMANT REAGENT. NEW THF SOLUBLE METHYL COPPER(I)ATE COMPLEXES BY REACTION OF "CH_3MgBr" AND $(CH_3)_2Mg$ WITH CUPROUS BROMIDE

E.C. ASHBY*, A.B. GOEL and R. SCOTT SMITH

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332 (U.S.A.)

(Received February 25th, 1981)

Summary

The composition of the Normant reagent in THF has been studied resulting in the identification of the species in solution as halogen-free copper-magnesium "ate" complexes of type $Cu_mMg_nMe_{(m+2n)}$ (m = 1, 2, 3, 4, 6; n = 1, 2).

Applications of lithium organocuprate reagents in organic synthesis over the past few years have been the subject of numerous reports [1, 2]. More recently, magnesium organocuprate reagents (Normant reagents) derived from the reaction of Grignard reagents with cuprous halides, have attracted a great deal of interest and have been utilized very imaginatively in organic synthesis [2—6]. However, the precise composition of the Normant reagent or the identification of the reactive species present in the reaction mixture has not been reported. Due to our continuing interest in the chemistry of organocuprates [7], we decided to perform a detailed investigation of the composition of the Normant reagent, particularly the reaction of "MeMgBr" and Me_2Mg with CuX (where X = Cl, Br, I and Me). During our investigation, we observed the formation of several methylmagnesium copper(I)ate complexes depending upon the reaction conditions. Surprisingly, we have noticed no halide component in any of these methylcuprates, contrary to earlier suggestions. A brief account of our studies is presented here.

When "MeMgBr" was allowed to react with CuBr in THF at temperatures ranging from —78 to —30°C, formation of several THF soluble complexes i.e., $CuMgMe_3$, $Cu_3Mg_2Me_7$, Cu_2MgMe_4, Cu_3MgMe_5, Cu_4MgMe_6 and Cu_6MgMe_6, were observed by PMR spectroscopy. At the same time, unreacted cuprous bromide and/or MeCu were observed as insoluble solids. The characterization of these complexes was established by complete elemental analysis of both the solution phase as well as the solid phase of the reaction mixtures at selected

0022-328X/81/0000—0000/$02.50, © 1981, Elsevier Sequoia S.A.

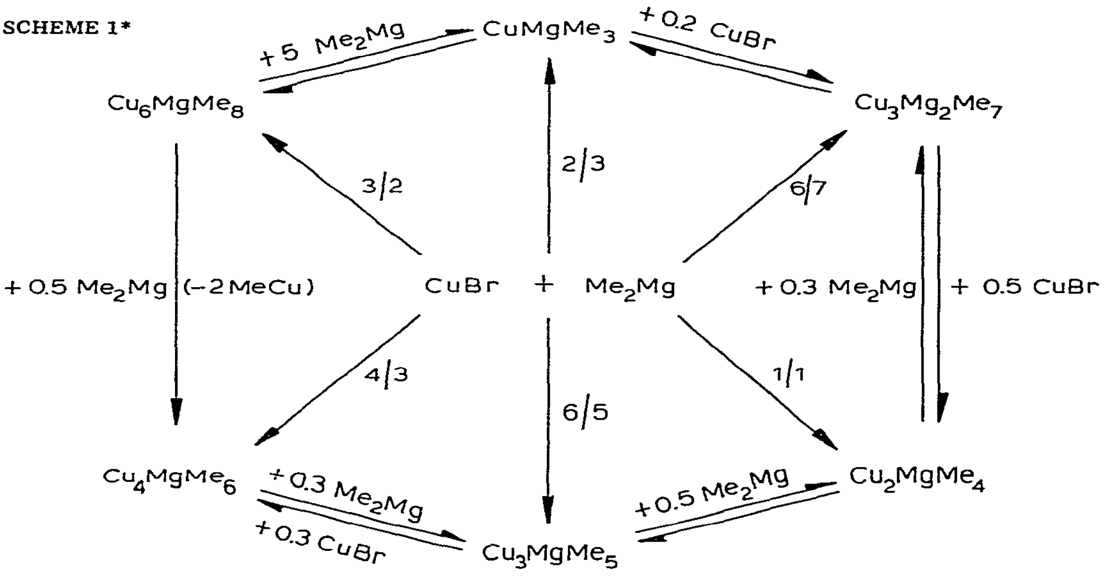
times and intervals and at certain reaction temperatures. The analytical results were then compared to the low temperature NMR spectra of the soluble complexes with those of authentic samples prepared independently by the reactions of cuprous halides or MeCu with Me_2Mg in the appropriate stoichiometry as shown in Scheme 1. The spectrum of each complex, $Cu_mMg_nMe_{(m+2n)}$ (Where $m = 1, 2, 3, 4, 6$ and $n = 1, 2$), matched perfectly with the product prepared by the reaction of Me_2Mg and MeCu in the proper stoichiometry.

Thus, when equimolar amounts of "MeMgBr" and CuBr in THF were mixed at −78°C and the reaction mixture allowed to react at −60°C for about 15—20

$$\text{CuBr} + \text{“MeMgBr”} \rightarrow \text{Products} \tag{1}$$

min., about one-third of the CuBr dissolved, resulting in the formation of soluble $CuMgMe_3$ in addition to free $MgBr_2$. The low temperature NMR spectrum at (−85°C) of this solution showed a singlet at δ 3.34 ppm upfield to the THF multiplet which was found to be identical to the spectrum of the complex prepared from the reaction of CuX (X = Cl, Br, I) or MeCu with Me_2Mg in the ratios 2/3 or 1/1, respectively.

SCHEME 1*



Alternatively, when CuBr and "MeMgBr" in THF were mixed in a 1/3 molar ratio and allowed to react at −30°C for about 5 min, all the CuBr dissolved and $CuMgMe_3$ was formed. On allowing the reaction mixture from eq. 1 to stand for approximately 0.5 h at −60°C, about 30% more CuBr dissolved. The stoichiometry and the PMR spectrum of the solution were found to be consistent with the formulation of $Cu_3Mg_2Me_7$. Similarly, allowing this reaction mixture to react further by warming to −50 and −40°C, in time other complexes i.e., Cu_2MgMe_4, Cu_3MgMe_5 and Cu_4MgMe_6 were generated as more CuBr went into

---

*$CuMgMe_3$ trhough Cu_6MgMe_8 also prepared from two mole equivalents of "MeMgBr" in place of Me_2Mg.

solution. It is important to mention here that at certain times, in solution one may find a mixture of two complexes observable by NMR. By integration of the NMR spectrum and elemental analysis of the solution and the solid, the relative amounts of each complex can be determined.

In the course of reaction 1, at —30° C, there was a time when over 75% of the CuBr was in solution giving a clear, very light yellow colored solution of Cu_6MeMe_8. However, this complex at —30° C persisted only a few minutes and then MeCu precipitated from solution. After 15 min, the solution contained Cu_4MgMe_6 and Cu_6MgMe_8 in about 6/1 ratio. The observation was better understood when we examined the nature of Cu_6MgMe_8 prepared separately by the reaction of CuBr with Mg_2Mg in 3/2 ratio. We found that Cu_6MgMe_8 had a tendency to disproportionate in the presence of a small amount of CuBr and also by itself on dilution to give insoluble MeCu leaving behind Cu_4MgMe_6 in solution (eq. 2). The amount of insoluble MeCu increased slowly as the reaction proceeded. This observation can be explained on the basis of the reaction of Cu_4MgMe_6 with remaining unreacted CuBr to form Cu_6MgMe_6 which in turn disproportionates to give MeCu and Cu_4MgMe_6. After the reaction of CuBr and

$$Cu_6MgMe_8 \rightleftharpoons 2MeCu + Cu_4MgMe_6 \qquad (2)$$

"MeMgBr" proceeded for 1 h at —30° C, only about 30% of the copper as Cu_4MgMe_6 and Cu_6MgMe_8 (in 6/1 ratio) was found in solution and the insoluble solid contained mainly MeCu contaminated with magnesium ($\leqslant$ 10%) and the remaining unreacted CuBr. After ~ 2 h reaction, it appeared that equilibrium was reached and approximately 20% of the copper was in solution. However, on adding a small amount of "MeMgBr" or Me_2Mg, more copper was formed in solution.

In the reactions of CuBr with either "MeMgBr" or Me_2Mg, we have found in solution the same complexes, $Cu_mMg_nMe_{(m+2n)}$. The only observable difference between Me_2Mg and "MeMgBr" reaction is that Me_2Mg reacted at a faster rate than "MeMgBr". These complexes can be prepared halide free from the reaction of MeCu with Me_2Mg, however, the reactions to prepare Cu_3MgMe_5 and higher copper containing complexes, are slow probably because of the loss of the reactivity of MeCu, once isolated. The reactivity among the cuprous halides followed the trend CuCl > CuBr > CuI*.

All the cuprates reported here are soluble in THF and are reasonable stable at low temperature. The solubility and the stability in solution decreases as the Cu/Mg ratio increases and follows the sequence $CuMgMe_3 > Cu_3Mg_2Me_7 > Cu_2MgMe_4 > Cu_3MgMe_5 > Cu_4MgMe_6 > Cu_6MgMe_8$. PMR spectra of all the complexes show only one peak at the highest temperature of their stability indicating a rapid methyl group exchange, however upon cooling to approximately —50° C this exchange can be stopped where splitting of the signals is observed (Table 1). The spectra at —85° C, show sharp signals. However, in order to ascertain the absence of an exchange process, dimethyl ether was introduced in order to make it possible to obtain spectra at —120° C where no further splitting in the signals was observed. Molecular association studies performed under reduced

---

*By means of kinetic studies comparing the reaction rates of copper(I)ate complexes and the Normant reagents with 1-alkynes, we have determined the reactive copper species responsible for addition to the triple bond. These results will be reported shortly.

TABLE 1

PROPERTIES OF SOLUTIONS OF "ATE" COMPLEXES

Complex	^{1}H NMR (−85°C) (ppm, upfield from THF)	Ratio of signals	Stability
CuMgMe$_3$	3.34(s)		Stable at room temp. over 2 days; at 0°C, more than 4 weeks
Cu$_3$Mg$_2$Me$_7$	3.33(s), 2.21(s)	3/1	Stable at room temp. over one day; at 0°C, more than a week
Cu$_2$MgMe$_4$	3.04(s), 2.08(s)	3/1	Stable at room temp. for a few hours; at −10°C for 2 days
Cu$_3$MgMe$_5$	3.03(s), 2.07(s)	5/2	Stable at −25°C for 1 day
Cu$_4$MgMe$_6$	3.03(s), 2.06(s)	2/1	Stable at −25°C for 10 h
Cu$_6$MgMe$_8$	3.03(s), 2.18(s), 2.06(s)	2/1/1	Stable below −40°C for a few hours with dissociation into MeCu and Cu$_4$MgMe$_6$

pressure in THF reveals that CuMgMe$_3$ and Cu$_3$Mg$_2$Me$_7$ are monomeric whereas Cu$_2$MgMe$_4$ is dimeric. Molecular weights of the other complexes could not be carried out successfully due to their instability above 0°C.

References

1 J.F. Normant, Synthesis, 63 (1972); G.H. Posner, Org. Reaction, 19 (1972) 1; G.H. Posner, Org. Reaction, 22 (1975) 253; H.O. House, Accounts Chem. Res., 9 (1976) 60.

2 J.F. Normant and D. Seyferth (Eds.), Organo-copper Reagents in Organic Synthesis, in New Applications of Organometallic Reagents in Organic Synthesis, Elsevier, Amsterdam, 1976, p. 219 (J. Organometallic Chem. Literary 1).

3 J.K. Crandall and F. Collonges, J. Org. Chem., 41 (1976) 4089.

4 D.E. Bergbreiter and J.M. Killough, J. Org. Chem., 41 (1976) 2750.

5 A. Martat , P.R. McGuirk and P. Helquist, J. Org. Chem., 44 (1979) 3888 and ref. therein.

6 M.T. Rahman, A.K.M.M. Hogue, I. Siddique, D.A.N. Chowdhury, S.K. Nahar and S.L. Sahar, J. Organometal. Chem., 188 (1980) 293.

7 E.C. Ashby and J.J. Watkins, J. Amer. Chem. Soc., 99 (1977) 5312; E.C. Ashby and J.J. Lin, J. Org. Chem., 42 (1977) 2805; E.C. Ashby, J.J. Lin and J.J. Watkins, J. Org. Chem., 42 (1977) 1099.