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ORGANOMAGNESIUM–ORGANOALUMINUM COMPLEXES

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Summary

Preparation of hydrocarbon-soluble complexes of diorganomagnesium compounds has been studied. Organoaluminum compounds were added to the reaction products of organic halides with magnesium in hydrocarbon. After filtration of the reaction mixtures, the resultant solutions of complexes were typically clear, colorless, and mobile, and contained negligible soluble halide when organic chlorides were employed as starting materials. Diorganomagnesium compounds constituted from 50 to 95 mole percent of organometallics in solution. Maximum isolated yields of solubilized diorganomagnesium compounds ranged from 60 to 77%. Proton NMR analysis showed that alkyl group exchange occurs between the organoaluminum and organomagnesium compounds. Cryoscopic molecular weight determinations indicate that the state of association increases as the magnesium/aluminum ratio in the complex increases.

Introduction

Complexes between magnesium alkyls and aluminum alkyls have been known since 1957. Ziegler and Holzkamp [1] prepared and characterized complexes of the types $RMg(AlR_4)$ and $Mg(AlR_4)_2$ wherein R was methyl or ethyl. Unlike pure Me_2Mg and Et_2Mg, the complexes exhibited high solubility in hydrocarbons. The complexes were prepared by reaction of R_3Al with Grignard reagents from which ether had been removed.

In order to determine crystal structures, Atwood and Stucky [2] prepared Me_5AlMg and Me_8Al_2Mg, i.e., the 1/1 and 1/2 complexes of Me_2Mg with Me_3Al. The complexes, prepared by direct reaction of Me_3Al with Me_2Mg, possessed significantly different properties than those reported by Ziegler and Holzkamp. This may be attributable to incomplete removal of ether from the Grignard reagents employed by Ziegler and Holzkamp.

This paper reports the results of an expanded investigation of complexes involving diorganomagnesium compounds and aluminum alkyls employing a more convenient synthetic approach.

Results and discussion

Complexes of organomagnesium compounds were prepared by interaction of aluminum alkyls with the reaction products of organic halides with magnesium in hydrocarbon media as in eqn. 1.

$$2RX + 2Mg \rightarrow R_2Mg\downarrow + MgX_2\downarrow \xrightarrow{R'_3Al} (R_2Mg)\cdot(R'_3Al) \quad (1)$$

The aluminum alkyls rendered normally insoluble organomagnesium compounds highly soluble in hydrocarbon via complex formation.

Product solution was isolated from by-product magnesium halide by filtration, although in some cases, yield was determined by analysis of the supernatant of centrifuged aliquots from the reaction mixture. Magnesium/aluminum ratios in the complexes ranged from 1 to about 20 depending upon the nature of the organomagnesium compound and the aluminum alkyl solubilizing reagent. Complexes prepared from organic chlorides showed only trace quantities of soluble chloride (< 0.1%), but the amount of soluble halide was significant when alkyl bromides or iodides were used as reactants. Maximum yields of solubilized R_2Mg compounds ranged from 60-77% while organoaluminum solubilizing agents were recovered typically in 90-99% yields. Use of fine magnesium powder (100 to 325 mesh) gave maximum yields of R_2Mg. Magnesium turnings or coarse mesh powder gave poor yields of R_2Mg. Results are summarized in Table 1. In cases where the aluminum alkyl solubilizing agent is relatively unreactive toward the organic halide employed, e.g., ethyl and phenyl halides, the organoaluminum compound may be present during the RX—Mg reaction. n-Butyl chloride, however, is reactive toward aluminum alkyls undergoing a complex set of reactions [3] and hence, the solubilizing agent must be added after the BuCl—Mg reaction is completed.

In eqn. 1 and throughout the following discussion, the complexes are presented for the sake of simplicity as if discrete complexes form between R_2Mg and R'_3Al. Actually, the complexes undergo alkyl group exchange resulting in a complex mixture. Evidence for this is as follows. Proton NMR analysis of a n-Bu_2Mg/n-Bu_3Al complex (Mg/Al = 5) at 37°C shows a broad unresolved absorption centered at about τ10.1. Similar results were obtained with a n-Bu_2Mg/Et_3Al complex (Mg/Al = 4). Other than a gradual broadening of the absorption in the organometallic region, little change in the spectra was observed as the temperature was lowered to —60°C. Since the absorption due to CH_2—Al in pure n-Bu_3Al occurs as a well-resolved multiplet at τ9.58 [4], and the triplet due to CH_2—Mg in pure n-Bu_2Mg (in cyclohexane—ether, 98/2) absorbs at τ10.15 [5], the observed broad unresolved resonances in the organometallic region indicate that alkyl group exchange is taking place (albeit slowly on the NMR time scale) resulting in several magnetically non-equivalent environments for the alkyl groups.

Diethylmagnesium and triethylaluminum formed complexes with magnesium/aluminum ratios of 1 to 1.5. In some cases, product solutions of $Et_2Mg\cdot Et_3Al$ complexes appeared to be metastable, particularly those which had magnesium/aluminum ratios greater than one or high concentrations (⩾ 40%) of complex. These solutions are initially clear and colorless but gradually assume

TABLE 1

PREPARATION OF ORGANOMAGNESIUM—ORGANOALUMINUM COMPLEXES

Reactants[a]			Product solution analyses			
RX (mol)	Mg[b] (mol)	R_3Al (mol)	% yield[c] R_2Mg	% recovery R_3Al	Wt% R_2Mg	Mg/Al atomic ratio
EtCl[d] (2.728)	3.27	Et_3Al (0.313)	30	93	2.2	1.4
EtCl[d] (2.90)	3.60	Et_3Al (0.37)	34[e]	90[e]	5.6	1.5
EtCl[d] (2.59)	3.13	Et_3Al (0.828)	60	92	11.7	1.0
EtBr[f] (0.407)	0.489	Et_3Al (0.084)	38	92	6.6	1.1[g]
EtBr[f] (1.011)	1.205	n-Bu_3Al (0.067)	43[e]	90[e]	11.0	3.5
EtI[h] (0.209)	0.242	Et_3Al (0.052)	50	82	6.2	1.2[i]
n-BuCl (0.20)	0.24	Et_3Al (0.017)	60	93	14.7	3.8
n-BuCl (1.93)	2.40	Et_3Al (0.385)	67	99	11.3	1.7
n-BuCl (5.98)	7.27	Et_3Al (0.439)	77	87	20.7	6.1
n-BuCl (6.13)	7.36	Et_3Al (0.425)	68	70	18.6	6.7
n-BuCl (1.01)	1.39	Et_3Al (0.018)	26	—[j]	9.0	20.0[k]
n-BuCl (1.00)	1.23	Et_3Al (0.016)	19	—[j]	10.1	20.0[k]
n-BuCl (0.402)	0.489	Et_2AlOEt (0.159)	59[e]	90[e,l]	16.0	0.8
n-BuCl (1.01)	1.22	Et_2AlOEt (0.139)	76[e]	90[e,l]	18.5	3.0
n-BuCl (1.99)	2.39	i-Bu_3Al (0.354)	65	93	12.4	2.0
n-BuCl (4.14)	4.81	i-Bu_3Al (0.741)	58	86	13.5	2.0
n-BuCl (4.13)	4.81	i-Bu_3Al (0.732)	66	96	18.3	2.0
n-BuCl (0.40)	0.48	i-Bu_3Al (0.028)	33[e]	90[e]	10.3	2.7
n-BuCl (4.09)	4.85	i-Bu_3Al (0.608)	55	90	13.7	2.0
n-BuCl (0.40)	0.48	TIHAL[m] (0.028)	63[e]	90[e]	39.3[n]	5.7
n-BuCl[f] (2.00)	2.41	n-Bu_3Al (0.207)	56[e]	90[e]	13.3	3.0
PhCl (0.192)	0.243	Et_3Al (0.073)	62	90	11.2	0.9
PhCl[p] (0.193)	0.243	Et_3Al (0.075)	70	90	12.5	1.0
PhCl (0.215)	0.243	Et_3Al (0.051)	53	83	12.6	1.4

(continued)

TABLE 1 (cont'd)

[a] Reaction of RX with Mg for 2-4 h at reflux temperature of heptane unless otherwise noted; solubilization step conducted at 70-100°C except with heat sensitive organoaluminum compounds, e.g. triisobutylaluminum.

[b] Usually present in 16-24% excess.

[c] Isolated yield determined from analysis of filtered solutions unless otherwise noted. Yield based on alkyl halide.

[d] Reaction conducted in an autoclave at 77-98°C. Optimum yield realized by allowing 16 h for EtCl—Mg reaction.

[e] Reaction mixture not filtered; estimated yield based on analysis of clear supernatant assuming 90% recovery of R_3Al.

[f] Hexane solvent.

[g] Product solution contained ca. 0.8% soluble bromide.

[h] Cyclohexane solvent.

[i] Product solution contained ca. 2.3% soluble iodide.

[j] Indeterminate by direct titration owing to dilute concentration of R_3Al.

[k] Organometallic composition in solution determined by GC analysis of hydrolysis gas.

[l] Analysis showed essentially no loss of alkoxide.

[m] TIHAL = tris(2-methylpentyl)aluminum.

[n] Sample concentrated by partial evaporation of solvent; solution remained clear even at this concentration.

[p] Toluene solvent.

an opaque, milky appearance due to precipitation of solids. Although Et_2Mg and Et_3Al apparently form a specific 1/1 complex, n-Bu_3Al is able to solubilize at least 3.5 mole-equivalents of Et_2Mg.

Di-n-butylmagnesium formed complexes with Et_3Al, n-Bu_3Al and tris(2-methylpentyl)aluminum with Mg/Al ratios ranging as high as 20, i.e., n-Bu_2Mg constituted as much as 95 mole percent of the organometallic species in solution, although n-Bu_2Mg prepared from n-butyl chloride is normally insoluble in hydrocarbons*. The solutions were clear and colorless and were completely mobile**. even in concentrations as high as 40-50%. Determinations on 25% solutions of n-Bu_2Mg complexes in heptane showed viscosities of only 1-2 centipoise at ambient temperature.

Unlike other trialkylaluminum compounds investigated, triisobutylaluminum solubilizes only about 2-3 mole-equivalents of n-Bu_2Mg, even in the presence of excess unsolubilized n-Bu_2Mg. This was especially surprising in view of the results with the structurally similar tris(2-methylpentyl)aluminum, which can solubilize at least 5.7 mole equivalents of n-Bu_2Mg under identical reaction conditions and stoichiometry.

Although maximum isolated yields of n-Bu_2Mg compounds ranged from 60-77%, considerably lower yields are obtained when preparation of n-Bu_2Mg complexes with greater than 90 mole percent n-Bu_2Mg in solution is attempted. The maximum amount of n-Bu_2Mg available in solution without sacrificing yield, appears to be about 86-87% mole percent, or a magnesium/aluminum ratio of ca. 6-7.

Use of dialkylaluminum chloride compounds as solubilizing agents results in alkylation by the magnesium alkyl as in eqn. 2. Any excess magnesium dialkyl is then solubilized by the unsymmetrical aluminum alkyl (eqn. 3). For

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* Solutions of "n-Bu_2Mg" in hydrocarbons can be prepared from n-butyl bromide or iodide and magnesium, but these solutions contain significant amounts of magnesium halide [6].

** Pure di-n-alkylmagnesium compounds (C_5 and above) exhibit some solubility in hydrocarbon solvents, but the solutions (ca. 0.1 to 0.3 *M*) are highly viscous and difficult to handle [6].

example, diethylaluminum chloride was added to an equimolar amount of n-Bu_2Mg. Analysis of the clear supernatant showed no chloride ($< 0.1\%$) and a magnesium/aluminum ratio of 0.46. Gas chromatographic analysis of the hydrolysis gas showed 52 mole percent ethane and 48 mole percent n-butane indicating information of the complex n-$Bu_2Mg \cdot 2\ Et_2Al$ n-Bu (theoretical values: Mg/Al = 0.5; hydrolysis gas composition of 50 mole % n-butane and 50 mole % ethane). Dialkylaluminum hydrides acted similarly, although the precipitation of MgH_2 was much slower than for $MgCl_2$. In contrast to organoaluminum chlorides and hydrides, use of alkylaluminum alkoxides afforded good yields of complexes. Diethylaluminum ethoxide was employed as solubilizing agent for n-Bu_2Mg in two experiments with essentially no loss of ethoxide.

$$2\ R'_2AlCl + R_2Mg \rightarrow 2\ R'_2AlR + MgCl_2\downarrow \qquad (2)$$

$$R_2Mg + R'_2AlR \rightarrow (R_2Mg)\cdot(R'_2AlR) \qquad (3)$$

Preparation of complexes between diphenylmagnesium and Et_3Al was briefly studied. Like Et_2Mg, diphenylmagnesium apparently formed a specific 1/1 complex with Et_3Al. Phenyl chloride and magnesium required a long reaction time (16 h) and a reaction temperature of 100-110°C for maximum yields. The resultant solutions were pale yellow and clear, although slow precipitation of crystalline solids from the filtered solutions was sometimes noted.

Most of the complexes prepared in this study were stable indefinitely. A 20% solution of 2(n-Bu_2Mg)$\cdot$(i-Bu_3Al) was re-analyzed after 6 months storage at ambient temperatures and showed no loss of soluble magnesium or aluminum. Similar results were obtained with a 39% solution of (Et_2Mg)$\cdot$(Et_3Al) complex in heptane which had been in storage for 32 months.

Molecular weights were determined for complexes of n-Bu_2Mg and triethylaluminum having various Mg/Al ratios over the range of 1-10. Vacuum stripping of solvent and n-octane by-product (Wurtz coupling) gave a clear, mobile liquid for the 1/1 complex, a viscous liquid for the 3/1 complex, a white, waxy semisolid for the 6/1 complex, and a dry, white powder for the 10/1 complex. The isolated complexes were redissolved in cyclohexane for molecular weight determinations and the results are summarized in Table 2.

At a Mg/Al ratio of 1, the molecular weight approaches the calculated value of 504 for a 1/1 complex of dimeric n-Bu_2Mg and dimeric Et_3Al possibly associated as shown below. Fig. 1 illustrates graphically the manner in which

TABLE 2

CRYOSCOPIC MOLECULAR WEIGHT DETERMINATIONS[a] FOR n-$Bu_2Mg \cdot Et_3Al$ COMPLEXES

Mg/Al atomic ratio	Observed molecular weight
0	229
1.1	538
2.8	820
5.9	1210
10.1	1650

[a] Cyclohexane solvent.

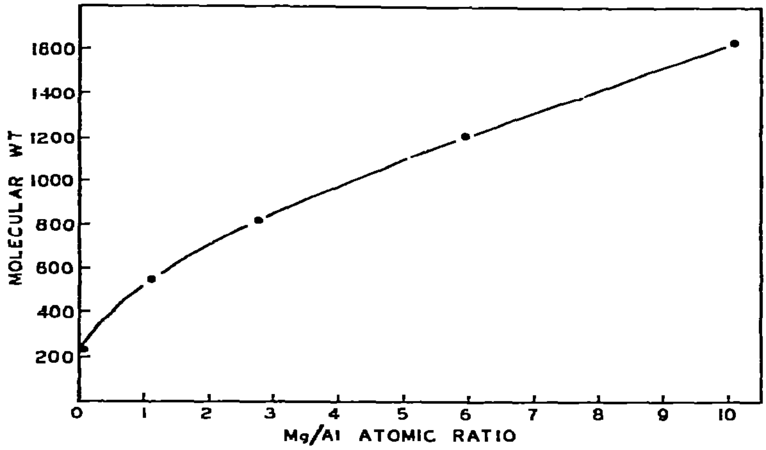
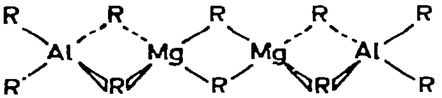


Fig. 1. Molecular weight of n-$Bu_2Mg \cdot Et_3Al$ complexes versus Mg/Al atomic ratio.

the apparent molecular weight increases as the Mg/Al ratio increases.



The ability of small quantities of aluminum alkyls to render n-Bu_2Mg soluble in hydrocarbon may be explained as follows. The lower magnesium alkyls (C_1-C_3 and n-C_4) exist as highly associated polymers [7] (solids) and for this reason are virtually insoluble in hydrocarbons. However, magnesium alkyls in which the organic radicals possess large steric bulk cannot associate beyond the dimeric state [8]. Thus, s-Bu_2Mg and t-Bu_2Mg are completely miscible in all proportions with hydrocarbons [8]. The findings in this study indicate that aluminum alkyls, which are largely dimeric [9], interact with polymeric n-Bu_2Mg through complex formation, reducing the magnesium alkyl to smaller oligomeric units (eqn. 4) which are soluble in hydrocarbon.

$$(\text{n-Bu}_2\text{Mg})_x \xrightarrow{R_3Al} x/y\,(\text{n-Bu}_2\text{Mg})_y \qquad (x \gg y) \qquad (4)$$

Experimental

Reagents. Organic halides were reagent grade and dried over 4A Molecular Sieves before use. Magnesium powder (100, 200, and 325 mesh) was obtained from Reade Manufacturing Co. Hydrocarbon solvents were high purity and were dried to less than 20 ppm water (by Karl Fisher analysis) with Molecular Sieves (4A). Organoaluminum compounds used were commercial products of Texas Alkyls, Inc. and were used without further purification.

Analytical. Aluminum and magnesium were determined by EDTA titration of the aqueous portion of hydrolyzed samples at pH 4.5 and 10 respectively. Aluminum was masked by triethanolamine when determining magnesium. Eriochrome Black T was used as indicator for magnesium and dithizone for aluminum. Halide determination employed the standard Volhard procedure. Gas chromatographic analysis of the hydrocarbon gas produced upon hydrolysis utilized the procedure of Watson, Mudry and Philipp [10]. Ethoxide content was determined by GC analysis of the aqueous phase resulting from hydrolysis with distilled water using 2-propanol as internal standard. Proton NMR spectra were recorded on a Varian A-60 spectrometer.

Molecular weights were determined cryoscopically in cyclohexane (K_f = 20.0) using a Philadelphia differential thermometer inserted through a rubber serum cap into a nitrogen-blanketed tube. A confidence limit was established by determining molecular weights of the following known dimers with the found results followed by calculated values in parentheses: $[(CH_3)_3Al]_2$, 143 (144); $[(C_2H_5)_3Al]_2$, 229 (228); and $[(C_2H_5)_2AlCl]_2$, 241 (241). Cyclohexane solutions of the magnesium—aluminum alkyl complexes supercooled as much as 0.5°C, even with vigorous agitation. Intersection of the slopes of the freezing point curves usually gave values that agreed within 0.1°C with the melting points and the results were averaged.

Preparation of the n-Bu_2Mg—Et_3Al complex. The following experiment illustrates the general procedures used in the preparation of complexes. To a nitrogen-purged 5 l Morton flask equipped with a 500 ml pressure-equalizing addition funnel, thermometer well, reflux condenser, and mechanical stirrer were charged 176.7 g (7.27 mol) of 100 mesh magnesium powder and 3 l of high purity (99 mole percent) n-heptane dried to less than 10 ppm water (by Karl Fisher Analysis). A few crystals (0.2 g) of iodine and 4 g of n-butyl chloride were added for initiation. The reaction mixture was then heated to reflux. Initiation occurred within 30 min, after which the remainder of the n-butyl chloride was added dropwise over a 3.5 h period. A total of 554.0 g (5.98 mol) of n-butyl chloride was added while maintaining the pot temperature at 97.8-99.1°C. External heat was required during the addition of the last half of the n-butyl chloride. A total of 50.1 g (0.439 mol) of triethylaluminum was added and the mixture was heated to 85-95°C for 2 h. Filtration of the total reaction mixture through a fritted glass filter funnel under nitrogen afforded a clear, colorless filtrate. The grey solids from the reaction mixture were washed with approximately 1 l of n-heptane and the wash combined with the filtrate. The solution was then concentrated by distillation of approximately 1 l of n-heptane. Analysis of the solution (1537 g) at this point showed no chloride (< 0.1%), 3.64% magnesium (or 1.09 *M*), and 0.68% aluminum (or 0.18 *M*), or Mg/Al = 5.98. The yield of solubilized n-Bu_2Mg was 77% based on n-butyl chloride, and the charged Et_3Al was 87% recovered. Gas chromatographic analysis of the gas resulting from hydrolysis of the complex revealed the following composition (normalized mole percent): 19.7% ethane, 80.2% n-butane. Theoretically a 6/1 complex of n-Bu_2Mg and Et_3Al contains 20% ethane and 80% butane.

Isolation of n-Bu_2Mg—i-Bu_3Al complex (Mg/Al = 2). 56.0 g of a (n-Bu_2Mg)·(i-Bu_3Al) (Mg/Al = 2) complex in n-heptane was vacuum stripped at 50 torr initially, and 0.3 torr overnight to remove last traces of solvent. Pot temperature was kept near ambient during stripping to avoid possible decomposition. A total of 15.0 g of a white, syrupy semi-solid (approx. density 0.84 g/cm^3) was isolated which analysis showed to contain 9.7% magnesium and 5.6% aluminum (theory for 2(n-Bu_2Mg)·(i-Bu_3Al): 10.23% magnesium and 5.67% aluminum). Analysis by GC of the hydrolysis gas showed 59.4 mole percent n-butane and 39.4 mole percent isobutane with the remainder being small amounts of hydrogen, methane, ethane, 1-butene and isobutylene (theory for $n\text{-}Bu_2Mg\cdot i\text{-}Bu_3Al$ (Mg/Al = 2): 59.14 mole percent n-butane and 42.86 mole percent isobutane). The complex was reactive with air but did not ignite, and reacted explosively with water. The complex redissolved in hexane with essentially no insoluble residue.

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