THE PREPARATION OF ORGANOMAGNESIUM FLUORIDES BY ORGANOMETALLIC EXCHANGE REACTIONS AND THE COMPOSITION IN SOLUTION OF ALKOXY(METHYL)MAGNESIUM AND DIALKYLAMINO(METHYL)MAGNESIUM COMPOUNDS

A THESIS

Presented To

The Faculty of the Graduate Division

by

John A. Nackashi

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

In the School of Chemistry

Georgia Institute of Technology

May, 1974

THE PREPARATION OF ORGANOMAGNESIUM FLUORIDES BY ORGANOMETALLIC EXCHANGE REACTIONS AND THE COMPOSITION IN SOLUTION OF ALKOXY(METHYL)MAGNESIUM AND DIALKYLAMINO(METHYL)MAGNESIUM COMPOUNDS

Approved:

E. C. Ashby, Chairman

A. Bertrand

C. L. Liotta

Date approved by Chairman: 7/13/74

ACKNOWLEDGMENTS

The author is grateful to Dr. E. C. Ashby for his guidance, direction and patience during this research. The reading of this thesis by Dr. A. Bertrand and Dr. C. Liotta is greatly appreciated. The author is also indebted to John P. Oliver for his assistance and friendship, and to the members of the research group who made the successes of this research a joy and the failures acceptable. The warm friendship expressed by the research group will always be cherished.

Financial assistance by the Georgia Institute of Technology and the National Science Foundation is gratefully acknowledged.

The author acknowledges a special appreciation to his parents and particularly his wife, Bryan. Their gentle encouragement and patient understanding throughout the entire period of study has made this thesis possible.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF ASSOCIATION PLOTS

LIST OF SPECTRA

SUMMARY

PART I

THE PREPARATION OF ORGANOMAGNESIUM FLUORIDES BY ORGANOMETALLIC EXCHANGE REACTIONS

Methyl-, ethyl-, and phenylmagnesium fluoride were prepared in high yield by the reactions of dimethyl-, diethyl-, and diphenylmagnesium with boron trifluoride diethyl etherate in tetrahydrofuran. Borane-free hexylmagnesium fluoride in diethyl ether was also prepared by this method, but only in low yield.

Methylmagnesium fluoride was readily prepared from dimethylmagnesium and silicon tetrafluoride in tetrahydrofuran; however, i-propylmagnesium fluoride could not be prepared from silicon tetrafluoride.

Tri-n-butyltin fluoride was allowed to react with di-n-butyl- and diphenylmagnesium in tetrahydrofuran. n-Butylmagnesium fluoride was prepared in 100% yield; however, phenylmagnesium fluoride was prepared in only 50% yield.

n-Butylmagnesium fluoride was prepared in 60% yield by the reaction of di-n-butylmagnesium and triphenylsilicon fluoride in tetrahydrofuran. The reaction between diphenylmagnesium and triphenylsilicon fluoride in tetrahydrofuran

resulted in a 100% yield of phenylmagnesium fluoride.

Tin tetrafluoride was found to be an ineffective fluorinating agent when allowed to react with diphenylmagnesium in tetrahydrofuran.

Aluminum free ethylmagnesium fluoride could not be prepared by the reaction of diethylmagnesium and diethylaluminum fluoride in benzene, hexane or tetrahydrofuran.

PART II

THE COMPOSITION IN SOLUTION OF ALKOXY(METHYL)MAGNESIUM AND DIALKYLAMINO(METHYL)MAGNESIUM COMPOUNDS

Molecular association and variable temperature NMR studies on a series of alkoxy(methyl)magnesium and dialkylamino(methyl)magnesium compounds in diethyl ether were carried out. It was observed that the degree of association is a function of the size of the bridging group and that as the size of the bridging group decreased, the molecular association increased. For the methylmagnesium alkoxides, $MeMgOCPh_2Me$ was the least associated and $MeMgOPr^n$ was the most highly associated. For the dialkylamino(methyl)magnesium compounds, diphenylamino(methyl)-magnesium was the least associated and di-i-propylamino-(methyl)magnesium was the most highly associated. In all cases, the addition of an equimolar quantity of Me_2Mg to the associated compounds resulted in a complex. Low tem-

perature NMR data indicated that the composition of the alkoxy(methyl)magnesium and dialkylamino(methyl)magnesium compounds in solution varied with the temperature.

PART I

THE PREPARATION OF ORGANOMAGNESIUM FLUORIDES BY ORGANOMETALLIC EXCHANGE REACTIONS

CHAPTER I

INTRODUCTION

Background

For many years chemists have been interested in the preparation of organomagnesium fluorides; however, all attempts to synthesize this class of Grignard reagents failed. In 1921 Swarts[1] reported the first attempt to prepare an organomagnesium fluoride by the reaction between amyl fluoride and iodine-activated magnesium in diethyl ether. Decane and magnesium fluoride were produced after one hundred hours of reflux. Schiemann and Pillarsky[2] reported in 1931 that phenylmagnesium fluorides could not be prepared by the reaction of magnesium with fluorobenzene or its o-methyl or p-nitro derivatives. During the same year Gilman[3] and Heck reported that a small quantity of biphenyl was formed when fluorobenzene and magnesium were allowed to react without solvent in a sealed tube at 300°C for two hundred hours. Gilman in 1930 reported the sealed tube reaction of fluorobenzene with an activated magnesium-copper alloy in diethyl ether at room temperature. After six months, no active organomagnesium compound was formed, but after eighteen months the color test for an active reagent was positive.[4] Several pathways directed toward the preparation of benzylmagnesium

fluoride were investigated by Bernstein and co-workers.[5] They found that benzyl fluoride and magnesium did not react in refluxing diethyl ether solvent and that the reaction was not activated by the addition of phenylmagnesium bromide or iodine crystals. The use of di-n-butyl ether and more vigorous reaction conditions resulted in polymerization of the benzyl fluoride. It was also observed that the reaction between benzyl fluoride and activated magnesium in an autoclave at 100° for ten days resulted in a coupling reaction producing bibenzyl. In 1969 Respess and Tamborski[6] reported a series of reactions which suggested the intermediacy of perfluoroarylmagnesium fluorides. These workers examined the reaction of perfluoroaryl compounds with two molar equivalents of ethylmagnesium bromide in tetrahydrofuran with a catalytic amount of certain transition metal halides. They also allowed hexafluorobenzene in THF and in diethyl ether to react with magnesium and an equimolar quantity of ethylene bromide. The hydrolysis of the reaction product produced pentafluorobenzene, which can be accounted for by assuming the intermediate formation of perfluorophenylmagnesium fluoride; however, the formation of this intermediate product was neither suggested nor established.

Before the report by Respess and Tamborski, workers in our laboratory had prepared organomagnesium fluorides for the first time by reaction of alkyl fluorides with magnesium in ether solvents employing catalysts.[7] It was found that

the reaction rate was dependent on the solvent, reaction temperature and catalyst. The most effective solvents were tetrahydrofuran and dimethoxyethane and the most effective catalyst was iodine. Under the most favorable conditions, fluorobenzene and benzyl fluoride would not react with magnesium. The composition in solution of the alkylmagnesium fluorides was also examined. Whereas alkylmagnesium chlorides, bromides and iodides are monomeric in tetrahydrofuran over a wide concentration range, it was found that the alkylmagnesium fluorides are dimeric in diethyl ether and tetrahydrofuran over a similar concentration range. Low temperature NMR, ir, fractional crystalization and dioxane precipitation studies indicated that, although the Schlenk equilibrium describes other alkylmagnesium halides in solution, alkylmagnesium fluorides are best represented by a single dimeric species. The dimeric nature of alkylmagnesium fluorides in solution and the absence of the Schlenk equilibrium is best rationalized as the result of strong Mg-F-Mg bridge bonds. It was found that alkylmagnesium fluorides react with H_2O, O_2, CO_2, PhCN and Ph_2CO in a manner similar to the corresponding bromo Grignard compounds.

Purpose

The preparation of organomagnesium fluorides involving organometallic exchange reactions was examined. A variety of dialkylmagnesium compounds and diphenylmagnesium were allowed to react with a series of commercially available

metal and non-metal fluorides. The preparation of phenyl-magnesium fluoride was investigated.

CHAPTER II

EXPERIMENTAL

Apparatus

All operations were carried out either in a Kewaunee nitrogen filled glove box equipped with a recirculating system to remove oxygen and moisture or at the bench using typical Schlenk Tube and syringe techniques.[8] All glassware was heated to dryness and flushed with nitrogen prior to use.

NMR spectra were obtained on a Varian A-60D NMR spectrometer. All infrared spectra were obtained using a Perkin Elmer 621 high resolution grating spectrophotometer. Cesium and potassium iodide absorption cells were used.

Analyses

Active alkyl groups were analyzed by hydrolyzing samples with aqueous HCl on a high vacuum line. The volume of evolved gas was determined by transferring the gas to a calibrated bulb via a toepler pump. Active phenyl groups were analyzed by adding a known amount of acid and back titrating with standard base using methyl red as an indicator. The same sample was then analyzed for total magnesium by a conventional EDTA complexiometric titration at pH 10 with Eriochrome Black T indicator. Some of the active alkyl groups also were analyzed in this manner. Magnesium in the

presence of aluminum was determined by an EDTA titration in which the aluminum was complexed by triethanolamine. In order to analyze solutions containing both aluminum and fluoride, the analyses were preceded by a Willard-Winter distillation in which fluoride was separated as fluorosilicic acid by steam distillation from perchloric acid.[9] The distillation was performed in the recommended distilling apparatus. Fluoride was analyzed by the precipitation of lead chloride-fluoride (PbClF) followed by a Volhard chloride determination or potentiometric titration.[10]

Chemicals

Magnesium (Grignard-grade turnings, Fisher) was washed with ether and dried prior to use. Ethylbromide (Baker Analyzed Reagent), i-propylchloride (Eastman Organic Chemicals), n-butylchloride (Fisher Certified), n-hexylbromide (Fisher, Highest Purity) and bromobenzene (Fisher Purified) were washed with a sodium bicarbonate solution, dried over magnesium sulfate and distilled from 4-A molecular sieves through a packed column. Boron trifluoride diethyl etherate (Eastman Practical) was distilled under vacuum. A lecture bottle of diethylaluminum fluoride in heptane (Texas Alkyls) was taken into the dry-box, emptied into a round-bottom flask and used without further purification. Silicon tetrafluoride (Matheson) was used without further purification. Tri-n-butyltin fluoride (Alfa Inorganics and M

and T Chemicals), triphenylsilicon fluoride (Peninsular Chem. Research) and tin tetrafluoride (Peninsular Chem. Research) were dried by subjecting to vacuum prior to use. Tetrahydrofuran (Fisher Certified), 1,4-dioxane (Fisher Certified) and benzene (Fisher Certified thiophene free) were distilled from $NaAlH_4$. Hexane (Fisher Certified ACS) was stirred with concentrated sulfuric acid to remove olefins. The sulfuric acid was then removed and the hexane solution washed with an aqueous solution of sodium bicarbonate followed by distilled water, dried over magnesium sulfate and then distilled from $NaAlH_4$ through a packed column. Dimethylmercury (Orgmet) was used without further purification. Diethyl ether (Fisher Anhydrous) was distilled from $LiAlH_4$.

Preparation of Dialkyl and Diarylmagnesium Compounds

Magnesium (Grignard-grade turnings) was rinsed with diethyl ether and dried. The magnesium turnings (5g, 0.2 mole) were placed in a 250 ml round bottom flask equipped with a reflux condenser. The flask contained an egg-shaped stirring bar. The magnesium and apparatus were evacuated, heated with a flame and finally purged with nitrogen. Dimethylmercury (7.5 ml, 0.1 mole) was added to the magnesium through a three-way stopcock attached to the top of the condenser. The reaction mixture was allowed to stir until the magnesium became white and powder-like. The mixture was then placed under vacuum for one hour in order to remove the

unreacted dimethylmercury. The dimethylmagnesium was extracted with tetrahydrofuran and filtered through a fritted filter funnel. The active methyl to magnesium ratio = 2.02:1.00.

Except for dimethylmagnesium, the dialkylmagnesium compounds and diphenylmagnesium were prepared by the dioxane precipitation method.[11] The preparation of diethylmagnesium will illustrate this method. Ethyl bromide (165 ml, 2.2 moles) and diethyl ether (1.5 liters) were added to magnesium (80 g, 3.3 moles) in a two liter flask equipped with a dropping funnel and reflux condenser. After the Grignard reaction was complete, 2.2 moles of 1,4-dioxane was added slowly. The mixture was stirred overnight to allow complete reaction. When the solid product had settled, the solution was analyzed for active alkyl groups, magnesium and halide (active alkyl:magnesium:halide = 2:1:0). The solution was then filtered through a medium size fritted funnel filled with one inch of pre-dried filter-aid. The dioxane was removed under vacuum at 80-100° overnight. The residual solid was redissolved in tetrahydrofuran and the solution was standardized.

Reaction of Dimethylmagnesium and Boron Trifluoride Diethyl Etherate

To 130.1 ml of 0.384 M dimethylmagnesium (49.96 m-moles) in tetrahydrofuran was added 108 ml of 0.149 M boron trifluoride diethyl etherate (16.10 m-moles) in tetrahydro-

furan. The boron trifluoride was added slowly through a dropping funnel and a white solid precipitated from solution after the addition of approximately 60% of the boron trifluoride. The reaction was allowed to proceed for twenty-four hours. The solution was filtered from the solid and placed under vacuum to remove the solvent and the trimethylborane by-product. The resultant solid was washed with hexane to insure complete remove of the boron product. The solid dissolved in tetrahydrofuran, and a boron flame test indicated the absence of boron. An absorption band at 530 cm^{-1} was observed in the ir spectrum and a singlet at 11.71τ in the NMR spectrum of the solution. There was a 100% completion of reaction and a 80% yield of methylmagnesium fluoride. Analysis of the solution indicated an active methyl:magnesium:fluoride ratio of 1.0:1.1:1.0.

Reaction of Diethylmagnesium and Boron Trifluoride Diethyl Etherate

To 335 ml of 0.0803 M diethylmagnesium (26.9 m-moles) in tetrahydrofuran was added 100 ml of 0.0897 M boron trifluoride etherate (8.97 m-moles). No precipitation occurred during the addition. The solvent was removed under vacuum and the resultant solid was washed with hexane. The solid was then redissolved in tetrahydrofuran and a boron flame test of the resulting solution was negative. The infrared spectrum of the solution exhibited a C-Mg stretching band

at 480 cm^{-1}, and the NMR spectrum contained a quartet centered at 10.65τ. Analysis of the solution indicated an active ethyl:magnesium:fluoride ratio of 1.11:1.00:1.24 indicating complete reaction and 100% yield of ethylmagnesium fluoride.

Reaction of Diphenylmagnesium and Boron Trifluoride Diethyl Etherate

To 58.5 ml of 0.500 M diphenylmagnesium (29.25 m-moles) in tetrahydrofuran was added 1.23 ml of neat boron trifluoride diethyl etherate (9.75 m-moles). Solid precipitated during the addition and was filtered from the solution. The infrared spectrum of the solution exhibited a C-Mg absorption at 400 cm^{-1}, and the NMR spectrum contained a complex aromatic multiplet with the absorption of highest intensity centered at 3.21τ. The solution gave a negative boron flame test. Analyses of the solution gave an active phenyl:magnesium:fluoride ratio of 1.00:1.03:0.763, indicating 100% completion of reaction and a 74% yield of phenylmagnesium fluoride.

Reaction of Dihexylmagnesium and Boron Trifluoride Diethyl Etherate

To 24.8 ml of 0.474 M dihexylmagnesium (117.43 m-moles) in diethyl ether was added 4.93 ml of neat boron trifluoride diethyl etherate (39.10 m-moles). No solid formation occurred during the reaction. Removal of solvent by vacuum resulted in a viscous oil which dissolved in hexane

preventing the separation of the borane from the product. A high vacuum distillation (10^{-5}mm) was then attempted to remove the borane product. No distillate was observed until a temperature of 120° was reached and then only a small quantity of a liquid distilled. The viscous oil remained in the reaction mixture, but solid on the sides of the flask looked oil-free and was analyzed, giving an active hexyl:magnesium:fluoride ratio of 1.12:1.00:1.21. The reaction proceeded to 100% completion, but the borane by-product could not be removed.

Reaction of Dimethylmagnesium with Silicon Tetrafluoride

All reactions involving silicon tetrafluoride were run in a hood. The volume of silicon tetrafluoride was measured at atmospheric pressure and the number of m-moles was calculated. An apparatus consisting of calibrated bulbs and a calibrated buret filled with mercury and attached to mercury equalizing bulbs was used to measure the volume of silicon tetrafluoride. The apparatus was directly attached to a gas diffusion tube (fritted disc) allowing for the slow diffusion of gas into the dialkylmagnesium solution. The entire apparatus (except for the section containing mercury) was heated with a flame, and then purged with nitrogen gas and finally purged with silicon tetrafluoride. The three-neck round bottom flask containing the dialkylmagnesium solution was equipped with a three-way stopcock and a dry-ice conden-

ser. A piece of dry-ice was placed in the condenser to create a vacuum in the closed system in order to start the flow of silicon tetrafluoride through the gas diffusion tube into the dialkylmagnesium reagent. To 80 ml of 1.530 M dimethylmagnesium (122.3 m-moles) was added 768 ml of silicon tetrafluoride (30.6 m-moles). The NMR spectrum showed the formation of the tetramethylsilane by-product and methylmagnesium fluoride. The silane by-product was removed by the gentle warming of the solution. No solid formation occurred and the analysis of the solution indicated an active methyl:magnesium ratio of 1.07:1.00 indicating a 100% completion of reaction and 100% yield of methylmagnesium fluoride.

Reaction of Di-i-propylmagnesium and Silicon Tetrafluoride

Silicon tetrafluoride (418 ml, 16.67 m-moles) was added to 119 ml of 0.420 M di-i-propylmagnesium (50 m-moles) in tetrahydrofuran. No precipitation of solid occurred during the addition and the NMR of the solution exhibited a doublet for the i-propyl methyl groups centered at 8.54τ (di-i-propylmagnesium exhibited the same signal). The reaction mixture was placed under vacuum at room temperature, resulting in the formation of an oil and suspended solid. The material was washed with hexane and redissolved in tetrahydrofuran. On standing, solid precipitated from the solution almost immediately. Analysis of the solution indicated active i-propyl:magnesium = 1.45:1, and 30% of the magnesium

remained in solution. The reaction was carried out a second time. Again no solid precipitated during the reaction. The solvent was removed under vacuum at room temperature resulting in an oil and suspended solid: the mixture was washed four times with hexane to remove the silicon by-product. Tetrahydrofuran was added to the washed reaction mixture and only part of the solid redissolved. Analysis of the solution indicated an active i-propyl:magnesium ratio of 1.39:1.00, and 24% of the magnesium was found in solution.

Reaction of Di-n-butylmagnesium and Tri-n-butyltin Fluoride

Tri-n-butyltin fluoride (29.965 g, 97 m-moles) was added in the dry box to 77.3 ml of 1.255 M di-n-butylmagnesium (97 m-moles) in tetrahydrofuran. The solid tri-n-butyltin fluoride, which is insoluble in tetrahydrofuran, dissolved immediately and the reaction was stirred overnight at room temperature. No precipitate was formed in the reaction and the infrared spectrum of the solution showed an absorption band at 520 cm^{-1} characteristic of a C-Mg band and two bands at 500 and 580 cm^{-1} characteristic of tetra-n-butyltin. The solvent was removed under vacuum resulting in an amorphous solid and a colorless liquid which was washed with hexane repeatedly to remove the tetra-n-butyltin product. The amorphous solid was then dried and redissolved in tetrahydrofuran. The infrared spectrum of the solution exhibited a band at 520 cm^{-1} characteristic of a C-Mg band

and no absorption bands characteristic of tetra-n-butyltin. Analysis of the solution indicated an active butyl:magnesium: fluoride ratio of 1.00:1.18:1.35, indicating 100% reaction. After the work-up, 55% of the magnesium remained in solution, resulting in a 55% yield of n-butylmagnesium fluoride.

In order to obtain a higher yield of product a vacuum distillation was attempted to remove the tin product. At 1-2 mm, tetra-n-butyltin quantitatively distilled from the flask at 101.5° to 108°. The resultant solid would not redissolve in refluxing tetrahydrofuran. The reaction was repeated and after the completion of the reaction the solvent was removed under vacuum at room temperature resulting in the formation of an amorphous solid and a colorless liquid. The amorphous solid and liquid were placed in benzene and a suspension formed making the separation of the product difficult. The suspension was then placed in a soxhlet thimble and extracted with benzene for 24 hours in order to remove the tin product. After the completion of the soxhlet extraction procedure, the solid in the thimble would not redissolve.

Reaction of Diphenylmagnesium and Tri-n-butyltin Fluoride

Tri-n-butyltin fluoride (26.423 g, 85.6 m-moles) was added to 95.9 ml of 0.893 M diphenylmagnesium (85.6 m-moles) in tetrahydrofuran. The tri-n-butyltin fluoride only partially dissolved after stirring overnight at room temperature.

The reaction mixture was then refluxed for four days and the tri-n-butyltin fluoride remained unreacted. The infrared spectrum of the solution indicated that the two bands at 435 and 380 cm^{-1} characteristic of diphenylmagnesium had decreased in intensity, but the band characteristic of the fluoro Grignard could not be seen (the 400 cm^{-1} absorption is generally a weak absorption). The solution was analyzed giving an active phenyl:magnesium:fluoride ratio of 1.52:1.00:0.79 indicating 50% reaction (analysis calculated for 50% reaction gives 1.5:1.0:0.5.

Reaction of Di-n-butylmagnesium and Triphenylsilicon Fluoride

Triphenylsilicon fluoride (5.284 g, 19.02 m-moles) was added to 15.05 ml of 1.264 M di-n-butylmagnesium (19.02 m-moles) in tetrahydrofuran. The infrared spectrum of the solution after 1.5 hours reaction time at room temperature indicated that the strong band at 510 cm^{-1} characteristic of triphenylsilicon fluoride was still present. The reaction mixture was then heated overnight at 40° after which the infrared spectrum of the solution indicated a slight decrease in the 510 cm^{-1} band. The reaction mixture was then refluxed for 3 days. The infrared spectrum of the resulting solution indicated that tri-phenylsilicon fluoride was still present. Analysis of the solution indicated an active butyl:magnesium:fluoride ratio of 1.4:1.0:0.78 indicating 60% reaction (analysis calculated for 60% reaction is 1.4:1.0:0.6).

Reaction of Diphenylmagnesium and Triphenylsilicon Fluoride

To 20.7 ml of 0.934 M diphenylmagnesium (19.31 m-moles) in tetrahdyrofuran was added 5.369 g of triphenylsilicon fluoride (19.31 m-moles). Precipitation occurred with stirring overnight, and analysis of the solution indicated that the reaction had proceeded to 50% completion (active phenyl: magnesium = 1.5:1.0). The solution was then refluxed for an additional 24 hours with the result that the white precipitate dissolved on heating and reprecipitated on cooling. Analysis of the solution after refluxing gave an active phenyl:magnesium:fluoride ratio of 1.14:1.00:1.06 indicating 100% completion of reaction. All the magnesium remained in solution, therefore the solid was tetraphenylsilane. The precipitate was filtered and dried and it was found that 60% of the silicon by-product precipitated from solution. The reaction mixture was stripped of solvent by vacuum, and benzene was added to the resultant solid. The mixture was allowed to stir overnight and a great deal of the solid dissolved in the benzene making the removal of the tetraphenylsilane impossible. The benzene was removed from the solution, forming a solid which redissolved in tetrahydrofuran. The infrared spectrum of the solution showed an absorption at 400 cm^{-1} indicating that the phenylmagnesium fluoride had dissolved in the benzene. A slow fractional crystallization was attempted in order to separate the tetraphenylsilane from the fluoro Grignard compound. Solvent was very slowly

removed until precipitation occurred. The precipitate was removed from the solution and the crystallization procedure was repeated two more times. With each successive crystallization, the 400 cm^{-1} band for phenylmagnesium fluoride increased in intensity relative to the 510^{-1} band characteristic of tetraphenylsilane, however, phenylmagnesium fluoride co-precipitated with tetraphenylsilane. The quantity of silicon product present with phenylmagnesium fluoride was estimated by combustion of the mixture to silicon dioxide (phenylmagnesium fluoride was hydrolyzed with ammonium chloride to isolate the tetraphenylsilane), and 18% of the silicon product was found in solution.

Reaction of Diphenylmagnesium and Tin Tetrafluoride

To 66.4 ml of 0.893 M diphenylmagnesium (59.32 m-moles) in tetrahydrofuran was added 2.888 g of tin tetrafluoride (14.83 m-moles). The tin tetrafluoride only partially dissolved. After 24 hours of stirring at room temperature, analysis of the solution indicated that no reaction occurred (active phenyl:magnesium = 1.96:1.00). The mixture was refluxed for four days and the tin tetrafluoride did not appear to dissolve. After the four days of refluxing, the analysis of the solution showed an active phenyl:magnesium ratio of 1.76:1 indicating 24% reaction.

Reaction of Diethylaluminum Fluoride and Diethylmagnesium

To 22.3 ml of 0.455 M diethylmagnesium (101.5 m-moles)

in tetrahydrofuran was added 27 ml of 3.76 M diethylaluminum fluoride (101.5 m-moles). The reaction was allowed to stir overnight, and precipitation of solid occurred. Analysis of the solution indicated an active ethyl:magnesium:aluminum: fluoride ratio of 3.79:5.60:1.08. Analysis of the solid showed an active ethyl:magnesium:aluminum:fluoride ratio of 9.0:1.0:11.0:14.0. Found in solution was 31% of the aluminum and 75% of the magnesium. The reaction was repeated in hexane and the reaction mixture was stirred for 24 hours. Analysis of the solution indicated an active ethyl:magnesium: aluminum ratio of 8:1:3. The solid analyzed for magnesium: aluminum = 2.57:1.00. In solution was found 25% of the aluminum and 20% of the magnesium. Diethylmagnesium was also allowed to react as a slurry in benzene. The reaction mixture contained a precipitate throughout the time of reaction. In solution was found 20% of the aluminum and 25% of the magnesium.

In the reactions involving diethylaluminum fluoride, it was found that the analyses were reproducible only within 10-15%. Hydrolysis of the samples always lead to an insoluble polymer which would not dissolve completely even in boiling acid for long periods of time, therefore decreasing the accuracy of the analysis.

CHAPTER III

RESULTS AND DISCUSSION

The various exchange reactions investigated involve the reactions of dialkyl and diarylmagnesium compounds with readily available metal and non-metal fluorides in an attempt to develop a route to fluoro Grignard compounds. Tetrahydrofuran was chosen as the solvent since preliminary work indicated that organomagnesium fluorides can be prepared and are stable in this solvent. Identification of the prepared organomagnesium fluorides involved elemental analyses (C-Mg: Mg:F = 1:1:1), observation of infrared absorption bands in the C-Mg stretching region, and the presence of appropriate chemical shifts in the NMR spectrum characteristic of organomagnesium compounds.

Reaction of Dialkylmagnesium Compounds and Diphenylmagnesium with Boron Trifluoride Diethyl Etherate

In order to determine the usefulness of boron trifluoride etherate as a fluorinating agent, reactions between boron trifluoride etherate and dimethyl-, diethyl-, dihexyl- and diphenylmagnesium were examined. The following general reaction stoichiometry was employed.

$$3\ R_2Mg + BF_3 \cdot Et_2O \xrightarrow{THF} 3\ RMgF + R_3B \qquad (1)$$

The principle of the reaction is that the borane by-product is hydrocarbon-soluble and can be removed, leaving behind the hydrocarbon-insoluble organomagnesium fluoride. Methyl-, ethyl and phenylmagnesium fluoride were successfully prepared by this route. Although, hexylmagnesium fluoride has been prepared in diethyl ether and in tetrahydrofuran by the reaction of hexylfluoride and magnesium, borane-free hexylmagnesium fluoride was produced only in low yield by the reaction of dihexylmagnesium and BF_3 etherate.

During the addition of boron trifluoride etherate in tetrahydrofuran to dimethylmagnesium, a precipitate was formed which was filtered from the solution. Borane-free methylmagnesium fluoride was formed in 80% yield. Analysis of the solution indicated an active methyl:magnesium:fluoride ratio of 1.0:1.1:1.0. The NMR spectrum of the solution exhibited a singlet at 11.71τ (dimethylmagnesium in tetrahydrofuran exhibited a singlet at 11.76τ). An infrared spectrum of the solution exhibited a band at 530 cm^{-1} which is characteristic of the C-Mg stretching frequency exhibited by alkyl Grignard compounds. The yield of methylmagnesium fluoride was 80%.

Ethylmagnesium fluoride was also prepared by the above method and in quantitative yield. No solid formation occurred during the reaction and the borane product was readily removed by hydrocarbon extraction. Elemental analysis indicated an active ethyl:magnesium:fluoride ratio of

1.11:1.00:1.24. The NMR spectrum showed a quartet at 10.65τ. The infrared spectrum contained an absorption band at 480 cm^{-1}.

The direct preparative route (fluorobenzene and magnesium) proved to be unsuccessful in the preparation of phenylmagnesium fluoride, however, phenylmagnesium fluoride was prepared in approximately 74% yield by the reaction of boron trifluoride etherate in tetrahydrofuran with diphenylmagnesium. A white solid formed during the reaction which was filtered from solution leaving behind a boron-free solution with an active phenyl:magnesium:fluoride ratio of 1.0:1.0:0.76. The NMR spectrum of the solution exhibited a complex, aromatic multiplet with the absorption of highest intensity being centered at 3.21τ (3.02τ for the signal of highest intensity for diphenylmagnesium). This reaction is best explained by the following equations:

$$3\ Ph_2Mg + BF_3 \quad 3\ PhMgF + Ph_3B \qquad (2)$$

$$3\ PhMgF + Ph_3B \quad Ph_4BMgF + 2\ PhMgF \qquad (3)$$

Hexylmagnesium fluoride was prepared in low yield in diethyl ether by the reaction of dihexylmagnesium with boron trifluoride etherate. It was found that the borane by-product could not be removed as was done in the other cases. Removal of the solvent resulted in a viscous oil which completely dissolved in hexane, preventing the separation of

the borane by-product. A high vacuum distillation (10^{-5} mm) was attempted to remove the borane, but was unsuccessful. After the distillation, solid collected around the sides of the flask. The solid, which looked oil-free, was isolated and analyzed. The analysis of the solid showed active hexyl: magnesium:fluoride = 1.12:1.00:1.21.

Reaction of Dimethylmagnesium and Di-i-propylmagnesium with Silicon Tetrafluoride

Silicon tetrafluoride is a readily available and inexpensive fluorinating agent and is easily handled in a hood. Methylmagnesium fluoride was easily prepared by reacting dimethylmagnesium with SiF_4 in tetrahydrofuran.

$$4\ Me_2Mg + SiF_4 \longrightarrow 4\ MeMgF + Me_4Si \qquad (4)$$

The reaction has the inherent advantage of producing four moles of the Grignard reagent to one mole of tetramethylsilane and thus the amount of by-product to be removed is small relative to the desired product. In addition, $(CH_4)_4Si$ is low boiling (34^oC) and therefore easy to remove from the reaction mixture. The formation of tetramethylsilane was readily followed by analysis of the NMR spectrum. Tetramethylsilane was removed from the methylmagnesium fluoride by gentle heating of the reaction mixture. Methylmagnesium fluoride was produced in 100% yield by this method.

Silicon tetrafluoride was added to a tetrahydrofuran solution of di-i-propylmagnesium. A reaction stoichiometry of 3:1 was employed since it is difficult to replace the fourth fluorine atom in silicon tetrafluoride with a secondary alkyl group. The uptake of the gas by the di-i-propylmagnesium solution occurred very readily.

$$3\ Pr^{i}_{2}Mg + SiF_4 \longrightarrow 3\ Pr^{i}MgF + Pr^{i}_{3}SiF \qquad (5)$$

The clear solution was worked up by the removal of solvent at room temperature, followed by the washing of the reaction mixture with hydrocarbon. After this procedure, the residual product redissolved in tetrahydrofuran; however, on standing, a precipitate appeared rapidly. Analysis of the solution indicated an active i-propyl:magnesium ratio of 1.45:1.00. Only 30% of the theoretical amount of magnesium was in solution. The reaction was repeated using the same stoichiometry and, after the work up, the new reaction mixture only partially redissolved. The active i-propyl:magnesium ratio of the solution was 1.39:1.00. Only 24% of the theoretical amount of magnesium was in solution. These reactions indicate that i-propylmagnesium fluoride disproportionates, resulting in the formation of di-i-propylmagnesium and insoluble magnesium fluoride. It was found in another reaction that the addition of the fluorinating agent beyond the stoichiometry of 3:1 resulted in a greater

loss of the active alkyl group in solution and this observation indicates that the i-propyl:magnesium ratio of 1.45:1.00 is not due to incomplete reaction.

Reaction of Di-n-butylmagnesium and Diphenylmagnesium with Tri-n-butyltin Fluoride

Tri-n-butyltin fluoride was allowed to reaction with di-n-butyl- and diphenylmagnesium according to the equation:

$$R_2Mg + n\text{-}Bu_3SnF \longrightarrow RMgF + n\text{-}Bu_3SnR \qquad (6)$$

The fluorine atom is the only readily exchangeable group in tri-n-butyltin fluoride, allowing the compound to act only as a fluorinating agent. n-Butylmagnesium fluoride was readily formed by this method; however, phenylmagnesium fluoride formed in only 50% yield.

Tri-n-butyltin fluoride, which is insoluble in tetrahydrofuran, dissolved immediately in the presence of di-n-butylmagnesium. The infrared spectrum showed a strong absorption band at 570 cm^{-1} characteristic of the C-Mg band and two strong absorption bands at 500 cm^{-1} and 586 cm^{-1} characteristic of tetra-n-butyltin. Solvent removal under vacuum left behind an amorphous solid and colorless liquid. The mixture was extracted with hexane and redissolved in tetrahydrofuran. The infrared spectrum of the resulting solution did not exhibit absorption bands characteristic of

tetrabutyltin; however, weak absorption bands characteristic of butylmagnesium fluoride were observed. Only 55% of the theoretical magnesium was found in the tetrahydrofuran solution, indicating that n-butylmagnesium fluoride THF etherate must have some solubility in hexane. Analysis of the solution showed an active butyl:magnesium:fluoride = 1.00:1.18:1.35, indicating 100% completion of the reaction. Distillation at 1-2 mm was attempted in order to remove the tin product without loss of the n-butylmagnesium fluoride. Tetra-n-butyltin distilled quantitatively at 101.5-108° (ir of distillate identical to ir of tetra-n-butyltin), but the Grignard reagent would not redissolve in tetrahydrofuran.

Tri-n-butyltin fluoride did not completely dissolve in the presence of diphenylmagnesium even after refluxing in tetrahydrofuran for four days. Elemental analysis indicated that the reaction proceeded to 50% completion and that the active phenyl:magnesium:fluoride = 1.52:1.00:0.79.

Reaction of Di-n-butylmagnesium and Diphenylmagnesium with Triphenylsilicon Fluoride

Di-n-butylmagnesium and triphenylsilicon fluoride were allowed to react in 1:1 ratio. After 24 hours, analysis indicated little reaction. The solution was then refluxed for three days, and analysis indicated 60% reaction (active butyl:magnesium:fluoride = 1.4:1.0:0.784).

Triphenylsilicon fluoride was added to diphenylmagne-

sium, and a solid precipitated with stirring overnight. Analysis of the solution indicated that the reaction proceeded to 50% completion (active phenyl:magnesium = 1.5:1.0). The solution was then refluxed for 24 hours, and the white solid redissolved on heating and reprecipitated from solution on cooling. All the magnesium was in solution and analysis indicated a 100% yield of phenylmagnesium fluoride (active phenyl:magnesium:fluoride = 1.14:1.00:1.06). The solution contained 40% of the produced tetraphenylsilane. The solution was stripped of solvent, resulting in the isolation of a solid product. On stirring, almost all of the solid dissolved in benzene, preventing the separation of the tetraphenylsilane from the Grignard reagent. A fractional crystallization was then attempted to remove the silicon product since tetraphenylsilane should be less soluble than phenylmagnesium fluoride in tetrahydrofuran. After three fractions had been removed from solution, the infrared spectrum of the resulting filtrate showed an increase in intensity of the 400 cm^{-1} band of phenylmagnesium fluoride relative to the 510 cm^{-1} band of tetraphenylsilane. The infrared spectrum and the elemental analyses indicated that both products were co-precipitating. Phenylmagnesium fluoride appears to crystallize from solution slower than tetraphenylsilane; however, with each crystallization too much of the Grignard product comes out of solution to make the method attractive. The infrared spectrum indicated the presence of the by-product

and analysis indicated that 18% of tetraphenylsilane remained in solution.

Reaction of Tin Tetrafluoride and Diphenylmagnesium

Tin tetrafluoride was found to be ineffective as a fluorinating agent. After 24 hours, tin tetrafluoride and diphenylmagnesium showed no reaction in tetrahydrofuran (active phenyl:magnesium = 1.96:1.00). In addition, tin tetrafluoride showed only partial solubility in the reaction solution. Refluxing for four days resulted in only a 24% yield of phenylmagnesium fluoride (active phenyl:magnesium = 1.76:1.00).

Reaction of Diethylmagnesium with Diethylaluminum Fluoride

Diethylmagnesium and diethylaluminum fluoride (50% in heptane) were allowed to react in tetrahydrofuran, benzene and hexane. Diethylmagnesium is soluble in tetrahydrofuran, but insoluble in benzene and hexane; diethylaluminum is soluble in all three solvents. The reaction in tetrahydrofuran resulted in solid formation. Both the solution and solid contained aluminum and no aluminum-free ethylmagnesium fluoride could be isolated. The reactions in hydrocarbon were pursued, hoping that the fluoro Grignard would precipitate and the aluminum product would stay in solution. Again, sizeable quantities of aluminum were found in both the solid product and in solution. The result could possibly be due to the formation of a complex between triethylaluminum and

ethylmagnesium fluoride which would be difficult to separate from the fluoro Grignard product.

$$Et_2Mg + Et_2AlF \longrightarrow EtMgF + Et_3Al \qquad (7)$$

$$EtMgF + Et_3Al \longrightarrow FMgAlEt_4 \text{ or } EtMgAlEt_3F \qquad (8)$$

CHAPTER IV

CONCLUSION

Organomagnesium fluorides have been prepared in high yield by the exchange reactions of metal and non-metal fluorides with dialkylmagnesium compounds and diphenylmagnesium in tetrahydrofuran. Phenylmagnesium fluoride was prepared for the first time.

Boron trifluoride diethyl etherate was found to be convenient for the preparation of methyl-, ethyl, and phenylmagnesium fluoride. Silicon tetrafluoride led to a facile preparation of methylmagnesium fluoride and was used to prepare i-propylmagnesium fluoride which could not be isolated from the silicon by-product. Tri-n-butyl tin fluoride was successfully employed in preparing n-butylmagnesium fluoride. Triphenylsilicon fluoride and diphenyl magnesium produced phenylmagnesium fluoride in 100% yield, but the silicon by-product could not be removed. Tin tetrafluoride and diethylaluminum fluoride were not successfully used in preparing the reagent in a state separated from the metal alkyl by-product.

LITERATURE CITED

1. F. Swarts, Bull. Soc. Chim. Belges, 30, 302 (1921).
2. G. Schiemann and R. Pillarsky, Chem. Ber., 64B, 1340 (1931).
3. H. Gilman and L. H. Heck, J. Amer. Chem. Soc., 53, 377 (1931).
4. H. Gilman and N. B. St. John, Rec. Trav. Chim., 49, 717 (1930).
5. J. P. Bernstein, et al, J. Amer. Chem. Soc., 70, 2310 (1948).
6. W. L. Respess and C. Tamborski, J. Organometal. Chem., 18, 263 (1969).
7. E. C. Ashby, S. Yu and R. Beach, J. Amer. Chem. Soc., 92, 433 (1970).
8. D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill Book Company, New York, N. Y., 1969.
9. T. S. Ma and J. Gwirtsman, Anal. Chem., 29, 1940 (1957).
10. J. M. Hogan and F. Tortoric, Anal. Chem., 39, 221 (1967).
11. W. Schlenk and W. Schlenk, Jr., Ber., 62B, 920 (1929).

PART II

THE COMPOSITION IN SOLUTION OF ALKOXY(METHYL)MAGNESIUM AND DIALKYLAMINO(METHYL)MAGNESIUM COMPOUNDS

CHAPTER I

INTRODUCTION

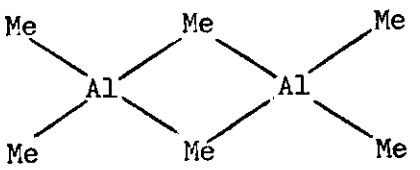
Background

Since the discovery of Grignard reagents, organomagnesium compounds have been of great interest with respect to their utility as alkylating agents as well as their unusual ability to form so called electron deficient compounds. Synthetically these reagents are very useful as alkylating agents toward many different types of organic substrates. In order to use these reagents to their full advantage, the nature of the species in solution must be known. This information will allow one to determine the mechanisms of reactions and to predict subsequent stereochemical courses with organic substrates.

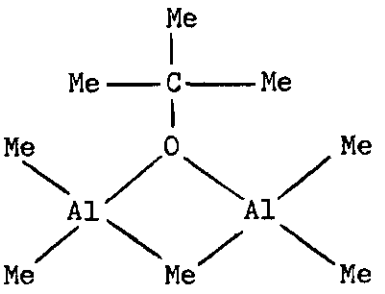
The most widely examined class of organometallic compounds is the Grignard reagent and its compositions in solution have been determined in hydrocarbon,[1] diethyl ether,[2] tetrahydrofuran[3] and triethylamine.[4] Early composition studies involved the determination of the degree of association of the Grignard compounds, however, no additional information was available which could be used in conjunction with the association data in order to determine the structure of the reagent in solution. Logical structures

were offered; however, studies involving the direct observation of the reagent species in solution were not fruitful. Spectroscopy offered the best means of directly observing the organometallic species in solution. Unfortunately, infrared spectroscopy[3d] was not helpful when applied to Grignard reagents in diethyl ether, and until recently, NMR spectroscopy resulted in a limited amount of information.[5-9] The difficulty has been that organomagnesium compounds are characteristically associated in solution and are involved in labile equilibria involving several distinct chemical species.

The structures in solution of non-magnesium organometallic compounds have been determined successfully by variable temperature NMR spectroscopy.[10,11,12] In general, it has been found that in associated compounds, alkyl groups bridging two metal atoms resonate downfield from alkyl groups in terminal positions. The NMR spectrum of the trimethylaluminum dimer in hydrocarbon at low temperature exhibits the bridging methyl signal downfield from the terminal methyl signal with a relative area ratio of 1:2.



In the complex between Me_2AlOBu^t and Me_3Al[13] the NMR spectrum shows the bridging methyl signal downfield from the terminal methyl signal with a relative area ratio of 1:4. Apparently, 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.

A number of workers have carried out studies on alkylmagnesium alkoxides.[8,14,15] The degree of association of a number of these compounds has been determined cryoscopically in benzene and ebulliscopically in diethyl ether. On the other hand, the NMR spectra of these compounds have received little attention, and no one has studied their low temperature NMR spectra in ether solvents.

Alkylmagnesium alkoxides are the addition products formed in the reactions of dialkylmagnesium compounds with ketones. This class of compounds is important in as much as structural knowledge of these compounds would increase the

understanding of the mechanism of the reaction between dimethylmagnesium and ketones[16] since these compounds are intermediates in the reaction. Secondly, alkoxides have potential as stereoselective alkylating agents.[17] All of the organometallic alkoxides of the Group II elements reported in the literature are associated due to the strong bridging characteristics of the alkoxy group. Alkylmagnesium alkoxides in diethyl ether have been found to be generally tetrameric, but a few are dimeric and some trimeric. In benzene, compounds with straight-chain alkoxy groups are oligomeric, whereas tetrameric species are found when there is chain branching at the carbon alpha to oxygen.[15]

Dialkylamino(alkyl)magnesium compounds possess a great propensity toward association due to the strong bridging characteristics of dialkylamino groups. The majority of the compounds studied are insoluble indicating possible polymeric constitutions.[18] Dimeric compounds have been found when the groups attached to nitrogen are relatively large; for example, in benzene the THF etherates of diethylamino(ethyl)magnesium and di-i-propylamino(ethyl)magnesium were found to be dimeric and diphenylamino(ethyl)magnesium was found to be monomeric. The NMR spectra of these compounds have not been investigated in diethyl ether at low temperature, and their potential as stereoselective alkylating agents has not been evaluated.[17]

Purpose

The present investigation involved the systematic examination of a series of methylmagnesium compounds in diethyl ether solvent by both variable temperature NMR and molecular association studies while varying the size and nature of the groups bonded to magnesium in an effort to determine the effect of the nature of the groups on solution composition. The compounds investigated can be represented as MeMgX where X is an alkoxy or dialkylamino group. Alkoxy and dialkylamino groups are considered strong bridging groups; thus, it was hoped that these groups would allow the study of associated species in solution involving equilibria slow enough to be observed by low temperature NMR. Such a study would allow for the determination of the chemical shift of an alkyl group in various environments resulting in a basis for inferring the structure in solution of methylmagnesium compounds by NMR spectroscopy.

CHAPTER II

EXPERIMENTAL

Apparatus

All work was performed at the bench under a nitrogen atmosphere, or in a glove box equipped with a recirculating system. The recirculating system used manganese oxide to remove oxygen and dry ice-acetone traps to remove solvent vapors from the dry box atmosphere.[19,20]

Spectra were obtained on a Varian A-60D NMR spectrometer equipped with the standard variable temperature unit. The accuracy of the temperature reading was $\pm$ 2°.

NMR Techniques

The variable temperature unit was calibrated with a methanol sample prior to obtaining each spectrum. TMS was used as a reference. The NMR samples were prepared on a high vacuum line by first freezing the samples in the NMR tube with liquid nitrogen. The frozen samples were then placed under vacuum and sealed with a torch.

Ebullioscopic Determination of the Molecular Association

The molecular association of the compound was determined ebullioscopically at 740 mm employing a modified Cottrell boiling point elevation apparatus.[21] Temperature changes

were observed using a Beckman differential thermometer and the pressure was measured using a precision Wallace-Tiernan manometer. Solvent loss was prevented by the recirculation of ice-water through the condenser. Specific details of the procedure have been described.[21]

Calculations of the i-values were made using the following equation:

$$i = \frac{W_2 M_1}{W_1 M_2} \left[\frac{1}{e^{\Delta T_b M_1 / 1000 K_{b-1}}} \right]$$

The equation was derived in the usual manner by assuming an ideal solution which is not necessarily dilute. The terms include M_2, the formula weight of the solute; M_1, the molecular weight of the solvent (74.12 g for diethyl ether); and K_b, the molal boiling point elevation constant (2.01 for diethyl ether at an internal nitrogen pressure of 740.0 mm).

Analyses

Active methyl groups were analyzed by hydrolyzing samples with HCl on a high-vacuum line. The volume of evolved methane was determined by transferring the gas to a calibrated bulb via a Toepler pump. Magnesium analyses were carried out by EDTA titrations.

Chemicals

Benzophenone (Eastman Reagent Grade) was distilled under vacuum. t-Butyl alcohol and i-propyl alcohol (Fisher Certified) were dried over 4-A molecular sieves and distilled on a spinning band column (the respective boiling points were 82.5-83.5 and 82.8). n-Propyl alcohol was distilled from magnesium di-n-propoxide through a helix-packed column. Diphenylamine (Fisher Certified ACS Special Indicator Grade) was dried by exposure to a vacuum for 24 hours and was used without further purification. Di-i-propylamine, di-n-butylamine (Eastman) and diethylamine (Fisher Reagent Grade) were dried over anhydrous magnesium sulfate and 4-A molecular sieves prior to distillation through a packed column. Diethyl ether (Fisher Anhydrous) was distilled from $LiAlH_4$. Fisher Certified thiophene-free benzene was distilled from $NaAlH_4$.

Preparation of Dimethylmagnesium

Doubly-sublimed magnesium turnings were rinsed with diethyl ether and dried. The magnesium, 15 g (0.6 mole) was placed in a 500 ml round bottom flask containing an egg-shaped stirring bar and equipped with a reflux condenser. The apparatus was then evacuated, heated with a flame and finally flushed with nitrogen. Dimethylmercury, 22.5 ml (0.3 mole), was added to the magnesium through a three-way stopcock attached to the top of the condenser. The

reaction was allowed to proceed for 24 hours until the magnesium became white and powder-like. The mixture was then placed under vacuum for one hour using a liquid nitrogen trap to remove any unreacted dimethylmercury. The dimethylmagnesium was then extracted with diethyl ether and filtered through a fritted filter funnel. Analysis of the solution indicated an active methyl to magnesium ratio of 1.96:1.00.

Preparation of Alkoxy(methyl)magnesium and Dialkylamino-(methyl)magnesium Compounds

The alkoxy(methyl)magnesium and dialkylamino(methyl)-magnesium compounds investigated were prepared by the addition of the ketone, alcohol or amine to dimethylmagnesium in diethyl ether which had been cooled to approximately -79°C by a dry ice-acetone bath. At the dry ice-acetone bath temperature, the dimethylmagnesium precipitated from solution, and the organic substrate was added slowly to the precipitate. The dry ice bath temperature was maintained during the addition of the organic substrate, and after the completion of the addition, the reaction mixture was allowed to slowly warm to room temperature. It was found that cooling during the reaction enhanced the solubility of the compound at room temperature (when the reactions were run at room temperature precipitation of the product occurred, resulting in a lower concentration of the organomagnesium compound in solution).

Preparation of 1,1-Diphenylethoxy(methyl)magnesium

To 50 ml of 0.356 M dimethylmagnesium (17.80 m-moles) in diethyl ether, cooled to approximately -78°C (the dimethylmagnesium crystallized) by a dry ice-acetone bath, was added 69.40 ml of 0.256 M benzophenone (17.76 m-moles) in diethyl ether. The first drop of benzophenone solution resulted in a yellow solution, and as more benzophenone was added, the solution became violet. On warming to 0°C the solution became colorless and the dimethylmagnesium precipitate completely dissolved. On warming to room temperature the clear solution began to precipitate a white solid. Analysis of the solution gave an active methyl to magnesium ratio of 1.00:1.04.

Preparation of 1,1-Diphenylethoxy(methyl)magnesium-dimethylmagnesium

To 100 ml of 0.07648 M 1,1-diphenylethoxy(methyl)-magnesium (7.64 m-moles), cooled to a dry ice-acetone bath, was added 11.61 ml of 0.6586 M dimethylmagnesium (7.64 m-moles) in diethyl ether. At dry ice-acetone and room temperature, no precipitate was formed, yielding a clear solution. Analysis of the solution gave an active methyl to magnesium ratio of 1.51:1.00.

Preparation of t-Butoxy(methyl)magnesium

To 75 ml of 0.356 M dimethylmagnesium (26.70 m-moles) in diethyl ether, cooled to dry ice-acetone temperature,

was added 80.69 ml of 0.33 M (26.62 m-moles) t-butyl alcohol in diethyl ether. At the dry ice temperature precipitate was formed after the addition of the alcohol, and on warming to room temperature the precipitate partially dissolved. Analysis of the clear solution gave an active methyl to magnesium ratio of 1.04:1.00.

Preparation of t-Butoxy(methyl)magnesium-dimethylmagnesium

To 64.20 ml of 0.5646 M t-butoxy(methyl)magnesium (36.2 m-moles) in diethyl ether at room temperature was added 55.0 ml of 0.658 M dimethylmagnesium (36.2 m-moles) in diethyl ether. No precipitation occurred during the addition and, after stirring overnight, analysis of the solution gave an active methyl to magnesium ratio of 1.53: 1.00.

Preparation of i-Propoxy(methyl)magnesium

To 49.83 ml of 0.7057 M dimethylmagnesium in diethyl ether (35.16 m-moles) cooled by a dry ice-acetone bath was added 7.92 ml of 4.440 M i-propyl alcohol (35.16 m-moles) in diethyl ether. A precipitate was formed at low temperature which partially dissolved on warming to room temperature. Analysis of the clear solution gave an active methyl to magnesium ratio of 0.997:1.000.

Preparation of i-Propoxy(methyl)magnesium-dimethylmagnesium

To 50.49 ml of 0.7057 M dimethylmagnesium (35.6 m-

moles) in diethyl ether, cooled by a dry ice-acetone bath, was added 4.02 ml of 4.440 M i-propyl alcohol (17.8 m-moles) in diethyl ether. On warming to room temperature no precipitation occurred, and analysis of the solution resulted in an active methyl to magnesium ratio of 1.51:1.00.

Preparation of n-Propoxy(methyl)magnesium

To 250 ml of 0.399 M dimethylmagnesium (99.7 m-moles) in diethyl ether cooled by a dry ice-acetone bath was added 5.986 g of n-propyl alcohol (99.7 m-moles). At low temperature a precipitate was present, but dissolved on warming to room temperature. Analysis of the clear solution gave an active methyl to magnesium ratio of 0.954:1.000.

Preparation of n-Propoxy(methyl)magnesium-dimethylmagnesium

To 40 ml of 0.3561 M dimethylmagnesium (14.24 m-moles) in diethyl ether at room temperature was added 42.63 ml of 0.3341 M n-propoxy(methyl)magnesium (14.24 m-moles) in diethyl ether. No precipitation occurred and analysis of the clear solution indicated an active methyl to magnesium ratio of 1.55:1.00.

Preparation of Diphenylamino(methyl)magnesium

To 50 ml of 0.4609 M dimethylmagnesium (23.05 m-moles) in diethyl ether at dry ice-acetone temperature was added 24.06 ml of 0.9576 M diphenylamine (23.05 m-moles) in diethyl ether. No precipitate was observed after the addi-

tion of the amine or on warming to room temperature. In order to analyze for magnesium it was found necessary to make a hydrolyzed solution basic with ammonium hydroxide and to steam distill out the diphenylamine prior to analysis. Analysis of the solution gave an active methyl to magnesium ratio of 0.977 to 1.000.

Preparation of Diphenylamino(methyl)magnesium and Dimethylmagnesium

To 60 ml of 0.4609 M dimethylmagnesium (27.65 m-moles) in diethyl ether at dry ice-acetone temperature was added 14.44 ml of 0.9576 M diphenylamine (13.83 m-moles) in diethyl ether. At low temperature a precipitate was present which dissolved on warming to room temperature. Analysis of the solution gave an active methyl to magnesium ratio of 1.48:1.00.

Preparation of Di-i-propylamino(methyl)magnesium

To 30 ml of 0.4946 M dimethylmagnesium (14.83 m-moles) in diethyl ether at dry ice-acetone temperature was added 5.96 ml of 2.486 M di-i-propylamine (14.82 m-moles) in diethyl ether. At low temperature a precipitate formed which increased in quantity on warming. After one hour of stirring at room temperature the precipitate dissolved leaving a clear solution. Analysis of the solution indicated an active methyl to magnesium ratio of 1.06:1.00.

Preparation of Di-i-propylamino(methyl)magnesium-dimethylmagnesium

To 60 ml of 0.4946 M dimethylmagnesium (29.67 m-moles) in diethyl ether at dry ice-acetone temperature was added 5.97 ml of 2.486 M di-i-propylamine (14.84 m-moles) in diethyl ether. Precipitate was present at low temperature and on warming to room temperature additional precipitation occurred. Analysis of the solution gave an active methyl to magnesium ratio of 1.43:1.00.

Preparation of Di-n-butylamino(methyl)magnesium

To 40.66 ml of 0.356 M dimethylmagnesium (14.47 m-moles) in diethyl ether at dry ice-acetone temperature was added 30 ml of 0.4825 M di-n-butylamine (14.47 m-moles) in diethyl ether. At the dry ice-acetone temperature no precipitate was present, but precipitation occurred on warming to room temperature. The solution was filtered and analysis of the clear solution indicated a low concentration of the compound (the concentration of magnesium in solution was 0.033 M).

Preparation of Diethylamino(methyl)magnesium

To 15.79 ml of 0.4946 M dimethylmagnesium (7.81 m-moles) in diethyl ether at dry ice-acetone temperature was added 10.0 ml of 0.7809 M diethylamine (7.81 m-moles) in diethyl ether. At low temperature no precipitate was observed, but on warming to room temperature, massive preci-

pitation occurred. The solution was filtered and the resultant clear solution was analyzed for magnesium. Analysis showed that the concentration of magnesium in solution was 0.0079 M, and therefore the majority of the organomagnesium compound had precipitated.

CHAPTER III

RESULTS

$MeMgOCPh_2Me$ is the addition product of the reaction of Me_2Mg and benzophenone. Association measurements on $MeMgOCPh_2Me$ in diethyl ether in the concentration range 0.0537-0.155 m show that this compound has an i-value of 1.32 at the lower concentration range, increasing and then leveling off at 2.01 at the higher concentrations indicating a monomer-dimer equilibrium at the lower concentration and predominantly dimeric species at the higher concentrations. The stoichiometric addition of Me_2Mg to $MeMgOCPh_2Me$ results in the formation of a complex in solution, $MeMgOCPh_2 \cdot Me_2Mg$, as determined by the measurement of its molecular association (i = 0.90-1.06, m = 0.0196-0.098). Throughout the thesis the spectra and molecular association data are listed in the Appendix. The NMR chemical shifts and relative area ratios are shown in Table 1.

The complex $MeMgOCPh_2Me \cdot Me_2Mg$ is best described in terms of $MeMgOCPh_2Me$ being bound to Me_2Mg by the donation of the lone pair electrons on the alkoxide oxygen of $MeMgOCPh_2Me$ to the empty orbitals on the magnesium atom in dimethylmagnesium. At $+40^{\circ}$ the complex exhibits one signal at 11.48τ which is in the region where methyl groups

Table 1.[a,b] Low Temperature NMR Data for $MeMgOCPh_2Me \cdot Me_2Mg$ and $MeMgOCPh_2Me$

		$MeMgOCPh_2Me \cdot Me_2Mg$		
+40°			11.48	
+30°	11.16[c]		11.48	
-80°		11.24(1)		11.56(4.9)
		$MeMgOCPh_2Me$		
+40°		11.46		
-80°	11.18(1)			11.51(20)

a. All chemical shifts are τ values.

b. Relative area ratios are in parenthesis.

c. The 11.16τ signal is very small relative to the 11.48τ signal.

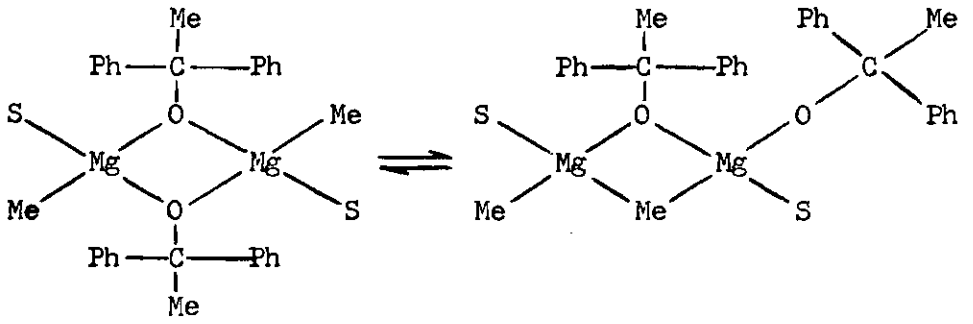
directly bonded to magnesium atoms absorb. The methyl group attached to the alkoxide carbon atom was not observable, whereas the other alkoxy(methyl)magnesium compounds to be discussed show an absorption for the methyl group attached to the alkoxide carbon between 8-8.5τ. At +30° a small signal is observed at 11.16τ while the 11.48τ signal remains unchanged. Temperature lowering to -80° resulted in a shifting of the 11.16τ and 11.48τ signals to 11.24τ and 11.56τ with a relative area ratio of 1.0:4.9 respectively.

The signal at 11.48τ observed in the +40° spectrum represents an averaged signal. The 11.16τ signal observed at +30° is assigned to a bridging environment and the 11.48τ signal is assigned to a terminal methyl environment. The +30° spectrum indicates an equilibrium between a mixed bridged structure (I) and an open structure (II). At -80°

the equilibrium shifts from II to I as indicated by the increase in concentration of bridging methyl groups. There-

fore, as the temperature is lowered, the mixed bridged system increases in concentration. This data can be used to help understand the structure in solution of $MeMgOCPh_2Me$.

Examination of the spectrum of $MeMgOCPh_2Me$ in the concentration range in which it is a dimer, indicates an equilibrium between structures III and IV.

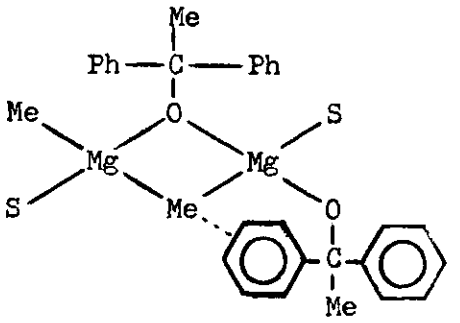


III IV

The temperature dependence of this equilibrium is readily observed by examination of the +40° and -80° spectra. At +40° one signal is observed in the methylmagnesium absorption region at 11.46τ. Again the absorption for the methyl group attached to the alkoxide carbon could not be observed. Temperature lowering to -80° results in the formation of two peaks, a minor one at 11.18τ and a major one at 11.51τ. The 11.18τ signal represents a deshielded methyl environment and is assigned to the bridging methyl in IV. The 11.51τ signal represents terminal methyl groups and accounts for 95% of all the methyl groups, indicating that the struc-

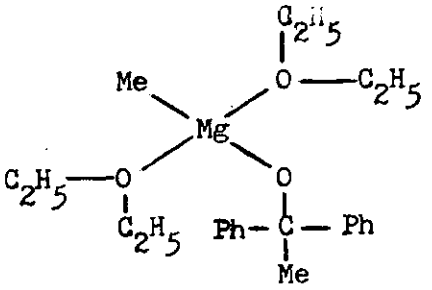
ture of dimeric $MeMgOCPh_2$ may be represented almost entirely by III.

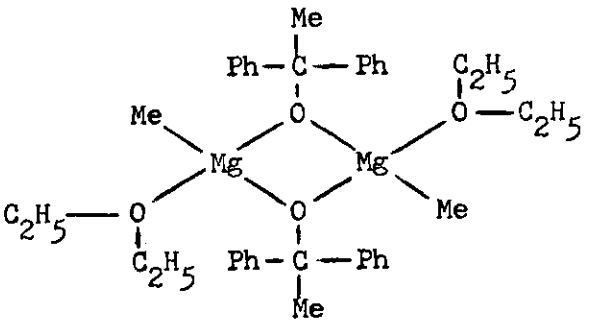
It is interesting to observe that the bridging methyl group signal in ($MeMgOCPh_2Me_2$) is downfield from the bridging methyl signal in $MeMgOCPh_2Me \cdot Me_2Mg$. The difference in chemical shift may be due to an anisotropic effect between the bridging methyl group and the benzene ring that can occur only in the dimer $(MeMgOCPh_2Me)_2$.



The molecular association data for $MeMgOCPh_2Me$ in ether indicates monomeric species in solution at the low concentration range of the study (i = 1.32, m = 0.053). In order to directly observe monomeric $MeMgOCPh_2Me$ the NMR spectra of a 0.05 m solution were examined at ambient and low temperatures. The spectra at the different temperatures for the low and high concentration $MeMgOCPh_2Me$ solutions were identical. Consideration of the structural differences between monomeric and dimeric $MeMgOCPh_2Me$ with respect to the environments of the methyl groups suggests that the

observation of identical spectra is reasonable. The environments of the terminal methyl group of the dimer and the methyl group of the monomer differ in that the monomeric molecule may have two ethers of solvation whereas the dimer is solvated by one ether molecule and one alkoxy group which may resemble an ether molecule.





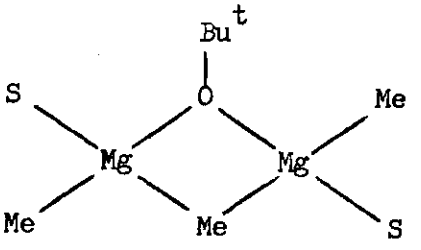
Accompanying these small environmental differences is a rapid equilibrium at room temperature preventing the observation of separate signals for monomeric and dimeric species. The averaged NMR signal observed reflects the exchange of methyl groups in the monomer and in the terminal and bridging sites of the dimer. The presence of bridging methyl groups in the methyl group exchange between monomers and dimers may decrease the sensitivity of the NMR signal to reflect changes in concentration of monomers and dimers, since three types of methyl environments are present rather than just two distinct types: monomer and terminal.

Throughout this study of alkoxy(methyl)magnesium compounds it was observed that the composition in solution was very temperature dependent. It was hoped that temperature lowering of the dilute and concentrated solutions of $MeMgOCPh_2Me$ would result in slower exchange between the methyl groups resulting in the observation of distinct monomeric molecules. Also it was hoped that the solvation differences between the monomers and dimers would be enhanced at low temperatures aiding in the observation of the monomeric $MeMgOCPh_2Me$ species. As the temperature was lowered the dilute and more concentrated solutions of $MeMgOCPh_2Me$ exhibited the same temperature dependence and yielded identical spectra. Apparently the solutions approach the same composition at low temperature preventing the observation of different spectra.

The direct observation of monomeric $MeMgOCPh_2Me$ in solution was unsuccessful through NMR spectroscopy, but the work of Bell and Coates[22] supports the plausibility of a monomeric structure. These workers found that when $MeBeOCPh_2H\cdot Et_2O$ was placed in benzene it existed as a monomer (determined cryoscopically). This observation indicates that large groups attached to the carbon atom alpha to the oxygen atom may prevent association due to their bulkiness thus resulting in a monomeric compound. Comparison of $MeBeOCPh_2H\cdot Et_2O$ with $MeMgOCPh_2Me$ is reasonable especially since the magnesium compound has a more bulky alkoxy group.

$MeMgOBu^t \cdot Me_2Mg$ is a complex in diethyl ether solvent (i = 0.975-1.04, m = 0.104-0.301) and is prepared by the addition of $MeMgOBu^t$ to Me_2Mg. The association values for $MeMgOBu^t$ (i = 1.7-2.04, m = 0.034-0.101)[23] indicate that dimeric species are an important part of the composition in solution and suggest that monomers may exist in equilibrium with dimers. The i-values for $MeMgOBu^t$ therefore may be interpreted in terms of monomer-dimer, dimer, or oligomeric composition in solution. Table 2 contains the NMR data for $MeMgOBu^t$ and $MeMgOBu^t \cdot Me_2Mg$.

At $+30^o$ the NMR spectrum of $MeMgOBu^t \cdot Me_2Mg$ consists of three signals, one of which is in the t-butoxy region (8.46τ) while the other two are in the methylmagnesium absorption region at 11.10τ and 11.38τ. The lower field signal at 11.10τ is assigned to a bridging methyl environment and the high field signal at 11.38τ is assigned to a terminal methyl group environment. The area ratio of the bridging to terminal methyl environments is 1:2 indicating that at room temperature the complex exists in solution as a stable, mixed t-butoxy-methyl bridged organomagnesium compound V.



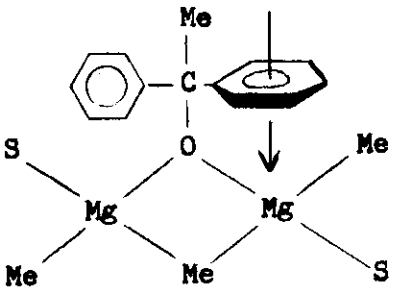
V

Table 2. Low Temperature NMR Data for $MeMgOBu^t \cdot Me_2Mg$ and $MeMgOBu^t$

		$MeMgOBu^t \cdot Me_2Mg$			
+30°	8.46(3)	11.10(1)		11.38(2)	
-80°		11.15(1)	11.21	11.36	11.57(2.3)
		$MeMgOBu^t$			
+40°	8.45	11.11(6.3)	11.18(1)	11.47(8)	
-80°		11.10(3)	11.30(1)		11.60(11)

At -80° $MeMgOBu^t \cdot Me_2Mg$ exhibits two signals (11.15τ and 11.57τ) with relative area ratio of 1:2.3 indicating the mixed bridged species at low temperature. Two other signals are observed at 11.21τ and 11.36τ with a relative area ratio of 1:2. These two signals contribute only to a minor degree in the equilibrium (4% of the methyl groups) and may be due to the production of new species in solution through increased association at -80°.

The difference between $MeMgOBu^t \cdot Me_2Mg$ and MeMgOCPhMe• Me_2Mg is very interesting. Both are complexes, but $MeMgOBu^t \cdot Me_2Mg$ exhibits separate bridging and terminal methyl signals at +30° whereas $MeMgOCPh_2Me \cdot Me_2Mg$ requires a temperature of -80° before the exchange process is slowed down enough to observe separate signals for the bridging and terminal methyl group environments. This observation is consistent with Mole's[13] work involving $Me_2AlOCR_2Me \cdot Me_3Al$ systems. He found that exchange was very much slower than -OR = OBu^t than when -OR = $-OCPh_2Me$ and -OCPhHMe. Mole rationalized that the phenyl rings on the alkoxy group may labilize the mixed bridge compound by donating electrons to the metal atom, therefore satisfying its tetravalence. This same argument is suggested in the present work and the effect is represented by the structure below:

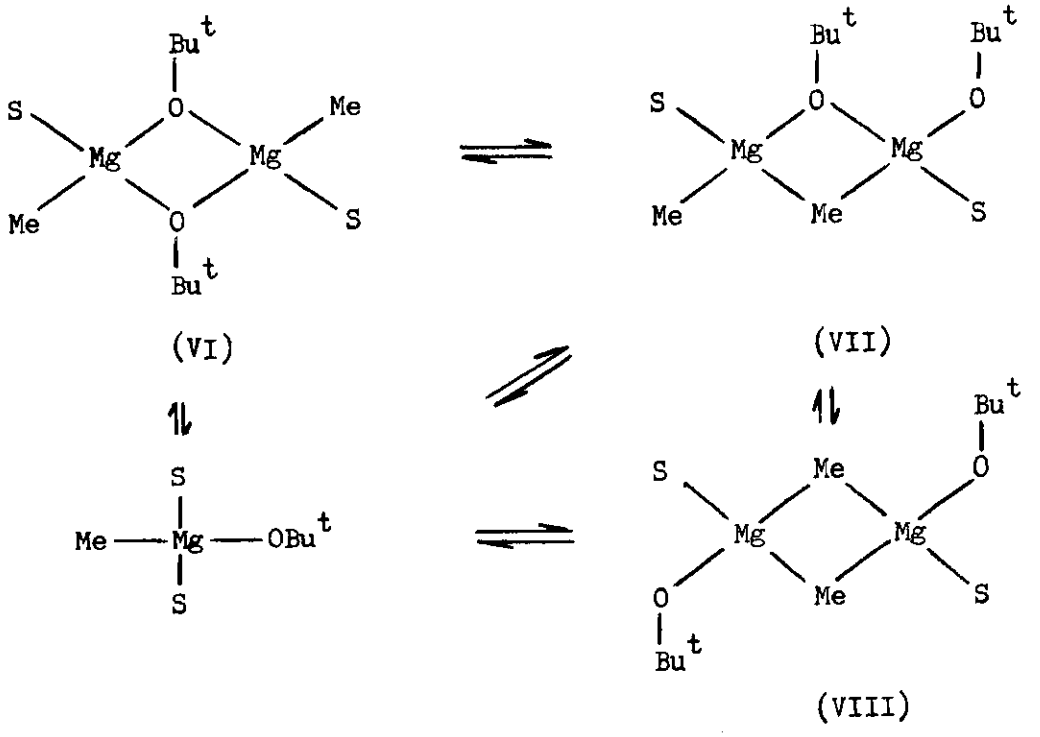


Donation of electrons by the π-cloud of the benzene ring into the magnesium orbitals should enhance the formation of the open bridge system allowing for a rapid exchange process involving the open bridge and mixed bridge structure (the phenyl and methyl group would compete for the magnesium site). Therefore, only at low temperature is the exchange process slow enough to observe both bridging and terminal groups.

The t-butoxy group attached to magnesium has proven to be a very interesting system to examine. The alkoxide group is generally considered to be a better bridging group than alkyl groups due to the unshared lone-pair electrons on oxygen. In the case of the t-butoxy group there is a counter-balancing effect between the size of the alkoxy group and its ability to share its lone-pair of electrons. The $MeMgOBu^t \cdot Me_2Mg$ complex may be considered a model system in that it allows one to observe the chemical shift of bridging and terminal methyl environments at room temperature. $MeMgOBu^t$ allows one to examine the counter-

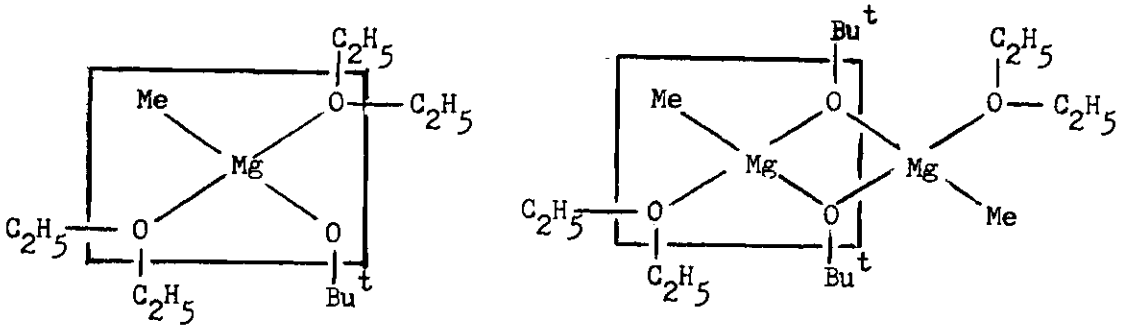
balancing effect of the t-butoxy group since the methyl and t-butoxy groups may compete as bridging groups.

At +40° $MeMgOBu^t$ exhibits one signal in the alkoxy group region. In the methylmagnesium absorption region the signals at 11.11τ(6.3) and 11.18τ(1) represent bridging methyls. The signal at 11.47τ(8) represents terminal methyl groups and methyl groups in monomeric $MeMgOBu^t$. The following monomer-dimer description is consistent with the data.



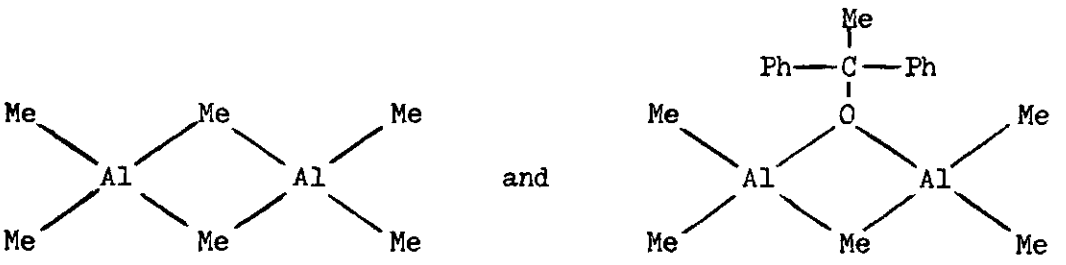
All non-bridging methyl groups (methyl groups in the monomer and in the terminal sites of the dimer) resonate at the

same position at ambient temperature due to their apparent electronically equivalent environments.



Again the environmental equivalence would be due to the structural similarities between the monomer and dimer with respect to the methyl groups. The boxed in areas of the monomer and dimer shown, indicate the structural similarities.

Structures VII and VIII both contain bridging methyl groups and the assignment of the two observed bridging methyl signals to the appropriate bridging methyl environment was based on the NMR spectra of Me_3Al and $Me_2AlOCPh_2Me \cdot Me_3Al$.[24]



The methyl groups in the double methyl bridge of Me_3Al absorb 5 Hz upfield from the methyl group in the methyl-alkoxide bridge in $Me_2AlOCPh_2Me \cdot Me_3Al$. Therefore, the methyls in the double methyl bridge of VIII are best represented by the 11.18τ signal and the signal at 11.11τ is assigned to the methyl-alkoxide bridging environment in VII.

Terminal type methyl sites are the predominant sites insolution at $+40^{\circ}$ as is indicated by the area ratio of the 11.47τ signal to the bridging signals (6.3 bridging:1 bridging:8 terminal). The major species in solution is the t-butoxy(methyl)dimer (VII) which has a bridging group resonating at 11.11τ. The terminal methyl signal at 11.47τ is made up of terminal type methyl groups from the monomer and dimers VI and VII. Of the eight terminal methyl groups 6.3 must be due to the t-butoxy-methyl dimer VII, leaving behind 1.7 groups to be represented by both the monomer and VI. Therefore, in terms of the area ratio the composition in solution is composed of 6.3 molecules of VII to 1 molecule of VIII to 1.7 molecules of monomer and VI taken together, indicating the predominance of VII.

The spectra of $MeMgOBu^t$ indicate a temperature dependence and at -80° three signals are present in the methylmagnesium absorption region. The t-butoxy absorption has shifted into the ether peak and is not observable. Two of the three signals are due to bridging environments (11.10τ and 11.31τ) and the third signal represents a terminal type

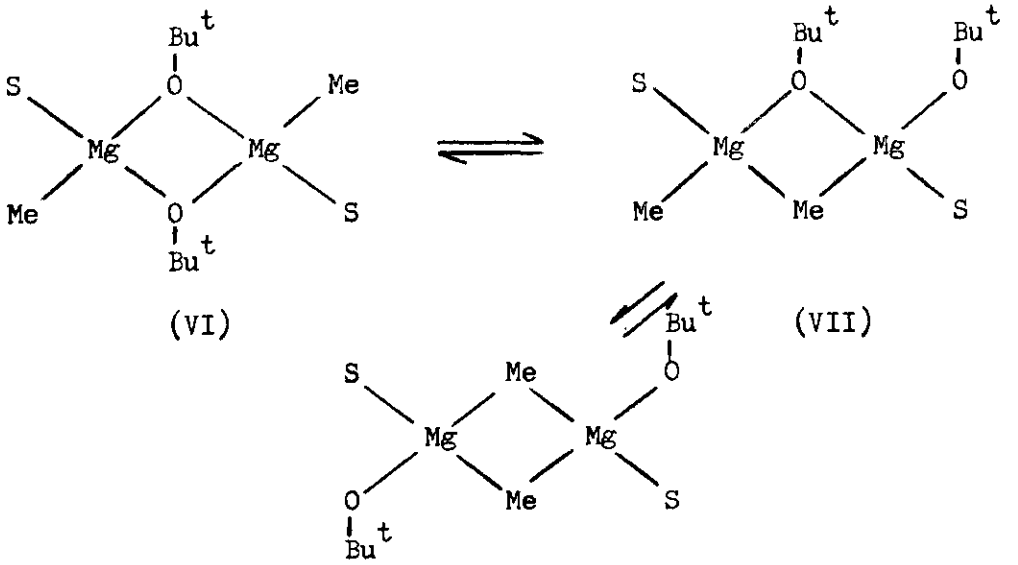
methyl position (11.60τ). The area ratio of bridging methyls to terminal type methyls is 1:2.7 (at +40° the ratio is 1:1.1) indicating a shift in the equilibrium to species with a greater preponderance of terminal type methyl groups with a decrease in temperature. The terminal type methyl signal at 11.60τ accounts for 73% of the methyl groups whereas, only 52% of the methyl groups were in terminal type environments at +40°. No distinct signals were seen upfield specifically for monomers and for dimers. With temperature lowering increased association is expected over a dissociation equilibrium which would yield monomer, therefore it is assumed that the temperature dependence of the spectra reflects an increase in the concentration of dimers with cooling. On the other hand, temperature lowering produces increased solvation which could lead to less association at the lower temperature.

In order to investigate the existence of monomers in solution, the spectra of a 0.034 m solution of $MeMgOBu^t$ in ether was examined. The spectra of the low and high concentration solutions were found to be identical at ambient and low temperatures. Again temperature lowering changes the composition in solution preventing the observation of monomeric $MeMgOBu^t$ in the less concentrated solution (0.034 m). The lack of separate signals at room temperature for methyls in the monomer and in the terminal positions of the dimer may be due to the apparent electronic

equivalence of the methyl groups in the monomer and dimer.

The composition in solution may be oligomeric. This conclusion is based on the examination of the association data plot (p. 148) for $MeMgOBu^t$. The slope does not level off, but rather is continuous, indicating that we are examining only a small part of the composition in solution. The monomer-dimer interpretation in case of an oligomeric $MeMgOBu^t$ would only then apply in the concentration range of 0.034-0.101 m, and at higher concentrations the degree of aggregation would increase.

The description of the composition in solution as consisting only of dimers is based on the observation that the spectra do not show a temperature dependence (assuming that the electronically equivalent description of the methyls in the monomer and dimer is incorrect). The interpretation of the NMR data for the composition in solution consisting of only dimers is identical to that interpretation given for the monomer-dimer equilibrium (except that no monomer is present). The scheme is consistent with the data. Just as in the monomer-dimer description, the 11.11τ signal represents the bridging methyl in VII, the 11.18τ signal represents the bridging methyl in VIII and the 11.47τ signal represents the terminal methyl groups in VI and VII (VII has no terminal methyl groups). Structure VII is the predominant species in solution as is shown by the relative area ratio of the NMR signals.



(VI) (VII)

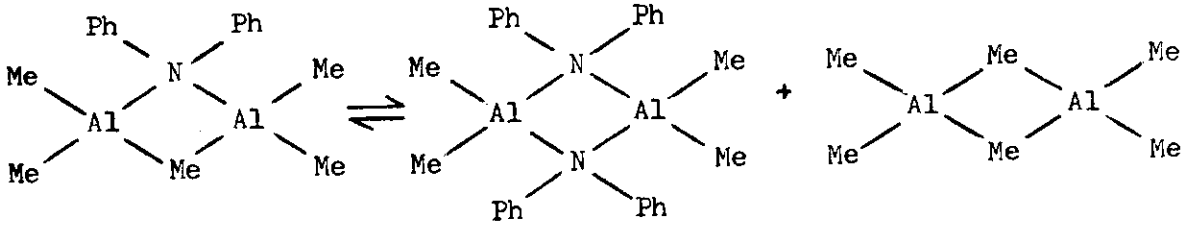
(VIII)

Consideration of the low temperature spectra results in the same description for the dimer as for the monomer-dimer scheme at low temperature. With temperature lowering there is a shift in the equilibrium toward species with terminal methyl positions such as structures VI and VII (structure VIII does not have any terminal methyls). In terms of relative numbers of molecules, eight molecules of structure VI gives sixteen terminal methyl groups, six molecules of VII gives six bridging methyl groups and six terminal methyl groups, and one molecule of VIII results in two bridging methyl groups which are different from the methyl bridge in VII. This results in six methyl bridges in VII, two methyl bridges in VIII and a total of twenty-two methyl groups which is consistent with the experiment-

ally observed ratio of 3:1:11 (bridging methyl in VII: bridging methyl in VIII:terminal methyls). With temperature lowering structure VI increases in concentration in the monomeric-dimer, dimer and oligomeric composition descriptions.

The NMR data and association values indicate that dimers represent the composition in solution of $MeMGOBu^t$ totally or at least to a major degree. At room temperature the t-butoxy(methyl) bridging system seems to predominate the composition in solution, and at low temperature the incorporation of two t-butoxy groups as bridging groups seems to be favored. It is interesting to speculate on the possible reasons for these structural preferences at room and low temperature.

It has been reported that μ-diphenylamino-μ-methyl-tetramethyldialuminum exists in cyclohexane in equilibrium with the dimethylaluminum diphenylamide dimer.[25]

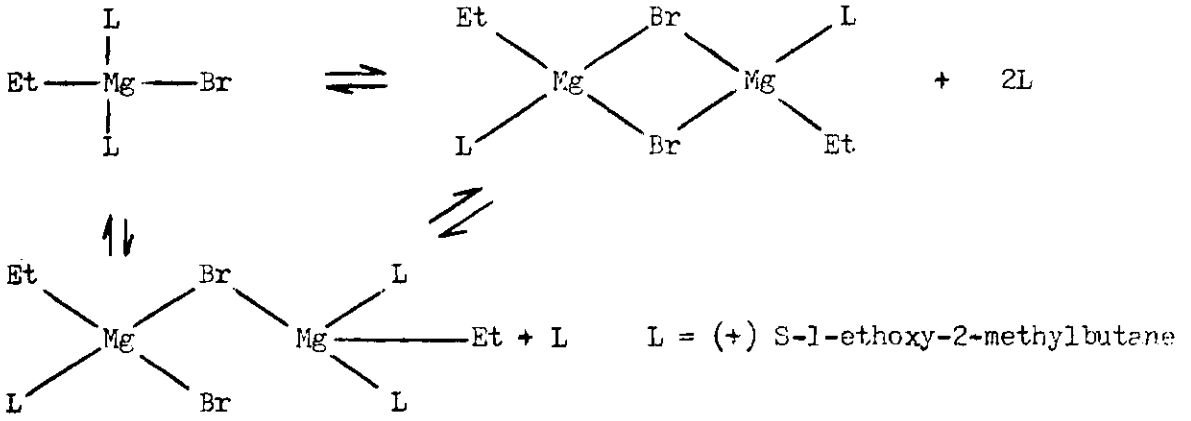


In this case the mixed bridged system is thermodynamically stable to disproportionation. It has been suggested that the driving force for this stability may be due to strong

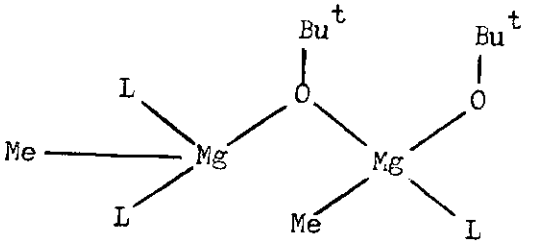
steric interactions in the dimethylaluminum diphenylamide dimer. The absence of such a steric factor in mixed bridged compounds involving weakly bridging (alkyl) and strongly bridging (alkoxy or amino) groups may result in bridging systems stable to disproportionation. Possibly for $MeMgOBu^t$ an analogous argument can be made concerning the preference of the t-butoxy-methyl bridging system at room temperature. The use of a methyl group as a bridging group results in the placement of one t-butoxy group in a terminal position. The terminal t-butoxy group is farther away from neighboring groups than when it is in a bridging site, therefore making the μ-t-butoxy-μ-methyl system more stable than the double t-butoxy bridging system at room temperature. Dimer VIII involves weakly bridging groups and therefore accounts for only a minor part of the composition in solution. Molecular models of VI, VII and VIII do not show strong steric interactions of the t-butoxy group while in a bridging site, but these models indicate that the t-butoxy group is farther away from neighboring groups while in the terminal position. The preference for VI at low temperature may be due to a decrease in the molecular vibrations of the molecule, allowing for the utilization of two t-butoxy bridges (the maximum number). It appears that with temperature lowering the strongest bridging system VI becomes more favorable.

The low temperature NMR data for $MeMgOBu^t$ may also be explained in terms of solvation effects. Recently Vink,

Blomberg and Brickelhaupt[26] reported evidence indicating an equilibrium consisting of monomer and dimer dietherates and dimer trietherates for ethylmagnesium bromide.



Calculations indicated that the trietherated dimer was a major constituent of the composition in solution of ethylmagnesium bromide. This evidence suggests that the increase in concentration of terminal methyl groups for $MeMgOBu^t$ with temperature lowering may result from the formation of an analogous trietherated dimer or a shifting of the equilibrium in favor of the monomer.



In this dimer the methyl groups are terminal, and the increase in formation of such species would account for the increase in concentration of terminal methyl groups at low temperature. The double alkoxy bridged dimer and the trietherated dimer description are both possible and no preference can be stated at this time. Kovar and Morgan[12] have studied the composition of dimethylberyllium adduct species in dimethyl sulfide solution by NMR. These workers have reported the observation of separate signals for the methyl groups in 1:1 and 1:2 adducts of dimethylberyllium and dimethylsulfide. The methyls in $Me_2Be{:}SMe_2$ absorb at 10.77τ and in $Me_2Be{:}(SMe_2)_2$ absorb at 11.30τ. The upfield shift in the 1:2 adduct is expected since the diamagnetic shielding of two coordinating dimethylsulfide molecules should be greater than one molecule. Analogous results have been reported for the methyl signals in $Me_2Be{:}NMe_3$ and in $Me_2Be{:}(NMe_3)_2$.[27] In t-butoxy(methyl)magnesium only one terminal signal is observed at low temperature. In fact in all four alkoxy(methyl)magnesium compounds studied only one signal is observed at low temperature in the region where monomer methyl sites and terminal sites for associated species absorb. Since only one signal is observed in this region, the observation of different solvates for the alkoxy(methyl)magnesium compounds is not possible.

Kovar and Morgan found that the equilibrium between $Me_2Be{:}SMe_2$ and $Me_2Be{:}(SMe_2)_2$ is quite temperature dependent.

In fact the equilibrium between the 1:1 and 1:2 adducts is operative only above -65°. At lower temperatures, polymerization occurs as described by the following equilibrium:

$$n\ Me_2Be{:}(SMe_2)_2 \rightleftharpoons (Me_2Be)_n{:}(SMe_2)_2 + (2n-2)SMe_2$$

$$n = 2,3,4...$$

At low temperature polymerization competes well with adduct formation as a coordination process. The dimethylberyllium system exemplifies the thermodynamic stability of bridging, electron-deficient bonds in associated species at low temperature. Since electron-deficient bridging bonds are favored over the solvation process at low temperature, then the formation of bridging bonds via the donation of the lone pair electrons of the alkoxy groups may be expected to be even more favorable. Parris and Ashby reported that in dimethylmagnesium in diethyl ether, highly associated species precipitated from solution at low temperature.[9] This resulted in an effective higher concentration of monomeric dimethylmagnesium at low temperature than present at room temperature. The NMR spectra at low temperature showed two terminal type methyl group signals at 11.69τ and 11.74τ. The 11.69τ signal was assigned to terminal methyl groups in associated species and the 11.74τ signal was assigned to monomeric species. It was concluded that some form of en-

hanced solvation for monomeric dimethylmagnesium at low temperature may also be responsible for the observed NMR. The dimethylberyllium-dimethyl sulfide system indicates the preference of the formation of bridging bonds over increased solvation at low temperatures, whereas the dimethylmagnesium and alkoxy(methyl)magnesium compounds in diethyl ether do not lead to a single description. Consideration of the dimethylberyllium-dimethyl sulfide data suggests that the double alkoxy bridged dimer at low temperature may be the best description, but for the alkoxy(methyl)magnesium compounds either description is still operative.

It is interesting to observe that the alkoxy(methyl)-magnesium compounds show only one signal for a terminal like methyl group at room temperature. The approach used to explain why the methyl groups in monomeric and dimeric $MeMgOCPh_2Me$ and $MeMgOBu^t$ respectively may absorb at the same chemical shift also may explain why different solvates may be indistinguishable in NMR study. In the tightly bridged dimers, (consider structures III and VI), each magnesium atom is coordinated to three oxygen atoms. The trietherated dimer has an extra ether of solvation, but each magnesium is still coordinated to three oxygen atoms. The alkoxy oxygens may have a similar diamagnetic shielding effect as the oxygen atom in the ether solvent molecules, and therefore, the proximity of methyl groups to one or two solvent molecules results in an inconsequential change

in the electronic environment. In the case of $MeMgOR \cdot Me_2Mg$ compounds, the presence of the bridging alkoxy oxygen may dampen the shielding effect of the addition of another solvent molecule if a trisolvated complex is formed. The dimethylberyllium and dimethylmagnesium compounds do not contain sulfur or oxygen atoms respectively, and the presence of one or two dimethylsulfide or diethyl ether molecules may readily change the shielding around the methyl groups.

$MeMgOPr^i \cdot Me_2Mg$ is a complex in solution (i = 0.93-1.06, m = 0.078-0.232), and is prepared by adding $MeMgOPr^i$ to Me_2Mg. The molecular association determination indicated that $MeMgOPr^i$ has concentration dependent i-values varying from 2.29 (m = 0.0537) to 2.76 (m = 0.265). A change in the degree of association with a change in concentration indicates an equilibrium in solution between distinct chemical species.

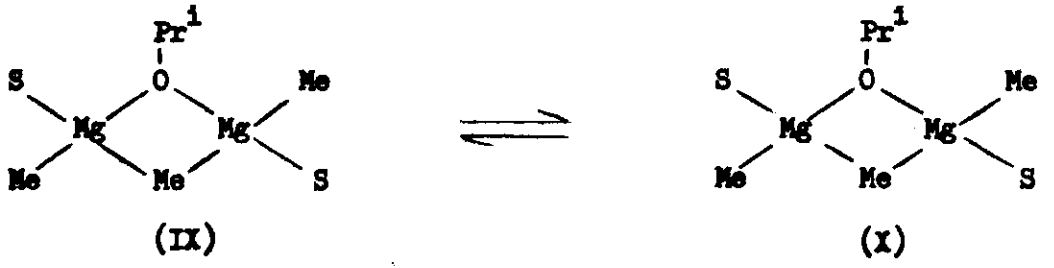
The $MeMgOPr^i \cdot Me_2Mg$ complex exhibits one signal in the methylmagnesium absorption region (11.40τ) at $+40^\circ$ (see Table 3). The doublet of the i-propoxy group is seen at 8.57τ. Temperature lowering to -80° resulted in a shift of the 11.40τ signal to 11.51τ. At -100° the 11.51τ signal shifted to 11.58τ and broadened while the i-propoxide signal remained unchanged. Further temperature lowering to -120° resulted in the splitting of the 11.58τ signal into a signal at 11.38τ and 11.68τ with a relative area ratio of 1:7. The NMR spectra and association data indicate that the complex

Table 3. Low Temperature NMR Data for $MeMgOPr^i \cdot Me_2Mg$ and $MeMgOPr^i$

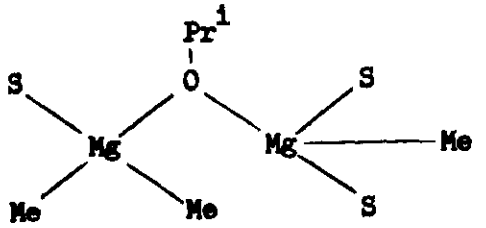
			$MeMgOPr^i \cdot Me_2Mg$		
+40°	8.57	11.40			
-80°	8.58		11.51		
-100°	8.58			11.58(broad)	
-120°[a]		11.38(1)			11.68(7)
			$MeMgOPr^i$		
+40°	8.56	11.30			
-30°	8.56	11.33			
-60°		11.35(2)		11.60(1)	
-80°		11.37(1)		11.63(1)	

a. Approximate temperature

is involved in a rapid equilibrium as follows:



The open bridged system (X) predominates at +40° resulting in an averaged signal at a field indicative of predominately terminal methyl groups. The direct observation of distinct chemical species IX and X were observed; however, only at low temperatures. The presence of IX was inferred by the observation of a bridging methyl signal (11.38τ) at -120°. Structure IX by itself would result in an area ratio of 1:2 (bridging to terminal methyl groups), and structure X alone would exhibit only a terminal methyl signal. The NMR spectrum at -120° exhibits a relative area ratio of 1:7 (bridging to terminal methyls) indicating that an equilibrium does indeed exist and that at -120° the open bridged system still predominates. The predominance of the open bridged dimer X even at -120° may be due to an enchanced solvation effect resulting in a trietherated complex.



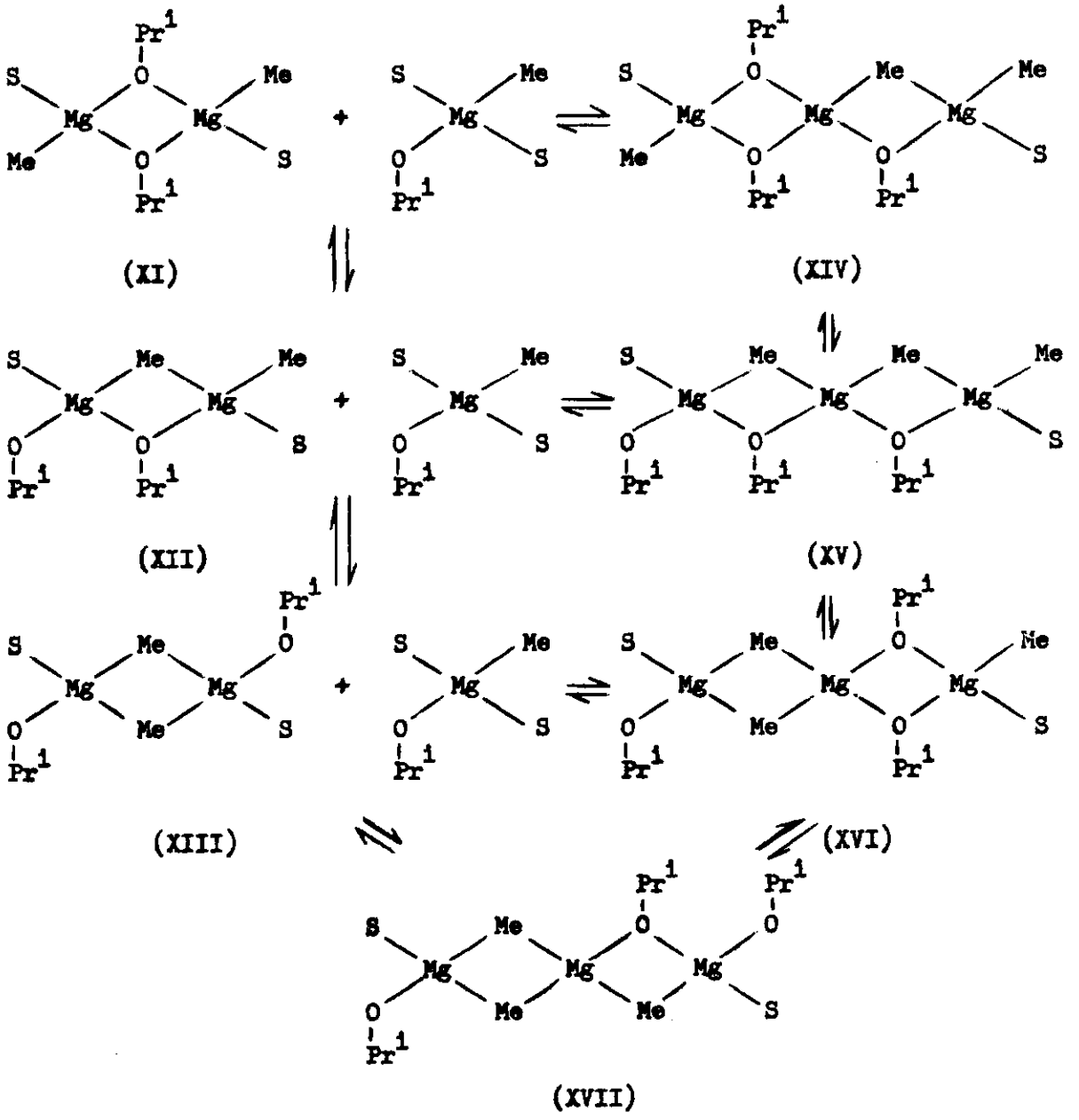
In this complex, the diethyl ether solvent molecules may compete very favorably with the methyl groups for coordination sites resulting in the low concentration of the mixed i-propoxy-methyl bridged system. These results are especially interesting when they are compared to results observed for $MeMgOBu^t \cdot Me_2Mg$. The structural difference between these two complexes is one methyl group on the alkoxide bridge, but the difference in the exchange rates is very large. $MeMgOBu^t \cdot Me_2Mg$ exhibits two distinct signals at $+30^o$; one for the bridging methyl group and the other for the terminal methyl group, whereas -120^o is needed to observe the two different types of methyl groups in $MeMgOPr^i \cdot Me_2Mg$. This indicates that a small structural difference may result in a large difference in the methyl group exchange rates in solution.

The concentration dependent molecular association values of $MeMgOPr^i$ indicate that an equilibrium in solution exists between distinct chemical species. At the lower concentration range the compound appears to be predominantly dimeric (2.29) and as the concentration increases the association increases to a maximum of 2.78 (the last association

value recorded is 2.76). A value of 2.78 is an averaged molecular weight which may be interpreted by various equilibria. A dimer-trimer, dimer-tetramer, cyclic trimer or an oligomeric composition in solution appear to be the best alternatives in describing the composition in solution.

The NMR spectrum of a 0.265 m solution of $MeMgOPr^i$ at $+40^o$ exhibits a doublet at 8.56τ (doublet of the i-propoxide group) and a signal at 11.30τ representing the methylmagnesium region. At -30^o solid formation occurred resulting in a decrease of the signal intensity and a shift of the 11.30τ signal to 11.33τ (the i-propoxide chemical shift remained effectively unchanged with temperature lowering). On warming the solid was isolated, analyzed and found to be $MeMgOPr^i$. At -60^o the 11.33τ signal shifts to 11.35τ and a new signal appears at 11.60τ which is smaller in intensity than the 11.35τ signal (2:1). Temperature lowering to -80^o causes the 11.35τ signal to shift to 11.37τ and the 11.60τ peak to shift to 11.63τ with the peak intensities being approximately equal.

Description of the composition of this system by a dimer-trimer equilibrium appears to be quite reasonable since $MeMgOPr^i$ is smaller than $MeMgOBu^t$ and should be more highly associated. The following scheme contains representative dimers and trimers in solution:



(XI) (XIV)

(XII) (XV)

(XIII) (XVI)

(XVII)

The NMR spectra indicate an averaged signal at +40° and the presence of different methyl environments at -60° and below. A dimer-trimer equilibrium would result in an averaged signal at room temperature as is observed. The spectra show at -60° a preference for bridging methyl sites

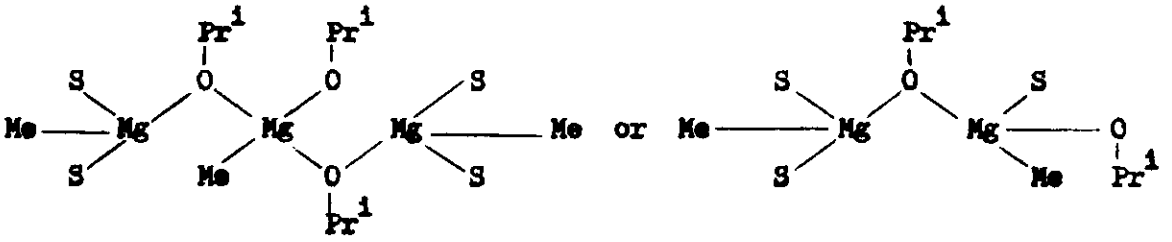
(11.35τ) over terminal sites in a 2:1 ratio. The continued temperature dependence of the composition in solution is shown by temperature cooling to -80°. At -80° the terminal methyl environment (11.63τ) increases relative to the bridging methyl sites (11.37τ) resulting in a 1:1 ratio. The bridging to terminal methyl ratio of 2:1 at -60° can be accounted for by the trimers XV and XVI alone, by a mixture of all the dimers and trimers, or by a mixture of all the trimers (XV through XVII) alone. The existence of only dimers at -60° is not considered to be a meaningful description since the temperature lowering would not be expected to result in less association than found at room temperature. Since bridging methyl sites predominate at -60° then those structures with at least two bridging sites to every terminal site must be the **major** species in solution. Structures XIII, XV, XVI and XVII meet this criterion. At -80° the 1:1 equivalence of bridging and methyl positions can be accounted for by an increase in concentration of those structures with more terminal than bridging sites. This is necessary in order to compensate for those structures in solution with more bridging methyl than terminal methyl sites. Structures XI and XIV have more terminal than bridging methyl sites. Trimers, XV, XVI and XVII taken collectively cannot give a 1:1 ratio. Dimer XII has a 1:1 ratio of bridging to terminal methyl sites and XI has only terminal methyl sites, but these structures are not expected to be major constituents

at -80°. Therefore, with temperature lowering trimer XIV should be increasing in concentration.

The alternative interpretation of the temperature dependence of the spectra at -80° suggesting that dimer XII is the major species in solution since it will give the appropriate area ratio of 1:1, has been examined. It was observed that at -30° solid formation occurred, and it may be argued that the more highly associated species in solution precipitated leaving behind predominantly dimeric species. This description must then account for the 2:1 ratio of bridging to terminal groups at -60° by a predominance of dimer XIII. Of the three dimers, XIII should be the least favorable since the two strong alkoxy bridging groups are not utilized. To further investigate this possibility, a dilute sample (0.05 m) or $MeMgOPr^i$ was examined. With temperature lowering no solid formation occurred, and at -60° and at -80° the 0.05 m and 0.265 m solution exhibited the same signals. The signals of the two samples were of the same intensity at the same amplitude indicating that the same shift in equilibrium occurred. These results indicate that the precipitation of more highly associated species resulting in the leaving behind of dimers does not occur since the 0.05 m sample did not produce a precipitate, but gave the same spectrum as the 0.265 m sample.

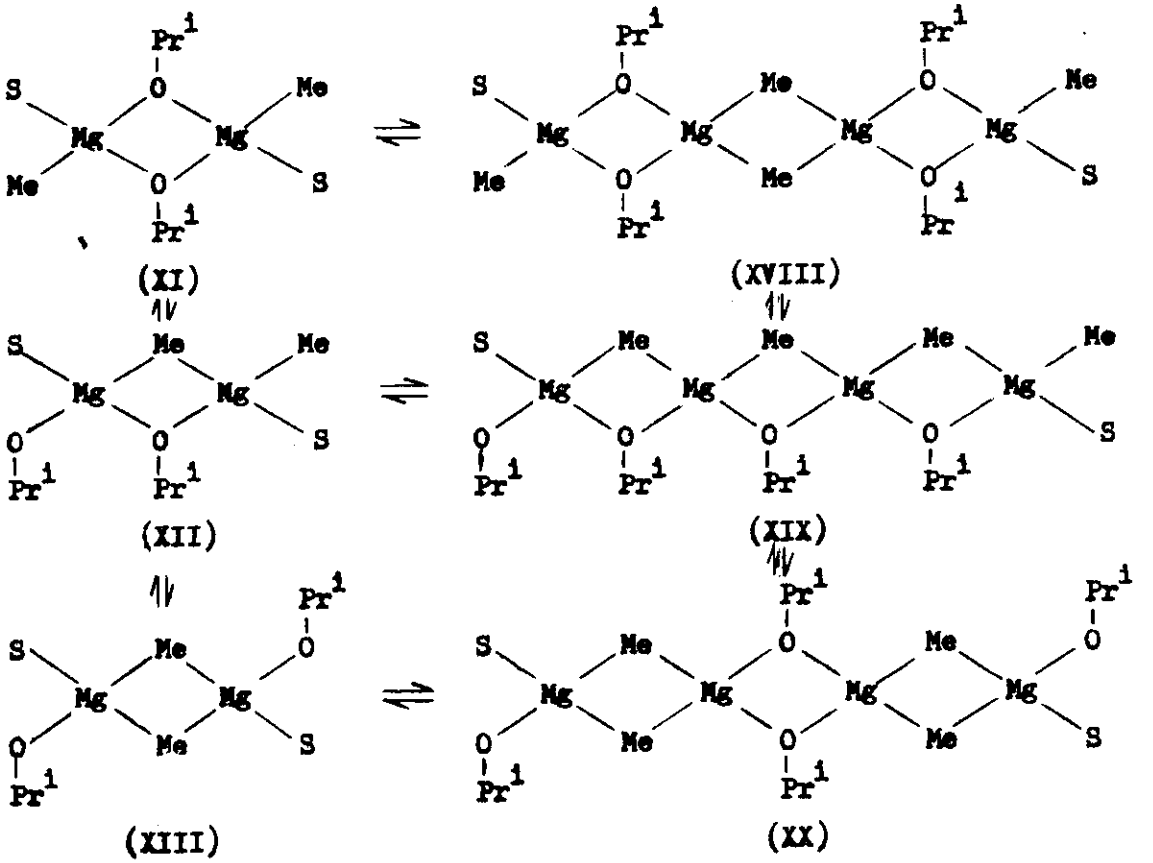
In this and in the following descriptions of the composition in solution of $MeMgOPr^i$, the increase in concen-

tration of terminal methyl groups with temperature lowering may be considered to be due to the formation of new solvates such as:



Such solvates may also explain the temperature dependence of the spectra from -60° to -80°.

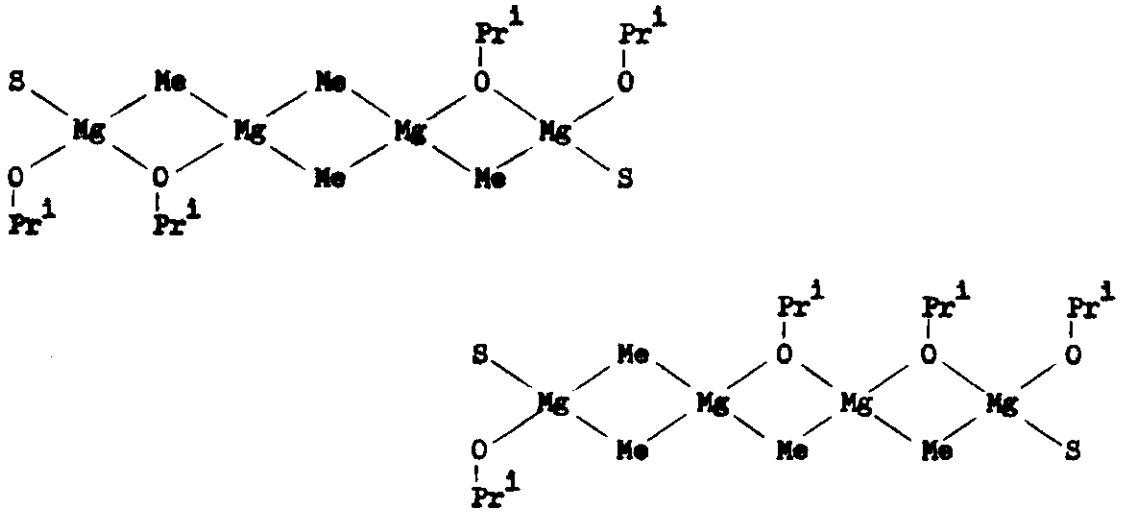
The association of $MeMgOPr^{i}$ indicates the possibility of a dimer-tetramer equilibrium. The following scheme is consistent with the NMR spectra and association data. The tetramers shown are representative of the types of structures which may exist in solution, and represent those structures with one, two or no terminal alkoxy groups. The structures shown represent tetramers which are formed by the coming together of two dimers via two alkoxy bridges, one alkoxy and one methyl bridge, and two methyl bridges. At $+40^{\circ}$ the equilibria involve fast methyl group exchange processes resulting in an averaged signal. The exchange process occurs intramolecularly and intermolecularly. The intramolecular process occurs between dimers XI, XII and XIII and between tetramers XVIII, XIX and XX.



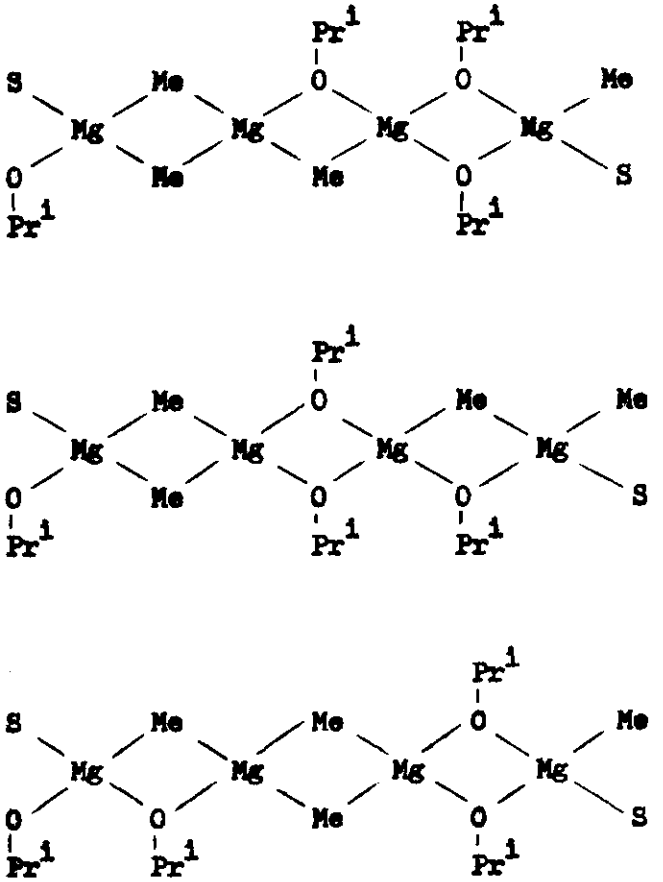
The intermolecular exchange occurs through the equilibria between the dimers and tetramers in which the terminal methyl in the dimer becomes a bridging methyl in the tetramers. The two methylmagnesium signals at 11.35τ(2) and 11.68τ(1) at -60° can be related to all the structures. The i-values of 2.78 indicates an equilibrium in solution consisting of dimers and tetramers at room temperature, but the exact composition in solution at -60° is not known. The relative area ratio at -60° indicates a predominance of bridging methyl environments (2:1), and this is best

explained by an equilibrium favoring the species with the greatest number of bridging methyl environments relative to terminal positions (XIII, XIX and XX). The dimeric species cannot account for the methyl bridge predominance unless the dimer possess some double methyl bridge species which is highly unlikely based on the results with $MeMgOBu^t$ and the significantly greater bridging tendency of alkoxy groups compared to methyl groups. At -80^o the two signals represent bridging and terminal methyl environments of the same concentration. These data are consistent with structures XII and XVIII, which would exhibit bridging and terminal methyl environments of the same intensity. The most favorable bridging system is one involving the maximum number of alkoxide bridges and at low temperature atomic and molecular motion is slowed down sufficiently to eventually allow for the utilization of all four alkoxide bridges in XVIII; therefore, lower temperatures (-80^o) should increase the concentration of XVIII compared to the other structures.

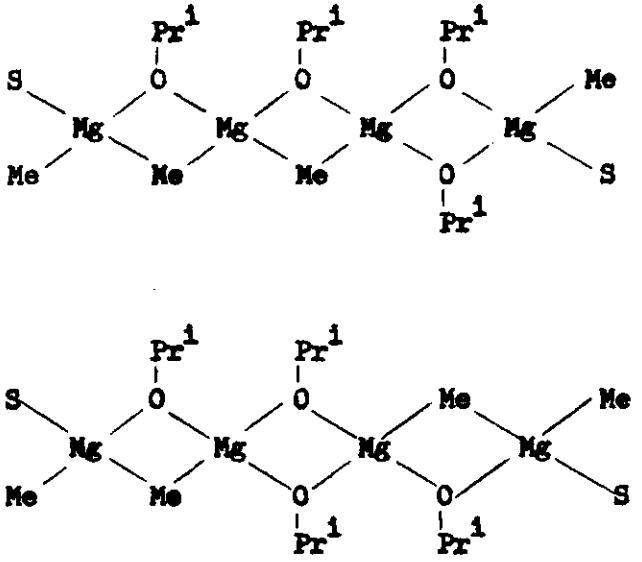
Other tetramers are also possible and may be in solution along with XVIII, XIX and XX. For example, possible tetramers with two terminal i-propoxy groups like XX are:



Structures with one terminal and one bridging group like XIX are:



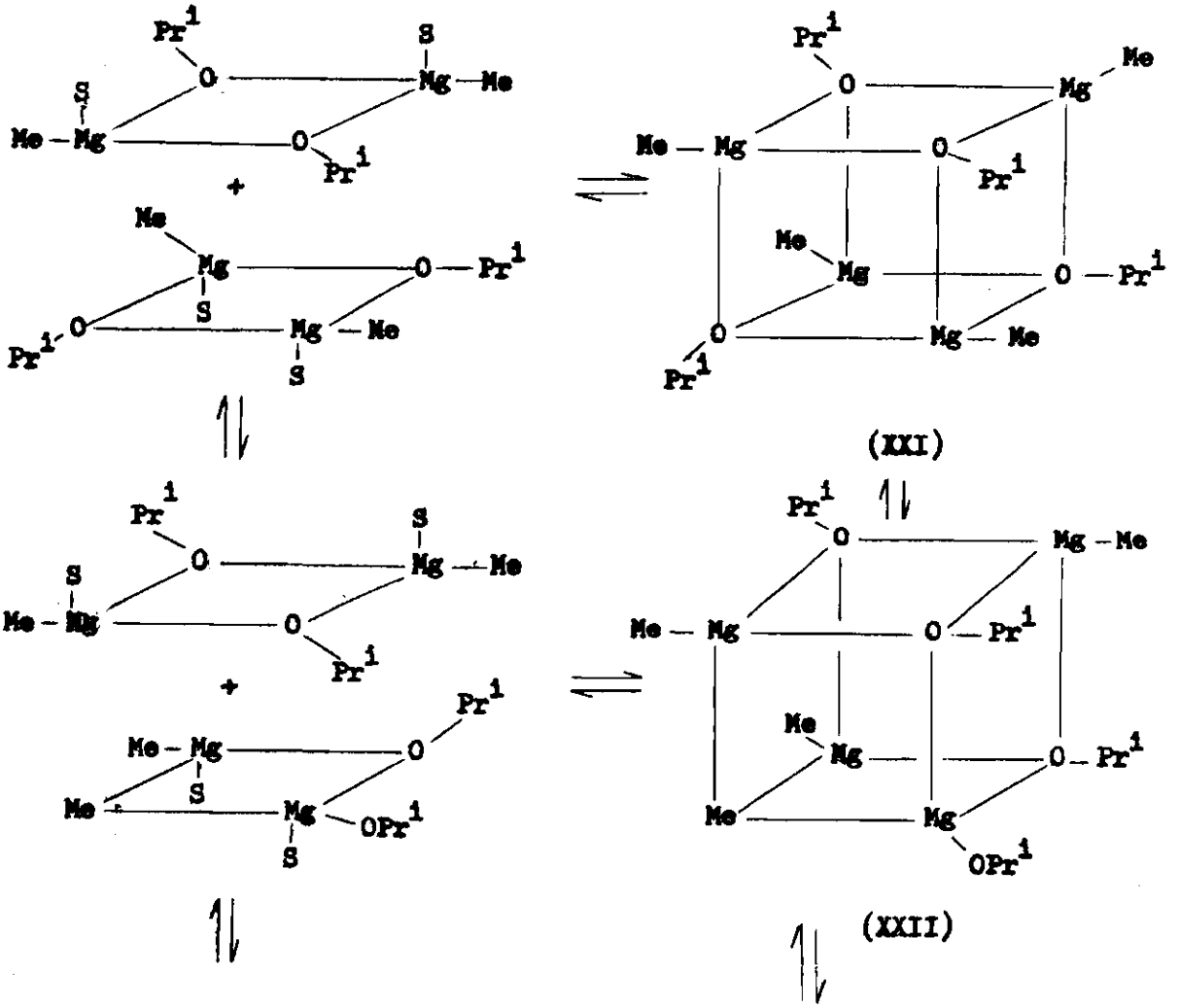
Structures with two terminal methyl groups and all bridging alkoxy groups like XVIII are:

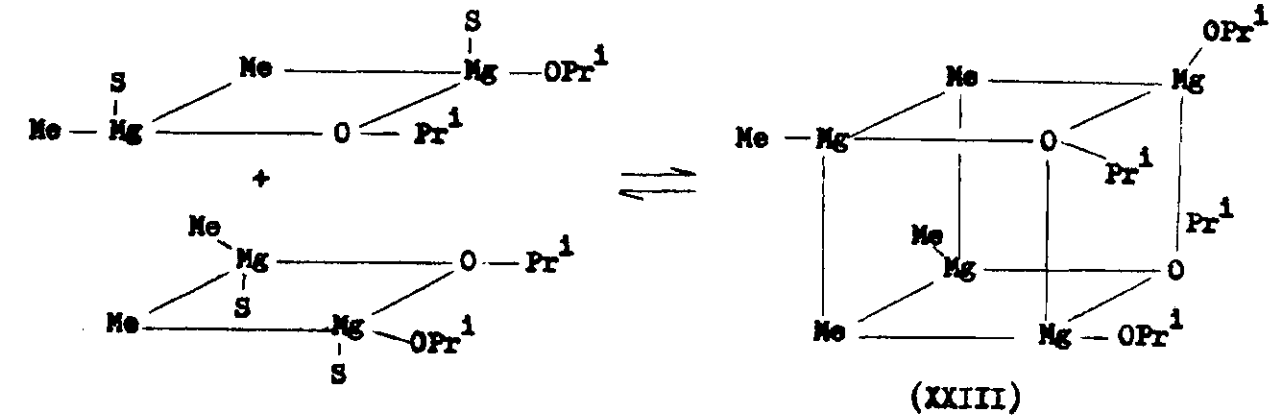


Other possible structures may be conceived which are reasonable. The point to be made is that as the temperature is lowered to -60°, tetramers like XIX and XX are favored which have more bridging methyl sites than terminal methyl sites. As the temperature is lowered to -80° tetramers like XVIII are favored which utilize all four alkoxy groups as bridging groups (such tetramers have a 1:1 ratio of bridging to terminal methyl groups). Tetramers XVIII, XIX and XX have been used to describe the equilibrium since these structures are easily formed by the coming together of two dimers (2 XI, 2 XII or 2 XIII). Tetramers XVIII, XIX and XX fit the

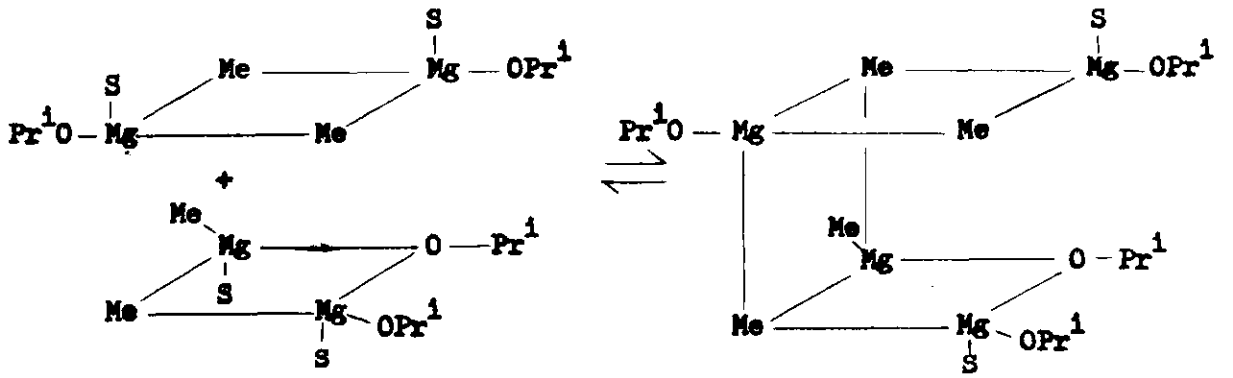
NMR data, but all the tetramers shown are equally important.

In describing the composition in solution of $MeMgOPr^i$ as consisting of a dimer-tetramer equilibrium a possible tetrameric structure is the cubane structure. The following scheme contains representative cubanes which fit the data:

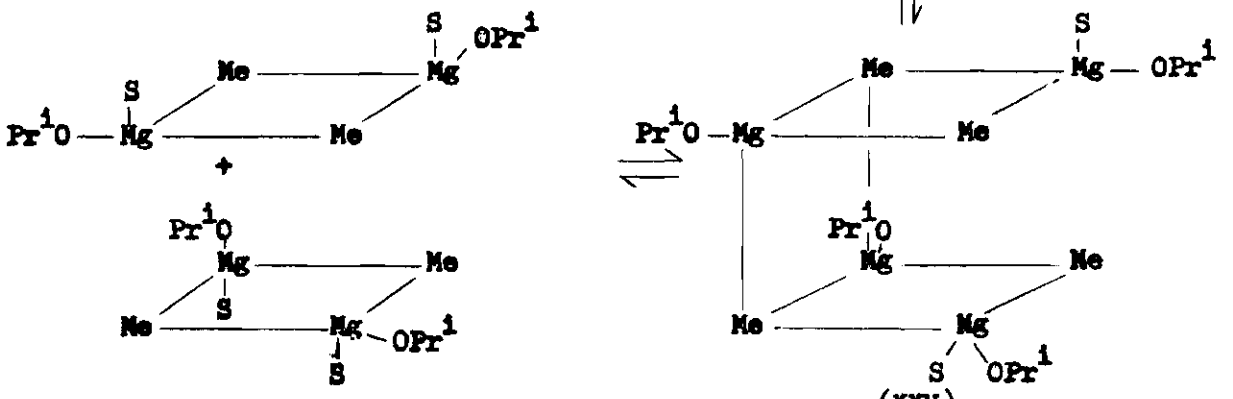




(XXIII)



(XXIV)



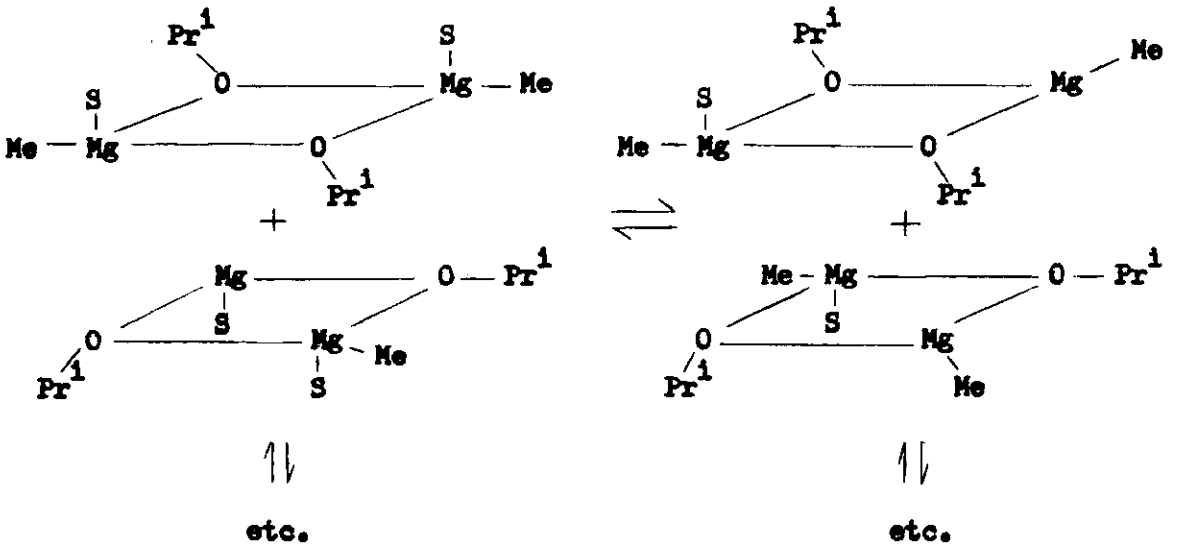
(XXV)

The chemical shift of a μ_3 bridging methyl group in diethyl ether has not been reported. The prediction of the chemical shift would be difficult since the hybridization of the magnesium atom is not known. It is reasonable to assume that a μ_3 bridging methyl would absorb downfield from the non-bridging methyl in the cubane, since the μ_3 methyl just as the μ_2 methyl bridge is involved in electron deficient bonding. The bridging methyls in the cubane description are best represented by the 11.35τ(-60°) and 11.37τ (-80°) signals, and the non-bridging methyls are represented by the 11.60τ(-60°) and 11.63τ(-80°) signals. Cubane XXI and tetramer XVII are analogous in that all of the alkoxy groups are involved in bridging, and both structures are favored at -80°. The area ratio shows an increase in non-bridging methyl groups (11.63τ) during cooling to -80°, and cubane XXI has all of its methyls in non-bridging sites. At -60° bridging groups are present in 2:1 ratio with respect to the non-bridging methyls. Structure XXV (just as XX) has all the methyls in bridging positions, and may at least partially account for the predominance of bridging methyls at -60°. Cubanes XXII, XXIII and XXIV are intermediate between XXI and XXV. As the temperature is lowered from -60° to -80° the equilibrium shifts from cubanes like XXIV and XXV to cubanes like XXI and XXII. Again an important point to be made is that other cubanes may be possible. The most important point to be made is that other cubanes with a pre-

dominance of bridging methyl groups at -60^{o} are favored and temperature lowering to -80^{o} results in an increase in non-bridging methyl sites. The cubanes discussed represent these observations and the types of cubanes which account for the NMR data.

In the cubane structure both magnesium and oxygen are four coordinate with oxygen donating both lone pairs of electrons. The important question arises concerning solvation of $MeMgOPr^{i}$ since the cubane has no sites for specific solvation. When an ether solution of $MeMgOPr^{i}$ is placed in benzene and the ether is co-distilled, the $MeMgOPr^{i}$ rapidly precipitates from solution. The precipitation indicates that ether is involved in some manner in the solvation process, and therefore specific solvation is present in diethyl ether solvent to some degree.

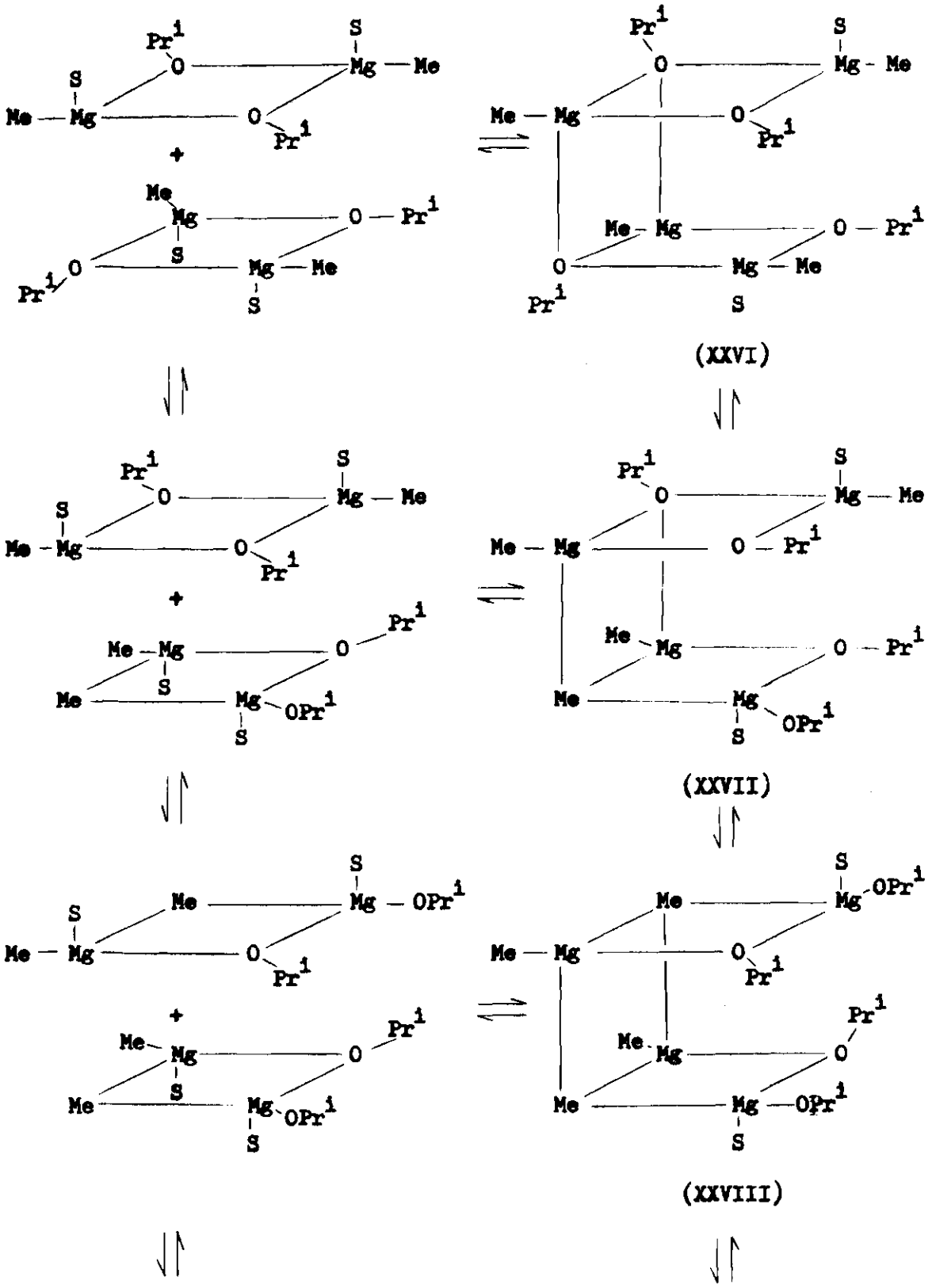
Perhaps a better possibility of the composition in solution would involve a modified cubane structure which allows for specific solvation. The modified cubane structure may exist in all six possible forms in a state of dynamic interconversion. This interconversion would result in an averaged NMR signal at room temperature as is observed.



Coates suggests a similar cubane description for some alkoxy(alkyl) zinc compounds.[28] Competition for solvation sites on magnesium by ether and the alkoxy groups as shown in the modified cubane description is reasonable since at room temperature the basicity of the alkoxy oxygen and ether oxygen may be very close. Experimentally it has been found that $MeMgOPr^i$ loses ether of solvation readily when placed under vacuum and no definite solvate is formed. This ease of desolvation is indicative of the weak specific solvation suggested for $MeMgOPr^i$.

The modified cubane description allows for solvation while bringing together positive and negative centers resulting in favorable non-bonded interactions between the oxygen and magnesium atoms. By breaking two bonds, the modified cubane becomes two dimers resulting in the dimer-tetramer

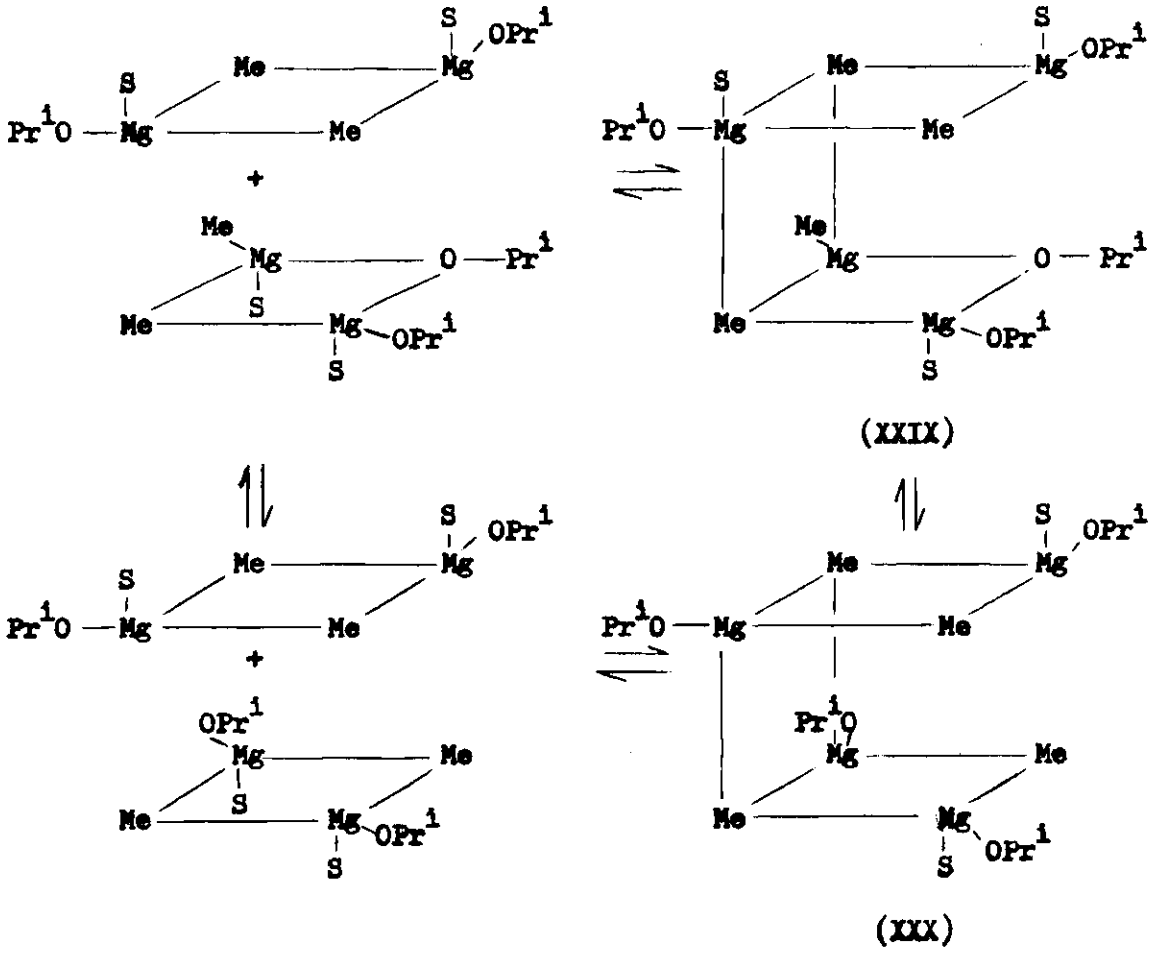
equilibrium.



(XXVI)

(XXVII)

(XXVIII)



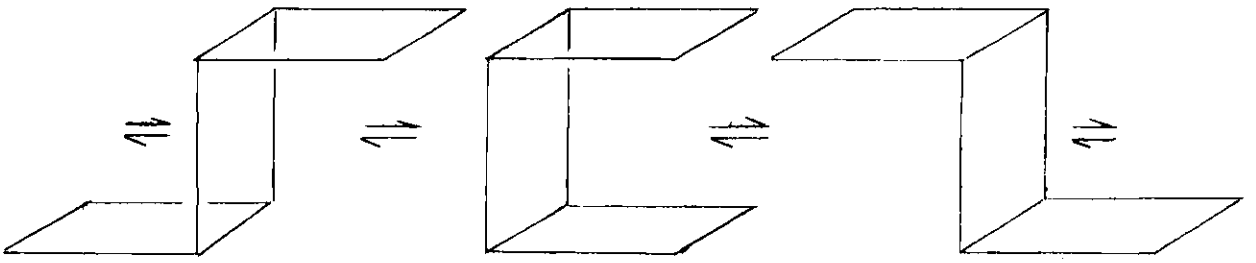
(XXIX)

(XXX)

The modified cubane description is analogous to the classical cubane and the bridging methyls in the modified structure are represented by the 11.35τ(-60°) and 11.37τ(-80°) signals. The non-bridging methyls are represented by the 11.60τ(-60°) and 11.63τ(-80°) signals. As the temperature is lowered from -60° to -80°, the equilibrium shifts from XXIX and XXX which have more bridging than terminal methyls to XXVI, XXVII and XXVIII which either have more terminal than bridging methyls or at least a 1:1 ratio of the two types of sites (XXVIII gives a 1:1 area ratio). Structure

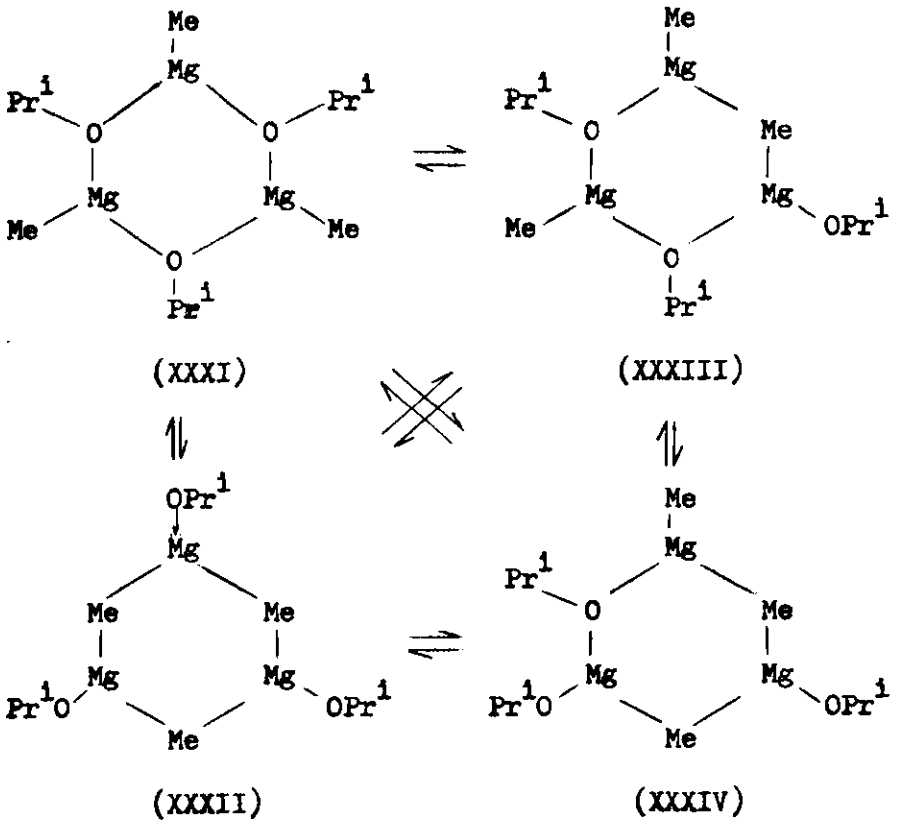
XXVIII alone fits the NMR data, and this observation is interesting since the two dimers comprising the modified cubane have an i-propoxy-methyl mixed bridged system. At -80° the exact composition in solution is not known and all the dimers and modified cubanes shown may exist in solution.

The modified cubane may exist in a variety of interconvertible forms in which no bond breaking is necessary.



The association plot for $MeMgOPr^i$ represents the type of slope expected for a cyclic trimer. The plot shows an increase in association then a leveling out around 2.76. A plateau at 2.76 is approximately described by a trimer since a value of 2.76 is relatively close to 3.0, and a dimer-trimer, dimer-tetramer equilibrium may be expected to show a greater increase in association with an increase in concentration. A cyclic trimer rather than an open-chain trimer might be preferred since the open-chain structure has sites for additional association whereas, the cyclic structure does not. The following cyclic trimer schem fits the

data.



At +40° rapid equilibrium among the species results in an averaged NMR signal. The increase in terminal methyl groups with temperature lowering indicates a shift in equilibrium from structures XXXII and XXXIV to XXXI and XXXIII at low temperature. The 2:1 bridging to terminal methyl ratio at -60° may be explained solely by XXXIV or by a composition in solution consisting of all four trimers. At -80° the 1:1 ratio indicates an increase in concentration of species with terminal methyl groups. At -80° the composition in solution

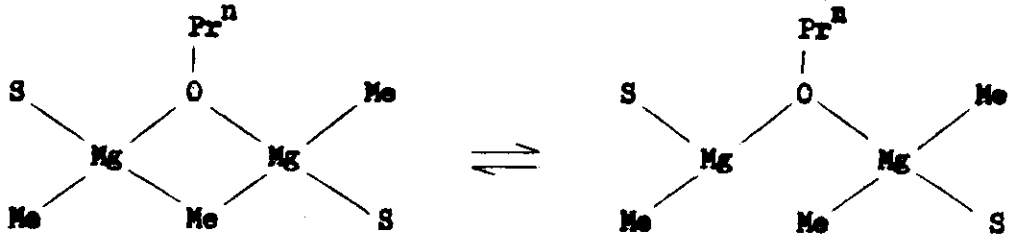
cannot be explained by the presence of just one of the trimers in solution, since no single structure can account for the 1:1 area ratio at -80°. The composition must therefore consist of an equilibrium between molecular species XXXI, XXXIII, XXXIV and possibly XXXII, (this trimer should be the least favorable trimer since no bridging alkoxy groups are present). Trimers XXXI and XXXIII possess more terminal than bridging methyl groups, whereas XXXII and XXXIV possess more bridging than terminal methyl groups. Together in an equilibrium they may give the 1:1 area ratio observed.

Possibly the association is oligomeric and these observations may involve the concentration range involving only dimers and trimers. If this is the case then association measurements at higher concentrations may indicate higher i-values. The association values and NMR data therefore represent the composition in solution between 0.0537 to 0.265 m. Since the $MeMgOPr^i$ solution was added to the ether during the ebullioscopic determinations, the solution was not saturated during the association measurement.

$MeMgOPr^n$ and Me_2Mg form a complex as determined by association measurements (i = 1.05-0.96, m = 0.068-0.11). $MeMgOPr^n$ exhibits the highest associated state of the alkoxides examined with i-values ranging from 3.36 to 3.8 (m = 0.134-0.235). The higher degree of aggregation is reasonable in that the smaller the steric requirement of

the alkoxide group the better chance for aggregation. The association values for $MeMgOPr^n$ indicate a trimer-tetramer, dimer-tetramer or oligomeric species in solution. The variable temperature NMR signals for both systems are shown in Table 4.

The +40 NMR spectrum of the $MeMgOPr^n \cdot Me_2Mg$ complex shows an averaged signal at 11.43τ. On temperature lowering to -40° a new signal appears at 11.26τ and the 11.43τ signal shifts to 11.45τ. The 11.26τ signal is assigned to the bridging methyl position in XXXV and the 11.43τ signal is assigned to the terminal methyl environment in XXXV and XXXVI.



(XXXV) (XXXVI)

Temperature lowering to -80° resulted in little change, and at -90° the complex precipitated. At-85° the bridging methyl signal resides at 11.28τ and the terminal methyl group is at 11.53τ. The 11.26τ signal is quite small compared to the 11.45τ signal, indicating the predominance of structure XXXVI in the above equilibrium.

Table 4. Low Temperature NMR Data for $MeMgOPr^n \cdot Me_2Mg$ and $MeMgOPr^n$

$MeMgOPr^n \cdot Me_2Mg$				
+40°			11.43	
-40°	11.26		11.45[a]	
-60°	11.27		11.48[a]	
-80°	11.27		11.51[a]	
-85°	11.28		11.53[a]	
$MeMgOPr^n$				
+40°		11.33		
0°	11.26	11.33[b]		
-40°	11.28	11.34[b]	11.42	
-60°	11.28	11.34[b]	11.42	
-80°	11.28	11.34		11.59
-100°	11.28[c]	11.35[c]		11.60
-110°	11.28[d]	11.35[d]		11.61

a. Large relative to the downfield signal.

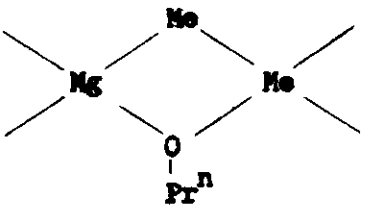
b. The 11.33τ-11.34τ signal is larger relative to the overlapping 11.26τ-11.28τ signal.

c. The relative area ratio of the 11.28τ and 11.35τ signals relative to the 11.60τ signal is 10:1.

d. The relative area ratio of the 11.28τ and 11.35τ signals relative to the 11.61τ signal is 8:1.

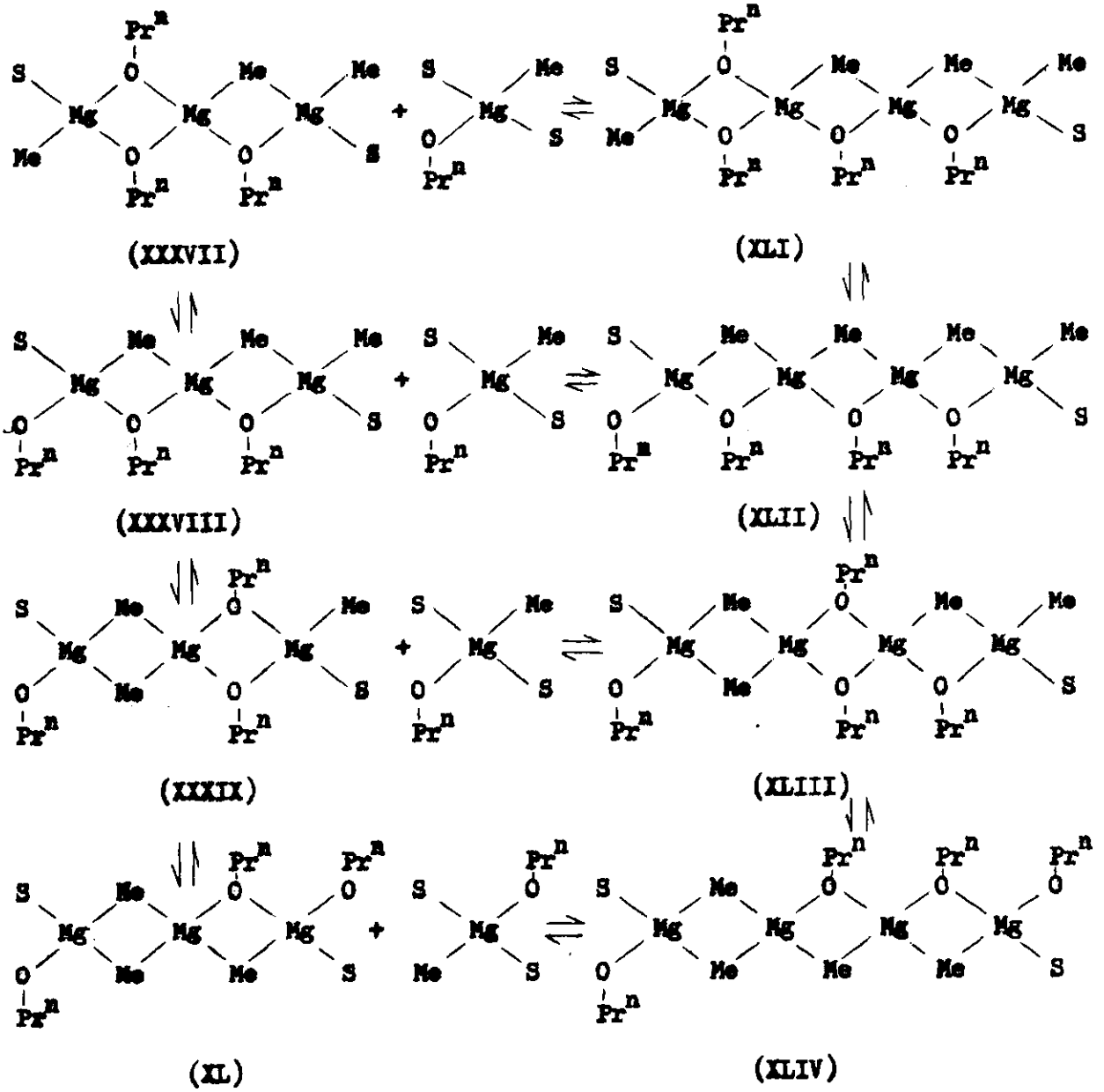
At +40° $MeMgOPr^n$ exhibits one signal at 11.33τ. Temperature lowering at 0° resulted in the formation of a small signal at 11.26τ overlapping with the signal at 11.33τ (the 11.33τ signal is much larger than the 11.26τ signal). This is interesting since $MeMgOPr^i$ showed collapsing of the signal only at -60° and below. At -40° a new signal at 11.42τ is observed overlapping with the large signal at 11.34τ and the 11.26τ signal shifts to 11.28τ. At -80° the 11.28τ and the 11.34τ signals remain unchanged while the 11.42τ signal moves to 11.59τ. The spectrum at -100° exhibits three signals: 11.28, 11.35 and 11.60τ.

Various structural generalizations may be inferred from the examination of the NMR data. At +40° the equilibrium must be fast relative to the NMR time scale since an averaged signal is observed. The 11.33τ signal at 0° is an averaged signal comprising both bridging and terminal methyl groups and at -40° the signal begins to collapse into a bridging signal at 11.34τ and a terminal signal at 11.42τ. As the temperature is lowered the concentration of species in solution with terminal methyl groups increases. This is indicated by the bridging:terminal methyl area ratio at -100° and -110° (10:1 at -100° and 8:1 at -110°). At -40° the small signal at 11.28τ represents a n-propoxy-methyl mixed bridge environment. This signal assignment is based on the observation that $MeMgOPr^n \cdot Me_2Mg$ exhibits a bridging methyl signal at 11.26τ-11.28τ from -40° to -85°. This



signal in the $MeMgOPr^n \cdot Me_2Mg$ spectrum can be accounted for only by a n-propoxy-methyl bridging situation. At -40° the 11.34τ signal represents a methyl bridge in a dimethyl bridge environment (based on the previously mentioned observation that the methyl group in a dimethyl bridge environment absorbs upfield from the methyl group in an alkoxy-methyl environment). It is interesting to note that the 11.28τ bridging signal is observed at 0°, whereas the 11.34τ bridging signal is observed only at -40° and below. This indicates that at 0° the bridging methyl at 11.28τ (a methyl group in an n-propoxy-methyl bridging system) does not exchange or exchanges more slowly than the methyl bridge represented by the 11.34τ signal (a dimethyl bridging system). This suggests that the n-propoxy-methyl bridge is more stable than the dimethyl bridging system.

The i-values for $MeMgOPr^n$ (3.36 to 3.8) clearly indicate the possibility of a trimer-tetramer equilibrium. The following scheme fits the data:



(XXXVII) (XLI)

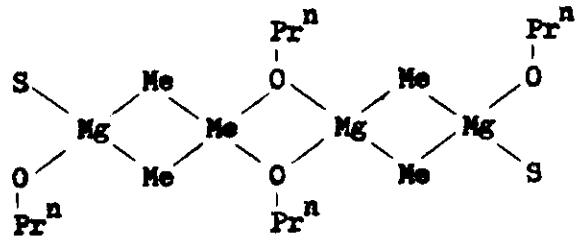
(XXXVIII) (XLII)

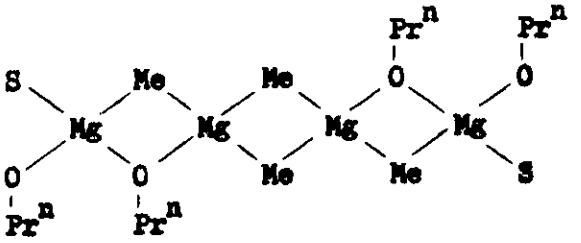
(XXXIX) (XLIII)

(XL) (XLIV)

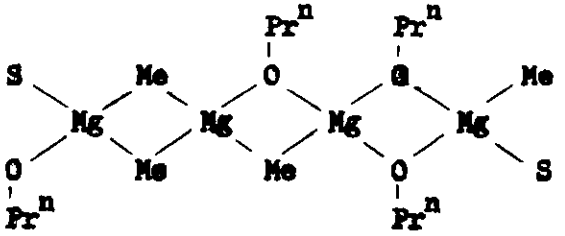
The scheme includes various possible trimers, and the tetramers represent the three general types of structures in solution: structures with one, two and no terminal alkoxy groups. Other possible tetramers with two terminal n-propoxy

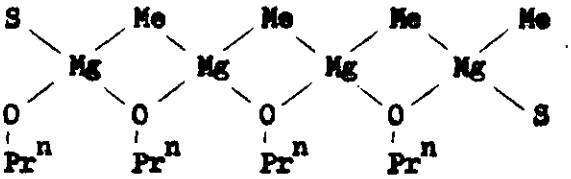
groups are:



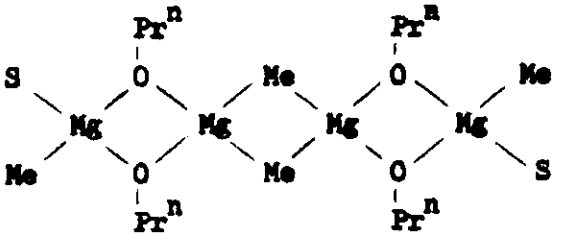


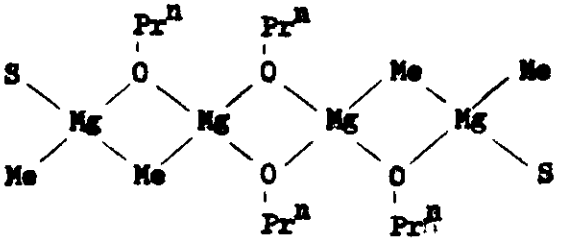
Structures with one terminal and one bridging group are:





Structures with two terminal methyl groups are:





For simplicity all the structures are not shown, but rather structures representing the three general types of structures. At the higher temperatures (+40° to -40°) structures such as XXXVIII, XXXIX, XL, XLII, XLIII and XLIV are favored since they contain just one or no terminal methyl groups. At the lower temperatures structures such as XXXVII and XLI are favored since they have two terminal methyl sites, and only those structures with two terminal methyl sites can account for the increase in terminal methyl concentration at low temperature (just as in the other compounds discussed).

The dimer-tetramer equilibrium of $MeMgOPr^n$ is analogous to the equilibrium used to describe $MeMgOPr^i$ and is sufficiently fast to give an averaged signal at +40°; (see structures XI, XII, XIII, XVIII, XIX, and XX for $MeMgOPr^i$).

The association values indicate a higher concentration of tetramers than present in the $MeMgOPr^i$ equilibrium. At the higher temperatures ($+40^\circ$ to -40° structures analogous to XIX and XX predominate and temperature lowering from -40° to 110° resulting in an increase in concentration of structures with terminal methyl groups analogous to XVIII. The signal at 11.34τ represents methyl groups in the dimethyl bridge in tetramers for $MeMgOPr^n$ which are analogous to XIII, XVIII and XX for $MeMgOPr^i$. The signal at 11.28τ represents methyl groups in n-propoxy-methyl bridge systems analogous to XII and XIX. An averaged signal between the bridging and terminal methyl groups is expected at the higher temperatures since the bridging methyls in the tetramers are the terminal methyls in the dimers.

There is a possibility that solvation effects rather than the utilization of all four alkoxy groups with temperature lowering may explain the increase in concentration of terminal methyl groups. Since even at -110° the percentage of terminal methyl sites in solution is small, the complete utilization of all four alkoxy groups and the possible solvation effects contribute to only a minor extent to the equilibrium.

The existence of a cubane or modified cubane structure for the tetrameric species in solution must also be considered for $MeMgOPr^n$. The description in solution would follow the scheme shown for $MeMgOPr^i$ except that there would be a

higher concentration of cubanes or modified cubanes in solution for $MeMgOPr^n$ compared to $MeMgOPr^i$. At -40^o to -80^o the 11.28τ signal represents the methyls in the n-propoxy-methyl bridges in the dimers and in the cubanes and modified cubanes. The 11.34τ signal represents the dimethyl bridges in the dimers and modified cubanes. Since species with terminal methyl groups increase in concentration with temperature lowering, cubanes and modified cubanes such as XXI and XXVI are favored (cubanes with four n-propoxy bridges). The n-propoxy group is smaller than the i-propoxy group and may fit into bridging sites easier resulting in the production of more cubanes in solution than for $MeMgOPr^i$. This may be the reason for the higher association values for $MeMgOPr^n$ relative to $MeMgOPr^i$.

The slope of association values for $MeMgOPr^n$ indicates the possibility of oligomeric species in solution. If this is the case then this study has examined only a part of the composition in solution. If the composition in solution is oligomeric then the trimer-tetramer equilibrium would be the most meaningful description in the concentration range from 0.134-0.235 m with the association increasing with higher concentrations.

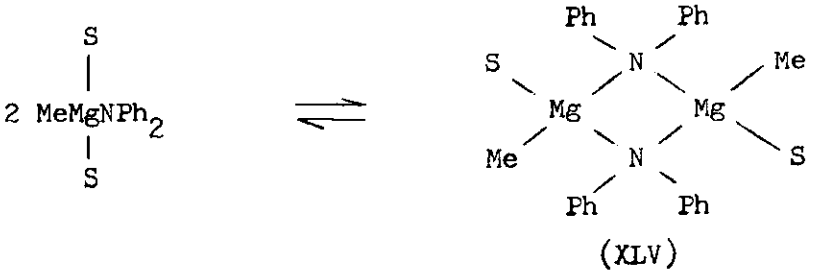
$MeMgNPh_2$ is prepared by the addition of diphenylamine to dimethylmagnesium and is monomeric in diethyl ether solvent (i = 1.16-1.26, m = 0.058-0.165). The addition of Me_2Mg to $MeMgNPh_2$ does not result in complex for-

mation as indicated by the observed i-values (i = 0.599-0.655, m = 0.035-0.113).

The NMR spectra of 0.137 m solution of $MeMgNPh_2$ are consistent with a monomeric compound in solution (Table 5).

$MeMgNPh_2$ exhibits a signal at 11.36τ at +40°. The diphenylamino signals are complex and are uninterpretable with temperature lowering. At -60° the 11.36τ signal shifts to 11.43τ. The spectra exhibit no temperature dependence from -60° to -100°, and the signal remains unsplit at 11.43τ. A single signal at -100° indicates a single type of methyl environment which is in keeping with a monomeric species.

The i-value range of 1.16-1.26 could also indicate a monomer-dimer equilibrium of the type shown below favoring the monomeric species.



(XLV)

The spectra do not show any signals in the bridging methyl absorption region and therefore a dimer would be best represented as having diphenylamino bridges and terminal methyl groups. In such an equilibrium the methyl groups are always

Table 5. Low Temperature NMR Data for $MeMgNPh_2$ Plus Me_2Mg and $MeMgNPh_2$

	$MeMgNPh_2$			
+40°	11.36			
-60°		11.43		
-80°		11.43		
-100°		11.43		
	Me_2Mg + $MeMgNPh_2$			
+40°	11.36		11.50	
-60°	11.30(1)		11.51(37)	
-80°	11.32[a]			11.60[b]
-100°	11.31[a]			11.68[c]
-110°		11.45[c]		

a. Very small

b. Broad

c. Overlapping signals

in a terminal methyl environment and if exchange is rapid only one methylmagnesium signal would be observed. With temperature lowering such a signal should broaden indicating a slowing down in the exchange process. At low temperatures monomeric and dimeric $MeMgNPh_2$ should be distinguishable. Me_2Mg in diethyl ether exhibits a signal for terminal methyl groups upfield from bridging methyl species, and $MeMgNPh_2$ should be analogous. The NMR spectra do not show line broadening even down to -100° thus corroborating the monomeric interpretation of the i-values. In addition, if monomer-dimer equilibrium existed then a shift to the dimeric species would be expected with an increase in concentration therefore allowing for the observation of both species. A low temperature NMR spectrum at -100° of a 0.543 m solution showed only one signal at -100°, unsplit and residing at 11.47τ. The signal was slightly broadened relative to the 0.137 m solution and the broadening can be easily explained as being due to increased viscosity of the more concentrated solution. It is possible that the i-value 1 is simply a result of the limits of capability of the association measurement and that for all practical purposes the i-value is 1 ± 0.2.

The NMR spectra of a 0.11 m solution of Me_2Mg and $MeMgNPh_2$ verifies the association data which indicates non-association of these two compounds. At $+40^{\circ}$ one signal in the methylmagnesium region is observed at 11.36τ indicating

rapid methyl group exchange between the two species in solution. At -60° the signal shifts to 11.50τ, and at -80° the signal collapses forming two signals. One signal is at 11.30τ(1) and the second signal is at 11.51τ(37). The 11.30τ signal shifts to 11.32τ and the 11.51τ broadens and shifts to 11.60τ at -100°. Temperature lowering to -110° splits the 11.60 τ signal into two overlapping signals of unequal intensity located at 11.45τ and at 11.68τ. The very small signal at 11.31τ does not change.

The splitting of the signal into three peaks at -110° indicates that the signals at the higher temperature are time averaged. The 11.31τ and 11.68τ signals are characteristic of Me_2Mg while the 11.45τ signal is characteristic of $MeMgNPh_2$ at that temperature. At -100° $MeMgNPh_2$ absorbs at 11.43τ and assignment of the 11.45τ signal to $MeMgNPh_2$ at -110° is reasonable. In order to further substantiate that the solution composition consists of unassociated Me_2Mg and $MeMgNPh_2$ an additional equivalent of Me_2Mg was added to the solution. At -100° to -110° the signals assigned to Me_2Mg grew in intensity relative to the $MeMgNPh_2$ indicating that the 11.31τ signal and 11.68τ signals are indeed due to uncomplexed Me_2Mg.

The monomeric nature of $MeMgNPh_2$ is quite interesting, and the reason for its propensity toward a monomeric composition has been considered. With respect to steric considerations, the diphenylamino group may be bulky enough

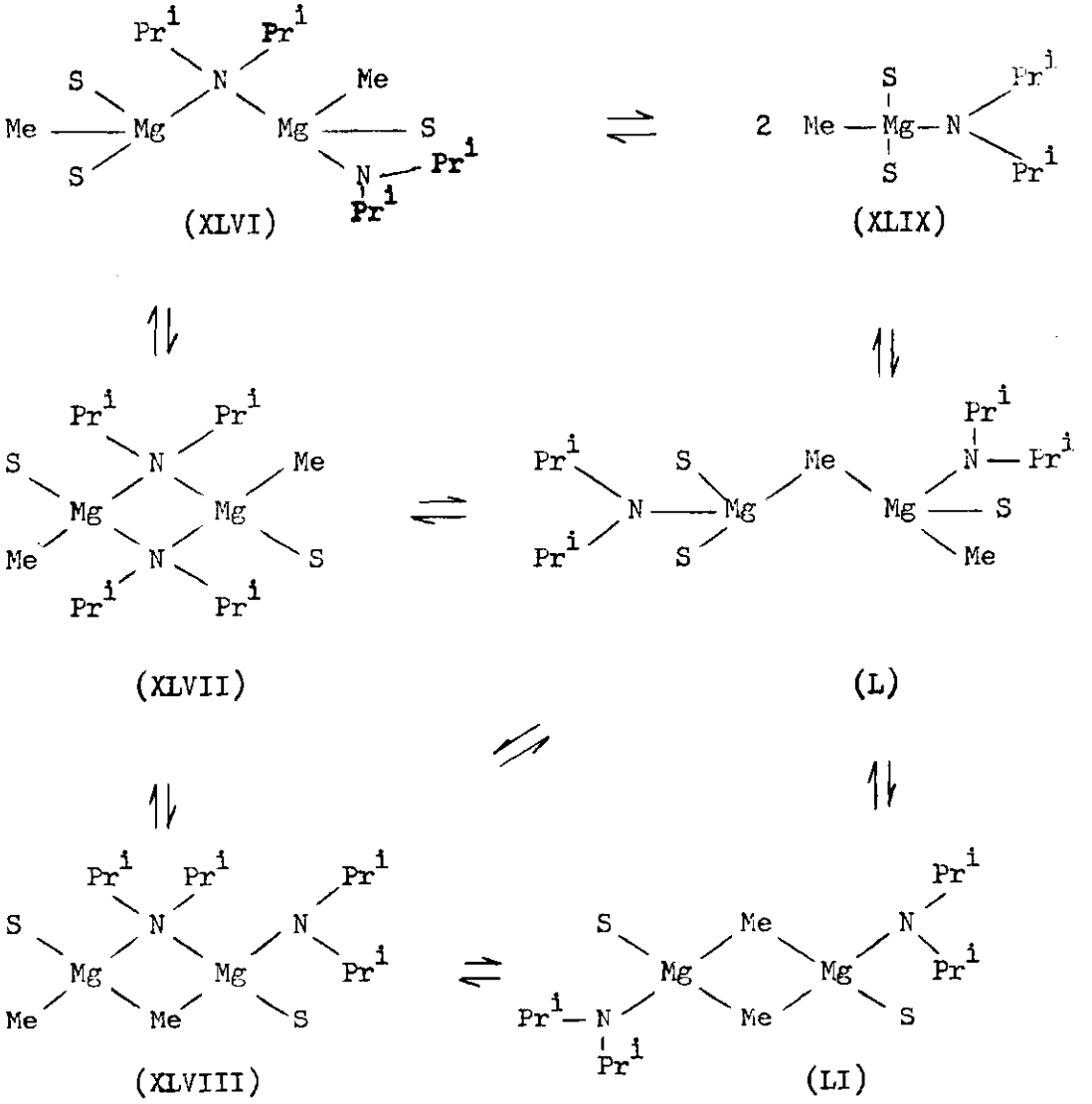
to prevent association. We have determined that di-i-propylamino(methyl)magnesium exists as a dimer in solution, and consideration of molecular models indicates that the steric bulk difference between the diphenylamino and the di-i-propylamino group are small. Probably more important factors are that the lone pair electrons may back-bond to the magnesium atom giving the magnesium-nitrogen bond double bond character, or that the phenyl rings may delocalize the lone pair electrons and therefore decreases the electron density (and hence basicity) of the amino group sufficiently to prevent association. A UV study was attempted to investigate the existence of magnesium-nitrogen back-bonding, but the large extinction coefficient (1.69×10^4) of the diphenylamino group necessitated working with dilute solutions (10^{-5}m). Meaningful data could not be obtained at such a low concentration.

Di-i-propylamino(methyl)magnesium ($MeMgNPr_2^i$) is dimeric in diethyl ether (i = 1.99-2.11, m= 0.143-0.455). The stoichiometric addition of Me_2Mg to $MeMgNPr_2^i$ results in complex formation yielding $MeMgNPr_2^i \cdot Me_2Mg$ (i = 0.9-1.32, m = 0.0201-0.0395). The low temperature NMR data for these compounds can be found in Table 6.

Table 6. Low Temperature NMR Data for $MeMgNPr_2^i \cdot Me_2Mg$ and $MeMgNPr_2^i$

	$MeMgNPr_2^i$						
+40°	8.76			11.24			
-20°	10.96(1)	11.03(5)		11.30(90)			
-40°	10.97(1)	11.03(6)		11.34(24)			
-60°	10.95(1)	11.05(5)	11.12(1)	11.38(38)			
-80°	11.00(1)		11.12(4)	11.18(1)	11.44(108)	11.54(10)	11.57(5)
	$MeMgNPr_2^i \cdot Me_2Mg$						
+40°				11.46			
-40°				11.54			
-60°				11.58			
-80°			11.15(2)	11.26(1)	11.55(16)	11.61(14)	
-100°			11.15(2)	11.26(1)	11.55(14)	11.63(15)	

The spectrum of $MeMgNPr_2^i$ (0.308m) at +40° shows a doublet centered at 8.76τ due to the i-propyl methyl groups and one signal in the methylmagnesium region at 11.24τ. At -20° three signals are observed: one at 10.96τ(1), one at 11.03τ(5) and one at 11.30τ(90). Relative to the other compounds studied in this report, the NMR spectra of $MeMgNPr_2^i$ exhibited the greatest temperature dependence. At -60° four signals are present in the methylmagnesium absorption region, and six signals are observed at -80°. The 11.24τ signal at +40° is an averaged signal involving bridging and terminal methyl groups. Temperature lowering to -20° slows down the equilibrium allowing for the observation of different methyl environments. It is very instructive to follow the temperature dependence of the 11.30τ signal below -20°. At -60° the signal shifts to 11.38τ and at -80° the signal collapses to form three signals residing at 11.44, 11.54 and 11.57τ. $MeMgNPr_2^i$ exists predominantly as a dimer in diethyl ether over a large concentration range, and therefore, the composition in solution is best described by dimeric structures. The following description is consistent with the NMR and association data.



At all temperatures below +40° the terminal methyl signals (the highest field signals) account for the largest percentage of methyl groups in solution. Both $MeMgNPr_2^i$ and $MeMgNPr_2^i \cdot Me_2Mg$ exhibit multiple terminal methyl signals at low temperatures, whereas the other compounds examined show only a single terminal methyl signal at all temperatures.

The observation of these terminal methyl signals only at low temperature may be explained by solvation effects occurring with temperature lowering. In addition, an equilibrium involving structures XLVI, XLVII, XLVIII, XLIX and L may also account for these multiple terminal methyl signals. Examination of the NMR spectra for $MeMgNPr_2^i$ indicates that those dimers with bridging methyl sites contribute to only a minor degree to the composition in solution (approximately 5% of the methyl groups are in bridging methyl environments at -80^o), and dimers XLVI and XLVII are therefore the most important species in solution. These two structures contain two different types of terminal methyl environments. Monomeric $MeMgNPr_2^i$ possesses one type of terminal methyl environment (the methyl in the monomer is not involved in bridging) and is assigned to the highest field signal at 11.57τ. This assignment is based on the already discussed observation that methyl groups in monomeric species absorb upfield from terminal methyl groups in associated species. Dimer XLVII contains identical terminal methyl groups: each methyl group is bonded to a magnesium atom coordinated to two di-i-propylamino groups and one ether molecule. Dimer XLVI contains two kinds of methyl groups; however, one of the terminal methyl groups is identical to the terminal methyl group in XLVII (a methyl group attached to a monosolvated magnesium), and the other methyl group is attached to a disolvated

magnesium atom. The methyl groups in XLVII and the methyl group attached to the monosolvated magnesium in XLVI are assigned to the downfield terminal methyl signal at 11.44τ, and the methyl group attached to the disolvated magnesium in the trisolvated dimer XLVI is assigned to the 11.54τ signal. The basis of these assignments is that the diamagnetic shielding effect of two coordinated ethers is expected to be greater than the effect from one ether molecule. This results in the methyl group attached to the disolvated magnesium in XLVI to absorb upfield from the methyl groups in XLVII and the methyl attached to the monosolvated magnesium in XLVI. At -80° the 11.44τ signal (a terminal methyl signal), accounts for 85% of the methyl groups in solution and must represent the major structure in solution which is XLVII. Structure XLVI cannot be the major structure in solution since it should exhibit two terminal methyl signals of equal intensity. The observation that only one signal accounts for 85% of the methyl groups in solution corroborates the suggestion that indeed XLVII is the major species in solution. The trisolvated dimer and the monomer account for approximately 7% and 4% of the methyl groups in solution respectively, as calculated from the relative area ratios. The three bridging methyl signals account for only 5% of the methyl groups in solution and represent species in very low concentration. Dimers XLVIII, L and LI contain three different types of

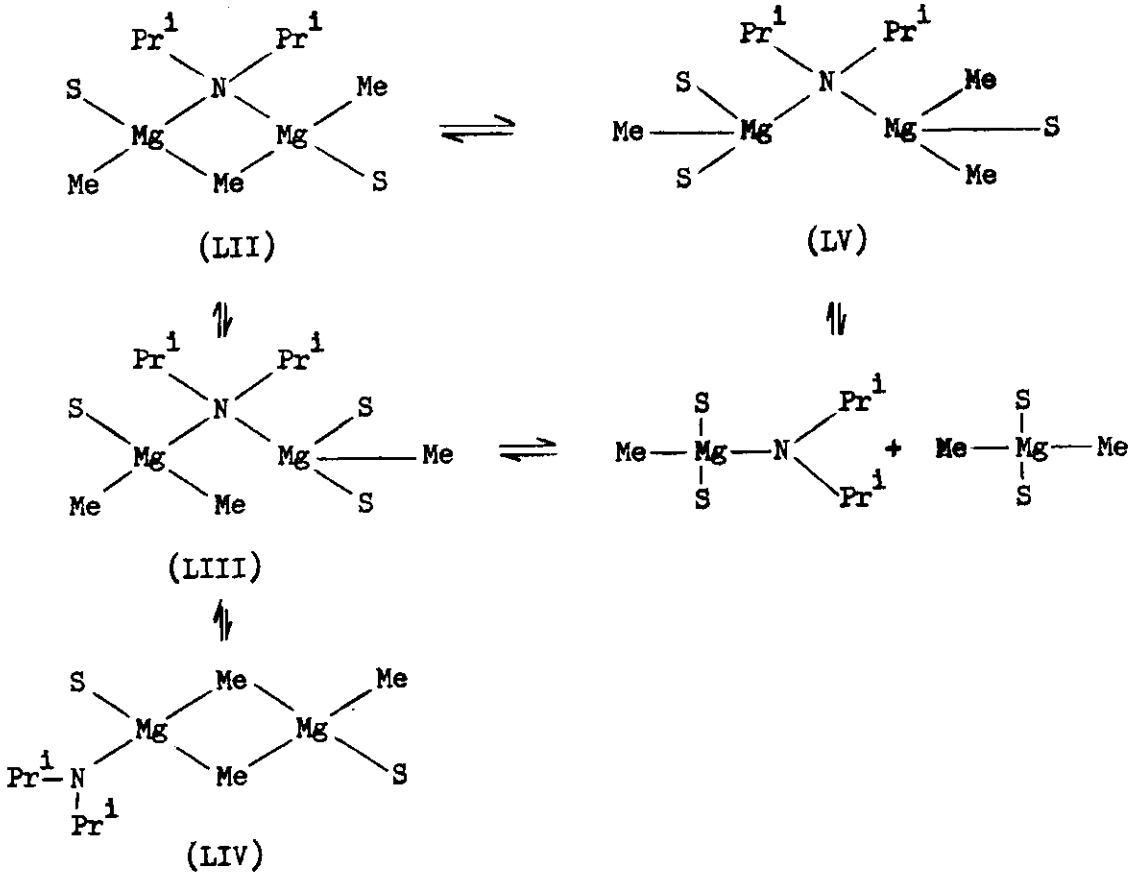
bridging methyl groups. Unequivocal assignment of these bridging methyl environments is not possible; however, using the MeMgOR and MeMgOR·Me_2Mg compounds as a basis for assignment, it is proposed that the dimethyl bridge in LI may be expected to resonate upfield from the bridging methyl group in XLVIII. The expected chemical shift of the bridging methyl in L relative to the bridging methyls in XLVIII and LI is not known. At the present time the most important consideration regarding the species in solution containing bridging methyl groups is that such species are in very low concentration.

Complexion occurs in solution between $MeMgNPr_2^i$ and Me_2Mg to form $MeMgNPr_2^i \cdot Me_2Mg$. Both $MeMgNPr_2^i$ and Me_2Mg are soluble in diethyl ether, but when they are mixed together precipitation occurs leaving behind a dilute solution. Due to the low solubility of the complex, the association measurements could be made only in a narrow concentration range. The i-values indicate approximately a monomeric species, but a plot of the i-values verses molality exhibits a relatively steep slope indicating that the species associate readily with an increase in concentration. In fact, solid formation always occurs when the attempt is made to prepare the complex at a higher concentration. Possibly, highly associated species precipitate from solution leaving behind less associated species in solution.

From $+40^\circ$ to -60° $MeMgNPr_2^i \cdot Me_2Mg$ exhibits a singlet

in the methylmagnesium absorption region. At -80° four signals are present at 11.15τ(3), 11.26τ(2), 11.55τ(16), and 11.61τ(14), and the spectrum is basically the same at -100°.

In the compounds examined so far in this study the NMR spectra of MeMgOR and $MeMgNPh_2$ could be interrelated with $MeMgOR \cdot Me_2Mg$ and $MeMgNPh_2$ plus Me_2Mg, respectively; however, the spectra of $MeMgNPr^i_2$ and $MeMgNPr^i_2 \cdot Me_2Mg$ are much more complicated. From $+40^{\circ}$ to -60° $MeMgNPr^i_2 \cdot Me_2Mg$ exhibits a time averaged signal. At -80° bridging methyl groups are observed and therefore, a mixed bridged compound exists in solution. Since two terminal methyl site signals, 11.55τ and 11.63τ account for 90% of the methyl groups in solution, the composition in solution consists mainly of species with terminal methyl environments. The two terminal methyl signals of approximately equal intensity indicate that two general types of terminal methyl sites are present in approximately equal concentration. Two different types of bridging methyl sites in low concentration must also be present in solution, as is indicated by the signals at 11.15τ and 11.26τ. The following scheme is suggested:



The molecular association data indicate that $MeMgNPr_2^i$. Me_2Mg exists primarily as a complex and therefore, at the higher temperatures ($+40^\circ$) the composition in solution is best described by structures LII, LIII, LIV and LV. Since species with bridging methyl sites are in very low concentration, structures LII, LIII and LIV must contribute only to a very limited degree to the composition in solution. Structures LII, LIII, LIV and LV comprise all the possible complexes in solution, and LV must be the complex of high-

est concentration in solution since it is the only structure which does not have a bridging methyl site. Complex LV contains two different terminal methyl environments which is congruous with the -80° spectrum, but LV by itself will give two terminal methyl signals in a 2:1 rather than a 1:1 ratio. Consequently, other species in solution must be present. Since multiple terminal methyl signals are seen only at low temperature, the presence of enhanced solvation with temperature lowering is quite reasonable. Enhanced solvation at low temperature may result in an equilibrium involving the complex LV and monomeric Me_2Mg and $MeMgNPr_2^i$. In $MeMgNPr_2^i$ the 11.57τ signal is assigned to monomeric $MeMgNPr_2^i$ and it is therefore reasonable to assign the 11.55τ signal in the $MeMgNPr_2^i \cdot Me_2Mg$ system to monomeric $MeMgNPr_2^i$. The high field signal at 11.63τ may represent monomeric Me_2Mg. Again, if the composition in solution is due entirely to monomeric $MeMgNPr_2^i$ and Me_2Mg, the relative area ratio again would be 2:1 (Me_2Mg:$MeMgNPr_2^i$). Another interpretation of the data is to assume that complex LV absorbs at 11.55τ just as monomeric $MeMgNPr_2^i$. The composition in solution consisting of an equilibrium involving LV and monomeric $MeMgNPr_2^i$ and Me_2Mg may be consistent with the data, if the concentration of each monomer is three times the concentration of the complex LV. Such an equilibrium would result in three methyls from one molecule of LV and three methyls from three $MeMgNPr_2^i$ molecules absorbing

at 11.55τ and six methyls from three Me_2Mg molecules absorbing at 11.63τ resulting in a 1:1 ratio of terminal methyl-type signals. The assignment of all three methyls in LV to a single signal at 11.55τ is not unequivocal, but is reasonable. At +40° $MeMgNPr_2^i \cdot Me_2Mg$ absorbs at 11.46τ whereas $MeMgNPr_2^i$ absorbs at 11.24τ. The 11.46τ signal indicates that the methyl groups in $MeMgNPr_2^i \cdot Me_2Mg$ absorb upfield from dimeric $MeMgNPr_2^i$ at +40°, and at -80° $MeMgNPr^i \cdot Me_2Mg$ may absorb upfield from $MeMgNPr_2^i$. At -80° dimeric $MeMgNPr_2^i$ is assigned to a signal at 11.44τ in the $MeMgNPr_2^i$ system and $MeMgNPr_2^i \cdot Me_2Mg$ is therefore assigned to the 11.55τ signal.

The composition in solution of $MeMgNPr_2^i \cdot Me_2Mg$ is best described as consisting of $MeMgNPr_2^i \cdot Me_2Mg$ complexes which are in equilibrium with monomeric $MeMgNPr_2^i$ and Me_2Mg at low temperature. The complex of higher concentration is LV which does not contain any bridging methyl sites. Unequivocal assignments of the bridging methyl groups is not possible and at the present time the only conclusion possible concerning species with bridging methyl environments is that they exist in low concentration and constitute a minor part of the composition in solution.

It is interesting to speculate why $MeMgNPr_2^i$ and $MeMgNPr_2^i \cdot Me_2Mg$ show multiple terminal methyl groups, whereas all the alkoxy(methylmagnesium compounds and the $MeMgNPr_2$ systems exhibit only a single signal for terminal-like

methyl environments. In the alkoxy(methyl)magnesium compounds, the magnesium atoms are bonded to oxygen atoms from the alkoxy groups and from the diethyl ether solvent molecules. The alkoxy and etheral oxygen atoms may result in the same diamagnetic shielding effect and mono- and disolvated structures may be indistinguishable. In $MeMgNPr_2^i$ solvation by the ether oxygen and/or coordination by the di-i-propylamino nitrogen atom may result in different electronic environments around the magnesium atoms yielding different terminal-type methyl group signals. $MeMgNPh_2$ exists as a monomer in solution and exhibits only one signal in its NMR spectra. The composition in solution of $MeMgNPr_2^i$ and $MeMgNPr_2^i \cdot Me_2Mg$ consists of a variety of species resulting in different electronic environments yielding terminal-type methyl groups. Since $MeMgNPh_2$ exists in diethyl ether only as a monomer, it possesses a single type of electronic environment yielding only one NMR signal. If $MeMgNPh_2$ was associated, then competition between the bridging groups and the ether molecules for coordination sites may result in different solvates observable in the NMR spectra. The spectra for $MeMgNPh_2$ exhibits a single signal at all temperatures corroboratin the monomeric association description.

In comparing the $MeMgNPh_2$ and $MeMgNPr_2^i$ systems it is important to note the different chemical shift assignments for monomeric $MeMgNPh_2$ and $MeMgNPr_2^i$. Monomeric

$MeMgNPh_2$ absorbs at 11.43τ (-80°) whereas monomeric $MeMgNPr_2^i$ has been assigned to a 11.57τ signal (-80°). If both monomers are equally solvated (most likely both are disolvates), then the different chemical shifts for the methyl groups must be due principally to the diphenylamino and di-i-propylamino groups. The methyl group in $MeMgNPh_2$ resonates downfield from the methyl group in $MeMgNPr_2^i$. This downfield shift indicates a decrease in the diamagnetic shielding due to a decrease in the electron density around the methyl group in $MeMgNPh_2$ compared to $MeMgNPr_2^i$. The most reasonable mechanism for a decrease in electron density around the methyl group in $MeMgNPh_2$ involves the delocalization of the lone pair electrons on the nitrogen atom to the phenyl rings. Back bonding of the lone pair electrons on nitrogen to the magnesium atom in $MeMgNPh_2$ would increase the electron density around the methyl group shifting the signal upfield. If this explanation is correct, then the cause for non-association in the $MeMgNPh_2$ system is the delocalization of the lone pair electrons around the phenyl rings rather than back bonding of the electrons from the nitrogen to the magnesium atom.

In order to further study the composition of dialkylamino(methyl)magnesium compounds in solution, both di-n-butylamino(methyl)magnesium and diethylamino(methyl)magnesium were prepared. These compounds were found to be very insoluble in diethyl ether, preventing the measurement of

their molecular association and the examination of the temperature dependence of their NMR spectra. Since the higher molecular weight compounds, $MeMgNPh_2$ and $MeMgNPr^i_2$, are quite soluble in ether it was somewhat surprising to find the di-ethyl and di-n-butylamino analogs to be so insoluble. The only difference in these compounds is the size of the dialkylamino group, and this indicates that perhaps association increases in these compounds as the dialkylamino group decreases in size rendering the compounds insoluble in ether.

Knowledge of the degree of solvation of the compounds studied would be very helpful in understanding their structure in solution. Various attempts were made in order to gain information along this line.

$MeMgOCPh_2Me$, $MeMgOBu^t$ and $MeMgOPr^i$ were disolvated by codistillation with benzene ($MeMgOPr^i$ rapidly precipitated when in benzene and was not investigated). The spectra for $MeMgOCPh_2Me$ and $MeMgOBu^t$ in benzene showed the complete absence of ether, and it was observed that the spectra in benzene and diethyl ether are quite different. A 0.13 M solution of $MeMgOCPh_2Me$ in benzene at ambient temperature exhibited very broad signals at 8.08τ and 11. 11.29τ of equal intensity and a small sharp signal at 9.63τ. A 0.17 M solution of $MeMgOBu^t$ in benzene showed signals at 8.54τ(3), 9.72τ(1) and 10.70τ(2). It was hoped that with the stoichiometric addition of diethyl ether to

Table 7. Molecular Weight Data for $MeMgOCPh_2Me$

0.13M $MeMgOCPh_2Me$ in Benzene			
+40°	8.08(1)[a]	9.63[b]	11.29(1)[a]
0.17M $MeMgOBu^t$ in Benzene			
+40°	8.54(3)	9.72(1)	10.70(2)

a. Very broad

B. Small sharp signal

these benzene solutions the number of ether molecules involved in specific solvation could be determined. In principle when the proper number of ether molecules is added to the benzene solutions, the spectra in ether and benzene-ether solutions should exhibit similar signals and signal intensities (the signal will resonate at different fields in the benzene solvent relative to the ether solvent due to the anisotropy of benzene; however, the number of signals and signal intensities should not be effected). Such an experiment would allow for the determination of the extent of ether solvation. Diethyl ether was added to the compound in molar ratios of 1:1, 2:1, 3:1, etc., (ether: CH_3MgOR), and the NMR spectra of each resultant solution recorded. Unfortunately, both $MeMgOCPh_2Me$ and $MeMgOBu^t$ exhibited no change in the spectra until the volume of diethyl ether approached the volume of benzene. Therefore, specific solvation could not be determined.

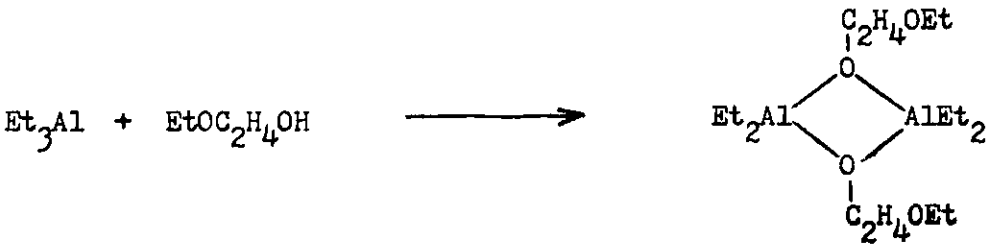
Since the degree of specific solvation could not be determined, cryoscopy was attempted to determine the degree of association of $MeMgOCPh_2Me$ and $MeMgOBu^t$ in benzene. $MeMgOBu^t$ precipitated near the freezing point of benzene preventing the cryoscopic measurements from being completed. These results indicate a higher degree of association in benzene relative to ether since in diethyl ether both $MeMgOCPh_2Me$ and $MeMgOBu^t$ do not precipitate at temperatures as low as -80^o.

Without association data meaningful interpretation of the NMR spectra is impossible. However, it can be inferred that solvation is extremely important since dissolution in benzene and diethyl ether resulted in different spectra, and different spectra indicate different compositions in solution.

CHAPTER IV

DISCUSSION

Our investigation of alkylmagnesium alkoxides in diethyl ether solvent indicates the existence of dimeric, trimeric and tetrameric species in solution. From this it is evident that the alkoxide group coordinates more strongly than diethyl ether with magnesium. The greater basicity of the alkoxy-oxygen relative to the ether-oxygen has been suggested by the nature of the product from the following reaction:[29]



Due to the greater coordinating ability of the alkoxy oxygen compared to ether oxygen, the alkoxy bridged dimer was formed rather than the chelate monomer and therefore, alkoxy group associated alkylmagnesium alkoxides stable in ether are quite reasonable (provided entropy considerations are minor).

In considering a bridging group such as x = $OCR_1R_2R_3$,

it is important to follow the changes in the composition and structure in solution as the nature of the R group is varied. Alkoxy bridging groups possess an inherent counterbalancing effect involving the size of the group and its ability to donate a lone electron pair. The smaller the size of the bridging group, the more readily it can approach another molecule thus increasing its effective bridging ability leading to associated species. This principle is quite apparent with dimethylmagnesium in diethyl ether. Dimethylmagnesium crystalizes from solution as an ether free polymer.[17] In the series of alkoxides examined, this principle is also followed. $MeMgOCPh_2Me$ has the largest alkoxy group and is the least associated, whereas the n-propoxy group is the smallest group resulting in $MeMgOPr^n$ being the most associated.

$MeMgOBu^t$ is dimeric and the NMR spectrum indicates that bridging occurs through both a methyl and t-butoxy group resulting in a stable methyl-t-butoxy bridged system at room temperature. The small methyl group competes well with the large t-butoxy group for a bridging position, and therefore one of the t-butoxy groups ends up in the less sterically hindered terminal environment. The i-propoxy and n-propoxy groups are smaller than the t-butoxy group, and therefore $MeMgOPr^i$ and $MeMgOPr^n$ are more highly associated than $MeMgOBu^t$. The composition in solution of these two compounds at room temperature involves equilibria be-

tween the double alkoxy and mixed methyl-alkoxy bridged dimers, trimers and tetramers. In both $MeMgOPr^i$ and $MeMgOPr^n$ an averaged signal is seen at room temperature, but temperature lowering initially results in the observation of species with a predominance of bridging methyl groups. This observation of bridging methyl groups can be accounted for only by the presence of an equilibrium involving mixed methyl-alkoxy bridges, indicating that at the higher temperatures (-60^o to $+40^o$) the mixed methyl-alkoxy system is preferred, and that the alkoxy groups tend toward terminal positions (just as one t-butoxy group is in a terminal position in $MeMgOBu^t$). This preference for mixed methyl-alkoxy bridges at the higher temperatures may be due primarily to the smaller size of the i-propoxy and n-propoxy groups. As the alkoxy group becomes smaller and therefore starts to approach the methyl group in size, the methyl and alkoxy groups start to compete more evenly for the bridging sites. At ambient temperature $MeMgOBu^t$ exhibits separate bridging and terminal methyl signals because the large alkoxy group cannot compete with the methyl group for the second bridging site and is forced to a terminal position. $MeMgOPr^i$ and $MeMgOPr^n$ exhibit an averaged signal since the methyl and alkoxy groups compete more evenly for the second bridging site resulting in a rapid exchange.

In $MeMgOBu^t$, $MeMgOPr^i$, and $MeMgOPr^n$ temperature lowering to -80^o results in a shift in the equilibria toward

species incorporating the maximum number of alkoxy groups in bridging positions. Temperature lowering to -80° and below slows down the molecular vibrations sufficiently so that the ability to donate the electron pairs overcomes the steric interactions, thus increasing the effective bridging ability of the alkoxy groups. Possibly more important is the fact that greater solvation would be expected at the lower temperatures, thus producing single alkoxy bridged compounds which of course will increase the concentration of terminal methyl signals.

$MeMgOCPh_2Me$ is dimeric at the higher concentrations examined and at +40° an averaged signal is seen in the methylmagnesium absorption region. At -80° a bridging methyl position is observed which accounts for approximately 5% of the bridging methyl groups in solution. Since a bridging methyl signal was observed only at low temperature and accounted for only a small percentage of the methyl groups in solution, this data has been interpreted to mean that an equilibrium exists between a double alkoxy bridged structure predominates. Consideration of the structures of the t-butoxy, i-propoxy and n-propoxy compounds taken together leads to a possible alternate description for $MeMgOCPh_2Me$. The $-OCPh_2Me$ group is larger than the OBu^t group and should show an even greater propensity toward a terminal position. At room temperature direct electron donation by the phenyl rings to the magnesium atoms may

result in a labile equilibrium between the double alkoxy and mixed methyl-alkoxy bridged structures yielding an averaged NMR signal, and therefore the mixed bridged structure is not observable (this is in keeping with the observation that $MeMgOCPh_2Me \cdot Me_2Mg$ requires a low temperature for the observation of a mixed bridged species at $+30^{\circ}$). At -80° the labile equilibrium is slowed down which should allow for the observation of the bridging methyl group, but the double alkoxy bridged dimer should become more favorable (just as the other compounds indicated a possible tendency toward the maximum use of alkoxy groups as bridging groups at low temperature) and therefore only 5% of the methyl groups in solution are involved in a bridging position. Therefore, $MeMgOCPh_2Me$ may exist in an equilibrium involving mixed methyl-alkoxy and double alkoxy bridged dimers at the higher temperatures and as a double alkoxy bridged compound at -80° and below. Such a description could not be developed solely from the NMR data for $MeMgOCPh_2Me$, but is based on the structural trends found in the methyl-magnesium alkoxides studied. Also the description involving enhanced solvation at low temperature may prevent the observation of a mixed bridge structure at -80°.

From this study of dialkylamino(methyl)magnesium compounds various relationships are observed concerning the bridging ability of the dialkylamino groups relative to themselves and to the methyl group.

In organomagnesium compounds the bridging group is intimately involved in the formation of associated species, and the degree of association often governs the solubility of a compound (as association increases, the molecular weight of the compound increases resulting in a decrease in solubility).

The dialkylamino(methyl)magnesium compounds studied show that the compounds with straight chain dialkylamino groups are much less soluble than those which have branching at the carbon alpha to the nitrogen atom. It was found that $MeMgNPr^{i}_{2}$ may be prepared readily to 0.5 M (no attempt was made to make higher concentrations), whereas the maximum solubility found for $MeMgNEt_2$ and $MeMgNPr^{i}_{2}$ is 0.0079 M and 0.033 M respectively. These solubility differences must be due to the dialkylamino group since the remainder of the compound is the same in all cases, and the order of bridging ability is therefore $-NEt_2 \rangle -Bu^{n}_{2} \rangle -NPr^{i}_{2}$. This conclusion is quite reasonable since alkyl substituents are directly attached to the bridging atom, and small structural differences in the substituents are important since the atoms in the bridging system are close to each other.

The diphenylamino group appears to be the weakest bridging group since $MeMgNPh_2$ in diethyl ether appears to be monomeric. The weak bridging ability may be due to both the large size of the phenyl rings and a decrease in electron density at the nitrogen atom. This electron density

decrease may occur either by delocalization of the lone pair electrons around the ring or inductively through the ring. Another possibility would be the presence of nitrogen - magnesium back bonding of the lone pair electrons forming a magnesium-nitrogen double bond ($-\overset{\ominus}{M}=\overset{\oplus}{N}\begin{matrix}Ph\\Ph\end{matrix}$) where the result- and double bond and positive charge would be stabilized by the conjugated phenyl rings. An expansion of the order of bridging ability of the dialkylamino groups to include the diphenylamino group is $-NEt_2$ $-NBu^n$ $-NPr_2^i$ $-NPh_2$.

Dimethylmagnesium is reasonably soluble in diethyl ether (0.7 M) and association measurements indicate that it is involved in a monomer-dimer equilibrium at room temperature. On the basis of solubilities, the diethylamino and di-n-butylamino groups are better bridging groups than the methyl group, and on the basis of association measurements, the di-i-propylamino group is a stronger bridging group than the methyl group, whereas the diphenylamino group is a weaker bridging group. The order of bridging ability of the dialkylamino groups and the methyl group is therefore:

$$-NEt_2 \rangle -NBu_2^n \rangle -NPr_2^i \rangle -Me \rangle -NPh_2$$

Throughout this work the Me-Mg portion of the molecule has been kept constant allowing us now to compare the bridging abilities of the methyl, alkoxy and dialkylamino

groups all together. In the methyl-magnesium alkoxide series the molecular association data indicate the following order of bridging ability: $-OPr^{n} > -OPr^{i} > -OBu^{t} > -OCPh_2Me$. On the basis of solubility, the $-NEt_2$ and NBu_2^{n} groups are the best bridging groups followed by the $-OPr^{n}$ and $-OPr^{i}$ based on the degree of association. Both $MeMgNPr_2^{i}$ and $MeMgOBu^{t}$ are dimeric at room temperature indicating approximately equal bridging abilities and therefore, are next in bridging tendency. $MeMgOCPh_2Me$ and Me_2Mg each exist in a monomer-dimer equilibrium (showing comparable bridging ability), and $MeMgNPh_2$ is the least associated (monomeric). The relative order of bridging ability of the groups in the methylmagnesium alkoxides and dialkylamino(methyl)magnesium compounds in diethyl ether at room temperature is:

$$-NEt_2 > -NBu_2^{n} > -OPr^{n} > -OPr^{i} > -OBu^{t} > -NPr_2^{i} > -OCPh_2Me > -Me > -NPh_2$$

A very interesting aspect of this work is its potential application in stereoselective alkylation studies. Very often stereochemical results in reactions between alkylating agents and organic substrates have been explained on the basis of steric bulk of the alkylating agent. If the steric bulk is important in determining the side of attack by an alkylating agent then the degree of associa-

tion of the alkylating agent may be very important since it will effect its molecular volume.

A compound which is monomeric or dimeric at room temperature and is much more highly associated at low temperature may induce different stereochemical results at the two temperatures. The inherent underlying principle of such an approach is that one organometallic alkylating agent may induce different stereochemical results, whereas traditionally two alkylating agents would be necessary.

CHAPTER V

CONCLUSION

Molecular association studies indicate that the degree of association for methylmagnesium alkoxy and dialkylamino(methyl)magnesium compounds is a function of the size of the alkoxy and dialkylamino group. Of the methylmagnesium alkoxy compounds studied $MeMgOCPh_2Me$ is the least associated, whereas $MeMgOPr^n$ is the most highly associated. $MeMgNPh_2$ is the least associated dialkylamino(methyl)magnesium compound and $MeMgNPr^i_2$ is the most highly associated. In all cases it was found that the addition of Me_2Mg to the associated compounds broke down their aggregation to form a complex. It was observed that the composition in solution is temperature dependent, and this change in composition was followed by the low temperature NMR spectra.

APPENDIX

Table 7. Molecular Weight Data for 1,1-Diphenylethoxy(methyl)magnesium (high concentration study)[a]

Fraction	W_2(g)	W_1(g)	ΔT_b^o(C°)	m	i
1	1.32	49.084	0.112	0.115	2.01
2	1.32	59.468	0.100	0.094	1.94
3	1.32	69.854	0.085	0.080	1.91
4	1.32	80.567	0.085	0.069	1.66
5	1.32	90.006	0.083	0.061	1.52
6	1.32	104.131	0.083	0.053	1.32
	Molecular Weight Data (low concentration study)[b]				
7	1.037	87.747	0.080	0.050	1.28
8	0.659	73.843	0.062	0.038	1.28

a. Due to the low concentration of the solution an inverse addition procedure was necessary. The boiling point of the solvent was measured, and the solvent was then removed by vacuum. The compound in ether was added and the first boiling point was determined. The boiling points of the subsequent fractions were determined by adding aliquots of ether to the solution followed by the boiling point measuremnts. Therefore the first fraction is the most concentrated and the last fraction is the most dilute.

b. Normal addition procedure.

Table 8. Molecular Weight Data for 1,1-Diphenylethoxy(methyl)magnesium-dimethylmagnesium

Fraction	W_2(g)	W_1(g)	$\triangle T_b^\circ$ (C°)	m	i
1[a]	0.298	52.599	0.043	0.019	0.90
2[a]	0.596	62.937	0.073	0.033	0.931
3[a]	0.894	73.287	0.096	0.042	0.890
4[a]	0.256	69.453	0.123	0.058	0.960
5[b]	0.256	55.353	0.146	0.073	1.02
6[b]	0.256	41.360	0.183	0.098	1.06

a. Inverse addition

b. Normal addition

Table 9. Molecular Weight Data for t-Butoxy(methyl)magnesium

Fraction	W_2(g)	W_1(g)	ΔT_b^o(C^o)	m	i
1	0.158	41.708	0.040	0.034	1.7
2	0.316	48.624	0.064	0.058	1.82
3	0.632	62.655	0.095	0.090	1.91
4	0.790	69.681	0.11	0.101	2.04

Table 10. Molecular Weight Data for t-Butoxy(methyl)magnesium-dimethylmagnesium

Fraction	W_2(g)	W_1(g)	$\Delta T_b^{\circ}(C^{\circ})$	m	i
1	0.714	41.534	0.213	0.104	0.975
2	1.787	51.346	0.415	0.207	1.01
3	3.216	64.462	0.587	0.301	1.02
4	4.645	77.426	0.693	0.361	1.04

Table 11. Molecular Weight Data for i-Propoxy(methyl)magnesium[a]

Fraction	W_2(g)	W_1(g)	$\triangle T_b^o(C^o)$	m	i
1	0.3294	55.620	0.053	0.0537	2.29
2	0.633	62.468	0.850	0.103	2.45
3	0.937	69.374	0.104	0.138	2.66
4	1.242	76.272	0.128	0.161	2.67
	Higher Concentration Range				
5	0.952	55.546	0.128	0.175	2.76
6	1.587	69.089	0.169	0.234	2.78
7	2.063	79.353	0.193	0.265	2.76

a. Normal addition procedure

Page missing from thesis

Table 13. Molecular Weight Data for n-Propoxy(methyl)magnesium

Fraction	W_2(g)	W_1(g)	ΔT_b^o(C^o)	m	i
1	0.642	48.454	0.08	0.134	3.36
2	0.962	55.291	0.101	0.176	3.5
3	1.283	62.092	0.113	0.209	3.7
4	1.604	68.939	0.124	0.235	3.8

Table 14. Molecular Weight Data for n-Propoxy(methyl)magnesium-dimethylmagnesium

Fraction	W_2(g)	W_1(g)	$\triangle T_b^o$(C°)	m	i
1	0.250	41.80	0.075	0.039	1.05
2	0.500	48.665	0.158	0.068	0.848
3	0.750	55.557	0.185	0.089	0.963
4	1.000	62.456	0.22	0.106	0.96

Table 15. Molecular Weight Data for Diphenylamino(methyl)magnesium

Fraction	W_2(g)	W_1(g)	$\triangle T_b^o$(C°)	m	i
1	0.615	51.448	0.100	0.057	1.16
2	1.229	58.206	0.162	0.102	1.26
3	1.844	65.056	0.220	0.137	1.25
4	2.459	71.784	0.263	0.165	1.26

Table 16. Molecular Weight Data for Diphenylamino(methyl)magnesium – dimethylmagnesium

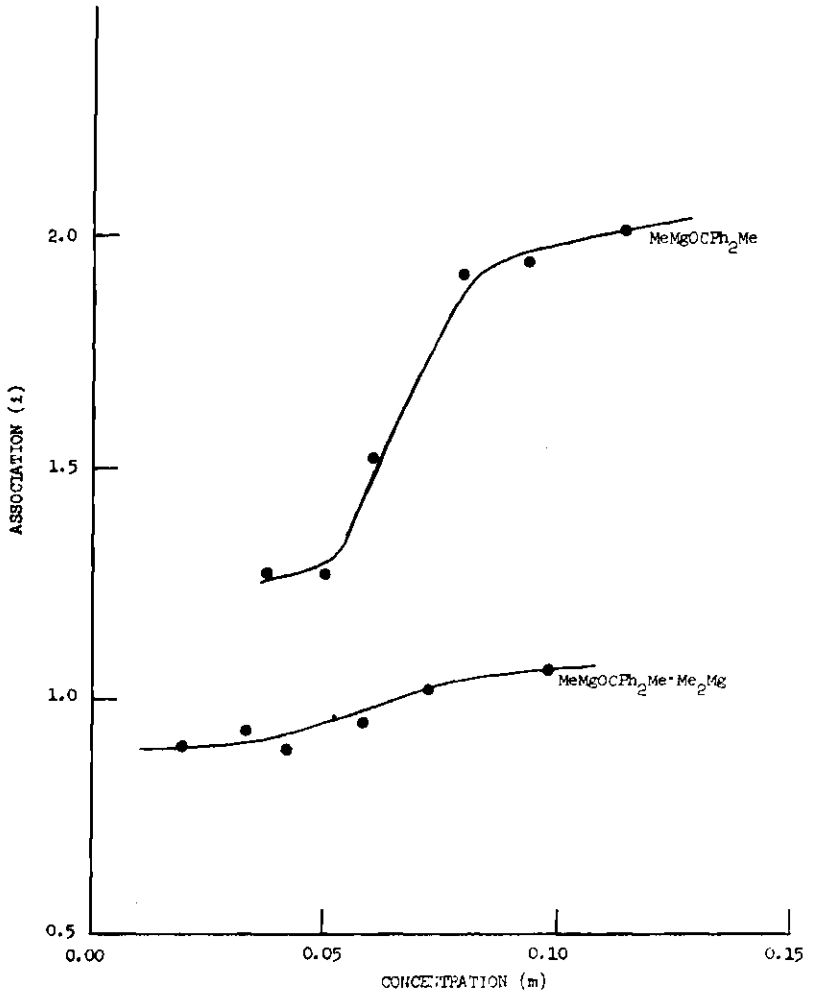
Fraction	W_2(g)	W_1(g)	ΔT_b°(C°)	m	i
1	0.456	49.610	0.118	0.035	0.599
2	0.912	56.508	0.195	0.063	0.636
3	1.369	63.424	0.255	0.082	0.649
4	2.281	77.157	0.345	0.113	0.655

Table 17. Molecular Weight Data for Di-i-propylamino(methyl)magnesium

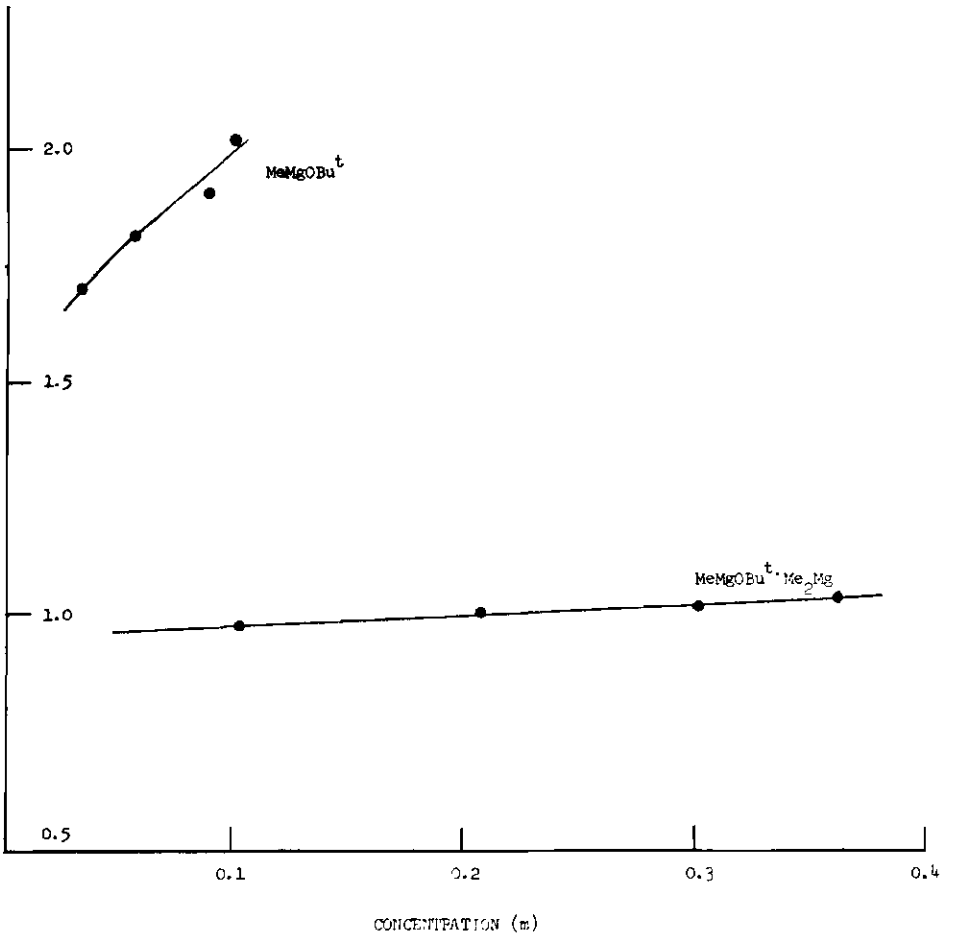
Fraction	W_2(g)	W_1(g)	$\triangle T_b^o$(C°)	m	i
1	1.013	50.830	0.145	0.143	1.99
2	2.571	63.846	0.287	0.289	2.02
3	4.129	76.909	0.371	0.386	2.08
4	5.687	89.919	0.430	0.455	2.11

Table 18. Molecular Weight Data for Di-i-propylamino(methyl)magnesium-dimethylmagnesium

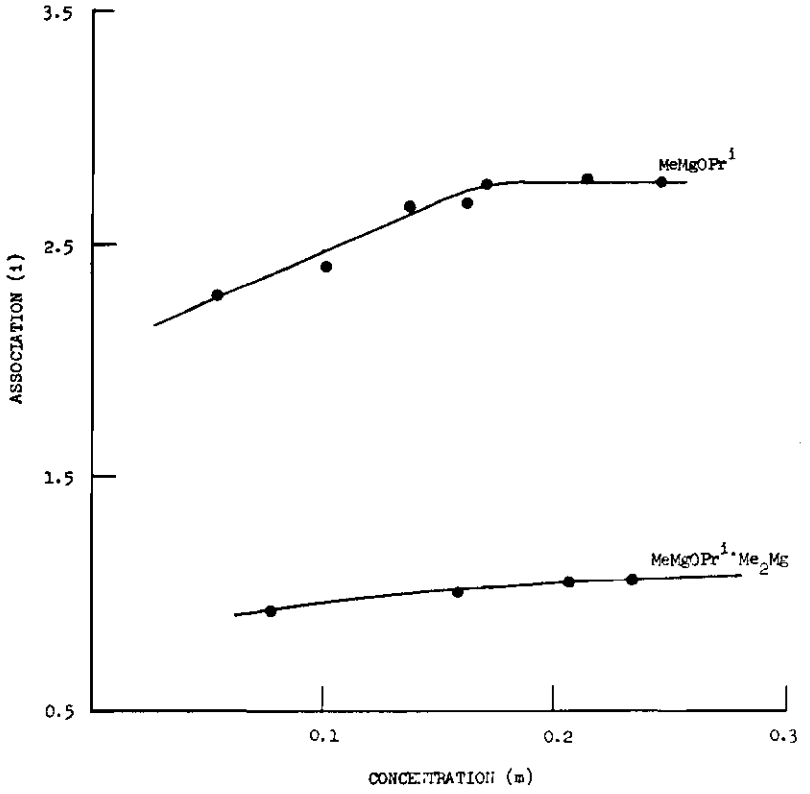
Fraction	W_2(g)	W_1(g)	$\triangle T_b^o$(C°)	m	i
1	0.309	40.660	0.060	0.0395	1.32
2	0.309	54.862	0.050	0.0292	1.17
3	0.309	69.057	0.040	0.0232	1.17
4	0.309	79.682	0.045	0.0201	0.9



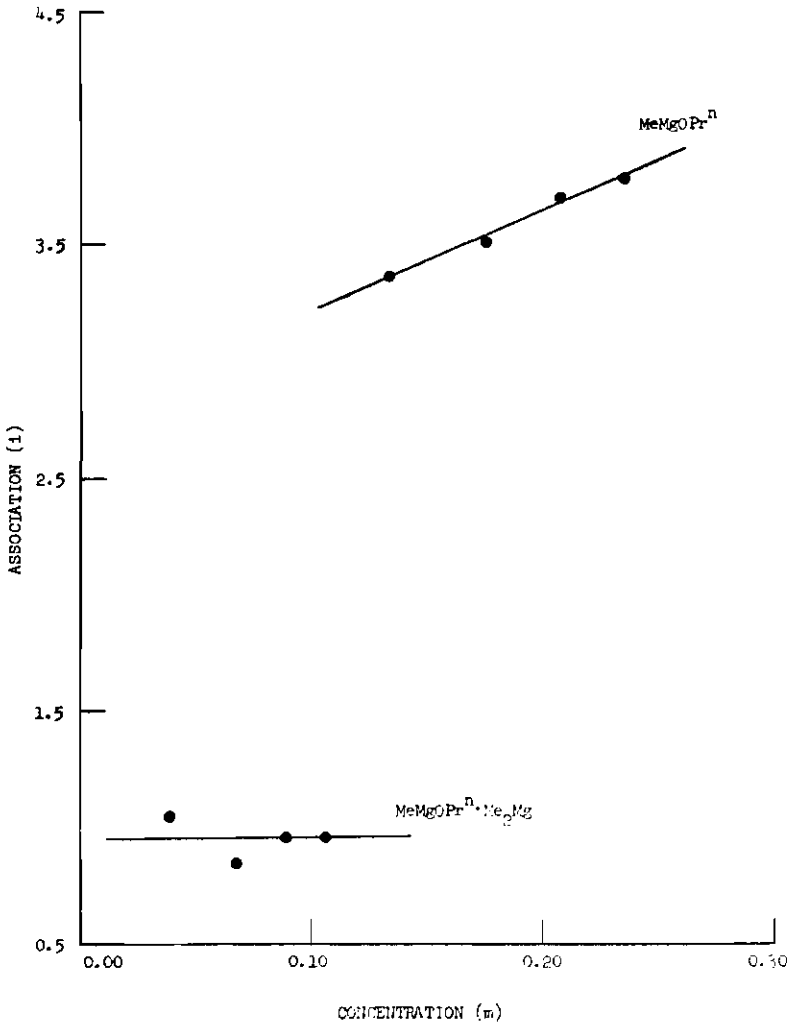
Plot 1. The Association of $MeMgOCPh_2Me$ and $MeMgOCPh_2Me \cdot Me_2Mg$.



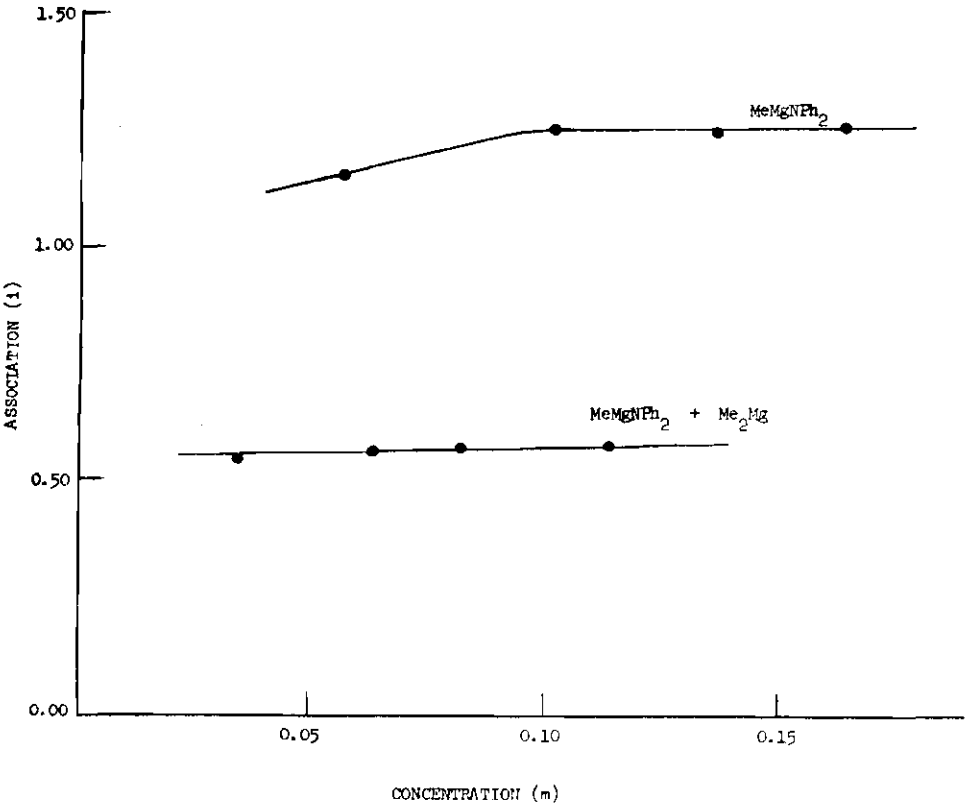
Plot 2. The Association of MeMgOBu^t and MeMgOBu^t·Me$_2$Mg.



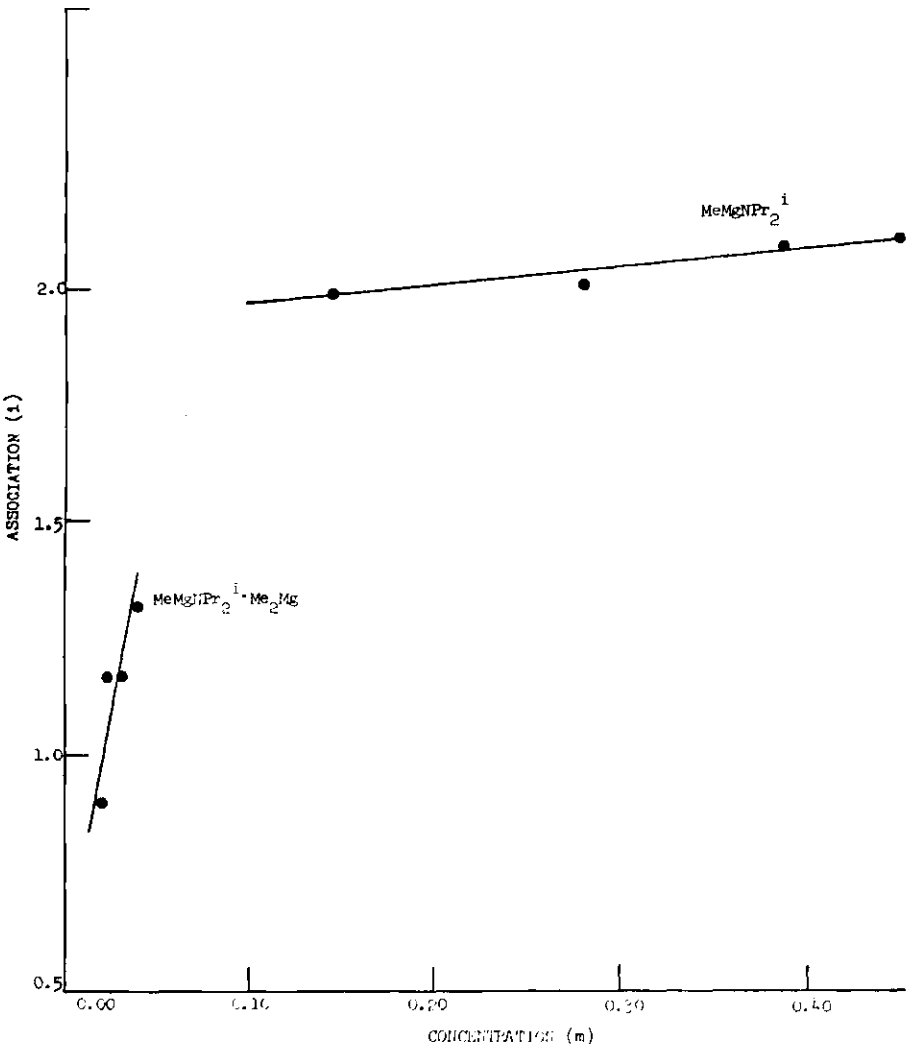
Plot 3. The Association of MeMgOPr^{i} and MeMgOPr^{i}·Me$_2$Mg.



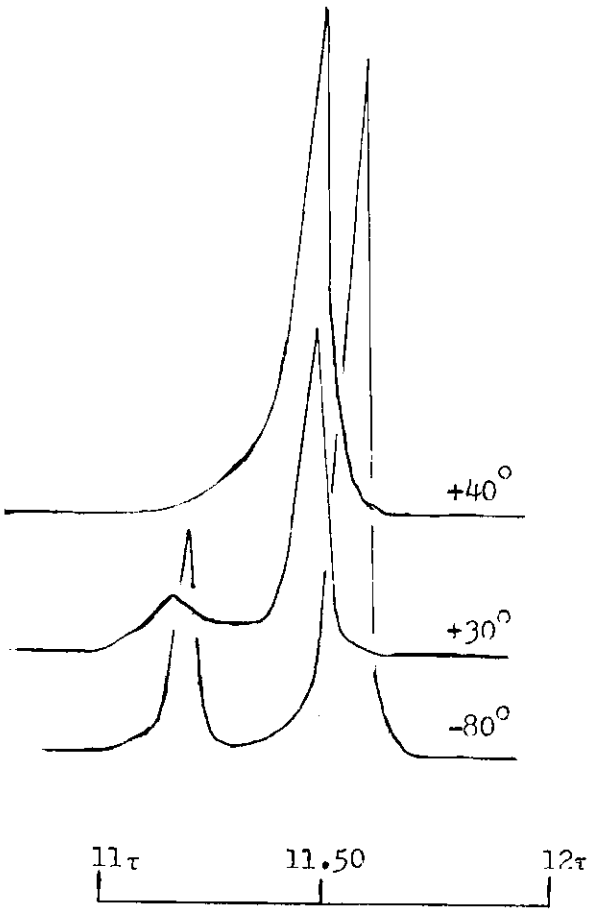
Plot 4. The Association of $MeMgOPr^n$ and $MeMgOPr^n \cdot Me_2Mg$.



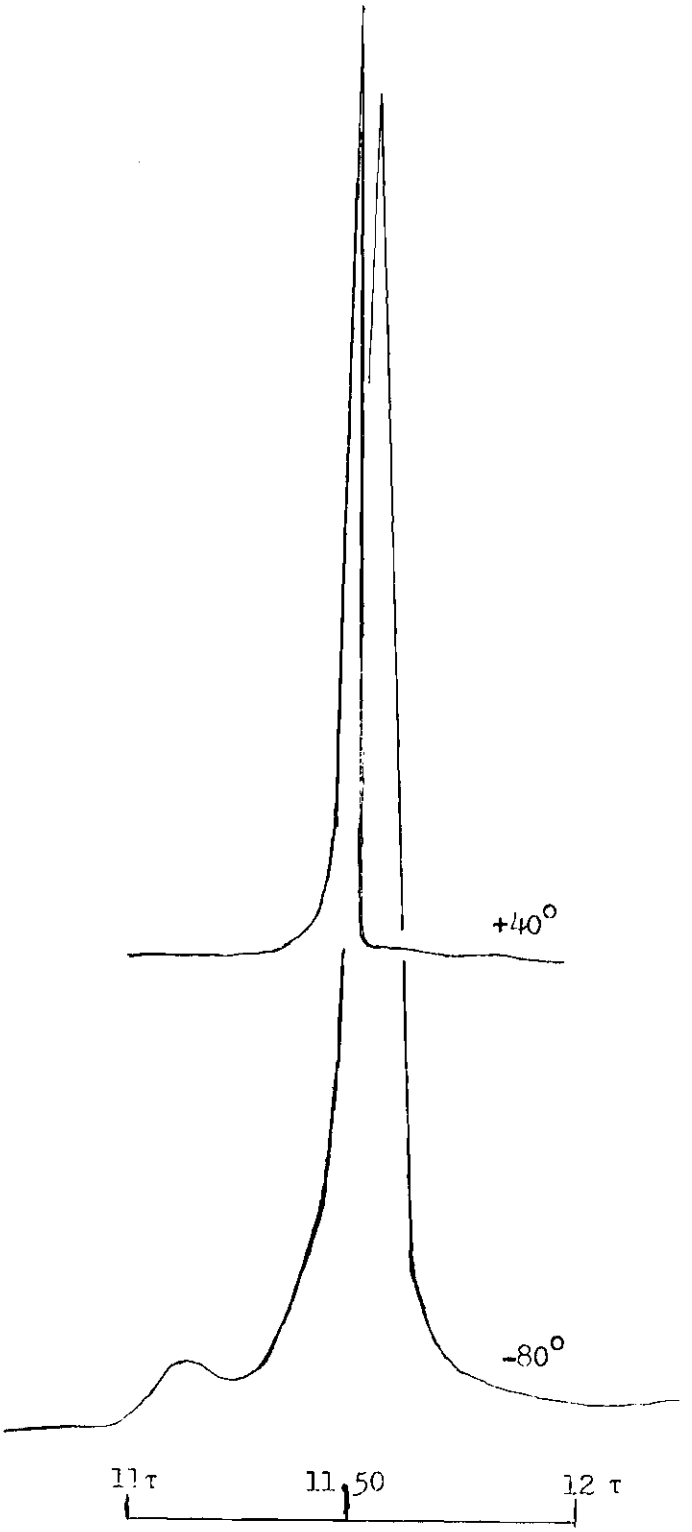
Plot 5. The Association of $MeMgNPh_2$ and $MeMgNPh_2 + Me_2Mg$.



Plot 6. The Association of $MeMgNPr_2^i$ and $MeMgNPr_2^i \cdot Me_2Mg$.

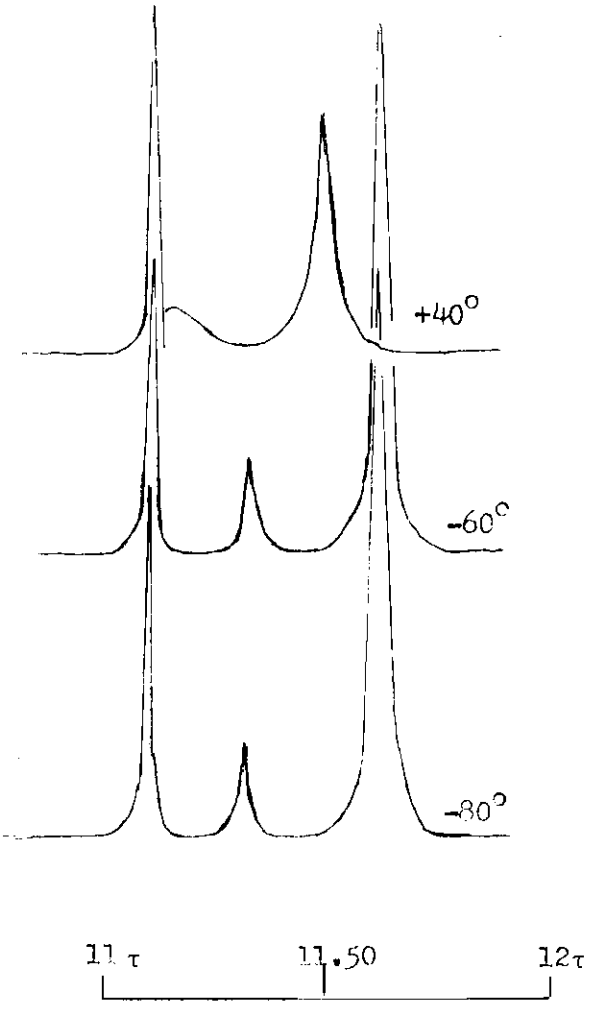


1. Spectra of $MeMgOCPh_2Me \cdot Me_2Mg$ in Diethyl Ether.

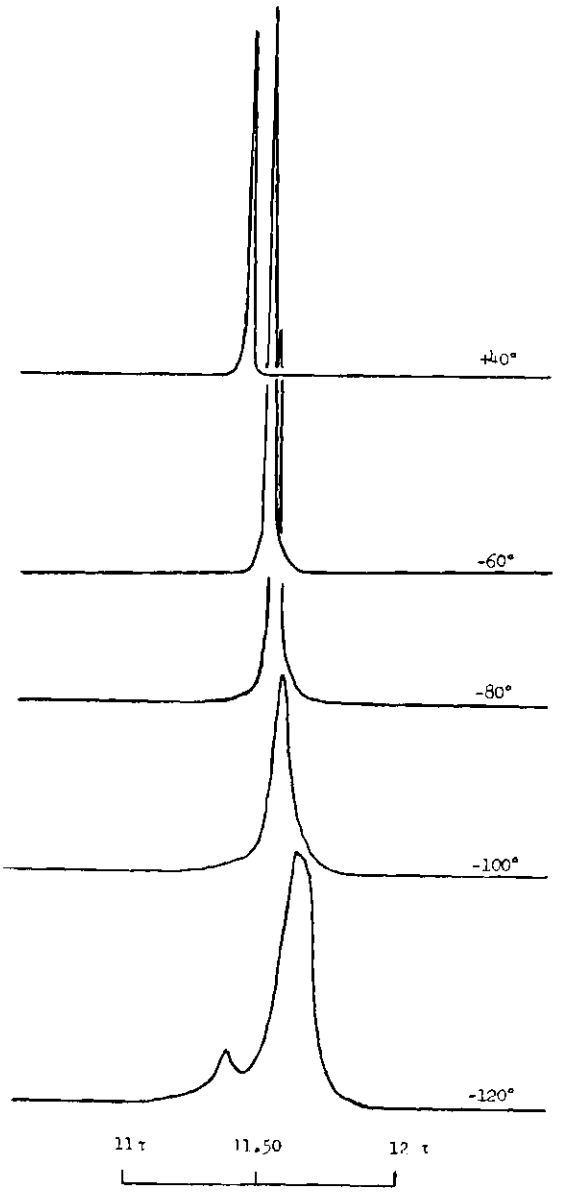


2. Spectra of $MeMgOCPh_2Me$ in Diethyl Ether.

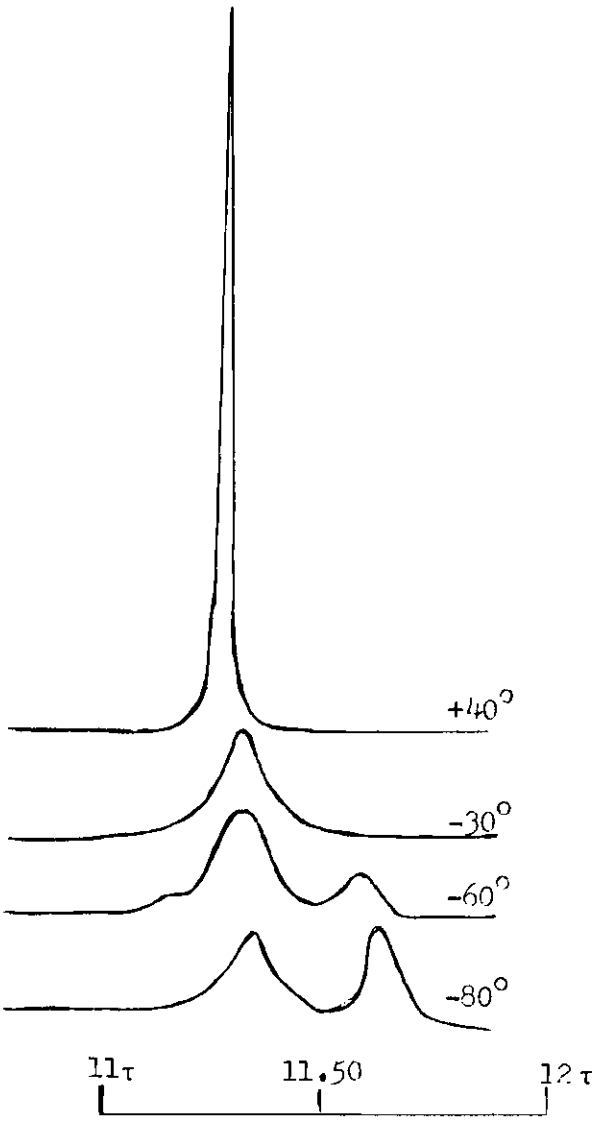
3. Spectra of $MeMgOBu^{t}\cdot Me_2Mg$ in Diethyl Ether.



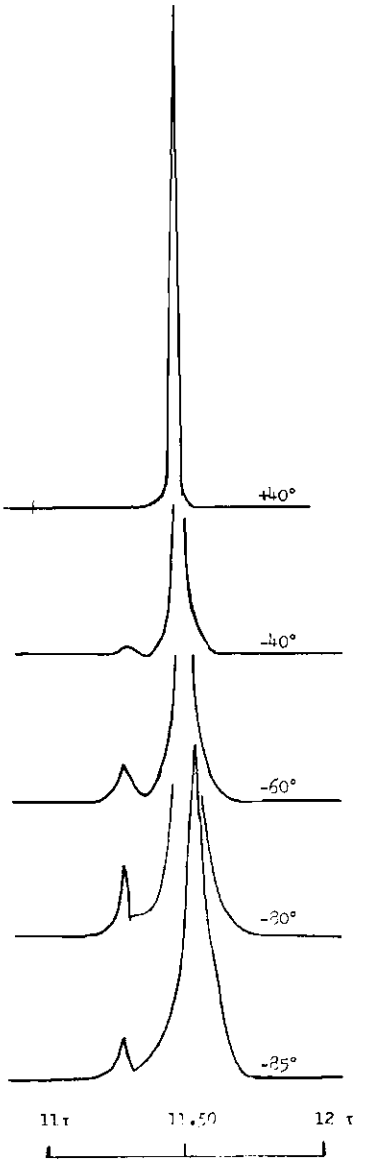
4. Spectra of $MeMgOBu^t$ in Diethyl Ether.



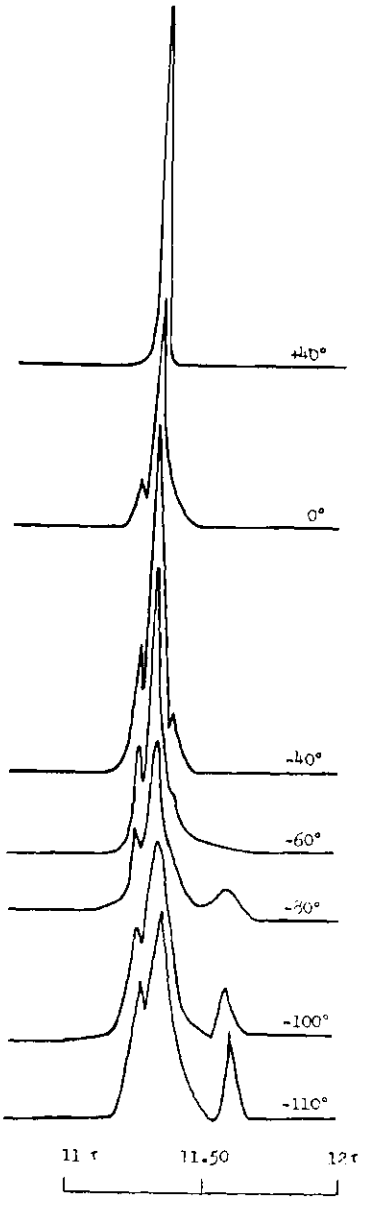
5. Spectra of $MeMgOPr^{i}\cdot Me_2Mg$ in Diethyl Ether.



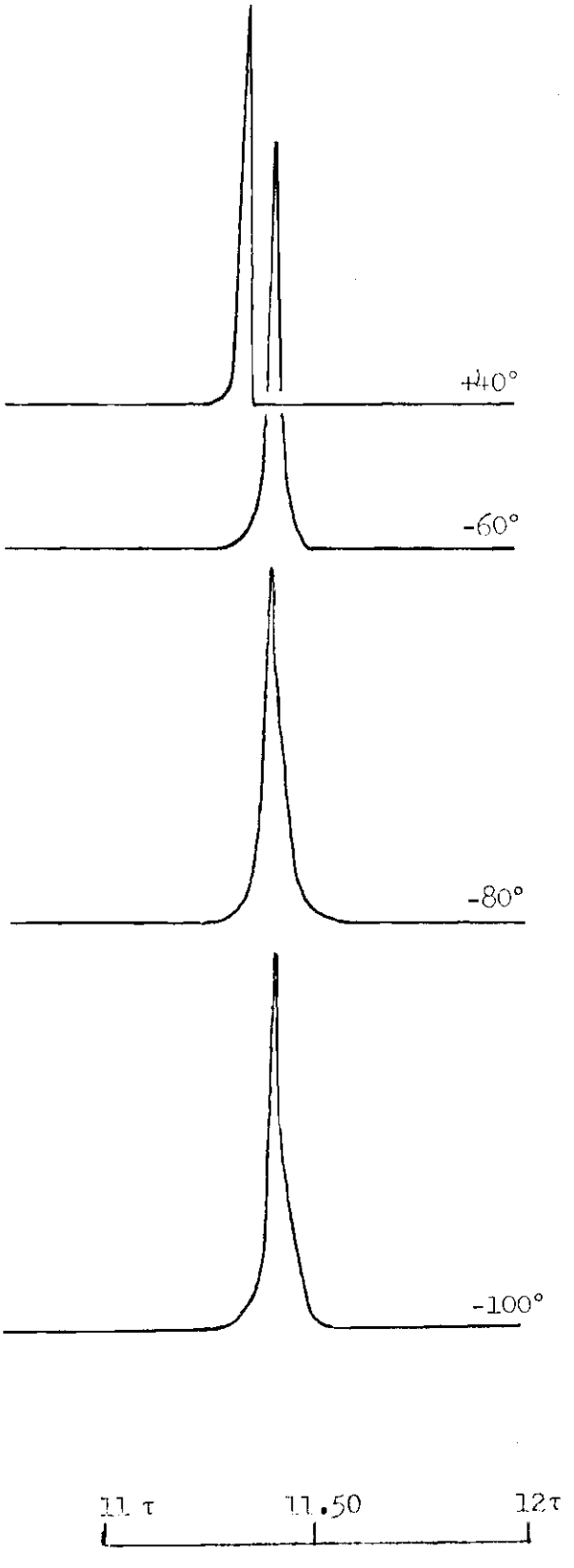
6. Spectra of $MeMgOPr^{i}$ in Diethyl Ether



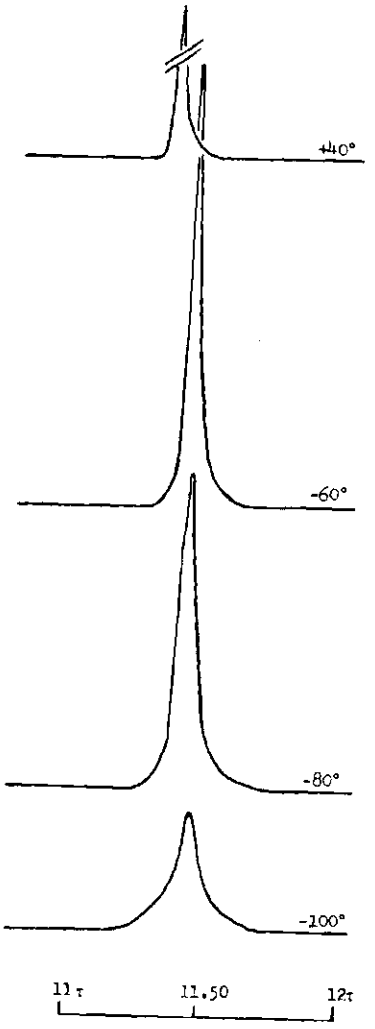
7. Spectra of $MeMgOPr^{n}\cdot Me_2Mg$ in Diethyl Ether.



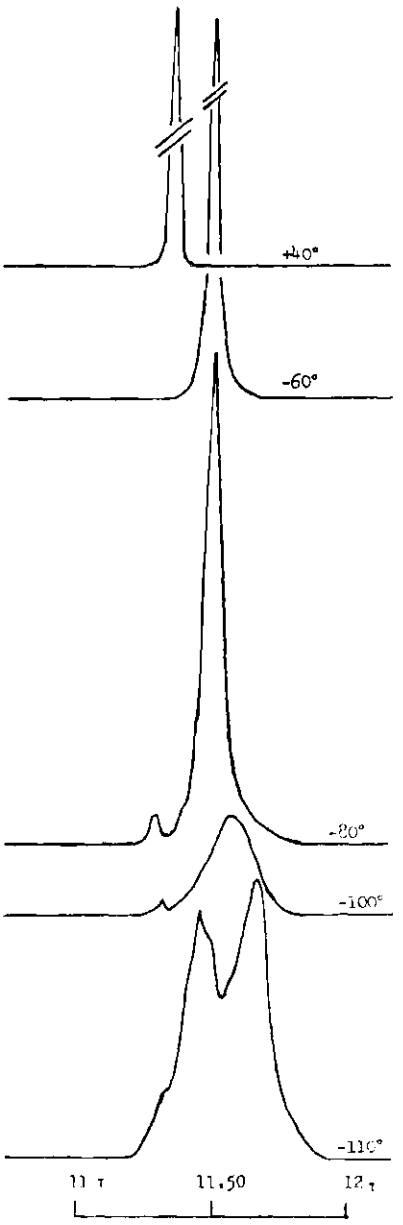
8. Spectra for $MeMgOPr^n$ in Diethyl Ether



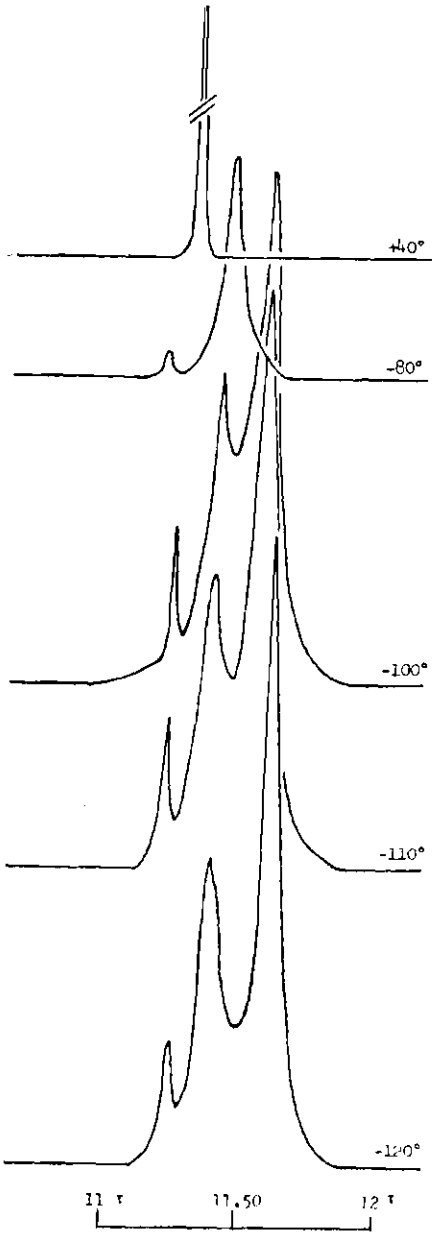
9. Spectra of 0.137 M $MeMgNPh_2$ in Diethyl Ether



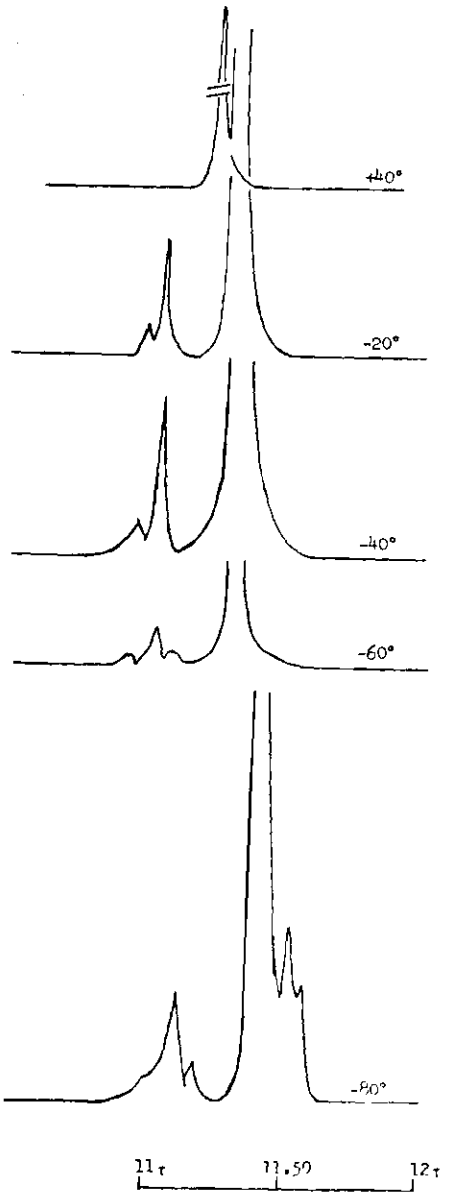
10. Spectra of 0.33 M $MeMgNPh_2$ in Diethyl Ether.



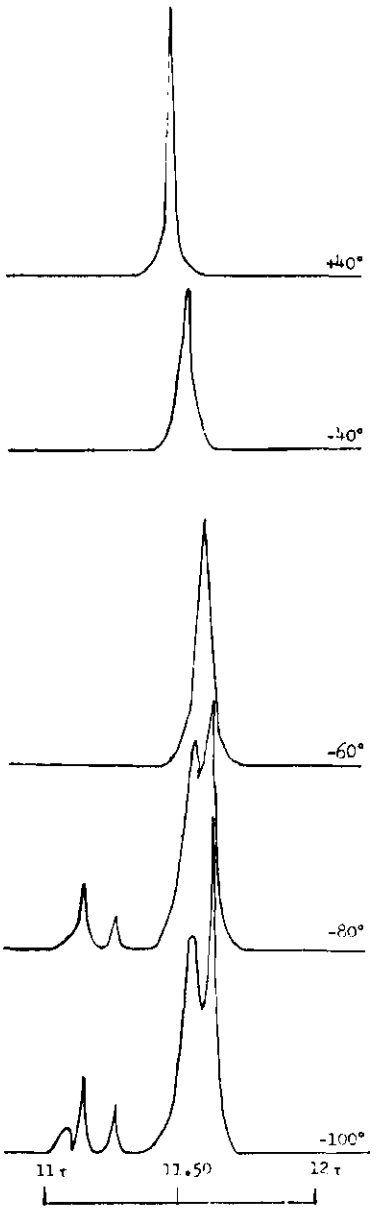
11. Spectra of $MeMgNPh_2$ + Me_2Mg in Diethyl Ether.



12. Spectra of $MeMgNPh_2$ + 2 Me_2Mg in Diethyl Ether.



13. Spectra of $MeMgNPr^{i}_{2}$ in Diethyl Ether.



14. Spectra for $MeMgNPr^{i}_{2} \cdot Me_2Mg$ in Diethyl Ether.

LITERATURE CITED

1. (a) E. C. Ashby and R. Read, J. Org. Chem., 31, 971 (1966).
   (b) L. I. Zakharkin, et al, Tetrahedron Lett., 631 (1962).

2. E. C. Ashby and M. B. Smith, J. Amer. Chem. Soc., 86, 4363 (1963).

3. (a) F. Walker and E. C. Ashby, J. Amer. Chem. Soc., 91, 3845 (1969).
   (b) R. E. Dessy, et al, Tetrahedron Lett., 1369 (1964).
   (c) E. C. Ashby and W. E. Becker, J. Amer. Chem. Soc., 85, 118 (1963).
   (d) R. M. Salinger and H. S. Mosher, J. Amer. Chem. Soc., 86, 1782 (1964).
   (e) M. B. Smith and W. E. Becker, Tetrahedron Lett., 3843 (1965).
   (f) M. B. Smith and W. E. Becker, Tetrahedron, 22, 3027 (1966).

4. (a) E. C. Ashby and F. Walker, J. Org. Chem., 33, 3821 (1968).
   (b) J. Toney and G. D. Stucy, Chem. Commun., 22, 1168 (1967).

5. D. F. Evans and J. P. Maher, J. Chem. Soc., 5125 (1962).

6. D. F. Evans and M. S. Khan, Chem. Commun., 67 (1966).

7. G. M. Whitesides, F. Kaplan and J. D. Roberts, J. Amer. Chem. Soc., 85, 2167 (1963).

8. H. O. House, R. A. Latham and G. M. Whitesides, J. Org. Chem., 32, 2481 (1967).

9. G. E. Parris and E. C. Ashby, J. Amer. Chem. Soc., 93, (5), 1206-13 (1971).

10. E. C. Ashby, J. Laemmle and G. E. Parris, J. Organometal. Chem., 19, 24-28 (1969).

11. K. C. Williams and T. L. Brown, J. Amer. Chem. Soc., 88, 4134 (1966).

12. R. A. Kovar and G. L. Morgan, J. Amer. Chem. Soc., 91, 7269 (1969).

13. E. A. Jeffery and T. Mole, Aust. J. Chem., 23, 715-24 (1970).

14. D. Bryce-Smith and I. F. Graham, Chem. Commun, 559 (1966).

15. G. E. Coates, et al, J. Chem. Soc. (A), 1118 (1968).

16. J. Laemmle, E. C. Ashby and H. M. Neumann, J. Amer. Chem. Soc., 93, 5120 (1971).

17. This study is presently being conducted.

18. G. E. Coates and R. Ridley, J. Chem. Soc. (A), 56 (1967).

19. D. F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N. Y., (1969).

20. T. L. Brown, et al., Rev. Sci. Instrum., 33, 491 (1962).

21. F. Walker and E. C. Ashby, J. Chem. Ed., 45, 654 (1968).

22. N. A. Bell and G. E. Coates, J. Chem. Soc. (A), 1069 (1966).

23. Coates (reference 15) reports $MeMgOBu^t$ to be tetrameric in ether (i = 4.04, M = 0.01-0.07). The different association values may be due to the different methods of preparation. Coates sublimed $MeMgOBu^t$ at 200° under vacuum, and reported that the compound forms a viscous solution in benzene which decomposes with the formation of a white precipitate. We did not sublime the compound and it initially dissolved in benzene (0.17M), but on standing for twenty minutes, partial precipitation did occur. Our analysis of the precipitate indicated that the white solid was $MeMgOBu^t$ and decomposition of $MeMgOBu^t$ was not occurring. Possibly Coates sublimation conditions were sufficiently stringent to desolvate the compound. The tetracoordinate valence of magnesium could then be satisfied by the intermolecular bridging by way of the t-butoxy groups resulting in polymerization. The t-butoxy oxygen being bonded directly to magnesium would be more basic than the ether oxygen. The t-butoxy oxygen bridges two magnesium atoms together displacing an ether molecule in the process. This would prevent the specific solvation of magnesium from occurring when placed back in ether, and a different structure in solution would be observed.

24. E. C. Ashby, J. Laemmle and G. E. Parris, J. Organometal. Chem., 19, 24 (1969).

25. T. Mole, Organometallic Reactions, I, 20 (1970).

26. P. Vink, C. Blomberg and F. Bickelhaupt, J. Organometal. Chem., 55, 57 (1973).

27. N. A. Bell, G. E. Coates and J. W. Emsley, J. Chem. Soc., (A), 49 (1966).

28. G. E. Coates and D. Ridley, J. Chem. Soc., (A), 1064, (1966).

29. E. G. Hoffman, Annalen, 629, 104 (1960).

VITA

John A. Nackashi was born in Jacksonville, Florida on November 20, 1944. He attended both primary and secondary schools there. His undergraduate work was done at Belmont Abbey College, Belmont, North Carolina, where he received a Bachelor of Science degree in chemistry in 1966. In 1966 he began work at the Georgia Institute of Technology and in 1967 started his research under the direction of Dr. E. C. Ashby. After the completion of his research in September, 1972, he assumed a faculty-staff position at Florida International University in Miami, Florida.

The author is married to the former Mary Bryan Brennan and they have two sons, John Joseph and Timothy.