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The Elimination–Condensation Reaction between Dimethylaluminum Hydride and Methylphenylphosphine

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The aluminum–phosphorus compound of simplest formula $Me_2AlPMePh$ has been prepared by an elimination–condensation reaction between Me_2AlH and PMePhH. The aluminum–phosphorus product has been characterized by elemental analyses and cryoscopic molecular weight measurements as well as infrared, ^1H NMR, and ^{31}P NMR spectral data. The product exists in benzene solution as a trimer, $(Me_2AlPMePh)_3$. However, the complexity of the spectral data suggests that $(Me_2AlPMePh)_3$ exists in benzene solution as a mixture of isomers due to different conformations of the ring and/or different orientations of the methyl and phenyl groups. It is also of interest that the nature of the aluminum–phosphorus product and its degree of association change when benzene is removed. An amorphous and possibly polymeric material that is no longer completely soluble in benzene at room temperature is formed. Sublimation of the amorphous material at 170 °C produces a transparent glass that is also only partially soluble in benzene. Extensive heating of the initial amorphous material or the transparent glass with benzene leads to complete dissolution and re-formation of the trimer $(Me_2AlPMePh)_3$. The nature of the elimination reaction between Me_2AlH and PMePhH has also been investigated by following the rate of formation of H_2 at 22 °C in isomeric xylenes solution. The kinetics data are consistent with a second-order rate law that is complicated by equilibria. The initial intermediate from the elimination reaction is a monomeric $Me_2AlPMePh$ species, which reacts in turn with Me_2AlH and/or $Me_2AlPMePh$ to eventually form the trimer. The equilibrium constant for the formation of the adduct $HMe_2Al{\cdot}PMePhH$ from monomeric alane and phosphine, K_a, has been evaluated from the kinetics data and has a value of 2.60 M^{-1} at 22 °C.

Introduction

The elimination–condensation reaction sequence that occurs between an organo group 13 derivative and a group 15 hydride is of fundamental importance in main-group chemistry and finds many significant applications, especially for the preparation of semiconductors such as GaAs and InP by the MOCVD process.[1] Despite the considerable importance of the elimination–condensation reaction, only four kinetic and mechanistic studies of reactions have been reported. The reaction[2] between Me_2AlH and NMePhH to form the dimer $(Me_2AlNMePh)_2$ and H_2 was studied in toluene solution at −63 °C. The observed kinetics data were consistent with a second-order rate law that was complicated by an equilibrium. The important steps of the mechanism for H_2 elimination (eq 1 and 2) required the prior dissociation of the

$$HMe_2Al{\cdot}NMePhH \overset{K_d}{\rightleftharpoons} HMe_2Al + NMePhH \qquad (1)$$

$$HMe_2Al + NMePhH \overset{k}{\rightleftharpoons} H_2 + Me_2AlNMePh \qquad (2)$$

adduct $HMe_2Al{\cdot}NMePhH$. Then, elimination occurred when the monomeric alane and amine recombined with the appropriate orientation. The dimer was then formed by a concerted π-cycloaddition reaction that minimized the interactions between the bulky phenyl groups. The second kinetics study[3] between Me_2AlH and $N(CH_2Ph)H_2$ to form another dimer $[Me_2AlN(CH_2Ph)H]_2$ in toluene solution at −63 °C led to a mechanism which was closely related to that proposed for the HMe_2Al–NMePhH system, but additional equilibria complicated the system. The higher basicity of benzylamine was considered to be responsible for the variety of equilibria, including the formation and dissociation of a five-coordinate aluminum species, $HMe_2Al{\cdot}2N(CH_2Ph)H_2$. The other two kinetics studies involved high-temperature gas-phase reactions of Me_3Ga–AsH_3[4] and Me_3Ga–PH_3.[5] An exceedingly important conclusion from all four of these kinetics studies is that elimination does not occur from a preformed adduct. Elimination results when the monomeric Lewis acid and the Lewis base combine with an appropriate energy and orientation.

As part of our continuing studies of the elimination–condensation reaction for group 13–15 compounds, we report the synthesis and characterization of the aluminum–phosphorus product from the reaction between Me_2AlH and PMePhH. In addition, the kinetics of the reaction have been investigated by following the evolution of H_2 for xylene solutions at 22 °C. Methylphenylphosphine, PMePhH, was especially selected for this study because of obvious comparisons with the NMePhH system[2] and for the possibility that the product might be trimeric. The comparisons of the mechanisms of the elimination reactions and of the intermediates in the condensation processes when dimers and trimers are formed would greatly enhance our understanding of the factors that influence the degree of association of the final product.

Experimental Section

General Data. All compounds were manipulated in a vacuum line or a purified argon atmosphere. Dimethylaluminum hydride (Me_2AlH) was prepared from $LiAlH_4$ and $AlMe_3$ and purified by vacuum distillation.[6,7] Methylphenylphosphine (PMePhH) was obtained from Strem Chemicals, Inc., was dried over $CaCl_2$, and was vacuum-distilled prior to use. Isomeric xylenes (bp 137–144 °C) and benzene were refluxed with and stored over sodium sand and finally vacuum-distilled from P_4O_{10} directly into the reaction vessel. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Nature and Stoichiometry of the Elimination Reaction. The stoichiometry of the elimination reaction was examined by combining the reagents, 0.2538 g (4.38 mmol) of Me_2AlH and 0.5426 g (4.38 mmol) of PMePhH in 7.99 g of benzene, in a sealed tube. After the resulting solution was maintained at 54 °C for 18 days, 4.37 mmol of H_2 (measured with a Toepler pump and gas-buret assembly) and the aluminum phosphide were formed. If solutions of reagents were heated for only 10 days at either 54 or 85 °C, only 0.94–0.96 mol of H_2/mol of $HMe_2Al{\cdot}PMePhH$ was formed. In 24 h at room temperature, approximately 40% of the H_2 was formed. Anal. Calcd for $Me_2AlPMePh$: C, 59.99; H, 7.85; Al, 14.97; P, 17.19. Found: C, 59.57; H, 7.93; Al, 14.75; P, 16.84.

Physical Properties of the Product. The physical properties of $(Me_2AlPMePh)_n$ are considered unusual and are described in detail. After benzene was completely removed from the clear, colorless solution formed after stoichiometric H_2 elimination, an amorphous material remained. When 11.815 g of benzene was readded to 0.5950 g of product, part of the product remained insoluble. After the suspension was stirred for 12 h at room temperature, 0.3866 g (65.0%) of insoluble material was isolated. Heating of a benzene suspension of the amorphous product at 50 °C readily solubilized the material. The original amorphous material had an apparent melting point of 222–223 °C, and it sublimed under high vacuum at 170 °C to yield a colorless, transparent glass with an apparent melting point of 188–189 °C. This glass, contained in a sealed tube with benzene, was insoluble after heating to 50 or 90 °C but dissolved when heated in an oven to 140 °C. These observations of solubility have been

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repeated numerous times and are not related to particle size of the product.

Spectral Properties. The spectroscopic properties of all materials described above were identical, regardless of their history. The ^1H NMR spectra were recorded at 90 and 300 MHz by means of a Varian Model EM-390 and a Nicolet Model NTC-300 spectrometer, respectively, and are reported in δ units downfield from $SiMe_4$ (0.00 ppm). The spectra of $(Me_2AlPMePh)_n$ are surprisingly complicated multiline patterns. In the 90-MHz spectrum, the AlMe region consisted of 13 well-defined lines centered at approximately −0.27 ppm, whereas the PMe region had 8 lines centered about 1.40 ppm. The 300-MHz spectrum revealed four distinct sets of Al–Me lines with four lines centered about −0.44 ppm (−0.453, −0.445, −0.438, −0.432), six lines at about −0.38 ppm (−0.400, −0.392, −0.385, −0.378, −0.369, −0.362), four lines at about −0.31 ppm (−0.322, −0.315, −0.310, −0.300), and nine lines at about −0.27 ppm (−0.292, −0.285, −0.280, −0.274, −0.270, −0.267, −0.260, −0.258, −0.255). The P–Me region had two groups of lines, one at about 1.37 ppm with nine lines (1.347, 1.353, 1.358, 1.363, 1.367, 1.373, 1.378, 1.384, 1.385) and the other centered at about 1.42 ppm with four lines (1.408, 1.415, 1.418, 1.425).

The ^{31}P NMR spectrum was recorded at 109.16 MHz by means of a JEOL Model FX-270 spectrometer and was referenced to 85% H_3PO_4. The proton-decoupled spectrum is reported in δ units (+ means downfield from H_3PO_4). The spectrum in C_6D_6 consisted of only two lines at 80.81 and 81.62 ppm with relative heights of 2.14 to 1, respectively.

The infrared spectrum of the amorphous material as a Nujol mull between CsI plates was recorded by means of a Perkin-Elmer Model 683 spectrometer in the range 4000–250 cm^{-1}. Absorption intensities are reported in cm^{-1} for bands below 1350 cm^{-1} with the abbreviations w (weak), m (medium), s (strong), vs (very strong), and sh (shoulder): 1260 (vw), 1185 (m), 1025 (w), 998 (w), 903 (w), 890 (m), 790 (vw), 730 (s), 717 (m), 702 (m), 687 (s), 660 (s), 640 (s), 567 (m), 475 (w), 385 (m), 315 (m), 250 (w).

Molecular Weight. Cryoscopic molecular weights were determined for benzene solutions by using an instrument similar to that described by Shriver.[8] Since $(Me_2AlPMePh)_3$ cannot be prepared, isolated, and then quantitatively redissolved in benzene without heating, molecular weights were determined for solutions obtained directly from the stoichiometric elimination reaction or for solutions formed by heating the isolated amorphous material in benzene. In all cases, the calculated molecular weights indicated an association that varied from 2.93 to 3.10. The degree of association was independent of the initial preparative concentration in the range 0.153–0.480 *m* (monomeric aluminum phosphide), the temperature of preparation, either 54 or 85 °C, or the concentration of the final solution in the range 0.0370–0.0830 *m* (trimeric aluminum phosphide). Similarly, solutions of amorphous materials prepared by heating the isolated material or the sublimed glass in benzene had apparent associations of 3.05 (0.134 *m* monomer) and 3.17 (0.200 *m* monomer), respectively.

Reactions of $(Me_2AlPMePH)_n$ with Excess Me_2AlH and PMePhH. To a benzene solution of $(Me_2AlPMePh)_3$ (0.339 mmol, 2.69 mL of C_6H_6) was added 0.534 g (0.921 mmol) of Me_2AlH. The ^1H NMR spectrum of the resulting solution was observed 2 h after the reagents were mixed. The spectrum consisted of a broadened Al–Me singlet at −0.38 ppm (width at half-height 9 Hz), four lines in the P–Me region at 1.24, 1.27, 1.28, and 1.38 ppm, and a very broad Al–H singlet at 3.13 ppm. After the above solution was heated for 84 h at 54 °C, the ^1H NMR spectrum revealed a well-defined pattern of lines. The Al–Me region had at least eight lines at −0.43, −0.40, −0.38, −0.36, −0.35, −0.32, −0.29, and −0.27 (most intense) ppm, the P–Me region had nine lines at 1.17, 1.25, 1.26, 1.28, 1.30, 1.32, 1.33, 1.38, and 1.40 ppm, and the Al–H region had a very broad line centered at 3.18 ppm.

The ^1H NMR spectrum of a benzene solution of 0.980 mmol of $(Me_2AlPMePh)_3$, 0.270 mmol of PMePhH, and 2 mL of C_6H_6 was a composite of the spectra of the three components with no change in chemical shift or coupling constant data from the individual components. Additional experiments demonstrated that the excess PMePhH can be quantitatively removed from $(Me_2AlPMePh)_3$ by vacuum distillation at room temperature.

The addition of either Me_2AlH or PMePhH to samples of isolated amorphous solid $(Me_2AlPMePh)_n$ indicated that neither reagent reacted with a stoichiometric quantity of alane or phosphine. A mixture of 0.2800 g (1.56 mmol) of $(Me_2AlPMePh)_n$ and 0.7411 g (12.78 mmol) of $AlMe_2H$ was heated at 55 °C for 3 h. The unreacted Me_2AlH was then removed by vacuum distillation while being heated at 40 °C for 3 h. Only 0.30 mmol of Me_2AlH (0.19 mol of Me_2AlH/mol of $Me_2AlPMePh$) was retained. After 0.1803 g (1.00 mmol) of $(Me_2AlPMePh)_n$ and 2.0 g of PMePhH were combined for 24 h at room temperature, 0.1806 g of material was isolated after the PMePhH was removed by vacuum distillation.

Investigation of Preliminary Reaction Products from Me_2AlH and PMePhH Mixtures before Quantitative Elimination of H_2. The ^1H NMR spectrum of a solution prepared from 0.1060 g (1.83 mmol) of Me_2AlH, 0.2247 g (1.82 mmol) of PMePhH, and 5 mL of benzene was observed within 1 h of reagent mixing, 90 MHz (δ, multiplicity, intensity, assignment): −0.40 (s, 6, Al–Me), 1.02 (dd, J = 7.5, 2.6 Hz, 3, PMe), 3.23 (s, 1, Al–H), 4.10 (dq, J = 220, 7.5 Hz, 1, P–H). The spectra of individual components are given for comparison. Me_2AlH (C_6H_6): δ −0.47 (s, 6, Al–Me), 2.87 (s, broad, 1, Al–H). PMePhH (C_6H_6): δ 1.07 (dd, J = 7.5, 2.6 Hz, 3, PMe), 4.10 (dq, J = 204, 7.5 Hz, 1, P–H).

The ^1H NMR spectrum of the above solution was also observed 48 h after the previously described spectrum. During this time interval with the sample at room temperature, elimination had occurred to the extent of approximately 75%. The Al–Me portion of the 90-MHz spectrum consisted of seven lines with the most intense line at −0.30 ppm and with at least six other lines upfield of this most intense line and separated by approximately 3 Hz but with progressively diminished intensity. The P–Me region exhibited three different groups of lines. One group was a doublet of doublets centered at 1.03 ppm (J = 7.5, 2.6 Hz) with an integrated intensity of 0.25 of the total P–Me integration. A second complex group of lines had its most intense resonance at 1.27 ppm with an integrated intensity of 0.25 of the total P–Me integration. The third group of P–Me lines was a complex set of at least six lines, separated by 1.5 Hz, centered at 1.36 ppm with an integrated intensity of 0.50 of the total P–Me integration. The P–H resonance was a doublet of quartets centered at 4.10 ppm (J = 220, 7.5 Hz).

Kinetics Experiments. The kinetics of the reaction between Me_2AlH and PMePhH in xylenes at 22.0 ± 0.1 °C was monitored by following the rate of H_2 evolution manometrically. The apparatus, general procedure, and experimental details for the preparation of the Me_2AlH solution were identical with those previously described.[2,3] The phosphine solution was prepared in a 10-mL graduated addition tube fitted with a Teflon valve and standard-taper joint for connection to the kinetics apparatus. The desired amount of preweighed PMePhH was distilled into the tube and was followed by distillation of 6.00 mL of xylene. The volume of the solution was measured with the calibrated tube. A constant-temperature bath with a circulating pump was used to feed water at 22.0 °C to a glass jacket surrounding the kinetics apparatus.

Results and Discussion

The stoichiometry of the elimination–condensation reaction between dimethylaluminum hydride and methylphenylphosphine in aromatic solvents is represented by eq 3. Hydrogen was formed

$$(Me_2AlH)_3 + 3PMePhH \xrightarrow[\text{solvents}]{\text{aromatic}} (Me_2AlPMePh)_3 + 3H_2 \qquad (3)$$

quantitatively after 0.1 M solutions of the alane and phosphine were heated at 54 °C for 18 days. A shorter reaction time of 10 days led to only a 94% yield of the expected hydrogen. The final aluminum–phosphorus product in benzene solution is a trimeric species according to cryoscopic molecular weight measurements. Samples for the molecular weight studies were prepared from the alane and phosphine without removal of the reaction solvent, benzene. The observed molecular weight of the product was independent of the concentration of the preparative solution in the range of 0.153–0.480 *m* (monomer), the concentration of the solution used for the cryoscopic measurements in the range of 0.0370–0.0830 *m*, and the preparative reaction temperature, either 54 or 85 °C. These data suggest that $(Me_2AlPMePh)_3$ is the ultimate product of the reaction that occurs in benzene solution. Equilibria between species of different degrees of association in solution seem unlikely.

The product $(Me_2AlPMePh)_3$ should exist as a six-membered ring in order to have donor–acceptor bonding between the three amphoteric monomers. In an attempt to define the solution structure of $(Me_2AlPMePh)_3$, a variety of spectroscopic data including ^1H NMR (90 and 300 MHz) and ^{31}P NMR spectra were collected. The complexity of the data suggests that the ring exists in more than one conformation with possibly multiple isomers for each conformation due to the orientation of the substituents on the aluminum and especially on the phosphorus atoms. Furthermore, the interconversion of the different orientations of substituents must also be slow. The 300-MHz ^1H NMR

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[8] Shriver, D. F. *The Manipulation of Air Sensitive Compounds*; McGraw-Hill: New York, 1969.

Table I. Kinetic Data for the Me_2AlH–PMePhH Reaction

$[Me_2AlH]_T$,[a] M	$[PMePhH]_T$, M	10^5k_0,[b] s^{-1}	$[Me_2AlH]_T$,[a] M	$[PMePhH]_T$, M	10^5k_0,[b] s^{-1}
0.0552	0.622	2.76	0.0746	0.874	3.14
0.0708	0.624	2.69	0.0735	0.878	3.14
0.0635	0.645	2.78	0.0888	0.907	3.01
0.0574	0.710	2.77	0.0847	0.928	3.23
0.0715	0.712	2.89	0.1183	1.170	3.30
0.0712	0.721	2.96	0.1700	1.202	3.34
0.0666	0.738	3.02	0.0798	1.206	3.39
0.0622	0.806	3.08	0.1030	1.206	3.33

[a] Concentrations of Me_2AlH are based on the number of moles of monomeric unit. [b] Calculated by dividing the initial rate by $[Me_2AlH]_T$.

spectrum had a minimum of 23 lines in the Al–Me region and 13 lines in the P–Me region with no major effect on the spectrum with heating. In contrast, the ^{31}P NMR spectrum consisted of two closely spaced lines with relative heights of 2.14/1. It is of interest that $(Me_2AlNMeH)_3$ exists as two isomers with both chair (cis isomer) and skew-boat (trans isomer) conformations being conclusively identified[9,10] by X-ray structural studies. The interconversion of the axial and equatorial substituents for each isomer was slow according to NMR data.[10] Similarly, the substituents on the six-membered ring of $(H_2GaNRH)_3$ (R = Me,[11] Et[12]) do not exhibit rapid interconversion of axial and equatorial positions in their proposed chair conformations. However, all attempts to make reasonable ^1H NMR assignments for $(Me_2AlPMePh)_3$ based on the spectra of the different isomers of $(Me_2AlNMeH)_3$[9,10] and $(H_2GaNRH)_3$[11,12] were unsuccessful. It is regrettable, but the structural problem for $(Me_2AlPMePh)_3$ cannot be solved by X-ray structural techniques because removal of solvent or sublimation changes the nature of the compound to produce an amorphous material rather than a crystalline solid.

The degree of association or polymerization of the aluminum–phosphorus product depends upon the state of the product. A trimer exists in benzene solution, but removal of benzene leads to the formation of an amorphous, colorless, apparently polymeric material. Upon readdition of the same solvent, the compound is no longer completely soluble. Mild heating is required for complete dissolution and re-formation of the trimer. If the isolated material had been composed of only trimeric species, complete dissolution would have been expected. Heating is probably necessary to rupture aluminum–phosphorus bonds in the more polymeric isolated material so that the thermodynamically more stable trimer can be reformed in solution. These observations suggest that aluminum–phosphorus bonds in the trimer can be broken more easily than those in the isolated polymeric material, possibly due to the presence of more strain in the six-membered ring than the larger polymer. It is also noteworthy that the amorphous material can be sublimed at 170 °C to yield a colorless, transparent glass. However, this glass is also insoluble in benzene at 50–90 °C but dissolves completely upon more extensive heating in a sealed tube to re-form the trimer, according to molecular weight measurements. The significantly different apparent "melting points" for the original amorphous material isolated by removal of the reaction solvent and for the transparent glass from sublimation, 222–223 °C vs. 188–189 °C, respectively, are also consistent with different degrees of polymerization for the two materials. The degree of polymerization of the nominal species $Me_2AlPMePh$ must be controlled by small differences between the changes in enthalpy and entropy for the different phases. However, it is also apparent that aluminum–phosphorus bonds in the trimeric species are readily broken and re-formed in order for removal of solvent to produce a species with a different degree of association.

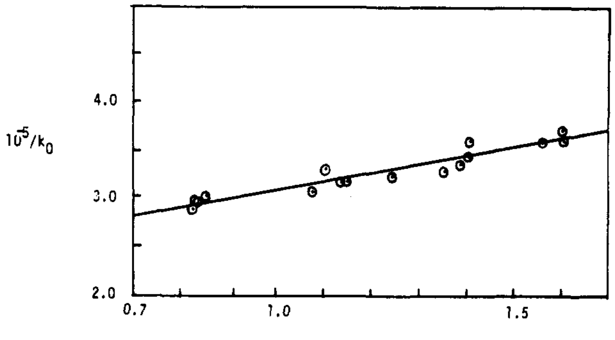

Figure 1. Dependence of k_0 on phosphine concentration (pseudo-first-order conditions, excess PMePhH; T = 22 °C; $\Delta P_{H_2}/\Delta t = k_0[AlMe_2H]_T$.

The nature of the reaction between $(Me_2AlH)_3$ and PMePhH to form a trimer has been examined in order to compare this system with the corresponding $(Me_2AlH)_3$–NMePhH system.[2] One major purpose of this aluminum–phosphorus study was to determine whether analogous intermediates from elimination reactions such as $Me_2AlYMePh$ (Y = N, P) lead to both dimers and trimers. The nitrogen dimers[2,3] $(Me_2AlNMePh)_2$ and $[Me_2AlN(CH_2Ph)H]_2$ are formed from the monomers $Me_2AlNMePh$ and $Me_2AlN(CH_2Ph)H$, respectively. The kinetics of the elimination reaction between $(Me_2AlH)_3$ and PMePhH in xylene solution at 22 °C were investigated by following the rate of evolution of H_2. Even though a variety of experimental conditions were attempted, the useful kinetics data were derived only from experiments that used a greater than 10-fold excess of PMePhH. The kinetics data are summarized in Table I. The plots of H_2 pressure vs. time for the early part of the reaction (10% conversion) give data that can be correlated with a rate law. (Typical first-order plots of log H_2 pressure vs. time for pseudo-first-order conditions with excess PMePhH had a distinct curvature.) The slope of the initial linear portion of the pressure vs. time plots gives an observed rate that is proportional to the initial Me_2AlH concentration for a given PMePhH concentration. A plot of $1/k_0$ vs. 1/[PMePhH] is linear with a finite intercept (Figure 1). The Me_2AlH and PMePhH concentrations were each varied by factors of 2. The rate law for the elimination of H_2 is given by the following equation and is analogous to that observed for the HMe_2Al–NMePhH reaction. This rate law (eq 4) is

$$\frac{dP_{H_2}}{dt} = \frac{k}{1 + K_a[PMePhH]_T}[Me_2AlH]_T[PMePhH]_T \quad (4)$$

consistent with a mechanism in which monomeric $Me_2AlPMePh$ is the product of the elimination reaction. However, the available kinetic data do not permit us to distinguish between two possible elimination reactions, a second-order elimination of H_2 between monomeric alane and phosphine (eq 5) as observed for the

$$HMe_2Al + PMePhH \rightarrow H_2 + Me_2AlPMePh \quad (5)$$

Me_2AlH–NMePhH[2] and Me_2AlH–$N(CH_2Ph)H_2$[3] systems or a first-order elimination of H_2 from the adduct $HMe_2Al{\cdot}PMePhH$ (eq 6). All previous kinetic studies[2-5] suggest that elimination

$$HMe_2Al{\cdot}PMePhH \rightarrow H_2 + Me_2AlPMePh \quad (6)$$

results when the monomeric Lewis acid and the Lewis base combine with the appropriate energy and orientation as in eq 5.

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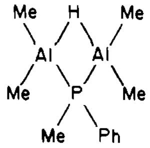
The observed kinetics data and rate law permit the equilibrium constant for the formation of the adduct, K_a, to be evaluated (eq 7). The magnitude of K_a at 22 °C (2.60 M^{-1}) is consistent with

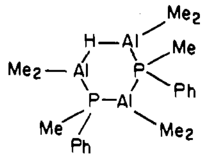
$$HMe_2Al + PMePhH \overset{22\ °C}{\rightleftharpoons} HMe_2Al\cdot PMePhH \qquad K_a = 2.60\ M^{-1} \tag{7}$$

the components of the system and other experimental observations. For comparison, the analogous constant in the HMe_2Al–NMePhH system[2] at −63 °C has a value of 110 M^{-1}. The amine is expected to be a significantly stronger base than the phosphine toward Me_2AlH. The calculated value of equilibrium constant K_a for $HMe_2Al\cdot PMePhH$ is also consistent with the small change in the P–H coupling constant from the free phosphine (204 Hz) to that observed for an equimolar mixture of Me_2AlH and PMePhH (220 Hz). The adduct $Me_3Al\cdot PMePhH$ has a much larger P–H coupling constant, 315 Hz, and suggests that $AlMe_3$ is a significantly stronger Lewis acid than Me_2AlH. Since the kinetics data for the HMe_2Al–NMePhH system[2] clearly suggested that the prior dissociation of the adduct is required for elimination of H_2, it is of interest to compare the equilibrium concentrations of monomeric Me_2AlH in the NMePhH and PMePhH systems. In the HMe_2Al–NMePhH system, the kinetic data[2] led to an equilibrium concentration of monomeric alane of 0.0286 M when the initial concentrations of alane and *N*-methylaniline were both 0.117 M. In comparison, when the initial concentrations of alane and phosphine are 0.100 M, the calculated equilibrium concentration of monomeric alane would be 0.0823 M. This high concentration would suggest that Me_2AlH monomers should form dimers (or trimers) and/or other Lewis acid–base adducts. When the initial concentration of alane was 0.0622 M and the phosphine was 0.806 M, our pseudo-first-order conditions, the calculated equilibrium concentration of alane would be 0.0211 M, a value comparable to that in the HMe_2Al–NMePhH system.[2]

A surprisingly long reaction time (18 days at 54 °C) is required for the complete conversion of Me_2AlH and PMePhH into $(Me_2AlPMePh)_3$ and H_2, even though 40% of the H_2 is formed during the first 24 h of reaction. The formation of cyclic complexes of the general formula $HMe_2Al(PMePhAlMe_2)_n$ (n = 1, 2, 3) with bridging phosphorus and hydrogen atoms is believed to be responsible for the extended reaction times for complete reaction and for the observed departure of the reaction kinetics from simple first order (under pseudo-first-order conditions) for the duration of the reaction. These unsymmetrically bridged complexes tie up Me_2AlH and hinder the further occurrence of the elimination reaction. The formation of these complexes is consistent with the calculated values of K_a (2.60 M^{-1}), the presence of many Lewis base sites in the system, the Lewis acidity of Me_2AlH, the ^1H NMR spectra of an equimolar HMe_2Al–PMePhH reaction mixture at different stages of the reaction, and the literature.[13-15] The spectrum of the equimolar reaction mixture after 1 h of mixing is of the apparent adduct. After 48 h, the spectrum compares favorably with a composite of spectra of a solution formed by reacting $(Me_2AlPMePh)_3$ with Me_2AlH in a 1/3 mole ratio in benzene and of a solution of the adduct $HMe_2Al\cdot PMePhH$ and free PMePhH. The ^1H NMR spectrum after 48 h (reaction 75% complete) had three distinct sets of lines in the diagnostic PMe proton region. The lines around 1.27 ppm are consistent with the presence of the cyclic species $HMe_2AlPMePhAlMe_2$:



Another complex set of lines around 1.36 ppm would suggest the trimer $(Me_2AlPMePh)_3$ or species with closely related PMe groups such as $HMe_2Al(PMePhAlMe_2)_n$, n = 2 (six-membered ring)



or 3 (eight-membered ring). The observed doublet of doublets at 1.03 ppm would be consistent with the adduct $HMe_2Al\cdot PMePhH$ and/or unreacted PMePhH. It is noteworthy that the ^1H NMR spectrum of the solution formed by combining $(Me_2AlPMePh)_3$ and Me_2AlH in a 1/3 molar ratio in benzene had two sets of PMe lines at the same chemical shifts as those above, 1.26 and 1.38 ppm. The lines around 1.26 ppm were significantly more intense than those at 1.38 ppm. Unsymmetrically bridged organoaluminum compounds analogous to $HMe_2AlPMePhAlMe_2$ with the four-membered ring are well-known for nitrogen derivatives,[13-15] but there are no previously well-characterized phosphorus compounds, possibly because so little has been reported on aluminum–phosphorus chemistry. It is also significant that $(Me_2AlPMePh)_3$ does not react with PMePhH to form complexes.

The reaction between Me_2AlH and PMePhH to form a trimer in benzene solution cannot be considered simple or straightforward. However, it is noteworthy that for the three systems that have been studied by kinetics data, the product of the actual H_2 elimination step is a simple monomeric amphoteric species, irrespective of whether the base site is nitrogen or phosphorus. It is also significant that both dimers and trimers are formed from the same type of monomeric amphoteric product of elimination. Thus, the degree of association of the product cannot be related to the mechanism of the elimination step. The formation of a trimer for the $Me_2AlPMePh$ system is apparently related to the basicity of the phosphorus in the amphoteric intermediate, which enables intermediate species such as the four-membered ring $HMe_2AlPMePhAlMe_2$ to form. The addition of more amphoteric $Me_2AlPMePh$ monomers provides a pathway whereby the size of the species can grow. Similar observations have been made in boron–nitrogen chemistry.[16] Eventually, the six-membered ring becomes the thermodynamically favored product in benzene solution. The dimer[17,18] $(Me_2AlPPh_2)_2$ is apparently formed when the steric effects of the phenyl substituents are sufficient to decrease either the basicity of the amphoteric intermediate, the stability of the longer intermediates, or the stability of the final six-membered ring. Thus, the dimer is the preferred product that minimizes the interactions between the bulkier substituents but still permits the formation of the maximum number of bonds in the system. Lastly, the nature of the association reaction, concerted π-cycloaddition reaction[2] for $Me_2AlNMePh$ and stepwise σ-bond formation for $Me_2AlPMePh$, might also be important for determining the degree of polymerization of the product. It is also clear that the major factors which influence the rate of elimination will be those that alter the equilibrium constant for adduct formation and the rate constant for elimination.

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Registry No. Me_2AlH, 865-37-2; PMePhH, 6372-48-1; $Me_2AlPMePh$, 101834-72-4; $(Me_2AlPMePh)_3$, 101834-71-3.

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