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SYNTHESIS AND CHARACTERIZATION OF ORGANOALUMINUM
COMPOUNDS CONTAINING THE... (U) STATE UNIV OF NEW YORK AT
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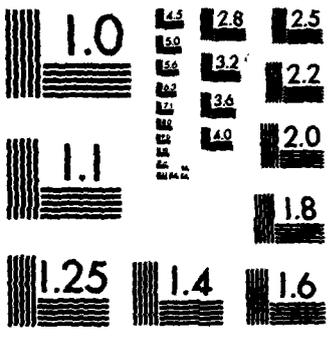
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Synthesis and Characterization of Organoaluminum Compounds
Containing the Trimethylsilylmethyl Substituent
 $Al(CH_2SiMe_3)_2Br$, $Al(CH_2SiMe_3)_2H$ and $(Me_3SiCH_2)_2AlPh_2$ and
a Reinvestigation of the Chemistry of Me_2AlPh_2 and Et_2AlPh_2 .

by

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in
Organometallics

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Introduction

The synthesis and characterization of $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{Al}(\text{CH}_2\text{SiMe}_3)_2\cdot\text{NMe}_3]^1$ has been described recently. This compound serves as a model for compounds in which a diphenylphosphide group bridges a transition metal and a main-group element moiety. Alternatively, this new compound may be considered to be a transition metal derivative of an organoaluminum phosphide, an amphoteric ligand. As part of this research effort, the chemistry of amphoteric ligands is of interest and consequently we have extended, reinvestigated and in some cases reassessed the chemistry of several organoaluminum diphenylphosphides.

Organoaluminum diphenylphosphides with methyl,² ethyl³ and aryl⁴ substituents have been prepared from triorganoaluminum compounds and PPh_2H by elimination reactions. The compounds R_2AlPPh_2 exist as dimers in benzene solution and are believed to have four-membered aluminum-phosphorus rings in analogy with similar compounds containing other Group 3 and Group 5 atoms.²⁻⁴ The four-membered rings reportedly can be disrupted by reaction with various Lewis bases to form adducts of formula $\text{Ph}_2\text{PAIR}_2\cdot\text{Base}$.²⁻⁴ However, no NMR or x-ray structural data have been reported to support the proposed structures of dimers or of their adducts. The lack of such data prompted us to undertake a reinvestigation of the properties and reaction chemistry of $\text{Me}_2\text{AlPPh}_2$ and $\text{Et}_2\text{AlPPh}_2$. The results of our initial attempts to synthesize $\text{M}(\text{CO})_5\text{PPh}_2\text{AlR}_2$ compounds defined the need for a more soluble organoaluminum diphenylphosphide. Our previous experience^{5,6} had indicated that the trimethylsilylmethyl ligand enhanced the solubility of its compounds in hydrocarbon solvents. Thus, we prepared $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$ from $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$, $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ and $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ in order to define the best and most useful route. Our new convenient synthesis of $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ has been reported.⁷

From this parent compound, the preparations of $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ and $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ have been accomplished. In this paper we also report the properties of the adducts $\text{R}_3\text{AlPPh}_2\text{H}$ ($\text{R} = \text{Me}, \text{Et}, \text{CH}_2\text{SiMe}_3$) and the chemistry of organoaluminum diphenylphosphides towards ethers (THF and Et_2O) and CH_3CN .

Experimental

Handling procedures, solvent purification and spectra were as previously described.¹ All molecular weights were measured cryoscopically in benzene solution.¹ Moles of hydrolyzable alkyl groups or hydrogens bound to aluminum were determined by measuring the gas (PVT) evolved upon acid hydrolysis from a weighed sample of compound¹ (mol). Attempts to analyze for aluminum via an EDTA titration² in the presence of phosphorus were unsuccessful. Immediately prior to its use AlMe_3 was vacuum distilled. AlEt_3 was obtained from a commercial 25% solution in hexane by removal of hexane by vacuum distillation. The compound AlMe_2H was obtained from the reaction of AlMe_3 and LiAlH_4 ⁸ and was purified by vacuum distillation. The reagents $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ ⁷ and PPh_2H ⁹ were synthesized by literature procedures. The liquids, AlEt_3 (0.835 g/mL)¹⁰ and $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ (0.802 g/mL),⁷ were measured by volume using graduated gas-tight syringes in the dry-box. The liquid PPh_2H (1.07 g/mL)¹¹ was similarly handled using Schlenk techniques. ¹H NMR spectra are reported in δ units (ppm) and are referenced to TMS as 0.00 and C_6H_6 as 7.27. Assignments are based on integration of spectra, where possible.

Synthesis of $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$

The compound $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ was synthesized by an exchange reaction between one mol AlBr_3 and two mol $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$. In the dry box, 1.75 mL (1.40 g, 4.87 mmol) $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ and 0.650 g (2.43 mmol) AlBr_3 were combined in

a 10 mL flask. Heat was evolved and a colorless liquid was produced. The flask was attached to a micro-scale distillation apparatus and $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ (1.926 g, 94%) distilled as a colorless liquid at 60-62°/0.01 mm. Density: 1.06 g/mL at 22°. Anal. Calc.: Al, 9.59; Br, 28.41; Me_4Si , 2.00 mol/mol. Found: Al, 9.45; Br, 27.73; Me_4Si , 1.98 mol/mol. ^1H NMR (benzene, δ): 0.27 (s, 9, CH_3), -0.16 (s, 2, CH_2). IR (Nujol, cm^{-1}): 1259(s), 975(s,b), 946(m), 858(vs,b), 763(s), 734(s), 668(m), 636(vs), 577(s), 315(w). Cryoscopic molecular weight. Formula weight $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$: 281.27. Molality, observed mol. wt., association: 0.1257, 644, 2.29; 0.0497, 405, 1.44; 0.0401, 335, 1.19; 0.0336, 295, 1.05. Solubility: soluble in aromatic, halogenated and aliphatic hydrocarbons and ethers. $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ readily reacts with absorbed water on glass. In order to obtain satisfactory analyses for this compound, the reaction flask had to be oven dried (>100°C) prior to being brought into the dry box and the flask containing the sample had to be evacuated at -196° to avoid loss of volatile Me_4Si and HBr which formed even with these precautions.

Synthesis of $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$

The reagents $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ (2.5 mL, 2.0 g, 6.9 mmol) and 0.3 g (7.9 mmol) LiAlH_4 (recrystallized from Et_2O) were heated at 90° for 18 h under vacuum. The reaction mixture solidified on cooling to room temperature. The product $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ (1.29 g, 92%) sublimed at 40-70° under high vacuum as a crystalline solid. Mp: 35-36°. Alternatively, $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ was isolated from the reaction mixture by extracting with hexane, concentrating the solution and cooling to 0° or -20°. Mp: 38-40°. Anal. Calc.: Al, 13.33; Me_4Si , 2.00 mol/mol; H_2 , 1.00 mol/mol. Found: Al, 11.36; Me_4Si , 2.04 mol/mol; H_2 0.99 mol/mol. ^1H NMR

(benzene, δ):[†] 0.33 (s, 9, CH₃), -0.25 (s, 2, CH₂). IR (Nujol mull, cm⁻¹): 1765 (vs, vb, Al-H), 1257 (vs), 970 (vs, b), 854 (vs), 838 (vs), 765 (vs), 733 (s), 702 (m), 661 (w), 575 (m). Cryoscopic molecular weight. Formula weight Al(CH₂SiMe₃)₂H: 202.35. Molality, obs. mol. wt., association: 0.1144, 607, 3.00; 0.144, 648, 3.20; 0.1702, 609, 3.01. Solubility: soluble in aromatic and aliphatic hydrocarbons. The analysis suggests a 5-9% impurity of Al(CH₂SiMe₃)₃ which could not be removed due to the similarities of its solubility and volatility with Al(CH₂SiMe₃)₂H.

Synthesis of R₃AlPPh₂H (R = Me, Et, CH₂SiMe₃)

Adducts of formula R₃Al·PPh₂H (R = Me, Et or Me₃SiCH₂) were obtained by combining equimolar quantities of the trialkylaluminum compound and Ph₂PH (see preparations of R₂AlPPh₂). All three adducts were colorless liquids at room temperature. ¹H NMR Me₃Al·PPh₂H (d⁸-toluene, δ): 7.46 (m, Ph), 7.20 (m, Ph), 5.53 (d, J = 299 Hz, 1, PH), -0.08 (s, 9, CH₃). ¹H NMR Et₃Al·PPh₂H (d⁶-benzene, δ): 7.45 (m, Ph), 7.18 (m, Ph), 5.55 (d, J = 295 Hz, 1, PH), 1.51 (t, J = 8 Hz, 9, CH₃), 0.53 (q, J = 8 Hz, 6, CH₂). ¹H NMR (Me₃SiCH₂)₃Al·PPh₂H (d⁶-benzene, δ): 7.55 (m, Ph), 7.24 (m, Ph), 5.62 (d, J = 300 Hz, 1, PH), 0.30 (s, 27, CH₃), -0.40 (s, 6, CH₂).

Synthesis of (Me₃SiCH₂)₂AlPPh₂

a) From Ph₂PH and Al(CH₂SiMe₃)₃

As in the preparation of Et₂AlPPh₂, a break-seal tube containing 1.00 mL (1.07 g, 5.74 mmol) Ph₂PH and 2.09 mL (1.68 g, 5.82 mmol) Al(CH₂SiMe₃)₃ was prepared. The tube was evacuated, sealed at -196° and then heated at 160-180° for about 18 h. The progress of the

reaction was followed by periodically cooling the tube to room temperature. At room temperature, $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$ is a solid and can be distinguished from the liquid adduct. The tube was opened under vacuum. Tetramethylsilane (5.45 mmol, 94.9%) and a trace of a noncondensable gas were evolved during the reaction. The solid was transferred from the tube to a flask by repeated extractions with one 5 mL portion of hexane and then washed once with the same hexane at -20° to remove unreacted adduct. The compound $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$ (1.63 g, 73.4%) was obtained as a white solid. Mp: $120-121^\circ$ a glass forms which melts at $136-139^\circ$; cooling this sample to room temperature gives crystals which when slowly heated melt at $141-143^\circ$. ^1H NMR (benzene, δ): 0.20 (s, 4.5, CH_3), 0.06 (q, $J = 2.7$ Hz, 1, CH_2). (See Results and Discussion for additional description of spectrum.) IR (Nujol mull, cm^{-1}): 1584 (m), 1263 (m), 1248 (s), 1097 (m,b), 1034 (m), 971 (s), 956 (m), 862 (vs), 832 (vs), 749 (vs), 733 (s,sh), 704 (m), 696 (m,sh), 652 (m), 636 (w), 567 (m), 470 (w), 451 (w), 430 (w), 398 (w), 313 (w). Cryoscopic molecular weight. Formula weight $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$: 386.54. Molality, obs. mol. wt., association: 0.0549, 665, 1.72; 0.0446, 638, 1.65; 0.0210, 545, 1.41.

b) From $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ and Ph_2PH

A sample of $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ (0.660 g, 3.26 mmol) was placed in a tube equipped with a Teflon valve. Toluene (5 mL) was distilled into the tube and then, under argon flush, the tube was attached to a two-neck flask containing 0.56 mL (0.60 g, 3.2 mmol) Ph_2PH . The flask was evacuated and the alane solution was added to the stirred phosphine. Evolution of a noncondensable gas took place very slowly at room

temperature in toluene solution. The toluene was removed by vacuum distillation and the reaction flask was heated with an oil bath. Gas evolution was rapid at 65° and a white solid formed. The flask was heated at 70-80° for 2 h to drive the reaction to completion. Hydrogen was evolved in greater than 91% yield. Unreacted adduct was removed by washing the solid with 5 mL hexane at -20°. Mp: 146-147°. Anal. Calc.: Me₄Si, 2.00 mol/mol. Found: Me₄Si, 2.02 mol/mol. Infrared and ¹H NMR spectra were identical to those obtained from the previous reaction.

c) From Al(CH₂SiMe₃)₂Br and KPPH₂

Potassium hydride (0.102 g, 2.54 mmol) was slowly added to a stirred solution of 0.64 mL (0.69 g, 3.7 mmol) Ph₂PH in 10 mL diethyl ether. An orange solid, KPPH₂, was precipitated and hydrogen was evolved in 95% yield in less than 12 hr. A solution of 0.97 mL (1.0 g, 3.7 mmol) Al(CH₂SiMe₃)₂Br in 3 mL diethyl ether, contained in a built-in addition tube of the reaction vessel, was added to the stirred KPPH₂ suspension. The orange solid disappeared immediately and a white precipitate was formed. After stirring for one-half hour, the solution was filtered from the KBr using a medium frit. Diethyl ether was removed by vacuum distillation and the remaining white solid was recrystallized from pentane. The compound (Me₃SiCH₂)₂AlPPh₂ was obtained in 71% yield. Mp: glass forms at 115° which melts completely by 138°. The ¹H NMR spectrum of the product in d⁶-benzene indicated (Me₃SiCH₂)₂AlPPh₂ and the presence of a small impurity of Br(Me₃SiCH₂)₂AlPPh₂H.

Syntheses of Me₂AlPPh₂

a) From PPh₂H and AlMe₃

The compound AlMe₃ (1.0117 g, 14.03 mmol) was distilled into a trap on the vacuum line. Then Ph₂PH (2.34 mL, 2.50 g, 13.4 mmol) was syringed into an argon filled break-seal tube. The preweighed AlMe₃ was vacuum distilled into the tube and the tube was sealed at -196°. On warming to room temperature, an exothermic reaction took place. The clear liquid adduct was heated for 16 h at 160°, producing a white solid and 13.4 mmol methane gas. The tube was opened under vacuum using a stainless steel breaker. The contents of the tube were transferred into a flask by repeated extractions with toluene. The resultant white solid was washed once with hexane (5 mL) yielding Me₂AlPPh₂ (2.812 g, 86%) as a white powder. Mp: 200-206° a glass forms, 211-222° the glass melts (lit. mp: 230°, sublimed).² Anal. Calc.: MeH, 2.00 mol/mol. Found: MeH, 1.99 mol/mol. ¹H NMR (d⁸-toluene, δ): 7.50 (m, Ph), 7.16 (m, Ph), 0.08 (q, J = 2 Hz, AlCH₃). (See Results and Discussion for additional description of spectrum.) IR (Nujol mull, cm⁻¹): 3081 (w), 3050 (w), 1587 (w), 1437 (s), 1264 (w), 1183 (m), 1042 (s,b), 1021 (s), 1005 (s), 950 (w), 926 (w), 804 (w), 757 (m), 730 (s), 685 (s,b), 554 (m), 487 (m), 423 (m), 355 (w), 332 (w). Solubility: moderately soluble in benzene or toluene, insoluble in hexane and diethyl ether. The compound Me₂AlPPh₂ reacts with halogenated hydrocarbons, THF and CH₃CN (vide infra), solvents in which it has only slight solubility. The attempted sublimation of a 1.79 g sample at 160° for 12 h under high vacuum produced 0.0347 g (2%) sublimed Me₂AlPPh₂ (mp: 228°).

b) From Ph_2PH and AlMe_3 in toluene.

As in the previous preparation, a break-seal tube containing 0.8315 g (11.53 mmol) AlMe_3 and 1.54 mL (1.65 g, 8.88 mmol) Ph_2PH was prepared. Toluene (10 mL) was vacuum distilled into the tube and the tube was sealed. The reaction mixture was heated at 140° for 18 h. Large crystals formed as the reaction vessel slowly cooled to room temperature. The tube was opened under vacuum. Methane was generated by the reaction. The crystals were washed out of the tube with toluene, recrystallized from this solvent and subjected to high vacuum for several hours. During this latter process the unreacted AlMe_3 was removed. The compound $\text{Me}_2\text{AlPPh}_2$ (1.40 g, 62%) was obtained as a white solid which melted at 228° . Identical ^1H NMR and infrared spectra were obtained as for the compound described in the previous preparation.

c) From Ph_2PH and AlMe_2H .

The reagent AlMe_2H (0.2789 g, 4.804 mmol) was vacuum distilled into a tube equipped with a Teflon stopcock. Under argon flush, the tube was attached to a 2-neck flask containing 0.83 mL (0.88 g, 4.8 mmol) Ph_2PH . The flask was evacuated and AlMe_2H was transferred to the flask by distillation. The reagents were allowed to slowly warm to room temperature. Vigorous bubbling took place and a white solid and a noncondensable gas formed. After 2 h at room temperature, the reaction flask was heated at 90° for 1 h to drive the reaction to completion. Using estimated volumes, the quantity of hydrogen evolved was nearly quantitative. A sublimation of this solid was attempted but after several hours at 160° only a trace of a liquid, identified as Ph_2PH , had distilled to the cold finger. The remaining solid was then recrystallized from toluene, yielding 0.235 g

(20%) $\text{Me}_2\text{AlPPh}_2$. Mp: 210-212° glass forms, which is completely melted by 225°. Identical infrared and ^1H NMR spectra were obtained as for the compounds described in the previous two preparations. A second crop of a slightly sticky solid (0.20 g) melting at 205-210°, was shown to contain Ph_2PH by its infrared spectra.

Synthesis of $\text{Et}_2\text{AlPPh}_2$

The reagent Ph_2PH (2.25 mL, 2.41 g, 2.9 mmol) was syringed into an argon filled break-seal tube. In the dry-box, 1.79 mL (1.49 g, 13.0 mmol) AlEt_3 was added to the tube. Heat was evolved due to adduct formation. Toluene (10 mL) was then vacuum distilled into the tube. The tube was sealed at -196° and then heated at 90° for 16 h. The tube was opened under vacuum and the ethane evolved (11.4 mmol, 88.4%) was measured. The toluene solution was filtered into a flask under vacuum. Solvent was removed by vacuum distillation leaving a sticky white solid. The solid was recrystallized from 6 mL 1:1 toluene/hexane yielding $\text{Et}_2\text{AlPPh}_2$ (2.374 g, 68%) as a white powder. Mp: 123-126° glass forms, 141-143° glass melts (lit. mp: 124-126°, from benzene).³ In other preparations, the sticky white solid was washed with hexane, leaving a solid which melted at 140-143°. Identical spectral and analytical data were obtained for both products.

Anal. Calc.: EtH, 2.00 mol/mol. Found: EtH, 2.02 mol/mol. ^1H NMR (d^8 -toluene, δ): 7.51 (m, Ph), 7.20 (m, Ph), 1.31 (t, $J = 7$ Hz, 1.5, CH_3), 0.80 (q, $J = 7$ Hz, 1, CH_2). (See Results and Discussion for additional description of spectrum.) ^{31}P NMR (d^8 -toluene, ppm from 85% H_3PO_4): -42.30 (s). IR (Nujol mull, cm^{-1}): 3052 (w), 1594 (w), 1441 (s), 1267 (w), 1236 (w), 1195 (m), 1137 (vs), 1051 (m,b), 1018 (m), 989 (m), 955 (m), 920 (w), 809 (w), 759 (m), 736 (s), 700 (s), 543 (m), 504 (m), 477 (m), 424 (w).

400 (w), 379 (vw), 284 (vw). Solubility: soluble in aromatic hydrocarbons and diethyl ether, slightly soluble in hexane, soluble in and reacts with halogenated hydrocarbons, THF and CH_3CN (vide infra).

Attempted Syntheses of $\text{Et}_2\text{AlPPh}_2 \cdot \text{OEt}_2$

A 0.3180 g (1.177 mmol) sample of $\text{Et}_2\text{AlPPh}_2$ was placed in a tube equipped with a Teflon valve and a magnetic stirring bar. The tube was evacuated and weighed. Diethyl ether (2 mL) was vacuum distilled into the tube. The solution was stirred until all the $\text{Et}_2\text{AlPPh}_2$ dissolved and then cooled to -78° for 48 h. Et_2O was removed by vacuum distillation and the tube was reweighed. No diethyl ether was retained by the sample. This observation was confirmed by the ^1H NMR spectrum which identified the presence of only $\text{Et}_2\text{AlPPh}_2$. The sample melted at $143\text{--}146^\circ$ (lit. mp $\text{Et}_2\text{AlPPh}_2 \cdot \text{OEt}_2$: 148°).³

Another sample of $\text{Et}_2\text{AlPPh}_2$ was recrystallized in Et_2O . The crystals were subjected to high vacuum at -78° until they appeared dry. A ^1H NMR spectrum of these crystals showed that no ether was retained. The crystals melted at $143\text{--}145^\circ$.

Reaction of $\text{Et}_2\text{AlPPh}_2$ with THF

A sample of $\text{Et}_2\text{AlPPh}_2$ and THF was stirred for 18 h in a flask equipped with a side-arm NMR tube. Solvent was removed by vacuum distillation and some of the resultant sticky white solid was washed into the NMR tube with benzene. The tube was sealed at -196° and the ^1H NMR spectrum was recorded. ^1H NMR (benzene, δ): 3.55 (t, $J = 6$ Hz, OCH_2), 2.02 (t, $J = 7$ Hz, PCH_2), 1.44 (m, other CH_2), 1.36 (t, $J = 9$ Hz, AlCH_2CH_3), 0.32 (m, b, AlCH_2), 0.21 (q, $J = 9$ Hz, AlCH_2). The sticky material remaining in the reaction tube was then treated with dilute hydrochloric acid and extracted with diethyl ether. Solvent was removed from the extract, the clear oil was dried under

high vacuum for three days and its infrared spectrum was recorded.

$\text{Ph}_2\text{PC}_4\text{H}_8\text{OH}$ plus PPh_2H . IR (neat, bands above 1400 cm^{-1}): 3380 (vs, b, OH), 3058 (s), 2964 (s), 2932 (s), 2866 (s), 2332 (m, PH); 1969 (w), 1899 (w), 1821 (w), 1720 (m), 1592 (m), 1583 (s), 1490 (m), 1442 (s).

Reactions of Organoaluminum Phosphides with Acetonitrile

Samples of organoaluminum phosphides (about 0.1 g) were stirred in CH_3CN (3 mL) for 48 h. The solvent was removed by vacuum distillation. Sticky white solids, which were soluble in toluene, were obtained.

Infrared spectra of Nujol mulls were recorded. Bands assignable to

carbon-nitrogen double or triple bonds are reported. $\text{Me}_2\text{AlPPh}_2 + \text{CH}_3\text{CN}$.

Mp: 80° red color, $138\text{-}140^\circ$ sample melts to a red liquid. IR (cm^{-1}):

$\nu_{\text{C=N}}$ 1601 (s). $\text{Et}_2\text{AlPPh}_2 + \text{CH}_3\text{CN}$. Mp: 125° glass forms, 137° sample

melts to a yellow liquid. IR (cm^{-1}): $\nu_{\text{C=N}}$ 1613 (s). $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2 +$

CH_3CN . Mp: $160\text{-}165^\circ$ to a yellow liquid. IR (cm^{-1}): $\nu_{\text{C=N}}$ 2186 (m),

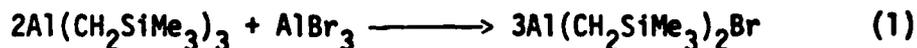
$\nu_{\text{C=N}}$ 1601 (s).

Results and Discussion

Standard reactions have been used for the preparation of $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ and $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ from the trialkylaluminum compound. The compound

$\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ was prepared in 94% yield by an exchange reaction between

$\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ and AlBr_3 in the absence of solvent (eq. 1).

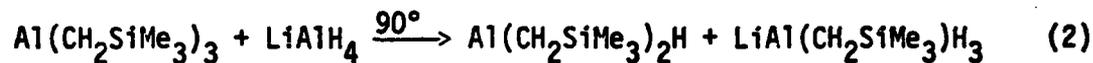


Exchange is exothermic and apparently occurs at room temperature.

Formulation of $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ as a discrete compound, rather than as a mixture of $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ and AlBr_3 is supported by the fact that $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ has a two degree boiling range about ten degrees higher than $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ under

high vacuum. The compound $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ exists as a mixture of monomeric and dimeric species in benzene solution in contrast to the dimeric association observed in hydrocarbon solutions of other organoaluminum halides,¹² $\text{In}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ ⁶ and $\text{Ga}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$.⁵ The lower association of $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ in comparison to these compounds can be attributed to a combination of the large steric size of the trimethylsilylmethyl substituents and the smaller size of the aluminum atom. The analogous chloro-substituted compound, $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$, was prepared from the reaction of one mole of AlCl_3 with two moles of $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$.¹³ The solution molecular weight of $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Cl}$ was not reported but mass spectral data showed a fragmentation pattern consistent with a monomeric species in the gas phase.

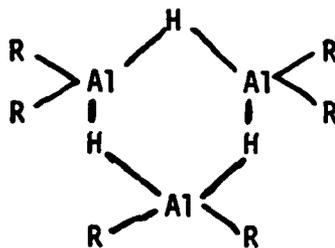
The synthesis of $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ has been achieved by the reaction of $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ with an excess of LiAlH_4 at 90° (eq. 2). This type of



reaction has also been used to prepare AlMe_2H .⁸ The compound $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ can be easily isolated in about 90% yield by sublimation or crystallization from hexane. However analysis of $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ indicates the presence of a 5-9% impurity of $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$, which cannot be removed by repeated sublimations or crystallizations due to similarities of volatility and solubility properties of $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ and $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$. This situation was not improved by altering the reaction conditions. Under the preparative reaction conditions, $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ apparently distills away from the LiAlH_4 to cooler parts of the reaction vessel to avoid reaction. The reaction has also been attempted several times using hexane or toluene as solvent in the hope that the solvent would wash unreacted $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ back down onto

the LiAlH_4 . Surprisingly, only very impure solids were isolated from these reactions. Use of longer reaction times or a larger excess of LiAlH_4 were also ineffective in reducing the amount of the impurity.

The compound $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ is the only dialkylaluminum hydride that exists as a solid at room temperature. Other dialkylaluminum hydrides, with alkyl groups ranging in size from methyl to iso-butyl, exist as viscous oils or as liquids.¹² Cryoscopic molecular weight data indicate that $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ is trimeric in benzene solution. A puckered 6-membered ring composed of alternating dialkylaluminum groups and hydrogen atoms has been proposed for the structure of other trimeric AlR_2H compounds ($\text{R} = \text{Me}$, et, *i*Bu).¹² The infrared spectrum of $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ shows a very broad and intense band

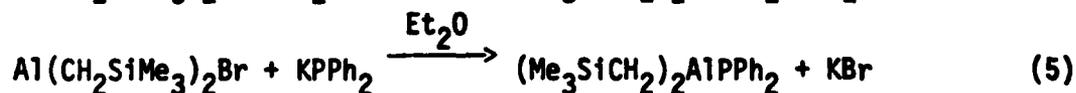
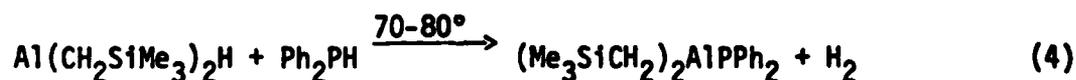
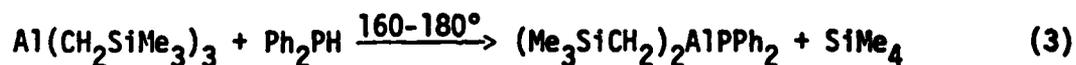


centered at 1765 cm^{-1} which can be attributed to the aluminum-hydrogen stretching frequency. Similarly broad and intense bands in the range of $1785\text{-}1775\text{ cm}^{-1}$ have been observed in the infrared spectra of other dialkylaluminum hydrides.¹⁴

The main route by which the compounds R_2AlPPh_2 ($\text{R} = \text{Me}$, Et, CH_2SiMe_3) have been synthesized involves an elimination-condensation reaction between AlR_3 and Ph_2PH . Formation of the intermediate adduct is an exothermic process giving a liquid product in all three cases. The adducts $\text{R}_3\text{Al}\cdot\text{PPh}_2\text{H}$ have been examined by ^1H NMR spectroscopy. Complexation of diphenylphosphine by aluminum is shown by the P-H ^1H NMR signal, a doublet due to $^{31}\text{P}\text{-}^1\text{H}$ coupling.¹⁵ The chemical shift for the P-H of Ph_2PH (δ 5.2-5.1) depending on solvent

moves to lower field upon coordination to the trialkylaluminum compounds ($\delta = 5.7-5.5$). The solvent dependency of the chemical shift makes it a less useful probe of complexation than the $^{31}\text{P}-^1\text{H}$ coupling constant, which is not only virtually solvent independent but is also highly sensitive to the degree of substitution on the phosphorus atom.¹⁵ In aromatic solvents, the $^{31}\text{P}-^1\text{H}$ coupling constant of PPh_2H is about 220 Hz. This value is in the 180-230 Hz range indicative of three coordinate phosphorus.¹⁵ The ^1H NMR spectra of $\text{R}_3\text{AlPPh}_2\text{H}$ in aromatic solvents show a substantial increase in the $^{31}\text{P}-^1\text{H}$ coupling constant to about 300 Hz. This value is within the 250-730 Hz range indicative of four coordinate phosphorus.¹⁵ As expected, the phenyl resonances are split by the phosphorus. As with other R_3AlPR_3 adducts^{16,17} no detectable splitting of the resonances for the alkyl groups bound to aluminum by phosphorus occurs.

The new organoaluminum phosphide $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$ has been prepared from appropriate reagents by the elimination of SiMe_4 at $160-180^\circ$ (eq. 3), hydrogen at $70-80^\circ$ (eq. 4) and KBr (eq. 5) at room temperature. The best



synthetic reaction based on the ease of preparation and purification of reagents, ultimate purity and percent yield of purified product is given by eq. 3. The purified product $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$, a colorless solid, is isolated in 78% yield, even though SiMe_4 is formed in 95% yield. If reaction temperatures higher than $160-180^\circ$, i.e. $180-200^\circ$, are used for the preparative

reaction, reaction is considerably faster. However, products indicative of the decomposition of the trimethylsilylmethyl ligand, H_2 and a solid product with a grey color are formed. The compound,⁷ $KAl(CH_2SiMe_3)_3H$, also decomposes around 200° .

The potentially amphoteric ligand, $(Me_3SiCH_2)_2AlPPh_2$, exists as a mixture of monomeric and dimeric species in benzene solution according to cryoscopic molecular weight studies. The compounds Me_2AlPPh_2 and Et_2AlPPh_2 are dimers. All other organoaluminum phosphides exist as either dimers or trimers in solution.¹² The decreased extent of association for $(Me_3SiCH_2)_2AlPPh_2$ is presumably due to the bulky CH_2SiMe_3 ligand. The compound, $(Me_3SiCH_2)_2AlPPh_2$ is the most soluble of the three organoaluminum phosphides discussed in this study, having moderate solubility in hexane and pentane and excellent solubility in aromatic hydrocarbons and diethyl ether. The spectral properties of these compounds are discussed later.

The compound $(Me_3SiCH_2)_2AlPPh_2$ exhibits an unusual behavior upon heating. The purified product from the $Al(CH_2SiMe_3)_3-PPh_2H$ reaction shows a solid to glass transformation at $120-121^\circ$ and this glass melts at $136-139^\circ$. If this sample is then permitted to cool slowly to room temperature, crystals form which upon reheating melt at $141-143^\circ$, no glass transition is observed. The purified product from the $Al(CH_2SiMe_3)_2H-PPh_2H$ reaction does not show the glass transition but melts sharply at $146-147^\circ$.

The compound Me_2AlPPh_2 is also readily prepared by a variety of routes, in the presence or absence of a solvent (toluene) or excess alane. All of the reactions are quantitative. All products have the same 1H NMR and infrared spectral properties and analyses but they have slightly different melting points. The different melting points observed for the

products from the different reactions and/or conditions are probably related to the detailed nature and extent of association of the aluminum-phosphide rather than impurities. Some samples of product melt sharply at 228°, whereas others form a glass at temperatures around 200° and then melt at higher temperatures, within the range of 210 to 225°. Since these temperatures are not considered to reflect a material impurity, the melting point of this type of compound should not be used for product identification and purity. The details of the melting point behavior of different products are given in the Experimental Section. The compound $\text{Et}_2\text{AlPPh}_2$ also exhibits this unusual glass transition at 123-126° prior to melting at 141-143°. Similar observations have been made for many other Group 3-5^{2,18,19} and 3-6²⁰ compounds.

The aluminum-phosphorus dimers have been reported to react with Lewis bases to form adducts, $\text{PPh}_2\text{AlR}_2 \cdot \text{Base}$. The compound, $\text{PPh}_2\text{AlEt}_2 \cdot \text{OEt}_2$, was first described by Issleib and Deyling.²¹ The compound was prepared by two different routes but the melting points of the two resulting solid products were slightly different, 148° and 151°. In a later paper Issleib and Krech²² reported $\text{PPh}_2\text{AlEt}_2 \cdot \text{OEt}_2$ as a solid with a melting point of 145-150°. This compound was characterized by analysis and curious cryoscopic molecular weight measurements in dioxane solution. Johnson, Larson and Dahl³ also reported $(\text{Et}_2\text{AlPPh}_2)_2$ (mp: 124-126°) and $\text{PPh}_2\text{AlEt}_2 \cdot \text{OEt}_2$ (mp: 148°). The formulation of the etherate was supported by cryoscopic molecular weight measurements and hydrolyzable ethane data but analysis for P and Al were consistent with the formula $\text{Et}_2\text{AlPPh}_2$, not the etherate. We have attempted to repeat the synthesis of $\text{PPh}_2\text{AlEt}_2 \cdot \text{OEt}_2$ but without success. All samples of $\text{Et}_2\text{AlPPh}_2$ combined with Et_2O produce a solid which melts in the temperature range reported for $\text{PPh}_2\text{AlEt}_2 \cdot \text{OEt}_2$. However, mass balance experiments and

^1H NMR spectra of products show conclusively that Et_2O does not react with $\text{Et}_2\text{AlPPh}_2$ to form an adduct. Our results suggest that the earlier workers^{3,21,22} were confused and misled by the unusual melting point behavior of $\text{Et}_2\text{AlPPh}_2$. The glass transition of $\text{Et}_2\text{AlPPh}_2$ at $123\text{-}126^\circ$ is the melting point previously reported³ for $\text{Et}_2\text{AlPPh}_2$, whereas the melting point of $\text{Et}_2\text{AlPPh}_2$ at $141\text{-}143^\circ$ is the melting point reported for the proposed ether adduct.^{3,21,22} Thus, neither $\text{Et}_2\text{AlPPh}_2$ nor $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$ form stable diethyl ether adducts.

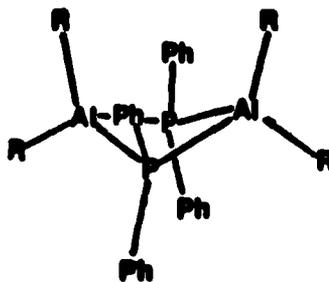
Our attempts to synthesize compounds²³ of the type $\text{Cr}(\text{CO})_5(\text{PPh}_2\text{AlR}_2)$ from $\text{KCr}(\text{CO})_5\text{PPh}_2 \cdot 2$ dioxane and AlR_2Br in tetrahydrofuran unexpectedly produced products containing a cleaved THF moiety, $\text{Cr}(\text{CO})_5[\text{PPh}_2\text{C}_4\text{H}_8\text{OAlR}_2]$. These results led us to question the claim that $\text{PPh}_2\text{AlEt}_2 \cdot \text{THF}$ can be prepared from LiPPh_2 and AlEt_2Br in THF. We have studied the reaction of $\text{Et}_2\text{AlPPh}_2$ with excess THF at room temperature. If the excess THF is removed after 18 h, a sticky white solid is isolated. Its ^1H NMR spectrum shows lines indicative of a cleaved THF moiety. Acid hydrolysis of the sticky white solid produces $\text{Ph}_2\text{PC}_4\text{H}_8\text{OH}$ and a small amount of PPh_2H . The former compound has been previously obtained after hydrolysis of the product from LiPPh_2 and THF.²⁴ The PPh_2H probably results from the hydrolysis of $[\text{Et}_2\text{AlPPh}_2]_2$ which did not react with THF rather than $\text{PPh}_2\text{AlEt}_2 \cdot \text{THF}$. The compounds $\text{Me}_2\text{AlPPh}_2$ and $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$ also cleave THF. The relative rates of cleavage of THF have been monitored by ^1H NMR experiments and have been found to increase in the order $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2 > \text{Me}_2\text{AlPPh}_2 > \text{Et}_2\text{AlPPh}_2$, with reaction ranging from one-half to essentially complete in 8 h. In all cases, the THF cleaved products $\text{R}_2\text{AlOC}_4\text{H}_8\text{PPh}_2$ exhibit several alkylaluminum ^1H NMR signals suggesting a mixture of variously associated oligomers.

Many organometallic main-group compounds²⁵ including various organoaluminum compounds¹² and alkali metal phosphides,^{24,25} cleave THF and other

ethers. In view of the generality of this reaction, it is surprising to note that there appears to be only one prior example involving a Group 3-5 compound as an ether cleaving reagent. The reaction mixture of B_2H_6 and $(CF_3)_2PH$ in dimethyl ether led to the formation of ether cleaved products at or below room temperature.²⁷ However, we believe that the THF cleavage reaction is probably more common in Group 3-5 chemistry than the literature suggests. The ether cleavage reaction appears to be very facile and the products are expected to have good thermodynamic stability.

The organoaluminum phosphides R_2AlPPh_2 ($R = Me, Et, CH_2SiMe_3$) are very reactive towards other common organic solvents as well as THF. Dichloromethane and chloroform solutions react to form grey precipitates after only 12 h at room temperature. Acetonitrile is reduced under equally mild conditions. Infrared spectra of the products from the reactions of all R_2AlPPh_2 with CH_3CN show strong absorbances around 1600 cm^{-1} attributable to the carbon-nitrogen double bond stretch. There are many examples of simple organoaluminum compounds such as $AlMe_3$ and $AlMe_2H$ reacting with CH_3CN to form dimeric aldimine derivatives $[RCH = NAlMe_2]_2$.²⁸ The reactions of Ar_2AlPPh_2 ($Ar = Ph, Me-C_6H_4$) with CH_3CN at or below room temperature have also been studied but adducts of the general formula $Ar_2AlPPh_2 \cdot NCCH_3$ were observed.²⁹

The 1H NMR spectra of $[R_2AlPPh_2]_2$ ($R = Me, Et, CH_2SiMe_3$) have been useful in revealing some details concerning the structures of these dimeric molecules in benzene solution. The data suggest that the four membered ring is nonplanar in solution with nonequivalent groups on aluminum and phosphorus.



The lines assigned to the hydrogens on the alkyl groups adjacent to aluminum are unexpectedly complex. The compound $[\text{Me}_2\text{AlPPh}_2]_2$ in benzene solution exhibits an apparently symmetrical quartet at 90 or 100 MHz at δ 0.08 for the aluminum-methyl group. However, closer inspection of these lines gives a separation between the lines of 2.2, 2.1 and 2.2 Hz. At 60 MHz, the quartet is less symmetrical with separations of 2.1, 2.6 and 2.3 Hz. These observations suggest that the methyl groups are not equivalent and that the quartet is due to the superposition of two ^{31}P - ^1H coupling patterns. Due to the fast relaxation of the ^{27}Al nucleus, spin-spin coupling is not usually observed.³⁰ The alkyl region of the ^1H NMR spectrum of $[(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2]_2$ shows a singlet for the silicon methyl groups and an unsymmetrical quartet for the methylene groups at 90 MHz. Expansion reveals a shoulder on the side of the line at lowest field. At 60 MHz, the signal due to the aluminum methylene groups simplifies to a fairly symmetrical triplet with a coupling constant of 2.6 Hz. The spectrum is independent of concentration in the range 0.102-0.361 m. At these concentrations virtually all $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$ should be in the form of dimers, with nonequivalent aluminum alkyl groups. The alkyl region of the spectrum of $[\text{Et}_2\text{AlPPh}_2]_2$ shows the expected splitting pattern for an ethyl group; a triplet at δ 1.31 for the methyl groups and a quartet at δ 0.80 for the methylene groups. The coupling constants are 7 Hz for both absorbances and are independent of spectrometer frequencies. However, further splitting of the methylene quartet is also observed. At all spectrometer frequencies, the methylene quartet lines are considerably broader than those due to the methyl groups. Expansion of the quartet does not reveal any details. The

phenyl resonances are not helpful in providing more information about any of the molecules. Two adjacent complex multiplets in the δ 7.7-7.1 region are observed. The complexity of these signals results from the overlap of the ^1H - ^{31}P and ^1H - ^1H coupling patterns for the ortho, meta and para ring hydrogens. The splitting of the lines for hydrogens on carbon adjacent to aluminum in the dimers may be explained by the existence of nonplanar, four-membered aluminum-phosphorus rings. A nonplanar dimer has been observed for the solid state structures of $[\text{I}_2\text{BPPH}_2]_2$ ³¹ and $[\text{Me}_2\text{AlN}(\text{iPr})\text{H}]_2$.³² The alkyl groups on aluminum are not equivalent and the hydrogens on the α -carbon atoms would be split by two equivalent phosphorus atoms giving rise to a triplet for each of the two types of alkyl groups. Long range ^{31}P - ^1H coupling is observed in other systems³³ but it has not been reported previously for other organoaluminum phosphides mainly because the NMR spectra have not been observed. The proposed structure is also consistent with the proton decoupled ^{31}P MMR spectrum of $[\text{Et}_2\text{AlPPh}_2]_2$, which consist of a single absorption at δ 42.3 (downfield from H_3PO_4) for two equivalent phosphorus atoms.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The new amphoteric ligand, $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$, has been prepared from the reactions of either $\text{Al}(\text{CH}_2\text{SiMe}_3)_3$ or $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ with PPh_2H or $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ with KPPH_2 and fully characterized by analysis, cryoscopic molecular weight measurements, IR and ^1H NMR data. This aluminum-phosphide is unique as it exists as a monomer-dimer equilibrium mixture in benzene solution. The syntheses and characterization of the new compounds $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{H}$ and $\text{Al}(\text{CH}_2\text{SiMe}_3)_2\text{Br}$ are also described. Since the chemistry of		

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of aluminum-phosphides as amphoteric ligands is of interest, the behavior of $(\text{Me}_3\text{SiCH}_2)_2\text{AlPPh}_2$, $(\text{Me}_2\text{AlPPh}_2)_2$ and $(\text{Et}_2\text{AlPPh}_2)_2$ toward common solvents, Et_2O , THF and CH_3CN , was investigated. The aluminum phosphides readily cleave THF and reduce the triple bond of CH_3CN at room temperature. However, neither THF nor Et_2O form isolable adducts with aluminum phosphides. The unusual melting point behavior of aluminum phosphides is also discussed.