84849-59-2; 1,2-diaminohexane, 13880-27-8; *cis*-1,2-diamino-1-methylcyclopentane, 84849-60-5; *trans*-1,2-diamino-1-methylcyclopentane, 84849-61-6; *cis*-1,2-diaminocyclohexane, 1436-59-5; *trans*-1,2-diaminocyclohexane, 1121-22-8; *d,l*-1,2-diamino-1-phenylpropane, 84849-62-7; *meso*-1,2-diamino-1-phenylpropane, 74745-66-7; (*Z*)-3,4-dideuterio-3-hexene, 76596-51-5; 2-methyl-1-phenyl-1-propene, 768-49-0; (*E*)-3-hexene, 13269-52-8; (*Z*)-3-hexene, 7642-09-3; 1-methylcyclopentene, 693-89-0; 1-phenyl-1-propene, 873-66-5; 2,3-dimethyl-2-butene, 563-79-1; 2-methyl-2-butene, 513-35-9; isobutylene, 115-11-7; (*E*)-2-butene, 624-64-6; (*Z*)-2-butene, 590-18-1; cyclopentene, 142-29-0; norbornadiene, 121-46-0; triphenylphosphine oxide, 791-28-6; hydroxylamine hydrochloride, 5470-11-1; 1-hexene, 592-41-6; cyclohexene, 110-83-8.

Synthesis and Characterization of Organoaluminum Compounds Containing the (Trimethylsilyl)methyl Substituent, $Al(CH_2SiMe_3)_2Br$, $Al(CH_2SiMe_3)_2H$, and $(Me_3SiCH_2)_2AlPPh_2$, and a Reinvestigation of the Chemistry of Me_2AlPPh_2 and Et_2AlPPh_2

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Received November 9, 1982

The new amphoteric ligand $(Me_3SiCH_2)_2AlPPh_2$ has been prepared from the reactions of either $Al(CH_2SiMe_3)_3$ or $Al(CH_2SiMe_3)_2H$ with PPh_2H or $Al(CH_2SiMe_3)_2Br$ with $KPPh_2$ and fully characterized by analysis, cryoscopic molecular weight measurements, and 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 $Al(CH_2SiMe_3)_2H$ and $Al(CH_2SiMe_3)_2Br$ are also described. Since the chemistry of aluminum phosphides as amphoteric ligands is of interest, the behavior of $(Me_3SiCH_2)_2AlPPh_2$, $(Me_2AlPPh_2)_2$, and $(Et_2AlPPh_2)_2$ 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.

Introduction

The synthesis and characterization of $Cr(CO)_5[PPh_2Al(CH_2SiMe_3)_2\cdot NMe_3]$[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] ethyl,[3] and aryl[4] 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 $Ph_2PAlR_2\cdot$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 Me_2AlPPh_2 and Et_2AlPPh_2. The results of our initial attempts to synthesize $M(CO)_5PPh_2AlR_2$ compounds defined the need for a more soluble organoaluminum diphenylphosphide. Our previous experience[5,6] had indicated that the (trimethylsilyl)methyl ligand enhanced the solubility of its compounds in hydrocarbon solvents. Thus, we prepared $(Me_3SiCH_2)_2AlPPh_2$ from $Al(CH_2SiMe_3)_3$, $Al(CH_2SiMe_3)_2Br$, and $Al(CH_2SiMe_3)_2H$ in order to define the best and most useful route. Our new convenient synthesis of $Al(CH_2SiMe_3)_3$ has been reported.[7] From this parent compound, the preparations of $Al(CH_2SiMe_3)_2Br$ and $Al(CH_2SiMe_3)_2H$ have been accomplished. In this paper we also report the properties of the adducts of R_3AlPPh_2H (R = Me, Et, CH_2SiMe_3) and the chemistry of organoaluminum diphenylphosphides toward ethers (THF and Et_2O) and CH_3CN.

Experimental Section

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 compound[1] (mol). Attempts to analyze for aluminum via an EDTA titration[2] 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

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$Al(CH_2SiMe_3)_3$[7] and PPh_2H[9] were synthesized by literature procedures. The liquids $AlEt_3$ (0.835 g/mL)[10] and $Al(CH_2SiMe_3)_3$ (0.802 g/mL)[7] were measured by volume with use of graduated gas-tight syringes in the drybox. The liquid PPh_2H (1.07 g/mL)[11] was similarly handled by using Schlenk techniques. ^1H NMR spectra are reported in δ units (ppm) and are referenced to Me_4Si as δ 0.00 and C_6H_6 as δ 7.27. Assignments are based on integration of spectra, where possible.

Synthesis of $Al(CH_2SiMe_3)_2Br$. The compound $Al(CH_2SiMe_3)_2Br$ was synthesized by an exchange reaction between 1 mol of $AlBr_3$ and 2 mol of $Al(CH_2SiMe_3)_3$. In the drybox, 1.75 mL (1.40 g, 4.87 mmol) of $Al(CH_2SiMe_3)_3$ and 0.650 g (2.43 mmol) of $AlBr_3$ were combined in a 10-mL flask. Heat was evolved, and a colorless liquid was produced. The flask was attached to a microscale distillation apparatus and $Al(CH_2SiMe_3)_2Br$ (1.926 g, 94%) distilled as a colorless liquid at 60–62 °C (0.01 mm): density, 1.06 g/mL at 22 °C; ^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), 698 (m), 668 (m), 636 (vs), 577 (s), 315 (w); cryoscopic molecular weight; formula weight $Al(CH_2SiMe_3)_2Br$, 281.27. Molality, obsd 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. Anal. Calcd: 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. $Al(CH_2SiMe_3)_2Br$ 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 drybox and the flask containing the sample had to be evacuated at −196 °C to avoid loss of voltile Me_4Si and HBr that formed even with these precautions.

Synthesis of $Al(CH_2SiMe_3)_2H$. The reagents $Al(CH_2SiMe_3)_3$ (2.5 mL, 2.0 g, 6.9 mmol) and 0.3 g (7.9 mmol) of $LiAlH_4$ (recrystallized from Et_2O) were heated at 90 °C for 18 h under vacuum. The reaction mixture solidified on cooling to room temperature. The product $Al(CH_2SiMe_3)_2H$ (1.29 g, 92%) sublimed at 40–70 °C under high vacuum as a crystalline solid, mp 35–36 °C. Alternatively, $Al(CH_2SiMe_3)_2H$ was isolated from the reaction mixture by extracting with hexane, concentrating the solution, and cooling to 0 or −20 °C: mp 38–40 °C; ^1H NMR (benzene, δ) 0.33 (s, 9, CH_3), −0.25 (s, 2, CH_2); IR (Nujol mull, cm^{-1}) 1765 (vs, vb, AlH), 1257 (vs), 970 (vs, b), 854 (vs), 838 (vs), 765 (vs), 733 (s), 702 (m), 661 (w), 575 (m); cryoscopic molecular weight; formula weight $Al(CH_2SiMe_3)_2H$, 202.35. Molality, obsd 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. Anal. Calcd: 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. The analysis suggests a 5–9% impurity of $Al(CH_2SiMe_3)_3$ that could not be removed due to the similarities of its solubility and volatility with $Al(CH_2SiMe_3)_2H$.

Synthesis of R_3AlPPh_2H (R = Me, Et, or CH_2SiMe_3). Adducts of formula $R_3Al{\cdot}PPh_2H$ (R = Me, Et, or Me_3SiCH_2) were obtained by combining equimolar quantities of the trialkylaluminum compound and Ph_2PH (see preparations of R_2AlPPh_2). All three adducts were colorless liquids at room temperature. ^1H NMR: $Me_3Al{\cdot}PPh_2H$ (toluene-d_8, δ); 7.46 (m, Ph), 7.20 (m, Ph), 5.53 (d, J = 299 Hz, 1, PH), −0.08 (s, 9, CH_3); $Et_3Al{\cdot}PPh_2H$ (benzene-d_6 δ); 7.45 (m, Ph), 7.18 (m, Ph), 5.55 (d, J = 295 Hz, 1, PH), 1.51 (t, J = 8 Hz, 9, CH_3), 0.53 (q, J = 8 Hz, 6, CH_2); $(Me_3SiCH_2)_3Al{\cdot}PPh_2H$ (benzene-d_6, δ), 7.55 (m, Ph), 7.24 (m, Ph), 5.62 (d, J = 300 Hz, 1, PH), 0.30 (s, 27, CH_3), −0.40 (s, 6, CH_2).

Synthesis of $(Me_3SiCH_2)_2AlPPh_2$. (a) From Ph_2PH and $Al(CH_2SiMe_3)_3$. As in the preparation of Et_2AlPPh_2, a break-seal tube containing 1.00 mL (1.07 g, 5.74 mmol) of Ph_2PH and 2.09 mL (1.68 g, 5.82 mmol) of $Al(CH_2SiMe_3)_3$ was prepared. The tube was evacuated, sealed at −196 °C, and then heated at 160–180 °C for about 18 h. The progress of the reaction was followed by periodically cooling the tube to room temperature. At room temperature, $(Me_3SiCH_2)_2AlPPh_2$ is a solid and can be distinguished from the liquid adduct. The tube was opened under vacuum. Tetramethylsilane (5.45 mol, 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 °C to remove unreacted adduct. The compound $(Me_3SiCH_2)_2AlPPh_2$ (1.63 g, 73.4%) was obtained as a white solid: mp 120–121 °C a glass forms that melts at 136–139 °C; cooling this sample to room temperature gives crystals that when slowly heated melt at 141–143 °C; ^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 $(Me_3SiCH_2)_2AlPPh_2$; 386.54. Molality, obsd mol wt, association: 0.0549, 665, 1.72; 0.0446, 638, 1.65; 0.0210, 545, 1.41.

(b) From $Al(CH_2SiMe_3)_2H$ and Ph_2PH. A sample of $Al(CH_2SiMe_3)_2H$ (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) of 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 °C, and a white solid formed. The flask was heated at 70–80 °C 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 of hexane at −20 °C; mp 146–147 °C. Anal. Calcd: Me_4Si, 2.00 mol/mol. Found: Me_4Si, 2.02 mol/mol. Infrared and ^1H NMR spectra were identical with those obtained from the previous reaction.

(c) From $Al(CH_2SiMe_3)_2Br$ and $KPPh_2$. 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) of Ph_2PH in 10 mL of diethyl ether. An orange solid, $KPPh_2$, was precipitated, and hydrogen was evolved in 95% yield in less than 12 h. A solution of 0.97 mL (1.0 g, 3.7 mmol) of $Al(CH_2SiMe_3)_2Br$ in 3 mL of diethyl ether, contained in a built-in addition tube of the reaction vessel, was added to the stirred $KPPh_2$ suspension. The orange solid disappeared immediately, and a white precipitate was formed. After being stirred for 0.5 h, the solution was filtered from the KBr by using a medium frit. Diethyl ether was removed by vacuum distillation, and the remaining white solid was recrystallized from pentane. The compound $(Me_3SiCH_2)_2AlPPh_2$ was obtained in 71% yield; glass forms at 115 °C that melts completely by 138 °C. The ^1H NMR spectrum of the product in benzene-d_6 indicated $(Me_3SiCH_2)_2AlPPh_2$ and the presence of a small impurity of $Br(Me_3SiCH_2)_2AlPPh_2H$.

Syntheses of Me_2AlPPh_2. (a) From PPh_2H and $AlMe_3$. The compound $AlMe_3$ (1.0117 g, 14.03 mmol) was distilled into a trap on the vacuum line. Then Ph_2PH (2.34 mL, 2.50 g, 13.4 mmol) was syringed into an argon-filled break-seal tube. The preweighed $AlMe_3$ was vacuum distilled into the tube, and the tube was sealed at −196 °C. When the tube was warmed to room temperature, an exothermic reaction took place. The clear liquid adduct was heated for 16 h at 160 °C, producing a white solid and 13.4 mmol of methane gas. The tube was opened under vacuum by 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 Me_2AlPPh_2 (2.812 g, 86%) as a white powder; mp 200–206 °C a glass forms, 211–222 °C the glass melts (lit.[2] mp 230 °C sublimed); ^1H NMR (toluene-d_8, δ) 7.50 (m, Ph), 7.16 (m, Ph), 0.08 (q, J = 2 Hz, $AlCH_3$) (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 and insoluble in hexane and diethyl ether. Anal. Calcd: MeH, 2.00 mol/mol. Found: MeH, 1.99 mol/mol. The compound Me_2AlPPh_2 reacts with halogenated hydrocarbons, THF, and CH_3CN (vide infra), solvents in which it has only slight solubility. The attempted sublimation

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of a 1.79-g sample at 160 °C for 12 h under high vacuum produced 0.0347 g (2%) of sublimed Me_2AlPPh_2 (mp 228 °C).

(b) From Ph_2PH and $AlMe_3$ in Toluene. As in the previous preparation, break-seal tube containing 0.8315 g (11.53 mmol) of $AlMe_3$ and 1.54 mL (1.65 g, 8.88 mmol) of 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 °C 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 Me_2AlPPh_2 (1.40 g, 62%) was obtained as a while solid that melted at 228 °C. 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 two-neck flask containing 0.83 mL (0.88 g, 4.8 mmol) of 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 °C 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 °C 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%) of Me_2AlPPh_2, mp 210–212 °C glass forms, which is completely melted by 225 °C. 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 °C, was shown to contain Ph_2PH by its infrared spectra.

Synthesis of Et_2AlPPh_2. The reagent Ph_2PH (2.25 mL, 2.41 g, 12.9 mmol) was syringed into an argon-filled break-seal tube. In the drybox, 1.79 mL (1.49 g, 13.0 mmol) of $AlEt_3$ 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 °C and then heated at 90 °C 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 of 1:1 toluene/hexane, yielding Et_2AlPPh_2 (2.374 g, 68%) as a white powder, mp 123–126 °C glass forms, 141–143 °C glass melts (lit.[3] mp 124–126 °C from benzene). In other preparations, the sticky white solid was washed with hexane, leaving a solid which melted at 140–143 °C. Identical spectral and analytical data were obtained for both products: ^1H NMR (toluene-d_8, 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 (toluene-d_8, 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, and soluble in and reacts with halogenated hydrocarbons, THF, and CH_3CN (vide infra). Anal. Calcd: EtH, 2.00 mol/mol. Found: EtH, 2.02 mol/mol.

Attempted Syntheses of $Et_2AlPPh_2 \cdot OEt_2$. A 0.3180-g (1.177-mmol) sample of Et_2AlPPh_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 Et_2AlPPh_2 dissolved and then cooled to −78 °C 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 that identified the presence of only Et_2AlPPh_2. The sample melted at 143–146 °C (lit. $Et_2AlPPh_2 \cdot OEt_2$, mp 148 °C).

Another sample of Et_2AlPPh_2 was recrystallized in Et_2O. The crystals were subjected to high vacuum at −78 °C until they appeared dry. A ^1H NMR spectrum of these crystals showed that no ether was retained. The crystals melted at 143–145 °C.

Reaction of Et_2AlPPh_2 with THF. A sample of Et_2AlPPh_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 °C, 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 3 days, and its infrared spectrum was recorded. $Ph_2PC_4H_8OH$ 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. Me_2AlPPh_2 plus CH_3CN: mp 80 °C red color, 138–140 °C sample melts to a red liquid; IR (cm^{-1}) $\nu_{C=N}$ 1601 (s). Et_2AlPPh_2 plus CH_3CN: mp 125 °C glass forms, 137 °C sample melts to a yellow liquid; IR (cm^{-1}) $\nu_{C=N}$ 1613 (s). $(Me_3SiCH_2)_2AlPPh_2$ plus CH_3CN: mp 160–165 °C to a yellow liquid; IR (cm^{-1}) $\nu_{C\equiv N}$ 2186 (m), $\nu_{C=N}$ 1601 (s).

Results and Discussion

Standard reactions have been used for the preparation of $Al(CH_2SiMe_3)_2Br$ and $Al(CH_2SiMe_3)_2H$ from the trialkylaluminum compound. The compound $Al(CH_2SiMe_3)_2Br$ was prepared in 94% yield by an exchange reaction between $Al(CH_2SiMe_3)_3$ and $AlBr_3$ in the absence of solvent (eq 1). Exchange is exothermic and apparently

$$2Al(CH_2SiMe_3)_3 + AlBr_3 \rightarrow 3Al(CH_2SiMe_3)_2Br \quad (1)$$

occurs at room temperature. Formulation of $Al(CH_2SiMe_3)_2Br$ as a discrete compound rather than as a mixture of $Al(CH_2SiMe_3)_3$ and $AlBr_3$ is supported by the fact that $Al(CH_2SiMe_3)_2Br$ has a 2-deg boiling range about 10 deg higher than $Al(CH_2SiMe_3)_3$ under high vacuum. The compound $Al(CH_2SiMe_3)_2Br$ exists as a mixture of monomeric and dimeric species in benzene solution in contrast to the dimeric association observed in hydrocarbon solutions of other organoluminum halides,[12] $In(CH_2SiMe_3)_2Cl$[6] and $Ga(CH_2SiMe_3)_2Br$.[5] The lower association of $Al(CH_2SiMe_3)_2Br$ in comparison to these compounds can be attributed to a combination of the large steric size of the (trimethylsilyl)methyl substituents and the smaller size of the aluminum atom. The analogous chloro-substituted compound, $Al(CH_2SiMe_3)_2Cl$, was prepared from the reaction of 1 mol of $AlCl_3$ with 2 mol of $Al(CH_2SiMe_3)_3$.[13] The solution molecular weight of $Al(CH_2SiMe_3)_2Cl$ was not reported, but mass spectral data showed a fragmentation pattern consistent with a monomeric species in the gas phase.

The synthesis of $Al(CH_2SiMe_3)_2H$ has been achieved by the reaction of $Al(CH_2SiMe_3)_3$ with an excess of $LiAlH_4$ at 90 °C (eq 2). This type of reaction has also been used

$$Al(CH_2SiMe_3)_3 + LiAlH_4 \xrightarrow{90\ °C} Al(CH_2SiMe_3)_2H + LiAl(CH_2SiMe_3)H_3 \quad (2)$$

to prepared $AlMe_2H$.[8] The compound $Al(CH_2SiMe_3)_2H$

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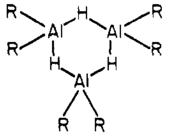
can be easily isolated in about 90% yield by sublimation or crystallization from hexane. However analysis of $Al(CH_2SiMe_3)_2H$ indicates the presence of a 5–9% impurity of $Al(CH_2SiMe_3)_3$, which cannot be removed by repeated sublimations or crystallizations due to similarities of volatility and solubility properties of $Al(CH_2SiMe_3)_2H$ and $Al(CH_2SiMe_3)_3$. This situation was not improved by altering the reaction conditions. Under the preparative reaction conditions, $Al(CH_2SiMe_3)_3$ 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 $Al(CH_2SiMe_3)_3$ 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 $LiAlH_4$ was also ineffective in reducing the amount of the impurity.

The compound $Al(CH_2SiMe_3)_2H$ 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 isobutyl, exist as viscous oils or as liquids.[12] Cryoscopic molecular weight data indicate that $Al(CH_2SiMe_3)_2H$ is trimeric in benzene solution. A puckered six-membered ring composed of alternating dialkylaluminum groups and hydrogen atoms has been proposed for the structure of other trimeric AlR_2H compounds (R = Me, Et, *i*-Bu).[12] The infrared spectrum of $Al(CH_2SiMe_3)_2H$ shows a very broad and intense hand centered at 1765 cm^{-1} that can be attributed to the aluminum–hydrogen stretching frequency. Similarly broad and intense bands in the range of 1785–1775 cm^{-1} have been observed in the infrared spectra of other dialkylaluminum hydrides.[14]



The main route by which the compounds R_2AlPPh_2 (R = 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 $R_3Al{\cdot}PPh_2H$ 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}P–^1H 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 (δ 5.7–5.5). The solvent dependency of the chemical shift makes it a less useful probe of complexation than the ^{31}P–^1H 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}P–^1H 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 R_3AlPPh_2H in aromatic solvents show a substantial increase in the ^{31}P–^1H 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 $(Me_3SiCH_2)_2AlPPh_2$ has been prepared from appropriate reagents by the elimination of $SiMe_4$ at 160–180 °C (eq 3), hydrogen at 70–80 °C (eq 4), and KBr (eq 5) at room temperature.

$$\mathrm{Al(CH_2SiMe_3)_3 + Ph_2PH \xrightarrow{160\text{–}180\ ^\circ C} (Me_3SiCH_2)_2AlPPh_2 + SiMe_4} \qquad (3)$$

$$\mathrm{Al(CH_2SiMe_3)_2H + Ph_2PH \xrightarrow{70\text{–}80\ ^\circ C} (Me_3SiCH_2)_2AlPPh_2 + H_2} \qquad (4)$$

$$\mathrm{Al(CH_2SiMe_3)_2Br + KPPh_2 \xrightarrow{Et_2O} (Me_3SiCH_2)_2AlPPh_2 + KBr} \qquad (5)$$

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 $(Me_3SiCH_2)_2AlPPh_2$, a colorless solid, is isolated in 78% yield, even though $SiMe_4$ is formed in 95% yield. If reaction temperatures higher than 160–180 °C, i.e., 180–200 °C, are used for the preparative reaction, reaction is considerably faster. However, products indicative of the decomposition of the (trimethylsilyl)methyl ligand, H_2, and a solid product with a gray color are formed. The compound[7] $KAl(CH_2SiMe_3)_3H$ also decomposes around 200 °C.

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 °C and this glass melts at 136–139 °C. If this sample is then permitted to cool slowly to room temperature, crystals form that upon reheating melt at 141–143 °C and 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 °C.

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 °C, whereas others form a glass at temperatures around 200 °C and then melt at higher

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temperatures, within the range of 210–225 °C. 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 Et_2AlPPh_2 also exhibits this unusual glass transition at 123–126 °C prior to melting at 141–143 °C. Similar observations have been made for many other group 3–5[2,18,19] and 3–6[20] compounds.

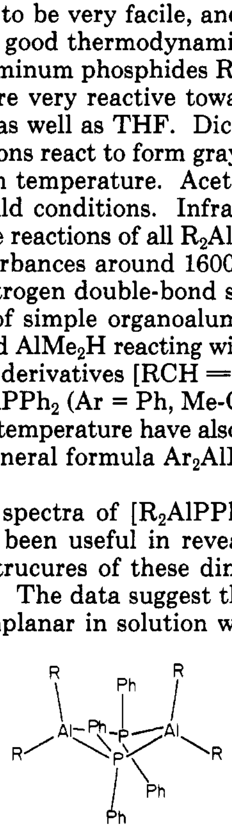
The aluminum–phosphorus dimers have been reported to react with Lewis bases to form adducts PPh_2AlR_2·base. The compound $PPh_2AlEt_2·OEt_2$ was first described by Issleib and Deyling.[21] The compound was prepared by two different routes, but the melting points of the two resulting solid products were slightly different, 148 and 151 °C. In a later paper Issleib and Krech[22] reported $PPh_2AlEt_2·OEt_2$ as a solid with a melting point of 145–150 °C. This compound was characterized by analysis and curious cryoscopic molecular weight measurements in dioxane solution. Johnson, Larson, and Dahl[3] also reported $(Et_2AlPPh_2)_2$ (mp 124–126 °C) and $PPh_2AlEt_2·OEt_2$ (mp 148 °C). The formulation of the etherate was supported by cryoscopic molecular weight measurements and hydrolyzable ethane data, but analyses for P and Al were consistent with the formula Et_2AlPPh_2, not the etherate. We have attempted to repeat the synthesis of $PPh_2AlEt_2·OEt_2$ but without success. All samples of Et_2AlPPh_2 combined with Et_2O produce a solid that melts in the temperature range reported for $PPh_2AlEt_2·OEt_2$. However, mass balance experiments and ^1H NMR spectra of products show conclusively that Et_2O does not react with Et_2AlPPh_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 Et_2AlPPh_2. The glass transition of Et_2AlPPh_2 at 123–126 °C is the melting point previously reported[3] for Et_2AlPPh_2, whereas the melting point of Et_2AlPPh_2 at 141–143 °C is the melting point reported for the proposed ether adduct.[3,21,22] Thus, neither Et_2AlPPh_2 nor $(Me_3SiCH_2)_2AlPPh_2$ forms stable diethyl ether adducts.

Our attempts to synthesize compounds[23] of the type $Cr(CO)_5(PPh_2AlR_2)$ from $KCr(CO)_5PPh_2·2$ dioxane and AlR_2Br in tetrahydrofuran unexpectedly produced products containing a cleaved THF moiety, $Cr(CO)_5[PPh_2C_4H_8OAlR_2]$. These results led us to question the claim that $PPh_2AlEt_2·THF$ can be prepared from $LiPPh_2$ and $AlEt_2Br$ in THF. We have studied the reaction of Et_2AlPPh_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 $Ph_2PC_4H_8OH$ 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 $[Et_2AlPPh_2]_2$, which did not react with THF rather than $PPh_2AlEt_2·THF$. The compounds Me_2AlPPh_2 and $(Me_3SiCH_2)_2AlPPh_2$ also cleave THF. The relative rates of cleavage of THF have been monitored by ^1H NMR experiments and have been found to decrease in the order $(Me_3SiCH_2)_2AlPPh_2 > Me_2AlPPh_2 > Et_2AlPPh_2$, with reaction ranging from half complete to essentially complete in 8 h. In all cases, the THF-cleaved products $R_2AlOC_4H_8PPh_2$ exhibit several alkylaluminum ^1H NMR signals suggesting a mixture of variously associated oligomers.

Many organometallic main-group compounds[25] including various organoaluminum compounds[12] 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 belive 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 toward other common organic solvents as well as THF. Dichloromethane and chloroform solutions react to form gray 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 $Ar_2AlPPh_2·NCCH_3$ 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 strucures 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 $[Me_2AlPPh_2]_2$ 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



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that the methyl groups are not equivalent and that the quartet is due to the superposition of two ^{31}P–^{1}H 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 ^{1}H NMR spectrum of $[(Me_3SiCH_2)_2AlPPh_2]_2$ 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 $(Me_3SiCH_2)_2AlPPh_2$ should be in the form of dimers, with nonequivalent aluminum alkyl groups. The alkyl region of the spectrum of $[Et_2AlPPh_2]_2$ 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 ^{1}H–^{31}P and ^{1}H–^{1}H 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 $[I_2BPPh_2]_2$[31] and $[Me_2AlN(i\text{-}Pr)H]_2$.[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–^{1}H coupling is observed in other systems[33] 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 NMR spectrum of $[Et_2AlPPh_2]_2$, which consist of a single absorption at δ 42.3 (downfield from H_3PO_4) for two equivalent phosphorus atoms.

Acknowledgment. This work was supported in part by the Office of Naval Research.

Registry No. $Al(CH_2SiMe_3)_2Br$, 85004-93-9; $Al(CH_2SiMe_3)_2H$, 85004-94-0; Me_3AlPPh_2H, 85004-96-2; Et_3AlPPh_2H, 85004-97-3; $(Me_3SiCH_2)_3AlPPh_2H$, 85004-98-4; $(Me_3SiCH_2)_2AlPPh_2$, 84537-82-6; Me_2AlPPh_2, 85004-95-1; Et_2AlPPh_2, 1024-73-3; THF, 109-99-9; CH_3CN, 75-05-8.

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Synthesis of Diynes, α,β-Unsaturated Monoacids, and Diacids by the Selective Palladium(0)-Catalyzed and Phase Transfer Catalyzed Reactions of Vinylic Dibromides

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Received December 21, 1982

Three new, mild, and highly selective phase-transfer reactions are described. Vinylic dibromides derived from aromatic aldehydes react with carbon monoxide, zerovalent palladium compounds as the metal catalyst, and a phase-transfer agent in a two-phase system (C_6H_6, 5 N NaOH) to give diynes in reasonable yields. α,β-Unsaturated monacids were the major or only products formed by using vinylic dibromides, derived from aliphatic aldehydes or ketones, as reactants. Dicarbonylation of all classes of vinylic dibromides to diacids occurred by using *tert*-amyl alcohol as the organic phase. Mechanisms are proposed for these selective transformations.

Phase-transfer catalysis has proved to be a useful method for effecting a number of reactions catalyzed by palladium complexes. For example, palladium bromide is a good catalyst for the phase transfer catalyzed synthesis of diphenyl carbonate from phenol, carbon monoxide, and oxygen (eq 1).[2] Halide displacement by cyanide ion can occur by using palladium(0) and crown ether catalysts.[3] The synthesis of aryl and alkenyl sulfides by displacement of halide by the thiolate ion is catalyzed by organopalladium(II) compounds under two-phase conditions (eq 2). A phase-transfer agent is not required in the latter reaction, although its presence improves the product yield in selected cases.[4] Phase transfer catalyzed isomerization[5]

$$2PhOH + CO + 0.5O_2 \xrightarrow[\substack{(n\text{-}C_4H_9)_4NBr,\ Mn(acac)_2 \\ \text{molecular sieves}}]{PdBr_2,\ NaOH,\ CH_2Cl_2} Ph_2CO_3 + H_2O \quad (1)$$

$$PhBr + PhSH/30\%\ NaOH \xrightarrow[Ph_3P,\ PhCH_3]{Ph(PPh_3)_2PdBr} PhSPh \quad (2)$$

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