Reactivity of R_2AlH (R = Me, Bu^i) and Me_3M (M = Al, Ga, In) toward the Silylphosphines $P(SiMe_3)_3$ and $HP(SiMe_3)_2$

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The reactivities of Me_2AlH with $P(SiMe_3)_3$ and of Me_3M (M = Al, Ga, In) and $Bu^i{}_2AlH$ with $P(SiMe_3)_3$ and $HP(SiMe_3)_2$ were monitored with multinuclear NMR to determine the trend for adduct formation and establish the role that the Me and Bu^i moieties and M play in influencing the nature of the possible 1,2-elimination product. 1:1 adducts were obtained in the $Me_3M/P(SiMe_3)_3$ systems with no tendency toward room-temperature, 1,2-elimination reactivity. Thermolysis at 100 °C gave the following order of reactivity for $SiMe_4$ elimination: $Me_3In{\cdot}P(SiMe_3)_3 > Me_3Ga{\cdot}P(SiMe_3)_3 >> Me_3Al{\cdot}P(SiMe_3)_3$. With the $Me_3M/HP(SiMe_3)_2$ systems, only Me_3Al gave an isolable adduct, which eliminated CH_4 upon heating to form $[Me_2AlP(SiMe_3)_2]_2$. Although NMR spectral data indicated adduct formation in the Me_3Ga and Me_3In systems, these underwent CH_4 elimination to yield the respective $[Me_2MP(SiMe_3)_2]_2$ species. The variable-temperature, multinuclear NMR study of the $Me_2AlH/P(SiMe_3)_3$ system indicated adduct formation at −90 °C and subsequent conversion to cyclic oligomeric $[Me_2AlP(SiMe_3)_2]_n[Me_2AlH]_m$ species at −80 °C that ultimately produced $[Me_2AlP(SiMe_3)_2]_2$. The reactivity of $Bu^i{}_2AlH$ toward $P(SiMe_3)_3$ and $HP(SiMe_3)_2$ is much slower then that of Me_2AlH. In the $Bu^i{}_2AlH/HP(SiMe_3)_2$ system, H_2 elimination is favored and $[Bu^i{}_2AlP(SiMe_3)_2]_2$ and $Bu^i{}_2AlP(SiMe_2)_2{\cdot}Bu^i{}_2AlP(H)SiMe_3$ are formed. An X-ray structure analysis of $[Bu^i{}_2AlP(SiMe_3)_2]_2$ establishes the planarity of the $(AlP)_2$ core.

Introduction

There has been an increasing interest in silylated phosphines for use in the synthesis of single source group 13−phosphide precursors for material science applications.[1−3] $P(SiMe_3)_3$ has been used to synthesize a wide variety of organo Al,[4−6] Ga,[7−14] and In[9,15−23] silylphosphine derivatives via adduct formation and 1,2-elimination reactions. For example, Et_2AlCl,[4] $AlCl_3$,[6] Ph_3Ga,[8] $(Me_3CH_2)_2GaCl$,[14] and Me_3In[15] form isolable adducts with $P(SiMe_3)_3$. Thermolysis of $Me_2GaCl/P(SiMe_3)_3$,[13] sonication of $GaCl_3/P(SiMe_3)_3$,[12] and stirring of $(Me_3CCH_2)_2GaCl/P(SiMe_3)_3$[14] mixtures produce $[Me_2GaP(SiMe_3)_2]_2$, $[Cl_2GaP(SiMe_3)_2]_2$, and $[(Me_3CCH_2)(Cl)GaP(SiMe_3)_2]_2$, respectively, via a 1,2-elimination or dehalosilylation process. Thermolysis of the $Me_3In/P(SiMe_3)_3$ adduct results in Me_4Si elimination and formation of $[Me_2InP(SiMe_3)_2]_2$.[15] With Al−H bond-containing systems, i.e. Cl_2AlH and Me_2AlH, Et_2PSiMe_3 readily undergoes $HSiMe_3$ elimination to form $[Cl_2AlPEt_2]_3$ and $[Me_2AlPEt_2]_2$, respectively.[24] However, in the reaction of $Bu^i{}_2AlH$ with H_2PSiPh_3 the 1,2-elimination of H_2 produces $[Bu^i{}_2AlP(H)SiPh_3]_2$.[25] Thus, both P−Si and P−H bonds can be involved in 1,2-elimination reactions in $H_xP(SiR_3)_{3-x}$ systems, depending upon the nature of the group 13 species.

Recently we reported the reactivity of Me_2AlH with $HP(SiMe_3)_2$,[26] wherein the preferred mode of reactivity is $HSiMe_3$—as opposed to H_2—elimination. Transpho-

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(1) Buhro, W. E. *Polyhedron* **1994**, *13*, 1131.
(2) Fritz, G. *Comments Inorg. Chem.* **1982**, *1*, 329.
(3) David, L. D. U.S. Patent 4 798 701, 1989; *Chem. Abst.* **1989**, *110*, 714.
(4) Wells, R. L.; McPhail, A. T.; Self, M. F.; Laske, J. A. *Organometallics* **1993**, *12*, 3333.
(5) Rösch, L.; Schmidt-Fritsche, W. *Z. Anorg. Allg. Chem.* **1976**, *426*, 99.
(6) Wells, R. L.; McPhail, A. T.; Laske, J. A., White, P. S. *Polyhedron* **1994**, *13*, 2737.
(7) Dillingham, M. D. B.; Burns, J. A.; Byers-Hill, J.; Gripper, K. D.; Pennington, W. T.; Robinson, G. H. *Inorg. Chim. Acta* **1994**, *216*, 267.
(8) Wells, R. L.; Aubuchon, S. R.; Self, M. F.; Jasinski, J. P.; Woudenberg, R. C.; Butcher, R. J. *Organometallics* **1992**, *11*, 3370.
(9) Wells, R. L.; Baldwin, R. A.; White, P. S. *Organometallics* **1995**, *14*, 2123.
(10) Burns, J. A.; Pennington, W. T.; Robinson, G. H. *Organometallics* **1995**, *14*, 1533.
(11) Aubuchon, S. R.; McPhail, A. T.; Wells, R. L.; Giambra, J. A.; Bowser, J. R. *Chem. Mater.* **1994**, *6*, 82.
(12) Wells, R. L.; Self, M. F.; McPhail, A. T.; Aubuchon, S. R.; Woudenberg, R. C.; Jasinski, J. P. *Organometallics* **1993**, *12*, 2832.
(13) Wiedmann, D.; Hausen, H.-D.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1351.
(14) Wells, R. L.; Baldwin, R. A.; White, P. S.; Pennington, W. T.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 91.
(15) Stuczynski, S. M.; Opila, R. L.; Marsh, P.; Brennan, J. G.; Steigerwald, M. L. *Chem. Mater.* **1991**, *3*, 379.
(16) Self, M. F.; McPhail, A. T.; Jones, L. J. III; Wells, R. L. *Polyhedron* **1994**, *13*, 625.
(17) Wells, R. L.; McPhail, A. T.; Jones, L. J., III; Self, M. F. *J. Organomet. Chem.* **1993**, *449*, 85.
(18) Jones, L. J., III; McPhail, A. T.; Wells, R. L. *Organometallics* **1994**, *13*, 2504.
(19) Wells, R. L.; Aubuchon, S. R.; Kher, S. S.; Lube, M. S. *Chem. Mater.* **1995**, *7*, 793.
(20) Wells, R. L.; McPhail, A. T.; Self, M. F. *Organometallics* **1992**, *11*, 221.
(21) Wells, R. L.; McPhail, A. T.; Self, M. F. *Organometallics* **1993**, *12*, 3363.
(22) Healy, M. D.; Laibinis, P. E.; Stupik, P. D.; Barron, A. R. *J. Chem. Soc. Chem. Commun.* **1989**, 359.
(23) Douglas, T.; Theopold, K. H. *Inorg. Chem.* **1991**, *30*, 594.
(24) Fritz, G.; Emül, R. *Z. Anorg. Allg. Chem.* **1975**, *416*, 19.
(25) Cowley, A. H.; Jones, R. A.; Mardones, M. A.; Atwood, J. L.; Bott, S. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1409.
(26) Krannich, L. K.; Watkins, C. L.; Schauer, S. J. *Organometallics* **1995**, *14*, 3094.

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sphination with $HP(SiMe_3)_2$ produced several intermediate $Me_2AlP(SiMe_3)_2$-containing species with the major product being $[Me_2AlP(H)SiMe_3]_2 \cdot Me_2AlP(SiMe_3)_2$. In this paper, we report the extension of this study to the reactivities of Me_2AlH with $P(SiMe_3)_3$ and of Me_3M (M = Al, Ga, In) and Bu^i_2AlH with $P(SiMe_3)_3$ and $HP(SiMe_3)_2$ to note the tendency for adduct formation and the role that R and M play in influencing the nature of the 1,2-elimination product. Reactions of Me_2AlH and Bu^i_2AlH with $P(SiMe_3)_3$ and of Bu^i_2AlH with $HP(SiMe_3)_2$ were monitored by NMR to elucidate the reaction pathways to the stable products. All new isolable compounds were characterized using melting points, ^1H, ^{13}C, and ^{31}P NMR, IR, EI MS or cryoscopic molecular weight determinations, and elemental analyses. The X-ray structure of the dimeric phosphinoalane $[Bu^i_2AlP(SiMe_3)_2]_2$ was determined, and the structural data are compared with those of $[Me_2AlP(SiMe_3)_2]_2$[27] and $[Et_2AlP(SiMe_3)_2]_2$.[4]

Experimental Section

General Information. All reagents and products were handled using standard inert-atmosphere techniques. $P(SiMe_3)_3$ and $HP(SiMe_3)_2$ were purchased from Quantum Design, Inc., Austin, TX, and their purity was checked by ^1H, ^{13}C, and ^{31}P NMR. Me_2AlH and Me_3Ga were obtained as a gift from Morton Advanced Materials, Danvers, MA. Me_3Al (Ethyl Corp.), Bu^i_2AlH (Texas Alkyls), and Me_3In (Morton Advanced Materials) were used without further purification. Benzene-d_6 and toluene-d_8 (Aldrich) were stored over molecular sieves. $[Me_2AlP(SiMe_3)_2]_2$ was prepared by an alternate synthetic route as described below. $Me_3In \cdot P(SiMe_3)_3$ was prepared as previously reported.[15] ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a GE (Nicolet) 300 MHz multinuclear FT NMR operating at 300.1, 75.4, and 121.5 MHz, respectively. ^{31}P NMR spectra were externally referenced to H_3PO_4 with downfield shifts assigned to positive δ's. Low-resolution EI-MS data were recorded on a HP5986A GC/MS spectrometer operating at 70 eV with a 2400 V electron multiplier. IR data were recorded as Kel-F and Nujol mulls on KBr plates using a Nicolet IR/42 FT spectrophotometer. Carbon and hydrogen elemental analyses were obtained from E+R Microanalytical Laboratory, Inc., Corona, NY.

Synthesis of Adducts. $Me_3Al \cdot P(SiMe_3)_3$, $Me_3Ga \cdot P(SiMe_3)_3$, and $Me_3Al \cdot HP(SiMe_3)_2$ were synthesized by the following general procedure. Approximately 2.5 mmol of Me_3M and an equal amount of the respective phosphine were combined with 10 mL of hexane. The solution was stirred for 30 min, followed by removal of the solvent under vacuum. $Me_3Al \cdot P(SiMe_3)_3$, $Me_3Ga \cdot P(SiMe_3)_3$, and $Me_3Al \cdot HP(SiMe_3)_2$ were isolated as clear crystalline solids and purified by sublimation at 50 °C under vacuum, with yields of 94, 85, and 92%, respectively.

$Me_3Al \cdot P(SiMe_3)_3$. Mp: 215−217 °C. NMR (C_6D_6): ^1H δ 0.25 (d, J_{PH} = 4.87 Hz, 27 H, $SiCH_3$), −0.26 (s, 9 H, $AlCH_3$); ^{13}C δ 2.88 (d, J_{PC} = 8.33 Hz, $SiCH_3$), −4.85 ($AlCH_3$); ^{31}P δ −233.6. IR (cm^{-1}): 2956 (s), 2929 (s), 2884 (s), 2815 (w), 1305 (w), 1251 (m), 1177 (m), 972 (w, br), 845 (s), 827 (s), 756 (m), 721 (m), 626 (m), 516 (w), 455 (m). EI-MS: m/z 307 ($M - CH_3^+$). Anal. Calcd for $C_{12}H_{36}AlPSi_3$: C, 44.67; H, 11.25. Found: C, 44.12; H, 10.99.

$Me_3Ga \cdot P(SiMe_3)_3$. Mp: dissociation above 80 °C. NMR (C_6D_6): ^1H δ 0.29 (d, J_{PH} = 4.53 Hz, 27 H, $SiCH_3$), 0.10 (s, 9 H, $GaCH_3$); ^{13}C δ 3.75 (d, J_{PC} = 10.23 Hz, $SiCH_3$), −2.07 ($GaCH_3$); ^{31}P δ −231.9. IR (cm^{-1}): 2961 (m), 2903 (w), 1419 (w), 1256 (s), 1212 (s), 1097 (s), 1038 (s), 851 (s), 760 (m), 696 (w), 596 (m), 543 (m), 491 (w). Cryoscopic molecular weight: Calcd M_r, 365.73; obsd M_r (m), 360 (0.169), 353 (0.083). Due to the instability of the solid complex, a satisfactory elemental analysis could not be obtained.

$Me_3Al \cdot HP(SiMe_3)_2$. Mp: melts with decomposition and evolution of gas at 175 °C. NMR (C_6D_6): ^1H δ 0.14 (d, J_{PH} = 5.6 Hz, 18 H, $SiCH_3$), 1.28 (d, J_{PH} = 262.9 Hz, 1 H, PH), −0.27 (s, 9 H, $AlCH_3$); ^{13}C δ 1.77 (d, J_{PC} = 9.0 Hz, $SiCH_3$), −5.43 ($AlCH_3$); ^{31}P δ −201.8. IR (cm^{-1}): 2956 (s), 2927 (vs), 2885 (s), 2817 (m), 2317 (w), 1411 (m), 1322 (w), 1253 (vs), 1178 (s), 1053 (w), 1024 (w), 994 (w), 942 (m), 846 (vs), 760 (m), 689 (vs), 688 (s), 516 (m), 447 (m), 407 (m). Anal. Calcd for $C_9H_{28}AlPSi_2$: C, 43.16; H, 11.27. Found: C, 42.88; H, 11.05.

Synthesis of $[Me_2AlP(SiMe_3)_2]_2$. A solution of Me_2AlH (0.119 g, 2.05 mmol) and $P(SiMe_3)_3$ (0.513 g, 2.05 mmol) in 10 mL of toluene was stirred at room temperature for 24 h and then concentrated by removal of solvent under vacuum. Recrystallization at −15 °C gave colorless crystals of $[Me_2AlP(SiMe_3)_2]_2$ (0.131 g, 83% yield). Anal. Calcd for $C_{16}H_{48}Al_2P_2Si_4$: C, 40.99; H, 10.32. Found: C, 40.85; H, 10.25. Melting point and ^1H and ^{13}C NMR spectra are consistent with those previously reported;[27] however, the ^{31}P NMR chemical shift, reported as −226.7 ppm, was observed here at −240.5 ppm.

Synthesis of $[Bu^i_2AlP(SiMe_3)_2]_2$. Bu^i_2AlH (0.286 g, 2.01 mmol) and $P(SiMe_3)_3$ (0.506 g, 2.02 mmol) were combined with 25 mL of hexane. The resultant solution was stirred and heated to reflux for 6 h, after which the volume of the solution was reduced by removal of solvent under vacuum. Upon cooling of the solution to −30 °C, crystalline $[Bu^i_2AlP(SiMe_3)_2]_2$ (0.461 g, 72% yield) was obtained. Mp: 235−236 °C. NMR (C_6D_6): ^1H δ 2.17 (m, 4 H, CH), 1.24 (d, 24 H, CH_3), 0.62 (d, 8 H, CH_2), 0.45 (d, J_{PH} = 1.2 Hz, 36 H, $SiCH_3$); ^{13}C δ 28.52, (CH_3), 27.55 (CH), 26.62 (CH_2), 4.82 (vt, J_{PC}(sum) = 8.47 Hz, $SiCH_3$); ^{31}P δ −245.3. IR (cm^{-1}): 2950 (s), 2861 (m), 1460 (m), 1401 (w), 1376 (w), 1359 (w), 1319 (w), 1247 (m), 1157 (w), 1061 (s), 942 (w), 847 (s), 760 (m), 661 (m), 624 (w), 456 (w), 424 (w). EI-MS: m/z 579 ($M - Bu^+$). Anal. Calcd for $C_{28}H_{72}Al_2P_2Si_4$: C, 52.78; H, 11.39. Found: C, 52.37; H, 11.46.

Reactions of Me_3M (M = Al, Ga) with $HP(SiMe_3)_2$ and of Me_3M (M = Al, Ga, In) with $P(SiMe_3)_3$. Each of the reaction systems was carried out in toluene-d_8 using solutions that were 0.2 M in each reactant. Each of the reaction systems was then monitored by ^1H, ^{13}C, and ^{31}P NMR spectroscopy. Identification of the respective $[Me_2MP(SiMe_3)_2]_2$ (M = Al,[27] Ga,[7,13] In[15]) product was determined by comparison of NMR spectral data with those reported in the literature. The $Me_3Al/HP(SiMe_3)_2$ system was followed at 90 °C, the $Me_3Ga/HP(SiMe_3)_2$ system at room temperature, and the $Me_3M/P(SiMe_3)_3$ (M = Al, Ga, In) systems at 100 °C.

Variable-Temperature Reactions. VT studies were carried out on the $Me_3In/HP(SiMe_3)_2$, $Bu^i_2AlH/HP(SiMe_3)_2$, $Me_2AlH/P(SiMe_3)_3$, and $Bu^i_2AlH/P(SiMe_3)_3$ systems using 1:1 mol ratios of the reactants in toluene-d_8. An additional reaction for the $Me_2AlH/P(SiMe_3)_3$ system at a 2:1 mol ratio was also carried out. The reactants were loaded into J Young NMR tubes at −115 °C using a previously published procedure.[28] The NMR tube was then placed into the precooled (−95 °C) probe of the NMR spectrometer, and the reaction was monitored by ^1H, ^{13}C, and ^{31}P NMR spectroscopy with respect to temperature and time.

^{31}P NMR Data. The following is a list of additional ^{31}P NMR chemical shift data (ppm) independently determined in our laboratory at room temperature in benzene-d_6 solution for compounds used in this study: $P(SiMe_3)_3$, −251.7; $HP(SiMe_3)_2$, −236.3; $Me_3In \cdot P(SiMe_3)_3$, −230.0; $Me_3Ga \cdot HP(SiMe_3)_2$, −203.0; $Me_3In \cdot HP(SiMe_3)_2$, −213.3 (−40 °C, toluene-d_8); $[Me_2AlP(SiMe_3)_2]_2$, −240.5; $[Me_2GaP(SiMe_3)_2]_2$, −217.8; $[Me_2InP(SiMe_3)_2]_2$, −238.4; $Bu^i_2AlP(H)SiMe_3 \cdot Bu^i_2AlP(SiMe_3)_2$, −214.9 (P(H)Si, J_{PH} = 261.4 Hz, J_{PP} = 203.9 Hz), 237.9 (PSi_2).

X-ray Structure Analysis for $[Bu^i_2AlP(SiMe_3)_2]_2$. A crystal (dimensions: 0.25 mm × 0.25 mm × 0.20 mm) was

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[27] Hey-Hawkins, E.; Lappert, M. F.; Atwood, J. L.; Bott, S. G. *J. Chem. Soc. Dalton Trans.* **1991**, 939.

[28] Krannich, L. K.; Watkins, C.. L.; Srivastava, D. K. *Polyhedron* **1990**, *9*, 289.

Table 1. Experimental Parameters for the X-ray Diffraction Study of $[Bu^i_2AlP(SiMe_3)_2]_2$

empirical formula	$AlPSi_2C_{14}H_{36}$
cryst size, mm	$0.35 \times 0.30 \times 0.20$
cryst system	monoclinic
space group	*C*2/*c*
unit cell dimens	
a, Å	19.0263(34)
b, Å	12.4408(36)
c, Å	19.2032(19)
β, deg	106.8760(117)
V, Å^3	4351(2)
Z	4
fw	637.1
ρ_{calc}, g/cm^3	0.973
abs coeff, mm^{-1}	0.265
F(000)	1408
2θ range, deg	5.0−45.0
scan type	ω
index ranges	$0 \leq h \leq 20$; $0 \leq k \leq 13$; $-20 \leq l \leq 20$
reflcns collcd	2956
indepdt reflcns	2838 ($R_{merge} = 2.46\%$)
obsd reflcns	1704 ($F > 4.0\sigma$)
min/max transm	0.8384/0.8950
no. of params	164
final R (obsd data)	$R = 5.07\%$, $R_w = 7.37\%$
final R (all data)	$R = 9.27\%$, $R_w = 9.72\%$
goodness of fit	0.90
largest Δ/σ	0.001
mean Δ/σ	0.000
data to param ratio	17.3:1
largest diff peak (e Å^{-3})	0.51
largest diff hole (e Å^{-3})	−0.41

sealed into a thin-walled capillary under anaerobic conditions. It was then mounted and aligned on an Enraf Nonius CAD4 diffractometer with κ-geometry. Details of the data collection are given in Table 1.

The crystal belongs to the monoclinic crystal system (2/*m* diffraction symmetry) with space group *C*2/*c* (No. 15). Although systematic absences *hkl* for $h + k = 2n + 1$ and *h*0*l* for $l = 2n + 1$ define either the centrosymmetric space group *C*2/*c* (No. 15) or the noncentrosymmetric space group *Cc* (No. 9), intensity statistics favored the former. The choice was subsequently verified by successful solution and refinement of the crystal structure. All crystallographic calculations were carried out with the use of the Siemens SHELXTL-PC[29] program package. The analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion.[30] The structure was solved by the use of direct methods. Positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were not located directly but were input in calculated positions with $d(C-H) = 0.96$ Å[31] and with the appropriate staggered-tetrahedral geometry. The isotropic thermal parameter of each hydrogen atom was defined as equal to the U_{eq} value of that carbon atom to which it was bonded. Following refinement, the extreme features left on the difference-Fourier map were a peak of height 0.51 e Å^{-3} and a negative feature of −0.41 e Å^{-3}. Refinement of the model converged with $R = 5.07\%$ and $R_w = 7.37\%$ for 164 parameters refined against those 1704 reflections with $|F_o| > 4.0\sigma|F_o|$ and $R = 9.27\%$ for all data.

Results and Discussion

A. Reaction of Me_3M (M = Al, Ga, In) with $P(SiMe_3)_3$ and $HP(SiMe_3)_2$. The 1:1 reactions of Me_3M (M = Al, Ga, In) with $P(SiMe_3)_3$ produced high yields of the 1:1 adducts $Me_3Al{\cdot}P(SiMe_3)_3$, $Me_3Ga{\cdot}P(SiMe_3)_3$, and $Me_3In{\cdot}P(SiMe_3)_3$, respectively, which are stable in solution at room temperature. The NMR data indicated the formation of 1:1 adducts. The ^1H and ^{13}C NMR spectral data for $Me_3In{\cdot}P(SiMe_3)_3$ agreed with those previously reported.[15] For each adduct, the ^{31}P NMR chemical shift value was downfield from that of the uncomplexed $P(SiMe_3)_3$ (−251.7 ppm). This is consistent with such data for other Al,[4−6] Ga,[8,9,14] and In[9,16] containing adducts of $P(SiMe_3)_3$. The Me−Al ^{13}C NMR data for $Me_3Al{\cdot}P(SiMe_3)_3$ are representative of those for coordination of a very sterically demanding phosphine in $Me_3Al{\cdot}PR_3$ adducts[32] and are similar to that reported for $Me_3Al{\cdot}PBu^t_3$ and $Me_3Al{\cdot}P(c\text{-}C_6H_{11})_3$.

Although $Me_3Al{\cdot}P(SiMe_3)_3$ and $Me_3In{\cdot}P(SiMe_3)_3$ are stable as neat solid adducts at room temperature in an inert atmosphere, $Me_3Ga{\cdot}P(SiMe_3)_3$ dissociates upon standing. Because of its high volatility, the Me_3Ga slowly evaporates, which leaves behind liquid $P(SiMe_3)_3$ that wets the solid adduct. This may explain the ill-defined melting point and our inability to obtain a satisfactory elemental analysis of the compound. However, cryoscopic molecular weight data in benzene indicated that a 1:1 $Me_3Ga{\cdot}P(SiMe_3)_3$ adduct exists in solution.

Solution NMR studies of the three adducts in benzene-d_6 indicated room-temperature adduct stability with respect to dissociation or 1,2-elimination of tetramethylsilane. This is consistent with the reactivity reported for $Me_3In{\cdot}P(SiMe_3)_3$,[15] which required heating to induce the 1,2-elimination reaction. However, these results are inconsistent with the reported room-temperature tetramethylsilane elimination of $Me_3Ga{\cdot}P(SiMe_3)_3$ to form $[Me_2GaP(SiMe_3)_2]_2$.[7] Thermolysis of the adducts at 100 °C in toluene-d_8 suggested the following trend toward $SiMe_4$ elimination: $Me_3In{\cdot}P(SiMe_3)_3 > Me_3Ga{\cdot}P(SiMe_3)_3 >> Me_3Al{\cdot}P(SiMe_3)_3$. $Me_3In{\cdot}P(SiMe_3)_3$ reacted within 4.5 days to produce $[Me_2InP(SiMe_3)_2]_2$. After 10 days of heating, $Me_3Ga{\cdot}P(SiMe_3)_3$ showed only partial conversion (∼10%) to $[Me_2GaP(SiMe_3)_2]_2$, while $Me_3Al{\cdot}P(SiMe_3)_3$ displayed no observable reactivity.

The 1:1 reactions of Me_3Al, Me_3Ga, and Me_3In with $HP(SiMe_3)_2$ were carried out in benzene-d_6 or toluene-d_8 and monitored by NMR. At room temperature, Me_3Al and $HP(SiMe_3)_2$ form an isolable adduct. Heating a toluene solution of this adduct at 90 °C for 2 months resulted in 1,2-elimination of CH_4 and a 50% conversion to $[Me_2AlP(SiMe_3)_2]_2$,[27] which was identified by comparison of the NMR data with the dimer prepared from the reaction of Me_2AlH with $P(SiMe_3)_3$ (see Experimental Section). The combination of Me_3Ga and $HP(SiMe_3)_2$ resulted in the elimination of CH_4 at room temperature. The NMR chemical shift data indicated initial $Me_3Ga{\cdot}HP(SiMe_3)_2$ adduct formation with a slow quantitative conversion to $[Me_2GaP(SiMe_3)_2]_2$[7] over a period of 2 months. Mixing Me_3In and $HP(SiMe_3)_2$ resulted in rapid CH_4 evolution and quantitative conversion to $[Me_2InP(SiMe_3)_2]_2$[15] at room temperature within 10 min. A variable-temperature NMR study was then conducted on the reaction mixture between −60 and 0 °C. Adduct formation was noted at −60 °C and $[Me_2InP(SiMe_3)_2]_2$ formation was first observed at −40 °C. The reaction was almost complete within 1 h upon raising the temperature to −20 °C. Thus these studies indicate the

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(29) *Siemens SHELXTL-PC Manual*, release 4.1; Siemens Analytical Instruments: Madison, WI, 1990.

(30) *International Tables for X-Ray Crystallography;* Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99−101, 149−150.

(31) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(32) Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1988**, 3047.

following order of increasing ease of CH_4, 1,2-elimination for the reactions of Me_3M with $HP(SiMe_3)_2$: $Me_3Al < Me_3Ga < Me_3In$.

B. Reaction of Me_2AlH with $P(SiMe_3)_3$ and of Bu^i_2AlH with $P(SiMe_3)_3$ and $HP(SiMe_3)_2$. Variable-temperature NMR studies of the reactions of Me_2AlH with $P(SiMe_3)_3$ and of Bu^i_2AlH with $P(SiMe_3)_3$ and $HP(SiMe_3)_2$ were carried out in toluene-d_8. The 1:1, 2:1, and 1:2 $Me_2AlH/HP(SiMe_3)_2$ reaction systems have been previously reported.[26] The progress of each reaction was monitored by ^1H, ^{13}C, and ^{31}P NMR as a function of temperature and time.

The variable-temperature ^1H, ^{13}C, and ^{31}P NMR spectra suggest that the following reactions occur in the 1:1 $Me_2AlH/P(SiMe_3)_3$ reaction system:[33]

$$Me_2AlH + P(SiMe_3)_3 \rightleftharpoons Me_2AlH{\cdot}P(SiMe_3)_3 \quad (1)$$

$$Me_2AlH + P(SiMe_3)_3 \rightleftharpoons \text{“}Me_2AlP(SiMe_3)_2\text{”} + HSiMe_3 \quad (2)$$

$$n\text{“}Me_2AlP(SiMe_3)_2\text{”} + m Me_2AlH \rightleftharpoons [Me_2AlP(SiMe_3)_2]_n[Me_2AlH]_m \quad (3)$$

$$2\text{“}Me_2AlP(SiMe_3)_2\text{”} \rightleftharpoons [Me_2AlP(SiMe_3)_2]_2 \quad (4)$$

At −90 °C, an equilibrium is initially established (eq 1) that can be characterized by slow exchange owing to the presence of individual ^{31}P NMR peaks for free and complexed phosphine at −255.3 and −232.6 ppm, respectively. The presence of a very low intensity peak in the ^{13}C NMR spectrum at −2.67 ppm indicates the formation of a trace amount of $HSiMe_3$. Above −60 °C, 1,2-elimination of $HSiMe_3$ readily proceeds (eq 2) with conversion of the adduct to cyclic oligomeric species of the general form $[Me_2AlP(SiMe_3)_2]_n[Me_2AlH]_m$ (eq 3). Analogous oligomeric species have been observed for the $Me_2AlH/HP(SiMe_3)_2$[26] reaction system as well as for other Al−N[34−37] and Al−P[38] systems where Me_2AlH is involved. With increasing temperature, there is a change in relative intensities of the peaks associated with the various oligomeric species as Me_2AlH is consumed in the $HSiMe_3$ elimination reaction (eq 2). At −20 °C, the NMR spectrum indicates the presence of $[Me_2AlP(SiMe_3)_2]_2$ which is the final product in the reaction. As has been observed previously for analogous reaction systems involving Me_2AlH,[34−38] the final dimeric product does not form until sufficient Me_2AlH has been consumed to permit dimerization of “$Me_2AlP(SiMe_3)_2$”[33] (eq 4). Upon increase of the reaction mixture temperature to room temperature, 60% conversion to $[Me_2AlP(SiMe_3)_2]_2$ had occurred, and greater than 90% is observed after 12 h at room temperature.

Further evidence to support the suggested route to $[Me_2AlP(SiMe_3)_2]_2$ was obtained by studying the reaction system at 2:1 stoichiometry. With this higher stoichiometric ratio of $Me_2AlH:P(SiMe_3)_3$, the NMR spectra indicated that all the $P(SiMe_3)_3$ was complexed at −90 °C. The presence of NMR peaks associated with $HSiMe_3$ and the $[Me_2AlP(SiMe_3)_2]_n[Me_2AlH]_m$ species were observed at −80 °C. Upon warming of the sample to room temperature, the intensities of the peaks associated with $HSiMe_3$ and the oligomeric species increase and those assigned to $Me_2AlH{\cdot}P(SiMe_3)_3$ decrease. At room temperature, only a trace of $[Me_2AlP(SiMe_3)_2]_2$ is observed and the major Al−P-containing products are the oligomeric species.[26] Thus, the additional Me_2AlH in the 2:1 system complexes “$Me_2AlP(SiMe_3)_2$” (eq 3) and precludes its dimerization (eq 4).

A variable-temperature NMR study of the 1:1 $Bu^i_2AlH/P(SiMe_3)_3$ system was carried out to note what effect the steric demand of R has on the R_2AlH reactivity with $P(SiMe_3)_3$. Between −90 and −20 °C, the spectra indicate the presence of only the starting materials. Above −20 °C, peaks assignable to trace amounts of $HSiMe_3$ and oligomeric Al−P species are observed. Reactivity proceeds very slowly at room temperature. After 2 months, the spectra indicate only a trace of $[Bu^i_2AlP(SiMe_3)_2]_2$ and a large amount of unreacted $P(SiMe_3)_3$. Thus, adduct formation and 1,2-elimination are greatly influenced by the steric demand of the Bu^i group in Bu^i_2AlH. $[Bu^i_2AlP(SiMe_3)_2]_2$ was independently synthesized from the thermolysis of a hexane solution of Bu^i_2AlH and $P(SiMe_3)_3$ (see Experimental Section). In each case, the pathway to the $[R_2AlP(SiMe_3)_2]_2$ dimer involves the association of R_2AlH with “$R_2AlP(SiMe_3)_2$” to form oligomeric species that are ultimately converted to the dimer as the associated R_2AlH is consumed in reaction with $P(SiMe_3)_3$.

The 1:1 $Bu^i_2AlH/HP(SiMe_3)_2$ reaction system was also followed by variable-temperature NMR to compare results with those previously reported for the $Me_2AlH/HP(SiMe_3)_2$ system wherein $HSiMe_3$ elimination was the preferred mode of reactivity.[26] Below −40 °C, the spectra indicate the presence of only the starting materials. Above −40 °C, the ^{13}C NMR spectra indicate the formation of $HSiMe_3$, while the ^{31}P spectra indicate the concurrent formation of both “$Bu^i_2AlP(H)SiMe_3$”- and “$Bu^i_2AlP(SiMe_3)_2$”-containing oligomers arising from $HSiMe_3$ and H_2 elimination, respectively. Spectral identification was made using coupled and decoupled ^{31}P spectra to note the presence of H bound to P. Reactivity increases with increasing temperature, and spectral intensities suggest that H_2-elimination products are formed in greater yield than $HSiMe_3$-elimination species. There was no evidence for transphosphination reactions involving species such as H_2PSiMe_3 and PH_3 which were observed in the $Me_2AlH/HP(SiMe_3)_2$ system.[26] Peaks assignable to Al−P oligomeric species were observed in the NMR spectra. These species are postulated to be analogous to those previously discussed for the Me_2AlH reaction system. At 0 °C, spectral peaks for $[Bu^i_2AlP(SiMe_3)_2]_2$ are observed and these grow in intensity with increasing temperature and consumption of $HP(SiMe_3)_2$ at room temperature. The reaction goes to completion within 2 weeks to give $[Bu^i_2AlP(SiMe_3)_2]_2$ and a species having the composition $Bu^i_2AlP(SiMe_3)_2{\cdot}Bu^i_2AlP(H)SiMe_3$ as the major (85%) and minor (15%) products, respectively. Although the minor product could not be isolated, peak assignments were made on the basis of coupled and decoupled ^{31}P spectra. This

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[33] Due to the presence of mixed oligomeric Al−P species, specific monomers will be referred to as single species (i.e. “$Me_2AlP(SiMe_3)_2$”) without implying that they exist as true monomers in solution.

[34] Watkins, C. L.; Krannich, L. K.; Thomas, C. J.; Srivastava, D. *Polyhedron* **1994**, *13*, 3299.

[35] Glore, J. D.; Hall, R. E.; Schram, E. P. *Inorg. Chem.* **1972**, *11*, 550.

[36] Glore, J. D.; Schram, E. P. *Inorg. Chem.* **1972**, *11*, 1532.

[37] Bernstein, J. D. Ph.D Thesis, SUNY at Buffalo, Buffalo, NY, 1975.

[38] Beachley, O. T.; Victoriano, L. *Inorg. Chem.* **1986**, *25*, 1948.

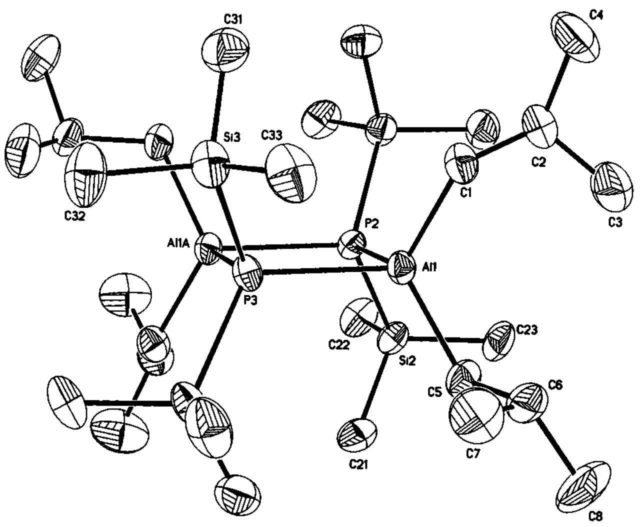

Figure 1. Molecular structure of $[Bu^i_2AlP(SiMe_3)_2]_2$.

species could arise from the combination of the "$Bu^i_2AlP(SiMe_3)_2$" and "$Bu^i_2AlP(H)SiMe_3$" units after the consumption of Bu^i_2AlH bound in the oligomers by analogy to the formation of $[Me_2AlP(H)SiMe_3]_2 \cdot Me_2AlP(SiMe_3)_2$, which was isolated and characterized in the $Me_2AlH/HP(SiMe_3)_2$ system.[26] Whereas $HSiMe_3$ elimination is the preferred mode of reactivity of Me_2AlH with $HP(SiMe_3)_2$,[26] H_2 elimination is favored in the $Bu^i_2AlH/HP(SiMe_3)_2$ system. In both cases, oligomeric species containing associated R_2AlH serve as precursors to the final products.

C. Crystal Structure of $[Bu^i_2AlP(SiMe_3)_2]_2$. The unit cell consists of four dimeric molecules of $[Bu^i_2AlP(SiMe_3)_2]_2$ each of which are separated by normal van der Waals distances. The labeling of the atoms is presented in Figure 1. Selected interatomic distances and angles are given in Table 2. The dimeric molecule has precise C_2 symmetry with the atoms P(2) and P(3) lying on a crystallographic 2-fold axis (0, *y*, $^1/_4$). This feature demonstrates the planarity of the $(AlP)_2$ core. The distances associated with this ring are Al(1)−P(2) = Al(1A)−P(2) = 2.469(2) Å and Al(1)−P(3) = Al(1A)−P(3) = 2.483(2) Å, and the internal angles are P(2)−Al(1)−P(3) = P(2)−Al(1A)−P(3) = 89.0(1)°, Al(1)−P(2)−Al(1A) = 91.3(1)°, and Al(1)−P(3)−Al(1A) = 90.7(1)°. The cross-ring distances are clearly nonbonding, with Al(1)···Al(1A) = 3.532 Å and P(2)···P(3) = 3.471 Å.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Bu^i_2AlP(SiMe_3)_2]_2$

Al(1)−P(2)	2.469(2)	Al(1)−C(1)	1.976(4)
Al(1)−P(3)	2.483(2)	Al(1)−C(5)	1.978(5)
Al(1)···Al(1A)	3.532	P(2)···P(3)	3.471
P(2)−Si(2)	2.255(2)	P(3)−Si(3)	2.267(2)
P(2)−Al(1)−P(3)	89.0(1)	C(1)−Al(1)−C(5)	117.1(2)
Al(1)−P(2)−Al(1A)	91.3(1)	Si(2)−P(2)−Si(2A)	107.3(1)
Al(1)−P(3)−Al(1A)	90.7(1)	Si(3)−P(3)−Si(3A)	105.2(1)

Table 3. Comparison of Average Structural Data (Å, deg) for $[R_2AlP(SiMe_3)_2]_2$ (R = Me, Et, Bu^i)

	$[Me_2AlP(SiMe_3)_2]_2$	$[Et_2AlP(SiMe_3)_2]_2$	$[Bu^i_2AlP(SiMe_3)_2]_2$
Al−P	2.457(2)	2.458(1)	2.476(2)
Al−C	1.959(4)	1.972(4)	1.977(5)
P−Si	2.259(1)	2.260(1)	2.261(2)
P−Al−P	89.4(3)	89.83(4)	89.0(1)
C−Al−C	113.4(2)	114.2(2)	117.1(2)
Al−P−Al	90.60(5)	90.17(4)	91.0(1)
Si−P−Si	108.35(6)	107.95(5)	106.3(1)

A comparison of several bond distances and angles for $[Bu^i_2AlP(SiMe_3)_2]_2$ and the related compounds $[Me_2AlP(SiMe_3)_2]_2$[27] and $[Et_2AlP(SiMe_3)_2]_2$[4] are given in Table 3. As the R groups on aluminum become increasingly more bulky, there is a corresponding increase in the interligand angle about the aluminum atoms (C−Al−C) and a decrease associated with the Si−P−Si angles of the bridging phosphido groups. It is interesting to note that all three structures possess planar four-membered $(AlP)_2$ cores and that the increase of the steric bulk of the alkyl groups associated with the aluminum atoms (ranging from Me to Bu^i) does not appear to cause significant distortions among the internal angles of the $(Al-P)_2$ ring. The Al−P, Al−C, and P−Si bonds for the series of compounds $[R_2AlP(SiMe_3)_2]_2$ show no statistically significant increase in bond length with increasing size of R.

Supporting Information Available: Tables listing positional and thermal parameters and complete bond distances and angles (4 pages). Ordering information is given on any current masthead page.

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