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Synthesis of trialkyl-gallium and -indium adducts of tetramethyldiphosphine

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Abstract

Trimethyl- and triethyl-gallium and -indium reacted with tetramethyldiphosphine to form 2/1 addition compounds. Characterization studies have included elemental analyses, molecular weight measurements, infrared, NMR, and mass spectra. In addition, vapor pressure measurements have been carried out between 50 and 100 °C. Attempts to isolate and identify 1/1 compounds were inconclusive.

Introduction

Although compounds of group 13 elements form numerous addition compounds, or adducts, with Lewis bases of group 15 elements [1], there are only a few examples involving bidentate bases containing a direct bond between the group 15 atoms. Reactions of hydrazines with R_3B and R_3Al produced isolable 1/1 adducts [2], whereas those of Me_4P_2 with borane gave both the 2/1 and the less-well-characterized 1/1 complexes [3]. Later studies involving tertiary diamines with nitrogen atoms separated by one or more methylene groups demonstrated that both 2/1 and 1/1 adducts could be formed with Me_3Ga and Me_3In [4]. More recently, 2/1 complexes of bis(diphenylphosphine)alkanes have also been reported [5,6]. We wish to report the synthesis of four new 2/1 addition compounds between trialkyl-gallium and -indium compounds and Me_4P_2. We believe these are the first isolable 2/1 adducts between group 13 alkyls and a bidentate base in which there are no methylene groups between the group 15 elements. We have also attempted to isolate and identify the 1/1 adducts of these compounds but have been unable to obtain conclusive evidence for their existence. Our interest in these compounds is related to recent work at this laboratory which has indicated that such bases with comparatively weak bonds between the group 15 atoms are good source materials for organometallic chemical vapor deposition (OMCVD) processes [7]. We are currently investigating the chemistry of several systems of bidentate bases and group 13 alkyls for OMCVD purposes.

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Experimental

All compounds were handled using standard vacuum system or inert-atmosphere techniques. Trimethyl- and triethyl-gallium were prepared by treating the appropriate alkyl aluminums with gallium trichloride [8], and trimethylindium was prepared by alkyl exchange between In and $(CH_3)_2Hg$ [9]. Triethylindium was obtained from Alfa Products, Danvers, MA. Tetramethyldiphosphine was purchased from Organometallics, Inc., East Hampstead, NH and purified by vacuum distillation using a series of traps at −23, −45, and −196 °C. Material stopping in the −45 °C trap was used. The purity of all materials was checked by mass spectrometry.

For the 2/1 adducts, the stoichiometries of reactions involving Me_3Ga, Et_3Ga, and Me_3In were determined by quantitative vacuum techniques. Tetramethyldiphosphine was condensed into a container with excess alkylmetal, and the mixture was warmed to ambient temperature resulting in a mildly exothermic reaction. After 30 minutes, the excess alkyl metal was quantitatively recovered. The very low volatility of Et_3In made it impractical to use it in excess since recovery was incomplete, even after attempting to remove it for several hours. Consequently, the reactants were mixed in a 2/1 stoichiometric quantity, and the resulting product was characterized. Ratios of reactants, percent yields of products, and melting points of solid products are given in Table 1. Melting points were determined using samples sealed in vacuo in capillary tubes.

Attempts to synthesize 1/1 adducts involved mixing both 1/1 stoichiometric and excess quantities of Me_4P_2 with the alkylmetals. The stoichiometric additions produced liquids for both the trimethyl and triethyl systems. Exposure of these materials to a dynamic vacuum resulted in the slow removal of Me_4P_2 and the formation of the 2/1 adducts.

Elemental analyses. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY. Results for Me_3Ga and Me_3In compounds were obtained using tared capillaries that were chemically dried, filled under an inert atmosphere, and sealed in vacuo.

$(Me_3Ga)_2P_2Me_4$ Found: C, 34.40; H, 8.63; P, 16.10. $C_{13}H_{30}Ga_2P_2$ calcd.: C, 34.15; H, 8.60; P, 17.61%.

$(Et_3Ga)_2P_2Me_4$: Found: C, 43.05; H, 9.37; P, 14.55. $C_{16}H_{48}Ga_2P_2$ calcd.: C, 44.09; H, 9.71; P, 14.21%.

$(Me_3In)_2P_2Me_4$: Found: C, 26.98; H, 6.84; P, 14.22. $C_{13}H_{30}In_2P_2$ calcd.: C, 27.18; H, 6.84; P, 14.02%.

$(Et_3In)_2P_2Me_4$: Found: C, 35.66; H, 7.67; P, 10.99. $C_{16}H_{48}Ga_2P_2$ calcd.: C, 36.53; H, 8.05; P, 11.77%.

Table 1

Reactions of trialkylmetals with tetramethyldiphosphine

Compound	R_3M/Me_4P_2	Yield of products (%)	M.p. (°C)
$(Me_3Ga)_2P_2Me_4$	2.00	99.5	118–121
$(Et_3Ga)_2P_2Me_4$	2.04	101.0	–
$(Me_3In)_2P_2Me_4$	2.01	100.9	109–111
$(Et_3In)_2P_2Me_4$	2.01	–	–

Table 2

Vapor pressure data

Compound	A	B	ΔH (kcal mol^{-1})	ΔS * (cal mol^{-1} K^{-1})
$(Me_3Ga)_2P_2Me_4$	4220	12.51	−19	44
$(Et_3Ga)_2P_2Me_4$	3689	10.55	−17	35
$(Me_3In)_2P_2Me_4$	4964	14.04	−23	51
$(Et_3In)_2P_2Me_4$	3294	9.61	−15	31

[a] By extrapolation of the vapor pressure equation.

Molecular weight studies. Molecular weights were determined at ambient temperatures by the vapor pressure depression of benzene that had been distilled from CaH_2 and stored over activated 4Å molecular sieves.

$(Me_3Ga)_2P_2Me_4$: FW, 351.7; Molality, 0.658; obsd. mol wt, 374.

$(Et_3Ga)_2P_2Me_4$: FW, 435.9; Molality, 0.828; obsd. mol wt, 457.

$(Me_3In)_2P_2Me_4$: FW, 441.9; Molality, 0.533; obsd. mol wt, 432.

$(Et_3In)_2P_2Me_4$: FW, 526.1; Molality, 0.830; obsd. mol wt, 514.

Vapor pressure studies. Vapor pressures were measured in a constant temperature bath between 50 and 100 °C using a mercury tensimeter similar to one described by Shriver [10]. Glass surfaces were passivated with Me_3Ga, and after the sample was loaded, the mercury columns were warmed in vacuo to remove dissolved He. Pressures near 50 °C were close to the limit of detectability with this method (0.1 torr), resulting in a greater degree of uncertainty in the lower temperature regions in comparison to other techniques such as effusion [11] or entrainment [12]. Measurements were not made above 100 °C in order to avoid decomposition and reaction with mercury. Of the compounds examined, only $(Et_3In)_2P_2Me_4$ indicated the onset of decomposition at 100 °C. Constants for the general vapor pressure equation $\log_{10}P(\text{torr}) = -(A/T) + B$ are given in Table 2 together with enthalpy and entropy values.

Infrared spectra. Infrared spectra were recorded on a Perkin–Elmer 1430 spectrophotometer. The solid trimethyl-gallium and -indium compounds were examined as smears between KBr plates, whereas the liquid triethyl compounds were run as thin films between CsI disks.

$(Me_3Ga)_2P_2Me_4$: 2950(m), 2925(m,sh), 2860(w), 1425(w), 1385(w), 1310(m), 1305(m), 1200(s,sh), 1150(vs,br), 1060(vs), 1030(m,sh), 950(m), 878(m), 735(m), 595(m), 545(m) cm^{-1}.

$(Et_3Ga)_2P_2Me_4$: 2940(vs), 2900(vs), 2865(vs), 2810(m), 2725(w), 1470(m), 1425(s), 1375(m), 1300(w), 1295(m), 1235(w), 1190(vw), 990(m), 955(s), 935(m), 895(m,sh), 885(s), 830(vw), 745(m), 680(m,sh), 645(s), 535(vs), 490(w), 285(m), 255(m) cm^{-1}.

$(Me_3In)_2P_2Me_4$: 2960(m), 2930(m), 2910(m), 2840(w), 2815(w), 1420(m), 1385(vw), 1300(s), 1145(vs,br), 1055(s,br), 945(m), 865(m), 780(w,sh), 740(m,sh), 705(m), 528(m), 475(m) cm^{-1}.

$(Et_3In)_2P_2Me_4$: 2930(vs), 2895(vs), 2855(vs), 2815(m), 2720(w), 1465(m), 1425(m), 1375(m), 1300(w), 1290(w), 1230(m), 1160(w), 1000(m), 955(s), 925(m), 908(m), 895(m), 882(m), 828(vw), 745(vw,sh), 735(w), 710(vw), 680(vw), 622(s), 465(s), 340(vw) cm^{-1}.

Infrared spectra of the liquids resulting from 1/1 addition reactions were very similar to those of products from the 2/1 reactions but offered no distinguishing characteristics on which to confirm an identity.

Table 3

^1H NMR data of trialkyl-gallium and -indium adducts of Me_4P_2

Adduct	$\frac{Me_3M}{Me_4P_2}$[a] or $\frac{Me(M)}{CH_2(M)+Me(P)}$	$\delta(MeM)$[b,c]	$\delta(CH_2M)$[b,c]	$\Delta[\delta(CH_2M) - \delta(MeM)]$	$\delta(MeP)$[b]
Me_3Ga		-0.15			
$(Me_3Ga)_2P_2Me_4$	1.47(1.50)	-0.22			0.73
Me_3In		-0.15[d]			
$(Me_3In)_2P_2Me_4$	1.48(1.50)	-0.20			0.75
Et_3Ga		1.15	0.41	0.74	
$(Et_3Ga)_2P_2Me_4$	0.73(0.75)	1.29	0.43	0.86	0.83
Et_3In		1.35	0.46	0.89	
$(Et_3In)_2P_2Me_4$	0.76(0.75)	1.45	0.61	0.84	0.85
Me_4P_2					0.90

[a] Values in parentheses are calculated. [b] Chemical shifts are reported as δ units in ppm and referenced to Me_4Si (0.00) and C_6H_6 (7.13). Sample concentrations were 5–10 mol% in C_6H_6. [c] Chemical shifts for the ethyl groups were determined on the basis of first-order approximation using the center line of the methyl triplet and the average of the two center lines of the methylene quartet. [d] N. Muller and A.L. Ottermat, Inorg. Chem., 2 (1963) 1075; calculated from δ(cyclopentane) (1.55 ppm).

NMR spectra. Proton NMR spectra were obtained at ambient temperature as 5–10 mole% benzene solutions on a Varian EM-390 spectrometer. Chemical shifts (Table 3) are reported as δ units in ppm and referenced to Me_4Si (0.00) with C_6H_6 at 7.13 ppm.

Proton chemical shifts and integration data of liquids from the 1/1 addition reactions were as follows for R_3M and P_2Me_4: $Me_3GaP_2Me_4$: -0.22 (0.69), 0.75 (1.00); $Et_3GaP_2Me_4$: 1.44 (0.47), (0.56, 0.82) (1.00); $Me_3InP_2Me_4$: -0.17 (0.70), 0.80 (1.00); $Et_3InP_2Me_4$: 1.46 (0.50), (0.63, 0.81) (1.00). In most instances, the differences in these values and those of the 2/1 adducts were within the limits of error of the spectrometer, thus making it impossible to confirm identities using these data.

Mass spectra. Mass spectra were obtained at 40 °C and 70 eV using a CVC MA-2 time-of-flight spectrometer equipped with a direct-insert probe. Fragmentation patterns (*m/e*, formula, percent abundance) reported here contain peaks whose intensities are at least 10% of the most abundant peak. No other significant peaks were observed at lower intensities.

$(Me_3Ga)_2P_2Me_4$: 99, $C_2H_6{}^{69}Ga$, 100; 101, $C_2H_6{}^{71}Ga$, 66; 107, $C_3H_9P_2$, 38; 122, $C_4H_{12}P_2$, 31; 69, ^{69}Ga, 24; 61, C_2H_6P, 21; 46, CH_3P, 21; 45, CH_2P, 21; 71, ^{71}Ga, 17; 62, C_2H_7P, P_2, 17; 59, C_2H_4P, 15; 57, C_2H_2P, 10.

$(Et_3Ga)_2P_2Me_4$: 127, $C_4H_{10}{}^{69}Ga$, 100; 129, $C_4H_{10}{}^{71}Ga$, 69; 18, H_2O, 66; 69, ^{69}Ga, 41; 28, C_2H_4, N_2, CO, 36; 71, ^{71}Ga, 27; 107, $C_3H_9P_2$, 24; 46, CH_3P, 21; 27, C_2H_3, 21; 122, $C_4H_{12}P_2$, 20; 62, C_2H_7P, P_2, 18; 61, C_2H_6P, 17; 45, CH_2P, 17; 17, OH, 16; 29, C_2H_5, 15; 99, $C_2H_6{}^{69}Ga$, 13; 59, C_2H_4P, 11; 26, C_2H_2, 10.

$(Me_3In)_2P_2Me_4$: 107, $C_3H_9P_2$, 100; 122, $C_4H_{12}P_2$, 80; 45, CH_2P, 66; 61, C_2H_6P, 65; 18, H_2O, 65; 28, C_2H_4, N_2, CO, 50; 46, CH_3P, 48; 59, C_2H_4P, 42; 145,

C_2H_6In, 40; 62, C_2H_7P, P_2, 40; 15, CH_3, 39; 57, C_2H_2P, 31; 79, CH_5P_2, 27; 115 ^{115}In, 22; 29, C_2H_5, 21; 16, CH_4, 21; 75, C_3H_8P, 18; 47, CH_4P, 16; 44, C_3H_8, CO_2, 16; 17, OH, 16; 14, CH_2, 11.

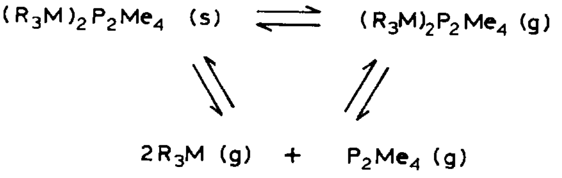
$(Et_3In)_2P_2Me_4$: 62, C_2H_7P, P_2, 100; 28, C_2H_4, N_2, CO, 67; 27, C_2H_3, 54; 173, $C_4H_{10}In$, 44; 115, ^{115}In, 37; 29, C_2H_5, 36; 90, $C_2H_4P_2$, $C_4H_{11}P$, 34; 75, C_3H_8P, 34; 46, CH_3P, 33; 18, H_2O, 31; 43, C_3H_7, PC, 27; 41, C_3H_6, 27; 61, C_2H_6P, 25; 59, C_2H_4P, 21; 57, C_2H_2P, 20; 26, C_2H_2, 19; 159, C_3H_8In, 15; 107, $C_3H_9P_2$, 13; 122, $C_4H_{12}P_2$, 127, InC, 12; 69, C_3H_2P, 11; 89, $C_4H_{10}P$, 144, C_2H_5In, 10.

Spectra of vapor above the liquids from the 1/1 reactions resembled very closely that of Me_4P_2. In the Me_3Ga system, there was evidence of Me_2Ga^+ at 40 °C, but heating between 40 and 100 °C was required to see similar fragments in others.

Results and discussion

The reactions of excess trimethyl- and triethyl-gallium and -indium with Me_4P_2 in the absence of solvent yielded thermally stable, air- and moisture-sensitive 2/1 adducts. The trimethyl derivatives were white solids that sublimed at ambient temperatures and 10^{-5} torr, whereas the triethyl compounds were low-volatile liquids that transferred with difficulty. This qualitative difference in melting points between the two groups of compounds appeared to be related to the different alkyl groups attached to the metal. Molecular weight values in benzene indicated no appreciable dissociation of the adducts in solution. Since all compounds exhibited low vapor pressures (< 0.1 torr) at ambient temperature, their use as precursors in CVD processes would require heating.

Mass spectra of vapors produced in the ionization chamber at approximately 40 °C indicated the presence of uncoordinated metal alkyls and phosphine. Gentle heating of samples up to 100 °C produced very weak additional peaks of higher mass values that could possibly be assigned to metal-phosphorus containing fragments for the trimethyl-gallium and -indium and triethylindium derivatives. However, the low intensities of these peaks made their assignments uncertain. Reducing the ionizing voltage to 10–15 eV had no significant effect on the fragmentation pattern. The lack of parent ions, or ions with masses near those of the parent species for the adducts may have resulted from their instability in the electron beam or from a shift in an equilibrium system involving the adduct and its components, e.g.:



as the latter were removed under a dynamic vacuum. Under a static vacuum, such as found in the closed volume of the tensimeter, the vapor would be expected to contain an equilibrium mixture of the adduct and free species. Consequently, the enthalpy values obtained from the vapor pressure plots would have contributions from heats of vaporization and dissociation, and the entropy values would be questionable since they depend on extrapolated boiling points which are not accurate when vaporization is accompanied by dissociation [13].

A comparison of the vapor pressures (torr) of these adducts calculated at 90 °C reveals a decrease with the alkylmetal component as follows: Me_3Ga(7.7), Et_3In(3.4), Et_3Ga(2.4), Me_3In(2.3). As might be expected, the lightest member of the series is the most volatile, and the Et_3Ga and Me_3In derivatives which are comparably heavier show reduced volatility with almost identical vapor pressures. A qualitative interpretation of the latter observation suggests that the M–P bond strength is about the same in these compounds [14]. The intermediate volatility for the heaviest adduct containing Et_3In implies that it has the weakest M–P bond, which is not unexpected from either electronic or steric considerations.

Liquids from the 1/1 reaction systems exhibited some interesting qualitative behavior as exemplified by that of $Me_3Ga_2Me_4$. Exposure of this material to a dynamic vacuum for several hours resulted in a quantitative removal of Me_4P_2 and formation of $(Me_3Ga)_2P_2Me_4$. This could have occurred by removal of excess Me_4P_2 in the presence of the 2/1 adduct or by an equilibrium shift favoring formation of the 2/1 adduct as the more volatile Me_4P_2 was removed. The latter is described in the following equation and has been observed in other 1/1 systems [4,15]:

$$2Me_3GaP_2Me_4 \rightleftharpoons (Me_3Ga)_2P_2Me_4 + Me_4P_2$$

Given the reasonable volatility of Me_4P_2 (vapor pressure at ambient temperature is approximately 10 torr) [3], it would be hard to explain the slow removal if it were not coordinated. Unfortunately, this could not be corroborated by other evidence, and the existence of the 1/1 adducts remained unconfirmed.

Data from NMR spectra are summarized in Table 3. Integration of the individual alkyl-metal and -phosphine peaks, or combined peaks as in the ethyl derivatives, gave ratios consistent with the expected values for the particular formulae. The use of benzene as a solvent in these samples resulted in relatively small changes in chemical shifts for "free" versus phosphine-complexed R_3M signals as a result of the interaction between benzene and the alkylmetals [16]. Internal chemical shifts of approximately 0.85 ppm for the ethyl derivatives were similar to that observed for the Et_3GaPMe_3 adduct [17]. Proton spectra of the phosphine portion of the adducts appeared as pseudo triplets similar to Me_4P_2 [18], but with a broader center peak. Chemical shifts were measured from the center peak.

Infrared spectra consisted essentially of composite spectra of the alkylmetal and -phosphine. These included C–H stretching and bending vibrations, as well as bands in the 750–650 cm^{-1} and 550–450 cm^{-1} regions that are associated primarily with P–C and M–C stretches [19]. Spectra of liquid films of the triethyl derivatives between CsI plates were examined for M–P stretching vibrations that would be expected below 350 cm^{-1} [20], the cut-off for KBr. Although weak bands were observed at 285 and 255 cm^{-1} for $(Et_3Ga)_2P_2Me_4$, these coincided with GaCC deformations in Et_3Ga [21]. No definitive bands were seen for the triethylindium compound. Exposure of the plates to atmospheric conditions for short periods of an hour or less produced intense, broad bands centered near 3450 cm^{-1}, indicative of the OH stretch, and other spectral changes suggesting sample decomposition.

The use of these materials to grow metal-phosphide films in chemical vapor deposition experiments has not been explored in our laboratories at this time, in part because of their low vapor pressures. However, experiments using Me_4P_2 as an alternative source of P have proved somewhat successful. Initial experiments have shown that polycrystalline GaP was grown on Si and GaP substrates between 625 and 769 °C [22]. Additional studies are needed, however, for more complete film characterization and optimization of deposition parameters.

We have thus shown the existence of 2/1 addition compounds between trimethyl- and triethyl-gallium and -indium and tetramethyldiphosphine. From the characterization of these materials, it is concluded that their use as precursors in OMCVD processes would require moderately heated transport lines. Alternatively, Me_4P_2 may be a viable source of P in these systems, in which case the chemistry of these materials remains an important issue. We are continuing our studies of group 13 alkyls and group 15 bidentate species.

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