PREPARATION AND PROPERTIES OF DIETHYL(DIPHENYLPHOSPHINYL)ALUMINIUM[1]

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Dedicated to Professor R. B. Sandin on the Occasion of his Sixty-Eighth Birthday

ABSTRACT

Two methods of preparing diethyl(diphenylphosphinyl)aluminium have been investigated. This compound exists as a dimer which can be cleaved to monomeric complexes by a variety of Lewis bases. The structure of the dimer and its chemical transformations are discussed.

INTRODUCTION

Considerable effort has been expended examining the chemistry of inorganic molecules which are isoelectronic with olefins. These studies have involved the formation of compounds by the bonding of an atom from group III with one from group V of the periodic table, both atoms often carrying organic substituents. Interest has centered on the chemical and physical properties of such systems but it has focused especially on the nature of the bonding between the group III and group V atoms. The major efforts in this area have involved studies of the B—N system (mainly trimeric) (1) and the B—P system (mainly trimeric) (2). Less is known about the Al—N system (3, 4). No "double bonding" has been observed to date.

When our work was started only three reports could be found on the chemistry of compounds containing aluminium–phosphorus bonds. Davidson and Brown (5) observed that trimethylphosphine and trimethylaluminium formed a stable adduct which eliminated methane, but only at high temperatures, to form dimethyl(dimethylphosphinyl)-aluminium, $Me_2Al—PMe_2$.[5] This compound was reported to be trimeric and not subject to cleavage by trimethylamine or dimethyl ether. In 1960 Burg and Mödritzer (6) attempted to prepare dimethylphosphinylalane, $Me_2P—AlH_2$, by a variety of methods but failed. Fritz and Trenczek (7) found that treatment of aluminium chloride with lithium diethylphosphide afforded dichloro(diethylphosphinyl)aluminium. They reported that this substance existed as a trimer but it must be noted that this conclusion was based on cryoscopy in phosphorus oxychloride, a solvent with which the compound in question reacted, albeit slowly.

Our purposes in studying the chemistry of aluminium–phosphorus compounds were: 1, to develop useful and general methods of synthesis of the compounds; 2, to investigate the nature of the bonding in these systems; and 3, to study the chemical behavior of aluminium–phosphorus compounds. Since the ultimate goal of most of the work in this field has been to detect the presence or absence of double bonding in the inorganic systems,

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[5] *Abbreviations used: Me = methyl, Et = ethyl, Ph = phenyl, THF = tetrahydrofuran.*

that became one of our goals as well. There was virtually no information available about the chemical properties of the aluminium–phosphorus compounds. In fact, most compounds reported were, at best, poorly characterized and nothing was known of their reactions.

RESULTS

In our study of the chemistry of aluminium–phosphorus compounds we decided to use diethyl(diphenylphosphinyl)aluminium (I), $Et_2Al—P(Ph)_2$, as our model compound. This choice was dictated primarily by the availability of starting materials but it was thought its chemistry would be typical nonetheless.

Lithium diphenylphosphide was required for one of our synthetic approaches to I. The only previous reports regarding the preparation of lithium diphenylphosphide involved either the cleavage of triphenylphosphine with metallic lithium (8) or the reaction of phenyllithium with diphenylphosphine (9). The former method has the distinct disadvantage of cost and the presence of phenyllithium. The latter method is tedious since the diphenylphosphine usually has to be prepared from the metal phosphide or from diphenylphosphinous chloride (8, 10). Methods are known for the preparation of sodium or potassium diphenylphosphide directly from the diphenylphosphinous chloride (11, 12) but these involved the use of the molten metals.

It was found that metallic lithium would react with diphenylphosphinous chloride in tetrahydrofuran solution to afford lithium diphenylphosphide. This reaction appeared to be rather specific in that it would not occur in diethyl ether or in dioxane solution. A convenient method of assaying for the phosphide was to react an aliquot with methyl iodide and isolate the diphenyldimethylphosphonium iodide. By this method, it was determined that the yield of the phosphide was normally 95%. The diphenylphosphinous chloride was shown not to react under these conditions. The solution of phosphide was stable for several hours and gave no indication of reacting with the solvent (13).

Diphenylphosphine at first was prepared according to literature procedures by the reduction of diphenylphosphinous chloride with lithium aluminium hydride (10). However, this reduction took place in only 47–67% yields. We found that conversion of the chloride into lithium diphenylphosphide followed by treatment of the latter with gaseous hydrogen chloride until the color of the phosphide was discharged led to the formation of diphenylphosphine in 83% overall yield. No attempt was made to maximize this yield. These methods developed for the synthesis of diphenylphosphine and lithium diphenylphosphide are much simpler, experimentally, than those presently in the literature (14). In addition, the yields are high and the products uncontaminated. They appear to be the methods of choice.

Reaction of lithium diphenylphosphide with diethylaluminium bromide (15) gave lithium bromide (91%) and an amorphous tetrahydrofuran etherate of I. Reaction of the potassium diphenylphosphide with diethylaluminium bromide initially afforded uncomplexed I but crystallization from ether gave an etherate of I. Issleib and Deylig (12) first carried out this reaction and obtained the etherate directly. Microanalytical data indicated that the etherate was converted to its uncomplexed dimer before analysis. However, ethane analysis and cryoscopy in benzene confirmed the monomeric etherate structure.

$$Ph_2P^-Li^+ + Et_2AlBr \rightarrow Ph_2P—AlEt_2 + LiBr. \quad [1]$$

Mixing diphenylphosphine and triethylaluminium either neat or in a solvent led to the instantaneous evolution of ethane and the formation of dimeric diethyl(diphenylphosphinyl) aluminium (eq. [2]). The dimer gave satisfactory aluminium and phosphorus analyses but the carbon and hydrogen values were consistently low, probably due to hydrolysis. The compound also gave satisfactory ethane analyses and cryoscopy in benzene confirmed the dimeric structure.

$$[2] \qquad Et_3Al + Ph_2PH \rightarrow [Et_3\overset{-}{Al}—\overset{+}{P}HPh_2] \rightarrow Et_2Al—PPh_2 + EtH.$$

The dimer of I was very sensitive to moisture. Protolysis with ethanol then water led to the evolution of ethane and the formation of diphenylphosphine. The latter was not isolated as such but was permitted to oxidize during the work-up to diphenylphosphinic acid. The yield of this acid could be increased by the addition of dilute hydrogen peroxide to the hydrolysis mixture prior to work-up. The dimeric structure could be cleaved by the action of a variety of Lewis bases. Simple crystallization of the dimer from diethyl ether at low temperatures led to the isolation of the diethyl etherate of monomeric I. This sample was identical to one prepared directly from diethylaluminium chloride and potassium diphenylphosphide (12).

In a similar manner the dimer (I) reacted with acridine to form a 1:1 complex between the acridine and the monomeric aluminium–phosphorus compound. This complex was an amorphous material but after purification it gave satisfactory phosphorus, aluminium, and ethane analyses. The dimer appeared to form complexes with a variety of amines but most were not crystalline. Evidence was obtained for some reaction between the dimer and trimethylamine in the form of a color change but only unreacted dimer could be isolated from the reaction mixture.

The dimer (I) was cleaved readily by *n*-butyllithium to *n*-butyldiethylaluminium and lithium diphenylphosphide. The presence of the latter was confirmed by trapping it in a reaction with iodobenzene to form triphenylphosphine (eq. [3]). Authentic lithium diphenylphosphide was shown to afford triphenylphosphine upon reaction with iodobenzene. The dimer was shown not to react with iodobenzene.

$$[3] \qquad \underset{\text{I}}{Et_2Al—P(Ph)_2} + C_4H_9Li \rightarrow Et_2AlC_4H_9 + (Ph)_2P^-Li^+ \xrightarrow{Ph—I} (Ph)_3P$$

Diethyl(diphenylphosphinyl)aluminium (I) also was shown to react with methyl iodide and the resulting diphenyldimethylphosphonium iodide was isolated in 90% yield. No attempt was made to isolate the aluminium-containing product.

DISCUSSION

When we began our work on the aluminium–phosphorus system the only known compounds of this type, $Me_2Al—P(Me)_2$ (5) and $Cl_2Al—P(Et)_2$ (7), had been reported to be trimeric. These observations appeared somewhat anomalous in view of Gillespie's arguments that valency-angle deformation from the tetrahedral (109°) hybridization to a square (90°) hybridization should occur rather readily with elements of the second and lower periods (16). Nonetheless, only trimeric aluminium–phosphorus compounds had been reported, those presumably having a six-membered ring structure.

Since our work was undertaken there have been three publications, including this one, reporting studies on aluminium–phosphorus compounds. Interestingly, all three of these independent reports indicated that the substances under study existed as *dimers* rather than trimers as had been reported earlier. Issleib and Deylig (12) prepared $Et_2Al—P(Et)_2$, Coates and Graham (17) prepared $Me_2Al—P(Ph)_2$, and we have prepared $Et_2Al—P(Ph)_2$.

It should be noted that Issleib and Deylig (12) earlier had failed to obtain the dimer of $Et_2Al{-}P(Ph)_2$ and had reported only the monomeric etherate. It would appear that the recent trend in the aluminium–phosphorus compounds is in accord with Gillespie's arguments (16) favoring the dimeric structures as the most common.

The aluminium atom in the dialkyl(disubstitutedphosphinyl)aluminium compounds obviously is very acidic and tends to be complexed by a Lewis base. In spite of the presence of an adjacent phosphorus atom with an unshared pair of electrons potentially available for sharing with the vacant orbital of aluminium, thereby satisfying the electron demand of the aluminium, there has been no evidence provided for the existence of a free monomeric structure (III). In other words, there is no evidence to indicate that multiple bonding exists in the aluminium–phosphorus series.

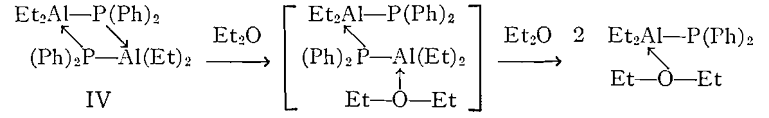
$$R_2Al{-}\ddot{P}R_2 \leftrightarrow R_2\overset{-}{Al}{=}\overset{+}{P}R_2$$

III

Instead, the compounds dimerize (e.g. IV) and a phosphorus atom acts as a Lewis base to complex with the aluminium atom of another molecule, both atoms probably being tetrahedrally hybridized. This apparent lack of double bonding is in spite of the fact that the size relationship of the two atoms, phosphorus and aluminium, should be favorable for overlap and double bonding. Lack of appreciable overlap may be due to the hybridization of the two atoms being incompatible with pi bonding.

We have been able to demonstrate that the dimer of I is readily converted into the monomeric etherate. It appears that the ether is sufficiently nucleophilic to displace the diphenyl(diethylaluminio)phosphine molecule as a complexing group for the other aluminium atom (eq. [4]). Such was not the case for the tetraethyl analog of IV, $(Et_2Al{-}PEt_2)_2$, since Issleib and Deylig (12) reported obtaining only the dimer with no mention made of a monomeric etherate. This is to be expected since the diethylphosphorus group in the latter case should be a stronger nucleophile than the diphenylphosphorus group in IV and more difficult to displace with ether.

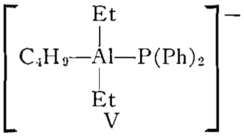
[4]



It was somewhat surprising to find that our dimer (IV) appeared to react only slightly with trimethylamine, a stronger nucleophile than ether. Under no conditions could a stable complex be isolated. In contrast, Coates and Graham (17) reported that $Me_2Al{-}P(Ph)_2$ would complex with trimethylamine (stable to 65°) but there was no indication of the stoichiometry of the product. We did find, however, that acridine would cleave the dimeric form of I and form a stable complex with the monomeric form. It may be that the steric requirements of a trimethylamine complex were too large and that acridine, while even less basic, does have a lower steric requirement.

Very little work has been published on the reactions undergone by aluminium–phosphorus compounds. We have found that diethyl(diphenylphosphinyl)aluminium (I) is very sensitive to moisture. Hydrolysis of I led to the initial cleavage of the aluminium–carbon bonds and then to the cleavage of the aluminium–phosphorus bond, resulting in the formation of ethane and diphenylphosphine. In view of our observations on the hydrolytic instability of I it is interesting to note that Fritz and Trenczek (18) recently reported, in a communication devoid of experimental data, that $H_2Al{-}P(Et)_2$, thought to exist as a trimer, was stable in the atmosphere. This is particularly surprising since the indications from all previous work on aluminium–phosphorus compounds are that all of these compounds are very moisture sensitive.

We have found that I is subject to cleavage by other nucleophiles, especially organolithium reagents. Reaction of I with *n*-butyllithium apparently proceeded by nucleophilic attack of the butyl carbanion on the aluminium atom resulting in the formation of *n*-butyldiethylaluminium and lithium diphenylphosphide (eq. [3]). Since the solution containing the colorless dimer acquired the orange coloration typical of the diphenylphosphide anion immediately upon the addition of *n*-butyllithium and it exhibited reactions characteristic of that anion (reaction with iodobenzene to form triphenylphosphine), it appears unlikely that an intermediate of the type V had an appreciable lifetime. This observation is somewhat surprising in view of the acidity of the aluminium atom. However, credence was lent to our observation by the recent report that $Et_3Ge{-}P(Ph)_2$ reacted similarly, affording *n*-butyltriethylgermane and the diphenylphosphide ion (19).



$$\left[\begin{array}{c} \mathrm{Et} \\ | \\ \mathrm{C_4H_9{-}Al{-}P(Ph)_2} \\ | \\ \mathrm{Et} \end{array}\right]^-$$

V

In accord with the observation initially made by Issleib and Deylig (12) we have confirmed that the aluminium–phosphorus bond is cleaved readily by methyl iodide, compound I forming diphenyldimethylphosphonium iodide and, presumably, diethyliodoaluminium. Again the reaction is not unique for the aluminium–phosphorus system since $Et_3Ge{-}P(Ph)_2$ was cleaved in an analogous manner (19). These cleavages most likely occurred by initial quaternization of the phosphorus atom followed by nucleophilic attack of the iodide on the aluminium or germanium atom (eq. [5]).

[5]
$$\mathrm{Et_2Al{-}P(Ph)_2 + MeI \rightarrow [Et_2Al{-}\overset{+}{P}(Me)(Ph)_2\ I^-] \rightarrow Et_2Al{-}I + MeP(Ph)_2,}$$
$$\mathrm{MeP(Ph)_2 + MeI \rightarrow Me_2\overset{+}{P}(Ph)_2\ I^-.}$$

EXPERIMENTAL

General Manipulative Methods

All operations were carried out under a blanket of oxygen-free nitrogen. Mechanical manipulations were done in a nitrogen-filled plastic "dry bag" (available from I²R, Inc., Cheltenham, Penna.). All solvents were meticulously purified and dried by standard procedures. Molecular weights were determined cryoscopically in benzene. It was necessary to degas the solvent thoroughly before use. Samples for elemental analysis were first oxidized with sodium peroxide in a Parr bomb. The oxidation solution was acidified with nitric acid, then an aliquot was analyzed for phosphorus essentially as described by Bachofer and Wagner (20). A second aliquot was analyzed for aluminium using the 8-hydroxyquinoline reagent in a standard manner. Ethane analyses were carried out by treating the compounds with *n*-butyl alcohol then 6 *N* hydrochloric acid and determining the volume of the liberated ethane.

Aluminium Starting Materials

Ethylaluminium sesquibromide was obtained by the procedure of Grosse and Mavity (15) in 73% yield as a colorless liquid, b.p. 140° (10 mm).

Using the procedure of the same authors we obtained diethylaluminium bromide in 75% yield as a colorless liquid, b.p. 64° (1.0 mm).

Anal. Calcd. for $C_4H_{10}AlBr$: Al, 16.35; Br, 48.5; ethane, 35.7. Found: Al, 15.65; Br, 48.0; ethane, 34.9.

Triethylaluminium was at first prepared by treatment of diethylaluminium bromide with sodium (15) but was later purchased from Texas Alkyls, Inc. It was redistilled as a colorless liquid, b.p. 54° (0.5 mm).

Anal. Calcd. for $C_6H_{15}Al$: ethane, 83.6. Found: ethane, 83.4.

Lithium Diphenylphosphide

To a stirred slurry of 2.0 g (0.29 g-atoms) of finely divided lithium metal in 250 ml of dry tetrahydrofuran was added 25 g (0.11 mole) of diphenylphosphinous chloride over a period of 30 min. After heating under reflux for 30–45 min the solution was siphoned away from the excess lithium and stored under nitrogen until needed. To 1.0 ml of the above orange solution was added excess methyl iodide in 2 ml of THF. The color rapidly disappeared and a colorless precipitate appeared simultaneously. After the mixture was warmed for a few minutes under a hot water tap the precipitate was filtered and dried. The yield of diphenyldimethyl phosphonium iodide was 0.135 g (95%) and it crystallized from ethanol–water as colorless needles, m.p. 240° (lit. (21) m.p. 241°).

Diphenylphosphine

To the stored solution of lithium diphenylphosphide prepared exactly as described above was added gaseous hydrogen chloride through a straight bore adapter until the orange color of the phosphide had just disappeared. A distillation head was then attached to the flask and the THF was removed. Distillation under vacuum afforded 17.5 g (83%) of diphenylphosphine as a colorless liquid, b.p. 84–86° (0.5 mm), n_D^{20} 1.6279, λ_{max} 4.5 μ (lit. (21) b.p. 280°).

Diethyl(diphenylphosphinyl)aluminium (I)

A solution of lithium diphenylphosphide was prepared as described above from 20.9 g (0.095 mole) of diphenylphosphinous chloride and 3.8 g (0.55 g-atom) of lithium. To this stirred solution was gradually added 15.6 g (0.095 mole) of diethylaluminium bromide, during which time the color faded to a golden yellow. The solvent was evaporated and replaced by benzene then the lithium bromide (7.5 g, 91%) was removed by filtration. Evaporation of the benzene left an oily residue which was taken up in ether. After 24 h a precipitate appeared which could not be recrystallized and which did not afford a satisfactory melting point.

Anal. Calcd. for $C_{16}H_{20}AlP \cdot C_4H_8O$: Al, 7.9; P, 9.06. Found: Al, 7.76; P, 8.1.

To a cold solution of 8.25 g (0.05 mole) of diethylaluminium bromide in 120 ml of diethyl ether was added slowly 20 g (0.05 mole) of $(Ph)_2PK \cdot (dioxane)_2$ (9). After the mixture was stirred for 2 h the potassium bromide was removed by filtration and the ether filtrate evaporated, leaving 8.0 g (60%) of crude diethyl(diphenylphosphinyl)aluminium (I), m.p. 121–122°. The solid crystallized from diethyl ether at −70° as colorless needles of the monomeric diethyl etherate of I, m.p. 148° (lit. (12) m.p. 151°).

Anal. Calcd. for $C_{16}H_{20}AlP \cdot (C_2H_5)_2O$: P, 9.02; Al, 7.85; mol. wt. 344; ethane, 16.8. Found: P, 11.31; Al, 9.66; mol. wt. 340, 358, 340, 345; ethane, 16.6.

To 15.1 g (0 081 mole) of diphenylphosphine cooled to 0° was added, with stirring, 9.27 g (0.081 mole) of triethylaluminium over a period of 30 min. Some gas was evolved but the rate of evolution increased when the temperature was raised to 90°. After 2 h at this temperature the oily mass solidified. The crude solid (21 g, 96%) was taken up in warm benzene, then the dimer of diethyl(diphenylphosphinyl)aluminium (I) was crystallized as colorless needles upon the addition of petroleum ether, m.p. 124–126°.

Anal. Calcd. for $(C_{16}H_{20}AlP)_2$: C, 71.2; H, 7.42; P, 11.5; Al, 10.0; mol. wt. 540; ethane, 21.5. Found: C, 66.6; H, 6.74; P, 11.39; Al, 9.96; mol. wt. 540, 550, 555; ethane, 20.9.

Dimeric I was dissolved in a minimum of warm diethyl ether. After cooling for 1 day the monomeric etherate of I crystallized as colorless needles, m.p. 148–150°, shown to be identical to the sample prepared above by admixture melting point and a comparison of the infrared spectra.

To a solution of 5.0 g of the dimer (I) in 25 ml of benzene was added 3.4 g of freshly sublimed acridine. The solution became a green-brown but it was warmed gently until all of the acridine had dissolved. After the solution stood overnight at room temperature the benzene was evaporated *in vacuo* and the residue was washed with a benzene – petroleum ether solution to remove unreacted acridine. Additional unreacted acridine was removed by heating the residue to 120° *in vacuo*. The presumed complex of monomeric I and acridine remained as a black porous solid, m.p. 130–145°.

Anal. Calcd. for $C_{29}H_{29}AlPN$: Al, 6.03; P, 6.91; ethane, 12.92. Found: Al, 5.95; P, 6.67; ethane, 13.0.

Hydrolysis of I

A solution of 3.0 g of I in 5 ml of benzene was treated with 10 ml of ethanol then 20 ml of water. A very strong phosphine odor was evident. The solvent mixture was replaced with pure benzene and this solution was extracted with dilute sodium hydroxide. Acidification of the aqueous layer afforded 0.4 g (20%) of crude diphenylphosphinic acid, m.p. 175–190°. The acid crystallized from ethanol–water as colorless needles, m.p. 190–193° (lit. (21) m.p. 195°). The yield of acid was increased to 43% when the additon of water was followed by the addition of 10% aqueous hydrogen peroxide.

Reaction of I with Methyl Iodide

To a solution of 5.0 g (9.3 mmoles) of dimeric I in 10 ml of cold benzene was added 11.5 g of methyl iodide. No visible reaction occurred but upon allowing the mixture to warm to room temperature and stand overnight a mass of colorless needles precipitated. When the supernatant liquid was treated with ethanol or dilute hydrochloric acid a gas was evolved. The precipitate was filtered, affording 7.0 g (90%) of crude diphenyldimethylphosphonium iodide, m.p. 235–239° (lit. (21) m.p. 241°).

Reaction of I with n-Butyllithium

To a solution of 6.0 g (0.22 mole) of I in 10 ml of benzene was added 0.07 mole of *n*-butyllithium in 20 ml of hexane. The solution immediately became yellow and the color darkened to orange with gentle warming.

A 10 ml aliquot of this solution was treated with excess iodobenzene whereupon the orange color gradually disappeared. The addition of ethanol and then water led to the evolution of a gas. The organic layer was separated, the aqueous layer extracted with benzene, and the combined organic layers were chromatographed on alumina to afford 0.7 g (38%) of crude triphenylphosphine, m.p. 65–72°. The phosphine crystallized from benzene–ethanol as colorless plates, m.p. 77–78°. It was identified by admixture melting point with an authentic sample, a comparison of its infrared spectrum with that of an authentic sample, and oxidation to triphenylphosphine oxide, m.p. 151–152°.

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