

SECTION 5:

SYNTHESIS OF ARSINE-PHOSPHONIUM LIGANDS

Introduction

Bidentate ligands containing the heavy group VB atoms have been studied for years because of their interesting coordination chemistry. Most of these have been homogeneous, however, with bis-phosphines the most common. Of the mixed group VB ligands, amine-phosphines are the most prevalent.^{1,2,3,4,5} While mixed arsine-phosphine bidentate ligands are known, the majority contain aromatic backbones.^{5,6,7,8,9,10,11,12} There are correspondingly few ligands of this type containing alkyl backbones.^{6,13,14,15,16} It was hoped that a novel synthetic route could be found by which mixed arsine-phosphine ligands containing alkyl backbones could be created.

Results & Discussion

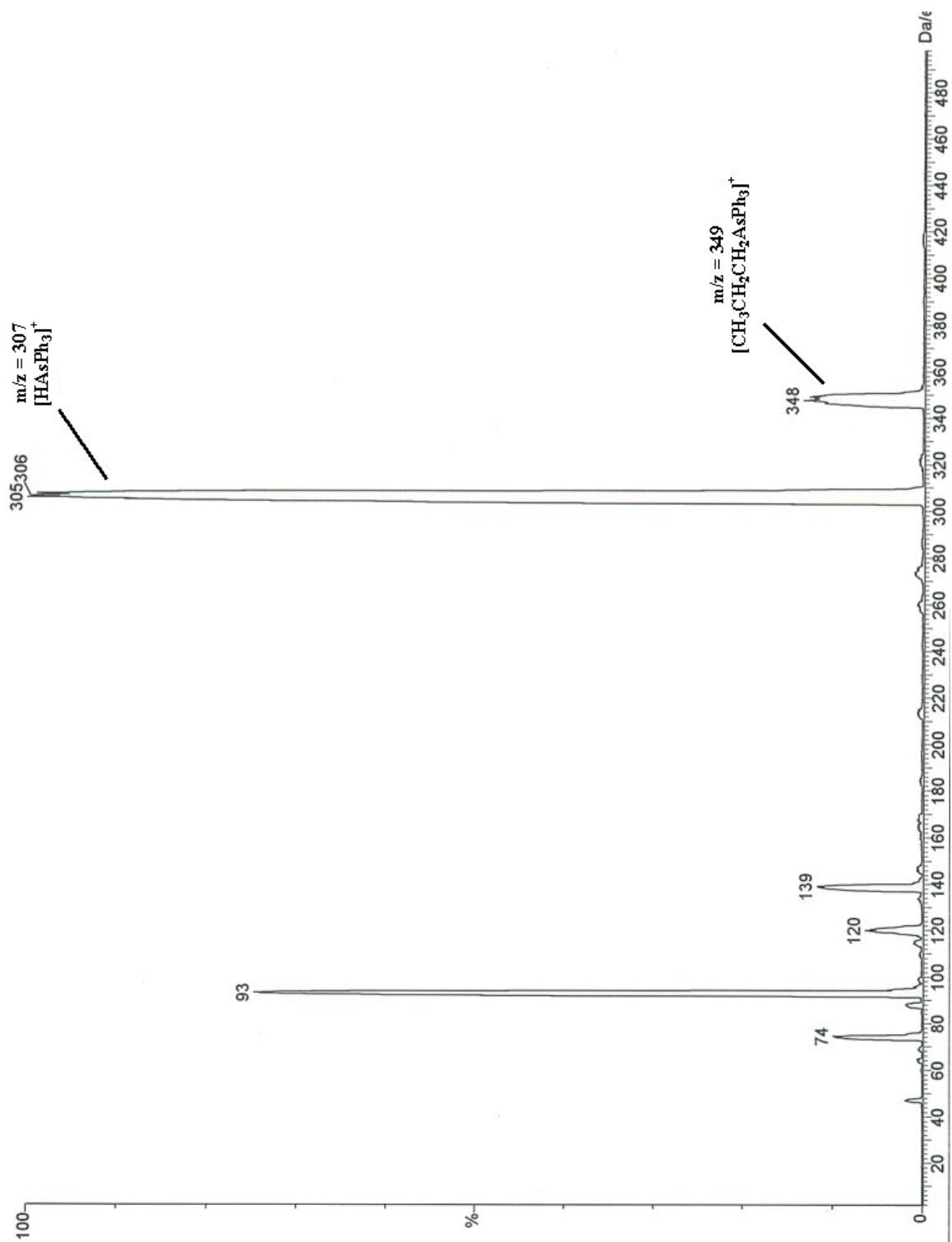
Arsonium Salts

Work began by trying to form arsonium salts from reaction of triphenylarsine with alkyl halides and dihalides.^{17,18} Both bromo- and iodo- containing chemicals were used such as CH_3I , $\text{I}-(\text{CH}_2)_2\text{CH}_3$, $\text{I}-(\text{CH}_2)_n-\text{I}$, cyclohexyl bromide, and $\text{Br}-(\text{CH}_2)_n-\text{Br}$ to list but a few. It was hoped that dihaloalkane would react in a 1:1 ratio with triphenyl arsine followed by triphenyl phosphine to form $[\text{Ph}_3\text{As}(\text{CH}_2)_n\text{PPh}_3]^{+2}$. This could then be reduced to the arsine-phosphine product.

First, simple arsonium formation reactions of triphenylarsine with $\text{Br}-(\text{CH}_2)_6-\text{Br}$ were attempted to see how easily the formation of the arsonium salt would be. Upon just stirring in a 2:1 ratio neat at room temperature no reaction took place. After heating for 24 hours there was still no change observed in the ^1H NMR. DMF was added as a solvent and the solution heated for another 24 hours but still no change was detected.

Work then switched from bromo-alkanes to iodo-alkanes, knowing from hard-soft acid-base theory¹⁹ that they should be more vulnerable to attack by the arsine. The first iodo-alkane studied was CH_3I which saw some change in the ^1H NMR. Encouraged by these results, triphenylarsine was added to an excess of $\text{CH}_3\text{CH}_2\text{CH}_2-\text{I}$ and heated to reflux for 24 hours. Positive electrospray of the solution in a 1:1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ solvent mix gave a complicated spectrum, but when run in ethanol resulted in a clean spectrum showing the hoped for $[\text{CH}_3\text{CH}_2\text{CH}_2\text{AsPh}_3]^+$ product at $m/z = 349$ (Figure 54). The base peak was protonated triphenylarsine ($m/z = 307$).

Figure 54

ESMS (+) Spectrum of $[\text{CH}_3\text{CH}_2\text{CH}_2\text{AsPh}_3]^+$ in Ethanol at 20 V

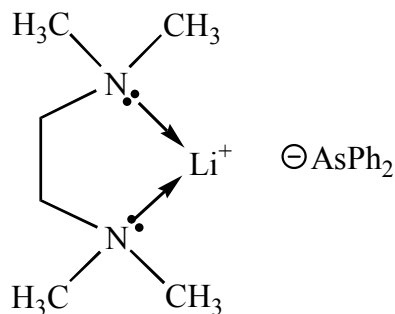
Next, the formation of mixed arsine-phosphine ligands was begun. It was hoped that phosphonium salts such as $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{I}]\text{I}$ could be used and then reduced from the phosphonium to a phosphine. However, it was first necessary to make sure that the base hydrolysis step used to reduce the phosphonium would leave the arsine intact. To test this triphenylarsine was placed in a 20% NaOH solution in water and heated overnight. This was then filtered and a white solid was collected which showed only unreacted triphenylarsine via FAB as hoped.

Based on this knowledge a reaction was set-up between $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{I}]\text{I}$ and LiAsPh_2 . Triphenylarsine was reacted in dry THF with a tenfold excess of lithium metal. Excess lithium was removed and the now dark red solution cooled to 0°C before adding the phosphonium salt in portions, as it is not soluble in THF. The solution was then heated to reflux for 2 hours. It remained reddish-brown, and very little product was obtained, most likely due to the presence of the lithium phenide (LiPh) byproduct competing for the phosphonium.

To improve the yield two additional steps were included in the reaction scheme. First, after removing the unreacted lithium metal, t-butyl chloride was added to scavenge the lithium phenide byproduct, converting it to lithium chloride, benzene, and isobutane gas. Second, tetramethylethylenediamine (TMEDA) was added to the LiAsPh_2 as a means of increasing the nucleophilic strength of the $[\text{AsPh}_2]^-$ (Figure 55).

Figure 55

Interaction of TMEDA with LiAsPh_2 to Increase Nucleophilic Strength of $[\text{AsPh}_2]^-$



This time upon adding the phosphonium salt to the LiAsPh_2 with TMEDA the solution turned immediately from dark red to yellowish-white. No long periods of heating and stirring were required. Positive electrospray showed the phosphonium salt starting material and the expected phosphonium-arsine product (Figures 56 and 57) along with the base peak at approximately $m/z = 303$. At first it was thought this must be unreacted triphenylarsine but such a neutral species would not be observable, and the m/z (306) and isotopic pattern did not match. However, the fragment $[\text{Ph}_3\text{P}(\text{CH}_2)_3]^+$ did match. While it is unusual to see this type of fragmentation at a cone voltage of only 20V, both the m/z (304) and isotopic pattern agreed with the experimental results (Figure 58). ^{31}P NMR produced some very interesting results. In addition to the two expected phosphonium peaks, triphenylphosphine was also observed in 18% yield (Table 38). Apparently the $[\text{AsPh}_2]^-$ is such a good nucleophile when coupled with TMEDA that it can even attack and replace the triphenyl phosphonium end of $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{I}]\text{I}$. Of course any $\text{Ph}_2\text{As}(\text{CH}_2)_3\text{AsPh}_2$ formed would not show up in ESMS, as it is a neutral species.

Figure 56

ESMS (+) Spectrum of Reaction of $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{I}] + \text{LiAsPh}_2$ with TMEDA
in Acetone at 20 V

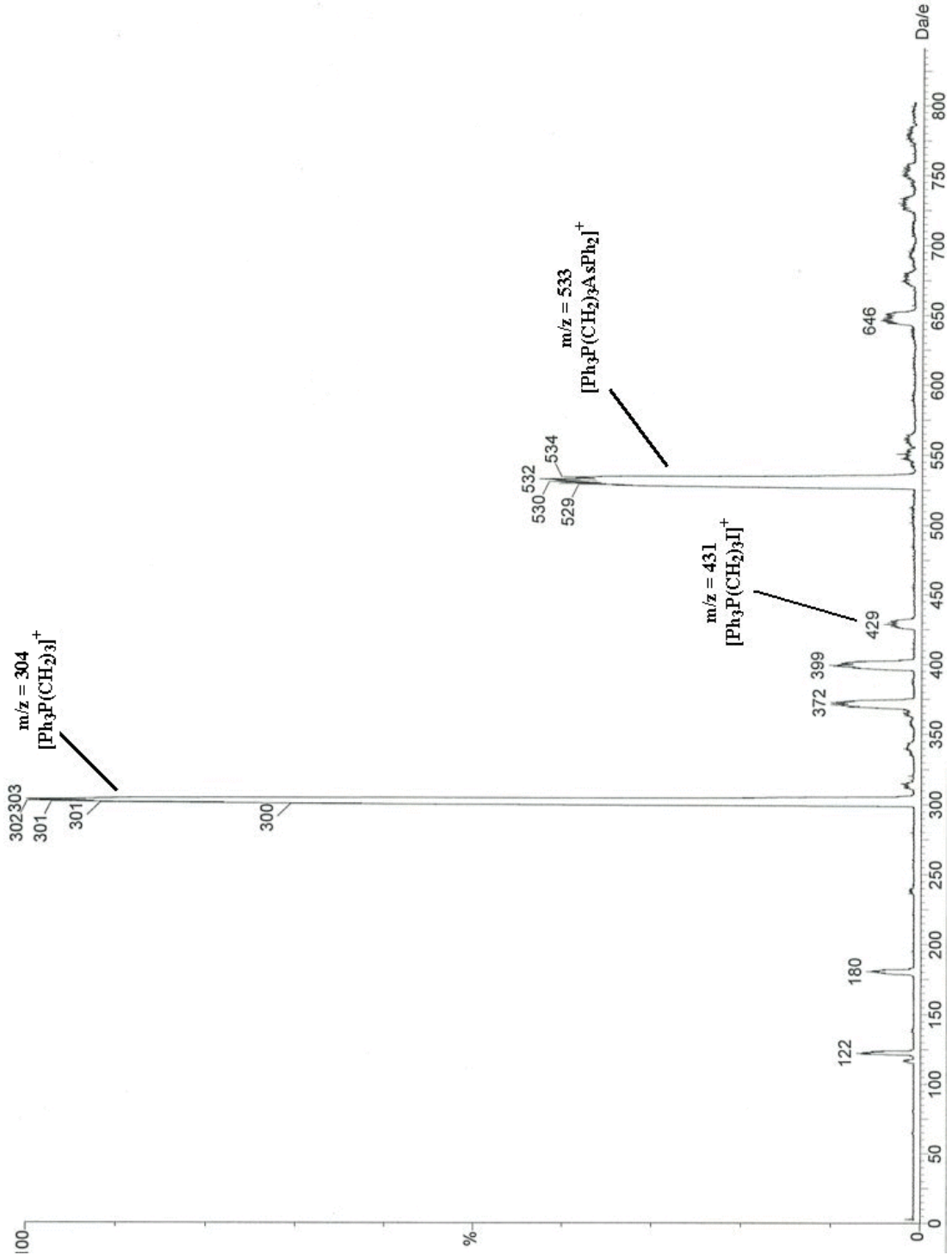


Figure 57

Calculated and Observed Isotopic Patterns of $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{AsPh}_2]^+$
in Acetone at 20 V

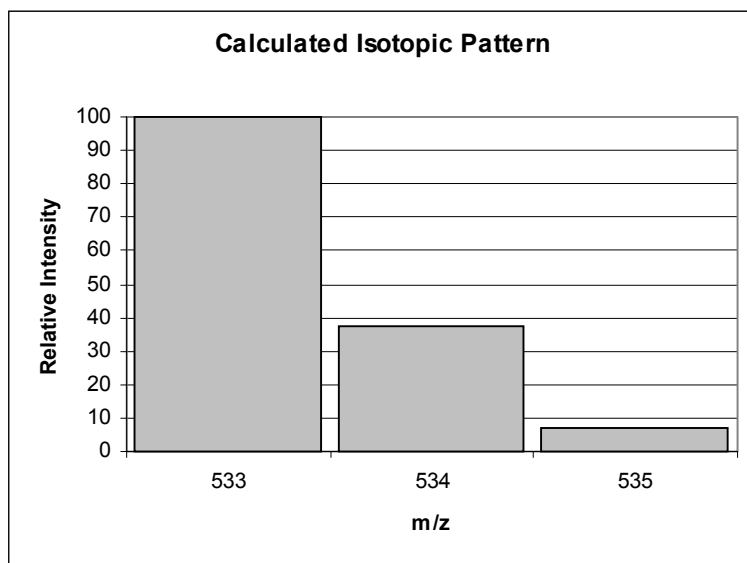
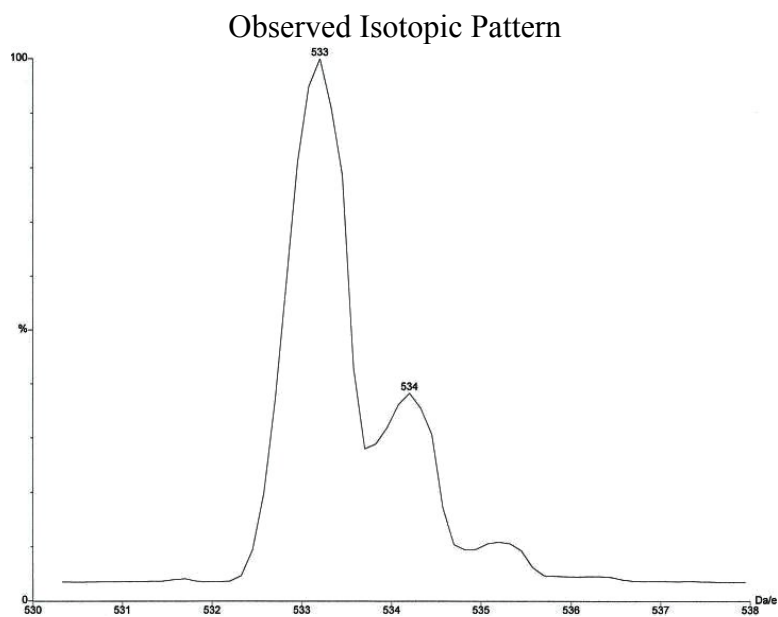


Figure 58

Calculated and Observed Isotopic Patterns of $[\text{Ph}_3\text{P}(\text{CH}_2)_3]^+$
in CH_3CN at 20 V

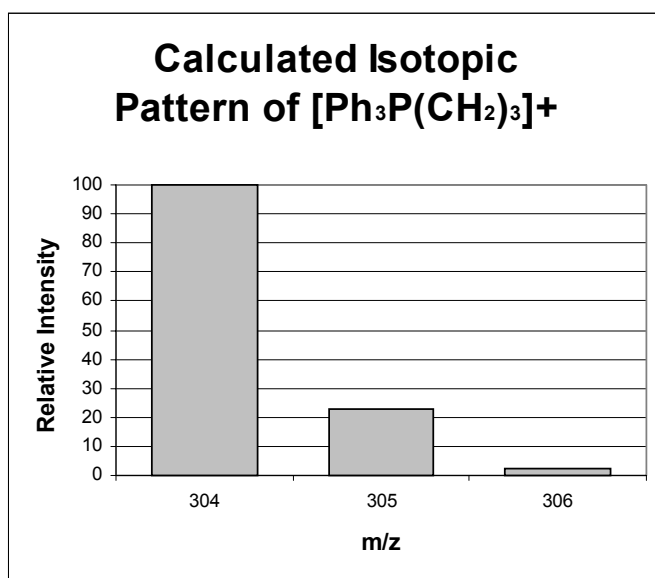
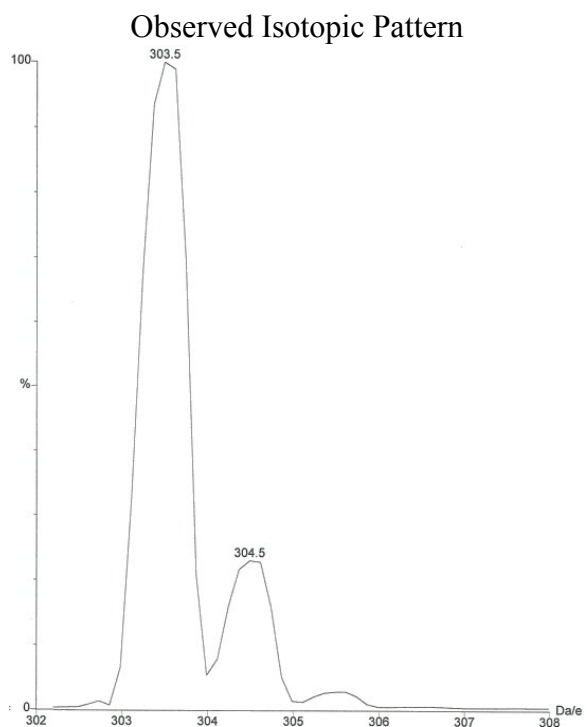


Table 38

³¹P NMR Results of Reaction of [Ph₃P(CH₂)₃I]I + LiAsPh₂ with TMEDA

Chemical Shift (ppm)	Species	Integral	% Composition
28.4	[Ph ₃ P(CH ₂) ₃ AsPh ₂] ⁺	76.3	51.6
22.6	[Ph ₃ P(CH ₂) ₃ I] ⁺	45.2	30.6
-6.1	PPh ₃	26.4	17.8

To try to improve the yield of the phosphonium-arsine product the reaction was repeated exactly as before but the LiAsPh₂ solution was cooled in an ice bath before adding the phosphonium salt. This time upon addition the solution did not immediately change colors but rather changed from deep red to the same yellowish-white over 20 minutes. After recrystallizing the product from isopropanol the ³¹P NMR showed 55% [Ph₃P(CH₂)₃I]I (δ = 23.2 ppm) and 45% [Ph₃P(CH₂)₃AsPh₂]I (δ = 29.1 ppm), along with a trace amount of triphenylphosphine. DCI MS, a relatively soft technique, shows both Ph₂As(CH₂)₃AsPh₂ (m/z = 501) and [Ph₃P(CH₂)₃AsPh₂]⁺ (m/z = 533) present at low intensities (Figure 59). The isotopic patterns were not a precise match (Figure 60) but considering the low intensity some deviation is to be expected. PPh₃ was again detected in significant amounts.

To further test the ability of LiAsPh₂ with TMEDA to attack and displace phosphonium groups, the same reaction as above was run again but with [Ph₃P(CH₂)₄PPh₃]I₂ hoping to form Ph₂As(CH₂)₄AsPh₂. Upon addition of the phosphonium salt the reddish solution of LiAsPh₂ slowly changed to clear-white but ³¹P

Figure 59

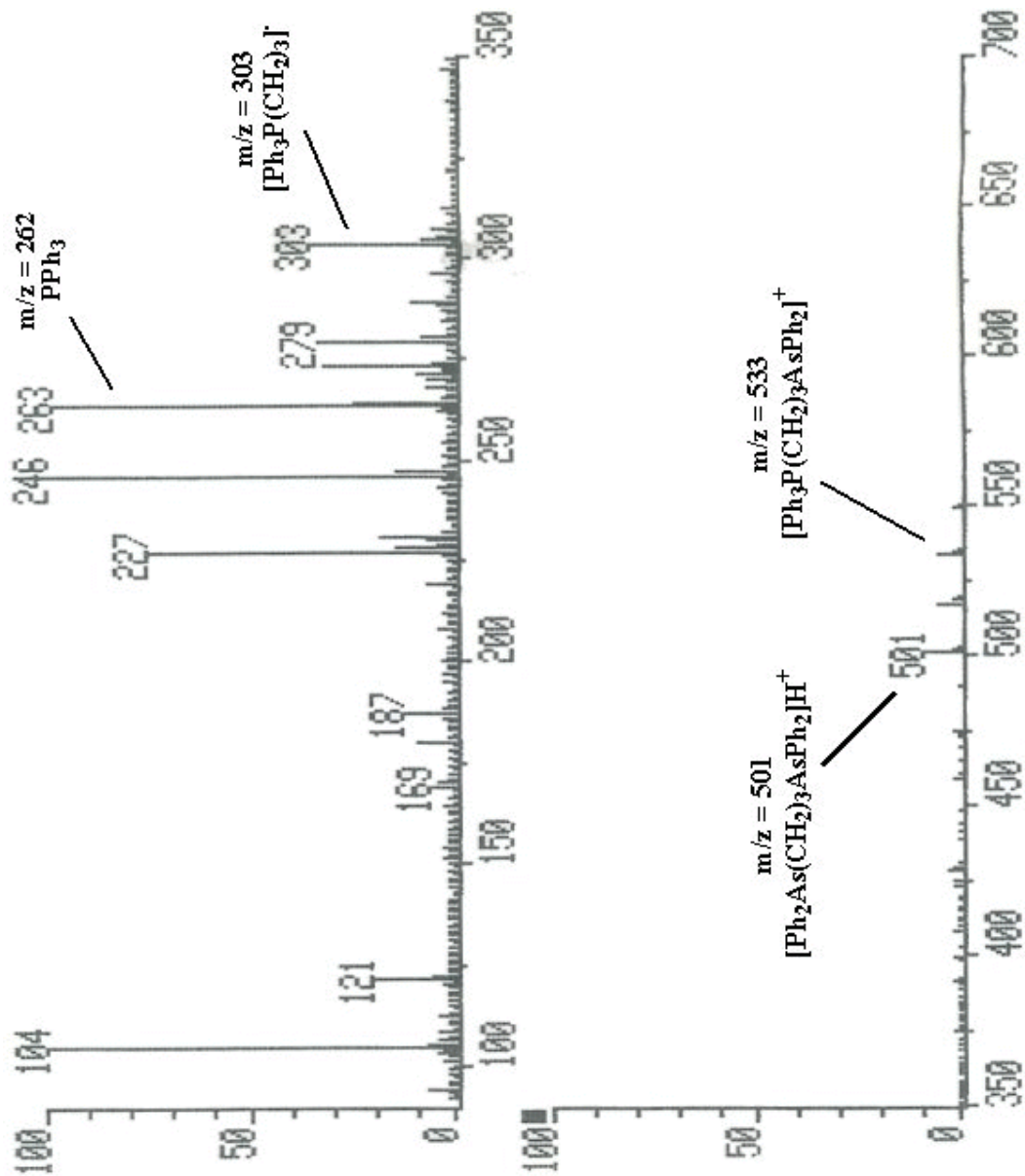
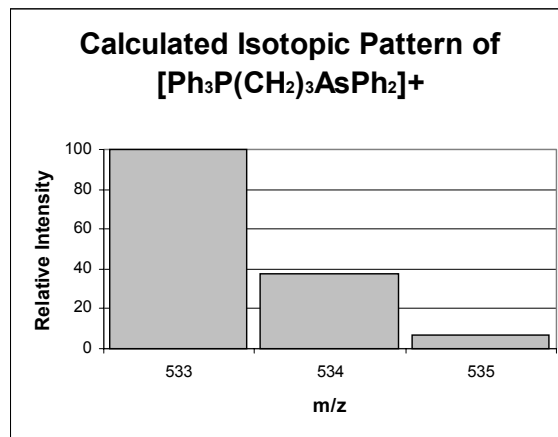
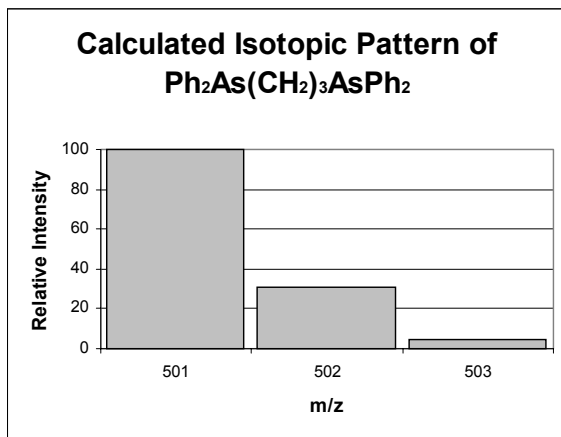
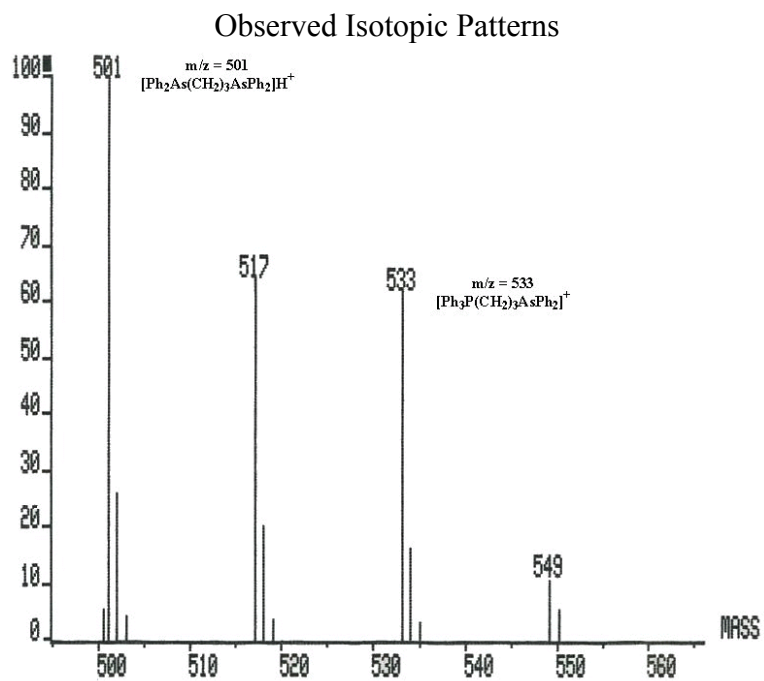
DCI MS Spectrum of Reaction of $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{I}]\text{I} + \text{LiAsPh}_2$ with TMEDA

Figure 60

Calculated and Observed Isotopic Patterns of $\text{Ph}_2\text{As}(\text{CH}_2)_3\text{AsPh}_2$
and $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{AsPh}_2]^+$ via DCI



NMR of the recovered white/brown solid product showed no triphenylphosphine. The reaction was also run with $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{PPh}_2(\text{CH}_2)_4\text{PPh}_2(\text{CH}_2)_3\text{PPh}_3]\text{I}_4$ in an attempt to synthesize $[\text{Ph}_2\text{As}(\text{CH}_2)_3\text{PPh}_2(\text{CH}_2)_4\text{PPh}_2(\text{CH}_2)_3\text{AsPh}_2]\text{I}_2$. Upon addition of the phosphonium the solution turned a clear-white but positive electrospray and ^{31}P NMR both showed only the phosphonium starting material and no triphenylphosphine. The reason for the color change in these two cases is unclear since no new products were discerned and must be the result of an undetected side reaction, possibly with impurities in the phosphoniums or an air oxidation.

Since LiAsPh_2 with TMEDA did not seem to be effective with other phosphoniums, work again returned to $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{I}]\text{I}$, but the reaction was run without TMEDA, all other reaction conditions the same as before. Phosphorus-31 NMR was run immediately after the addition of the phosphonium salt and triphenylphosphine (16%) was observed. Spectra were again taken 4 and 6 days later (Table 39). Triphenylphosphine was still observed in 11-12%, based on total product. So apparently TMEDA is not a prerequisite for the loss of triphenylphosphine.

Table 39

^{31}P NMR Results of $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{I}]\text{I} + \text{LiAsPh}_2$ without TMEDA

Species	% Composition After 4 days	% Composition After 6 days
$[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{AsPh}_2]^+$	60.3	61.8
$[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{I}]^+$	39.7	38.2

Conclusions

Synthesis of mixed arsine-phosphine bidentate ligands containing alkyl backbones was attempted. It was determined that triphenyl arsines were impervious to base hydrolysis, so work began by reacting bromo-alkanes with arsine but arsonium salts were not produced. However, by switching to an iodo-alkane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$, the arsonium salt was obtained.

Reactions between $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{I}]\text{I}$ and LiAsPh_2 did proceed, but only very slowly. However, with the addition of TMEDA the mixed group VB species $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{AsPh}_2]\text{I}$ was rapidly obtained and characterized by ^{31}P NMR, ESMS, and DCI MS.

Triphenylphosphine was also observed, leading to the conclusion that the phosphonium group was being attacked and replaced by $[\text{AsPh}_2]^-$. However, this could not be reproduced with $[\text{Ph}_3\text{P}(\text{CH}_2)_4\text{PPh}_3]\text{I}_2$ or $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{PPh}_2(\text{CH}_2)_4\text{PPh}_2(\text{CH}_2)_3\text{PPh}_3]\text{I}_4$. An explanation to this phenomenon is not readily apparent. It is assumed that in the reaction between $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{I}]\text{I}$ and LiAsPh_2 that the first product formed is $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{AsPh}_2]\text{I}$ which is then subsequently attacked again by LiAsPh_2 . It seems that the $:\text{AsPh}_2$ group in $[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{AsPh}_2]\text{I}$ must somehow activate the phosphonium end (perhaps forming a P-As bond) to make it accessible to nucleophilic attack though the mechanism is not understood. Since this activation step cannot occur in the diphosponiums no reaction is observed.

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