Reactions of N-Methylated Amino Acids and Benzylammonium Ions with P_7^{3-} and As_7^{3-}: Unusual Stereospecific Alkyl Group Transfers in the Synthesis of $R_2P_7^-$ and $R_2As_7^-$ Ions

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Ethylenediamine (en) solutions of E_7^{3-}, where E = P (**1**) or As (**2**), react with excess $(PhCH_2)Me_3NBr$ to give NMe_3 and a single diastereomer of the $(PhCH_2)_2E_7^-$ ions, where E = P (**3**) or As (**4**), in good yields. X-ray crystal structures of the $[PPh_4]$**3** and [K(2,2,2-crypt)]**4** salts showed that both anions adopt the sterically favored symmetrical structure. DMF solutions of **1** also react with ethyl esters of N-methylated amino acids, $(EtOCOCHR)Me_3N^+$, where R = H (glycine) or Me (alanine), to give $(EtOCOCHR)_2P_7^-$ ions where R = H (**7**) or Me (**8**). The transfer of Me^+ to give the known $Me_2P_7^-$ ion (**5**) is competitive with $(EtOCOCHR)^+$ transfer when R is not a proton such that **5** is favored over the formation of **8** (**5**:**8** = 2.5:1), but **5** is only a trace impurity for R = H (**5**:**7** ≈ 1:48). Reactions of *R* and *S* enantiomers of the alanine esters were conducted to probe the stereochemistry at carbon in these reactions, but the three different diastereomers of **8** (i.e., (*R*,*R*)- or (*S*,*S*)-, (*R*,*S*)-, and (*S*,*R*)-$(EtOCOCHR)_2P_7^-$) were indistinguishable by NMR spectroscopy. These studies advance the alkylation chemistry of the polypnictides by (1) unequivocally showing which isomer is formed in the alkyl transfer reaction, (2) showing that the alkylammonium alkylations proceed with As_7^{3-} with the same stereospecificity, and (3) demonstrating that the chemistry can be extended to N-methylated amino acid esters. Crystallographic data for $[PPh_4]$**3**: orthorhombic, space group *Pbca*, a = 17.6049(13) Å, b = 17.1910(12) Å, c = 23.798(2) Å, V = 7202.4(9) Å^3, Z = 8, $R(F)$ = 4.03%, $R(wF^2)$ = 10.41% ($F_o > 4\sigma F_o$). For [K(2,2,2-crypt)]**4**: monoclinic, space group *I*2/*a*, a = 25.527(2) Å, b = 13.292(2) Å, c = 24.687(2) Å, β = 96.836(11)°, V = 8317(2) Å^3, Z = 8, $R(F)$ = 6.47%, $R(wF^2)$ = 15.85% ($F_o > 4\sigma F_o$).

There are numerous examples of polyphosphorus anions that are isolable and relatively stable.[1−3] In contrast, the number of *isolable* neutral hydrogen polyphosphane analogues is few due to their inherent instability.[4,5] The alkylated derivatives are somewhat more stable, and neutral alkyl polyphosphanes are known.[4,6−8] The synthesis of the first trialkylheptaphosphane(3) was accomplished by Baudler and co-workers through reactions of Li_3P_7 and methyl bromide.[9] Subsequent studies by Fritz et al. showed that several R_3P_7 species could be prepared by this method where R = Me, Et, *i*-Pr, $SiMe_3$, $SnMe_3$, and $PbMe_3$ (eq 1).[6−8,10] Further studies showed that alkyl group

$$Li_3P_7 + 3RCl \rightarrow R_3P_7 + 3LiCl \qquad (1)$$

$$R = Me, Et, Bu, i\text{-}Pr$$

transfers between anions were facile and partially alkylated compounds (e.g., $R_2P_7^-$, RP_7^{2-}) could be prepared by alkyl exchange (eq 2).[11] Although eq 2 chemistry clearly gives the

$$2R_3P_7 + P_7^{3-} \rightarrow 3R_2P_7^- \qquad (2)$$

$$R = Me, Et, Bu$$

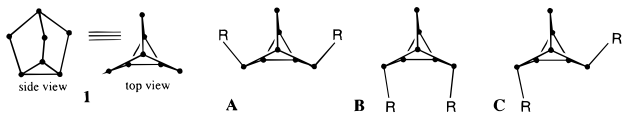
desired products, the reactions are hampered by distributions of compounds, and pure partially alkylated polyphosphides have not been isolated by this method.

Subsequent to their work, we discovered that tetraalkylammonium salts serve as alkylating agents in reactions with P_7^{3-} (**1**) but give only the $R_2P_7^-$ dialkylated products where R = Me, Et, Bu (eq 3).[12] Equation 3 chemistry is notable in that

$$\text{excess } NR_4^+ + P_7^{3-} \rightarrow R_2P_7^- + 2NR_3 \qquad (3)$$

$$R = Me, Et, Bu$$

it gives a single product (no monosubstituted or trisubstituted compounds) and only one of three possible isomers (**A**−**C**) is formed. NMR spectral analysis allowed us to eliminate the unsymmetrical isomer C but we were unable to differentiate between A or B based on spectroscopy.[12]



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Herein we report the synthesis and characterization of four new dialkylated compounds, namely, $(PhCH_2)_2P_7^-$, $(PhCH_2)_2As_7^-$, $(EtOCOCH_2)_2P_7^-$, and $(EtOCOCHMe)_2P_7^-$. This study advances the chemistry of alklyated polyphosphides in three important ways. First, the X-ray structure of $(PhCH_2)_2P_7^-$ confirms which isomer is formed in eq 3 chemistry. Second, the synthesis and structural analysis of $(PhCH_2)_2As_7^-$ show that this chemistry can be extended to arsenic while the product selectivity and stereospecificity are retained. Third, we show that eq 3 chemistry can be extended to N-methylated amino acid esters as evidenced by the formation of $(EtOCOCH_2)_2P_7^-$ and $(EtOCOCHMe)_2P_7^-$. The latter chemistry sets the groundwork for a series of peptide-supported polyphosphides and arsenides.

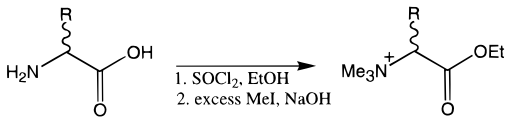
Synthesis

Ethylenediamine (en) solutions of E_7^{3-}, where E = P (**1**) or As (**2**), react with $(PhCH_2)Me_3NBr$ to give $(PhCH_2)_2E_7^-$ ions where E = P (**3**) or As (**4**) according to eq 4. The polyphosphide **3** was isolated as an orange PPh_4^+ salt in 58% yield and is moderately air sensitive in solution and in the solid state. The polyarsenide **4** was isolated in 53% yield as an orange $[K(2,2,2\text{-crypt})]^+$ salt and is also moderately air sensitive in solution and in the solid state. The salts have been characterized by ^1H NMR, ^{13}C NMR, and ^{31}P NMR (for **3**) spectroscopic studies, elemental analysis, and single-crystal X-ray diffraction.

$$\text{excess } (PhCH_2)Me_3N^+ + E_7^{3-} \rightarrow (PhCH_2)_2E_7^- + 2NMe_3 \quad (4)$$
$$E = P\ (\mathbf{3}),\ As\ (\mathbf{4})$$

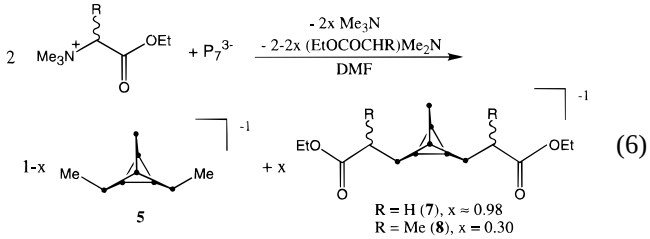
Both syntheses involve the transfer of the more electrophilic benzyl group from the benzyltrimethylammonium ion in lieu of the less sterically encumbered methyl group. NMR analysis (^{31}P and ^1H) shows that both reactions give trace amounts (<5%) of the methyl compounds, $Me_2P_7^-$ (**5**) or $Me_2As_7^-$ (**6**), as a result of Me^+ transfer. However, mixed Me/CH_2Ph compounds of formula $Me(PhCH_2)E_7^-$ have not been detected.

The preferential transfer of the most electrophilic alkyl groups can be exploited to attach amino acid derivatives to the P_7^{3-} ion by using N-methylated amino acid esters, $(EtOCOCHR)Me_3N^+$. The N-methylated amino acid esters were prepared from the amino acids glycine (R = H) and alanine (R = Me) by an initial thionyl chloride esterification and subsequent permethylation using methyl iodide (eq 5). DMF solutions of



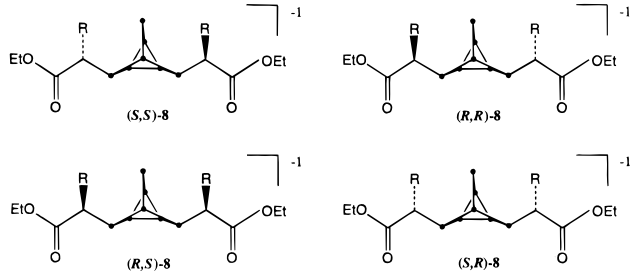
(5)

1 react with the esters to give $(EtOCOCHR)_2P_7^-$ ions where R = H (**7**) or Me (**8**) according to eq 6. Because the reactions require excess ammonium ion esters, the products were contaminated with $(EtOCOCHR)Me_3N^+$ salts. The $(EtOCOCHR)_2P_7^-$ ions have been characterized by ^1H NMR, ^{13}C NMR, ^{31}P NMR, and negative ion electrospray mass spectrometry (EMS). NMR and EMS analysis of the reaction mixtures showed that Me transfer to give the $Me_2P_7^-$ ion (**5**) becomes competitive when R is not a hydrogen atom. For the glycine reaction (eq 6, R = H), ester transfer is almost quantitative and only trace amounts of **5** (<2%) are detected spectroscopically. The 390.9 amu EMS peak for **7** was the parent ion in the spectrum with only trace (<5% of **7**) peaks between 100 and 600 amu. For the alanine reaction (eq 6, R = Me), methyl transfer prevails over ester transfer such that **5** is favored over **8** by a 2.5:1.0 ratio (NMR analysis). The EMS peak heights of **5** (247.1 amu) and **8** (418.9 amu) were in a 2.4:1.0 ratio. However, an unidentified third anion with m/z = 332.9 represented the parent ion. Mixed methyl−ester compounds of formula $(EtOCOCHR)(Me)P_7^-$ have not been detected either spectroscopically or by EMS. Reactions of the permethylated carboxylate zwitterions $(^-O_2CCHR)Me_3N^+$ give the methyl compound **5** as the exclusive product.



(6)

In an attempt to determine the fate of the stereochemistry at carbon in eq 6 chemistry, we studied the reactions of the *R* and *S* enantiomers of the alanine esters both individually and as racemic mixtures. Reactions involving a racemic mixture of alanine esters should give four isomers of **8**, namely, (*R*,*R*)-**8**, (*S*,*S*)-**8**, (*R*,*S*)-**8** and (*S*,*R*)-**8**. These four isomers represent three different diastereomers where (*R*,*R*)-**8** and (*S*,*S*)-**8** are an enantiomeric pair. It is important to note that the (*R*,*S*)-**8** and (*S*,*R*)-**8** diastereomers are not simple mesoforms due to asymmetry in the mirror plane (i.e., they are distinct diastereomers in which the Me groups are externally diastereotopic).[13] The situation is analogous to the 2,4-dinitrobenzenesulfenyl derivatives of meso amines with two chiral centers.[13,14] The (*R*,*R*)-**8** and (*S*,*S*)-**8** enantiomers have C_1 point symmetry, whereas the (*R*,*S*)-**8** and (*S*,*R*)-**8** diastereomers have mirror C_s point symmetry.



Assuming the reactions proceed by an S_N2 mechanism to give complete inversion of configuration at the α-carbon, 2 equiv of (*S*)-$Me_3NCHMeCO_2Et^+$ would give (*R*,*R*)-$(EtOCOCHMe)_2P_7^-$ ((*R*,*R*)-**8**). Likewise, two (*R*)-$(EtOCOCHMe)Me_3N^+$ would give (*S*,*S*)-$(EtOCOCHMe)_2P_7^-$ ((*S*,*S*)-**8**), and reactions of two different $(EtOCOCHMe)Me_3N^+$ enantiomers with P_7^{3-} would give all four stereoisomers in statistical mixtures. However, reactions involving the racemic mixtures of the alanine esters were identical to those of the enantiomerically pure compounds, and we were unable to differentiate between the diastereomers by either ^{13}C NMR, $^1H\{^{31}P\}$ NMR, or ^{31}P NMR spectroscopic analysis. Additional studies involving chiral esters are in progress in order to address this problem.

Solid State Structures

The single-crystal X-ray structures of $(PhCH_2)_2P_7^-$ (**3**) and $(PhCH_2)_2As_7^-$ (**4**) ions have been determined as the Ph_4P^+ and

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Table 1. Crystallographic Data for $[PPh_4][(PhCH_2)_2P_7]$ and $[K(2,2,2\text{-crypt})][(PhCH_2)_2As_7]$

empirical formula	$C_{38}H_{34}P_8$	$C_{32}H_{50}As_7KN_2O_6$
fw	738.41	1122.28
temp (K)	153(2)	153(2)
wavelength (Å)	0.710 73	0.710 73
space group	*Pbca*	*I*2/*a*
unit cell dimens		
a (Å)	17.6049(13)	25.527(2)
b (Å)	17.1910(12)	13.292(2)
c (Å)	23.798(2)	24.687(2)
β (deg)	90	96.836(11)
vol (Å^3), *Z*	7202.4(9), 8	8317(2), 8
density (calcd) (Mg/m^3)	1.362	1.793
abs coeff (mm^{-1})	0.415	5.697
F(000)	3056	4432
Θ range (deg)	2.31−25.00	2.33−25.02
reflns collected	12 680	4037
indep reflns	6342 [*R*(int) = 0.0357]	3849 [*R*(int) = 0.0466]
max. and min. transm	0.7718 and 0.6583	0.9317 and 0.1146
data/restraints/params	6333/25/595	3844/6/428
goodness-of-fit on F^2	1.055	1.040
final *R* indices [$I > 2\sigma(I)$][a]	R1 = 0.0403	R1 = 0.0647
	wR2 = 0.0923 [4689 data]	wR2 = 0.1585 [2807 data]
R indices (all data)	R1 = 0.0659	R1 = 0.0960
	wR2 = 0.1041	wR2 = 0.1813

[a] $R1 = \sum|F_o - F_c|/\sum F_o$, $wR2 = (\sum w|(F_o)^2 - (F_c)^2|^2/\sum wF_o^2)^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the $(PhCH_2)_2P_7^-$ and $(PhCH_2)_2As_7^-$ Ions

bond	**3** (E = P)	**4** (E = As)
E(2)−C(1)	1.863(6)	2.000(1)
E(3)−C(8)	1.878(3)	1.960(6)
E(2)−E(1)	2.2004(11)	2.447(2)
E(2)−E(5)	2.2053(12)	2.420(2)
E(5)−E(6)	2.2076(12)	2.431(2)
E(5)−E(7)	2.2320(13)	2.452(3)
E(7)−E(4)	2.1234(13)	2.357(3)
E(7)−E(6)	2.2225(14)	2.445(3)
E(6)−E(3)	2.2110(12)	2.421(2)
E(3)−E(1)	2.2043(12)	2.438(2)
E(1)−E(4)	2.1451(12)	2.331(2)
angle	**3** (E = P)	**4** (E = As)
C(1)−E(2)−E(1)	100.24(13)	98.10(4)
C(1)−E(2)−E(5)	99.26(14)	94.90(4)
C(8)−E(3)−E(1)	102.52(12)	99.00(13)
C(8)−E(3)−E(6)	96.11(10)	94.60(6)
E(1)−E(2)−E(5)	101.04(4)	100.59(6)
E(2)−E(5)−E(6)	100.19(5)	101.03(6)
E(2)−E(5)−E(7)	103.91(5)	104.66(8)
E(6)−E(5)−E(7)	60.08(4)	60.09(7)
E(4)−E(7)−E(6)	109.28(5)	108.97(9)
E(4)−E(7)−E(5)	109.00(5)	108.54(10)
E(6)−E(7)−E(5)	59.42(4)	59.53(8)
E(5)−E(6)−E(3)	101.31(5)	99.83(6)
E(5)−E(6)−E(7)	60.51(4)	60.38(7)
E(3)−E(6)−E(7)	104.29(5)	104.09(8)
E(1)−E(3)−E(6)	100.29(4)	101.31(6)
E(4)−E(1)−E(2)	105.86(4)	106.37(7)
E(4)−E(1)−E(3)	106.23(5)	106.19(7)
E(2)−E(1)−E(3)	86.98(4)	85.21(6)
E(7)−E(4)−E(1)	99.12(4)	99.60(8)

$[K(2,2,2\text{-crypt})]^+$ salts, respectively. Summaries of the crystallographic data are given in Table 1, and selected bond distances and angles are given in Table 2. ORTEP drawings of the ions are given in Figures1 and 2. A common numbering scheme is used for both compounds.

The $[PPh_4][(PhCH_2)_2P_7]$ salt is orthorhombic, space group *Pbca*, whereas the $[K(2,2,2\text{-crypt})][(PhCH_2)_2As_7]$ salt is monoclinic, space group *I*2/*a*. Both **3** and **4** have virtual C_s point symmetry, but in neither case is the mirror symmetry crystallographically imposed. The X-ray structure of $[PPh_4][(PhCH_2)_2P_7]$ was complicated by a minor (<5%) disorder in the P_7C_2 unit that was successfully modeled as an independent orientation of the anion in the crystal lattice. Only the data for the major orientation are given here. The P−P bond distances in **3** are in the range 2.123(1)−2.232(1) Å whereas the As−As bond distances in **4** are in the range 2.331(2)−2.452(3) Å. These contacts are typical for polypnictides of this type.[2,3,8,10,15−17] The phosphorus−carbon bonds of **3** average 1.87 Å and are similar

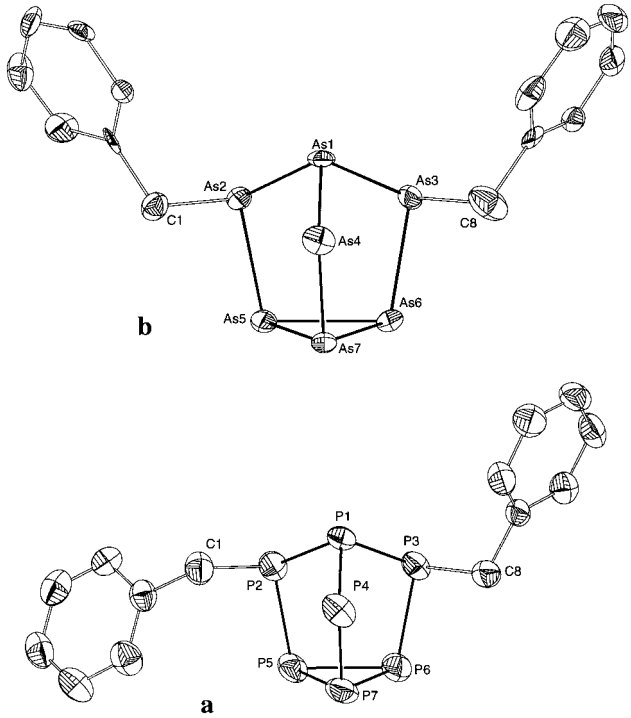

Figure 1. (a) ORTEP drawing of the $(PhCH_2)_2P_7^-$ ion (side view). (b) ORTEP drawing of the $(PhCH_2)_2As_7^-$ ion (side view).

(15) Hönle, W.; Wolf, J.; von Schnering, H.-G. *Z. Naturforsch. B* **1988**, *43*, 219.
(16) Hönle, W.; von Schnering, H.-G.; Fritz, G.; Schneider, H.-W. *Z. Anorg. Allg. Chem.* **1990**, *584*, 51.
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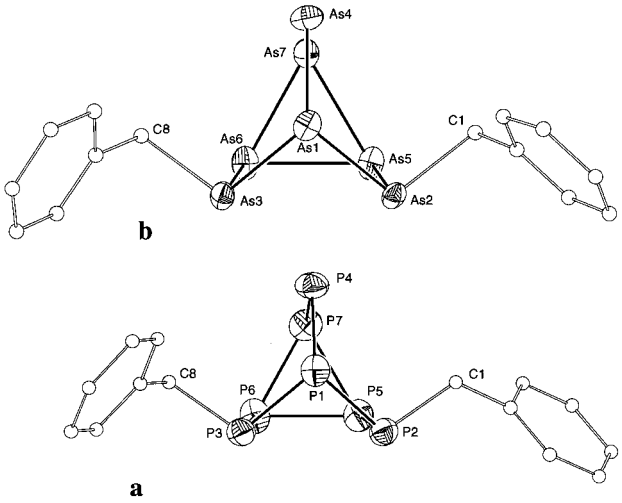
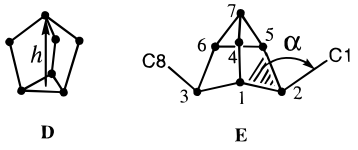


Figure 2. (a) ORTEP drawing of the $(PhCH_2)_2P_7^-$ ion (top view). (b) ORTEP drawing of the $(PhCH_2)_2As_7^-$ ion (top view).

to the P−C distances in the $[EtP_7W(CO)_3]^{2-}$ ion (1.858(7) Å)[12] and trialkylphosphines.[18] The As−C distances in **4** average 1.98 Å and are similar to those of related compounds (e.g., 1.96 Å in [*cyclo*-$(MeAs)_{10}Mo_2(CO)_6$]).[19]

The general structures of **3** and **4** are quite similar and show marked distortions from the parent E_7^{3-} ions (E = P, As)[20−22] and the R_3E_7 molecules (R = Me_3Si, Me_3Ge, Me_3Sn; E = P, As).[6−8,15,23] The benzyl groups in both ions point "up" toward the lone two-coordinate atom E4, giving rise to a virtual mirror plane defined by E1−E4−E7 (see Figure 2 and drawing **E**). The alkyl groups impart a major asymmetry into the central E_7 units as evidenced by the ∼20° compression of the E3−E1−E2 angles (87° for **3**, 85.2° for **4**) relative to the E4−E1−E3 and E4−E1−E2 angles (106.0°, average for **3**; 106.2°, average for **4**). For comparison, the corresponding angles in the R_3E_7 (R = Me_3Si, Me_3Ge, Me_3Sn) are all equivalent at 98.8° (R_3As_7)[15] and 98.6° (R_3P_7, average).[24] The distortions in the present compounds presumably result from the steric pressure between the benzyl groups and the E4 atom and the reduced electronic repulsion between the formally neutral E2 and E3 atoms. Similar but less pronounced distortions are present in the E_7^{3-} ions present in Ba_3P_{14} and Ba_3As_{14}.[20−22]



In addition to the angular distortions about the E_7 cages, there are also distortions in height. As indicated by von Schnering and Korber,[25] the distances from the apical phosphorus atom to the center of the basal triangular plane (see *h* in drawing **D**) are elongated by 0.15 Å in the neutral R_3P_7 molecules (*h* = 3.15 Å)[6−8,23] relative to the parent P_7^{3-} ion (*h* = 3.00 Å).[21,25,26] Korber and von Schnering recently showed that the height of the $H_2P_7^-$ ion (*h* = 3.09 Å) was intermediate to the two limiting cases as expected.[25] The height of **3** is 3.08 Å, which is similar to that of $H_2P_7^-$, as expected. However, the "legs" of **3** are asymmetric in that the P1−P4 and P4−P7 distances are 0.06 and 0.08 Å shorter than the corresponding distances involving P2 and P3. The same asymmetries exist in **4**. The height of **4** (*h* = 3.40 Å) is only slightly greater than that of the As_7^{3-} ion in Ba_3As_{14} (*h* = 3.38 Å)[20] and is relatively compressed with respect to the neutral R_3As_7 compounds (*h* = 3.47 Å, average).[15] The angular distortions and the asymmetries in height were not identified (or are not present) in the $H_2P_7^-$ ion presumably due to the complicated disorder present in the crystal structure.[25]

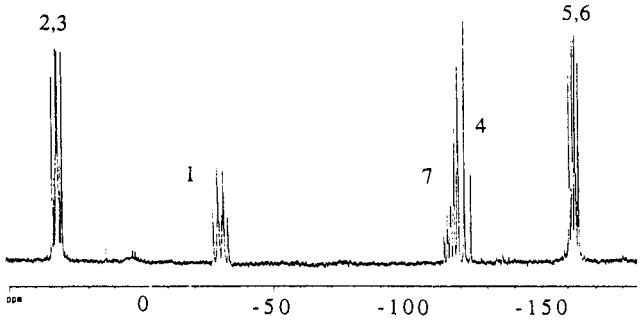


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of $(EtOCOCH_2)_2P_7^-$ (crude reaction mixture) recorded in DMSO-d_6 at 25 °C and 161.96 MHz. The peak assignments correspond to the atomic-numbering scheme used in Figures 1 and 2.

Finally, there is a subtle difference in bond angles in the two structures at the E2 and E3 atoms (see Table 2). The angle formed between the E2−C1 bond vector and the plane defined by E1, E5, and E2 (see α, drawing **E**) varies from 110.0° (average) for **4** to 113.3° for **3**.[27] The more acute angle in the arsenide is consistent with the reduced hybridization of As relative to P as has been seen in many alkyl−pnictogen compounds.[28,29]

Spectroscopic Studies. The NMR spectral data, including assignments, are given in the Experimental Section. The data are quite similar to those of the $R_2P_7^-$ ions (R = Me, Et, Bu) described previously. Brief discussions of the present data are given below.

The $^{31}P\{^1H\}$ NMR spectra for compounds **3**, **7**, and **8** show five second-order resonances with relative intensities of 2:1:1:1:2, which is consistent with their solid state structures. The spectrum of **7** is shown in Figure 3 as an example. Proton-coupled ^{31}P NMR and 2-D $^{31}P-^{31}P$ COSY NMR experiments allow for the unequivocal assignment of the five resonances in the ^{31}P NMR spectrum (labeled in Figure 3). The resonance of intensity 2 that is downfield of H_3PO_4 arises from the chemically equivalent alkylated phosphorus atoms P2 and P3 and varies in chemical shift between 32.0 and 58.6 ppm for the three ions. The P2/P3 resonance for $Me_2P_7^-$ is further upfield

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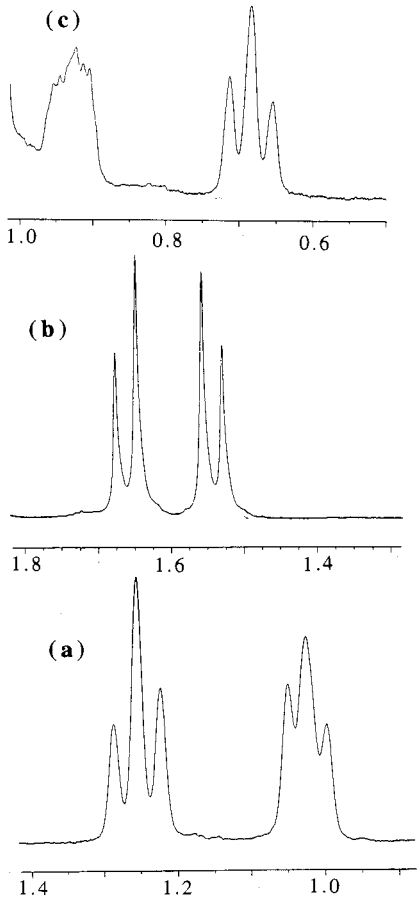

Figure 4. ^{1}H NMR spectra of α-CH_2 methylene regions of (a) $(PhCH_2)_2P_7^-$, (b) $(PhCH_2)_2As_7^-$, and (c) $(EtOCOCH_2)_2P_7^-$ showing the AB patterns of the diastereotopic methylene protons. All spectra were recorded in DMSO-d_6 at 25 °C and 400.13 MHz.

at 12 ppm.[12,30] The chemical shifts of the other four phosphorus resonances do not vary significantly from compound to compound (±5 ppm).[12]

The ^{1}H NMR spectra for **7** and **8** were assigned by using a combination of ^{1}H{^{31}P}NMR and ^{1}H−^{1}H COSY experiments. The ^{1}H NMR spectra for **3** and **4** were assigned on the basis of the solid state structures. For **3**, **4**, and **7**, the CH_2 protons of the α-carbon atoms are diastereotopic, as expected, giving rise to characteristic AB patterns (see Figure 4). In all cases, these resonances move upfield from the ammonium ion precursors. For example, the α-CH_2 protons in $(EtOCOCH_2)Me_3N^+$ give rise to a singlet at 4.75 ppm but appear as AB multiplets at 0.69 and 0.91 in **7** (see Figure 4). The resonances are complicated due to multiple couplings to phosphorus ($^2J_{^1H-^{31}P} \approx 12$ Hz, plus smaller three-bond couplings) as well as geminal hydrogen coupling ($^2J_{^1H-^1H} \approx 11$ Hz). The ethyoxy methylene protons are also diastereotopic in **7** and **8**, giving rise to AB multiplets instead of the quartets observed in the $(EtOCOCHMe)Me_3N^+$ precursors.

The ^{13}C NMR spectra were assigned with the aid of ^{13}C−^{1}H HMQC and standard ^{13}C{^{1}H} NMR experiments. The α-carbons of **3** and **4** resonate at 28.0 and 29.1 ppm, respectively, with the former being broad due to unresolved coupling to phosphorus. The α-carbons of **7** and **8** resonate at 26.6 and 30.5 ppm, respectively, and are also broadened due to unresolved coupling to phosphorus. The carbonyl carbons of **7** and **8** appear at 171.1 and 174.0 ppm, respectively.

The different diastereomers of **8** were indistinguishable by either ^{31}P NMR, ^{13}C NMR, or ^{1}H{^{31}P} NMR spectral analysis.

Discussion

Although the basicity of the E_7^{3-} ions is relatively modest (i.e., they do not deprotonate acids with $pK_a > \sim 20$ in DMSO),[31] their nucleophilicity is exceptional. The transfer of R^+ from tetraalkylammonium ions has been noted before in sulfide chemistry[32−34] and in the decomposition of Sn_9,[4−35] but we know of no other anions that possess the nucleophilicity to effect the transfer of 2 equiv of R^+ and for such a generic range of R. More importantly, the reactions are stereospecific, giving only one of the three possible isomers; however, the origin of the stereospecificity of these reactions is not clear at present.

Although the extension of the chemistry to arsenic is not in itself remarkable, the fact that 2 equiv is again transferred with the same product stereoselectivity was not altogether expected. The Brønsted and Lewis basicity of arsenic is known to be less than that of phosphorus,[36] and one might have anticipated some change in reactivity (i.e., the transfer of only one R^+).

The structures of the $(PhCH_2)_2E_7^-$ ions confirm which isomer is formed in eq 4 chemistry and show that there are significant asymmetries in the E_7 cages of the compounds. The change in formal charge at the E2 and E3 atoms upon alkylation causes a slight asymmetry in height, but the largest distortion in the compounds is the variation in angles about E1. The acute E2−E1−E3 angles give rise to rather short E2−E3 separations. The reduced E2−E3 separations in **3** and **4** relative to the parent E_7^{3-} ions is reminiscent of the norbornadiene-like $[E_7M(CO)_3]^{3-}$ complexes[37] and the Ba_3As_{14} and Ba_3P_{14} solids.[20−22]

Finally, the reactions of methylated amino acid esters with the E_7^{3-} ions indicate that we can transfer chiral carbon centers directly to the E_7 framework. Although we were unable to discern the stereochemistry at carbon through the preparation of the different diastereomers, the fact that the electrophilic $CHRCO_2Et$ is transferred preferentially to Me in eq 7 chemistry is consistent with the proposed[12] S_N2 mechanism. Supporting this hypothesis is the reaction of the carboxylate zwitterion $Me_3N^+CH_2COO^-$ with P_7^{3-} to give exclusively the methyl compound **5**. The electron-donating carboxylate group renders the α-C less electropositive than the Me groups, and thus Me transfer is observed. The ethyl ester $(EtOCOCH_2)Me_3N^+$, however, renders the α-C more electropositive than the Me groups, and $EtOCOCH_2$ transfer is observed. Only when the α-carbon becomes sterically hindered (and/or more electron rich) does Me transfer become competitive with ester transfer. For alanine (eq 7, R = Me), **5** is the dominant product and is formed in relative excess to **8** by a 2.5:1 ratio. Statistically, the ratio of **5** to **8** should be 3:1 in eq 7 chemistry if there were no steric or electronic preference. Since the observed concentration of **5** is less than what is statistically expected, it can be inferred

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that ester transfer is still kinetically favored in eq 7 chemistry (R = Me) even though the Me transfer product is formed in higher concentration. For leucine (eq 7, R = *i*-Bu), the Me compound **5** is the only product.[38]

Studies designed to probe the stereochemistry at carbon are in progress as are efforts to attach polypeptides to the P_7 cage.[38]

Experimental Section

General. Standard operating procedures used in our laboratory have been described elsewhere.[37] All reactions involving arsenic and phosphorus were conducted in an inert atmosphere drybox. Proton (^{1}H), ^{31}P, and ^{13}C NMR spectra were recorded at ambient temperatures on Bruker AF200, AMX 400, AMX 500, and AM400 spectrometers. ^{1}H−^{1}H and ^{31}P−^{31}P COSY experiments and the ^{13}C−^{1}H HMQC experiments were run on an AMX 500. For the NMR data that follows, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, pt = pseudo triplet arising from a doublet of doublets, and 2nd ord mult = second-order multiplet. Peak assignments correspond to the atomic-numbering scheme used in the text, tables, and figures. Elemental analyses were performed under inert atmospheres by Desert Analytics, Tucson, AZ. Electrospray mass spectra were recorded from DMF solution on a Finnigan LCQ mass spectrometer through direct injection. The samples were ionized by using an ESI probe and detected in the negative mode. DMF and DMSO were distilled under nitrogen at reduced pressure from K_4Sn_9. Ethylenediamine was distilled several times from CaH_2 under N_2 at reduced pressure and finally from K_4Sn_9.

Synthesis. Melts of nominal composition K_3P_7 and K_3As_7 were prepared by fusing the elements at ∼1000 °C in sealed, evacuated silica tubes. **CAUTION**: Polypnictides are known to spontaneously detonate even under anaerobic conditions.[3] Extreme care must be used when preparing alkali polypnictides by this method. The synthesis of the $Me_2P_7^-$ was reported previously.[30] The (EtOCOCHR)Me_3N^+ ions were prepared as I^- salts from the corresponding amino acids (*R*)-alanine, (*S*)-alanine, and glycine according to published procedures.[39,40] The amino acids were purchased from BaChem and used as received.

Preparation of [(PhCH$_2$)$_2$P$_7$][PPh$_4$]. K_3P_7 (100 mg, 0.30 mmol) and (PhCH$_2$)Me_3NBr (140 mg, 0.61 mmol) were stirred in en (ca. 3 mL) at room temperature for 16 h. The resulting yellow-orange solution was then evaporated to dryness and the residue extracted in ca. 3 mL of acetonitrile containing PPh_4Br (130 mg, 0.31 mmol) to give a yellow solution and a white precipitate. The solution was then filtered through tightly packed glass wool in a pipet. After ca. 5 h, the reaction vessel contained transparent yellow crystals. The crystals were isolated and dried under vacuum. Yield: 126 mg (58%). Anal. Calcd for $C_{38}H_{34}P_8$: C, 61.79; H, 4.63. Found: C, 61.12; H, 4.71.

^{31}P{^{1}H} (DMSO-d_6): δ (ppm) 40.5 [2nd ord mult, 2P, P(1)], 25.0 [s, PPh_4], −35.5 [2nd ord mult 1P, P(2)], −116.0 [2nd ord mult, 1P, P(3)], −128.0 [2nd ord mult 1P, P(4)], −165.0 [2nd ord mult, 2P, P(5)]. ^{1}H NMR (DMSO-d_6): δ (ppm) 1.02 [pt, 1 H, $^2J_{H-P} \approx 10$ Hz, $^2J_{H-H} \approx 12$ Hz: *CH*$_2$Ph], 1.26 [pt, 1 H, $^2J_{H-P} \approx 12$ Hz, $^2J_{H-H} \approx 12$ Hz: *CH*$_2$Ph], 6.90−7.17 [CH$_2$*Ph*], 7.61−7.94 [P*Ph*$_4$]. ^{13}C{^{1}H} (DMSO-d_6): δ (ppm) 28.0 [br, *CH*$_2$Ph], 129.3, 128.3, 127.7 [CH$_2$*Ph*], 141.2 [CH$_2$*Ph*, ipso].

Preparation of [K(2,2,2-crypt)][(PhCH$_2$)$_2$As$_7$]. K_3As_7 (50 mg, 0.078 mmol), 2,2,2-crypt (30 mg, 0.079 mmol), (PhCH$_2$)Me_3NBr (36 mg, 0.16 mmol), and en (ca. 3 mL) were stirred for 18 h in a vial at room temperature. The resulting dark-red brown colored solution contained an orange precipitate. The mixture was then heated to ca. 60 °C until the precipitate dissolved to give a red colored solution. The heated solution was then filtered through tightly packed glass wool in a pipet. After 24 h the reaction vessel contained red colored crystals, which were isolated and dried under vacuum. Yield: 46.1 mg (53%). Anal. Calcd for $C_{32}H_{50}N_2O_6KAs_7$: C, 34.24; H, 4.45. Found: C, 34.36; H, 4.43.

^{1}H NMR (DMSO-d_6): δ (ppm) 1.53 [d, 1 H, $^2J_{H-H} = 10.8$ Hz, *CH*$_2$Ph], 1.64 [d, 1 H, $^2J_{H-H} = 10.8$ Hz, *CH*$_2$Ph], 6.90−7.17 [CH$_2$*Ph*], 3.47, 3.45, 2.44 [m, (2,2,2-crypt)]. ^{13}C{^{1}H} (DMSO-d_6): δ (ppm) 29.1 [*CH*$_2$Ph], 128.8, 128.3, 125.2 [CH$_2$*Ph*], 143 [CH$_2$*Ph*, ipso], 70.3, 67.5, 53.7 [K(2,2,2-crypt)]$^+$.

Preparation of K[(EtOCOCH$_2$)$_2$P$_7$]. K_3P_7 (30 mg, 0.089 mmol) and (EtOCOCH$_2$)Me_3NCl (35 mg, 0.19 mmol) were stirred in DMF at room temperature for 12 h, yielding a yellow-orange solution. An aliquot of the solution was used for EMS analysis. The remaining solution was evaporated to dryness to give an orange oil. The oil was extracted into DMSO-d_6 and the solution used for NMR studies.

^{31}P{^{1}H} (DMSO-d_6): δ (ppm) 32.0 [2nd ord mult, 2P, P(1)], −29.5 [2nd ord mult, 1P, P(2)], −116.7 [2nd ord mult, 1P, P(3)], −119.1 [2nd ord mult, 1P, P(4)], −161.9 [2nd ord mult, 2P, P(5)]. ^{1}H NMR (DMSO-d_6): δ (ppm) 0.69 [pt, 1 H, $^2J_{H-P} \approx 12$ Hz, $^2J_{H-H} \approx 12$ Hz, P$_7$C*H*$_2$CO$_2$Et], 0.91 [br, 1 H, P$_7$C*H*$_2$CO$_2$Et], 1.06 [t, 3H, $^2J_{H-H} = 6.8$ Hz, OCH$_2$*CH*$_3$], 3.89 [q, 3H, $^2J_{H-H} = 7.2$ Hz, O*CH*$_2$CH$_3$]. ^{13}C{^{1}H} (DMSO-d_6): δ (ppm) 14.6 [OCH$_2$*CH*$_3$], 26.6 [br, P$_7$*CH*$_2$CO$_2$Et], 60.39 [O*CH*$_2$CH$_3$], 171.1 [P$_7$CH$_2$*C*O$_2$Et].

Preparation of K[(EtOCOCHMe)$_2$P$_7$]. A procedure identical to that described for K[(EtOCOCH$_2$)$_2$P$_7$] was followed except (EtOCOCHMe)Me_3NI (50 mg, 0.17 mmol) was used instead of (EtOCOCH$_2$)Me_3NCl. *R* and *S* enantiomers were prepared independently by the same procedures. The reactions were identical.

^{31}P{^{1}H} (DMSO-d_6): δ (ppm) 58.58 [2nd ord mult, 2P, P(1)], −32.0 [2nd ord mult, 1P, P(2)], overlapping peaks at ca. −118 and −126 [2nd ord mult, 2P, P(3), P(4)], −159.0 [2nd ord mult, 2P, P(5)].

^{1}H NMR (DMSO-d_6): δ (ppm) 0.30 [br, 1H,P$_7$C*H*Me], 0.93 [m, 3H, P$_7$CH*Me*] , 1.02 [t, 3H, $^2J_{H-H} = 8$ Hz, OCH$_2$*CH*$_3$], 3.81 [m, 2H, O*CH*$_2$CH$_3$]. ^{13}C{^{1}H} (DMSO-d_6): δ (ppm) 14.64 [OCH$_2$*CH*$_3$], 19.24 [br, P$_7$CH*Me*], 30.53 [br, P$_7$*C*HMe], 60.08[O*CH*$_2$CH$_3$], 174.0 [*CO*$_2$Et].

Crystal Structure Determination for (PPh$_4$)3. An orange-rust colored irregular block with approximate dimensions 0.50 × 0.50 × 0.50 mm was placed on the Enraf-Nonius CAD-4 diffractometer. Data were collected [Mo Kα] with ω/2θ scans over the θ range 2.3−25.0° with a scan width of (0.90 + 0.45tan θ)° and a variable scan speed of 4.1−5.5 deg min.$^{-1}$ A total of 12 680 reflections were collected; 6342 unique [*R*(int) = 0.0357]. Minor, 1−3%, variations in intensity were observed; data were not corrected. Nine ψ-scan reflections were collected over the θ range 5.5−17.8°, and the absorption correction was applied with transmission factors ranging from 0.6583 to 0.7718. Data were corrected for Lorentz and polarization factors and reduced to F_o^2 and $\sigma(F_o^2)$.

The systematic absences clearly indicated the centrosymmetric space group *Pbca* (No. 61), which was confirmed by successful solution and refinement of the structure. The structure was determined by direct methods using the program XS,[41] which resulted in the successful location of many of the non-hydrogen atoms comprising the ion of interest and the cation. An initial difference Fourier map revealed the locations of the remaining non-hydrogen atoms. The structure was refined with XL.[41] Hydrogen atoms were placed in calculated positions. As the refinement converged with all non-hydrogen atoms anisotropic, several peaks continued to appear within the P_7 core with peak heights as large as $|\Delta\rho| \leq -0.97$ e Å^{-3} indicating potential disorder. The phosphorus atoms within the P_7 complex were set isotropic and modeled with a minor constituent present. The final major:minor was 0.9542: 0.046. SAME instructions were used to force the second minor constituent to mirror the major. The carbon atoms attached to the P7 core were also input with a major:minor presence thereby allowing the correct calculation of the hydrogen atoms. The minor constituent atoms had their thermal parameters fixed to be equivalent (EADP). All of the non-hydrogen atoms were refined anisotropically, and the structure was refined to convergence. A final difference Fourier map was featureless with $|\Delta\rho| \leq 0.41$ e Å^{-3}, indicating that the structure is both correct and complete.

Crystal Structure Determination for [K(2,2,2-crypt)]4. An orange colored block with dimensions 0.52 × 0.50 × 0.16 mm was placed and optically centered on the Enraf-Nonius CAD-4 diffractometer. The data were collected and corrected as described above. One form of

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data was collected, indices $\pm h,-k,l$; resulting in the measurement of 4037 reflections; 3849 unique [R(int) = 0.0466]. Nine ψ-scan reflections were collected over the θ range 4.9−18.7°; the absorption correction was applied with transmission factors ranging from 0.1146 to 0.9317.

Intensity statistics and systematic absences clearly indicated the centrosymmetric monoclinic space group *I*2/*a* (No. 15); nonstandard setting for *C*2/*c*. The structure was determined by direct methods with the successful location of the seven arsenic atoms and one potassium atom using the program XS.[41] The structure was refined with XL.[41] After several cycles of refinement, all of the non-hydrogen atoms were refined anisotropically, except for C16 and O21. The structure was refined to convergence. A final difference Fourier map was essentially featureless, with the largest peak, $|\Delta\rho| \leq -1.01$ e Å^{-3}.

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Supporting Information Available: A complete listing of positional parameters, thermal parameters, bond distances and angles for (PPh_4)**3** and [K(2,2,2-crypt)]**4** (26 pages). Ordering information is given on any current masthead page.

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