Tetraalkylammonium Salts as Stereospecific Alkylating Agents for Highly Nucleophilic Polyphosphide Zintl Anions: Preparation of $[RP_7W(CO)_3]^{2-}$, $[R_2P_7]^-$, and $R_2R'P_7$ Compounds from R_4N^+ Reagents

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Abstract: $[K(2,2,2\text{-crypt})]_3[P_7W(CO)_3]$ reacts with R_4N^+ salts (R = Me, Et, *n*-Bu) in ethylenediamine (en) or dimethylformamide (DMF) solutions to give the $[RP_7W(CO)_3]^{2-}$ ions (**4**) and R_3N in high yields. Similar reactions involving $Me(n\text{-}C_8H_{17})_3N^+$ and $(CH_2Ph)Me_3N^+$ give the $[MeP_7W(CO)_3]^{2-}$ and $[(CH_2Ph)P_7W(CO)_3]^{2-}$ ions, respectively. Reactions of $[HP_7W(CO)_3]^{2-}$ with olefins did not affect insertions into the P−H bond to give compounds **4**. These data indicate that the alkylations proceed by way of nucleophilic attack at the α-carbon of the tetraalkylammonium ions and not by a radical electron transfer pathway or a Hofmann elimination/olefin insertion pathway. Compounds **4** were characterized by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopic studies, microanalyses, and representative crystallographic studies. They possess C_1 symmetry in the solid state but display C_s symmetry in solution due to an intramolecular wagging process. The $^{31}P\{^1H\}$ NMR spectra for **4** reveal an AA′BB′MM′X spin system. Crystal data for $[K(2,2,2\text{-crypt})]_2[EtP_7W(CO)_3] \cdot$ en: triclinic, space group $P\bar{1}$, a = 12.176(3) Å, b = 15.106(2) Å, c = 18.975(2) Å, α = 93.509(10)°, β = 98.833(13)°, γ = 111.472(12)°, V = 3183.1(9) Å^3, Z = 2; $R(F)$ = 4.29% and $R_w(F^2)$ = 10.34%. The P_7^{3-} ion reacts with excess R_4N^+ (R = Me, Et, *n*-Bu) in en or DMF solutions to give symmetrical $[R_2P_7]^-$ ions (**5**) in quantitative yields. The reactions are stereospecific in that only one of three possible isomers is formed in each case. Compounds **5** have been characterized by ^1H, ^{13}C, and ^{31}P and 2-D $^{31}P-^{31}P$ COSY NMR spectroscopic studies. Compounds **5** react with alkyl halides, R′X where R′ = CH_2Ph, X = Cl; R′ = Me, X = I; R′ = *n*-Bu, X = Br to give mixtures of the symmetric and asymmetric isomers (~1:10 ratios) of $R_2R'P_7$ compounds (**6**). The symmetric and asymmetric isomers are formed competitively from compounds **5** and do not interconvert in solution. Spectroscopic studies on the formation of the $(n\text{-}Bu)_3P_7$ compound (**6e**) show virtually quantitative "one pot" syntheses of compounds **6** from the P_7^{3-} parent ion but studies of the other members of compounds **6** were hampered by their low solubilities. All compounds **6** are thermally unstable to some extent with the sterically hindered compounds being somewhat more robust than their less hindered analogs. They have been characterized by ^{31}P NMR spectroscopy and FAB-MS (M + 1 molecular ions).

Introduction

The polyphosphide Zintl ions represent a remarkable class of compounds that have a rich structural diversity and a unique chemistry.[1−3] For example, K_3P_7 dissolves congruently in ethylenediamine (en) to give discrete P_7^{3-} ions (**1**) that adopt the nortricyclane structure.[3] In a valence bond formalism, one can assign a negative charge to each two-coordinate phosphorus atom. Surprisingly, addition of PPh_4Br to an en solution of P_7^{3-} affects an unusual oxidative coupling to give the P_{16}^{-2} ion in low but reproducible yields.[4] The P_{16}^{2-} structure (see Chart 1) contains two nortricyclic P_7 units fused by a central P_2 fragment, however, the mechanism of its formation is unclear. Baudler,[5−7] Hönle,[8−10] von Schnering,[2,9] and Fenske[11] have shown that P_7^{3-} can be derivatized in a systematic fashion to give various alkylated, protonated, and metalated compounds (*e.g.* R_3P_7, H_3P_7, $(Me_3Pb)_3P_7$). Recently, we and others have begun investigating the transition metal chemistry of the E_7^{3-} polypnictide anions where E = P, As, Sb.[12−17] These studies have yielded many new compounds that include the series of $[E_7M(CO)_3]^{3-}$ ions[13,14,17] where E = P, As, Sb and M = Cr, Mo, W as shown in eq 1. Equation 1 chemistry requires 2,2,2-

$$K_3E_7 + M(CO)_3L + 3\ (2,2,2\text{-crypt}) \rightarrow [K(2,2,2\text{-crypt})]_3[E_7M(CO)_3] + L \quad (1)$$

M = Cr, Mo, W; E = P, As, Sb; L = arene, cycloheptatriene

crypt or 18-crown-6 "activators" to break the E_7^{3-}/K^+ ion

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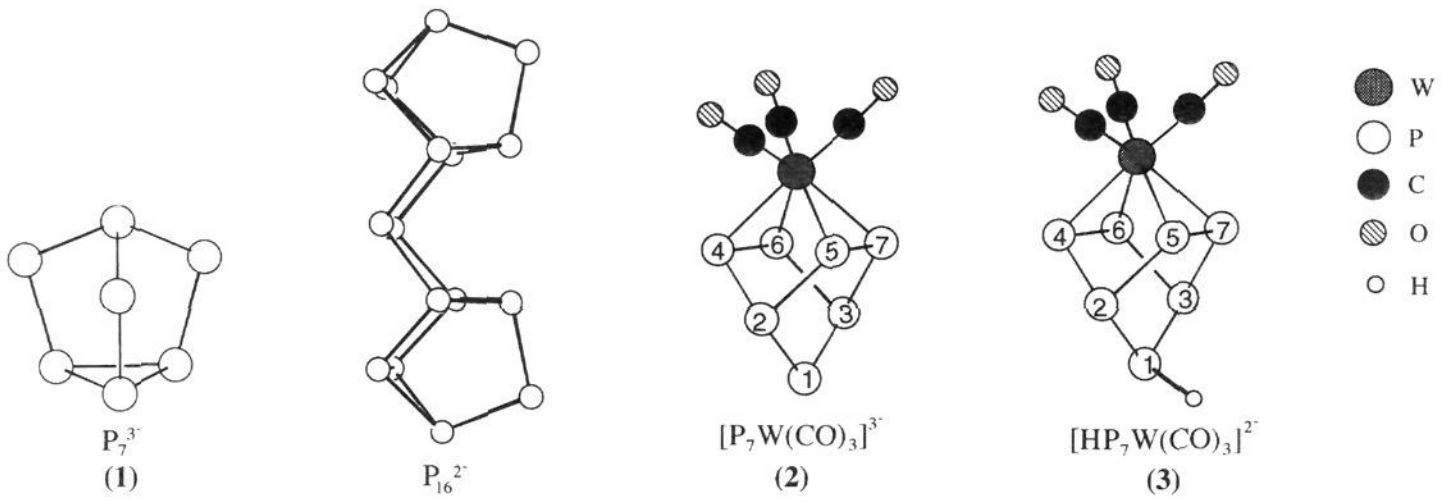
Chart 1



P_7^{3-} (**1**) P_{16}^{2-} $[P_7W(CO)_3]^{3-}$ (**2**) $[HP_7W(CO)_3]^{2-}$ (**3**)

pairing in solution before complexation to the transition metal can occur. The $[E_7M(CO)_3]^{3-}$ compounds have norbornadiene-like E_7 fragments, {*e.g.* $[P_7W(CO)_3]^{3-}$ (**2**)}, with a formal negative charge associated with the unique two-coordinate E atom furthest from the transition metal (the E(1) site). The pnictogen atom remains highly nucleophilic and is the site of attack by various electrophiles. For example, the $[P_7W(CO)_3]^{3-}$ ion (**2**) can be protonated to give the $[HP_7W(CO)_3]^{2-}$ ion (**3**) in which the hydrogen is attached to the nucleophilic P(1) atom (see drawing of **3** and eq 2).[13,18]

$$\underset{\mathbf{2}}{[P_7W(CO)_3]^{3-}} + H^+ \rightarrow \underset{\mathbf{3}}{[HP_7W(CO)_3]^{2-}} \qquad (2)$$

During the course of our studies of the $[P_7M(CO)_3]^{3-}$ compounds, we observed an unusual reaction with tetraalkylammonium salts in which the R_4N^+ ions served as alkylating agents. Herein, we describe the ambient temperature alkylations of the $[P_7M(CO)_3]^{3-}$ compounds and their P_7^{3-} precursor using R_4N^+ salts (where R = Me, Et, *n*-Bu) as R^+ sources.

Results

Syntheses. Ethylenediamine solutions of $[P_7W(CO)_3]^{3-}$ (**2**) react with excess R_4NBr to give dark red $[RP_7W(CO)_3]^{2-}$ compounds where R = Me (**4a**), Et (**4b**), *n*-Bu (**4c**) in *ca.* 37–69% crystalline yields (eq 3) as the $[K(2,2,2\text{-crypt})]^+$ salts. ^{31}P NMR spectroscopic studies show modest rates of reaction (t_∞

$$\underset{\mathbf{2}}{[P_7W(CO)_3]^{3-}} + \text{excess } R_4N^+ \rightarrow \underset{\substack{\mathbf{4a},\ R = Me\\ \mathbf{4b},\ R = Et\\ \mathbf{4c},\ R = n\text{-}Bu}}{[RP_7W(CO)_3]^{2-}} + R_3N \qquad (3)$$

$\approx$ 1 h) and virtually quantitative conversions to compounds **4** at ambient temperatures when R = Et, *n*-Bu. Because of the limited solubility of the Me_4N^+ ion in en, the formation of **4a** required gentle heating (*ca.* 40 °C) to obtain similar reaction rates. Like the protonation reactions, alkylation occurs at the P(1) site (see drawing of **2**) which is the most nucleophilic site on the precursor **2**. The mixed alkylammonium ions $Me(n\text{-}C_8H_{17})_3N^+$ and $(CH_2Ph)Me_3N^+$ gave quantitative conversions to the $[MeP_7W(CO)_3]^{2-}$ and $[(CH_2Ph)P_7W(CO)_3]^{2-}$ ions, respectively, as shown in eqs 4 and 5. Equation 4 chemistry

$$\underset{\mathbf{2}}{[P_7W(CO)_3]^{3-}} + \text{excess } Me(n\text{-}C_8H_{17})_3N^+ \rightarrow \underset{\mathbf{4a}}{[MeP_7W(CO)_3]^{2-}} + (n\text{-}C_8H_{17})_3N \qquad (4)$$

$$\underset{\mathbf{2}}{[P_7W(CO)_3]^{3-}} + \text{excess } (CH_2Ph)Me_3N^+ \rightarrow \underset{\mathbf{4d}}{[(CH_2Ph)P_7W(CO)_3]^{2-}} + Me_3N \qquad (5)$$

$$\underset{\mathbf{3}}{[HP_7W(CO)_3]^{2-}} + \text{excess ethylene} \not\rightarrow \underset{\mathbf{4b}}{[EtP_7W(CO)_3]^{2-}} \qquad (6)$$

affords a higher yield of **4a** (49% crystalline yield) than that obtained from eq 3. Attempts to prepare compounds **4** from olefin insertions into the P–H bond of **3** (eq 6) were unsuccessful. Attempted alkylations of **2** with alkyl halides were also unsuccessful. The implications of reactions 4–6 will be presented in the Discussion section.

Tetraalkylphosphonium ions such as Ph_4P^+ and $(n\text{-}Bu)_4P^+$ are unreactive towards compounds **2** and, in fact, aid in crystal growth of related *tri*anionic metalated Zintl ion compounds by replacing $[K(2,2,2\text{-crpyt})]^+$ cations in the crystal lattice.[19] Compounds **4** are air and moisture sensitive and have been characterized by ^1H, ^{13}C, and ^{31}P NMR and IR spectroscopic studies, microanalyses, and a representative single-crystal X-ray diffraction study.

Because of the unusual nature of the above alkylation reaction, we wondered if the use of alkylammonium salts would affect multiple alkylations of P_7^{3-} in analogy to the alkyl halide chemistry described by Baudler and von Schnering.[7,9,20] Surprisingly, reactions of P_7^{3-} with excess R_4N^+ give quantitative conversions (one product by ^{31}P NMR spectroscopy) to the symmetrical *di*substituted $[R_2P_7]^-$ products (eq 7) where R =

$$\underset{\mathbf{1}}{P_7^{3-}} + \text{excess } R_4N^+ \rightarrow \underset{\substack{\mathbf{5a},\ R = Me\\ \mathbf{5b},\ R = Et\\ \mathbf{5c},\ R = n\text{-}Bu}}{[R_2P_7]^-} + 2R_3N \qquad (7)$$

Me (**5a**), Et (**5b**), and *n*-Bu (**5c**). These alkylation reactions proceed slowly at room temperature (t_∞ = 6–12 h) but, unlike the metalation reactions, do not require crypt or crown ether activators. However, the use of crypt or crown ethers appears to accelerate the reaction rates and all three compounds have been prepared as the K^+, $[K(18\text{-crown-6})]^+$, and $[K(2,2,2\text{-crypt})]^+$ salts. The use of only 1 equiv of R_4N^+ in eq 7 results in mixtures of compounds **5** and unreacted starting material **1**.

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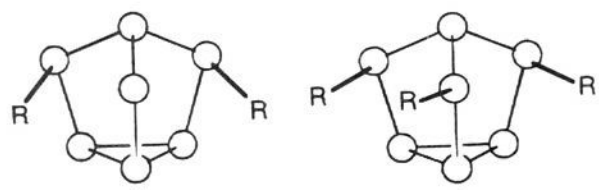
Table 1. FAB-MS Data for $R_2R'P_7$ Compounds (**6**)[a]

compd	*m/z*	% intensity	ion	
Me_3P_7 (**6a**)	263	20.8	$[C_3H_{10}P_7]^+$	(HM^+)
	247	11.7	$[C_2H_6P_7]^+$	$(M^+ - CH_3)$
$(CH_2Ph)Me_2P_7$ (**6b**)	339	64.7	$[C_9H_{14}P_7]^+$	(HM^+)
	323	18.8	$[C_8H_{10}P_7]^+$	$(M^+ - CH_3)$
	247	26.3	$[C_2H_6P_7]^+$	$(M^+ - CH_2Ph)$
$(n\text{-Bu})_2MeP_7$ (**6c**)	347	61.6	$[C_9H_{22}P_7]^+$	(HM^+)
	331	12.2	$[C_8H_{18}P_7]^+$	$(M^+ - CH_3)$
	289	31.6	$[C_5H_{12}P_7]^+$	$(M^+ - C_4H_9)$
$(CH_2Ph)(n\text{-Bu})_2P_7$ (**6d**)	423	10.1	$[C_{15}H_{26}P_7]^+$	(HM^+)
	365	8.39	$[C_{11}H_{16}P_7]^+$	$(M^+ - C_4H_9)$
	331	12.5	$[C_8H_{18}P_7]^+$	$(M^+ - CH_2Ph)$
$(n\text{-Bu})_3P_7$ (**6e**)	389	57.0	$[C_{12}H_{28}P_7]^+$	(HM^+)
	331	53.1	$[C_8H_{18}P_7]^+$	$(M^+ - C_4H_9)$

[a] See Experimental Section for experimental details.

Alkylphosphonium salts do not alkylate the P_7^{3-} ion, however, Ph_4P^+ affects an oxidative coupling to give P_{16}^{2-} as previously mentioned. Compounds **5** have been characterized by ^1H, ^{13}C, ^{31}P NMR, and 2-D ^{31}P-^{31}P COSY NMR spectroscopic studies. Compounds **5** were isolated as oily solids that were contaminated with trialkylamine byproducts and presumably potassium bromide. Repeated attempts to purify the compounds by crystallization/precipitation and sublimation were unsuccessful, and we could therefore only characterize the compounds by spectroscopic methods and by derivatization (see below). Attempts to prepare transition metal derivatives are currently in progress.



5 **6**

Compounds **5** can be alkylated further through reactions with alkyl halide reagents to give neutral $R_2R'P_7$ trialkyl compounds (**6**) (eq 8). For example, **5c** reacts cleanly with *n*-BuBr in DMF to give $(n\text{-Bu})_3P_7$ (**6e**) in good yield. Equation 8 chemistry appears to give virtually quantitative conversions to mixtures

$$\underset{\mathbf{5}}{[R_2P_7]^-} + R'X \rightarrow \underset{\substack{\mathbf{6a},\ R = R' = Me \\ \mathbf{6b},\ R = Me,\ R' = CH_2Ph \\ \mathbf{6c},\ R = n\text{-Bu},\ R' = Me \\ \mathbf{6d},\ R = n\text{-Bu},\ R' = CH_2Ph \\ \mathbf{6e},\ R = R' = n\text{-Bu}}}{R_2R'P_7} + X^- \qquad (8)$$

of isomers, which requires inversion at one alkylated phosphorus position. Due to the extreme insolubility and thermal instability of most of compounds **6**, determination of percent conversions and diasteromeric distributions were quite difficult. Compounds **6a**−**d** are pale orange to white solids that are moderately air sensitive, thermally unstable, and sparingly soluble or insoluble in most solvents (THF, toluene, en, DMF). The *n*-Bu compound **6e** is appreciably soluble in DMF and en and is sparingly soluble in toluene. Compounds **6** have been characterized by ^{31}P NMR spectroscopy and fast atom bombardment mass spectroscopy (FAB-MS). The FAB-MS analyses of compounds **6** showed protonated molecular ions for all compounds along with secondary ions due to loss of various alkyl groups. The data are summarized in Table 1. Because of the thermal instability of compounds **6**, microanlyses were not possible.

Structural Studies. The structure of the $[K(2,2,2,\text{-crypt})]^+$ salt of $[EtP_7W(CO)_3]^{2-}$ (**4b**) was determined by single-crystal X-ray diffraction. An ORTEP drawing of the anion is shown

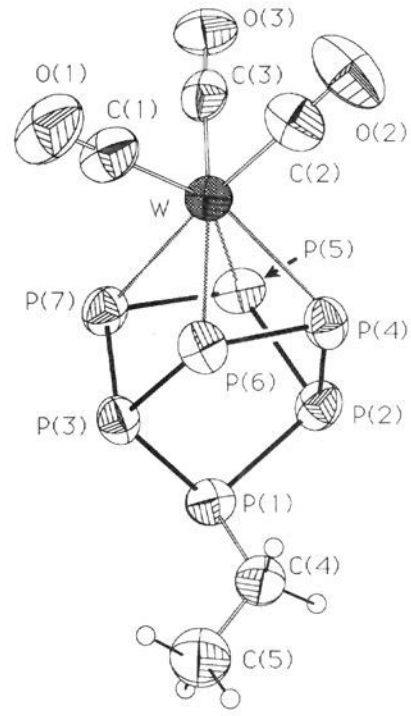


Figure 1. ORTEP drawing of the $[EtP_7W(CO)_3]^{2-}$ ion.

Table 2. Crystallographic Data for $[K(2,2,2\text{-crypt})]_2[EtP_7W(CO)_3]\cdot en$

empirical formula	$C_{43}H_{85}K_2N_6O_{15}P_7W$
formula wt	1405.01
temp, K	293(2)
radiation	Mo Kα($\lambda = 0.71073$ Å)
space group	$P\bar{1}$
cell dimensions	
a, Å	12.176(3)
b, Å	15.106(2)
c, Å	18.975(2)
α, deg	93.509(10)
β, deg	98.833(13)
δ, deg	111.472(12)
volume, Å^3	3183.1(9)
Z	2
density (calcd), g/cm^3	1.466
absorption coeff, mm^{-1}	0.391
crystal size, mm	0.50 × 0.25 × 0.20
reflcns collected	8776
independent reflcns	8301 [*R*(int) = 0.0224]
data/restraints/parameters	8301/0/670
goodness-of-fit on F^2	1.066
final *R* indices [$I > 2\sigma(I)$]	$R(F) = 0.0420$,[a] $wR(F^2) = 0.1023$[b] [6746 data]
largest diff peak and hole, e/Å^3	1.352 and −0.907

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R(wF) = (\sum w(|F_o|^2 - |F_c|^2)^2/\sum wF_o^2)^{1/2}$.

in Figure 1. A summary of the crystallographic data is given in Table 2 and a listing of selected bond distances and angles is given in Table 3. The structure contains a $P_7W(CO)_3$ core that is virtually unperturbed from the parent complex **2**.[13] The attachment of the ethyl group lowers the virtual point symmetry of the ion from C_s to C_1 in the solid state but virtual C_s symmetry is observed in solution (see below). The W−P and P−P bond distances and angles are remarkably similar to those observed for type **2** compounds. The P(4)−P(5) and P(6)−P(7) separations of 2.923(3) and 3.299(3) Å, respectively, are highly asymmetric as is also observed in type **2** compounds.[13] The P−C bond of 1.858(7) Å is typical for compounds of this type and those in trialkylphosphines.[21] The en solvate molecule and the $[K(2,2,2\text{-crypt})]^+$ ions were crystallographically well behaved and were well separated from the anion.

The $[K(2,2,2\text{-crypt})]^+$ salt of **4c** crystallizes with cubic crystal symmetry ($a = 19.0824(7)$ Å) but we were unable to solve the structure.

The alkyl groups of **5** reside on two of the three two-coordinate phosphorus atoms of the parent P_7 cage. Only one

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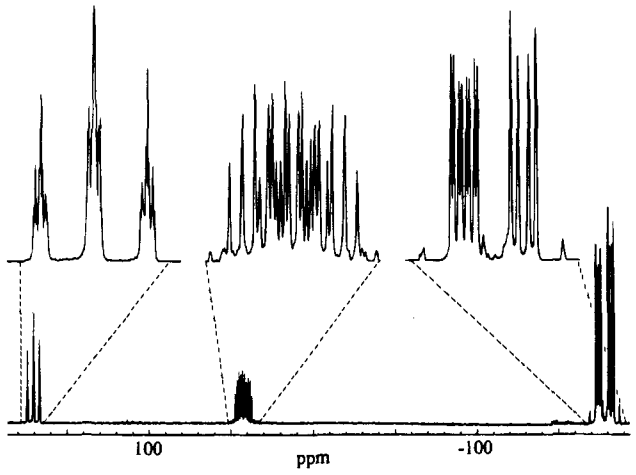
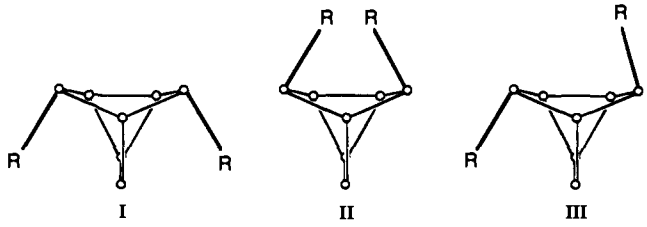
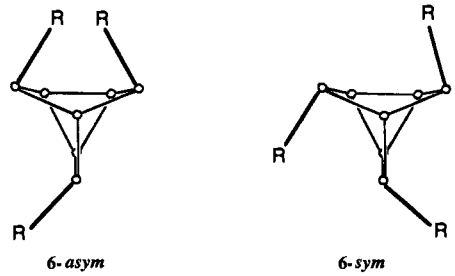


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of $[EtP_7W(CO)_3]^{2-}$ recorded in DMF-d_7 at 28 °C and 81.0 MHz.

two-coordinate P atom remains in compounds **5** (see **I** and the previous drawing of **5**) and it bears a formal negative charge. There are three possible isomers for compounds **5** as illustrated in structures **I**−**III** below (viewed down the former C_3 axis of **1**). Structures **I** and **II** both have C_s point symmetry with mirror planes bisecting the alkyl groups. In both structures, there are two pairs of equivalent phosphorus atoms with the remaining three being unique. In structure **III**, all seven phosphorus atoms are inequivalent. The NMR data show only one isomer in solution (see Spectroscopic Studies) and its spectral features are consistent with both structures **I** and **II**. Based on steric arguments, we believe that **I** is the structure adopted by compounds **5**.



Compounds **6** possess three alkyl groups that are attached to the former two-coordinate phosphorus atoms of **1**. There are two possible isomers of compounds **6**, **6-*sym***, and **6-*asym***, as illustrated below. ^{31}P NMR spectroscopic studies monitoring the formation of **6e** at −20 °C in DMF show that mixtures of isomers **6-*sym*** and **6-*asym*** are present in a 1:10 molar ratio at all stages of conversion. The 1:10 ratio of isomers is independent of temperature (−20 to +50 °C) and solvent (DMF, toluene, en).



Spectroscopic Studies. The ^{31}P NMR spectroscopic data for compounds **4**−**6** are summarized in Table 4 and the remaining spectroscopic data are given in the Experimental Section.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for the $[EtP_7W(CO)_3]^{2-}$ Ion

distances					
W-P(4)	2.581(2)	C(2)-O(2)	1.201(9)	P(5)-P(2)	2.212(2)
W-P(5)	2.584(2)	C(3)-O(3)	1.171(8)	P(6)-P(3)	2.200(3)
W-P(6)	2.673(2)	P(4)-P(6)	2.137(3)	P(7)-P(3)	2.185(3)
W-P(7)	2.676(2)	P(5)-P(7)	2.163(3)	P(1)-P(2)	2.173(3)
W-C(1)	1.918(8)	P(4)-P(5)	2.923(3)	P(1)-P(3)	2.176(3)
W-C(2)	1.911(9)	P(6)-P(7)	3.299(3)	P(1)-C(4)	1.858(7)
W-C(3)	1.953(8)	P(4)-P(2)	2.215(3)	C(4)-C(5)	1.474(10)
C(1)-O(1)	1.183(8)				

angles			
C(2)-W-C(1)	92.9(3)	P(3)-P(6)-W	92.99(7)
C(2)-W-C(3)	81.8(3)	P(6)-P(4)-W	68.28(7)
C(1)-W-C(3)	93.6(3)	P(2)-P(4)-W	103.17(8)
C(1)-W-P(4)	130.8(2)	P(7)-P(5)-W	67.97(7)
C(3)-W-P(4)	133.7(2)	P(2)-P(5)-W	103.16(8)
C(2)-W-P(5)	125.6(2)	P(4)-P(6)-P(3)	103.77(10)
C(1)-W-P(5)	140.6(3)	P(6)-P(4)-P(2)	106.53(10)
C(3)-W-P(6)	175.0(2)	P(1)-P(2)-P(5)	99.07(10)
C(2)-W-P(7)	173.8(2)	O(1)-C(1)-W	177.4(8)
P(5)-W-P(7)	48.53(6)	O(3)-C(3)-W	177.0(6)
P(6)-W-P(7)	76.15(6)	O(2)-C(2)-W	177.4(7)
P(4)-P(6)-W	63.75(7)		

Based on the crystal structure of **4a**, one would anticipate seven ^{31}P resonances due to the seven inequivalent phosphorus atoms observed in the solid state. However, the ^{31}P NMR spectra for **4** (Figure 2) show AA′BB′MM′X spin patterns due to a fluxional process that generates a virtual mirror plane of symmetry. The compounds remain fluxional at −60 °C in DMF-d_7. The data indicate that the $M(CO)_3$ fragments rotate rapidly in the P_4 face of compounds **4** as is common for similar $[E_xM(CO)_3]^{n-}$ complexes[13,22] and related organometallic compounds. The data also indicate that the P(4)−P(5)/P(6)−P(7) asymmetries observed in the solid state are time averaged in solution due to an intramolecular wagging process (see Scheme 1), but inversion at P(1) is not observed on the NMR time scale. These conclusions are based on the following: (1) rapid inversion at P(1) without the wagging process would render P(2) and P(3) *in*equivalent, which is not observed, and (2) rapid wagging *and* inversion at P(1) would make P(4), P(5), P(6), and P(7) all chemically equivalent, which is also not observed. The ^{13}C NMR spectra show a single carbonyl resonance at 229 ppm with $^1J_{W-C} = 167$ Hz and $^2J_{P-C} \leq 4$ Hz. Both coupling constants are only slightly diminished relative to **2** ($^1J_{W-C} = 180$ Hz and $^2J_{P-C} \approx 5$ Hz), which is surprising in view of the significant decrease in charge and the large blue shift in the ν(CO) bands (*ca.* 40 cm^{-1}). This P−C coupling indicates that $W(CO)_3/P_7^{3-}$ dissociation is not occurring on the NMR time scale. The $^1J_{P-C}$ coupling constants to the α-carbons of the alkyl groups range from 26 to 30 Hz which is also typical for alkyl polyphosphorus compounds but larger than the 10−15 Hz coupling observed in trialkylphosphines.[23] The α-hydrogens of **4b**, **4c**, and **4d** are non-diastereotopic in that they are bisected by a mirror plane generated by the wagging process described above.

The IR spectra for compounds **4** each contain three ν(CO) bands between 1874 and 1750 cm^{-1}. Due to the relative decrease in negative charge, these vibraitons are blue shifted by *ca.* 40 cm^{-1} from the parent trianion **2**.

The P−P coupling constants and the general features of the ^{31}P NMR spectra of compounds **5** are quite similar to those of the symmetrical $[H_2P_7]^-$ ion reported by Baudler *et al.*[5] The $^{31}P\{^1H\}$ NMR spectra for compounds **5** show five second-order resonances with relative intensities of 2:1:1:1:2 (Figure 3). The

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(23) Mann, B. E. *J. Chem. Soc., Perkin Trans. 2* **1972**, 30.

Table 4. ^{31}P NMR Data for Compounds **4**, **5**, and **6**[a–c]

compd **4a–d**	P(1)[a]	P(2), P(3)[a]	P(4)/P(5), P(6)/P(7)[a]
$[MeP_7W(CO)_3]^{2-}$ (**4a**)	142 (ttt ^1J(P,P) = 279 Hz, ^2J(P,P) = 28 Hz, ^2J(P,P) = 8.7 Hz)	51 (m)	−178.2 (m), −178.9 (m)
$[EtP_7W(CO)_3]^{2-}$ (**4b**)	170 (ttt, ^1J(P,P) = 290 Hz, 42 (m) ^2J(P,P) = 34 Hz, ^2J(P,P) = 8.4 Hz)	42 (m)	−175 (m), −180 (m)
$[n\text{-}BuP_7W(CO)_3]^{2-}$ (**4c**)	162 (tt, ^1J(P,P) = 296 Hz, ^2J(P,P) = 28 Hz)	41 (m)	−177 (m), −185 (m)
$[(CH_2Ph)P_7W(CO)_3]^{2-}$ (**4d**)	166 (ttt, ^1J(P,P) = 295 Hz, ^2J(P,P) = 28 Hz, ^2J(P,P) = 9.5 Hz)	45 (m)	−176 (m), −184 (m)

compd **5a–c**	P(1)[b]	P(2)[b]	P(3)[b]	P(4)[b]	P(5)[b]
$[Me_2P_7]^-$ (**5a**)	12	−26	−126	−137	−153
$[Et_2P_7]^-$ (**5b**)	25	−38	−123	−135	−165
$[nBu_2P_7]^-$ (**5c**)	28	−35	−121	−131	−161

asymmetric compd **6a**, **b**, **d**, **e**	P(1)[c]	P(2)[c]	P(3)[c]	P(4)[c]	P(5)[c]	P(6)[c]	P(7)[c]
Me_3P_7 (**6a**)	102	76	8	−65	−112	−152	−169
$(CH_2Ph)Me_2P_7$ (**6b**)	131	95	5	−70	−112	−160	−170
$(CH_2Ph)Bu_2P_7$ (**6d**)	132	92	27	−72	−112	−158	−163
$n\text{-}Bu_3P_7$ (**6e**)	122	92	22	−75	−115	−155	−167

symmetric compd **6a**, **e**	P(alkylated)	P(apical)	P(basal)[d]
Me_3P_7 (**6a**)	70	−89	(−152)
Bu_3P_7 (**6e**)	84	−100	(−155)

[a] See Figure 1 for atomic numbering schemes. [b] See Figure 4 for atomic numbering scheme. [c] Atoms P(1–3) are alkylated, P(4) is apical, P(5–7) are basal. [d] Resonance is hidden beneath the P(6) resonance of the asymmetric isomer.

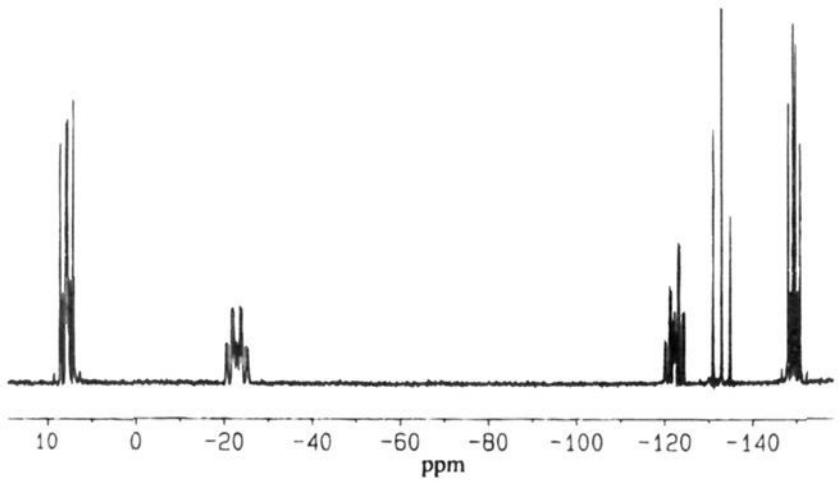
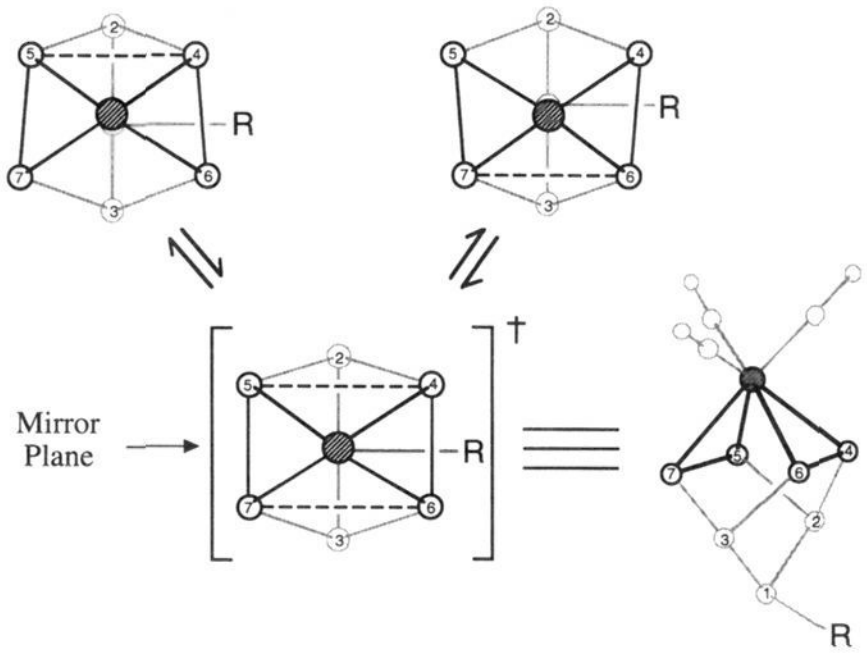


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of $[Me_2P_7]^-$ from a crude reaction mixture of P_7^{3-} and Me_4N^+ recorded in DMF-d_7 at 28 °C and 202.4 MHz.

Scheme 1



solution structure is clearly that of a symmetrical isomer (**I** or **II**) in that seven different ^{31}P resonances of intensity one would be expected for the unsymmetrical isomer (**III**). Through the use of proton coupled ^{31}P NMR and 2-D $^{31}P-^{31}P$ COSY NMR experiments, one can assign all five resonances in the ^{31}P NMR spectrum. The proton-coupled spectrum of **5a** shows splitting of the downfield resonance at 12 ppm due to coupling to the α-hydrogens of the alkyl groups. Thus, the two resonances of

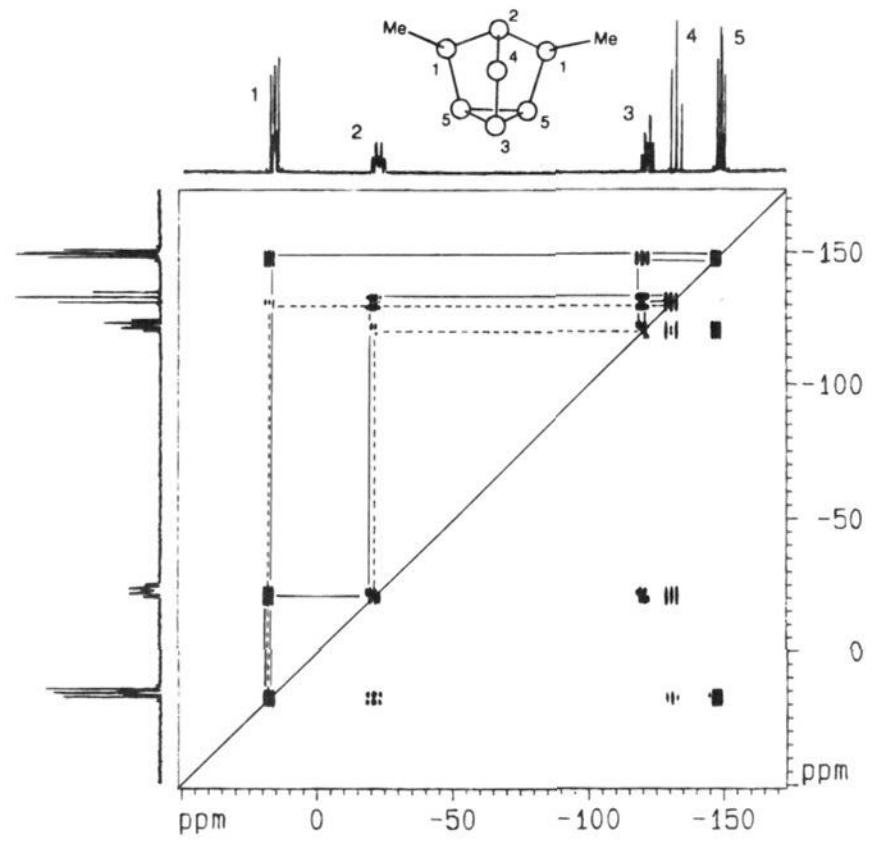


Figure 4. $^{31}P-^{31}P$ COSY NMR spectrum of $[Me_2P_7]^-$ recorded in DMF-d_7 at 28 °C and 202.4 MHz. The atomic labeling scheme is shown in the inset. The solid lines denote cross peaks due to one-bond P–P couplings. The dashed lines represent the two-bond couplings.

relative intensity two at 12 and −153 ppm can be assigned to the alkylated and the non-alkylated equivalent pairs, respectively. The $^{31}P-^{31}P$ COSY NMR spectrum (Figure 4) then allows for the assignments of the remaining resonances. Each resonance shows two principal cross peaks due to strong coupling between bound phosphorus neighbors and can be assigned as shown in Figure 4. Two additional weaker cross peaks are observed for the two-bond P(2)–P(3) and P(1)–P(4) interactions. Because bonds to two-coordinate phosphorus atoms are typically 0.1 Å shorter than those to three-coordinate phosphorus, these two interactions are enhanced in that they couple to or through the two-coordinated P(4). Thus, the relatively large P(2)–P(3) and P(1)–P(4) two-bond couplings are quite consistent with the expected structural features.

The $^{13}C\{^1H\}$ NMR spectrum of **5a** shows a large $^1J_{^{13}C-^{31}P}$ value of 45 Hz with smaller $^2J_{^{13}C-^{31}P}$ coupling of ≤2 Hz. As

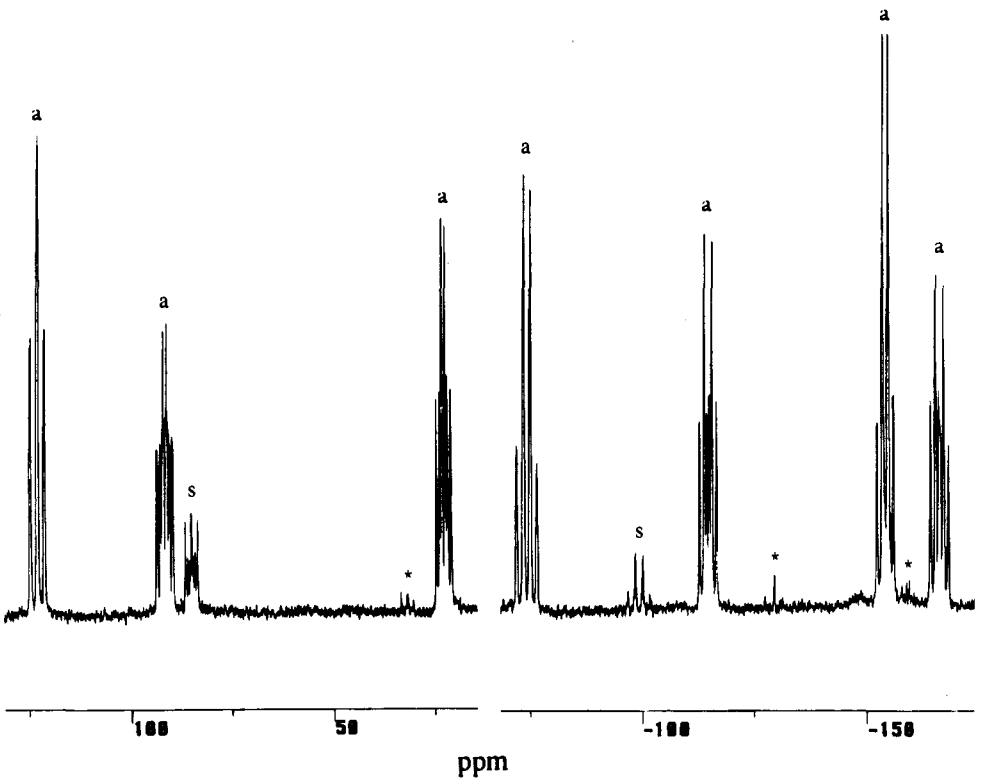


Figure 5. $^{31}P\{^1H\}$ NMR spectrum of $(n\text{-Bu})_3P_7$ from a crude reaction mixture of $[(n\text{-Bu})_2P_7]^-$ and *n*-BuBr in DMF at −20 °C and 202.4 MHz. The resonances marked with "s" and "a" arise from the symmetrical isomer **6-*sym*** and asymmetrical isomer **6-*asym***, respectively. The asterisks denote unreacted $[(n\text{-Bu})_2P_7]^-$.

anticipated from structural considerations, the α-hydrogens of **5b** and **5c** are diastereotopic and give rise to AB patterns ($\delta \approx 0$ ppm) that are broadened due to coupling to phosphorus.

Spectroscopic characterization of compounds **6** was hampered by their limited solubility and thermal instability. In addition, both isomers of the mixed alkyl compounds **6b−d** possess seven inequivalent phosphorus atoms (*i.e.* both **6-*sym*** and **6-*asym*** have C_1 point symmetry), giving rise to 14 overlapping multiplets in their respective ^{31}P NMR spectra. In contrast, the symmetrical isomer **6-*sym*** for the homoleptic alkyl compounds (*e.g.* **6a** and **6e**) as C_3 point symmetry with only three chemically distinct phosphorus nuclei in a 3:3:1 ratio. Thus, the symmetric and asymmetric isomers of **6a** and **6e** can easily be differentiated by ^{31}P NMR spectroscopy. Because of the extreme insolubility and thermal instability of **6a**,[24] only **6e** was studied in detail.

The $^{31}P\{^1H\}$ NMR spectrum of **6e** (Figure 5) shows a preponderance of the asymmetric isomers as evidenced by the seven equal intensity multiplets between 122 and −167 ppm. The spectrum of the minor isomer **6-*sym*** is quite similar to those of related symmetrical X_3P_7 compounds[5,9,11] and is characterized by the three resonances at 84, −100, and −155 ppm. The latter resonance is hidden beneath a peak from isomer **6-*asym***. The −100 ppm resonance of intensity one arises from the unique apical phosphorus atom of isomer **6-*sym***. The proton coupled spectrum shows broadening of the 84 ppm resonance due to alkylated phosphorus atoms with the upfield peak at −155 ppm assignable to the basal atoms.

For the resonances associated with the asymmetric isomer, the proton coupled spectrum shows significant broadening of the three downfield resonances at 122, 92, and 22 ppm, indicating they arise from the alkylated phosphorus atoms. Through comparisons with related compounds (*e.g.* isomer **6-*sym***), we can assign the −75 ppm resonance to the apical phosphorus and the three upfield resonances at −115, −155, and −167 ppm to the basal atoms. These assignments are in accord with those for $(i\text{-Pr})_3P_7$ previously reported by Fritz *et al.*[9]

(24) In our hands, the *in situ* preparation of Me_3P_7 gives very dilute solutions and weak NMR signals. The spectra reported by Baudler et al. (ref 5) were clearly more concentrated presumably due to the difference in synthetic procedure. The ^{31}P chemical shifts were the same in both cases.

Discussion

The transfer of R^+ from the R_4N^+ ions to the polyphosphide complexes described herein occurs by a nucleophilic displacement mechanism involving nucleophilic attack at the α-carbon of the R_4N^+ ions. Two other likely mechanisms that are encountered in related chemistry, the $S_{RN}1$ radical pathway and a Hofmann elimination/olefin insertion pathway, are not consistent with the observed experimental results. These findings are discussed individually below.

Because the steric congestion at the $(n\text{-Bu})_4N^+$ ion would hinder nucleophilic attack, we were concerned that the reactions might be occurring by a radical pathway such as an $S_{RN}1$ process.[25] A single-electron oxidation of $[P_7W(CO)_3]^{3-}$ appears to form a reactive radical that underoges rapid abstractions of hydrogen atoms to form $[HP_7W(CO)_3]^{2-}$.[18] It was therefore of concern that the alkylammonium alkylations described herein might occur via a similar radical pathway: either a single-electron transfer reaction or an initiated radical process.[25] The formation of the Me complex **4a** from $Me(n\text{-}C_8H_{17})_3N^+$ (eq 4) clearly shows that free alkyl radicals are *not* liberated from alkylammonium ions. The $n\text{-}C_8H_{17}$ radical is inherently more stable than the Me radical and the $[(n\text{-}C_8H_{17})P_7W(CO)_3]^{2-}$ complex would be the expected product from eq 4 if free alkyl radicals were involved. Moreover, if alkyl transfer occurred from caged radicals formed in tight-ion pairs (*i.e.* a

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$R_4N^+ \cdots [P_7W(CO)_3]^{3-}$ ion pair), transfer of the least sterically hindered alkyl group may be anticipated in a radical mechanism. The formation of the benzyl complex **4d** from $(CH_2Ph)Me_3N^+$ in eq 5 suggests that ion pairing is not a determining factor in the formation of compounds **4** in that the most electrophilic alkyl group is transferred despite the unfavorable steric factors.

Dealkylations of R_4N^+ ions are known to occur by a Hofmann elimination process[26] involving an initial deprotonation of an alkyl β-hydrogen followed by an olefin elimination to give H^+, R_3N, and olefin. Although the formation of the Me and CH_2-Ph compounds **4a**, **4d**, **6a**, and **6b** cannot proceed via this mechanism, the Et and *n*-Bu transfers could occur by way of a Hofmann elimination from the R_4N^+ ion (*i.e.* formation of $[HP_7W(CO)_3]^{2-}$, olefin, and R_3N) followed by an olefin insertion into the P−H bond of **3**. This mechanism can be discounted in that olefins do not insert into the P−H bonds to form compounds **4** (see eq 6). Although olefins appear to affect some type of transformation of compounds **3**, it is clear that compounds **4** are not formed in these reactions.

The data are consistent with a nucleophilic attack at the α-carbon of an R_4N^+ alkyl group in that the most electrophilic alkyl substituent is transferred in each case. Tetraalkylammonium ions are extremely weak electrophiles and are not known for their alkylating abilities. They are of course frequently used as "inert" spectator cations in various organic and inorganic reactions. In a related system, Haushalter and co-workers described the thermal decomposition of $(Me_4N)_4Sn_9$ to give Me_3N, Sn_2Me_6, and other methylated tin compounds that presumably result from Me^+ transfer from Me_4N^+ to Sn_9^{4-}.[27] An example of RS^- methylation by Me_4N^+ under mild conditions has also been reported,[28−30] but nucleophilic alkyl transfer from $(n\text{-Bu})_4N^+$ is, to our knowledge, unprecedented. Clearly, compounds **1** and **2** are potent nucleophiles, however, their basicity is relatively modest. Neither **1** nor **2** will deprotonate MeOH and **3** is cleanly deprotonated by MeO^- in DMF to give **2**. A detailed discussion of the formation and properties of the $[HE_7M(CO)_3]^{2-}$ compounds (M = Cr, Mo, W) will be presented elsewhere.[18]

Because of the extremely weak electrophilicity of alkylammonium salts, the degree of alkylation and isomeric distributions can be controlled in these reactions. In particular the alkylations of **1** are stereospecific, giving quantitative conversions to single isomers. This selectivity is observed even for the least sterically demanding alkyl group, Me.

Preliminary investigations on other systems suggest that the alkylation of anionic polyphosphides is quite generic although exhaustive studies of the various R groups were not initiated. The chemical selectivity and the ease of subsequent alkylations give this approach a decided advantage over the previously reported methods that utilize alkyl halides (eq 9).[5,8]

$$P_7^{3-} + 3\ RBr \rightarrow R_3P_7 + 3\ Br^- \qquad (9)$$

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

Equation 9 chemistry gives mixtures of isomers, and only certain alkyl groups are amenable to the synthetic conditions. For example, Et, CH_2Ph, and *n*-Bu derivatives cannot be prepared from alkyl halide reactions and disubstituted products are unattainable with any R. Through the combined use of R_4N^+ and RX alkylating agents, a large variety of mixed alkyl compounds can presumably be prepared in high yield.

Based on steric arguments, one must assume that the symmetrical structure ***6-sym*** is the thermodynamically favored isomer for the $R_2R'P_7$ compounds **6**. The $(R_3E)_3P_7$ compounds containing the bulky stannyl and silyl substituents Me_3Sn and $(Me_3Si)_3Si$ gave exclusively the symmetric isomer (*e.g.* $(Me_3Sn)_3P_7$,[9] $[(Me_3Si)_3Si]_3P_7$[11]). The addition of R′ to isomer **I** (or **II**) at the two-coordinate phosphorus site of compounds **5** in eq 8 chemistry would require the formation of ***6-asym*** as the kinetic product. The formation of isomer ***6-sym*** in eq 8 requires inversion at one of the alkylated phosphorus atoms of $[R_2P_7]^-$ during the course of reaction. Because the two do not interconvert after several hours at room temperature, one must assume that isomers ***6-sym*** and ***6-asym*** are formed competitively in a stereoselective reaction (eq 8) and do not represent an equilibrium mixture.

In summary, the reactions described herein reveal a novel method for alkylating highly nucleophilic polyphosphide compounds through the use of R_4N^+ alkylating agents. The reactions give virtually quantitative conversions to the alkylated products and appear to be quite genertic for a variety of "R^+" electrophiles and polyphosphide nucleophiles. The use of this methodology in the formation of other alkylated polypnictides and heterosubstituted phosphines from phosphide anion precursors may be worthy of future investigations.

Experimental Section

General Data. General operating procedures used in our laboratory have been described elsewhere.[13] Proton (^1H) NMR spectra were recorded at ambient temperature on both Bruker WP200 (200.133 MHz) and AM400 (400.136 MHz) spectrometers. Carbon (^{13}C) NMR spectra were recorded at ambient temperature on a Bruker Am400 (100.614 MHz) spectrometer. Phosphorus (^{31}P) NMR spectra were recorded on Bruker WP200 (81.015 MHz) and AMX500 (202.458 MHz) spectrometers. The $^{31}P-^{31}P$ COSY NMR experiments were conducted on an AMX500 in DMF-d_7 at 28 °C. The mass spectra were obtained on a VG7070E magnetic sector mass spectrometer in the fast atom bombardment (FAB) mode utilizing a Xe^+ beam (8 kV) and a *m*-nitrobenzyl alcohol (mNBA) matrix.

The following IR spectral data are common to all compounds containing $[K(2,2,2\text{-crypt})]^+$: IR (KBr pellet) 3126 (m), 2957 (m), 2885 (m), 2817 (m), 2209 (w), 1655 (m), 1597 (w), 1476 (m), 1459 (m), 1444 (m), 1400 (m), 1387 (s), 1362 (s), 1354 (s), 1299 (m), 1260 (m), 1238 (w), 1173 (w), 1132 (s), 1103 (s), 1081 (s), 1059 (m), 1030 (w), 950 (m), 933 (m), 830 (m), 820 (w), 806 (m), 754 (w), 667 (m), 638 (w), 614 (w), 572 (w), 546 (w), 525 cm^{-1} (w). The following NMR spectral data are common to all compounds containing $[K(2,2,2\text{-crypt})]^+$ and/or en: ^1H NMR (DMF-d_7) δ 3.61 (s, 12 H, 2,2,2-crypt), 3.58 (t, 12H, 2,2,2-crypt), 2.57 (t, 12H, 2,2,2-crpt), 2.54 (s, en), 1.26 ppm (br s, en). $^{13}C\{^1H\}$ NMR (DMF-d_7) δ 71.0 (s, 2,2,2-crypt), 68.3 (s, 2,2,2-crypt), 54.6 (s, 2,2,2-crypt), 46.3 ppm (s, en).

Chemicals. The preparation of the K_3P_7 has been previously reported.[13] **CAUTION:** alkali polyphosphorus compounds are known to spontaneously detonate even under rigorously anaerobic conditions.[10] These materials should only be prepared in small quantities and should be handled with caution. Mesitylene tungsten tricarbonyl, 4,7,13,16,-21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (2,2,2-crypt), tetraalkylammonium halides, and alkyl halides were purchased from Aldrich and used without further purification. Ethylenediamine (en) was purchased from Fisher (Anhydrous), distilled several times from CaH_2 under N_2 and then from K_4Sn_9 at reduced pressure, and finally stored under N_2 over molecular sieves. DMF was purchased from Burdick & Jackson (High Purity), distilled at reduced pressure from K_4Sn_9, and stored over molecular sieves. DMF-d_7 was purchased from

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(27) Teller, R. G.; Krause, L. J.; Haushalter, R. C. *Inorg. Chem.* **1983**, *22*, 1809.
(28) Shamma. M.; Deno, N. C.; Remar, J. F. *Tetrahedron Lett.* **1966**, 1375.
(29) Kametani, T.; Kigasawa, K.; Hiiragi, M.; Wagatsuma, N.; Wakisaka, K. *Tetrahedron Lett.* **1969**, 635.
(30) Hutchins, R. O.; Dux, F. J. *J. Org. Chem.* **1973**, *38*, 1961.

Cambridge Isotope Laboratories, degassed, and dried over molecular sieves. The preparation of **2** has been described elsewhere.[13]

Synthesis. Preparation of [K(2,2,2-crypt)]$_2$[MeP$_7$W(CO)$_3$] · en. Method A: K_3P_7 (29.6 mg, 0.089 mmol), 2,2,2-crypt (100.0 mg, 0.27 mmol), and $[C_6H_3(CH_3)_3]W(CO)_3$ (34.4 mg, 0.089 mmol) were dissolved in en (*ca.* 3 mL) and stirred for 12 h at ambient temperature yielding a red solution. An equivalent of solid Me(*n*-$C_8H_{17})_3$NBr (39.9 mg, 0.089 mmol) was added. The reaction mixture was stirred for 1 h producing a dark red solution. Solvent was concentrated *in vacuo* to 2 mL and filtered through tightly packed glass wool in a pipet. After 24 h, the reaction vessel contained rectangular maroon crystals that were removed from the mother liquor, washed with toluene, and dried *in vacuo* (crystalline yield, 49 mg, 39%). **Method B:** A procedure identical to that described in Method A was followed except solid Me_4NBr (13.8 mg, 0.089 mmol) was used and the reaction mixture was stirred for 4 h at *ca.* 40 °C, concentrated *in vacuo* to 2 mL, and filtered through *ca.* 0.25 in. of tightly packed glass wool in a pipet. After 24 h, the reaction vessel contained rectangular maroon crystals that were removed from the mother liquor, washed with toluene, and dried *in vacuo* (crystalline yield, 39 mg, 32%). IR (KBr pellet) 1871 (s), 1786 (s), 1757 cm^{-1} (s). ^{1}H NMR (DMF-d_7) δ 0.53 ppm (dt, 3H, CH_3). ^{13}C{^{1}H} NMR (DMF-d_7) δ 229.4 (br s, CO), −3.3 ppm (d, ^1J(C,P) = 30.4 Hz; CH_3).

Preparation of [K(2,2,2-crypt)]$_2$[EtP$_7$W(CO)$_3$] · en. A procedure identical to that described for [K(2,2,2-crypt)]$_2$[MeP$_7$W(CO)$_3$] · en (Method A) was followed except solid Et_4NBr (18.7 mg, 0.089 mmol) was used. After 24 h, the reaction vessel contained rectangular maroon crystals that were removed from the mother liquor, washed with toluene, and dried *in vacuo* (crystalline yield, 46 mg, 37%). Anal. Calcd for $C_{43}H_{85}N_6O_{15}K_2P_7W$: C, 36.76; H, 6.10; N, 5.98. Found: C, 36.92; H, 6.09; N, 5.93. IR (KBr pellet) 1866 (s), 1787 (s), 1750 cm^{-1} (s). ^{1}H NMR (DMF-d_7) δ 0.96 (dq. 2H, ^2J(H,P) = 14.2 Hz, ^3J(H,H) = 7.1 Hz; CH_2CH$_3$), 0.84 ppm (dt, 3H, ^3J(H,P) = 13.6 Hz, ^3J(H,H) = 7.1 Hz; CH$_2$CH_3). ^{13}C{^{1}H} NMR (DMF-d_7) δ 229.4 (p, ^1J(C,W) = 167 Hz, ^2J(C,P) = 4 Hz; CO), 15.6 (dt, ^1J(C,P) = 10.8 Hz, ^2J(C,P) = 5.4 Hz; CH_2CH$_3$), 8.0 ppm (d, ^2J(C,P) = 26.0 Hz; CH$_2$CH_3).

Preparation of [K(2,2,2-crypt)]$_2$[*n*-BuP$_7$W(CO)$_3$] · en. A procedure identical to that described for [K(2,2,2-crypt)]$_2$[MeP$_7$W(CO)$_3$] · en (Method A) was followed except solid (*n*-Bu)$_4$NBr (28.7 mg, 0.089 mmol) was used. After 24 h, the reaction vessel contained octahedral maroon crystals that were removed from the mother liquor, washed with toluene, and dried *in vacuo* (crystalline yield, 91 mg, 69%). Anal. Calcd for $C_{47}H_{97}N_8O_{15}K_2P_7W$: C, 37.81; H, 6.55; N, 7.50; P, 14.52. Found: C, 37.73; H, 6.51; N, 7.91; P, 13.95. IR (KBr pellet) 1874 (s), 1787 (s), 1753 cm^{-1} (s). ^{1}H NMR (DMF-d_7) δ 1.16 (m, 4H, *n*-Bu), 1.01 (m, 2H, *n*-Bu), 0.74 ppm (t, 3H, *n*-Bu). ^{13}C{^{1}H} NMR (DMF-d_7) δ 229.4 (br s, CO), 33.7 (m, *n*-Bu), 24.6 (d, J(C,P) = 8.1 Hz; *n*-Bu), 14.6 (d, J(C,P) = 27 Hz; *n*-Bu), 14.0 ppm (s, *n*-Bu).

Preparation of [K(2,2,2-crypt)]$_2$[(CH$_2$Ph)P$_7$W(CO)$_3$]. [K(2,2,2-crypt)]$_2$[(CH$_2$Ph)P$_7$W(CO)$_3$] · en was prepared by two separate reactions from two different ammonium salts, (CH$_2$Ph)Me$_3$NBr and (CH$_2$Ph)Et$_3$NBr. A procedure identical to that described for [K(2,2,2-crypt)]$_2$[MeP$_7$W(CO)$_3$] · en (Method A) was followed except solid (CH$_2$Ph)Me$_3$NBr (20.5 mg, 0.089 mmol) was added to one reaction and (CH$_2$Ph)Et$_3$NBr (24.2 mg, 0.089 mmol) to the other. After 24 h, the reaction vessels contained rectangular maroon crystals that were removed from the respective mother liquors, washed with toluene, and dried *in vacuo*. Crystalline yields were 42 mg (32%) for each. Anal. Calcd for $C_{46}H_{80}N_4O_{15}K_2P_7W$: C, 39.24; H, 5.73; N, 3.98. Found: C, 39.18; H, 5.73; N, 4.19. IR (KBr pellet) 1874 (s), 1792 (s), 1755 cm^{-1} (s). ^{1}H NMR (DMF-d_7) δ 7.17−7.00 (CH$_2$*Ph*), 2.38 ppm (m, 2H, CH_2Ph). ^{13}C{^{1}H} NMR (DMF-d_7) δ 229.3 (br s, CO). 141.0 (s, CH$_2$*Ph*, ipso), 129.2, 128.4, 125.5 (s, *CH$_2$Ph*), 21.2 ppm (d, ^1J(C.P) = 29.8 Hz; CH_2Ph).

Preparation of KMe$_2$P$_7$. In a 5 dram vial in a drybox, K_3P_7 (29.6 mg, 0.089 mmol) and Me_4NBr (27.6 mg, 0.178 mmol) were combined in en (*ca.* 3 mL) and stirred for 12 h yielding a bright yellow solution. ^{31}P NMR spectra of the crude reaction mixtures showed quantitative conversion to a single product. The solvent was removed *in vacuo* leaving a yellow film on the vial that was redissolved in DMF-d_7 (*ca.* 1 mL). The NMR data for the dried films showed residual en. ^{1}H NMR (DMF-d_7) δ −0.39 ppm (m, CH_3). ^{13}C{^{1}H} NMR (DMF-d_7) δ 42.1 ppm (d, ^1J(C,P) = 44.6 Hz; CH_3).

Preparation of KEt$_2$P$_7$. A procedure identical to that described above for KMe$_2$P$_7$ was followed except Et_4NBr (37.3 mg, 0.178 mmol) was used. ^{31}P NMR spectra of the crude reaction mixtures showed quantitative conversion to a single product. The solvent was removed *in vacuo* leaving a yellow film on the vial that was redissolved in DMF-d_7 (*ca.* 1 mL). The NMR data for the dried films showed residual en. ^{1}H NMR (DMF-d_7) δ 0.71 (m, 2H, CH$_2$CH_3), −0.07, −0.24 ppm (br m, 1H, CH_2CH$_3$).

Preparation of K(*n*-Bu)$_2$P$_7$. A procedure identical to that described above for KMe$_2$P$_7$ was followed except (*n*-Bu)$_4$NBr (57.3 mg, 0.178 mmol) was used. ^{31}P NMR spectra of the crude reaction mixtures showed quantitative conversion to a single product. The solvent was removed *in vacuo* leaving a yellow film on the vial that was redissolved in DMF-d_7 (*ca.* 1 mL). The NMR data for the dried films showed residual en. ^{1}H NMR (DMF-d_7) δ 1.73 (m, 2H, *n*-Bu), 1.37 (m, 2H, *n*-Bu), 1.06 (m, 3H *n*-Bu), −0.12, −0.24 ppm (br m, 1H, C$H_2C_3H_7$).

Preparation of Me$_3$P$_7$. KMe$_2$P$_7$ (0.089 mmol) was prepared in en (*ca.* 3 mL) as described above except a 25 mL Schlenk flask was used. The en was removed *in vacuo* leaving a yellow film in the flask. This film was redissolved in DMF (*ca.* 4 mL). MeI (5.5 μL, 0.089 mmol) was syringed into the stirring reaction mixture yielding a colorless solution and white precipitant (ppt). An aliquot of the solution was immediately removed and taken for MS analysis while the remainder of the solution was used for ^{31}P NMR analysis.

Preparation of (CH$_2$Ph)Me$_2$P$_7$. A procedure identical to that described earlier for Me$_3$P$_7$ was followed except (CH$_2$Ph)Cl (10.2 μL, 0.089 mmol) was syringed into the stirring reaction mixture yielding a colorless solution and white ppt. An aliquot of the solution was immediately removed and taken for MS analysis.

Preparation of (*n*-Bu)$_3$P$_7$. K(*n*-Bu)$_2$P$_7$ (0.089 mmol) was prepared in DMF (*ca.* 3 mL) as described above except a 25 mL Schlenk flask was used. (*n*-Bu)Br (17.2 μL, 0.089 mmol) was syringed into the stirring reaction mixture yielding a red solution. An aliquot of the solution was immediately removed and taken for MS analysis while the remainder of the solution was used for ^{31}P NMR analysis.

Preparation of Me(*n*-Bu)$_2$P$_7$. A procedure identical to that described earlier for (*n*-Bu)$_3$P$_7$ was followed except methyl iodide (5.5 μL, 0.089 mmol) was syringed into the stirring reaction mixture yielding a colorless solution and white ppt. An aliquot of the solution was immediately removed and taken for MS analysis.

Preparation of (CH$_2$Ph)(*n*-Bu)$_2$P$_7$. A procedure identical to that described earlier for (*n*-Bu)$_3$P$_7$ was followed except benzyl chloride (10.2 μL, 0.089 mmol) was syringed into the stirring reaction mixture yielding a colorless solution and white ppt. An aliquot of the solution was immediately removed and taken for MS analysis.

Crystallographic Experimental Details for [K(2.2.2-crypt)]$_2$[EtP$_7$W(CO)$_3$] · en. A dark, rectangular crystal with dimensions 0.50 × 0.25 × 0.20 mm was sealed in a glass capillary and placed on the Enraf-Nonius CAD-4 diffractometer. The crystals' final cell parameters and crystal orientation matrix were determined from 25 reflections in the range 23.7° < 2θ < 30.4°; these constants were confirmed with axial photographs. Data were collected [Mo Kα] with θ−2θ scans over the range 1.7° < θ < 22.5° using a variable scan speed of 2.75−4.12 min^{-1} with each scan recorded in 96 steps with the outermost 16 steps on each end of the scan being used for background determination. Three check reflections showed no change in intensity during data collection and the data were therefore not corrected for decay. Four ψ-scan reflections were collected over the range 6.7° < θ < 13.7°. An absorption correction was applied with transmission factors ranging from 0.8108 to 0.998, average 0.9091. One form of unique data were collected in the hemisphere *hkl*, resulting in the measurement of 8783 reflections−8304 unique.

Data were corrected for Lorentz and polarization factors and absorption and then reduced to observed structure−factor amplitudes using the program package NRCVAX. Intensity statistics clearly favored the centrosymmetric space group $P\bar{1}$ (no. 2). The structure was determined (SHELX)[31] with the successful location of the tungsten

(31) Sheldrick, G.; Siemens XRD: Madison, WI.

atom, the two potassium atoms, and seven phosphorus atoms. Subsequent difference–Fourier maps revealed the location of all of the remaining non-hydrogen atoms. Hydrogen atoms were placed in calculated positions, these being dependent on the type of bonding at the central atom, carbon or nitrogen, with $d(C-H_2) = 0.970$ Å and $d(N-H_2) = 0.890$ Å with U_H being set equal to $1.2U_{(parent)}$ and $d(C-H_3) = 0.960$ Å with U_H equal to $1.5U_{(parent)}$. The structure was refined to convergence by minimizing the function $w(F_o^2 - F_c^2)$ where $w = 1/[\sigma^2(F_o^2) + (0.0670P)^2 + 0.1341P]$ and $P = (\max(F_o^2,0) + 2F_c^2)/3$. A final difference–Fourier map possessed four peaks within 1.2 Å of the tungsten atom with $|\Delta\varrho| \leq 1.37$ eÅ^{-3}; heights for the remaining peaks had $|\Delta\varrho| \leq 0.46$ eÅ^{-3}.

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Supplementary Material Available: A complete listing of positional parameters, thermal parameters, and bond distances and angles for $[K(2,2,2\text{-crypt})]_2[EtP_7W(CO)_3]$ (14 pages); listing structure factor tables (24 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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