was described as mercury catalyzed. Our present studies indicate that traces of phosphinogermane oxidation products are in fact the catalyst instead of mercury.

(26) A referee suggested that the observed catalytic effects in this reaction may be the result of general acid catalysis. This possibility is being examined currently in our laboratories on model phosphinogermane systems.

(27) M. Baudler, H. Standeke, M. Borgardt, and H. Stravel, *Naturwissenschaften*, **52**, 345 (1965); M. Baudler, H. Standeke, M. Borgardt, H. Strahel, and J. Dobbers, *ibid.*, **53**, 106 (1966).

Structure and Dynamics of Catenated Phosphorus(III) Dianions

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Contribution No. 2731 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received April 9, 1975*

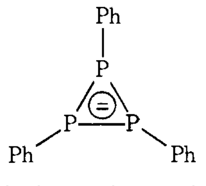
Abstract: ^{31}P NMR is used to study the structure of $M_2(PPh)_n$ (M = Li, Na, K, and Cs; n = 3 and 4) species in tetrahydrofuran. Analysis of phosphorus–phosphorus coupling constants at low temperatures shows that, for n = 4, the sodium and potassium compounds involve chelation of the metal ion by the phosphorus chain ("intimate ion pairing"), while the lithium compound has an acyclic structure. Exchange processes are evident in all three compounds at higher temperatures; for M = Na and K, the coupling constants indicate equilibration to acyclic structures. The compound $K_2(PPh)_3$, which is said to be a salt of the delocalized cyclic dianion $(PPh)_3{}^{2-}$, is found to exhibit concentration-dependent ^{31}P NMR spectra. This is attributed to "ion pairing" equilibria. Addition of a crown ether dramatically alters the phosphorus chemical shifts of $K_2(PPh)_3$ but leaves the coupling constants unchanged. It is concluded that $(PPh)_3{}^{2-}$ is in reality acyclic, with only two phosphorus–phosphorus bonds.

The synthesis and characterization of polyphosphine dianion "salts", $M_2(PR)_n$, is due almost exclusively to Issleib and coworkers.[1-10] When R = C_6H_5(Ph), the preparation involves reaction 1.

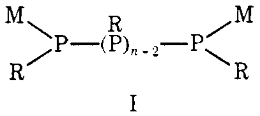
$$(PPh)_5 + \frac{10}{n}M \longrightarrow \frac{5}{n}M_2(PPh)_n \qquad (1)$$

Here M is an alkali metal and n = 1–4. The resultant phosphide compounds are extremely potent nucleophiles. They form cyclic condensation products with both alkyl[4,5,11,12] and aryl[13] dihalides. With monohalogenated reagents, the expected straight-chain species may be generated. However, if the final phosphorus chain length exceeds two, the primary product decomposes to the biphosphine, $(PPhR)_2$, and the cyclopolyphosphine, $(PPh)_5$. Reactions with transition metal complexes are also known.[6,14]

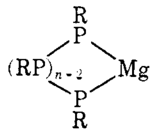
Earlier work[3,4,7-10,13] suggests that the species $M_2(PR)_n$ are acyclic. The compound $K_2(PPh)_3$ represents the only exception. The ^{31}P NMR singlet observed for this compound has been interpreted[6] in terms of a cyclic structure with two electrons delocalized in a π orbital. On the other hand, electrochemical experiments have been interpreted[15] as indicating that $K_2(PPh)_3$ does not produce a cyclic dianion in solution; the NMR result is attributed to an unspecified "rapid exchange".



These alkali metal compounds are conventionally written as I, implying a truly open chain structure with one metal associated with each chain terminus. The nature of the M-P bond is generally unspecified but "univalent" bonding is an implicit *assumption.* In the several instances where a magnesium salt was isolated,[7] cyclic structures (II) were written, consistent with the "divalency" of magnesium.



I



II

We now find that the phosphorus NMR spectra of $M_2(PPh)_n$ species are not consistent with simple straight-chain structures (I). The spectra exhibit complex cation and temperature dependencies. However, the long range coupling which exists in catenated phosphorus compounds serves as a somewhat unique structural probe which provides an insight into the solution geometry of $M_2(PPh)_n$ species.

Experimental Section

Phosphorus NMR spectra (Fourier transform) were recorded at 40.5 MHz as previously described.[16] Chemical shifts are reported with respect to 85% H_3PO_4, downfield chemical shifts being *positive.* Proton spectra were recorded at 220 MHz. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Iterative spectral calculations utilized the program LAOCN3.[17] For the AA′BB′ spectra, eight possible line assignments were typically made with iteration carried out on each. Typical root mean square errors for the best solution are 0.5 Hz, which is less than the error introduced by digitization. The parameters in Table I are therefore uniquely determined by the data.

Materials. Pentaphenylcyclopentaphosphine, $(PPh)_5$, was prepared and characterized as described previously.[18] All alkali and alkaline earth metals used were reagent grade and were rinsed well in the reaction solvent prior to use in order to remove any mineral oil. Other compounds were reagent grade and were used without further purification. Tetrahydrofuran (THF) was dried over Na/K alloy and distilled under N_2 prior to use. All reactions were carried out under prepurified N_2 which had been deoxygenated by activat-

Table I. Calculated ^{31}P NMR Parameters[a,b] for $M_2(PPh)_n$[c]

Compound	Temp (°C)	ν_A	ν_B	$J_{AA'}$	J_{AB}	$J_{AB'}$	$J_{BB'}$
$Li_2(PPh)_4$	−83	−83.4	−9.1	+8.4 (1)	−280.9 (1)	+128.4 (1)	−150.6 (1)
$K_2(PPh)_4$	30	−70.0	−21.3	+82.8 (3)	−323.3 (3)	+30.8 (3)	−301.8 (3)
$K_2(PPh)_4$	−50	−70.6	−24.4	+166.7 (2)	−337.8 (2)	−2.0 (2)	−315.1 (2)
$Na_2(PPh)_4$	−59.5	−91.4	−26.6	+310.6 (7)	−323.1 (6)	−12.3 (6)	−310.2 (6)
$K_2(PPh)_3$	30	−50.0	−46.8	–	268 (2)	–	–
$K_2(PPh)_3$ + crown ether	−85	−17.4	+12.8	–	269.9 (1)	–	–
$Cs_2(PPh)_3$	30	−42.5	−36.0	–	287.1 (1)	–	–

[a] Probable errors in the last digit shown appear in parentheses. [b] Chemical shifts in ppm; coupling constants in Hz. [c] In THF.

ed copper and dried by passage through P_2O_5. All glassware was flamed out and purged with N_2 prior to use.

$(PPh)_5 + xM$. Reactions were carried out with M = Li (x = 2.5), Na (x = 2.5), K (x = 2.0, 2.5, 3.0, 3.3, 4.0, 5.0), Cs (x = 2.5), Ca (x = 1.3), and Ba (x = 1.3). Since all preparations were identical, only a general scheme is given.

$(PPh)_5$ (0.5 g) was dissolved in 20 ml of THF, and the required amount of metal was added to the solution. The mixture was stirred at room temperature for 12 hr. If at the end of that time any unreacted metal remained, the reaction mixture was refluxed for an additional 12 hr. The mixture was then cooled to room temperature and filtered, and a portion of the filtrate was loaded into an NMR tube which was sealed under vacuum. When it was deemed necessary, the remaining filtrate was concentrated to approximately 5 ml, and a portion of this solution was loaded into an NMR tube and sealed under vacuum. In only one case was any solid ever isolated, that being where M = K and x = 5. This orange compound was washed with THF and dried under vacuum. Anal. Calcd for $K_2(PPh)_2 \cdot \frac{1}{2}THF$: C, 50.91; H, 4.24; P, 18.79. Found: C, 51.27; H, 4.46; P, 18.69.

The above procedure was altered in the case where M = K and x = 3.3. Upon addition of the potassium, the solution was immediately refluxed for 1 hr, cooled, filtered, and then loaded into NMR tubes as above.

Complexation of Potassium. A reaction was carried out as above for M = K and x = 2.5. The mixture was filtered into a flask containing the complexing agent (dibenzo-18-crown-6[19]) present in a 1:1 molar ratio to potassium taken. The resultant mixture was stirred for 10 min, and a portion of it was loaded into an NMR tube which was then sealed under vacuum.

Results and Discussion

Initially, the $K/(PPh)_5$ mole ratio was varied in order to determine the range of products possible. Of particular interest was the possibility of detecting $K_2(PPh)_5$.

The reactions of $(PPh)_5$ and potassium metal do not appear to proceed in exact stoichiometric ratios, and an excess of potassium is usually required in order to obtain the desired product free from impurities. This may be due to the heterogeneous nature of the reaction. Too much metal may react further producing smaller phosphide chain lengths. Only three phosphides were produced in these preparations, $K_2(PPh)_n$ where n = 2, 3, or 4.

$K_2(PPh)_4$. Reaction of $(PPh)_5$ with 2K yields an intensely red solution which in the ^{31}P NMR displays unreacted $(PPh)_5$ and an AA′BB′ pattern indicative of a four-phosphorus compound, $K_2(PPh)_4$. An increase in the $K/(PPh)_5$ ratio to 2.5 causes almost complete conversion to $K_2(PPh)_4$. The ^{31}P NMR spectrum of the $K_2(PPh)_4$ in THF at 30°C is shown in the top portion of Figure 1. An approximate solution to the AA′BB′ pattern can be obtained from known relationships.[20] The spectrum calculated from these parameters was iteratively fit to the experimental data to give the spectral parameters shown in Table I. Since $|J_{AA'}| < |J_{BB'}|$, the A and A′ spins are assigned as the terminal nuclei. The B (internal) chemical shift then lies closer to the chemical shifts of $(PPh)_5$ (−3 ppm)[16] and Ph_2PPPh_2 (−15.4 ppm)[21] than does ν_A.

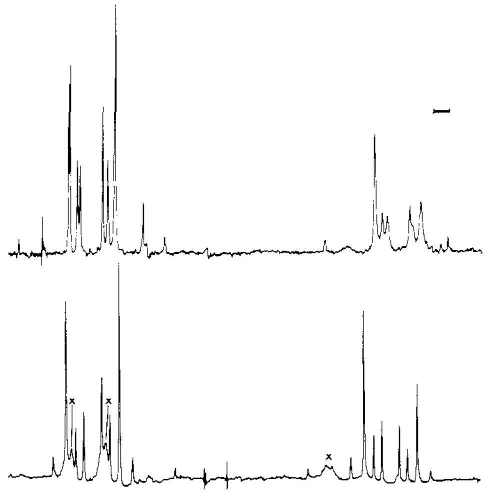
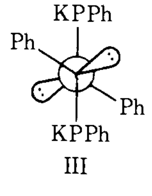


Figure 1. The 40.5-MHz $^{31}P\text{-}\{H\}$ NMR of $K_2(PPh)_4$ in THF at 30° (above) and −50° (below). × indicates an impurity. Calibration bar indicates 100 Hz.

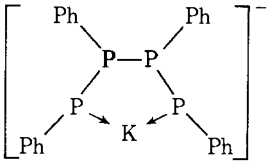
Relative signs of all J's are calculable in an AA′BB′ spin system, but absolute signs have been assigned following the absolute determination of $^1J_{P^{III}P^{III}}$ as negative.[20] Immediately evident in the 30°C spectrum is the broadness of the high field resonances. Lengthening the time between pulses in the data collection does not alter the pattern, thereby eliminating the possibility that different relaxation times cause loss of intensity.[22] Interaction with quadrupolar potassium ions or some type of potassium exchange (see below) might selectively broaden the resonances of the terminal phosphorus atoms. This confirms the conclusion (above) that the A and A′ nuclei possess the upfield chemical shift.

At −50°C (see bottom portion of Figure 1), $K_2(PPh)_4$ displays a different AA′BB′ pattern with peak amplitudes which are more nearly symmetric. The spectral parameters are obtained in the same manner as above and are listed in Table I. The assignment of resonances is identical with that of the 30°C spectrum. Immediately apparent is the dramatic increase in $J_{AA'}$ relative to the modest alterations in J_{AB} and $J_{BB'}$. The magnitude of $J_{AA'}$ is exceptionally large. It is large enough to warrant consideration as a possible one-bond interaction; this might suggest some direct bonding between the A and A′ nuclei. However, $J_{AA'}$ is *positive*, a result contrary to all previous data for ^1J values involving trivalent phosphorus. There can be no doubt that the value for $J_{AA'}$ excludes conventional linear chains such as III, re-



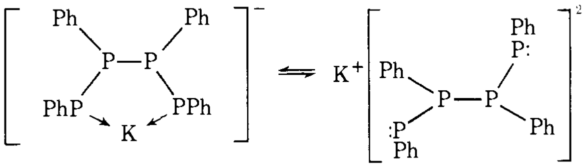
III

gardless of whether or not potassium ions are associated with the anionic termini; in III, $J_{AA'}$ is a three-bond interaction. Some association of K^+ with the dianion must occur, particularly in view of the relatively low dielectric constant of the solvent (THF). Phosphorus chemical shifts are cation-dependent for compounds of formula $MPPh_2$.[23] Conductivity measurements show that these compounds are not completely dissociated into ions even in dimethyl sulfoxide.[24] Initial interpretation of our spectral results in terms of solvent-separated ion pairs was soon abandoned since it provides no natural explanation of the strong temperature dependence of $J_{AA'}$. We now feel that the data are best interpreted in terms of equilibria involving coordinate-covalent bonds from anionic phosphorus to K^+. In contemporary terminology, this would be termed an "intimate" or "contact" ion pair structure,[25] but it seems unwise to apply this general term to a situation which is adequately characterized by the more familiar phrase "coordination complex". Further, in view of the dianionic nature of $(PPh)_4{}^{2-}$, it is most natural to consider one potassium ion to be chelated by the anion (IV).[26] The coordination shell of potassium will be completed by THF molecules which are always present in the solid materials isolated from these solutions. Chelation of alkali metal ions in the solid state has been established. Lithium is chelated by two 1,2-dimethoxyethane (DME) molecules in $Li(DME)_2[BH_2(C_9H_{11})_2]$.[27] *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) chelates to lithium in $Li(TMEDA)[C(C_6H_5)_3]$,[28] $[Li(TMEDA)]_2C_{10}H_8$,[29] and $[Li(TMEDA)C_4H_5]_2$.[30] Sodium is chelated by all three ligands in $Na[(Ph)_2P)O)CH_2P(O)(Ph)_2]_3Br\cdot H_2O$.[31] The diamine chelates to magnesium in $C_5H_5MgBr[(C_2H_5)_2N(CH_2)_2N(C_2H_5)_2]$.[32] One might hope to find an even closer structural analog to $K_2(PPh)_4$ among the metal polysulfides, M_2S_n. Unfortunately, no such pairwise bonding is found in the solid state. Both Na_2S_4[33] and $BaS_4\cdot H_2O$[34] exhibit ionic lattices composed of cations interacting at long distances with several different anions. However, the transition metal polysulfides $(C_5H_5)_2MoS_4$,[35] $(C_5H_5)_2TiS_5$,[36-38] and $Pt(S_5)_3{}^{2-}$[39] all contain chelating polysulfides. Finally, the ^{31}P NMR of $(C_5H_5)_2M(PPh)_3$ (M = Ti, Zr) is consistent with an MP_3 ring.[11]



IV

Structure IV provides a natural explanation for the strong coupling of the "terminal" phosphorus nuclei, since they are cyclized into a five-membered ring. However, it is likely that exchange of chelated with "free" (bulk solution) K^+ is rapid on the NMR time scale even at −50°.[40] This exchange must therefore occur without rotation about the central P-P bond; that is, potassium exchange must be a highly specific "insertion" process which never passes through a bridged transition state like III. The −50° spectrum thus implies nearly exclusive population of a cyclic species like IV. However, in order to account for the decrease in $J_{AA'}$ in the 30° spectrum, an acyclic species must be postulated (eq 2). The 30° spectrum provides information on the conformational reorganization of eq 2 under conditions of rapid exchange. The open chain species in eq 2 presumably resembles III and may have one- or two-coordinated potassium ions. The similarity of the ν_A values at −50 and 30° suggests similar environments. Thus, the acyclic species may be KP(Ph)(PPh)$_2$PK(Ph). The acyclic species finds an analogy in the structure of $LiX\cdot 2H_2NCH_2CH_2NH_2$, which contains both bridging and chelating ethylenediamine.[41]

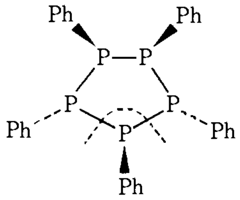


(2)

The temperature dependence of the ^{31}P NMR spectrum is typical of site exchange. As the temperature rises from −50°, both the upfield and downfield portions of the AA′BB′ pattern are altered, but in distinctly different ways. The downfield (central phosphorus) region exhibits minor broadening, but mainly a shift in line positions. The upfield portion, on the other hand, broadens so completely that it is nearly unobservable at 0°C. By 50°, all line widths are nearly identical. This complex behavior is not merely the alteration of relative populations in a rapidly exchanging system. Rather it is the passage from slow exchange to fast exchange in an equilibrium system. By the time fast exchange conditions are achieved (30–50°), this acyclic species has become appreciably populated ($J_{AA'}$, a population weighted average, is halved).[42]

$Na_2(PPh)_4$. This compound exhibits behavior similar to that of the potassium analog. Figure 2 shows the 30° and −59.5° spectra of the sodium compound in THF. The 30° spectrum has the same selectively broadened appearance as shown by $K_2(PPh)_4$ at 0°. At −59.5°, $Na_2(PPh)_4$ displays an AA′BB′ pattern whose parameters are listed in Table I. The line assignment is identical with that of the potassium compound. All coupling constants except $J_{AA'}$ are remarkably similar to those of $K_2(PPh)_4$. $J_{AA'}$, however, is now as large as a one-bond coupling constant although it is still of opposite sign. Again a five-membered ring is the major species detectable at low temperatures.[42] Comparison of the chemical shifts for the sodium and potassium compounds shows ν_B to be relatively invariant to the cation, while ν_A, the upfield resonance, is strongly affected. This, as well as the larger temperature effects in the upfield region, is again consistent with the A and A′ nuclei being the anionic phosphorus sites. The increased nuclear spin coupling between the A and A′ nuclei indicates a chemically distinct bridging atom in the two compounds. Until the theory of two-bond phosphorus-phosphorus coupling constants becomes better understood, it will be premature to attribute increasing $J_{AA'}$ to greater "covalency" in the sodium compound. However, the trends observed for ^{31}P chemical shifts of alkali metal diphenylphosphides have been rationalized in this fashion.[23] Independent of trends in covalency, the experimental data do show qualitatively that higher temperatures are required to populate the acyclic form when the metal ion is sodium. Thus, the sodium chelate is more resistant to ring opening.

It is noteworthy that both $Na_2(PPh)_4$ and $K_2(PPh)_4$ exhibit only one AA′BB′ spectrum at low temperature. As a result of asymmetry at each internal phosphorus, $M_2(PPh)_4$ may exist in *d-l* and meso isomers which would be expected to display different NMR patterns. *meso*-$M_2(PPh)_4$ results from reductive cleavage of $(PPh)_5$ at the bonds shown below. Removal of any other PPh group produces the *d-l*



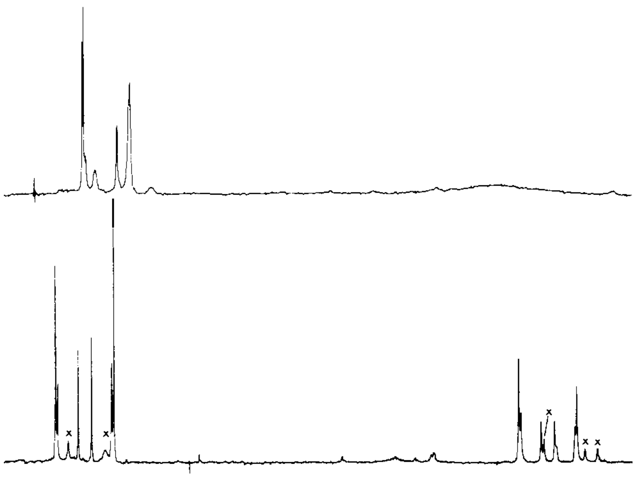


Figure 2. The 40.5-MHz ^{31}P-{H} NMR of $Na_2(PPh)_4$ in THF at 30° (above) and −59.5° (below). × indicates an impurity. Calibration bar indicates 100 Hz.

forms. Three-coordinate phosphorus ought to have high barriers to inversion.[43,44] Since only one pattern is observed,[42] it may be that $(PPh)_5$ reacts in a stereospecific fashion with these alkali metals to yield only one isomer. The similar values for J_{AB} and $J_{BB'}$ suggest that any two adjacent phosphorus atoms have the same substitutional stereochemistry, presumably trans.[45]

$Li_2(PPh)_4$. Reaction of $(PPh)_5$ with 2.5Li in THF yields a red solution. The ^{31}P NMR spectrum at 30° is similar to that reported previously for $Li_2(PPh)_4$,[3] being composed of doublets centered at −9.4 and −86.8 ppm. The spacing within each doublet is 214 Hz. Since all lines are broad (35 Hz), an exact spectral analysis is not possible. However, the doublet spacing does not directly correspond to any single coupling constant in an AA′BB′ spin system. Note that the downfield (ν_B) chemical shift is altered substantially from that in $Na_2(PPh)_4$ and $K_2(PPh)_4$

On cooling this sample to −83°, spectral patterns characteristic of two compounds are evident. Most prominent is a 24 line AA′BB′ pattern with the parameters shown in Table I. The chemical shift of the B nuclei, which are the internal phosphorus atoms in $Li_2(PPh)_4$, is similar to that of $(PPh)_5$ at −83°.[16,46] The coupling constants indicate that the structure of $Li_2(PPh)_4$ differs substantially from that of the sodium and potassium analogs. The coupling constant between anionic termini is very small for $Li_2(PPh)_4$, consistent with this being a true three-bond interaction. This is consistent with $Li_2(PPh)_4$ possessing a structure analogous to III. Thus, with lithium we for the first time observe an acyclic structure. This structural change from the sodium and potassium analogs is probably due to the small size of lithium; chelation of lithium might require an unfavorably small separation between the anionic phosphide groups.

The second spectral pattern observed at −83° is an especially simple example case of an AA′BB′ pattern. It is composed of four doublets, each with separation of 75 Hz, centered at +2.4, −3.4, −92.6, and −98.5 ppm. Since there are numerous degeneracies among the transitions, and since eight weak lines are not detected, it is not possible to solve for coupling constants. Although a structural assignment is not possible, this must be another species with four phosphorus nuclei. The similarity of these chemical shifts to those reported in Table I for "$Li_2(PPh)_4$" suggests that this may be an isomer, quite possibly *meso*-$Li_2(PPh)_4$.

$M_2(PPh)_3$. The reaction of $(PPh)_5$ with 3K produces a solution which exhibits a ^{31}P NMR spectrum of $K_2(PPh)_4$ and a *sharp* singlet at −48.80 ppm which has been previously assigned[6] as $K_2(PPh)_3$. When the reaction is performed with 3.3K, the resonances due to $K_2(PPh)_4$ are virtually gone, and the $K_2(PPh)_3$ resonance has changed to a "triplet" with an intensity ratio of 1:9:1. This pattern is near the limiting AB_2 pattern where $J/\Delta\nu$ approaches infinity. The ^{31}P spectrum of the $(PPh)_5$ + 4K mixture shows no trace of $K_2(PPh)_4$ but only the 1:9:1 AB_2 "triplet". The two outer peaks have a larger separation in the latter case (57.1 Hz as compared to 12.5 Hz from the 3.3K reaction). When this last sample is diluted to one-quarter its original concentration, the "triplet" becomes a more recognizable AB_2 pattern as shown in Figure 3. Spectral parameters are listed in Table I for this spectrum. At 220 MHz the ^{1}H NMR of pure $K_2(PPh)_3$ at any concentration shows two different types of phenyl groups with intensity ratios of 2:1. Ortho, meta, and para protons (two environments for each) are clearly resolved and appear as doublets, triplets, and triplets, respectively.

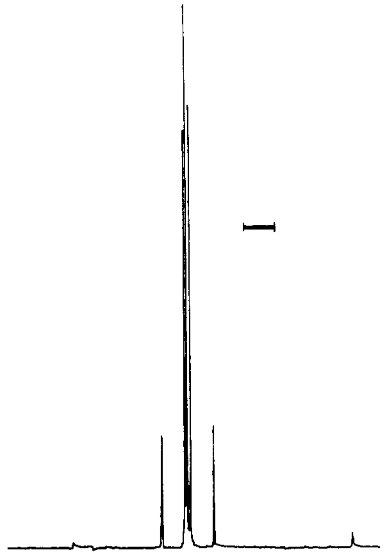
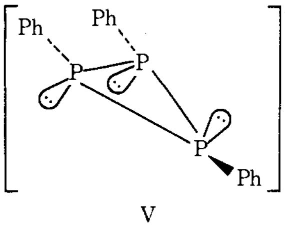


Figure 3. The 40.5-MHz ^{31}P-{H} NMR of $K_2(PPh)_3$ in THF at 30°. Calibration bar indicates 100 Hz.

A ^{31}P spectrum of the analogous cesium compound shows all eight lines of an AB_2 pattern; the spectral parameters are listed in Table I. The coupling constant is similar to $K_2(PPh)_3$ but ν_A−ν_B has increased twofold over the potassium compound.

The discovery that the ^{31}P NMR spectrum of $K_2(PPh)_3$ is concentration dependent is of crucial importance. Formerly,[6] $K_2(PPh)_3$ was said to contain a cyclic anion with three P–P bonds since only a single-line ^{31}P spectrum was observed. With the disclosure that this is actually only a case of accidental degeneracy in an AB_2 spin system, a chain structure must again be considered. The question of possible chelation of K^+ by such a chain remains unanswered, however, since the diagnostic J_{BB} coupling constant cannot be determined. While a chain structure is consistent with the data, so too is a cyclic dianion with conformation V. However, since we find $Cs_2(PPh)_3$ to exhibit inequivalent phosphorus environments and a P–P coupling constant similar to that of $K_2(PPh)_3$, we tentatively choose the more



V

conservative interpretation: the spectral data for both salts of $(PPh)_3^{2-}$ are most simply explained in terms of a chain structure with two P-P bonds.

In order to explain the concentration dependence observed for ν_A-ν_B we must assume that the 30° spectra fall in the rapid exchange category of *some* equilibrium, either coordinative or conformational. Then, as the relative populations of the two or more species vary with concentration, the chemical shift of the B nuclei will vary, and even become accidentally degenerate with that of the A nucleus. Since we have observed a singlet for $K_2(PPh)_3$ when it is in the presence of $K_2(PPh)_4$, the equilibrium which alters ν_B can actually be affected by "excess" K^+ alone (in such solutions the K^+ to $(PPh)_3^{2-}$ ratio exceeds 2:1). Finally, with regard to the question of cyclic vs. chain structure for $(PPh)_3^{2-}$, we note that the concentration dependence of ν_A-ν_B is more readily dealt with assuming a chain.

We attempted to verify our "chelation hypothesis" by adding alkali-metal-complexing agents in order to set up competitive equilibria. In this way it ought to be possible to populate significantly a species lacking metal-phosphorus bonds. The ^{31}P NMR spectrum of THF solution of $K_2(PPh)_3$ containing dibenzo-18-crown-6 in a "crown":K ratio of 1:1 shows *no* resonances at 30°. However, on cooling to −85°, a well-resolved AB_2 pattern (Table I) appears. No other species is detected. There are numerous remarkable features associated with this result. First J_{AB} is within 2 Hz of that observed in the absence of the crown ether. There can be no doubt that $(PPh)_3^{2-}$ in the presence or absence of the crown ether contains P-P bonds of identical character. Second, the environments of *both* types of phosphorus nuclei are extremely sensitive to potassium coordination. They undergo downfield shifts of 33 and 60 ppm when potassium is complexed by the crown ether. While the B nuclei are expected to be affected, transmission to the A nucleus is unusual. Finally, the total absence of any ^{31}P spectrum at 30° must be due to exchange broadening of unspecified nature. While the $M_2(PPh)_3$ species obviously exhibit exceedingly complex structural and dynamic behavior in solution, it is our subjective judgement that the totality of our observations are more consistent with a structure which contains two, not three P-P bonds. This point may remain controversial; a referee has suggested that structure V, with M^+ coordinated to a single phosphorus nucleus, is also consistent with our data.

$K_2(PPh)_2$. The reaction of $(PPh)_5$ with 5K is the first one in which any insoluble compound results. Analysis shows this orange product to be $K_2(PPh)_2\cdot\frac{1}{2}THF$. Appreciable $K_2(PPh)_3$ remains in solution, and no new resonances can be observed in the ^{31}P NMR. $(PPh)_5$ was found to be unreactive with either calcium or barium metal in THF.

Acknowledgment. We wish to thank the Research Corporation for continuing generous support of this work.

References and Notes

(1) J. W. B. Reesor and G. F. Wright, *J. Org. Chem.*, **22**, 385 (1957).

(2) P. R. Bloomfield and K. Parvin, *Chem. Ind.* (*London*), 541 (1959).

(3) E. Fluck and K. Isslieb, *Z. Anorg. Allg. Chem.*, **339**, 274 (1965).

(4) K. Issleib and K. Krech, *Chem. Ber.*, **98**, 2545 (1965).

(5) K. Issleib and K. Krech, *Chem. Ber.*, **99**, 1310 (1966).

(6) K. Issleib and E. Fluck, *Angew. Chem. Int. Ed. Engl.*, **5**, 587 (1966).

(7) K. Issleib, C. Rockstroh, I. Duchek, and E. Fluck, *Z. Anorg. Allg. Chem.*, **360**, 77 (1968).

(8) K. Issleib and F. Krech, *J. Prakt. Chem.*, **311**, 463 (1969).

(9) K. Issleib and F. Krech, *Z. Anorg. Allg. Chem.*, **372**, 65 (1970).

(10) K. Issleib and F. Krech, *Z. Anorg. Allg. Chem.*, **385**, 47 (1971).

(11) M. Baudler, J. Vesper, P. Junkes, and H. Sandmann, *Angew. Chem., Int. Ed. Engl.*, **10**, 940 (1971).

(12) M. Baudler, J. Vesper, and H. Sandmann, *Z. Naturforsch. B*, **27**, 1007 (1972).

(13) F. G. Mann and A. J. H. Mercer, *J. Chem. Soc., Perkin Trans. 1*, 1631 (1972).

(14) K. Issleib, G. Wille, and F. Krech, *Angew. Chem., Int. Ed. Engl.*, **11**, 527 (1972).

(15) T. J. DuPont and J. L. Mills, *Inorg. Chem.*, **12**, 2487 (1973).

(16) P. R. Hoffman and K. G. Caulton, *J. Am. Chem. Soc.*, **97**, 4221 (1975).

(17) Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind 47401.

(18) W. A. Henderson, M. Epstein, and F. S. Seichter, *J. Am. Chem. Soc.*, **85**, 2462 (1963).

(19) C. J. Pederson, *J. Am. Chem. Soc.*, **89**, 7017 (1967).

(20) E. F. Mooney, *Annu. Rep. NMR Spectrosc.*, **5B**, (1973); J. Günther, *Angew. Chem., Int. Ed. Engl.*, 11, 861 (1972).

(21) M. Crutchfield, C. Dungan, J. Letcher, V. Mark, and J. Van Wazer, *Top. Phosphorus Chem.*, **5**, (1967).

(22) This behavior is also not due to attenuation by filtering. This was established by collecting a "reflected" or "folded over" spectrum in a window of the same size as used originally.

(23) E. Fluck and K. Issleib, *Z. Naturforsch. B*, **20**, 1123 (1965).

(24) K. Issleib, G. Lux, and R. Stolz, *Z. Anorg. Allg. Chem.*, **350**, 44 (1967).

(25) G. Fraenkel and D. Watson, *J. Am. Chem. Soc.*, **97**, 231 (1975).

(26) The equilibrium constant for binding a second potassium ion to IV should be small.

(27) J. Hooz, S. A. Kiyama, F. J. Cedar, M. J. Bennett, and R. M. Tuggle, *J. Am. Chem. Soc.*, **96**, 274 (1974).

(28) J. J. Brooks and G. D. Stucky, *J. Am. Chem. Soc.*, **94**, 7333 (1972).

(29) J. J. Brooks, W. Rhine, and G. D. Stucky, *J. Am. Chem. Soc.*, **94**, 7346 (1972).

(30) R. P. Zerger and G. D. Stucky, *J. Chem. Soc., Chem. Commun.*, 44 (1973).

(31) W. Hewertson, B. T. Kilbourn, and R. H. B. Mais, *Chem. Commun.*, 952 (1970).

(32) C. Johnson, J. Toney, and G. D. Stucky, *J. Organomet. Chem.*, **40**, C11 (1972).

(33) S. C. Abrahams, *Acta Crystallogr.*, **7**, 423 (1954).

(34) R. Tegman, *Acta Crystallogr., Sect. B*, **29**, 1463 (1973).

(35) H. Köpf, *Angew. Chem., Int. Ed. Engl.*, **8**, 375 (1969).

(36) H. Köpf, B. Block, and M. Schmidt, *Chem. Ber.*, **101**, 272 (1968).

(37) H. Köpf and B. Block, *Chem. Ber.*, **102**, 1504 (1969).

(38) H. Köpf, *Chem. Ber.*, **102**, 1509 (1969).

(39) P. E. Jones and L. Katz, *Chem. Commun.*, 842, (1967).

(40) The lifetime of Na^+ in dibenzo-18-crown-6 is 10^{-5} sec at 25°: E. Shchori, J. Jagur-Grodzinski, Z. Luz, and M. Shporer, *J. Am. Chem. Soc.*, **93**, 7133 (1971). In "crypt", the lifetime increases to several milliseconds, but this would still yield averaged ^{31}P NMR spectra: J. M. Ceraso and J. L. Dye, *J. Am. Chem. Soc.*, **95**, 4432 (1973). Quite unexpectedly, however, there is evidence for lifetimes of chelated potassium on the order of seconds at −17° (see ref 25).

(41) F. Durant, P. Piret, and M. Van Meerssche, *Acta Crystallogr.*, **23**, 780 (1967).

(42) It is possible that the peaks marked "X" in the figures are due to (a) the acyclic form *or* (b) the *d-l* isomers. These lines are inadequate to fully define the spectra parameters, however.

(43) R. Baechler and K. Mislow, *J. Am. Chem. Soc.*, **93**, 773 (1971).

(44) J. Lambert, G. Jackson, and D. Mueller, *J. Am. Chem. Soc.*, **92**, 3093 (1970).

(45) J. P. Albrand and J. B. Robert, *J. Chem. Soc., Chem Commun.*, 644 (1974).

(46) The chemical shifts of $(PPh)_5$ are temperature dependent.