Conformational Stability and Ring-Size Integrity of Cyclic Polyphosphines

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In contrast to earlier reports, the compound $(PPh)_5$ exhibits a $^{31}P\{^1H\}$ NMR spectrum consistent with the known solid-state structure (a nonplanar five-membered ring). The compound $(PPh)_6$ has a ^{31}P chemical shift distinct from $(PPh)_5$ and undergoes ring-size redistribution reactions to other $(PPh)_n$ species only after months in solution at 30°. Conversely, melting $(PPh)_5$ produces small amounts of $(PPh)_6$ as well as a second phosphorus-containing species. The $^{31}P\{^1H\}$ spectra of $\overline{PhP(PPh)_3X}$ (X = CH_2, S) are analyzed completely. For X = CH_2, the proton NMR establishes that ring-puckering is slow on the NMR time scale. The $^1J_{PP}$ values are discussed in relation to possible delocalization within the ring.

The conformational stability and ring-size integrity of *cyclo*-polyphosphines are presently poorly understood.[1,2] It has been repeatedly claimed that the ^{31}P NMR spectrum of $(PPh)_5$ (Ph = C_6H_5) is a singlet.[3-5] Since the five-membered ring is known[6] to exist in the solid state in an envelope conformation with no molecular symmetry, the ^{31}P NMR result requires stereochemical nonrigidity. Time averaging of all five phosphorus nuclei, however, requires not only a torsional "ring puckering" motion (which yields only effective mirror symmetry) but also rapid inversion at phosphorus. It is now known that the latter process is generally much slower than "umbrella inversion" at nitrogen.[7] However, replacement of one R group in PR_3 by PR_2 to give a biphosphine, R_2PPR_2, lowers the barrier to inversion from ~32 to ~23 kcal mol^{-1}.[8] Although the quantitative effect of a second replacement of R by PR_2 is unknown, the barrier will probably decrease. Thus, rapid inversion about phosphorus in $(PPh)_5$ cannot be excluded, a priori. Finally, the problem of anomalously low solution molecular weights for $(PPh)_5$ has been suggested to result from rapid equilibria involving $(PPh)_5$ and $(PPh)_4$ or $PhPH_2$.[9] The possibility of ring expansion on coordination of *cyclo*-polyphosphines to a transition metal remains even in the recent literature,[10] and doubts persist as to whether $(PPh)_5$ and $(PPh)_6$ are different in solution.[5]

More recently Fourier transform ^{31}P NMR has been applied to the identification of $(R-P)_n$ species. The complex resonance patterns of $(CF_3P)_5$ and $(CH_3P)_5$ have been analyzed as AA'BB'C spin systems;[11,12] time-average *m* symmetry is implied. After the present work was completed, the resonance pattern of $(PhP)_5$ was described as a "complex multiplet".[13] We report here the application of Fourier transform ^{31}P NMR for the clarification of several stereochemical problems in *cyclo*-polyphosphine chemistry.

Experimental Section

Materials. $(PPh)_5$ was prepared by method c of Henderson[14] and recrystallized from carbon disulfide–ethanol; mp 148.5–151° (open tube). In a sealed evacuated capillary, the melting point is higher: 159.5–161°. Infrared[15] and mass spectra[16,17] confirm its purity. Anal. Calcd for $C_{30}H_{25}P_5$: C, 66.67; H, 4.63. Found: C, 66.69; H, 4.85. Since the reaction was kept near ambient temperature, $(PPh)_6$ was also formed and isolated from the acetone-insoluble material. It was recrystallized from carbon disulfide; mp 183.5–186.5° (open tube). The mass spectra (20 and 70 eV) show a molecular ion (m/e 648) and a fragmentation pattern similar to that of $(PPh)_5$. Anal. Calcd for $C_{36}H_{30}P_6$: C, 66.67; H, 4.63. Found: C, 65.27; H, 4.83.

$(PPh)_4CH_2$ was prepared by the method of Baudler[18] and recrystallized from carbon disulfide–ethanol; mp 136.5–139° (sealed tube). The mass spectrum (70 eV) shows the molecular ion and a fragmentation pattern as described previously. The ^{31}P NMR spectrum was recorded on a 0.33 M solution in CS_2.

Spectra. Fourier transform phosphorus-31 NMR spectra were obtained with a Varian Associates XL-100-15 spectrometer operating

at 40.5 MHz with a hexafluorobenzene external lock. Broad ^{31}P spectra recorded earlier[3-5] were complicated by unresolved coupling to protons. In order to avoid this problem, all protons were white-noise decoupled. Chemical shifts were measured relative to external 85% phosphoric acid. Peak positions are accurate to 0.5 Hz. Accessories similar to those above were also employed. Peak positions are accurate to 1.5 Hz. Downfield chemical shifts are denoted by *positive* values. While this is contrary to almost all previous papers on ^{31}P NMR, it conforms to the recommended convention.[19] NMR spectra were recorded on sealed evacuated samples. Solvent was freeze–thaw degassed and then vacuum transferred into 5-mm NMR tubes.

Mass spectra were recorded on a Varian Associates CH-7 spectrometer. Infrared spectra were taken as Nujol mulls on a Perkin-Elmer 137 spectrophotometer. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., and NMR spectra were simulated using the programs LAOCN3[20] and NMRCAL.[21]

Results and Discussion

The white-noise proton-decoupled ^{31}P spectrum of $(PPh)_5$ at 30° (Figure 1) is an asymmetric multiplet centered near −3 ppm indicative of three or more distinct chemical shifts with $J/\delta\nu$ large. Since we have not yet been successful in our attempts to fit the spectrum exactly with spin systems AA'BB'C or ABCDE,[22] we are presently unable to decide whether ring puckering, inversion, or both are "slow" processes at room temperature. The spectrum shows $(PPh)_4$, $(PPh)_6$, and $PhPH_2$ to be absent.

$(PPh)_6$ has been studied recently by ^{31}P NMR.[5] However, the material used was of low solubility (in contrast to our sample) and the resonance recorded coincided with that of $(PPh)_5$. These earlier results are apparently in error. A THF solution of $(PPh)_6$ exhibits a sharp ^{31}P singlet at −22.7 ppm (−21.7 ppm in CS_2), consistent with the sixfold symmetry observed for the all-equatorial isomer in the solid state.[23] No evidence is found for other conformers or geometrical isomers in solution, probably as a result of the large steric demands of the six phenyl rings. The observed change in ^{31}P chemical shift on going from $(PPh)_5$ to $(PPh)_6$ (18 ppm) is the order of magnitude observed in cyclic phosphonitrilic compounds, $[NPCl_2]_n$.[24] The resonance of $(PPh)_6$ falls outside the regions empirically assigned[13] to four- and five-membered rings.

To aid in interpreting the spectrum of $(PPh)_5$ we have recorded the spectrum of 1,2,3,4-tetraphenyl-*cyclo*-5-carba-1,2,3,4-tetraphosphane (1).[18] The white-noise proton-decoupled ^{31}P spectrum (Figure 2) is an AA'BB' pattern. The parameters in Table I result from an iterative fit of the line positions; the root-mean-square error for fitting 22 lines is 0.06 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.[19] Phosphorus nuclei bonded to the methylene carbon are presumed to be "A" spins since $|J_{AA'}| \ll |J_{BB'}|$, implying that B and B' are directly bonded. A pure AA'BB' spectrum does not allow assignment of δ_A and δ_B to particular nuclei. The
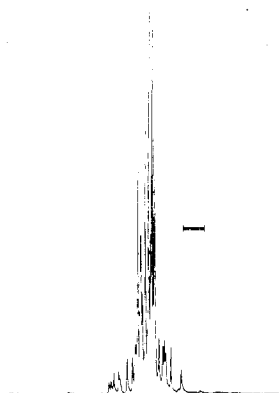
Figure 1. The 40.5-MHZ ^{31}P{H} NMR spectrum of 0.5 M (PPh)$_5$ in CS$_2$ at 30°. The calibration bar is 80 Hz, and the tallest peak has a chemical shift of -2.78 ppm.

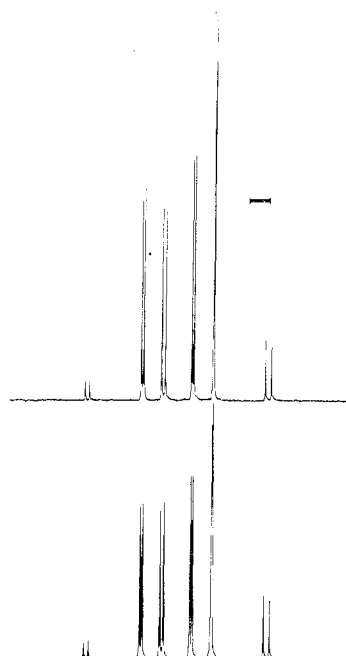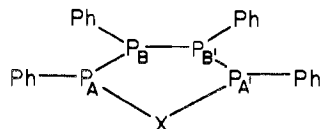**Figure 2.** The 40.5-MHz ^{31}P{H} NMR spectrum of 0.33 M (PhP)$_4$CH$_2$ in CS$_2$ at 30°. The calibration bar is 80 Hz. Only the low-field half of the spectrum is shown. The calculated spectrum appears below the observed spectrum.

Table I. ^{31}P NMR Parameters[a]

	X = CH$_2$ (I)	X = S (II)		X = CH$_2$ (I)	X = S (II)
δ_A	+46.66	+116.63	$J_{BB'}$	-316.2 (0.3)	-359.7 (2)
δ_B	+18.61	+69.13	$J_{AA'}$	-16.9 (0.2)	+14.6 (1)
J_{AB}	-285.0 (0.3)	-330.1 (2)	$J_{AB'}$	+7.26 (0.3)	+17.7 (2)

[a] Chemical shifts (δ) in ppm and coupling constants (J) in Hz. Estimated standard deviations in the last digit appear in parentheses.

assignment of Table I was made by selective decoupling of only the phenyl protons. The resulting spectrum was more broad and complex in the downfield (46.7-ppm) region, identifying this resonance as that of the phosphorus directly bonded to the methylene group. An AA'BB' spin system requires C$_2$ or m (mirror) symmetry. Case 1, a static structure based on a half-chair conformation of the five-membered ring with phenyl
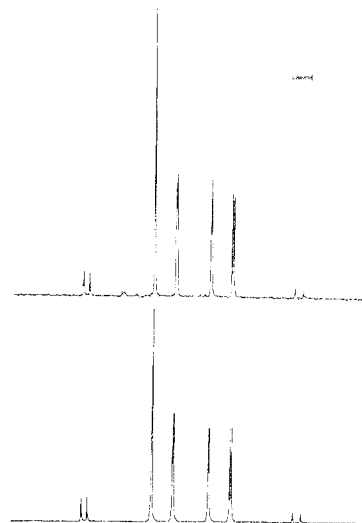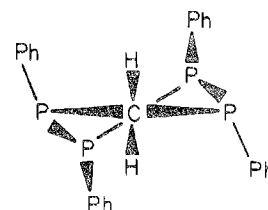

Figure 3. Observed (upper) and calculated (lower) upfield half of the 40.5-MHz ^{31}P{H} NMR spectrum of (PhP)$_4$S in CS$_2$ at 30°. The calibration bar is 80 Hz.

groups all axial, has C$_2$ symmetry. This is the structure found for (PPh)$_4$S.[25]

Case 2, rapid inversion at all phosphorus nuclei, produces time-averaged mirror symmetry. The ^{1}H{^{31}P} singlet reported earlier[18] does not distinguish between these two possibilities. The normal (phosphorus-coupled) proton spectrum resolves the ambiguity. Case 2 yields an AA'BB'X$_2$ spin system. Sample calculations at both 100 and 220 MHz show that the proton (X) spectrum is a first-order triplet (J_{AX}) of triplets (J_{BX}). The observed spectrum is the considerably more complex pattern[26] of an AA'BB'XX' spin system. The static orientation of phosphorus substituents (case 1) makes the two methylene protons magnetically inequivalent. A complete spectral analysis is not possible because of the large difference in the magnitudes of the J_{PP} and J_{PH} coupling constants. However, a partial analysis gives $|J_{HPB} + J_{HPB'}| = 9$ Hz and $|J_{HPA} + J_{HPA'}| = 19$ Hz. These values are consistent with the Karplus-type angular dependence observed for phosphorus–hydrogen coupling, since either J_{HPA} or $J_{HPA'}$ involves a near-zero dihedral angle.

The ^{31}P NMR spectrum of 1,2,3,4-tetraphenyl-*cyclo*-5-thia-1,2,3,4-tetraphosphane (II)[25] closely resembles that of the CH$_2$ analog (Figure 3). An iterative fit of the line positions yields the parameters shown in Table I; the root-mean-square error of the fit is 0.45 Hz.[27] Relative signs are again uniquely determined. Only $^2J_{AA'}$, the coupling "through the hetero group", changes sign in going from I to II.

Few data are available on NMR parameters of catenated phosphorus compounds. The *cyclo*-pentaphosphines (CH$_3$P)$_5$ and (CF$_3$P)$_5$ both show two types of $^1J_{PP}$, one with substituents cis and a second with substituents trans; the former exceed the latter by 60–100 Hz.[11,12] Only trans-type $^1J_{PP}$ values are found in I and II, and they are similar in magnitude within a given compound. The absolute values in I and II are markedly larger than for (CH$_3$P)$_5$ and (CF$_3$P)$_5$ suggesting a substantial effect due to substituent and the heteroatom in the ring. In both I and II, the two-bond $^2J_{PP}$ value with

substituents cis (J_{AB}) is more positive than when the substituents are trans ($J_{AA'}$), although the latter trend is nearly reversed for II. A similar relationship holds for the (RP)$_5$ species.[12] However, the "intervening atom" is not phosphorus for $J_{AA'}$ in I and II.

The theory for coupling constants of "heavy" ($Z > 1$) nuclei separated by several bonds is in its infancy.[19] Indeed, it is not clear whether $J_{AA'}$ should be designated as a three-bond (through P_B and $P_{B'}$) or a two-bond (through X) coupling constant due to the cyclic structure under consideration. It was in an attempt to understand this phenomenon that an NMR study of II was undertaken. Replacement of CH_2 (an "insulating" group along the two-bond path) by sulfur substantially alters $J_{AA'}$ toward more positive values. This suggests a possible two-bond "contribution" to $J_{AA'}$. J_{AB} also becomes more positive, although the magnitude of the effect is smaller.

The coupling of directly bonded nuclei becomes significantly more negative on going from I to II. Since this occurs to an equal extent in J_{AB} *and* $J_{BB'}$, it cannot be solely due to a substituent effect; the B nuclei are more distant and should be less affected. This effect is most easily explained on the basis of minor changes in the degree of delocalization in the ring. Delocalization has long been considered possible for *cyclo*-polyphosphines, but firm evidence is lacking. Some negative evidence exists.[28,29] The trends in J_{AB} and $J_{BB'}$ for I and II suggest greater s orbital character in the phosphorus–phosphorus bonds of II. This implies a greater sp^2 contribution to P–P bonds in II as a result of delocalization via the third p atomic orbital. The lone pairs on sulfur are more suited to such cyclic delocalization than the orbitals of the methylene group, thus making the observed trend plausible. Participation by d orbitals in the delocalization may occur but is not required to explain the data.

The evidence presented here shows that (PPh)$_5$ and (PPh)$_6$ retain their integrity in solution at 30°. It has been reported that two new ^{31}P resonances are detectable after heating solid (PPh)$_5$ above its melting point.[3] These have been attributed to PhP=PPh (−48.3 ppm) and PPh (−22.6 ppm). We have repeated the pyrolysis experiment and were able to reproduce the earlier results. However, an authentic sample of (PPh)$_6$ precisely reproduces the ^{31}P chemical shift of the species claimed to be PPh. Since it is demonstrated here and elsewhere[13] that the ^{31}P chemical shift is markedly dependent on ring size, we suggest that the sharp singlet observed at −48.3 ppm may be due to other (PPh)$_n$ rings (n even).[30] Although the species responsible for this peak remains to be identified, its constant intensity for periods of up to 2 months in solution at 30° suggests that it is not due to a reactive species such as PPh. No PhPH$_2$ is detected by ^{31}P NMR after pyrolysis of (PPh)$_5$. The ^{31}P spectrum of a mixture of five- and six-membered rings is the superposition of the individual species, proving that any ring-expansion equilibrium is only slowly established.[31] The high temperatures required and the small amount of new species produced suggest that the phosphorus–phosphorus bonds in (PPh)$_5$ are not particularly labile and lay to rest any thought that anomalously low solution molecular weights for this species are due to rapid equilibria involving either (PPh)$_4$ or PhPH$_2$.

Confusion continues to characterize the field of *cyclo*-polyphosphine chemistry. Even recent reports are suspect. The claimed[32] (PPh)$_3$ is observed to have a ^{31}P chemical shift identical with that of (PPh)$_5$; no comment is offered concerning this "accidental degeneracy". The problem lies in the similarity of commonly measured properties of those closely related oligomers. As ^{31}P NMR becomes the standard method of characterization, these ambiguities will hopefully disappear.

References and Notes

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(30) Professor Mills has noted that this singlet falls within the region apparently characteristic of four-membered rings.
(31) The −48.3-ppm resonance grows into a THF solution of a mixture of (PPh)$_5$ and (PPh)$_6$ sealed under vacuum after a period of 2 months at 25°. Over a period of 2.5 years, pure (PPh)$_6$ redistributes in CS$_2$ solution to an approximately equimolar mixture of (PPh)$_5$ and (PPh)$_6$, along with a trace of the higher field species. The initially colorless solution turns yellow during this transformation.
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