Carbon-13 Nuclear Magnetic Resonance Spectra of Some Polyphosphines with Ethane Bridges Between Trivalent Phosphorus Atoms

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The proton noise-decoupled pulsed Fourier transform ^{13}C n.m.r. spectra of $(C_6H_5)_2PCH_2CH_2PR_2$ (R = CH_3 and C_6H_5), $R_2PCH_2CH_2P(H)C_6H_5$ (R = CH_3 and C_6H_5), $(CH_3)_2PCH_2CH_2PH_2$, n-$C_6H_{13}PHCH_2CH_2PH_2$, $R'P(CH_2CH_2PR_2)_2$ (R' = CH_3, R = CH_3; R' = C_6H_5, R = CH_3 or C_6H_5), $(CH_3)_2PCH_2CH_2P(R)CH_2CH_2PH_2$ (R = H and C_6H_5), and $P(CH_2CH_2PH_2)_3$ have been examined. Replacement of alkyls by hydrogen in R_2P units consistently raises the ^{13}C n.m.r. chemical shifts (*i.e.*, lowers the δ values) of CH_2 groups attached to this phosphorus. The spin–spin splittings in the ^{13}C n.m.r. spectra by the phosphorus atoms in $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ must be analysed as second-order ABX systems whereas those in the remaining polyphosphines can be analysed as first-order AMX systems. The range of significant phosphorus–carbon coupling in these compounds is limited to three bonds. In most cases, the coupling constants ^1J(C–P) and ^2J(C–P) have nearly equal magnitudes but opposite signs. However, direct bonding of hydrogen to a trivalent phosphorus atom appears to decrease markedly its $|^2J(C\text{–}P)|$ while having much less effect on its $|^1J(C\text{–}P)|$. This indicates that substitution on phosphorus of alkyls or aryls by hydrogens has a major effect on the conformation of the PCH_2CH_2P chain.

RECENTLY Mann [1] reported ^{13}C n.m.r. chemical shifts and carbon–phosphorus coupling constants on an extensive series of tertiary phosphines. We were interested in extending such studies to polyphosphines containing PCH_2CH_2P structural units. Such compounds are now accessible through base-catalysed additions of phosphorus–hydrogen bonds to vinylphosphorus compounds.[2-7]

[1] B. E. Mann, *J.C.S. Perkin II*, 1972, 30.

[2] R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, 1969, **91**, 5191.

[3] R. B. King and P. N. Kapoor, *J. Amer. Chem. Soc.*, 1971, **93**, 4158.

[4] R. B. King, J. C. Cloyd, jun., and P. N. Kapoor, *J.C.S. Perkin I*, 1973, 2226.

[5] R. B. King, J. C. Cloyd, jun., and P. K. Hendrick, *J. Amer. Chem. Soc.*, 1973, **95**, 5083.

[6] R. B. King and J. C. Cloyd, jun., *J. Amer. Chem. Soc.*, 1975, **97**, 46.

[7] R. B. King and J. C. Cloyd, jun., *J. Amer. Chem. Soc.*, 1975, **97**, 53.

The ^{13}C chemical shifts and the carbon–phosphorus coupling constants involving the PCH_2CH_2P carbon atoms are of particular interest since these bridge carbon atoms can couple to both phosphorus atoms. Furthermore our synthetic procedures provide sources of many PCH_2CH_2P derivatives in which both phosphorus atoms are non-equivalent. Apparently the only polyphosphine to have been previously investigated by ^{13}C n.m.r. spectroscopy is $(CH_3)_2PCH_2CH_2P(CH_3)_2$ in which the phosphorus atoms are equivalent.[8]

TABLE 1

^{13}C N.m.r. spectra [δ (p.p.m.); J/Hz] of the terminal alkyl groups in some polyphosphines

		^{13}C N.m.r. spectrum					
		Methyl group		Phenyl group [a]			
Compound	Solvent	δ	^1J (P–C)	C-1	C (*ortho*)	C (*meta*)	C (*para*)
$Me_2PCH_2CH_2PMe_2$ [b]	$CD_3C_6D_5$	14.1	8				
$Ph_2PCH_2CH_2PPh_2$	CH_2Cl_2			139.9 (t, 7)	134.1 (t, 10)	129.9 (d, 5)	129.7 (s)
$Me_2PCH_2CH_2PPh_2$	Neat	15.4	16	140.2 (d, 15)	134.0 (d, 18)	129.7 (d, 5)	129.8 (s)
$Me_2PCH_2CH_2P(H)Ph$	Neat	15.3	16	136.9 (d, 13)	134.9 (d, 15)	129.8 (d, 6)	129.4 (s)
$Ph_2PCH_2CH_2P(H)Ph$ [c]	CH_2Cl_2			?	134.1 (Ph_2P, d, 18)	129.9 (d, 7)	130.0 (s)
$Ph_2PCH_2CH_2P(H)Ph$ [c]	CH_2Cl_2			?	135.1 (PhP, d, 15)	129.9 (d, 7)	130.0 (s)
$Me_2PCH_2CH_2PH_2$	Neat	15.6	16				
$MeP(CH_2CH_2PMe_2)_2$	Neat	16.0 (Me_2P)	16				
$MeP(CH_2CH_2PMe_2)_2$	Neat	13.2 (MeP)	18				
$PhP(CH_2CH_2PMe_2)_2$	Neat	15.7	16	139.9 (d, 18)	134.0 (d, 20)	129.9 (d, 7)	130.2 (s)
$PhP(CH_2CH_2PPh_2)_2$	CH_2Cl_2			140.0(Ph_2P, dd, 16, 7)	134.1 (dd, 18, 5)	129.8 (d, 6)	130.0 (s)
$PhP(CH_2CH_2PPh_2)_2$	CH_2Cl_2			139.1 (PhP, d, 17)	133.9 (d, ~17)	130.1 (d, ~6)	130.0 (s)
$Me_2PCH_2CH_2PHCH_2CH_2PH_2$	Neat	16.0	16				
$Me_2PCH_2CH_2PPhCH_2CH_2PH_2$	Neat	15.8	16	139.6 (d, 18)	134.0 (d, 18)	130.0 (d, 6)	130.4 (s)
n-$C_6H_{13}P(H)CH_2CH_2PH_2$	Neat	33.2 (n-C_6H_{13}, s),32.3 (d, 10), 29.9 (d, 11), 24.1 (s), 21.9 (d, 11), 15.7 (s)					

[a] s = singlet, d = doublet, t = triplet, dd = double doublet; coupling constants are given in parentheses. [b] Data taken from ref. 8. [c] This solution had to be freshly prepared to avoid decomposition.

TABLE 2

^{13}C N.m.r. spectra [δ (p.p.m.); J/Hz] of the ethane bridges of some polyphosphines

				^{13}C N.m.r. spectrum					
	$R_2PCH_2CH_2PR_2'$ Unit			δ		R_2PCH_2		CH_2PR_2'	
Compound	R_2	R_2'	^3J(P–P)	R_2PCH_2	CH_2PR_2'	^1J(C–P)	^2J(C–P)	^1J(C–P)	^2J(C–P)
$Me_2PCH_2CH_2PMe_2$ [a]	Me, Me	Me, Me		28.0	28.0	~1	~1	~1	~1
$Ph_2PCH_2CH_2PPh_2$	Ph, Ph	Ph, Ph		25.4	25.4	*b*	*b*	*b*	*b*
$Me_2PCH_2CH_2PPh_2$	Me, Me	Ph, Ph	26	29.1	25.3	15	15	14	14
$Me_2PCH_2CH_2P(H)Ph$	Me, Me	H, Ph		31.8	20.8	14	6	14	14
$Ph_2PCH_2CH_2P(H)Ph$	Ph, Ph	H, Ph		29.7	21.1	19	19	14	14
$Me_2PCH_2CH_2PH_2$	Me, Me	H, H		37.0	11.7	14	2	15	10
n-$C_6H_{13}PHCH_2CH_2PH_2$	n-C_6H_{13}, H	H, H		25.8	14.7	13	4	11	11
$MeP(CH_2CH_2PMe_2)_2$	Me, Me	Me, C_2H_4	20	29.2	26.7	12	12	~16	~12
$PhP(CH_2CH_2PMe_2)_2$	Me, Me	Ph, C_2H_4	23	29.2	25.3	12	12	14	14
$PhP(CH_2CH_2PPh_2)_2$	Ph, Ph	Ph, C_2H_4	27	25.0	24.9	~13	~13	~16	~16
$Me_2PCH_2CH_2PHCH_2CH_2PH_2$	Me, Me	H, C_2H_4		32.2	17.9	13	9	13	13
$Me_2PCH_2CH_2PHCH_2CH_2PH_2$	H, C_2H_4	H, H		25.8	14.8	15	4	9	9
$Me_2PCH_2CH_2PPhCH_2CH_2PH_2$	Me, Me	Ph, C_2H_4	23	29.3	25.1	13	13	14	14
$Me_2PCH_2CH_2PPhCH_2CH_2PH_2$	Ph, C_2H_4	H, H	14	33.4	12.1	17	<1	15	10
$P(CH_2CH_2PH_2)_3$	C_2H_4, C_2H_4	H, H		32.0	12.5	17	3	14	10

[a] Data taken from ref. 8. [b] This coupling could not be observed.

EXPERIMENTAL

The ^{13}C n.m.r. spectra (Tables 1 and 2) were taken in the indicated solvents using a JEOLCO PFT-100 spectrometer operating at 25.03 MHz in the Fourier transform mode with proton decoupling and a deuterium lock. The samples were placed in 10 mm n.m.r. tubes with internal tetramethylsilane for the standard and a capillary of deuterium oxide for the lock. The system was normally pulsed every 3—6 s with 45° pulses. An 8 K transform was used giving a channel width of 1.22 Hz. 25—1 200 pulses were used to obtain the spectra depending upon the concentration of the sample. The chemical shifts (δ) are reported in p.p.m. downfield from internal tetramethylsilane (Tables 1 and 2).

The ^3J(P–P) coupling constants listed in Table 2 were obtained directly from similar proton noise-decoupled pulsed Fourier transform ^{31}P spectra on the same spectrometer. Further details of these ^{31}P n.m.r. spectra are given elsewhere.[9]

The samples used in this work were prepared by procedures described elsewhere.[2-7] All preparations of the n.m.r. samples of the air-sensitive polyphosphines were done in the nitrogen-filled glove bag.

RESULTS AND DISCUSSION

The first step in the interpretation of the ^{13}C n.m.r. spectra of the polyphosphines was the assignment of all the observed resonances to either the carbons of the terminal alkyl groups or the carbons of the PCH_2CH_2P bridges. This posed no particular difficulty since with

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[8] M. Akhtar, P. D. Ellis, A. G. MacDiarmid, and J. D. Odom, *Inorg. Chem.*, 1972, **11**, 2917.

[9] R. B. King and J. C. Cloyd, jun., *Inorg. Chem.*, 1975, **14**, in the press.

the exception of n-$C_6H_{13}PHCH_2CH_2PH_2$ the only terminal alkyl groups present were methyl and phenyl groups which give well known spectra and which occurred in the phosphines studied by Mann.[1] All methyl carbon resonances in this work fell in the range 13—16 p.p.m. (Table 1) similar to the methyl groups in the phosphines studied by Mann [1] except for the unusual $[(CH_3)_2C]_2PCH_3$. The phenyl groups exhibited only three sets of carbon resonances because of overlap of the *meta*- and *para*-carbon resonances. In both our work and that of Mann the ranges of these three sets of phenyl resonances were consistently 138—144, 132—135, and 128—130 p.p.m.

The resonances remaining after elimination of the terminal alkyl carbon resonances must arise from the PCH_2CH_2P bridges. Most of the compounds studied in this work contain at least two different types of bridge carbons and thus exhibit at least two resonances from the PCH_2CH_2P bridge carbon atoms. These can be assigned by a systematic procedure using the symmetrical compounds $R_2PCH_2CH_2PR_2$ (R = CH_3 and C_6H_5) with only one type of bridge CH_2 group as models for the chemical shifts expected for a particular type of bridge carbon. The process of elimination can then be used to make assignments for the bridging CH_2 resonances of types for which symmetrical model compounds are not available.

Comparison of the chemical shifts of the CH_2 bridge carbons in the symmetrical derivatives $R_2PCH_2CH_2PR_2$ (R = C_6H_5 and CH_3) indicates that a bridging CH_2 adjacent to a dimethylphosphinyl group appears at a lower field (*i.e.* higher δ value) than a bridging CH_2 adjacent to a diphenylphosphinyl group. For this reason, the resonances at 29.1 and 25.3 p.p.m. in the unsymmetrical derivative $(CH_3)_2PCH_2CH_2P(C_6H_5)_2$ can be assigned to the bridge CH_2 groups adjacent to the dimethyl- and the diphenyl-phosphinyl group, respectively. In the tertiary–primary diphosphine $(CH_3)_2PCH_2CH_2PH_2$ the resonance at 37.0 p.p.m. is closest to the expected value for a bridge CH_2 adjacent to a dimethylphosphinyl group leaving the relatively high field (*i.e.* low δ) resonance at 11.7 p.p.m. for the remaining bridge CH_2 adjacent to the PH_2 group. Similar procedures can be used to assign the resonances at *ca.* 21 p.p.m. to the bridge CH_2 adjacent to the secondary phosphorus atom (*i.e.* the PHC_6H_5 group) in the tertiary–secondary diphosphines $R_2PCH_2CH_2P(H)C_6H_5$ (R = CH_3 and C_6H_5).

These assignments establish relatively high field chemical shifts (*i.e.* 10—15 p.p.m.) for CH_2 carbons directly bonded to PH_2 groups. This can then be used to assign the resonance at 25.8 p.p.m. to the CH_2 bridge carbon adjacent to the n-$C_6H_{13}PH$ group in the secondary–primary diphosphine n-$C_6H_{13}P(H)CH_2CH_2PH_2$ and the resonance at 32.0 p.p.m. to the CH_2 bridge carbon adjacent to the centre phosphorus in the tripod tertiary–triprimary tetraphosphine $P(CH_2CH_2PH_2)_3$. The bridge CH_2 of a $CH_2CH_2PH_2$unit bonded to a n-$C_6H_{13}PH$ unit is a useful approximation for the bridge CH_2 of a $CH_2CH_2PH_2$ unit bonded to a $(CH_3)_2PCH_2CH_2PH$ unit thus providing sufficient information along with the approximate chemical shifts of bridge CH_2 groups adjacent to $(CH_3)_2P$ and PH_2 units for assignment of all four bridge CH_2 resonances in the tertiary–secondary–primary triphosphine $(CH_3)_2PCH_2CH_2P(H)CH_2CH_2PH_2$.

The assignments of the PCH_2CH_2P ^{13}C resonances made by this method are summarized in Table 2. In this work the ^{13}C chemical shifts of CH_2 groups in PCH_2CH_2P bridges adjacent to $(C_6H_5)_2P$, $(CH_3)_2P$, RPH (R = alkyl or aryl), and PH_2 groups were found in the ranges 25—30, 26—27, 18—26, and 11—15 p.p.m., respectively. Thus replacement of alkyls by hydrogen in R_2P units consistently raises the ^{13}C chemical shifts (*i.e.* lowers the δ values) of CH_2 groups attached to this phosphorus.

The next step is the assignment of the carbon–phosphorus coupling constants. In all compounds except for the symmetrical derivatives $R_2PCH_2CH_2PR_2$ (R = CH_3 and C_6H_5) and the phenylated tritertiary phosphine $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$, the chemical shift differences between the phosphorus atoms are at least 400 Hz. These spectra can thus be analysed by first-order methods. The data of Mann [1] indicate that carbon–phosphorus coupling can be transmitted though a maximum of three bonds (at least relative to our programmed resolution of ~1 Hz). Thus, except for the symmetrical ditertiary phosphines and the phenylated tritertiary phosphine, all the spectra can be analysed as AMX systems realizing that in natural abundance the proportion of molecules containing two ^{13}C atoms will be negligible. Each carbon atom of either a bridging CH_2 group or a terminal alkyl or aryl group which is within the three-bond coupling range of two phosphorus atoms thus will be part of a different AMX system, since in the overwhelming majority of the cases an observed ^{13}C atom will occur in molecules containing no other ^{13}C atom within coupling distance.

In the ^{13}C n.m.r. spectra of these polyphosphines we are observing the X resonance of an AMX system. In the general case, this X resonance is a four line double doublet [10] with the equal separations between lines 1 and 2 or lines 3 and 4 corresponding to the absolute value of one of the coupling constants (say J_{AX}) and the equal separations between lines 1 and 3 or lines 2 and 4 corresponding to the other coupling constant involving X (*i.e.* J_{MX}). However, if the absolute values of the couplings J_{AX} and J_{MX} are equal, the X resonance becomes a 1 : 2 : 1 triplet. This is true in the spectra of many of the bridge carbons of the polyphosphines with PCH_2CH_2P units examined in this work indicating that the absolute values of their ^1J(C–P) and ^2J(C–P) coupling constants are nearly identical. This is consistent with Mann's observation [1] that $|^1J(C\text{–}P)|$ and $|^2J(C\text{–}P)|$ to saturated alkyl groups are nearly identical in most cases.

In our studies on the ^{13}C n.m.r. spectra of PCH_2CH_2P bridges (Table 2), the major exceptions to the near identity of $|^1J(C\text{–}P)|$ and $|^2J(C\text{–}P)|$ occur in bridges across a pair of phosphorus atoms, one of which has at least one, and preferably two, hydrogens bonded to it. However, the CH_2 group with the anomalously low $|J(C\text{–}P)|$ is the one

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[10] J. D. Roberts, 'An Introduction to the Analysis of Spin–Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra,' Benjamin, New York, 1962.

adjacent to the phosphorus bearing the least hydrogens rather than to the phosphorus bearing the most hydrogens. This suggests that hydrogens directly bonded to a trivalent phosphorus atom decrease its ability to couple through two bonds but do not have much effect on its ability to couple through only a single carbon–phosphorus bond. This is undoubtedly a consequence of conformational changes in the PCH_2CH_2P chain upon substitution on phosphorus of alkyls or aryls by hydrogens. However, a detailed interpretation of this phenomenon appears premature.

The chemical shift differences between the two phosphorus atoms in the symmetrical ditertiary phosphines $R_2PCH_2CH_2PR_2$ ($R = CH_3$ and C_6H_5) are very small since their CH_2 groups are equivalent. The only difference between the two phosphorus atoms in the symmetrical ditertiary phosphines is the fact that one is bonded to a $^{13}CH_2$ group and the other to a $^{12}CH_2$ group in the isotopic species observed 99% of the time in the ^{13}C n.m.r. spectrometer. These symmetrical ditertiary phosphines can thus be analysed as special ABX systems with an extremely small chemical shift difference between A and B.[8,11] In this special ABX system the X resonance appears as a triplet (or double doublet) with a separation between the outer lines of $J_{AX} + J_{BX}$. If J_{AX} and J_{BX} have equal magnitudes but opposite signs, this splitting will vanish and the X resonance will appear as a singlet. The $^{13}CH_2$ resonance in $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ is a singlet indicating that for the bridge CH_2 carbons the coupling constants $^1J(C-P)$ and $^2J(C-P)$ have equal absolute values but opposite signs. This compares with the previously reported [8] spectrum of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ where the bridge $^{13}CH_2$ resonance was a multiplet with a separation of ~1 Hz indicating similar, but slightly incomplete, cancelling of $^1J(C-P)$ and $^2J(C-P)$. Extrapolation of these results suggests that $^1J(C-P)$ and $^2J(C-P)$ in the unsymmetrical polyphosphines with PCH_2CH_2P units also have opposite signs and nearly equal absolute values in many cases like the symmetrical derivatives.

The chemical shift difference between the two different types of phosphorus atoms in the phenylated tritertiary phosphine $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ is 3.1 p.p.m. at 40 MHz which is small enough for this to be considered as an ABX rather than an AMX system. The multiplets from the two non-equivalent types of CH_2 bridges in this tritertiary phosphine appear to be overlapping triplets, but this overlap prevents determination of the fine structure.

The terminal methyl and phenyl carbons in the polyphosphines with PCH_2CH_2P units studied in this work which are AMX systems (*i.e.* all but the symmetrical derivatives $R_2PCH_2CH_2PR_2$ and the phenylated tritertiary phosphine) exhibit doublet resonances except for the *para*-carbon which exhibits only a singlet resonance. No carbon in a terminal alkyl or aryl bonded to the phosphorus of a PCH_2CH_2P unit can be closer than four bonds from the *far* phosphorus atom and thus can couple only with the near phosphorus atom. Furthermore the *para*-carbon of a $C_6H_5PCH_2CH_2P$ unit is four bonds away from even the closer phosphorus atom and thus is unable to couple with either of the two phosphorus atoms.

In the symmetrical $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, an ABX system, the resonances from the two types of phenyl carbons nearest to the phosphorus [C-1 and C-(*ortho*)] are triplets rather than the doublets observed for the unsymmetrical polyphosphines with PCH_2CH_2P units analysed as AMX systems. The separations between the outer lines of these triplets in $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ correspond to $J_{AX} + J_{BX}$ and are approximately equal to the separations of the doublets for similar phenyl carbon atoms in the unsymmetrical polyphosphines analysed as AMX systems. Since the coupling constant of any of the phenyl carbons to the far phosphorus atom in $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ must be negligible because the distance is at least four bonds, either J_{AX} or J_{BX} is zero thereby indicating that the separation between the outer triplet lines in $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ should correspond to the separations between comparable doublets in the unsymmetrical polyphosphines analysed as AMX systems in accord with observations.

The phenyl regions in the ^{13}C n.m.r. spectra of $(C_6H_5)_2PCH_2CH_2P(H)C_6H_5$ and $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ are more complex since both these compounds have two different types of phenyl groups. The resonances of the C-1 and C(*ortho*) atoms of the $(C_6H_5)_2P$ phenyls in the phenylated tritertiary phosphine $C_6H_5P[CH_2CH_2P(C_6H_5)_2]_2$ are double doublets in accord with expectations for the X resonance in an ABX system in cases where the two outer combination modes are too weak for observation.[10,11]

The six different carbon atoms of the n-hexyl group in $n-C_6H_{13}P(H)CH_2CH_2PH_2$ exhibit six distinct carbon-13 resonances. Three are doublets and the remaining three are singlets since only three of the six carbon atoms of this n-hexyl group are within coupling distance (three or less bonds) of a phosphorus atom.

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[11] R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 216.