Unsymmetrical Bisphosphorus Ligands. Phosphorus-31 and Carbon-13 Nuclear Magnetic Resonance and Mass Spectral Measurements

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The unsymmetrical bisphosphorus ligands of the type $RPhP[CH_2]_6PPh_2$ (R = Me, Et, and cyclohexyl), $R_2P[CH_2]_n$-PPh_2 (R = Me and Et, n = 3 and 4), $RPhP[CH_2]_4PPh_2$ (R = Me and Et), and $EtPhP[CH_2]_3PPh_2$ have been characterized by ^{31}P and ^{13}C n.m.r. spectroscopy and by mass spectral measurements. The variation in the ^{31}P chemical shift is explained in terms of the steric requirements of the substituent groups attached to phosphorus and the ^{13}C n.m.r. of the trimethylene-bridged diphosphines are compared and contrasted with their dimethylene-bridged analogues.

THERE is much current interest in the importance of steric effects in phosphorus ligands [1,2] and recent studies have demonstrated the crucial role that the steric bulk of substituent groups attached to the phosphorus donor atom plays in determining the pathway,[3] rate,[4] and product distribution [5] in chemical reactions. The bulk of a phosphine ligand is usually expressed in terms the ligand cone angle θ derived from CPK models [6] and calculations [7-12] have shown that predictions of θ from models are in good agreement with experimental results. The most common probe for examining the steric effect of substituent groups attached to phosphorus is ^{31}P n.m.r. and the value of the chemical shift parameter obtained from the spectra can best be correlated with the steric requirement of the substituents by calculation of the group contribution to the chemical shift (GC_i).[13] In this way ^{31}P spectral data can provide useful information about the change in the effective steric bulk around the phosphorus donor atom when subtle changes are made in the substituents groups bound to phosphorus. Symmetrical diphosphine ligands of the type $Ph_2P[CH_2]_n$-PPh_2 (n = 1—6) are well known and easily prepared [14] and have been characterized by ^{31}P n.m.r.[15] Recently Briggs and Dyer [16,17] have successfully prepared unsymmetrical diphosphines of the type $RPhP[CH_2]_6$-PPh_2 (R = Me, Et, and cyclohexyl), $RPhP[CH_2]_4PPh_2$ (R = Me and Et), and $EtPhP[CN_2]_3PPh_2$, all of which contain a chiral centre at phosphorus. Briggs and McAuliffe have similarly developed facile syntheses of unsymmetrical diphosphines of the type $R_2P[CH_2]_nPPh_2$ (R = Me and Et, n = 3 and 4).[18] These interesting new ligands provide an ideal system in which to study the effect of the steric bulk of substituent groups on the ^{31}P chemical shift parameter of two phosphorus nuclei in close proximity to one another and observe their mutual dependence. Also the variation of the methylene backbone chain allows a correlation to be made between $\delta(^{31}P)$ and the chain length. Finally, comparisons can be made between the steric bulk of substituents attached to the phosphorus nuclei to determine which combinations of substituent groups are the most sterically demanding.

The proton noise decoupled pulsed Fourier transform ^{13}C n.m.r. spectra of the trimethylene bridged diphosphines have been examined and compared with the values reported by King and Cloyd [19] for the dimethylene-bridged analogues. The range of significant phosphorus–carbon coupling is limited to three bonds. The diphosphines responded to analysis as AMX spin systems and the magnitude of the coupling constants ^1J(P-C), ^2J(P-C), and ^3J(P-C) are discussed. The ^{13}C n.m.r. spectra of the other diphosphines were also examined.

The mass spectral fragmentation patterns of the diphosphines were also obtained and the major fragmentation pathways are reported.

RESULTS AND DISCUSSION

^{31}P *N.m.r. Spectra.*—It has now been well established, from Grim's [13] and Tolman's [1] measurements on many monodentate tertiary phosphines PR_3 where R = alkyl or aryl, that the most important parameter determining ^{31}P chemical shifts is the steric bulk of the substituent groups attached to the phosphorus atom.† Thus $\delta(^{31}P)$ may be used as an extremely sensitive measure of the effective steric bulk of the substituents around the phosphorus atom.

The importance of steric effects on the chemical behaviour of phosphine ligands and their complexes have been increasingly appreciated over the last decade, and sophisticated applications to the control of homogeneous catalytic reactions (*e.g.* asymmetric induction) [20] may be expected in the future. The unsymmetrical diphosphines discussed here were developed to provide a range of bidentate ligands with different steric properties at each phosphorus atom, so that their complexes when used as catalysts, particularly with unsymmetrical substrate molecules, would give a more precisely defined host–guest steric interaction than would corresponding symmetrical bidentate phosphines. Some evidence for

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† The other important parameter affecting $\delta(^{31}P)$ in general is the electronegativity of substituents at phosphorus.[11] However, in this study, all substituents are of almost identical electronegativity to one another and to that of phosphorus,[13] and so this factor can be ignored. We can thus address ourselves solely to the effects of steric bulk on $\delta(^{31}P)$.

generally improved substrate recognition in catalytic hydrogenation by complexes of these new ligands has been obtained.[17]

Measurement of the effective steric bulk of the substituents at each of the two phosphorus atoms is then clearly of great interest to enable correlations with catalytic activity and other properties to be made. For the diphosphines described here, each phosphorus atom has two ' terminal ' substituents such as Me, Et, Ph, or cyclohexyl, and the third group is of the type $RR'P[CH_2]_n$–. The length of the polymethylene backbone therefore is expected to play a significant role in determining the effective size of the substituents at phosphorus, and hence the value of the ^{31}P chemical shift.

TABLE 1

^{31}P N.m.r. spectral data [a]

Ligand $RR'P[CH_2]_nPPh_2$	$\delta(^{31}P)$ (p.p.m.)	
	$RR'P$–	–PPh_2
$Me_2P[CH_2]_3PPh$ [b]	–52.69	–16.43
$Et_2P[CH_2]_3PPh_2$ [b]	–23.05	–16.33
$EtPhP[CH_2]_3PPh_2$ [c,d]	–21.21	–17.11
$Me_2P[CH_2]_4PPh_2$ [b,e]	–50.09	–15.47
$Et_2P[CH_2]_4PPh_2$ [b,e]	–21.72	–15.84
$MePhP[CH_2]_4PPh_2$ [b,f]	–38.19	–18.75
$EtPhP[CH_2]_4PPh_2$ [c,f]	–19.84	–16.13
$MePhP[CH_2]_6PPh_2$ [b]	–32.08	–18.50
$EtPhP[CH_2]_6PPh_2$ [b]	–17.44	–15.48
$CyPhP[CH_2]_6PPh_2$ [b]	–7.64	–15.52
$Ph_2P[CH_2]_3PPh_2$ [g]		–17.3
$Ph_2P[CH_2]_4PPh_2$ [g]		–16.3
$Ph_2P[CH_2]_6PPh_2$ [g]		–16.0

[a] Chemical shifts are in p.p.m. upfield from 85% H_3PO_4 external standard. [b] Solvent $CDCl_3$. [c] Solvent $CDCl_3$–C_6D_6. [d] In agreement with published values.[2,3] [e] $^5J_{PP}$ 1.3 Hz. [f] $^5J_{PP}$ 4.0 Hz. [g] Data from ref. 11.

The diphosphines examined, $R_2P[CH_2]_nPPh_2$ (R = Me and Et, $n = 3$ and 4), $EtPhP[CH_2]_nRPh_2$ ($n = 3$, 4, and 6), and also $C_6H_{11}PhP[CH_2]_6PPh_2$ can be classified in two ways: (a) those in which the terminal substituent groups vary along the series Me, Et, Ph, cyclohexyl, while the length of the polymethylene chain remains constant and (b) those in which the substituent groups remain constant while the length of the polymethylene chain varies.

Comparison of $Me_2P[CH_2]_nPPh_2$ with $Et_2P[CH_2]_nPPh_2$ ($n = 3$ and 4) shows that replacement of two methyl groups by two more bulky ethyl groups results in a very large decrease in the chemical shift of the alkyl-substitued phosphorus atom, from 52.69 to 23.05 p.p.m. for $n = 3$, and from 50.09 to 21.72 p.p.m. for $n = 4$ (Table 1). Replacement by two even more bulky phenyl groups gives the symmetrical ligands $Ph_2P[CH_2]_nPPh_2$ for which $\delta(^{31}P)$ is 17.3 for $n = 3$ and 16.3 p.p.m. for $n = 4$.[15]

The shift to lower field is also observed if one examines, say, the series $RPhP[CH_2]_6PPh_2$ where R = Me, Et, Ph, or cyclohexyl; the chemical shift of the RPhP–phosphorus atom decreases along this series thus: 38.19, 17.44, 16.0, 7.64 p.p.m. for R = Me, Et, Ph,[15] cyclohexyl, respectively.

The compounds studied also allow one to compare the steric requirements of one methyl and one phenyl substituent with those of two ethyl substituents at phosphorus the chemical shift of the MePhP phosphorus atom in $MePhP[CH_2]_4PPh_2$ is 32.08 and of the Et_2P phosphorus atom in $Et_2P[CH_2]_4PPh_2$ is 21.72 p.p.m., indicating that two ethyl groups are more bulky than one methyl and one phenyl.

Other similar comparisons may be made from Table 1. The general trend to lower values for ^{31}P chemical shifts as cone angles of substituents at phosphorus increase parallels that found earlier for monodentate phosphines.[1]

The new ligands also permit the first detailed study of the effective steric bulk of $RR'P[CH_2]_n$ groups. Both n and the substituents R and R' are variables in this study. The series $EtPhP[CH_2]_nPPh_2$ shows a decrease in chemical shift with increasing chain length for *both* phosphorus nuclei. Thus the longer the polymethylene chain, the greater is the effective steric bulk of the $RR'P[CH_2]_n$ group, presumably due to the greater flexibility of the backbone as the number of methylene units increases. The decrease is more marked at the PPhEt phosphorus atom (δ 21.21, 19.84, 17.44 p.p.m. for $n = 3$, 4, 6, respectively), than at the PPh_2 phosphorus atom (δ 17.11, 16.13, 15.48 p.p.m. for $n = 3$, 4, 6, respectively), indicating that in the latter more crowded case, the two phenyl groups restrict the degree of freedom of the $RRP[CH_2]_n$ group to a greater extent than do one phenyl and one ethyl group. Thus the effective cone angle of a $RR'P[CH_2]_n$ group is larger and varies more with n when this group is attached to PPhEt than when it is attached to PPh_2. This shows that a given substituent's cone angle is not necessarily constant from one compound to another, but may be influenced by the other substituents present.

TABLE 2

Group contributions [8] (GC values) to $\delta(^{31}P)$ for bisphosphorus ligands of the type $RR'P[CH_2]_nPPh_2$

Group	Attached to	GC value (p.p.m.)
$Ph_2P[CH_2]_3$	–PPhEt	11.2
$Ph_2P[CH_2]_4$	–PPhEt	9.8
$Ph_2P[CH_2]_6$	–PPhEt	7.4
$Ph_2P[CH_2]_3$	–PPh_2	11.3
$Ph_2P[CH_2]_4$	–PPh_2	10.3
$Ph_2P[CH_2]_6$	–PPh_2	10.0
$EtPh[CH_2]_3$	–PPh_2	11.1
$EtPh[CH_2]_4$	–PPh_2	10.1
$EtPh[CH_2]_6$	–PPh_2	9.5

A low GC value indicates a larger cone angle for the group.

Using Grim's ' group contributions ' to the ^{31}P chemical shifts,[13] we have calculated the group contributions (GC values) for the $EtPhP[CH_2]_n$ and $Ph_2P[CH_2]_n$ groups where $n = 3$, 4, and 6 (Table 2). A lower GC value indicates a larger cone angle for the group. In each series in Table 2, the GC values decrease as n increases, reflecting the greater steric requirements of the longer polymethylene chains. The decrease in GC value as n increases for the $Ph_2P[CH_2]_n$ groups is more marked when these groups are attached to PPhEt (GC value decreases from 11.2 to 7.4 as n increases from 3 to 6) than when they are attached to PPh_2 (GC value decreases from 11.3 to 10.0). This indicates (a) that the GC value of a given $Ph_2P[CH_2]_n$ group is not constant, being lower when that group is attached to PPhEt than when attached to PPh_2 and (b) that the two phenyl substituents of PPh_2 considerably restrict the degree of freedom of an attached polymethylene chain, so that with either the $EtPhP[CH_2]_n$ or $Ph_2P[CH_2]_n$ series of groups attached to PPh_2, the GC values of these groups vary relatively little with *n*: variation of *n* is appreciated far more by a PPhEt phosphorus atom than by a PPh_2.

TABLE 3

^{13}C Spectral data for the aromatic region of the diphosphines

Ligand	Chemical shift[a] and coupling constants[b] *ortho*	 *meta*	 *para*
$Ph_2P[CH_2]_6P(Et)Ph$	+132.89 (19.3 Hz) +132.78 (19.2 Hz)	+128.49	+128.21
$Ph_2P[CH_2]_6C_6H_{11}Ph$	+132.49 (19.3 Hz) +133.49 (17.7 Hz)	+128.61	+128.32
$Ph_2P[CH_2]_4P(Et)Ph$	+132.74 (18.5 Hz) +132.39 (18.3 Hz)	+128.48	+128.23
$Ph_2P[CH_2]_4PEt_2$	+132.81 (19.3 Hz)	+128.51	+128.34
$Ph_2P[CH_2]_4PEt_2$	+132.76 (18.5 Hz) +132.39 (18.6 Hz)	+128.49	+128.22
$Ph_2P[CH_2]_3PEt_2$	+132.82 (19.3 Hz)	+128.52	+128.26
$Ph_2P[CH_2]_4PMe_2$	+132.81 (19.3 Hz)	+128.58	+128.32

[a] Chemical shifts measured in p.p.m. relative to Me_4Si internal standard ($CDCl_3$ lock solvent). [b] Coupling only observed to the *ortho*-carbon, shown in parentheses.

^{13}C *N.m.r. Spectra.*—Mann has reported ^{13}C n.m.r. chemical shifts and carbon–phosphorus coupling constants for a range of monotertiary phosphines[21] and King and Cloyd have examined by ^{13}C n.m.r. some polyphosphines with ethane bridges (dimethylene bridges) between trivalent phosphorus atoms.[19] Assignments were made by comparison with these systems. The ^{13}C spectra of the diphosphines examined here can be divided into three distinct regions: (a) the aromatic region, (b) the aliphatic region where the methylene bridging carbon nuclei resonate, and (c) the aliphatic region where the carbon atoms in the methyl and ethyl groups attached to phosphorus resonate (see Tables 3—5).

TABLE 4

^{13}C Spectral data for the aliphatic region of the diphosphines containing the methyl and ethyl resonances

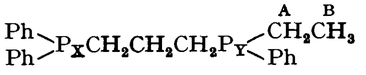
Ligand	Chemical shift[a] and P–C coupling constants[b] (1)	 (2)
$Ph_2P[CH_2]_6P(Et)Ph$	+20.73 (9.7 Hz)	+9.89 (13.6 Hz)
$Ph_2P[CH_2]_4P(Et)Ph$	+18.8 (9.3 Hz)	+9.51 (13.5 Hz)
$Ph_2P[CH_2]_4PEt_2$	+20.65 (9.9 Hz)	+9.90 (13.6 Hz)
$Ph_2P[CH_2]_3P(Et)Ph$	+20.63 (10.5 Hz)	+9.86 (13.6 Hz)
$Ph_2P[CH_2]_3PEt_2$	+18.84 (11.7 Hz)	+9.52 (13.4 Hz)
$Ph_2P[CH_2]_3PMe_2$	+14.00 (13.5 Hz)	

[a] Chemical shifts measured in p.p.m. relative to Me_4Si internal standard ($CDCl_3$ lock solvent). [b] Coupling constants shown in parentheses.

The aromatic region shows resonances for the *ortho*-, *meta*-, and *para*-carbons of the phenyl groups attached to phosphorus. The *ipso*-carbon does not possess a directly attached hydrogen atom and hence proton noise decoupling does not result in any nuclear Overhauser enhancement and this resonance is not observed. The *ortho*-carbon resonances appeared as two sets of doublets for ligands possessing a chiral phosphorus, *i.e.* of the type $Ph_2P[CH_2]_nP(R)Ph$ where there are two distinct types of phenyl group present and their position and the value of ^2J(P-C) is in good agreement with literature values.[19,21] The position of the *meta*- and *para*-carbon resonances are also reported but no carbon–phosphorus coupling was observed in these cases. In the case of the diphosphines of the type $Ph_2P(CH_2)P(R)$-Ph, the *meta*- and *para*-resonances for the two distinct phenyl groups overlap and cannot be resolved.

TABLE 5

^{13}C N.m.r. spectral data of trimethylene bridged diphosphines



$$\overset{\text{}}{Ph_2}P_XCH_2CH_2CH_2P_Y(\overset{A}{CH_2}\overset{B}{CH_3})Ph$$

Ligand	Chemical shift[a] and P–C coupling constants 1	 2	 3
$Ph_2P[CH_2]_3PEt_2$	+28.12 $^1J = {}^3J = 11.7$ Hz	+22.64 $^2J = {}^2J = 12.7$ Hz	+30.05 $^1J = {}^3J = 15.9$ Hz
$Ph_2P[CH_2]_3PMe_2$	+29.90 $^1J = {}^3J = 11.7$ Hz	+22.64 $^2J_{P_X\text{-}C}$ 13.8 Hz $^2J_{P_Y\text{-}C}$ 17.2 Hz	+33.89 ^1J 13.5 Hz
$Ph_2P[CH_2]_3PEtPh$	+29.2 $^1J = {}^3J = 11.6$ Hz	+22.48 $^2J_{P_X\text{-}C}$ 14.7 Hz $^2J_{P_Y\text{-}C}$ 16.7 Hz	+29.8 $^1J = {}^3J = 13.5$ Hz

[a] Chemical shifts measured in p.p.m. relative to Me_4Si internal standard.

The aliphatic region where the carbon nuclei present in the ethyl and methyl groups attached to phosphorus resonate is in the region 9—20 p.p.m. which is well upfield from the methylene backbone region.[19] In the case of the ethyl substituted derivatives ^2J(P-C) > ^1J-(P-C), in agreement with previous reports.

The aliphatic region in which the methylene bridge carbon nuclei resonate is too complicated by phosphorus–carbon coupling and signal overlap to allow analysis when $n > 3$. However, the ^{13}C resonances can be resolved for the compounds with trimethylene bridges between the trivalent phosphorus atoms. The individual assignments are made by comparison with the literature method of King.[19] The carbon atoms directly attached to phosphorus resonate at lower field than the central carbon, with the carbon directly bound to the most basic phosphine (*i.e.* the phosphine with alkyl substituents attached) resonating at lowest field (highest δ value). The chemical shift differences are such that the systems can be analysed by first-order methods and all spectra can be analysed as AMX spin systems. Each carbon atom of the bridging methylene backbone can be treated as a separate AMX system as the overwhelming majority of all the observed ^{13}C nuclei will occur in molecules with no other ^{13}C nucleus within coupling range. The ^{13}C n.m.r. spectra will comprise the X proton of the AMX spin system. Theoretical treatment of this spin system yields the X portion of the spectrum as a four line double doublet with equal separation between lines 1 and 2 or lines 3 and 4. This separation corresponds to one coupling constant, while separations between lines 1 and 3 or lines 2 and 4 correspond to the other coupling constant.[22] However, if the two coupling constants are of equal magnitude the X portion of the spectrum appears as a simple triplet. This has been observed for the dimethylene bridged analogues reported by King[19] and is consistent with earlier observations on the closeness of values for $^1J_{P\text{-}C}$ and $^2J_{P\text{-}C}$ in saturated alkylmonophosphines.[21]

TABLE 6

Mass spectral data for $Ph_2P[CH_2]_nPRPh$ [a]

	Relative intensities [c]				
m/*e* [b]	(I)	(II)	(III)	(IV)	Ion
107			3.26		C_6H_4P
108	192	4.04	10.40		C_6H_5P
109	1.15	2.93	8.97	0.76	C_6H_6P
121			3.74		C_7H_6P
138		0.23			$C_8H_{13}P$
152			1.63		$C_9H_{13}P$
183	1.14	2.36	12.25	0.47	$C_{12}H_8P$
185		0.34	6.99	0.47	$C_{12}H_{10}P$
186		2.64	5.08		$C_{12}H_{11}P$
193			2.17		$C_{12}H_{18}P$
199		2.84	1.30		$C_{13}H_{12}P$
200		0.88			$C_{13}H_{13}P$
203		1.73			$C_{13}H_{16}P$
212			1.87		$C_{14}H_{13}P$
214			7.21		$C_{14}H_{15}P$
221		20.18			$C_{14}H_{22}P$
222		1.37			$C_{14}H_{23}P$
239			4.78		$C_{16}H_{16}P$
241			3.55		$C_{16}H_{18}P$
269	2.83	13.07	0.17		$C_{18}H_{22}P$
270		0.88			$C_{18}H_{23}P$
271	5.03				$C_{18}H_{24}P$
301			2.24		$C_{18}H_{23}P_2$
335	2.92			17.91	$C_{21}H_{21}P_2$
336				1.94	$C_{21}H_{22}P_2$
349	0.89		100.00	2.74	$C_{22}H_{23}P_2$
350			22.61 [d]		
377	13.78	17.69			$C_{22}H_{27}P_2$
378	1.66	2.63			$C_{22}H_{28}P_2$

[a] (I) (R = C_6H_{11}, $n = 6$); (II) (R = Et, $n = 6$); (III) (R = Et, $n = 4$); (IV) (R = Et, $n = 3$). [b] *m*/*e* values less than 100 were not reported. [c] Relative intensities compared to *m*/*e* 28 base peak. [d] Isotopic ($A + 1$) peak.

TABLE 7

Mass spectral data for $Ph_2P[CH_2]_nPR_2$ [a]

	Relative intensities [c]			
m/*e* [b]	(I)	(II)	(III)	Ion
107	1.53	2.05		C_6H_4P
108	2.28		2.67	C_6H_5P
121	3.69	2.39		C_7H_6P
131		0.21		$C_7H_{16}P$
138	3.08		1.13	$C_8H_{11}P$
152	8.78			$C_9H_{13}P$
183	10.33	0.62		$C_{12}H_8P$
185	2.27	2.62	4.07	$C_{12}H_{10}P$
199		1.36	2.72	$C_{13}H_{12}P$
228		0.58		$C_{15}H_{17}P_2$
239		3.06		$C_{13}H_{21}P_2$
258		2.58	0.76	$C_{15}H_{16}P_2$
273	3.50		100.00	$C_{16}H_{19}P_2$
274			17.81 [d]	
287		100.00		$C_{17}H_{21}P_2$
288		18.26	16.93	$C_{17}H_{22}P_2$
289	49.01			$C_{17}H_{23}P_2$
301	11.27			$C_{18}H_{23}P_2$
316		0.59		$C_{19}H_{26}P_2$

[a] (I) (R = Et, $n = 4$); (II) (R = Et, $n = 3$); (III) (R = Me, $n = 3$). [b] *m*/*e* values less than 100 not reported. [c] Relative intensities compared to *m*/*e* 28 as base peak. [d] Isotopic ($A + 1$) peak.

In this study it appears that $^1J_{P\text{-}C}$ and $^3J_{P\text{-}C}$ are of comparable magnitude as the ^{13}C carbon atoms directly attached to phosphorus appear in all cases as a triplet. This is not unexpected as Mann's work[21] indicates that $^1J_{P\text{-}C}$ values are even closer to $^3J_{P\text{-}C}$ values than are the corresponding $^2J_{P\text{-}C}$ values. This is confirmed by studies on the ^{13}C n.m.r. spectra of diphosphines of the type $Ph_2P[CH_2]_nPPh_2$ (n = 6—12, and 16).[23] In the case of the ligand $Ph_2[CH_2]_3PEt_2$ it appears that both the $^2J_{P\text{-}C}$ values are identical as the resonance corresponding to the central carbon atom also appears as a triplet. In the cases of $Ph_2P[CH_2]_3PMe_2$ and Ph_2P-$[CH_2]_3P(Et)Ph$ the $^2J_{P\text{-}C}$ values are different and can be resolved into a pair of doublets.

Mass Spectral Data.—The major ion peaks and relative peak intensities for the diphosphines are shown in Tables 6 and 7. The major fragmentation pathways are shown in Figures 1 and 2. In all the diphosphines, the loss of the alkyl or cycloalkyl group from the parent molecule is a facile process; indeed for the phosphines $Ph_2P[CH_2]_nP(R)Ph$ the parent ion is not observed. In the case of the dialkyl-substituted diphosphines both $Ph_2P[CH_2]_3PEt_2$ and $Ph_2P[CH_2]_4PEt_2$ also do not exhibit strong parent ions in contrast to $Ph_2P(CH_2]_3PMe_2$ which does. Further cleavage by loss of PPh_2 is a common feature of the mass spectra.

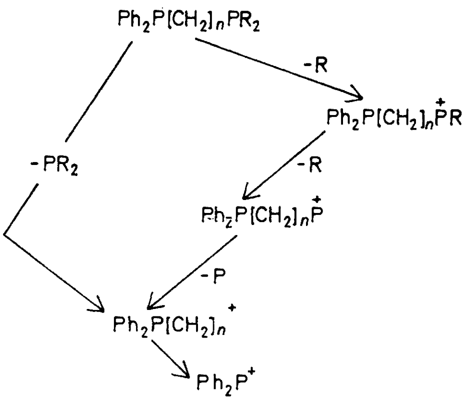


FIGURE 1 Mass spectral fragmentation patterns for diphosphines of the type $Ph_2P[CH_2]_nPR_2$

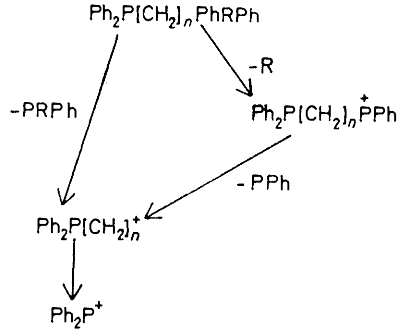


FIGURE 2 Mass spectral fragmentation patterns for diphosphines of the type $Ph_2P[CH_2]_nPRPh$

EXPERIMENTAL

^{31}P and ^{31}C n.m.r. spectra were obtained on a Varian CFT-20 spectrometer. Mass spectra were obtained on a Dupont 419B double focusing mass spectrometer equipped with a Finnigan Incos data system. Samples were run *via* the direct insertion probe.

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