

Chapter 6

Main Group Compounds

We would expect that phosphanes can utilize their electron lone pair to bond to Lewis acids (both from transition metals and from main group elements). However, they can also act as Lewis acids. The best known example is probably PF_5 , but similar molecules, like POCl_3 and PCl_5 , are known. PCl_5 is present as $[\text{PCl}_4][\text{PCl}_6]$ in the solid state, the result of PCl_5 acting as a Lewis acid toward itself, creating a PCl_6^- anion by abstraction of Cl^- and leaving a PCl_4^+ cation behind.

At left, the ^{31}P -NMR references of phosphorus chlorides are depicted in order of decreasing coordination number of phosphorus. However, the coordination number is not expected to be the only ordering principle, as PCl_4^- would fall outside the range of PCl_4^+ and the phosphonium salts are seen to resonate significantly upfield from PCl_4^+ .

The chapter is divided into Lewis basic behavior and Lewis acidic behavior, respectively. The concept overlaps somewhat at the end of Sect. 6.1, as we examine examples where both the Lewis base and the Lewis acid are phosphorus containing species.

Utilization of PF_5 as a fluoride abstracting Lewis acid is also mentioned in Chap. 7, where the fluoride is abstracted from a fluorophosphane bonded to a transition metal.

6.1 As Lewis Base

Phosphanes are characterized, among other things, by their electron lone pair. This electron lone pair can be expected to be utilized in a σ -donor interaction toward a Lewis acid, making the phosphane a Lewis base. In fact, that is the reason for the popularity of phosphanes in transition metal chemistry. Of course, the Lewis basicity not only makes them good ligands, but lets phosphanes develop a rich and diverse main group chemistry as well.

The most obvious choices for a Lewis acid to exploit the Lewis basicity of phosphanes are group 13 elements with their intrinsic electron deficiency. Looking at BH_3 as the Lewis acid component, we can easily discern the trends in the Lewis basicity of phosphanes. In the top part of Table 6.1, the phosphanes experience a pronounced coordination chemical shift of $\Delta\delta=60\text{--}135$ ppm from a well-shielded

Fig. 6.1 Chemical shift values for chlorophosphorus complexes

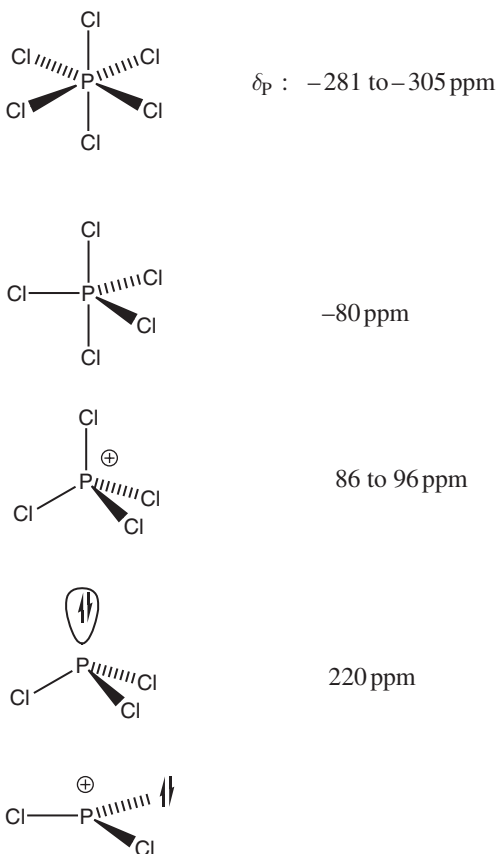


Table 6.1 ^{31}P -NMR resonances and coordination chemical shift values for phosphino boranes

Compound	δ_P phosphane [ppm]	δ_P complex [ppm]	$\Delta\delta$ [ppm]
PH_3BH_3	-246	-113	133
MePH_2BH_3	-163.5	-68.5	95
PhPH_2BH_3	-123.5	-49.3	74.2
Me_2PHBH_3	-98.5	-30.8	67.7
Me_3PBH_3	-62.8	-1.8	61
$\text{PhMe}_2\text{PBH}_3$	-46	49	95
$(\text{MeO})\text{PF}_2\text{BH}_3$	111.8	108.5	-3.3
PF_3BH_3	105	107	2
$(\text{Me}_2\text{N})_3\text{PBH}_3$	122.5	102.5	-20
$(\text{MeO})_2\text{PFBH}_3$	131.6	118.7	-12.9
$(\text{MeO})_3\text{PBH}_3$	140	118	-22
$(\text{Me}_2\text{N})\text{PF}_2\text{BH}_3$	143	130	-13
$(\text{Me}_2\text{N})_2\text{PFBH}_3$	153	134	-19
$(\text{CF}_3)\text{PF}_2\text{BH}_3$	158.1	148.5	-9.6

Table 6.2 ^{31}P -NMR resonances and coordination chemical shift values for phosphane chlorogallane adducts

R	δ_{p} ($\text{R}_2\text{ClPGaCl}_3$) [ppm]	δ_{p} (R_2ClP) [ppm]	$\Delta\delta$ [ppm]
Ph	41	81.5	−40.5
Me	57	92	−35
Et	79	119	−40
Pr ⁱ	91	—	—
Bu ^t	101	145	−44

resonance of $\delta_{\text{p}} = -46$ to -246 ppm as free ligands. In stark contrast, the phosphanes in the lower part of the table experience a moderate upfield coordination chemical shift of $\Delta\delta = -10$ to -22 ppm, with PF_3BH_3 and $(\text{MeO})\text{PF}_2\text{BH}_3$ somewhat in between with $\Delta\delta = 2$ and -3.3 ppm, respectively.

We would expect a considerable downfield shift upon coordination of the phosphane, and we are therefore not surprised to observe it in the ensuing adducts. However, why do we observe an upfield shift upon coordination to the borane with the phosphanes in the lower part of the table? The difference must lie in the behavior of the substituents on phosphorus, as this is the one parameter that changes as we look down the list. In the top part, the substituents are H, methyl, and phenyl, whereas in the lower part, the substituents are fluoride, amide, and methoxide. The latter three (F, NMe_2 , and MeO) are capable of a π -bonding interaction toward phosphorus that increases as the electron density on phosphorus diminishes upon coordination. Since the ^{31}P -NMR chemical shifts are more sensitive toward π -interactions than σ -interactions, the net result can very well be an upfield shift upon coordination of the phosphane, if substituents capable of “ π -backbonding” are present on phosphorus.

This argument is confirmed by a series of monochloro phosphane gallium(III) chloride adducts. The chemical shift values for the free ligand and the Ga(III) adduct change in accord with the alkyl or aryl substituent on phosphorus, but the coordination chemical shift stays in a very narrow range: $\Delta\delta = -35$ to -44 ppm upfield from the free ligand, indicative of a π -bonding contribution from the P—Cl substituent.

This Lewis base behaviour is not limited to group 13 complexes, but can be observed with all main group Lewis acids. A particularly interesting example is the intramolecular Lewis basicity toward another phosphorus group in bisphosphino ureas and thioureas. In Fig. 6.2, the PPh_2 group acts as a Lewis base toward the PF_2 group. The $^1J_{\text{pp}}$ coupling constant of 110 Hz can have its origin in a somewhat weak interaction that does not quite amount to a full single bond, or “through space” interactions of the two lone pairs. However, addition of PF_5 results in fluoride abstraction (PF_5 acts as a Lewis acid, see Sect. 6.2), and a proper P—P bond is formed ($^1J_{\text{pp}} = 304$ Hz). Interestingly, fluoride abstraction and formation of the cation results in an upfield shift for **both** phosphorus atoms, while the formal coordination number changes on **one** phosphorus atom only. The likely explanation is again a π -bonding interaction from fluorine and/or nitrogen. Hyperconjugation predicts donation from a non-bonding fluorine or nitrogen orbital into an antibonding P—P orbital, thus increasing the electron density on **both** phosphorus atoms.

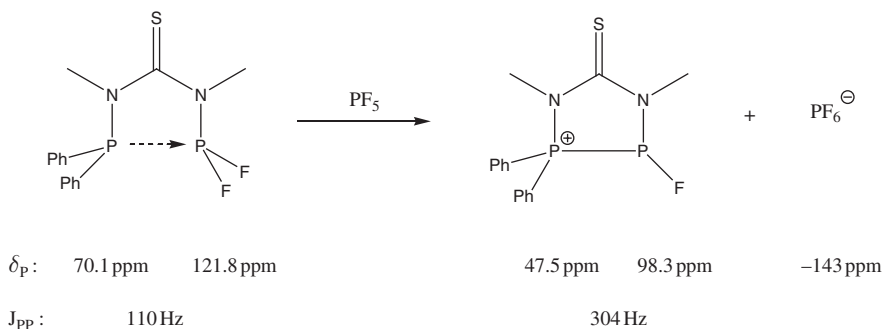


Fig. 6.2 Fluoride abstraction by PF_5 to form a phosphino phosphonium cation

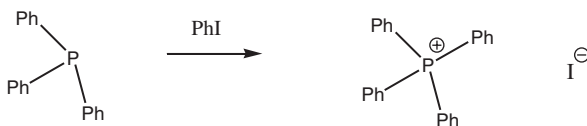
The same intramolecular Lewis base – Lewis acid interaction can be observed when a chlorophosphane is used instead of a fluorophosphane. However, the chloride is less strongly bonded than fluoride, resulting in the displacement of chloride by the phosphane without the use of an auxiliary Lewis acid. The chemical shift of the tricoordinate phosphorus atom is sensitive to the steric bulk of its carbon substituent. Evidently, sterically demanding substituents like *tert*-butyl hinder the π -bonding interaction from nitrogen, resulting in the observed downfield shift.

Phosphanes react with alkyl and aryl halides to form phosphonium salts. Their phosphorus chemical shifts are in a narrow range at $\delta_P = 20\text{--}60$ ppm (Ph_4P^+ : $\delta_P = 20$ ppm; Bu_4P^+ $\delta_P = 58$ ppm).

The lone pair on phosphorus is at the centre of its main group chemistry. The phosphorus atom can act as a Lewis acid when it is cationic or in an oxidation state other than +III (most likely +II or +I), but can also react with virtually any Lewis acid, including itself.

Table 6.3 Intramolecular Lewis base – Lewis acid behavior of phosphanes

R	$\delta_P (\text{P}^+)$ [ppm]	$\delta_P (\text{P})$ [ppm]	$^1J_{PP}$ [Hz]
Me	61.0	-12.0	310
Et	61.5	-5.3	303
Pr ⁱ	59.6	12.0	304
Bu ^t	55.4	36.2	302
Ph	59.8	1.7	278
CHCl_2	52.9	-11.4	304
CH_2SiMe_3	65.6	8.1	333

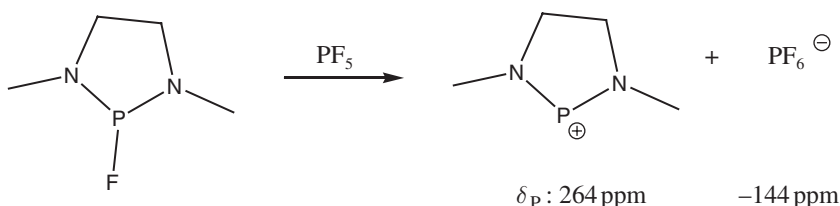
Fig. 6.3 Formation of phosphonium cations

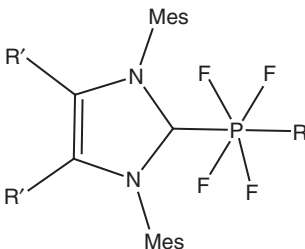
6.2 As Lewis Acid P(I), P(III), and P(V)

Arguably the best known phosphorus containing Lewis acid is PF_5 . It is often used to abstract a fluoride ion from another molecule, thus forming PF_6^- , a popular non-coordinating anion. Its ^{31}P -NMR resonance is observed at around $\delta_{\text{p}} = -144$ ppm.

If this other molecule is a fluorophosphane, a phosphonium cation is generated that is also a Lewis acid, but by necessity weaker than PF_5 . Halide abstraction from halophosphanes is a very popular method to obtain phosphonium Lewis acids.

Reaction of PF_4R ($\text{R} = \text{Me}, \text{Ph}, \text{F}$) with a carbene results in the six-coordinate phosphorus species $\text{PF}_4\text{R}(\text{carbene})$. The phosphorus compound acts as a Lewis acid toward the Lewis basic carbene, and the phosphorus resonance is shifted upfield by about $\Delta\delta = -100$ ppm. The fine structure of this upfield shift is of considerable interest. The electronegativity of the substituent R increases in the order $\text{Me} < \text{Ph} < \text{F}$ in accord with an upfield shift in the phosphorus resonance. Therefore, we again witness a case where the loss in electron density through the σ -backbone is partially compensated by an increased π -donor interaction, in the present case from the fluoride substituents on phosphorus. As the influence of the π -bonding interaction on the phosphorus chemical shift is larger than that of the σ -bonding interaction, we witness a net upfield shift.

**Fig. 6.4** Fluoride abstraction by the Lewis acid PF_5 **Table 6.4** Fluorophosphorane carbene adducts

	R	R'	δ_{p} [ppm]
	Me	H	-127.05
	Ph	H	-141.06
	F	H	-148.40
	F	Cl	-151.79

The argument is strengthened by comparison of the two carbenes. Introduction of chlorine atoms in 4,5-position lowers the nucleophilicity of the carbene. In turn, the electron density on phosphorus decreases, and we would expect a downfield shift of the resonance. However, we see a small upfield shift instead due to increased π -donation from the fluorine atoms. This trend is corroborated by the shortening of the P-F bonds by ≈ 2 pm going from $R = \text{Ph}$ to $R' = \text{Cl}$.

The same trend can be seen in the series of five-coordinate phosphorus compounds depicted in Table 6.5. Decrease of σ -donation along the series $\text{Me}_3\text{SiCH}_2 > \text{Me} > 2,5\text{-Me}_2\text{C}_6\text{H}_3 > \text{Ph}$ is accompanied by an increase of hyperconjugation from equatorial ligands (amine, F, pyrrole, Ph), resulting in an overall upfield shift.

Ring closure to the cationic species yields the expected downfield shift due to the introduction of a positive charge. The downfield shift is very moderate, because of the compensation from the amine functionality and the substituent R. The trend established by the substituent R remains essentially unchanged.

Note: In the cationic compound, the pyrrole group is in an axial position, and thus cannot contribute to a π -bonding interaction. In consequence, its phosphorus resonance is at the downfield end of the series, whereas it is at the upfield end of the neutral species.

The hypothetical phosphonium cation, PPh_2^+ , a P(III) species, has recently attracted great interest. It acts as Lewis acid toward a range of Lewis bases, amongst which the phosphanes and carbenes are possibly the best known. The phosphorus resonance of the PPh_2 part of the ensuing Lewis acid–Lewis base adduct is shifted upfield in accord with the nucleophilicity of the Lewis base employed. The Lewis base part, however, does not follow such a clear trend. In particular, PMe_3 shows the same chemical shift value as PPh_3 , an effect that is consistently observed in similar adducts.

Table 6.5 ^{31}P -NMR chemical shifts for λ^5 -fluorophosphoranes

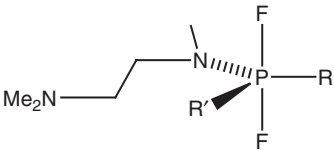
	R'	R	δ_p [ppm]
	F	Me_3SiCH_2	-33.0
	F	Me	-35.6
	F	$2,5\text{-Me}_2\text{C}_6\text{H}_3$	-44.5
	Ph	Ph	-51.9
	F	Ph	-58.0
	$\text{C}_4\text{H}_4\text{N}$	Ph	-66.4

Table 6.6 ^{31}P -NMR chemical shifts for intramolecularly Lewis base stabilized λ^5 -phosphonium cations

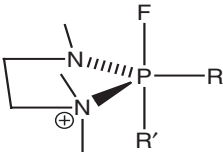
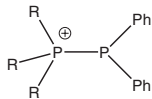
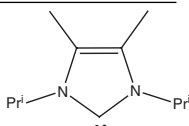
	R'	R	δ_p [ppm]
	F	Me_3SiCH_2	-13.3
	F	Me	-17.0
	F	Ph	-26.9
	$\text{C}_4\text{H}_4\text{N}$	Ph	-9.8

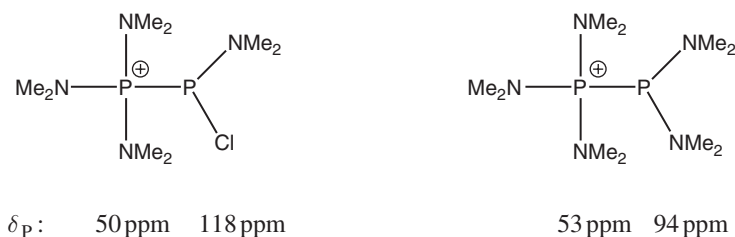
Table 6.7 ^{31}P -NMR chemical shift values for phosphino phosphonium cations

	CF_3SO_3^-	R	Ph	Cy	Me	
		$\delta_{\text{p}} (\text{R}_3\text{P})$	15	25	15	–
		$\delta_{\text{p}} (\text{PPh}_2)$	–10	–21	–23	–27
		$^1J_{\text{pp}} [\text{Hz}]$	350	361	289	–

Note: In the amine substituted phosphino-phosphenium cations, the four-coordinate phosphorus atom carrying the cationic charge resonates upfield from the tricoordinate phosphorus atom, while the reverse is the case in the phenyl substituted phosphino-phosphenium cations. The effect of the π -bonding interaction of the amino groups is clearly visible.

Of considerably greater interest from a spectroscopic point of view is the series of acyclic phosphenium cations shown in Fig. 6.6. Here, the phosphorus resonance is controlled by substituent effects, and ranges from $\delta_{\text{p}} = 264$ to $\delta_{\text{p}} = 513$ ppm. Diversion or hindrance of π -donation ability of the nitrogen substituents causes a noticeable downfield shift in the phosphorus resonance. Substitution of a dimethylamine functionality by a chloride causes a downfield shift of $\Delta\delta = 61$ ppm, whereas the substitution of the peripheral methyl groups on a dimethylamine functionality by silyl groups causes a considerably larger downfield shift of $\Delta\delta = 90.3$ ppm. The reason is that silicon is a far better π -acceptor toward the nitrogen atom than phosphorus. This is corroborated by the structures of $\text{E}(\text{SiMe}_3)_3$ ($\text{E} = \text{N}, \text{P}$), the amine is planar while the phosphine is not. As a result, the π -interaction is diverted from phosphorus to silicon, with a subsequent downfield shift in the phosphorus resonance. The effect is clearly additive, as successive substitution of the remaining two methyl groups by silyl functionalities results in an additional downfield shift of $\Delta\delta = 96$ ppm and $\Delta\delta = 186.3$ ppm, respectively.

One would expect that substitution of one dimethylamine functionality by a *tert*-butyl group would result in a very moderate downfield shift similar to the one caused by chlorine substitution. However, the downfield shift is a staggering $\Delta\delta = 249.2$ ppm, and thus the greatest observed in the series. What is at first surprising becomes clear upon closer inspection. In order for effective π -donor bonding to

**Fig. 6.5** ^{31}P -NMR chemical shifts for some amino-substituted phosphino phosphenium cations

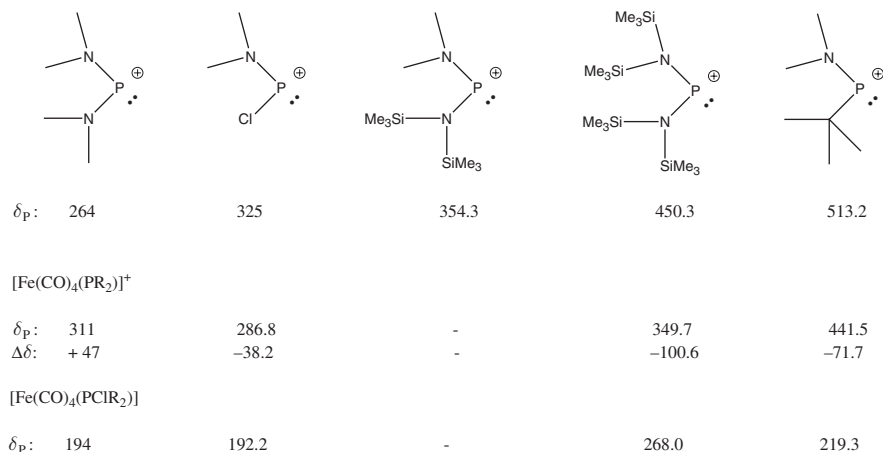


Fig. 6.6 Dependence of ^{31}P -NMR chemical shift values upon substitution in a series of amino phosphonium cations

occur between phosphorus and nitrogen, the methyl groups on nitrogen have to be in plane with the trigonal planar phosphorus atom, and would then collide with the methyl groups of the *tert*-butyl group. Steric crowding thus prevents π -donor bonding and causes the dramatic downfield shift. A description of the effect using the concept of hyperconjugation would discuss the chemical shift differences in terms of angle dependency. Of course, the largest upfield shift would be observed in the event of coplanarity (180°) in agreement with the π -donor concept.

Comparison of the free phosphonium cations with their $\text{Fe}(\text{CO})_4$ adducts is again very instructive. All phosphonium cations experience an upfield shift upon coordination to the $\text{Fe}(\text{CO})_4$ fragments (despite the strongly π -accepting carbonyl groups), with the exception of $(\text{NMe}_2)_2\text{P}^+$ which experiences a downfield shift of $\Delta\delta = 47$ ppm like an ordinary phosphane. Of course, with the π -bonding interaction of two dimethylamine functionalities already in place, backbonding from the metal is no longer substantial. M-P backbonding can be explained by hyperconjugation. However, the orbitals involved on phosphorus would be the same as those in the P-N interactions, and thus already engaged.

A similar system to the P(V) phosphoranes we have experienced in Tables 6.5 and 6.6 is also available for phosphorus (III) and presented in Table 6.8. The trends are absolutely analogous, with the exception of the different influences of equatorial and axial ligands, as such a distinction does not apply in λ^3 -phosphanes. The phosphorus resonances are shifted downfield by $\Delta\delta = 150\text{--}200$ ppm in accord with the difference in coordination numbers on phosphorus.

It can again be seen that the σ -withdrawing effect $\text{Me} < \text{Ph} < \text{CCl}_3 < \text{CF}_3$ is overcompensated by the additional π -bonding interaction from the nitrogen substituents, and that the same modulate the expected downfield shift upon introduction of a positive charge to a mere $\Delta\delta = 10\text{--}30$ ppm.

Table 6.8 Coordination chemical shifts upon formation of cyclo λ^3 -amino phosphonium cations

Y	δ_p [ppm]	δ_{p^+} [ppm]	$\Delta\delta$ [ppm]
Me	149.8	179.7	29.9
Ph	143.8	165.0	21.2
CCl ₃	118.5	130.2	11.7
CF ₃	98.6	119.3	20.7

We have already seen in the case of phosphino ureas that the interaction between a Lewis basic phosphane and a Lewis acidic phosphonium cation is not limited to intermolecular examples, but also occurs intramolecularly between neighboring phosphorus atoms in the same molecule. Two interesting examples are presented in Fig. 6.7. The phosphorus resonances are largely independent of the ring size (five- or six-membered), although the resonance of the neutral phosphorus atoms in the six-membered ring seem to be $\Delta\delta = -10$ ppm upfield from those in the five-membered ring. The $^1J_{PP}$ coupling constant predictably increases by 70–80 Hz upon changing the chloride substituent to an amino function.

R	δ_P	δ_{P^+}	$^1J_{PP}$
NEt ₂	62.6	28.6	349
NMe ₂	66.6	28.9	347
Cl	76.1	29.3	253

R	δ_P	δ_{P^+}	$^1J_{PP}$
Cl	66.9	37.6	268
NMe ₂	57.3	25.9	340

Fig. 6.7 Cyclic phosphino phosphonium cations with aromatic backbones

Table 6.9 Phosphino phosphonium cations with P(III) and P(I) cores

Compound	δ_p (PPh ₃) [ppm]	δ_p (P) [ppm]	$^1J_{PP}$ [Hz]
Ph ₂ P-PPh ₂	—	−14	—
[Ph ₃ P-PPh ₂] ⁺	15	−10	343
[Ph ₃ P-P-PPh ₃] ⁺	30	−174	502
[Ph ₃ P-PH-PPh ₃] ²⁺	23	−120	286

Going from a phosphonium (III) to a phosphonium (I) cation does not change the general concepts in the Lewis acidity of the cations, but causes a substantial upfield shift of $\Delta\delta = -150$ to -250 ppm as one moves from P(III) to P(I). This is not surprising, as the change in oxidation state in this case is equivalent to an additional electron lone pair on P(I).

Lewis base stabilization by phosphanes can lead to cyclic or acyclic species, with the cyclic compounds resonating some $\Delta\delta = -30$ to -60 ppm upfield from the acyclic compounds. With similar substituents on the P(I) atom, the magnitude of the upfield shift seemingly depends on the P(III)-P(I)-P(III) bond angle. Increasing the bond angle shifts the phosphorus resonance downfield as P(I)-P(III) backbonding becomes more feasible.

Protonation of the phosphonium cation occurs at the central P(I) phosphorus atom that has acquired a partial negative charge due to the σ -donor interaction with the flanking P(III) atoms. The resonance is duly shifted downfield by $\Delta\delta = 54$ ppm, and the $^1J_{PP}$ coupling constant almost halved from 502 Hz to 286 Hz, respectively. Despite the introduction of a second positive charge (protonation of a cation), the resonance of the P(III) centre is actually shielded by $\Delta\delta = -7$ ppm as one goes from [Ph₃P-P-PPh₃]⁺ to [Ph₃P-PH-PPh₃]²⁺.

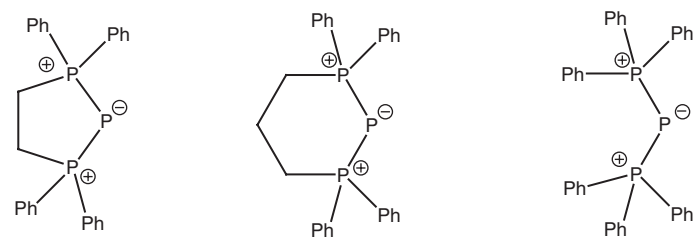
			
δ_p (+I) [ppm] :	−231.4	−209.5	−174
δ_p (+III) [ppm] :	64.4	22.4	30
$^1J_{PP}$ [Hz] :	453	423	502
P-P-P [°] :	88.4	97.8	

Fig. 6.8 Cyclic and acyclic phosphino phosphonium cations with a P(I) core

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