Bridgehead phosphorus chemistry: *in–out* inversion, intrabridgehead P · · · P bonding, and reactivity

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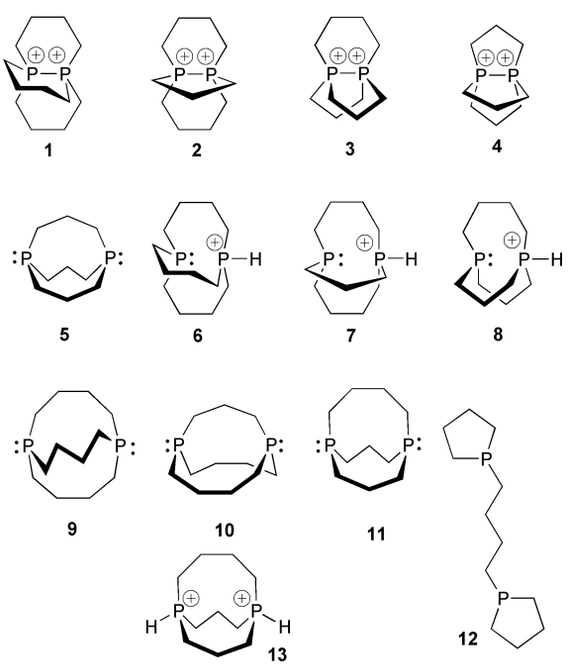
Propellane diphosphonium dications undergo addition reactions with a range of nucleophiles, and the products often have *in*,*out*-geometry with some P–P interaction, as shown by $^1J_{PP}$ values ranging from 46–253 Hz. X-Ray structures of 1-benzyl-6-phospha-1-phosphoniabicyclo[4.4.4]tetradecane trifluoromethanesulfonate, 1-benzyl-6-phospha-1-phosphoniabicyclo[4.4.3]tridecane hexafluorophosphate, and 1-hydroxy-6-phospha-1-phosphoniabicyclo[4.4.3]tridecane hexafluorophosphate are reported; these show that there is no simple relationship between P–P distance and $^1J_{PP}$ values, although the latter do correlate with the apicophilicity of the attached group. Hydride adducts, although formally protonated phosphines, can react as hydride sources, and salts of the 6-phospha-1-phosphoniabicyclo[4.4.3]tridecane ion, while stable in solution, undergo ring opening to the 1-propyl-1-phosphonia-6-phosphabicyclo[4.4.0]decane ion in the solid state. Addition of hydroxide to the 1,6-diphosphoniatricyclo[4.4.4.0^{1,6}]tetradecane ion leads, *via* a non-isolable hydroxide adduct, to *out*,*in*-1λ^5,6-diphosphabicyclo[4.4.4]tetradecane 1-oxide. Addition to the 1,6-diphosphoniatricyclo[4.4.3.0^{1,6}]tetradecane dication leads to isolable 1-hydroxy-6-phospha-1-phosphoniabicyclo[4.4.3]tridecane hexafluorophosphate, converted by excess hydroxide to the diphosphine monoxide which exists as a dynamic mixture of *out*,*in*- and *out*,*out*-isomers, the equilibrium being dependent on solvent polarity, the water content of the solvent, and the presence of metal ions. Addition of hydroxide to the 1,6-diphosphoniatricyclo[4.3.3.0^{1,6}]tetradecane dication leads to an *out*,*in*-hydroxide adduct which is rapidly converted to the *out*,*out*-monoprotonated phosphine oxide.

Introduction

The study of structure and reactivity at bridgeheads has a long and distinguished history.[1,2] In the 1970s and 1980s, our group studied the chemistry of medium-ring bicyclic diamines, and in particular the associated intrabridgehead chemistry,[3] finding examples of *in*,*in*-,[4] *in*,*out*-[5] and near *planar*,*planar*-diamines,[6] in addition to stable intrabridgehead N · · · N three-electron σ-bonds,[7] and N–H · · · N hydrogen bonds.[8] We have studied the corresponding diphosphine species more recently,[9,10] and we expected that the high barriers normally observed for phosphine inversion[11] would make it possible to study thermodynamically unstable *in*,*out*-invertomers.[12]

Synthetic access to the diphosphine species was mostly obtained *via* propellane diphosphonium dications such as 1,6-diphosphoniatricyclo[4.4.4.0^{1,6}]tetradecane bis(trifluoromethanesulfonate) **1**·2TfO, 1,6-diphosphoniatricyclo[4.4.3.0^{1,6}]tridecane bis(trifluoromethanesulfonate) **2**·2TfO, and 1,6-diphosphoniatricyclo[4.3.3.0^{1,6}]dodecane bis(trifluoromethanesulfonate) **3**·2TfO.[9] Although spectroscopic evidence for the 1,5-diphosphoniatricyclo[3.3.3.0^{1,5}]undecane dication **4** was obtained, this is extremely reactive and was not isolated in pure form. 1,5-Diphosphabicyclo[3.3.3]undecane **5** was prepared instead by a synthetic route involving ring closure.

We have reported that dications **1**–**3** undergo addition reactions with a range of nucleophiles, and that the adducts may retain some P–P interaction, as suggested by substantial $^1J_{PP}$ values, but structural data on these adducts have not been disclosed. We reported that hydride adducts **7** and **8** from **2** and **3** respectively could be deprotonated to diphosphines **10** and **11**, but that deprotonation of hydride adduct **6** did not lead to **9** (still unknown), but to rearrangement product **12**. We have also reported that hydride addition to dication **3** leads to inversion at both phosphorus atoms simultaneously to yield **13**, even though *in*,*out*-monoprotonated ion **8** is the thermodynamic product![13] The unusually high pK_a values of the hydride adducts (formally protonated phosphines) are discussed in an accompanying paper.[14]



Results and discussion

In this paper, we report structural data for a number of the nucleophilic adducts, consider the relationship between P–P distance and $^1J_{PP}$, and give further evidence for the hydridic nature of the hydride adducts, including an extraordinary solid

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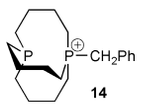
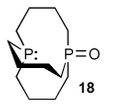
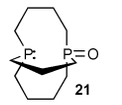
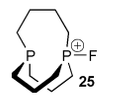
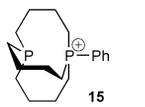
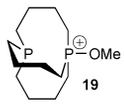
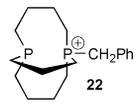
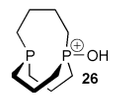
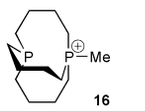
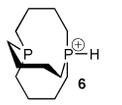
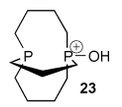
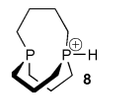
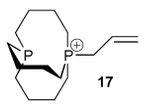
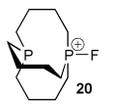
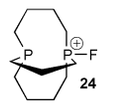
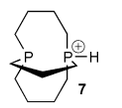
Table 1 P–P coupling constants in *in*,*out*-adducts

[4.4.4] adduct	$^1J_{PP}$/Hz	[4.4.4] adduct	$^1J_{PP}$/Hz	[4.4.3] adduct	$^1J_{PP}$/Hz	[4.3.3] adduct	$^1J_{PP}$/Hz
 **14**	46[a]	 **18**	108[a]	 **21**	46	 **25**	203
 **15**	46[a]	 **19**	139[a]	 **22**	139[a]	 **26**	237
 **16**	57	 **6**	178[a]	 **23**	192	 **8**	253[b]
 **17**	67[a]	 **20**	198[a]	 **24**	200		
				 **7**	249[a]		

[a] Ref. 9. [b] Ref. 13.

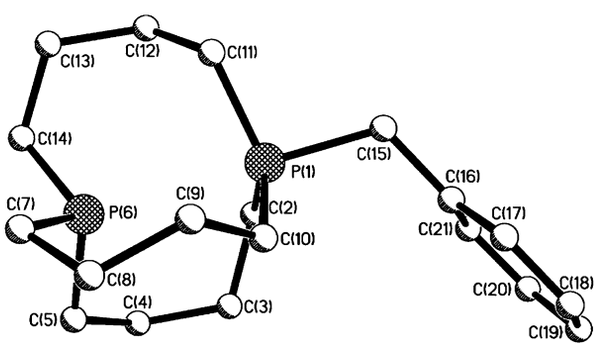


Fig. 1 X-Ray crystal structure of 1-benzyl-6-phospha-1-phosphoniabicyclo[4.4.4]tetradecane trifluoromethanesulfonate **14**. Hydrogen atoms have been omitted for clarity.

state rearrangement. We also discuss the hydroxide adducts and the associated diphosphine monoxides in the [4.3.3], [4.4.3], and [4.4.4] series, especially the [4.4.3] case where the *out*,*in*-–*out*,*out*-isomerisation of the diphosphine monoxide is solvent dependent. Finally, we describe some other cases of *in*,*out*-inversion.

Intrabridgehead P–P interaction in nucleophilic adducts to propellane dications

The ^{31}P NMR spectra of a number of adducts have been reported previously;[9] Table 1 includes this information, along with more recently acquired data. Isomers which are clearly *out*,*out*, such as **27**, **33**, **34**, **38**, and **39** (see later) never show detectable J_{PP}, and so we take observation of a substantial value for $^1J_{PP}$ as evidence for the *in*,*out*-nature of these adducts. In general, $^1J_{PP}$ values are larger when groups of higher apicophilicity are attached at one bridgehead, and it is tempting to speculate that $^1J_{PP}$ may correlate with the amount of P–P bonding, and the degree to which one phosphorus atom adopts trigonal bipyramidal geometry.

We report X-ray crystal structures (Figs. 1–3) of 1-benzyl-6-phospha-1-phosphoniabicyclo[4.4.4]tetradecane trifluoromethanesulfonate **14**, 1-benzyl-6-phospha-1-phosphoniabicyclo[4.4.3]tridecane hexafluorophosphate **22**, and 1-hydroxy-6-phospha-1-phosphoniabicyclo[4.4.3]tridecane hexafluorophosphate **23**. The structure of 6-phospha-1-phosphoniabicyclo[4.4.4]tetradecane hexafluorophosphate **6** is

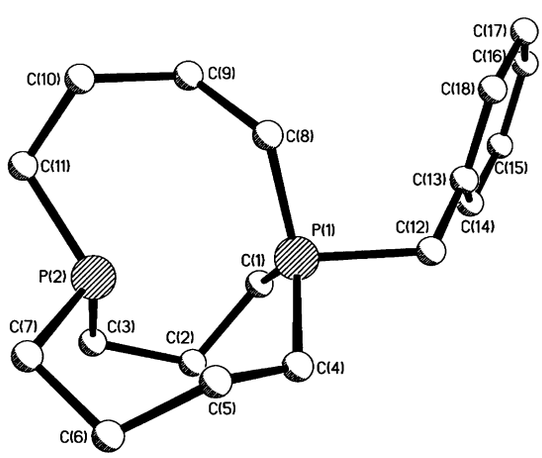


Fig. 2 X-Ray structure of 1-benzyl-6-phospha-1-phosphoniabicyclo-[4.4.3]tridecane hexafluorophosphate **22**. Hydrogen atoms have been omitted for clarity.

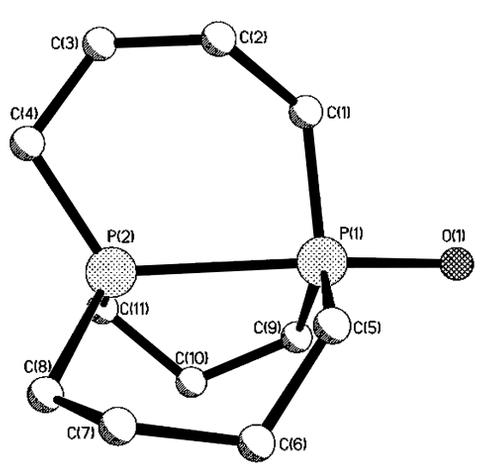


Fig. 3 X-Ray structure of 1-hydroxy-6-phospha-1-phosphoniabicyclo-[4.4.3]tridecane hexafluorophosphate **23**. Hydrogen atoms have been omitted for clarity.

reported in the accompanying paper concerning the basicity of these diphosphines,[14] and key features of these structures are summarised in Table 2. We also collected X-ray data for

Table 2 Selected structural data for adducts

Compound	P–P distance/Å	Average C–P(Nu)–C angle/°	Average C–*in*-P–C angle/°	Average C–C–C angle/°
6·PF_6	2.58	119.0	106.9	115.4
14·TfO	2.81	116.6	106.2	115.6
23·PF_6	2.51	119.4	108.7	114.1
22·PF_6	2.76	117.2	108.4	114.4

1λ⁵,6-diphosphabicyclo[4.4.4]tetradecane 1-oxide **18** as a monohydrate. Due to disorder problems associated with the three $(CH_2)_4$ bridges, the structure could not be fully refined, in spite of *R*-factors as low as 2.9% in some refinements. However, we believe that the data justify the conclusion that the molecule is *out*,*in*-1λ⁵,6-diphosphabicyclo[4.4.4]tetradecane 1-oxide, and we obtained values for the P–P bond length in the range of 2.976–3.027 Å during various attempts to treat the C-chain disorder. We feel it is safe to assume the bond distance is within the range of 2.9–3.1 Å, although unfortunately no reliable conclusions can be drawn on C–P–C angles. Nevertheless, it is clear that there is no correlation between P–P distance and $^1J_{PP}$ values. Thus for the three [4.4.4]adducts, P–P distances and $^1J_{PP}$ values are **6**: 2.58, 178; **14**: 2.81, 46; **18**, 2.9–3.1 Å, 108 Hz.

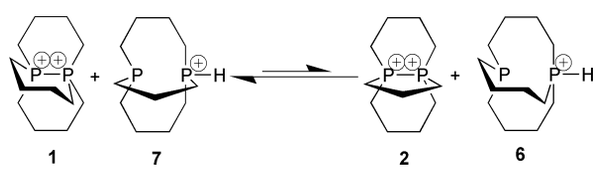
While different conformations might be adopted in solution, thus affecting NMR coupling constants, it seems likely that other factors are involved. Although the P–P distances in these adducts are much nearer to those of normal P–P single bonds (2.1–2.2 Å) than to twice the van der Waals radius of phosphorus (3.8 Å), it may be that actual P–P bonding is quite weak, so that the structure is determined by the strain in the rings and the apicophilicity of the groups attached to the P(v) atom, rather than the demands of the P–P bond. Evidence from B3LYP density functional calculations concerning the extent of P–P bonding in **6** is discussed in the accompanying paper.[14] Apicophilic groups (*e.g.* hydride) favour the phosphorus bearing the exocyclic substituent adopting a trigonal bipyramidal configuration, with flattening of the C–P–C angles at that centre. This also allows closer interaction with the other phosphorus atom giving short P–P distances. Where the exocyclic substituent is apicophobic (*e.g.* benzyl), the configuration at the substituted bridgehead phosphorus is more tetrahedral, and close interaction with the other bridgehead is not so effective. P–P Coupling constants are influenced by a number of factors including the hybridisation of the two centres involved, clearly linked to the C–P–C angles adopted at each bridgehead.

The unusual behaviour of dication **3** in giving diprotonated ion **13** on reaction with borohydride in CH_3CN–H_2O, mentioned above, prompted us to study the addition of other nucleophiles to **3**. Treatment with tetrabutylammonium difluoro(triphenyl)silicate, an anhydrous source of fluoride ion,[15] led to the formation of stable adduct **25** ($^1J_{PP}$ 203 Hz, clearly the *in*,*out*-isomer). Following the reaction by ^{31}P NMR showed no evidence for the initial formation of an *out*,*out*-species in this case. The initial product of the addition of hydroxide to dication **3** was also found to be *in*,*out*-species **26**; the rapid rearrangement of this to *out*,*out*-species **27** is discussed later.

The case of hydride addition to **3** is clearly due to a special kinetic effect. In contrast, the initial products of hydroxide and fluoride addition to **3** are both *in*,*out*-species. We suggest that addition of soft nucleophiles (*e.g.* BH_4^-) leads to extensive electron transfer into the σ* orbital of the P–P bond in the transition state, causing the phosphine leaving group to invert outwards where it is then trapped by a proton.[13] Addition of harder nucleophiles such as fluoride and hydroxide may lead to significantly less electron transfer into the P–P σ* orbital, thus giving *in*,*out*-products. The fact that this only occurs with the [4.3.3] ring system probably reflects the balance of strain between *in*,*out*- and *out*,*out*-structures; *in*,*out*-isomers are clearly more favourable in the larger [4.4.3] and [4.4.4] systems.

Hydride transfers from hydrido-species 6–8

As described in the introduction, hydride adducts **7** and **8** are converted to diphosphines **10** and **11**, and the remarkably low acidities of these *in*,*out*-systems are discussed elsewhere.[14] It should be noted that these reactions involve inversion at one phosphorus atom, which proceeds at ambient temperatures. We wondered if protonation would lead to *out*,*out*-diprotonated species, again *via* inversion. However, treatment of hydride adducts **6** and **7** with CF_3CO_2H results in the formation of the parent propellane dications **1** and **2** accompanied by the evolution of hydrogen gas. In these cases, the P–H is acting as a hydride source. Other examples of compounds with hydride P–H bonds have been recently reported,[16] although this type of umpolung behaviour is highly unusual. To test their abilities as hydride donors, reactions of adducts **6** and **7** with PhCHO were attempted, but there was no evidence of reduction of the carbonyl group. Similar studies involving **8** were not undertaken due to the instability of this system in solution. However, we found that hydride transfer did occur between the different ring systems. Thus addition of **6** to **2** led to an equilibrium mixture of all four species (Scheme 1) with the predominant

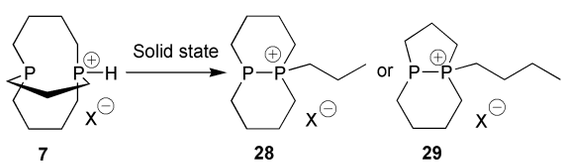


Scheme 1

species (~4:1) being [4.4.4.0] dication **1** and [4.4.3] hydride adduct **7**. This preference might be due to better accommodation of the *in*,*in*-geometry of the dication in the larger ring system. Since the equilibrium in Scheme 1 should not be strongly solvent dependent, we performed B3LYP/6-31G* density functional minimisation and frequency calculations on all four species. The calculations do favour **1** and **7**, but the calculated free energy difference (23.29 kJ mol^{-1}) is much too large to explain the 4:1 preference (ΔG° 3.43 kJ mol^{-1} at 298 K).

Solid state rearrangement of salts of 7

During the course of this work, it was noticed that stored solid samples of [4.4.3] hydride adducts **7**·TfO and **7**·PF_6 were both slowly converted to salts of a single new cation. The ^{31}P NMR spectrum of the new material consisted of two doublets at δ_P −79.42 and −1.38 with a coupling constant $^1J_{PP}$ 254 Hz, whilst the FAB^+ mass spectrum showed no change in mass from the hydride adduct **7** at *m*/*z* 217. We suspected a simple ring-opening process due to hydride transfer from phosphorus to carbon, forming one of two possible products **28** or **29** (Scheme 2).



Scheme 2

Cations **28** and **29** were prepared independently by appropriate alkylations of 1,6-diphosphabicyclo[4.4.0]decane and 1,6-diphosphabicyclo[4.3.0]nonane, and it was found that the spectroscopic data of the solid state rearrangement product agreed with that of [4.4.0] *n*-propyl derivative **28** and were quite distinct from those of **29**. The clean formation of **28** implies that only the ring-opening of the five-membered ring occurs whilst both six-membered rings remain intact.

All attempts to observe this rearrangement in solution failed, even on heating, strongly suggesting that the hydride transfer step is not an intramolecular process. Samples of **7**·PF_6 were found to rearrange more rapidly the more highly crystalline they were, with *ca*. 10% of **28** formed in a few hours from carefully recrystallised material. Experiments involving **7**·TfO gave similar results. We suspect that the orientation of the cations in the crystal state favours intermolecular hydride transfer resulting in the required ring-opening, but extensive attempts to obtain X-ray structural evidence from either salt for this proved fruitless. The preparation of **7**·BPh_4 was attempted with a view to disrupting the ordering of the cationic units in the crystal state, but this resulted only in decomposition to a number of unidentified species.

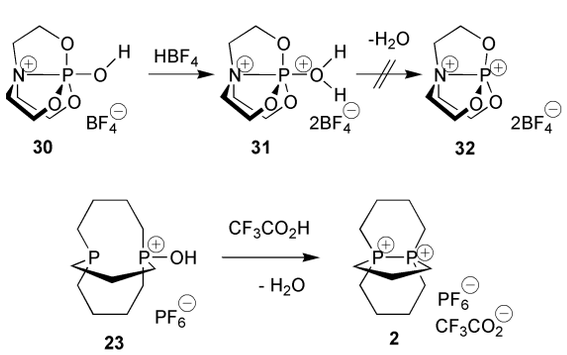
Hydroxide adducts

The behaviour of the hydroxide adducts of **1**, **2** and **3** and the formation of neutral diphosphine monoxides from them are discussed separately, since they give a particularly clear insight into the effect of ring strain on the behaviour of the [4.4.4], [4.4.3], and [4.3.3] ring systems. In general terms, the stability of dications **1**–**4** to water decreases sharply in that order, with **1** being stable up to pH 2, whereas we observed that **4** is instantly destroyed by traces of water in CH_3NO_2.

As reported previously, addition of two equivalents of hydroxide ion to [4.4.4.0] dication **1** leads to neutral monoxide **18**. Addition of hydroxide to an aqueous solution of **1** was followed in ^{31}P NMR as a function of pH. Dication **1**, stable up to pH 2, is fully converted to monoxide **18** by pH 8. At intermediate pH values the spectra correspond to rapid equilibrium between these species, and no convincing evidence for a discrete hydroxide adduct could be found; in particular the ^{31}P chemical shifts at intermediate acidities do not resemble those for the methoxide adduct **19**.

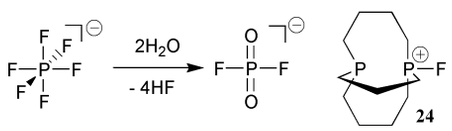
In contrast, addition of one equivalent of hydroxide ion to [4.4.3.0] dication **2** does give stable adduct **23**·TfO, the X-ray crystal structure of which was discussed earlier. Adduct **23** can be deprotonated with hydroxide ion or other bases to give **21**, a process discussed in more detail in a later section. Separation of the two stages of conversion of **2** to **21** is partly due to the greater reactivity of **2**, but it may also be that the trimethylene chain promotes closer intrabridgehead interaction, increasing electron density in the P–O–H function and perhaps stabilising the adduct with respect to proton loss.

Verkade and co-workers reported that **30**, an analogue of **23**, could be protonated with tetrafluoroboric acid giving stable dicationic species **31** (Scheme 3).[17] We attempted the preparation of a similar species by treating **23** with one equivalent of trifluoroacetic acid. However, ^{31}P NMR spectroscopy indicated that the parent dication **2** had been formed, presumably after initial protonation at oxygen and subsequent loss of water. In Verkade's example, similar loss of water would result in the formation of **32**, which may be quite strained.



Scheme 3

It was observed that a solution of **23**·PF_6 in dichloromethane slowly decomposed as it absorbed water, giving the fluoride adduct **24**. The appearance of the ^{31}P NMR signals for **24** were accompanied by another new triplet in the spectrum, due to $PF_2O_2^-$ (Scheme 4).[18] The hydrogen fluoride produced in the hydrolysis of hexafluorophosphate can then protonate **23** as discussed previously, liberating water and forming dication **2**. Unfortunately, the presence of mixed counterions prevented the use of this process as a practical preparation of **24**.



Scheme 4

Addition of hydroxide ion to dication **3** leads initially to **26** (δ_P −31.54 and −34.80 ppm, $^1J_{PP}$ 237 Hz), as described earlier. However analysis by ^{31}P NMR spectroscopy after one hour showed that an *out*,*out*-species had been formed, identified as protonated ion **27**. The presence of P(IV)–H functionality in **27** was confirmed by the proton-coupled ^{31}P NMR spectrum, which showed a doublet at δ_P 8.39 ppm with a P–H coupling constant J_{PH} 519 Hz. The clean conversion of *in*,*out*-species **26** into **27** is readily followed by ^{31}P NMR spectroscopy. As described later, the monoxide in the [4.3.3] series is exclusively *out*,*out*, so the thermodynamic preference for **27** is not surprising. The reaction proceeded in the same way even when a deficiency of hydroxide ion was used; in other words the proton transfers do not require free hydroxide as a base.

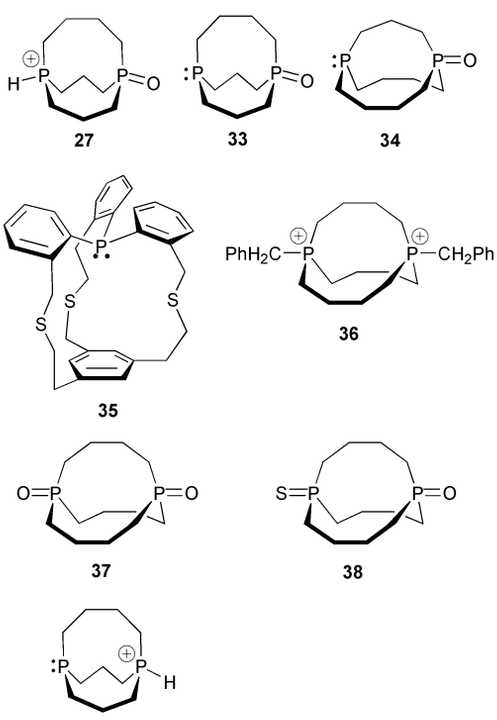
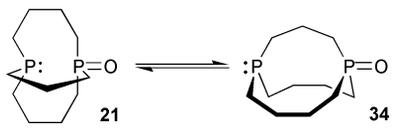


Table 3 Addition of water to a THF solution of the [4.4.3] monoxide



21 **34**

Amount of water added/μL	Concentration of [4.4.3] monoxide/M	Equivalents of water added	Ratio of isomers *in*,*out*-**21**–*out*,*out*-**34**
0	0.101	0	45:55
10	0.099	11	63:37
20	0.097	22	73:27
30	0.095	33	77:23
50	0.091	55	82:18
100	0.084	110	85:15

Phosphine oxides; *in*,*out*-inversion

Whilst [4.4.4] monoxide **18** exists in an *in*,*out*-conformation, the [4.3.3] analogue **33** exists in an *out*,*out*-conformation. Monoxide **33** can be prepared either by deprotonation of **27**, or more simply by direct treatment of [4.3.3.0] dication **3** with two equivalents of hydroxide ion. In keeping with its *out*,*out*-structure, monoxide **33** is readily oxidised to the corresponding dioxide.

The behaviour of the [4.4.3] monoxide is rather more intriguing. Deprotonation of **23** with $KN(SiMe_3)_2$ in THF, followed by analysis by ^{31}P NMR spectroscopy showed the presence of two species in approximately a 1:1 ratio. Four signals were observed in the ^{31}P NMR spectrum—a pair of singlets (δ_P −31.65 and 51.72 ppm) and a pair of doublets (δ_P −48.23 and 48.12 ppm, $^1J_{PP}$ 46 Hz). On the basis of our previous observations, we identified the species corresponding to the pair of singlets as the *out*,*out*-isomer **34**, whilst the pair of doublets were assigned to the corresponding *in*,*out*-isomer **21** (Table 1). In an initial experiment, deprotonation in CH_3CN gave a ratio **21**–**34** of 4:1, although repeating this in freshly distilled solvent gave a ratio of closer to 1:1. In pure water only **21** was observed. Addition of small quantities of water to a THF solution of the [4.4.3] monoxide led to a shift in the equilibrium as shown in Table 3; beyond the addition of 100 equivalents of water, only very small increases in the amount of *in*,*out*-isomer **21** are found. These observations imply that the two isomers are in equilibrium with each other, and the position of equilibrium can be shifted by the addition of water. In a similar fashion it was found that addition of lithium salts to mixtures of **21** and **34** led to an increase in the amount of *in*,*out*-isomer **21**. Five equivalents of $LiClO_4$ in THF gave a **21**–**34** ratio of 17:3, the same as produced by ~100 equivalents of water.

The establishment of this equilibrium implies a much reduced barrier to inversion at the P(III) centre. While there is no peak broadening in the ^{31}P NMR spectrum, equilibrium appears to be established within a minute at ambient temperature; this implies a rate constant of between 4×10^2 and 1.2×10^{-3} s^{-1} at 300 K, or a barrier of between 60 and 90 kJ mol^{-1}.

Phosphine oxides are known to be good hydrogen bond acceptors and ligands to hard metal centres, but *in*,*out*-isomer **21** is obviously markedly superior to *out*,*out*-isomer **34** in this respect. B3LYP/6-31G* density functional calculations predict dipole moments of 2.99 and 6.06 D for **21** and **34** respectively. The calculated ΔG° in the gas phase favours **34** but only by 1.52 kJ mol^{-1} at 298 K; such a small energy difference might be expected to be easily overcome by solvation effects. Thus the additivity effect of the phosphine and phosphine oxide dipoles in **21**, possibly accentuated by a contribution from P^+–P–O^- resonance structures, makes **21**, and similar species like **18**, "super" phosphine oxides.

Other cases of inversion and *in–out* isomerism

Even though an *in*,*out*-structure may be preferred for a given compound, its reactions may occur *via* low equilibrium concentrations of an *out*,*out*-isomer. Thus Pascal and co-workers have shown that reaction of **35** with sulfur to give the *out*-sulfide involves rate-limiting inversion of the phosphorus atom, the barrier (146 kJ mol^{-1}) here being relatively normal.[19] We reported the formation of *out*,*out*-dibenzyl dication **36** by heating *in*,*out*-benzyl adduct **14** with benzyl bromide at 150 °C.[9] We have found that *in*,*out*-[4.4.4] monoxide **18** can be converted to *out*,*out*-dioxide **37** and *out*,*out*-oxide sulfide **38** at more moderate temperatures.

In an NMR experiment, a solution of [4.4.4] monoxide **18** and one equivalent of hydrogen peroxide in degassed D_2O was heated at 85 °C for 20 minutes. ^{31}P NMR spectroscopy showed that **18** had been completely consumed, and the major product (>85%) formed gave a singlet in the spectrum (δ_P 70.7 ppm). This was shown by ^{13}C NMR spectroscopy and high resolution mass spectrometry to be **37**, although a number of decomposition products were evidently formed as well. Similarly, heating **18** with sulfur in 1:1 CH_3CN–D_2O at 80 °C leads rapidly to **38**. Although we have not carried out kinetic studies on these reactions, it can be estimated that the barrier to inversion in **18** must be ≤110 kJ mol^{-1} at 80 °C. Since this is an unfavourable equilibrium, the intrinsic barrier is probably at least 30 kJ mol^{-1} lower than typical barriers to inversion of trialkylphosphines.[11] We have previously discussed the conversion of *out*,*out*-**39** to *in*,*out*-**8**, where the barrier to (favourable) inward inversion is only 70 kJ mol^{-1}.[13] The order of magnitude calculation of the barrier for interconversion of **21** and **34** (see above) falls in the same range. We conclude that reduced phosphine inversion barriers in these bridgehead derivatives seem to be quite general, and that this is probably associated with considerable flattening at the phosphorus atoms.

Conclusions

Propellane diphosphonium dications **1**–**3** undergo addition reactions with a range of nucleophiles, and the products often have *in*,*out*-geometry with some P–P interaction (**6**–**8** and **14**–**26**). *in*,*out*-Isomers are more favoured by the larger ring systems, with *out*,*out*-isomers becoming more common in the [4.3.3] and especially the [3.3.3] series. Reduced phosphine inversion barriers in these bridgehead derivatives appear to be general, so that equilibration between *in*,*out*- and *out*,*out*-isomers is often rapid at ambient temperature.

Experimental

General procedures

Solvents and reagents used during the course of this work were purified according to standard literature procedures[20] and stored under nitrogen. Commercially available reagent solutions were used at the molarity stated and were titrated regularly. All solvents and solutions were dispensed with gas tight syringes. Due to the nature of this chemistry, the majority of reactions and work-ups were carried out under inert atmospheres using modified Schlenk techniques. The highly pyrophoric primary phosphines required special attention, and their manipulation was carried out in a fume-cupboard fitted with a military-grade filter designed for the removal of arsines and related materials. Melting points were determined on a Reichert apparatus using a thermocouple and digital readout and are uncorrected. Elemental combustion analyses were measured using a Perkin-Elmer 240C elemental analyser and were performed by the staff of the microanalytical department at the School of Chemistry, University of Bristol. Electron impact, chemical ionisation and fast atom bombardment mass spectra were recorded by Dr Ken MacNeil of the mass spectrometry service at the School of Chemistry, University

of Bristol. High resolution electrospray mass spectra were recorded by the staff of the EPSRC National Mass Spectrometry Service at the University of Wales, Swansea. NMR spectra were recorded on JEOL JNM-LA300 and JNM-GX400 spectrometers operated at 300 and 400 MHz for ^{1}H spectra, 121 and 162 MHz for ^{31}P spectra and 75 and 100 MHz for ^{13}C spectra. Chemical shifts are quoted in parts per million (δ) downfield from tetramethylsilane (TMS) in the case of ^{1}H and ^{13}C spectra, and externally referenced to 85% phosphoric acid in the case of ^{31}P spectra. Coupling constants (J) are expressed in hertz (Hz).

1-Propyl-1-phosphonia-6-phosphabicyclo[4.4.0]decane bromide 28·Br

A solution of 1,6-diphosphabicyclo[4.4.0]decane (180 mg; 1.03 mmol) in dichloromethane (2 mL) was treated with 1-bromopropane (1.2 eq. 153 mg). The mixture was stirred for 30 minutes, then pentane (10 mL) was added. The resulting white precipitate was collected by filtration and washed with cold dichloromethane. The product was obtained as a white solid (295 mg; 93%). The product was further purified by recrystallisation from acetonitrile and diethyl ether furnishing colourless needles; mp 174–176 °C (found: C, 44.0; H, 8.3. $C_{11}H_{23}BrP_2$ requires C, 44.5; H, 7.8%); δ_H(300 MHz; CD_3OD) 1.12–1.28 (3 H, t, $^{3}J_{HH}$ 7), 1.71–1.91 (4 H, m), 1.96–2.20 (8 H, m), 2.24–2.49 (6 H, m), 2.56–2.73 (2 H, m); δ_C(75 MHz; CD_3OD) 16.98 (1 C, d, $^{2}J_{PC}$ 11), 16.99 (1 C, s), 17.49 (2 C, d, $^{1}J_{PC}$ 35), 18.15 (2 C, dd, $^{1}J_{PC}$ 30, $^{2}J_{PC}$ 3), 22.10 (2 C, d, $^{2}J_{PC}$ 8), 22.36 (2 C, d, $^{2}J_{PC}$ 5), 23.37 (1 C, dd, $^{1}J_{PC}$ 41, $^{2}J_{PC}$ 9); δ_P(121 MHz; CD_3OD) −79.42 (d, $^{1}J_{PP}$ 254, P-6), −1.38 (d, $^{1}J_{PP}$ 254, P-1); *m/z* (FAB$^+$) 217 (M^+ − Br, 100%).

1-Methyl-6-phospha-1-phosphoniabicyclo[4.4.4]tetradecane trifluoromethanesulfonate 16·TfO. A solution of methyllithium in THF (1 M, 120 μL; 0.12 mmol) was added to a stirred suspension of 1,6-diphosphoniatricyclo[4.4.4.0^{1,6}]tetradecane bis(trifluoromethanesulfonate) in THF (4 mL). After stirring for 30 minutes, all volatiles were removed *in vacuo* and the residue extracted with dichloromethane (3 × 10 mL). Removal of solvent from the filtered extracts furnished the product as a white powdery solid (43 mg; 91%) contaminated with lithium trifluoromethanesulfonate which could not be removed; δ_H(400 MHz; CD_3OD) 1.29 (3 H, dd, $^{2}J_{PH}$ 9, $^{3}J_{PH}$ 2.5), 1.63–1.74 (6 H, m), 1.75–1.88 (6 H, m), 1.89–2.05 (6 H, m), 2.38–2.53 (6 H, m); δ_C(100 MHz) 21.64 (1 C, dd, $^{1}J_{PC}$ 38, $^{2}J_{PC}$ 31.5), 23.61 (3 C, dd, $^{1}J_{PC}$ 11, $^{2}J_{PC}$ 8), 23.73 (3 C, s), 26.45 (3 C, d, $^{2}J_{PC}$ 10), 32.72 (3 C, dd, $^{1}J_{PC}$ 82, $^{2}J_{PC}$ 33); δ_P(162 MHz) −25.87 (d, $^{1}J_{PP}$ 57), −13.06 (d, $^{1}J_{PP}$ 57); *m/z* (ES) 245.1587 ($M^+ - CF_3SO_3$. $C_{13}H_{27}P_2$ requires 245.1588).

1λ^5,6λ^5-Diphosphabicyclo[4.4.4]tetradecane 1,6-dioxide 37. An aqueous solution of hydrogen peroxide (30%; 5 μL; 2 eq.) was added to a solution of 1λ^5,6-diphosphabicyclo[4.4.4]-tetradecane 1-oxide (6 mg; 0.024 mmol) in D_2O (500 μL) in an NMR tube. The NMR tube was heated to 85 °C in a JEOL JNM-GX400 NMR spectrometer and the reaction monitored by ^{31}P NMR spectroscopy. The product was not discretely isolated; δ_C(100 MHz; D_2O) 24.2–24.5 (6 C, br), 32.94 (6 C, d, 58 Hz); δ_P(162 MHz) 70.72 (s); *m/z* (CI) 263.1324 (M^+ + 1. $C_{12}H_{25}P_2O_2$ requires 263.1330).

1λ^5,6λ^5-Diphosphabicyclo[4.4.4]tetradecane 1-sulfide 6-oxide 38. Finely powdered sulfur (1.3 mg; 2 eq.) was added to a solution of 1λ^5,6-diphosphabicyclo[4.4.4]tetradecane 1-oxide (6 mg; 0.024 mmol) in 1:1 CH_3CN–D_2O (500 μL) in an NMR tube. The NMR tube was heated to 80 °C in a JEOL JNM-GX400 NMR spectrometer and the reaction monitored by ^{31}P NMR spectroscopy. The product was not discretely isolated; δ_P(162 MHz; D_2O) 57.40 (s), 71.27 (s); *m/z* (CI) 279.1090 (M^+ + 1. $C_{12}H_{25}P_2OS$ requires 279.1101).

1-Hydroxy-6-phospha-1-phosphoniabicyclo[4.4.3]tridecane hexafluorophosphate 23·PF$_6$. Aqueous potassium hydroxide (1.7 M; 0.38 mL; 0.65 mmol) was added to a stirred solution of 1,6-diphosphoniatricyclo[4.4.3.0^{1,6}]tetradecane bis(hexafluorophosphate) (328 mg; 0.65 mmol) in acetonitrile (5 mL). A grey precipitate was formed immediately. After stirring for 1 hour, all volatiles were removed *in vacuo*. The solid residue was extracted with dichloromethane (2 × 10 cm^3) and filtered. Removal of solvent *in vacuo* gave a white waxy solid which was recrystallised from dichloromethane and ether furnishing the title compound as colourless needles (199 mg; 81%); mp 170–172 °C (found: C, 35.2; H, 6.2. $C_{11}H_{23}P_3F_6O$ requires C, 34.9; H, 6.1%); δ_C(100 MHz) 20.51 (1 C, d, $^{2}J_{PC}$ 3), 21.49 (1 C, dd, $^{1}J_{PC}$ 15, $^{2}J_{PC}$ 9), 24.85 (2 C, d, $^{2}J_{PC}$ 5), 25.33 (2 C, d, $^{2}J_{PC}$ 11), 25.37 (2 C, dd, $^{1}J_{PC}$ 17, $^{2}J_{PC}$ 8), 33.66 (1 C, dd, $^{1}J_{PC}$ 95, $^{2}J_{PC}$ 44), 39.13 (2 C, dd, $^{1}J_{PC}$ 101, $^{2}J_{PC}$ 29); δ_P(162 MHz) −21.41 (d, J_{PP} 192, P-1), −32.88 (d, $^{1}J_{PP}$ 192, P-6); *m/z* (ES) 242.15 ($M^+ + 1 - CF_3SO_3$. 80%). A crystal suitable for X-ray analysis was grown by slow diffusion of ether into a dichloromethane solution of the title compound.

1-Fluoro-6-phospha-1-phosphoniabicyclo[4.4.3]tridecane trifluoromethanesulfonate 24·TfO. Tetrabutylammonium difluoro(triphenyl)silicate (160 mg; 0.29 mmol) was added to a solution of 1,6-diphosphoniatricyclo[4.4.3.0^{1,6}]tridecane bis(trifluoromethanesulfonate) (152 mg; 0.29 mmol) and the reaction mixture stirred for 10 minutes. All volatiles were removed *in vacuo*, and the residue extracted with pentane to remove the triphenylsilyl fluoride. The solid residue was then extracted with dichloromethane (3 × 10 mL). Removal of solvent from the filtered extracts *in vacuo* yielded a white waxy solid which was shown to be the title compound contaminated with tetrabutylammonium trifluoromethanesulfonate, which could not be removed; δ_C(100 MHz; CD_2Cl_2) 18.2–18.6 (br m), 18.9–20.2 (br m), 21.6–21.9 (br m), 23.0–23.5 (br m); δ_P(162 MHz; CD_2Cl_2) −49.18 (dd, $^{1}J_{PP}$ 200, $^{1}J_{PF}$ 719, P-1), −15.55 (dd, $^{1}J_{PP}$ 200, $^{2}J_{PF}$ 218, P-6); *m/z* (ES) 235.1184 ($M^+ - CF_3SO_3$. $C_{11}H_{22}P_2F$ requires 235.1181).

1λ^5,6-Diphosphabicyclo[4.3.3]dodecane 1-oxide 33. Aqueous potassium hydroxide (1 M; 40 μL; 0.04 mmol) was added to a solution of 1,6-diphosphoniatricyclo[4.3.3.0^{1,6}]dodecane bis-(trifluoromethanesulfonate) (12 mg; 0.02 mol) in acetonitrile (1 mL) with stirring. After one hour, the solution was concentrated to half of its original volume, then filtered under nitrogen. All volatiles were removed *in vacuo* to give the product as a waxy white solid contaminated with potassium trifluoromethanesulfonate; δ_C(100 MHz; CD_3CN) 19.95 (2 C, t, $^{2}J_{PC}$ 4.5), 20.77 (1 C, d, $^{2}J_{PC}$ 3), 21.52 (1 C, d, $^{1}J_{PC}$ 24), 21.58 (2 C, d, $^{1}J_{PC}$ 24), 23.29 (1 C, d, $^{2}J_{PC}$ 5), 30.53 (2 C, $^{1}J_{PC}$ 59.5), 31.06 (1 C, d, $^{1}J_{PC}$ 60.5); δ_P(162 MHz; D_2O) −33.10 (1 P, s, P-6), 69.75 (1 P, s, P-1); *m/z* (CI) 219 (M^+ + 1, 100%). Attempts to remove the potassium trifluoromethanesulfonate by recrystallisation failed, hence an accurate microanalysis has not been obtained. Treatment of an acetonitrile solution of **33** with trifluoroacetic acid led to the formation of the trifluoroacetate salt of **27**.

1λ^5,6λ^5-Diphosphabicyclo[4.3.3]dodecane 1,6-dioxide. A solution of 1λ^5,6-diphosphabicyclo[4.3.3]dodecane 1-oxide (25 mg; 0.11 mmol) in acetonitrile (1 mL) was stirred in air overnight. All volatiles were removed *in vacuo* furnishing a white waxy solid in quantitative yield; δ_C(100 MHz; CD_3CN) 16.41 (2 C, t, $^{2}J_{PC}$ 3, C-8, C-11), 21.99 (2 C, d, $^{2}J_{PC}$ 3, C-3, C-4), 31.14 (4 C, d, $^{1}J_{PC}$ 58, C-7, C-9, C-10, C-12), 31.92 (2 C, d, $^{1}J_{PC}$ 58, C-2, C-5); δ_P(162 MHz) 57.38 (2 P, s); *m/z* (CI) 235.1013 (M^+ + 1. $C_{10}H_{20}P_2O_2$ requires 235.1017).

6-Oxo-6λ^5-phospha-1-phosphoniabicyclo[4.3.3]dodecane trifluoromethanesulfonate 27·TfO. Aqueous potassium hydroxide

(74 μL; 1 M; 0.07 mmol) was added to a solution of 1,6-diphosphoniatricyclo[4.3.3.0^{1,6}]dodecane bis(trifluoromethanesulfonate) (37 mg; 0.07 mmol) in acetonitrile (2 mL) with stirring. After one hour, the cloudy solution was filtered and the filtrate reduced *in vacuo* yielding the product as a waxy white solid contaminated with potassium trifluoromethanesulfonate; δ_H(300 MHz; CD_3CN) 1.84–1.90 (2 H, m), 1.91–2.25 (12 H, m), 2.35–2.60 (6 H, m), 6.14 (1 H, d, $^1J_{PH}$ 511); δ_C(75 MHz) 16.90 (2 C, dd, $^2J_{PC}$ 6, 4), 18.16 (2 C, d $^1J_{PC}$ 42), 19.34 (1 C, d, $^1J_{PC}$ 49.5), 20.51 (1 C, br), 21.04 (1 C, d, $^2J_{PC}$ 7), 30.39 (2 C, d, $^1J_{PC}$ 58), 32.23 (1 C, d, $^1J_{PC}$ 59); δ_P(121 MHz) 8.39 (1 P, d, $^1J_{PH}$ 511), 53.66 (1 P, s); *m*/*z* (ES) 219.1070 ($M^+ - CF_3SO_3$. $C_{11}H_{21}P_2O$ requires 219.1068).

1-Fluoro-6-phospha-1-phosphoniabicyclo[4.3.3]dodecane trifluoromethanesulfonate 25·TfO. Tetrabutylammonium difluoro(triphenyl)silicate (161 mg; 0.30 mmol) was added to a solution of 1,6-diphosphoniatricyclo[4.3.3.0^{1,6}]dodecane bis(trifluoromethanesulfonate) (149 mg; 0.30 mmol) and the reaction mixture stirred for 10 minutes. All volatiles were removed *in vacuo*, and the residue extracted with pentane to remove the triphenylsilyl fluoride. The solid residue was then extracted with dichloromethane (3 × 10 mL). Removal of solvent from the filtered extracts *in vacuo* yielded a white waxy solid which was shown to be the title compound contaminated with tetrabutylammonium trifluoromethanesulfonate, which could not be removed; δ_C(100 MHz; CD_2Cl_2) 20.3–21.0 (br m), 21.1–21.3 (br m), 22.1–22.4 (br m), 24.0–24.4 (br m); δ_P(162 MHz) −46.54 (dd, $^1J_{PP}$ 203, $^1J_{PF}$ 734, P-1), −18.37 (dd, $^1J_{PP}$ 203, $^1J_{PF}$ 185, P-6); *m*/*z* (ES) 221.1026 ($M^+ - CF_3SO_3$. $C_{10}H_{20}P_2F$ requires 221.1024).

Preparation of a mixture of *in*,*out*- and *out*,*out*-isomers of 1λ^5,6-diphosphabicyclo[4.4.3]tridecane 1-oxide 21 and 34. A suspension of potassium hydride (6 mg; 0.15 mmol) in THF (2 mL) was added to a stirred solution of 1-hydroxy-1λ^5-phospha-6-phosphoniatricyclo[4.4.3.0^{1,6}]tridecane hexafluorophosphate (40 mg; 0.11 mmol) in THF (2 mL). The solution was filtered to remove excess potassium hydride and all volatiles were removed *in vacuo*. The resulting waxy solid was extracted into d_8-toluene and analysed by NMR spectroscopy; δ_C(100 MHz) 20.92 (2 C, s), 20.98 (1 C, t, $^2J_{PC}$ 6), 21.12 (2 C, s), 22.82 (2 C, s), 22.86 (2 C, s), 24.36 (1 C, d, $^1J_{PC}$ 27, C-13, *out*,*out*-isomer), 25.69 (1 C, dd, $^1J_{PC}$ 34, $^2J_{PC}$ 9, C-13, *in*,*out*-isomer), 26.08 (1 C, br), 26.24 (2 C, dd, $^1J_{PC}$ 23, $^2J_{PC}$ 8, C-5, C-7, *in*,*out*-isomer), 28.64 (2 C, d, $^1J_{PC}$ 21, C-5, C-7, *out*,*out*-isomer), 32.35 (1 C, d, $^1J_{PC}$ 55, C-11, *out*,*out*-isomer), 35.31 (1 C, dd, $^1J_{PC}$ 79, $^2J_{PC}$ 28, C-11, *in*,*out*-isomer), 36.87 (2 C, d, $^1J_{PC}$ 58, C-2, C-10, *out*,*out*-isomer), 41.32 (2 C, dd, $^1J_{PC}$ 89, $^2J_{PC}$ 18, C-2, C-10, *in*,*out*-isomer); δ_P(162 MHz) −48.23 (1 P, d, $^1J_{PP}$ 46, P-6, *in*,*out*-isomer), −31.65 (1 P, s, P-6, *out*,*out*-isomer), 48.12 (1 P, d, $^1J_{PP}$ 46, P-1, *in*,*out*-isomer), 51.72 (1 P, s, P-1, *out*,*out*-isomer); *m*/*z* (EI) 231.1065 ($M^+ - 1$. $C_{11}H_{21}P_2O$ requires 231.1067).

X-Ray diffraction studies

X-Ray crystallographic studies were conducted using a Siemens SMART diffractometer at 173 K or Siemens P4 diffractometer at room temperature, using graphite monochromated Mo-Kα radiation. Structure solution and refinement were performed using SHELXTL software.[21] The data collected are summarised in Table 4.†

Theoretical methods

All calculations were performed with the Gaussian98 suite of programs.[22] The theoretical model used, denoted as B3LYP/6-31G*, is based on density functional theory (DFT) with Becke's three parameter exchange functional[23] and the Lee–Yang–Parr correlation functional,[24,25] and the 6-31G* basis set, which is of double-ζ type and contains an additional set of polarisation functions on all atoms, except hydrogens. All optimised molecular geometries are minima in the potential energy hypersurface (a frequency calculation on each optimised geometry resulted in no imaginary frequencies).

† CCDC reference numbers 152497–152499. See http://www.rsc.org/suppdata/p2/b0/b009007g/ for crystallographic files in .cif format.

Table 4 Summary of single crystal X-ray diffraction data

Compound	**14**·TfO	**22**·PF_6	**23**·PF_6
Formula	$C_{20}H_{31}F_3O_3P_2S$	$C_{18}H_{29}F_6P_3$	$C_{11}H_{22}F_6OP_3$
Formula weight	470.45	452.32	377.20
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$Pna2_1$	Cc	$Pbca$
a/Å	12.171(1)	9.094(3)	12.997(3)
b/Å	21.173(3)	18.975(7)	15.552(2)
c/Å	8.651(1)	12.045(5)	15.809(3)
β/°		91.296(1)	
V/Å^3	2229.4(4)	2078.2(10)	3195.3(11)
Z	4	4	8
μ/mm^{-1}	0.333	0.340	0.429
Temperature/K	173	173	293
Measured reflections	13743	6672	2822
Independent reflections	4984	4037	2822
R_{int}	0.0181	0.0395	0.0000
R	0.0303	0.0327	0.0524
Flack parameter	0.00(7)	0.02(7)	

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