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On the mechanisms of degenerate halogen exchange in phosphorus(III) halides

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Diazaphospholidine heterocycles of phosphorus(III) containing halogens or trifluoromethylsulfonate (triflate) display dynamic behaviour due to exchange of the X (Cl, OTf) groups. Full line-shape $^{13}C\{^1H\}$-NMR simulations on (3*R*,8*R*)-1-chloro-2,9-bis(4-*tert*-butylbenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane (**4a**) using the gNMR software package reveal proportionality between the rate of [P–Cl] exchange and the square of the concentration of the phosphorus compound, supportive of a second-order, bimolecular process. However, in the presence of an additional chloride ion source, a second, more rapid, process which is both first order in phosphorus compound and added chloride ion becomes competitive, consistent with a mechanism of the $S_N2(P)$ type. This tends to support the existence of parallel pathways which operate under slightly different conditions. Added nitrogen bases such as *N*-methylmorpholine do not affect the rate of exchange. Variable temperature full line-shape $^{13}C\{^1H\}$-NMR analyses on both **4a** and an analogue, (3*R*,8*R*)-1-chloro-2,9-bis(2,6-difluorobenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane (**4c**), reveal isothermal exchange rates at 206 K of 22.2 and 8.0 mol L^{-1} s^{-1} (0.36 M), respectively, suggesting that the exchange is slower for **4c**. Moreover, activation parameters ($\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 50.6(9), 20.8(9) kJ mol^{-1} and $-100(3)$ J K^{-1} mol^{-1}, respectively, for **4a** at 0.36 M and 55.8(1), 15.6(1) kJ mol^{-1} and $-135(5)$ J K^{-1} mol^{-1}, respectively, for **4c** at 0.36 M) are comparable and are more consistent, especially in terms of entropy change, with a bimolecular mechanism of exchange in the absence of added chloride ion. We argue on the basis of precedence that a bimolecular mechanism proceeding *via* a stabilised phosphenium intermediate is most probable, since it is well known that phosphorus(III) is capable of stabilising phosphenium centers. Finally, single-crystal X-ray diffraction analysis of (3*R*,8*R*)-1-chloro-2,9-bis(4-cyanobenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane (**4b**) reveals a fused ring system with a three-coordinate phosphorus atom in a distorted trigonal pyramidal geometry; the sum of the angles around P(1) is *ca.* 295°. The P–Cl, P–N and C(1)–C(2) bond lengths compare well with literature values for similar compounds; these range between 2.0–2.3, 1.6–1.7 and 1.5–1.56 Å, respectively.

Introduction

Throughout the 1950s and '60s, Van Wazer and co-workers published a series of seminal works on the reorganisation processes of phosphorus compounds, including phosphorus(III) halides.[1] Although this work focused on solution equilibria, Van Wazer tantalisingly speculated that the mechanism of group transfer in phosphorus(III) halides is bimolecular, although he was unable to provide direct evidence at that time.[1] Subsequently, in 1966, Fontal and Goldwhite reported semi-quantitative, variable-concentration studies on heterocyclic phosphorus halides,[2] which led them to propose a bimolecular [P–Cl] exchange process, although again, the necessary definitive experiments were not performed. In the intervening years, several reports have touched on the mechanistic aspects of phosphorus(III) halide exchange, although none in a definitive manner.[3] However, three works are especially revealing.

Verkade *et al*. examined dioxophosphocycle **A** (Fig. 1).[4] They argued, on the basis of solvent and dilution effects, that fluxionality involved a bimolecular phosphorus–halogen exchange mechanism. It was proposed further that chloride attack on phosphorus was an integral part of the rate-determining step. However, further experiments were not performed. Within a year, a parallel study by Newton *et al*. and Cavell and co-workers on a related dioxophosphocycle (**B**) suggested that [P–Cl] exchange does *not* occur in pure **B**, and that when exchange is observed, it is due to an impurity.[5] However, that impurity was not identified and to date no full study on this system has been published.

The most detailed [P–Cl] exchange study to date centers on chlorophosphines (**C**).[6] Hägele, Harris *et al*. examined inversion of stereochemistry at phosphorus by dynamic $^{31}P\{^1H\}$-NMR spectroscopy; variable temperature analysis revealing that [P–Cl] exchange leads to epimerisation at phosphorus.[6] Band-shape analysis of the $^{31}P\{^1H\}$-NMR signals due to (R_P)-R(Men)PCl and (S_P)-R(Men)PCl (R = Ph, Et; Men = L-menthyl) afforded energetic parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 68, 34 kJ mol^{-1} and -115 J K^{-1} mol^{-1}, respectively, for R = Ph and 61, 26 kJ mol^{-1} and -119 J K^{-1} mol^{-1} for R = Et, respectively. It was also observed that addition of chloride ion (as $^nBu_4NCl$) accelerated exchange. From these data, Hägele, Harris *et al*. analysed a range of mechanistic possibilities, as outlined in Scheme 1. From their data, they argued that the mechanism shown in Scheme 1(b), intermediate phosphenium ion formation *via* rate-determining [P–Cl] fission, although supporting evidence could not be provided at that time.

We were especially intrigued with this study, since the intermediacy of phosphenium ions [R_2P^+] is implicit in their proposed mechanism [Scheme 1(a)]. However, phosphenium ions bearing carbon substituents are known to be far less stable than those able to interact in a mesomeric manner with the positive phosphorus center (*e.g.* nitrogen groups) and, as such, might be considered to be a high-energy intermediate.[7] We supposed that, should the Hägele–Harris mechanism be correct, a phosphorus–halide system containing substituents better able to stabilise a phosphenium center should accelerate exchange. Consequently, we chose to examine [P–Cl] exchange in the 1,3-diazaphosphole system (**4**; Fig. 1), a system which we already know to stabilise phosphenium centres.[8] Here, we report our full kinetic and mechanistic investigation into the process of phosphorus–halogen exchange in this system; a study which we believe sheds light not only on [P–Cl] exchange in this

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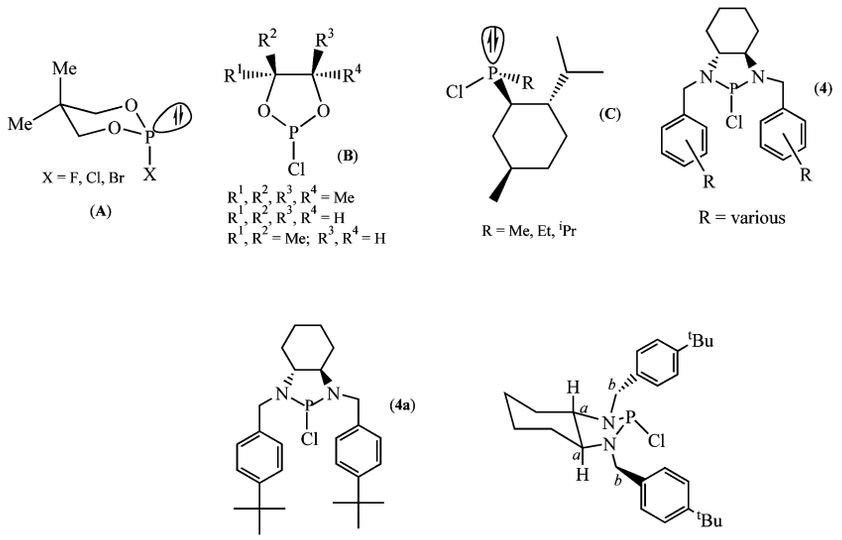
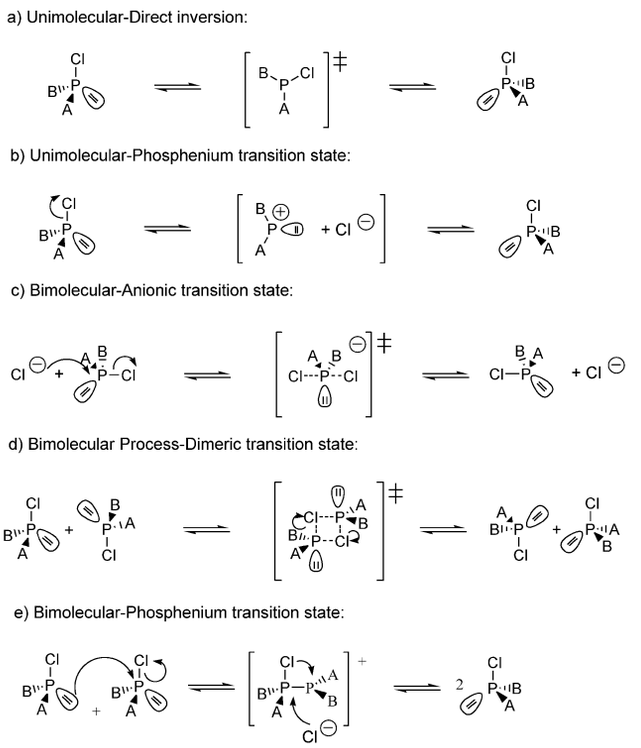


Fig. 1 Compounds which have been used to probe dynamic halogen exchange at phosphorus(III).



Scheme 1 Possible halogen exchange mechanisms at trivalent phosphorus(III).

particular heterocyclic family, but raises implications for halogen exchange in other phosphorus(III) systems.

Results and discussion

Syntheses and room temperature NMR behaviour of (3*R*,8*R*)-1-chloro-2,9-bis(4-*tert*-butylbenzyl)-2,9-diaza-1-phosphabicyclo-[4.0.3]nonane (4a), (3*R*,8*R*)-1-chloro-2,9-bis(4-cyanobenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane (4b) and (3*R*,8*R*)-1-chloro-2,9-bis(2,6-difluorobenzyl)-2,9-diaza-1-phosphabicyclo-[4.0.3]nonane (4c)

The title compounds **4a**–**c** have been synthesised using a procedure analogous to that reported previously by us for (3*R*,8*R*)-1-chloro-2,9-bis(4-*tert*-butylbenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane (Scheme 2).[8] During the syntheses, we find that precursor Schiff base **2** is difficult to obtain completely free of water, since water is a considerable and important part of the most effective work-up procedure.

Table 1 Selected interatomic distances (Å) and angles (°) of **4b** (s.u.s in parentheses)

Interatomic distances		Interatomic vectors	
P(1)–C(1)	2.2184(14)	N(1)–P(1)–N(2)	92.61(14)
P(1)–N(1)	1.664(3)	N(1)–P(1)–C(1)	102.56(11)
P(1)–N(2)	1.676(3)	N(2)–P(1)–C(1)	99.72(11)
N(1)–C(1)	1.469(4)	N(1)–C(1)–C(2)	103.8(3)
N(2)–C(2)	1.485(4)	N(2)–C(2)–C(1)	102.7(3)
N(1)–C(7)	1.473(4)	C(1)–N(1)–P(1)	113.5(2)
N(2)–C(15)	1.474(4)	C(2)–N(2)–P(1)	109.0(2)
C(14)–N(14)	1.147(5)	N(14)–C(14)–C(11)	178.8(5)
C(22)–N(22)	1.139(5)	N(22)–C(22)–C(19)	179.1(5)

Consequently, some of the microanalyses returned occasionally reflected this level of impurity; however, this does not in any way affect the subsequent chemistry, since it is possible to obtain both reduced derivative **3** and **4** completely free of water. Full synthetic and X-ray crystal structure studies on a range of Schiff bases **2** and their associated reduction products (**3**) are described in a separate paper.[9]

Molecular structure of (3*R*,8*R*)-1-chloro-2,9-bis(4-cyanobenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane (4b)

Unfortunately, neither **4a** or **4c** produced, in our hands, crystals suitable for single-crystal X-ray analysis, but fortunately compound **4b** provided suitable quality crystals. Our analysis (Fig. 2

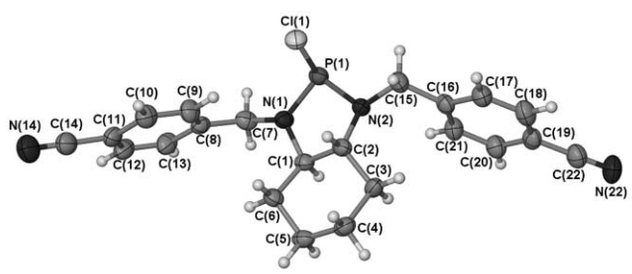
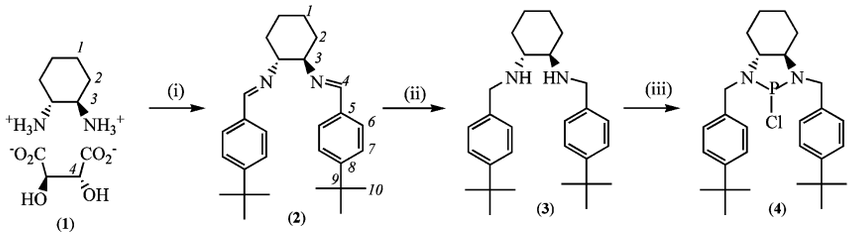


Fig. 2 Molecular structure of compound **4b**.

and Tables 1 and 2) reveals that the cyclohexyl ring adopts a chair conformation, as expected of the fused ring system with the sterically demanding NR groups occupying the more expected equatorial positions. In addition, the phosphorus atom is three-coordinate and adopts a distorted trigonal pyramidal geometry (see Tables 1 and 2 for selected bond lengths and angles), the sum of the angles around P(1) is *ca.* 295°. The sum of the angles around nitrogen atoms N(1)



Scheme 2 Synthesis of (3*R*,8*R*)-1-chloro-2,9-bis(4-*tert*-butylbenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane. (i) 4-^{t}BuC$_6$H$_4$CHO; (ii) NaBH$_4$; (iii) PCl$_3$, *N*-methylmorpholine.

Table 2 CH–π interaction parameters of **4b**

	H ··· Cg/Å	C–H ··· Cg/°
C(7)–H(7b) ··· Cg(3)[a]	2.8513	144.39
C(15)–H(15b) ··· Cg(4)[b]	2.9535	145.84

[a] Centroid Cg(3) = C(8)–C(9)–C(10)–C(11)–C(12)–C(13). [b] Centroid Cg(4) = C(16)–C(17)–C(18)–C(19)–C(20)–C(21).

and N(2) are *ca.* 356 and 343°, respectively, suggesting a strong preference for planar, sp^2-hybridised nitrogen.

The of [P–Cl], [P–N] and [C(1)–C(2)] bond lengths compare well with literature values for similar compounds; these range between 2.0–2.3, 1.6–1.7 and 1.5–1.56 Å, respectively, although, at 2.21 Å, the [P–Cl] bond is a little on the long side. The angles [N–P–N] of such five-membered rings range between 90–96°, and the other angles given Table 1 are also comparable to the corresponding literature values.[10] The presence of CH–π interactions between aliphatic hydrogen H(7b) and H(15b) bonded to methylene carbons C(7) and C(15), respectively (Fig. 3), seem to be the driving force in the way compound **4b** packs. Parameters of the interaction are provided in Table 2.

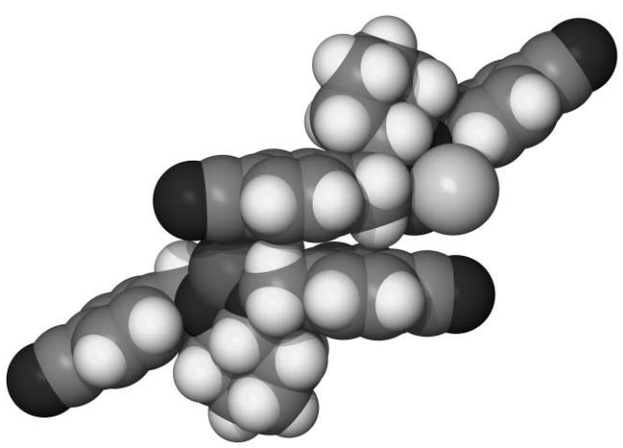


Fig. 3 CH–π interaction between two molecules of compound **4b**.

Mechanistic analysis of [P–Cl] exchange in (3*R*,8*R*)-1-chloro-2,9-bis(4-*tert*-butylbenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]-nonane (4a)

Selection of nucleus for examination. We recognise that the presence of a dynamic process involving [P–Cl] exchange in compounds of type **4** should, rate regime being favourable, afford changes in NMR spectra which can be analysed to reveal details of the mechanism of exchange. This is essentially the approach of Hägele and Harris. However, the first problem to address is the selection of the most appropriate nucleus for examination.

The ^{31}P{^{1}H}-NMR spectrum of **4a** is broadened at room temperature (CD_2Cl_2), but since **4** is C_2-symmetric, a single resonance is expected for **4a** at all temperatures, unlike **C**. Consequently, although line-shape analysis is possible, we feel that the risk of not being able to observe signals of sufficient distinction to be confident of accurate simulation is too great for us to proceed. Both ^{1}H and ^{13}C{^{1}H}-NMR spectra of **4a** reveal fluxional behaviour at room temperature, but signal overlap and complex spin systems make variable temperature ^{1}H-NMR analysis prohibitively complex. For example, the benzyl methylene hydrogens resonate as components of two distinct AA′BB′X spin systems.

^{13}C{^{1}H}-NMR spectroscopy is far more satisfactory than ^{1}H-NMR in this particular system. The benzyl (*b*, Fig. 1) and methine carbons (*a*, Fig. 1) are both magnetically distinct pairs in the absence of [P–Cl] exchange (as indeed found for the configurationally stable P–Ph derivative) and at low temperature (CD_2Cl_2), both sets of signals appear as pairs of doublets, coupling to phosphorus as part of two independent AX systems. Upon warming, each pattern coalesces and collapses to a single, average, doublet resonance. Interestingly, the aromatic carbons C^5, C^6 and C^8 (nomenclature as in Scheme 2) of **4a** also showed coalescing signals. These, however, were not simulated. Subsequently, we elected to analyse the dynamic properties of compound **4a** *via* full line-shape analysis using the gNMR software package (version 4.0, Cherwell Scientific), full details of which are described in the Experimental section; representative experimental and simulated pairs of spectra are reproduced for C_b in Fig. 4. The same situation is also observed for **4b** and **4c**, but due to the more favourable solubility properties of **4a**, especially at low temperature, we elected to perform full dynamic analyses only on **4a**. We have also performed a

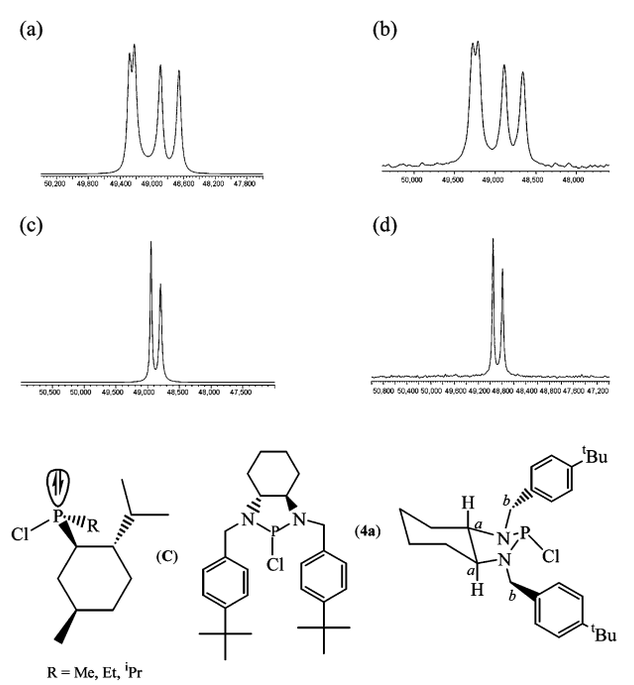


Fig. 4 Reproduction of part of the ^{13}C{^{1}H}-NMR spectra of compound **4a** at two temperatures, 185 [(a), (b)] and 312 K [(c), (d)]. (a) and (c) are simulations of experimental (CD_2Cl_2) signals for C_b, (b) and (d), at the respective temperatures. Chemical shift scale is in ppm. Concentration 0.36 M.

semi-quantitative analysis on **4c**, which will be discussed later. Although not as complete a study as for **4a**, we nevertheless feel that some valuable conclusions may still be drawn.

Variable concentration studies and exchange kinetics in 4a. Should phosphorus–halogen exchange in **4a** be unimolecular or bimolecular, then the respective rate equations for exchange should be rate = k·[**4a**] and rate = k·[**4a**]^2, where k is the appropriate rate constant. One should thus be able to differentiate between uni- and bimolecular rate expressions by measuring exchange rate as a function of the concentration of **4**; an experiment not reported on systems **A–C**. We have examined exchange rates of both C_a and C_b nuclei in **4** by $^{13}C\{^1H\}$-gNMR simulation at two temperatures (299 and 175 K) and at various concentrations between 0.01 and 0.36 mol L^{-1}. As is evident from Fig. 5, based on simulation of C_b at 299 K, there is a very

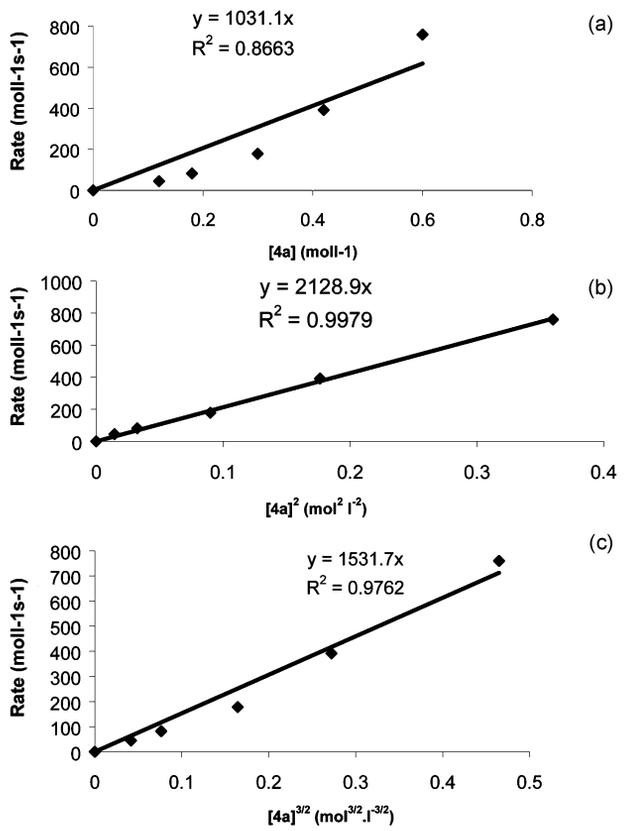


Fig. 5 Plots of rate *vs.* [**4a**] (a), rate *vs.* [**4a**]^2 (b) and rate *vs.* [**4a**]$^{3/2}$ for C_b of **4a** at 299 K.

poor linear relationship between rate and [**4a**], a result which seems to mitigate against both direct inversion [Scheme 1(a)] and the unimolecular phosphenium mechanism [Scheme 1(b)]. A far better linear relationship is obtained between rate and [**4a**]^2 [Fig. 5(b)], suggestive of a bimolecular exchange mechanism with a second-order rate constant of 2.1×10^3 L^2 s^{-1} mol^{-2}. Another possibility could result from a combination of mechanisms (b) and (c) in Scheme 1, involving dissociation of the [P–Cl] bond to afford an intermediate phosphenium cation (Scheme 1) and chloride anion, the latter then being able to attack another molecule of substrate, as in Scheme 1(c). Such a mechanism would have a rate expression of the form exchange rate = $2[k_1^{1/2}k_2/k_{-1}^{1/2}][\mathbf{4a}]^{3/2}$, where k_1 and k_{-1} are the rate constants for the forward and reverse reactions in Scheme 1(b), respectively, and k_2 is the rate constant for the forward reaction in Scheme 1(c). However, Fig. 5(c) reveals a poorer fit than in Fig. 5(b). Similar conclusions can be drawn for C_b exchange at 175 K.

From the above data, a bimolecular mechanism seems to be the best fit and from Scheme 1, two possibilities offer themselves: concerted exchange [Scheme 1(d)] and a stepwise process proceeding *via* a phosphenium intermediate [Scheme 1(e)]. In many ways, mechanisms (d) and (e) can be considered close relatives, since the transition state in (d) also may be viewed as a potential transition state for collapse of the chlorophosphine-stabilised phosphenium intermediate in mechanism (e). Our feeling at this stage is that (i) given the propensity for diazaphospholidine compounds to stabilise phosphenium cations[7] and (ii) the fact that chlorophosphine-stabilised phosphenium intermediates have been observed in solution[11] and derivatives isolated and analysed by single-crystal X-ray diffraction,[12] mechanism (e) is a distinct possibility.

The effect of added chloride on exchange kinetics of 4a. As mentioned earlier, several other workers have noticed that adding extra chloride to their systems accelerated [P–Cl] exchange.[5,6] To the best of our knowledge however, quantitative kinetic analyses have not been reported. In order to determine how the addition of extra chloride to our system affects the exchange kinetics, another variable concentration $^{13}C\{^1H\}$-NMR study was carried out. Tetrabutylammonium chloride was chosen as the source of chloride as it is an easily purifiable solid, is straightforward to manipulate and dissociates effectively in CD_2Cl_2 solution, as judged by solution conductivity in the concentration range of interest.

The concentration of **4a** was fixed at 0.3 M whereas that of $^nBu_4NCl$ was allowed to vary between 0 and 0.12 M. $^{13}C\{^1H\}$-spectra were recorded at 175 K and simulated using gNMR, as described in the Experimental. Plots of rates obtained from the simulation of C_a *vs.* [$^nBu_4NCl$] are shown in Fig. 6 and suggest a

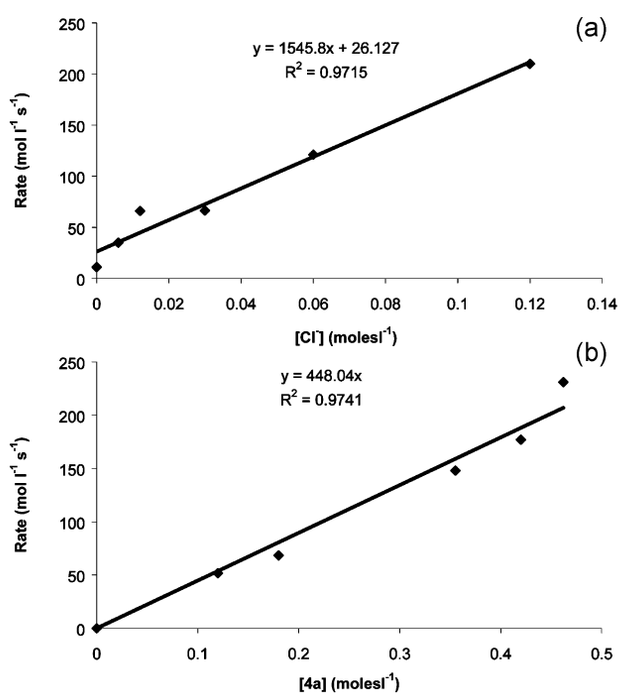


Fig. 6 (a) Rate *vs.* [$^nBu_4NCl$] for C_a of **4a** at 175 K. (b) Rate *vs.* [**4a**] for C_a at 175 K in the presence of [$^nBu_4NCl$] at 0.03 M.

linear relationship between exchange rate and chloride concentration; overall, suggestive of a mechanism first order in halide. The simulation on C_b gave similar results, although the R^2 value of 0.9399 was marginally less than for C_a (0.9715). According to these results, the exchange is considerably faster in the presence of extra chloride; the rate corresponding to [Cl^-] = 0.006 M is about three times faster than that for [Cl^-] = 0 M at 175 K.

In order to examine the exchange mechanism with respect to substrate concentration in presence of extra chloride, a variable concentration study with [**4a**] = 0.12–0.46 M and a fixed

amount of added chloride, [$^{n}Bu_4NCl$] = 0.03 M, was performed in CD_2Cl_2 at 177 K. The plot of rate *vs.* [**4a**] for C_a is shown in Fig. 6(b) and reveals a reasonably good linear fit ($R^2 > 0.97$, and also for C_b simulation), whereas the corresponding plots of the rate *vs.* [**4a**]^2 for carbons C_a and C_b have less satisfactory R^2 values of 0.9276 and 0.9195, respectively, and considerably worse fits compared to the same experiments performed in the absence of added chloride.

We suggest, therefore, that there are two parallel pathways for exchange in our system, a bimolecular mechanism in the absence of added chloride with overall second-order kinetics in [**4a**] (*vide supra*) and another, which is first order with respect to both [**4a**] and [Cl^-], presumably of the type outlined in Scheme 1(c).

The potential influence of impurities on exchange kinetics of 4a—chloride and base impurities? It has been reported for related halogeno–phosphorus systems that the presence of impurities can catalyse [P–X] exchange.[5] However, detailed kinetic studies do not appear to have been performed. It has been proposed that the presence of adventitious water leads to partial hydrolysis of the phosphorus(III) halide. This then releases hydrogen halide, which can act as an external halide source and/or source of proton-catalysed exchange. Whilst recognising this possibility, we have gone to considerable lengths to eliminate adventitious hydrolysis by the use of rigorous glove-box and inert atmosphere manipulations (see Experimental). At no time was any hydrolysis revealed by the presence of (3*R*,8*R*)-1-oxo-1-hydrido-2,9-bis(4-*tert*-butylbenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane, which gives rise to a peak at δ_P 20 ppm in the $^{31}P\{^1H\}$-NMR spectrum (CD_2Cl_2).

However, there could be two possible alternatives to water as potential impurities, based on the synthetic procedure used for **4a**. Since a nitrogen base (NEt_3 or *N*-methylmorpholine NMM) is used in the synthesis of **4a**, both the base and its protonated by-product ($NHEt_3^+Cl^-$ or $NMMH^+Cl^-$) are potential contaminants and both could, in theory, catalyse halogen exchange. We have already shown that added $^{n}Bu_4N^+Cl^-$ can greatly accelerate halogen exchange, but analysis of all samples of **4a** by ^1H-NMR and $^{13}C\{^1H\}$-NMR spectroscopy showed that at no time were detectable amounts of $NHEt_3^+Cl^-$ or $NMMH^+Cl^-$ present. However, in all cases, small amounts (*ca.* 1–2%) of NMM was found in samples of **4a** (by NMR) and which could be the cause of the slightly wavering microanalyses and possibly also have caused irregularities with our mechanistic analysis and conclusions above. Indeed, it is perhaps possible that NMM could catalyse halide exchange through a mechanism similar to (c) in Scheme 1, in which NMM replaces the chloride ion. A variable concentration NMR study of **4a** was therefore performed in the presence of NMM at various concentrations between 0 and 0.3 M in CD_2Cl_2 at 175 K, with a fixed concentration of substrate, [**4a**] = 0.3 M. No change in the broadening of the $^{13}C\{^1H\}$-NMR signals is observed upon addition of extra NMM, even when one equivalent of base is added. Consequently, NMM does not seem to affect the exchange and the base-induced mechanism (c) is unlikely to occur under these conditions.

Variable temperature studies and kinetic analysis of (3*R*,8*R*)-1-chloro-2,9-bis(4-*tert*-butylbenzyl)-2,9-diaza-1-phosphabicyclo-[4.0.3]nonane (4a) and (3*R*,8*R*)-1-chloro-2,9-bis(2,6-difluoro-benzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane (4c)

Two identical sets of variable temperature (VT), full line-shape $^{13}C\{^1H\}$-NMR analyses have been performed on **4a** at two different concentrations, 0.36 M and 0.53 M; calculated and experimental spectra for C_b at [**4a**] = 0.36 M are shown in Fig. 7(a) and (b), respectively, and corresponding Arrhenius and Eyring plots are shown in Fig. 8(a) and (b), respectively. Comparable parameters result from similar analysis on carbon resonance C_a. Rate constants and energetic parameters have been calculated using the gNMR package and are collected in Table 3.

From the Arrhenius equation, activation energies range from 16–22 kJ mol^{-1}, depending upon the resonance chosen for analysis. This is considerably less than the [P–Cl] bond energies in phosphorus(III) halides—for instance, the bond dissociation energy in PCl_3 is *ca.* 320 kJ mol^{-1} [12]—which might mitigate against a simple unimolecular [P–Cl] dissociative mechanism as outlined in Scheme 1(b). From the Eyring equation, we calculate $\Delta G^‡$, $\Delta H^‡$ and $\Delta S^‡$ of 49.5(9), 20.6(8) kJ mol^{-1} and −97(4) J K^{-1} mol^{-1} from the C_b signal at 0.53 M, and 50.6(9), 20.8(9) kJ mol^{-1} and −100(3) J K^{-1} mol^{-1} for the same resonance at 0.36 M. The values for C_a are comparable (Table 3), although the slight differences may result from variations in T_1 relaxation behaviour, since T_1 = 1 s for C_a and 0.5 s for C_b (298 K; 0.32 M in CD_2Cl_2).

Both $\Delta H^‡$ values from C_b and C_a, although comparable to those of chlorophosphines **3**, for which $\Delta H^‡$ ranges between 26–34 kJ mol^{-1}, are slightly lower than thes values. Hägele and Harris came down against a direct unimolecular inversion, option (a) in Scheme 1, since the energy barrier to pyramidal conversion in phosphines is known to be prohibitively high under normal conditions. Direct inversion of acyclic phosphines has been reported to require free energies of activation ranging between 120 and 150 kJ mol^{-1} at 130 °C,[12] and values of *ca.* 140 kJ mol^{-1} (at 130 °C) have been determined for four-membered ring phosphines.[13] Corresponding data for chlorophosphines is lacking in the current literature, but the $\Delta G^‡$ values of *ca.* 66 kJ mol^{-1} at 130 °C for **4a** suggest that the processes we are considering are not in the same energetic regime as direct inversion.

Of particular interest is the entropy data. Hägele and Harris' study returned quite large negative $\Delta S^‡$ values of between −115 and −119 J K^{-1} mol^{-1} (*vide supra*), which led these authors to conclude that mechanism (b) of Scheme 1 was the preferred option. Whilst it is quite rightly inappropriate to conclude mechanistic data solely from entropic data, we recognise that representative entropy values have been reported to range between 0 and −40 J K^{-1} mol^{-1} for unimolecular processes and between −70 and −140 J K^{-1} mol^{-1} for representative bimolecular processes.[14] For example, entropy of activation values of *ca.* −30 J K^{-1} mol^{-1} have been reported for the direct unimolecular inversion of four-membered ring phosphines.[15] The values of $\Delta S^‡$ reported for C–Et and C–Ph and those found for **4a** are both clearly more consistent with bimolecular exchange mechanisms.

When these energetic parameters are coupled with our concentration dependency studies on **4a** described above, there are now two pieces of evidence which mitigate against a unimolecular mechanism and both point more clearly towards a bimolecular mechanism (in the absence of added halide) in the case of a diazaphospholidine such as **4**. In an effort to provide a third piece of experimental evidence either for or against the intermediacy of phosphenium cations in the diazaphospholidine [P–Cl] exchange mechanism, we have explored the dynamic exchange behaviour of a related compound, (3*R*,8*R*)-1-chloro-2,9-bis(2,6-difluorobenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]-nonane (**4c**). Our reasoning here is that the presence of electron-pair donating fluoro substitutents in the benzyl arms should be able to help stabilise any putative phosphenium intermediate in the manner illustrated in Scheme 3. Similar intramolecular stabilisation of a phosphenium system has been shown to be possible *via* electron-pair donating methoxy-substituted benzyl groups within the same diazaphospholidine backbone.[16]

An identical variable temperature, full line-shape analysis has been carried out on **4c** at a concentration of 0.36 M. The calculated (a) and experimental (b) spectra for C_b are shown in Fig. 9

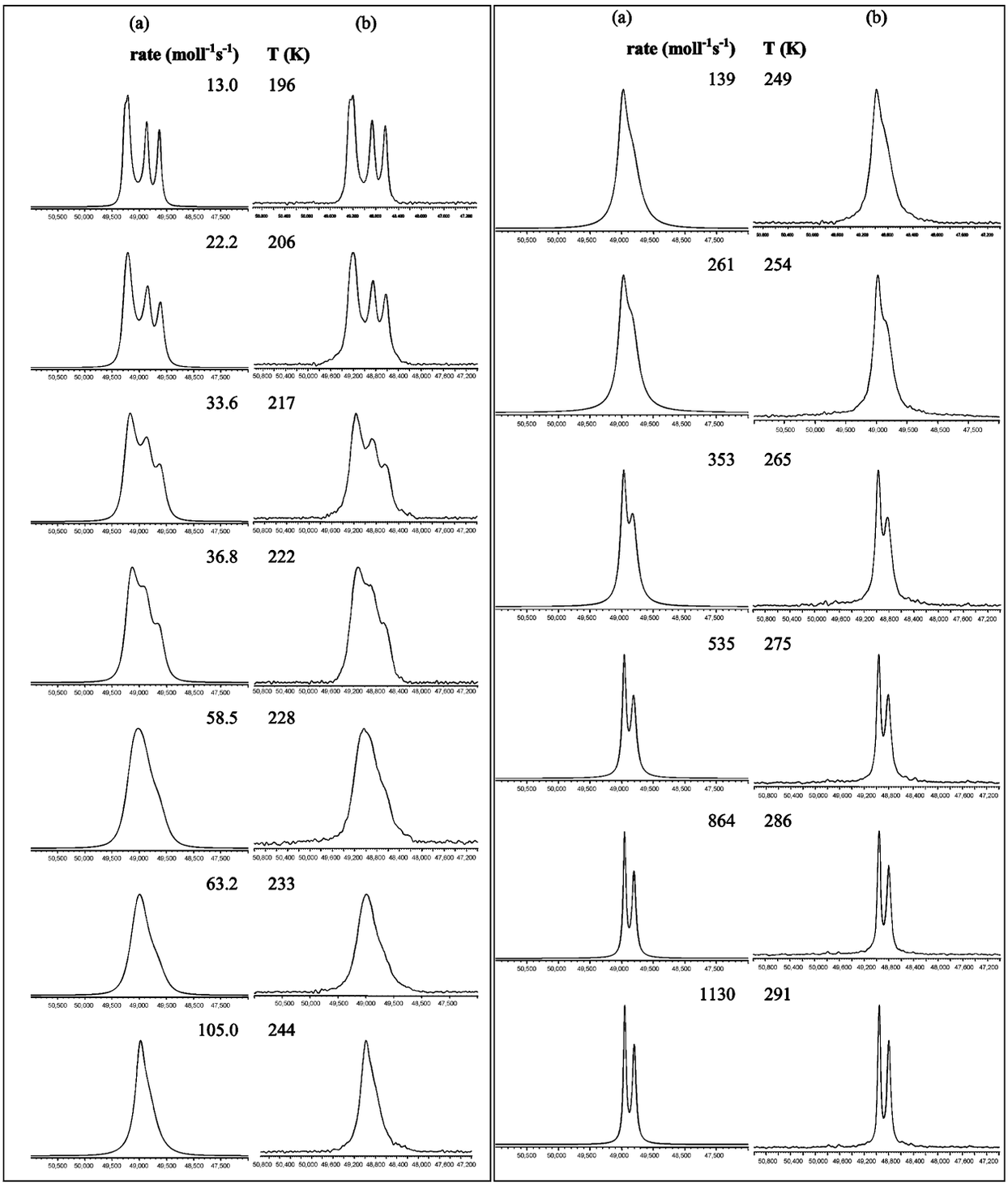


Fig. 7 Partial variable temperature $^{13}C\{^{1}H\}$-NMR spectra (C_b resonance only) of compound **4a** at 0.36 M; (a) calculated, (b) experimental. Rate (mol L^{-1} s^{-1}) = exchange rate at temperature T (K).

and associated Arrhenius and Eyring plots for C_a are reproduced in Fig. 10. The activation parameters computed from both C_a and C_b are collected in Table 4. Unfortunately, we were not able to observe the fast exchange-averaged doublet expected, but the data for the slow and medium exchange regimes are good. Both the fact that the "frozen" spectrum could be seen at a higher temperature than that of **4a** at the same concentration and the difference between the exchange rates at 206 K of similar samples of **4c** and **4a** (8.0 and 22.2 mol L^{-1} s^{-1} respectively; the chemical shift differences, $\delta\nu$, being similar) suggest that exchange is slower for **4c**. This result is more supportive of a bimolecular exchange mechanism in which the increased steric hindrance of *ortho*-disubstituted **4c** would make approach of two substrate molecules in a dimeric transition state relatively less favourable than for **4a**. In contrast, were a unimolecular phosphenium-intermediate mechanism such as (b) in Scheme 1 to be favoured, we might expect more facile [P–Cl] exchange in **4c** over **4a** and, consequently, a somewhat less negative entropy of activation.

Attempted variable temperature studies on related systems (3*R*,8*R*)-1-bromo-2,9-bis(4-*tert*-butylbenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane (4d) and (3*R*,8*R*)-1-trifluoro methylsulfonato-2,9-bis(2,6-difluorobenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane (4e)

Variable temperature analysis of the bromo analogue of **4a** was attempted to determine how the nature of the halogen affects

Table 3 Activation parameters for [P–Cl] exchange in **4a**, including standard errors in parentheses and R^2 values for Eyring and Arrhenius plots. Error values on Arrhenius activation parameter A were computed *via* standard propagation of error techniques using the equation $\sigma_A = \exp(I)\cdot\sigma_I$, where σ_A and σ_I are error values on A and the Arrhenius intercept (I), respectively[21]

	C_a		C_b	
	0.36 M	0.53 M	0.36 M	0.53 M
$\Delta G^{\ddagger}$(298 K)/kJ mol^{-1}	52.6(6)	52.9(5)	50.6(9)	49.5(9)
$\Delta H^{\ddagger}$/kJ mol^{-1}	14.5(6)	14.5(5)	20.8(9)	20.6(8)
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	−128(3)	−129(3)	−100(3)	−97(4)
Eyring plot, R^2	0.9771	0.9884	0.9797	0.9821
E_a/kJ mol^{-1}	16.4(6)	16.3(5)	22.8(9)	22.5(9)
A/s^{-1}	$2.8(8) \times 10^6$	$2.4(7) \times 10^6$	$8.4(33) \times 10^7$	$1.1(6) \times 10^8$
Arrhenius plot, R^2	0.9805	0.9907	0.9822	0.9844

Table 4 Activation parameters for [P–Cl] exchange in **4c** ([**4c**] = 0.36 M), including standard errors in parentheses and R^2 values for Eyring and Arrhenius plots. Error values on Arrhenius activation parameter A were computed as for **4a** (see Table 3)

	C_a	C_b
$\Delta G^{\ddagger}$(298 K)/kJ mol^{-1}	55.9(8)	55.8(1.3)
$\Delta H^{\ddagger}$/kJ mol^{-1}	16.6(8)	15.6(1.3)
$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	−132(3)	−135(5)
Eyring plot, R^2	0.981	0.9458
E_a/kJ mol^{-1}	18.7(9)	17.7(1.4)
A/L s^{-1} mol^{-1}	$1.9(8) \times 10^6$	$1.3(8) \times 10^6$
Arrhenius plot, R^2	0.9838	0.9548

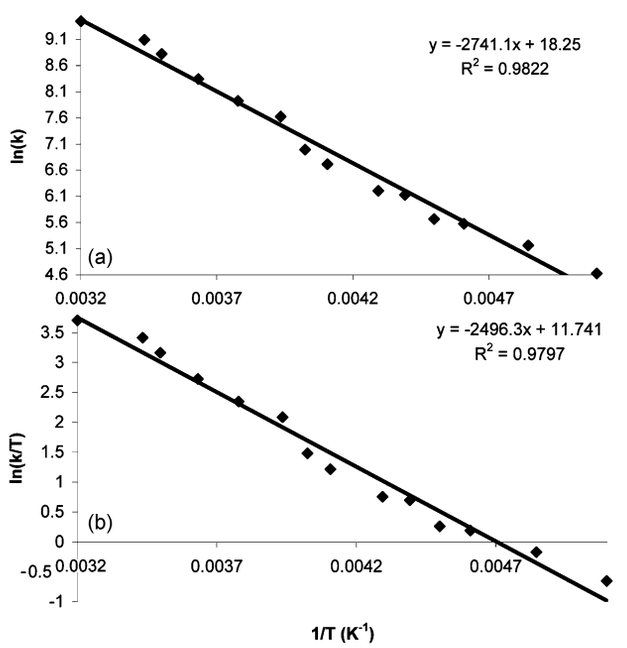
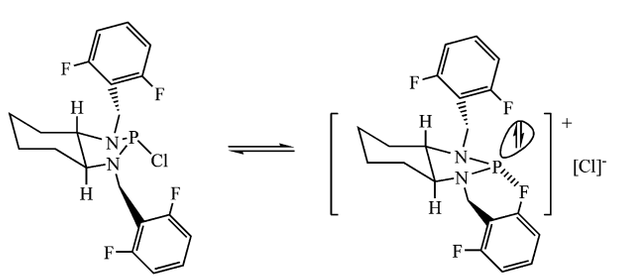


Fig. 8 Arrhenius (a) and Eyring (b) plots for C_b of **4a**, with [**4a**] = 0.36 M.



Scheme 3 Proposed intramolecular interactions between fluorine and a putative phosphenium centre in (8*R*, 9*R*)-1,3-bis(2,6-difluorobenzyl)-2-(chloro)octahydrobenzo[1,3,2]diazaphosphole (**4c**).

the phosphorus–halogen exchange. However, at 175 K in CD_2Cl_2 solvent, the C_a and C_b NMR signals are still too broad to determine precise coupling constants for the slow exchange limit, necessary as simulation input to gNMR. Consequently, no activation parameters could be evaluated. The phosphorus(III) triflate **4e** also shows dynamic behaviour in solution. Few VT-NMR studies have been reported on acyclic or cyclic phosphenium cations, but their dynamic behaviour is well known.[16] A VT-NMR study on compound **4e** at 0.36 M in deuterated dichloromethane was attempted in order to compare its dynamic behaviour with the corresponding chlorinated precursor **4a**. However, as in the case of the bromo derivative, at 175 K, both C_a and C_b NMR signals are too broad to determine the limiting coupling constants necessary for simulation. No quantitative information could be obtained, although one can conclude that this dynamic process for both bromo (**4d**) and triflate (**4e**) derivatives is to some degree faster than that of compounds **4a** and **4c**.[4,17]

Conclusions

We contend that proportionality between the rate of [P–Cl] exchange and [**4a**]^2 is supportive of a process which is second order in phosphorus in the absence of added chloride ions. By contrast, in the presence of an additional chloride ion source, a second, more rapid process becomes competitive, which is both first order in [**4a**] and in [Cl^-]. This tends to support parallel pathways in Scheme 1, which operate under different conditions. Added nitrogen bases such as *N*-methylmorpholine do not seem to affect the rate of exchange. Furthermore, variable temperature and full line-shape NMR simulation studies on derivatives **4a** and **4c** reveal activation parameters which are not inconsistent with the aforementioned mechanistic hypothesis. Our hypothesis, based on (i) our experimental results described above, (ii) precedence from related systems and (iii) the nature of the ligand framework in compounds **4**, is that a bimolecular exchange process proceeding *via* intermediate phosphine-stabilised phosphenium ions in the absence of added chloride ions [*i.e.* mechanism (e) in Scheme 1] generates chloride ions. These chloride ions can then induce exchange in either **4** *via* a bimolecular mechanism [Scheme 1(c)] or stabilised phosphenium ions *via* a bimolecular mechanism [Scheme 1(e)], whereas in the presence of excess added chloride ions, exchange becomes first order in both [**4a**] and [$Cl]^-$, consistent with mechanism (c) in Scheme 1.

Experimental

General

Manipulations were carried out under aerobic conditions unless specified otherwise. Solvents used were pre-dried over sodium wire or calcium chloride before being refluxed over sodium (toluene), sodium and benzophenone (tetrahydrofuran), lithium aluminium hydride (pentane) or calcium hydride (dichloromethane); all solvents were then deoxygenated by purging with dinitrogen gas prior to use. Reagents such as *cis*/*trans*-1,2-diaminocyclohexane, L-(+)-tartaric acid, lithium aluminium hydride and phosphorus trichloride were purchased

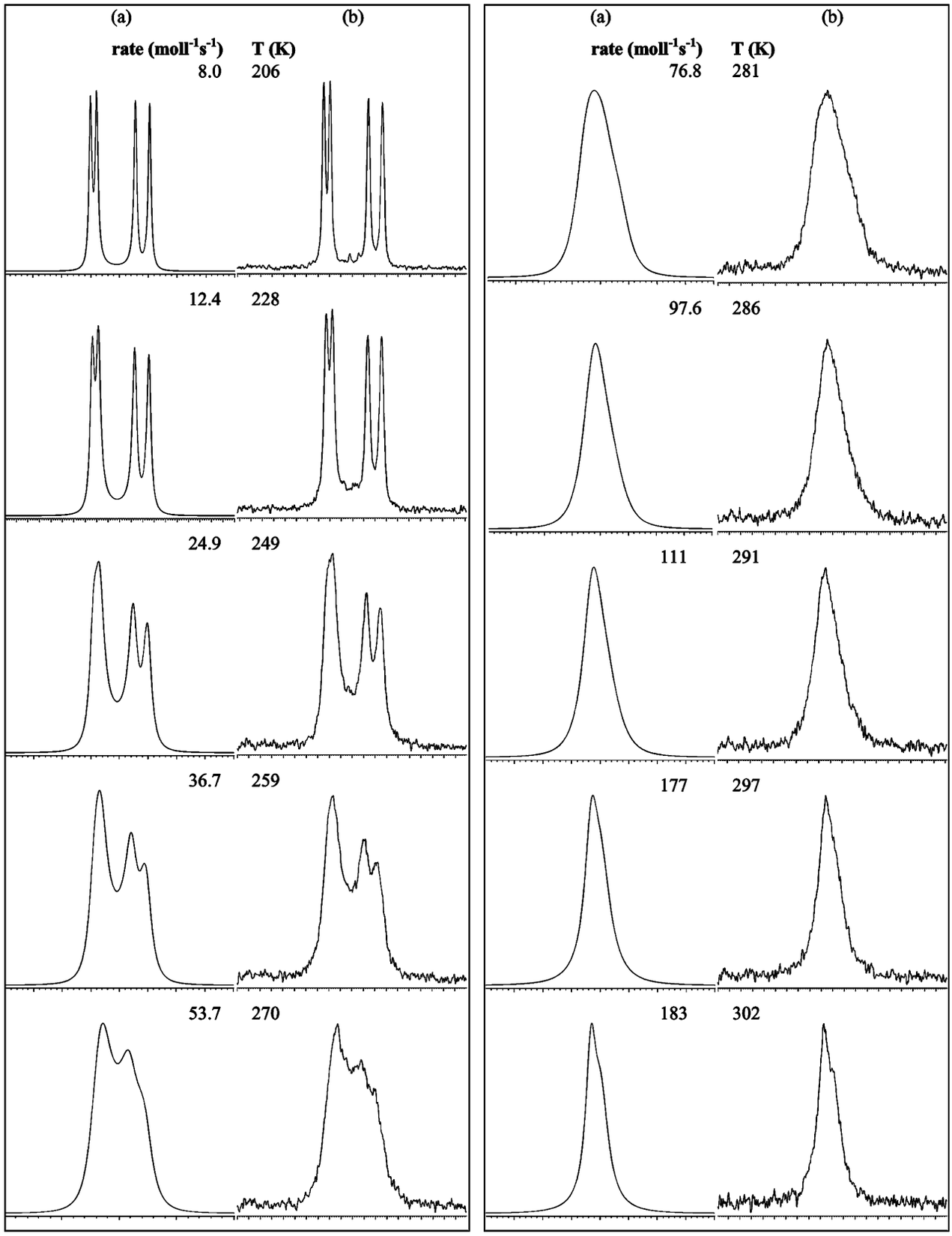


Fig. 9 Partial variable temperature $^{13}C\{^{1}H\}$-NMR spectra (C_b signal only) of compound **4c** at 0.36 M; (a) calculated, (b) experimental. Rate (mol L^{-1} s^{-1}) = exchange rate at temperature T (K).

from commercial sources and used as received. *N*-Methylmorpholine was distilled and stored over 4 Å molecular sieves under dinitrogen. Optical rotations were measured using an Optical Activity AA 10 polarimeter operating at 589.44 nm (sodium d-line). Microanalyses were performed in the School of Chemistry Microanalysis Laboratory (University of Leeds) by Mr M. Huscroft. Infrared spectra were recorded from KBr discs or Nujol mulls with a MIDAC FT-IR grating spectrophotometer (4000–600 cm^{-1}). Ms T. Marinko-Covell collected the mass spectrometric data on a VG Autospec instrument (operating at 70 eV for electron impact). All NMR spectra, except those involved in the quantitative dynamic analyses, were run at 298 K using a Bruker ARX 250 instrument (operating frequencies for ^{1}H, ^{13}C and ^{31}P of 250.1, 62.9 and 101.6 MHz,

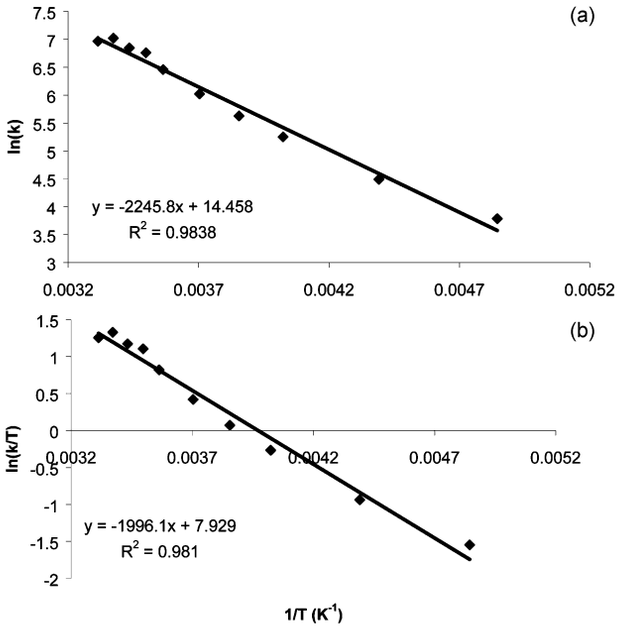


Fig. 10 Arrhenius (a) and Eyring (b) plots for C_a of **4c**, with [**4c**] = 0.36 M.

respectively). Chemical shifts are referenced either to residual protons in the solvent or to tetramethylsilane for ^{1}H and ^{13}C and to 85% H_3PO_4 for ^{31}P. Chemical shift values are given in ppm. All NMR assignments use the atom labelling shown in Scheme 2. We recognise that this numbering scheme is not identical to that implied by the correct IUPAC nomenclature. However, we feel in this case that there is considerable merit in maintaining some continuity of numbering for NMR assignment purposes throughout the sequence of compounds and it is with this intention in mind that we have used italicised superscript numbers for the NMR assignments below.

Preparations

Resolution of (1*R*,2*R*)-1,2-diaminocyclohexane (1). In a 500 cm^3 beaker, L-(+)-tartaric acid (40 g, 0.267 mol) was dissolved at room temperature in distilled water (130 cm^3). A mixture of *cis*/*trans*-1,2-diaminocyclohexane (62 cm^3, 57.7 g, 0.506 mol) was added so that the temperature reached 60 °C, followed by glacial acetic acid (24 cm^3, 24.85 g, 0.414 mol), generating a pale yellow solid. Stirring was maintained as the mixture cooled to room temperature over a period of *ca.* 2 h, after which it was cooled in an ice bath for a further 2 h (<5 °C). The white solid was collected by vacuum filtration, washed with cold distilled water (160 cm^3) and methanol (5 × 50 cm^3), and dried under reduce pressure overnight. Recrystallisation from distilled water afforded **1** as a white crystalline solid. Yield: 35 g, 50%. M.p.: 237–239 °C. $[\alpha]^D$ = +12.5 (c = 4 g dL^{-1}, H_2O), expected value for enantiopure compound +12.5. Found C: 45.45, H: 7.65, N: 10.45; $C_{10}H_{20}O_6N_2$ requires C: 45.45, H: 7.63, N: 10.60%. ν_{max}/cm^{-1}: 2926 (RNH_3^+). *m*/*z* (EI): 114 $[C_6H_{14}N_2]^+$, 97 $[C_6H_{14}N_2 - NH_3]^+$, 82 $[C_6H_{10}]^+$. ^{1}H-NMR (D_2O): 4.66 (s, 8H, NH and OH), 4.25 (s, 2H, C^4H), 3.34–3.22 (m, 2H, C^3H), 2.11–2.05 (m, 2H, C^2H_{eq}), 1.77–1.72 (m, 2H, C^1H_{eq}), 1.48–1.39 (m, 2H, C^1H_{ax}), 1.33–1.24 (m, 2H, C^2H_{ax}). ^{13}C{^{1}H}-NMR (D_2O): 178.92 (s, 2C, C^5), 74.29 (s, 2C, C^4), 52.61 (s, 2C, C^3), 29.81 (s, 2C, C^2), 23.22 (s, 2C, C^1).

(1*R*,2*R*)-*N*,*N*′-Bis(4-*tert*-butylbenzylidene)-1,2-diaminocyclohexane (2a). In a 1000 cm^3, three-necked flask equipped with magnetic stirrer, thermometer, condenser and 100 cm^3 adding funnel, anhydrous potassium carbonate (20.87 g, 0.151 mol) and the tartrate salt of **1** (20.00 g, 0.076 mol) were dissolved in distilled water (160 cm^3). Ethanol (300 cm^3) was added and the resulting white slurry heated under reflux. A solution of 4-*tert*-butylbenzaldehyde (24.50 g, 25.25 cm^3, 0.151 mol) in ethanol (70 cm^3) was added over 30 min. After refluxing for 5.5 h, the mixture was allowed to cool to room temperature, distilled water (160 cm^3) was added and the flask cooled to 5 °C overnight. A portion of the volatile materials was removed under reduced pressure and the resulting white crystals filtered off, recrystallised from pentane (180 cm^3) and dried under reduced pressure. Yield: 30.0 g, 99%. M.p.: 137–139 °C. Found C: 83.4, H: 9.5, N: 6.8; $C_{28}H_{38}N_2$ requires C: 83.5, H: 9.5, N: 7.0%. ν_{max}/cm^{-1}: 1639 (C=N, unsaturated, conjugated), 1500 (C=C, aromatic rings), 851 (C–H, *para*-disubstituted benzene). *m*/*z* (EI): 403 $[M]^+$, 402 $[M - H]^+$, 387 $[M - H - CH_3]^+$, 346 $[M - {}^tBu]^+$, 243 $[C_6H_{10}NCH_2C_6H_4{}^tBu]^+$, 186 $[C_6H_{10}NCHC_6H_5]^+$, 162 $[{}^tBuC_6H_4CHNH_2]^+$, 105 $[C_6H_5CHNH]^+$, 91 $[C_6H_5CH_2]^+$, 57 $[C(CH_3)_3]^+$. HRMS: calculated $[C_6H_{10}NCHPh]^+$ = 187.136100; found $[C_6H_{10}NCHPh]^+$ = 187.136192. ^{1}H-NMR ($CDCl_3$): 8.20 (s, 2H, C^4H), 7.52 (d, 4H, $^3J_{C^6H-C^7H}$ = 8.5 Hz, C^6H), 7.33 (d, 4H, $^3J_{C^6H-C^7H}$ = 8.5 Hz, C^7H), 3.40 (m, 2H, C^3H), 1.83 (m, 6H, C^2H and C^1H_{eq}), 1.46–1.25 (m, 2H, C^1H_{ax}), 1.30 (s, 18H, C^{10}H). ^{13}C{^{1}H}-NMR ($CDCl_3$): 160.6 (s, 2C, C^4), 153.5 (s, 2C, C^8), 133.8 (s, 2C, C^5), 127.8 (s, 4C, C^6), 125.3 (s, 4C, C^7), 74.0 (s, 2C, C^3), 34.8 (s, 2C, C^9), 33.2 (s, 2C, C^2), 31.2 (s, 6C, C^{10}), 24.6 (s, 2C, C^1).

(1*R*,2*R*)-*N*,*N*′-Bis(4-*tert*-butylbenzyl)-1,2-diaminocyclohexane (3a). In a 500 cm^3, three-necked flask equipped with magnetic stirrer, thermometer and condenser, lithium aluminium hydride (5.69 g, 0.150 mol) was diluted in dry tetrahydrofuran (40 cm^3) under dinitrogen and a solution of **2a** (20.00 g, 0.050 mol) in dry tetrahydrofuran (160 cm^3) was added dropwise. The mixture was heated under reflux for 24 h, followed by cooling to room temperature. Diethyl ether (150 cm^3) was added, followed by a slurry of sodium sulfate in distilled water until the mixture ceased effervescing. Stirring was maintained until a clear layer appeared. The insoluble lithium salts were filtered off over magnesium sulfate and the solvents removed to give **3a** as a colourless oil. Yield: 17.5 g, 86%. Found C: 82.0, H: 10.8, N: 6.5; $C_{28}H_{42}N_2$ requires C: 82.7, H: 10.4, N: 6.9%. ν_{max}/cm^{-1}: 3300 (N–H stretching), 3023 (aryl-H), 1393 and 1362 [C–H, $C(CH_3)_3$], 853 (C–H, *para*-disubstituted benzene). *m*/*z* (EI): 407 $[M]^+$, 406 $[M - H]^+$, 259 $[M - H - {}^tBuC_6H_4CH_2]^+$, 162 $[{}^tBuC_6H_4CH_2NH]^+$, 147 $[{}^tBuC_6H_4CH_2]^+$, 106 $[C_6H_5CH_2NH]^+$, 91 $[C_6H_5CH_2]^+$. HRMS: calculated for $C_{28}H_{42}N_2$ $[M]^+$ = 407.3426; found $[M]^+$ = 407.3430. ^{1}H-NMR ($CDCl_3$): 7.37 (d, 4H, $^3J_{C^6H-C^7H}$ = 6.6 Hz, C^7H), 7.29 (d, 4H, $^3J_{C^6H-C^7H}$ = 6.6 Hz, C^6H), 3.91 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, C^4H), 3.68 (d, 2H, $^2J_{H-H}$ = 13.1 Hz, C^4H), 2.34–2.30 (m, 2H, C^3H), 2.21–2.15 (m, 2H, C^2H_{eq}), 1.90 (s, 2H, NH), 1.80–1.75 (m, 2H, C^1H_{eq}), 1.36 (s, 18H, C^{10}H), 1.33 (m, 2H, C^1H_{ax}), 1.28 (m, 2H, C^2H_{ax}). ^{13}C{^{1}H}-NMR ($CDCl_3$): 149.5 (s, 2C, C^8), 138.3 (s, 2C, C^5), 127.8 (s, 4C, C^6), 125.0 (s, 4C, C^7), 61.0 (s, 2C, C^3), 50.6 (s, 2C, C^4), 34.5 (s, 2C, C^9), 31.7 (s, 2C, C^2), 31.5 (s, 6C, C^{10}), 25.1 (s, 2C, C^1).

(3*R*,8*R*)-1-Chloro-2,9-bis(4-*tert*-butylbenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane (4a). Diamine **3a** was dried in solution over basic alumina prior to use. To a mixture of phosphorus trichloride (0.44 cm^3, 0.70 g, 0.0051 mol) and *N*-methylmorpholine (1.68 cm^3, 1.55 g, 0.0153 mol) in dry pentane (10 cm^3), a solution of **3a** (2.07 g, 0.0051 mol) in dry pentane (30 cm^3) was added slowly at −78 °C under dinitrogen over 30 min. The solution was then allowed to warm to room temperature and stirred for a further 4 h, after this, the pentane solution was filtered under dinitrogen and the white chloride salt of hydrogenated *N*-methylmorpholine was washed out with dry pentane (2 × 15 cm^3). All the volatiles were removed under reduced pressure to leave **4a** as white microcrystals. Yield: 2.0 g, 83.3%. Found C: 70.6, H: 8.7; $C_{28}H_{40}N_2PCl$ requires C: 71.4, H: 8.6%. *m*/*z* (EI): 405 $[M - PCl]^+$, 259 $[M - PCl - CH_2C_6H_4{}^tBu]^+$, 162 $[{}^tBuC_6H_4CH_2NH]^+$, 147 $[{}^tBuC_6H_4CH_2]^+$, 106

$[C_6H_5CH_2NH]^+$, 91 $[C_6H_5CH_2]^+$. HRMS: calculated for $C_{28}H_{40}N_2PCl$ $[M]^+$ = 471.250991; found $[M]^+$ = 471.251976. ^{1}H-NMR ($CDCl_3$): 7.30 (m, 8H, C^6H and C^7H), 4.28 (m, 4H, C^4H), 2.95 (m, 2H, C^3H), 1.95 (m, 2H, C^2H_{eq}), 1.72 (m, 2H, C^1H_{eq}), 1.32 (s, 18H, C^{10}H), 1.23 (m, 2H, C^1H_{ax}), 0.88 (m, 2H, C^2H_{ax}). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 150.3 (s, 2C, C^8), 135.1 (d, 2C, $^3J_{P-C}$ = 6.5 Hz, C^5), 128.6 (s, 4C, C^6), 125.4 (s, 4C, C^7), 67.9 (m, 2C, C^3), 48.6 (m, 2C, C^4), 34.1 (s, 2C, C^9), 31.4 (s, 6C, C^{10}), 29.5 (s, 2C, C^2), 24.3 (s, 2C, C^1). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 183.0.

(1*R*,2*R*)-*N*,*N*′-Bis(4-cyanobenzylidene)-1,2-diaminocyclohexane (2b). The same procedure used to prepare **2a** was employed with K_2CO_3 (7.88 g, 0.057 mol), **1** (7.49 g, 0.028 mol) and 4-cyanobenzaldehyde (10.54 g, 0.057 mol), 8 h reflux. Yield: 8.4 g, 88% (white crystals). M.p.: 139–141 °C. ν_{max}/cm^{-1}: 2224 (aryl-C≡N), 1643 (C=N), 1593 (C=C), 843 and 832 (C–H, 1,4-disubstituted benzene ring). *m*/*z* (EI): 341 $[M + H]^+$, 340 $[M]^+$, 204 $[NH_3C_6H_{10}NHCH_2C_6H_4]^+$, 131 $[CNC_6H_4CH_2NH]^+$. HRMS: calculated for $C_{22}H_{20}N_4$ $[M]^+$ = 340.168797; found $[M]^+$ = 340.165693 (within 9.1 ppm). ^{1}H-NMR ($CDCl_3$): 8.28 (s, 2H, C^4H), 7.69 (d, 4H, $^3J_{C^6H-C^7H}$ = 8.3 Hz, C^6H), 7.60 (d, 4H, $^3J_{C^6H-C^7H}$ = 8.2 Hz, C^7H), 3.45 (m, 2H, C^3H), 1.82 (m, 6H, C^2H and C^1H_{eq}), 1.50 (m, 2H, C^1H_{ax}). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 159.0 (s, 2C, C^4), 140.0 (s, 2C, C^5), 132.3 (s, 4C, C^7), 128.3 (s, 4C, C^6), 118.4 (s, 2C, C^9), 106.8 (s, 2C, C^8), 73.9 (s, 2C, C^3), 32.6 (s, 2C, C^2), 24.2 (s, 2C, C^1).

(1*R*,2*R*)-*N*,*N*′-Bis(4-cyanobenzyl)-1,2-diaminocyclohexane (3b). Compound **2b** (4.00 g, 0.012 mol) was dissolved in methanol under a dinitrogen blanket (100 cm^3) and sodium borohydride (1.34 g, 0.035 mol) was added in small portions at room temperature. The mixture was heated under reflux for 6 h, followed by cooling to room temperature. Distilled water (80 cm^3) was added, which resulted in the decolouration of the solution. The solution was then heated to boiling point for 20 min and extracted with dichloromethane (3 × 80 cm^3). The combined organic layers were dried over magnesium sulfate. The solution was filtered and the volatiles removed to give **3b** as a pale yellow oil. The product was recrystallised from pentane in air to give white crystals. Yield: 2.0 g, 49%. M.p.: 73–75 °C. Found C: 76.2, H: 7.1, N: 16.1;$C_{22}H_{24}N_4$ requires C: 76.7, H: 7.0, N: 16.3%. ν_{max}/cm^{-1}: 3254 (N–H stretching), 3066 (aryl-H), 2227 (aryl-C≡N), 850–812 (C–H, 1,4-trisubstituted benzene ring). *m*/*z* (EI): 344 $[M]^+$, 228 $[M - NCC_6H_4CH_2]^+$, 211 $[NCC_6H_4CH_2NHC_6H_{10}]^+$, 133 $[NCC_6H_4CH_2NH_3]^+$, 116 $[NCC_6H_4CH_2]^+$, 96 $[C_6H_{10}N]^+$. ^{1}H-NMR ($CDCl_3$): 7.57 (d, 4H, $^3J_{C^6H-C^7}$ = 8.1 Hz, C^7H), 7.41 (d, 4H, $^3J_{C^6H-C^7H}$ = 8.0 Hz, C^6H), 3.82 (d, 2H, $^2J_{H-H}$ = 14.1 Hz, C^4H), 3.71 (d, 2H, $^2J_{H-H}$ = 14.5 Hz, C^4H), 2.22 (m, 2H, C^3H), 2.08 (m, 2H, C^2H_{eq}), 1.96 (s, 2H, NH), 1.70 (m, 2H, C^1H_{eq}), 1.24 (m, 2H, C^1H_{ax}), 1.02 (m, 2H, C^2H_{ax}). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 146.8 (s, 2C, C^5), 132.1 (s, 4C, C^7), 128.6 (s, 4C, C^6), 118.9 (s, 2C, C^9), 110.6 (s, 2C, C^8), 61.1 (s, 2C, C^3), 50.5 (s, 2C, C^4), 31.5 (s, 2C, C^2), 24.9 (s, 2C, C^1).

(3*R*,8*R*)-1-Chloro-2,9-bis(4-cyanobenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane (4b). The same procedure used to prepare **4a** was employed with PCl_3 (0.13 cm^3, 0.20 g, 0.0015 mol), triethylamine (0.61 cm^3, 0.44 g, 0.0044 mol) and **3b** (0.5 g, 0.0015 mol) in a mixture of dry pentane and toluene. Recrystallisation from pentane over several weeks at −35 °C afforded crystals suitable for single crystal X-ray analysis. Yield: 0.6 g, 98%. HRMS: calculated for $C_{28}H_{40}N_2PCl$ $[M]^+$ = 471.250991; found $[M]^+$ = 471.251976. ^{1}H-NMR ($CDCl_3$): 7.64 (d, 2H, $^3J_{C^6H-C^7H}$ = 8.3 Hz, C^7H), 7.48 (d, 4H, $^3J_{C^6H-C^7H}$ = 13.1 Hz, C^6H), 4.42 (m, 2H, C^4H), 4.15 (m, 2H, C^4H), 3.09 (m, 2H, C^3H), 1.76 (m, 4H, C^2H_{eq} and C^1H_{eq}), 1.14 (m, 4H, C^1H_{ax} and C^2H_{ax}). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 144.1 (d, 2C C^5), 132.4 (s, 4C, C^7), 128.7 (s broad, 4C, C^6), 118.7 (s, 2C, C^9), 111.5 (s, 2C, C^8), 68.1 (d, 2C, $^2J_{P-C}$ = 8.6 Hz, C^3), 49.1 (d, 2C, $^2J_{P-C}$ = 21.8 Hz, C^4), 29.8 (s, 2C, C^2), 24.0 (s, 2C, C^1). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 178.0.

(1*R*,2*R*)-*N*,*N*′-Bis(2,6-difluorobenzylidene)-1,2-diaminocyclohexane (2c). In a 250 cm^3, three-necked flask equipped with magnetic stirrer, thermometer, condenser and 50 cm^3 adding funnel, anhydrous potassium carbonate (5.23 g, 0.038 mol) and the tartrate salt of **1** (5.00 g, 0.019 mol) were dissolved in distilled water (40 cm^3). Ethanol (160 cm^3) was added and the resulting white slurry was heated to reflux. A solution of 2,6-difluorobenzaldehyde (5.4 g, 4.1 cm^3, 0.038 mol) in ethanol (40 cm^3) was added over 30 min. After refluxing for 4 h, the mixture was allowed to cool to room temperature, distilled water (40 cm^3) added and the flask cooled to 5 °C and allowed to stand overnight. The solvents were removed under reduced pressure to give a viscous yellow solid, which was dissolved in dichloromethane (50 cm^3). The organic layer was washed with distilled water (3 × 20 cm^3) and saturated brine (20 cm^3), and dried over magnesium sulfate. Dichloromethane was removed to afford a yellow oil which crystallised from pentane at −35 °C to give pale yellow crystals. Yield: 6.0 g, 90%. M.p.: 94–96 °C. Found C: 66.5, H: 5.0, N: 7.6; $C_{20}H_{18}N_2F_2$ requires C: 66.3, H: 5.0, N: 7.7%. ν_{max}/cm^{-1}: 3040 (aryl-H), 1640 (C=N), 1587 (C=C), 1462 and 680 (C–F), 783 (C–H, 1,2,3-trisubstituted benzene ring). *m*/*z* (ES): 385 $[M + Na]^+$, 363 $[M + H]^+$. ^{1}H-NMR ($CDCl_3$): 8.39 (s, 2H, C^4H), 7.23 (m, 2H, C^8H), 6.84 (m, 4H, C^7H), 3.46 (m, 2H, C^3H), 1.87 (m, 4H, C^2H), 1.77 (m, 2H, C^1H_{eq}), 1.36 (m, 2H, C^1H_{ax}). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 161.6 (dd, 4C, $^1J_{C-F}$ = 255.7, $^3J_{C-F}$ = 6.9 Hz, C^6), 151.6 (s, 2C, C^4), 130.9 (t, 2C, $^3J_{C-F}$ = 10.6 Hz, C^8), 114.1 (t, 2C, $^2J_{C-F}$ = 14.2 Hz, C^5), 111.6 (dd, 4C, $^2J_{C-F}$ = 23.5, $^4J_{C-F}$ = 2.0 Hz, C^7), 75.3 (s, 2C, C^3), 32.6 (s, 2C, C^2), 24.3 (s, 2C, C^1). ^{19}F-NMR ($CDCl_3$): −114.1 (m, 4F, C^6F).

(1*R*,2*R*)-*N*,*N*′-Bis(2,6-difluorobenzyl)-1,2-diaminocyclohexane (3c). The same procedure used to prepare **3b** was employed with **2c** (2.00 g, 0.006 mol) and $NaBH_4$ (0.63 g, 0.017 mol), 3 h reflux. Yield: 1.7 g, 84% (yellow liquid). Found C: 65.3, H: 6.1, N: 7.6; $C_{20}H_{22}N_2F_4$ requires C: 65.6, H: 6.1, N: 7.7%. ν_{max}/cm^{-1}: 3308 (N–H stretching), 3030 (aryl-H), 2930 and 2857 (CH_2), 1592 (C=C, aromatic rings), 1467 (C–F), 782 (C–H, 1,2,3-trisubstituted benzene ring). *m*/*z* (EI): 366 $[M]^+$, 222 $[C_6H_8NHCH_2C_6H_3F_2]^+$, 142 $[F_2C_6H_3CH_2NH]^+$, 127 $[F_2C_6H_3CH_2]^+$. ^{1}H-NMR ($CDCl_3$): 7.17 (m, 2H, C^8H), 6.83 (m, 4H, C^7H), 3.91 (d, 2H, $^2J_{H-H}$ = 12.8 Hz, C^4H), 3.77 (d, 2H, $^2J_{H-H}$ = 13.0 Hz, C^4H), 2.14 (m, 4H, C^3H and C^2H_{eq}), 1.90 (s, 2H, NH), 1.72 (m, 2H, C^1H_{eq}), 1.25 (m, 2H, C^1H_{ax}), 1.03 (m, 2H, C^2H_{ax}). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 161.8 (dd, 4C, $^1J_{C-F}$ = 247.7, $^3J_{C-F}$ = 9.0 Hz, C^6), 128.5 (t, 2C, $^3J_{C-F}$ = 10.5 Hz, C^8), 116.6 (t, 2C, $^2J_{C-F}$ = 20.6 Hz, C^5), 111.1 (d, 4C, $^2J_{C-F}$ = 25.7 Hz, C^7), 60.7 (s, 2C, C^3), 37.9 (s, 2C, C^4), 31.5 (s, 2C, C^2), 25.0 (s, 2C, C^1). ^{19}F-NMR ($CDCl_3$): −116.7 (broad t, 4F, *J* = 5.7 Hz, C^6F).

(3*R*,8*R*)-1-Chloro-2,9-bis(2,6-difluorobenzyl)-2,9-diaza-1-phosphabicyclo[4.0.3]nonane (4c). The same procedure used to prepare **4b** was employed with PCl_3 (0.12 cm^3, 0.19 g, 0.0014 mol), *N*-methylmorpholine (0.45 cm^3, 0.41 g, 0.0041 mol) and **3c** (0.5 g, 0.0014 mol) in pentane. Yield: 0.5 g, 85% (pale yellow liquid). Found C: 55.3, H: 4.9, N: 6.3, Cl: 8.0, P: 7.3; $C_{20}H_{20}N_2ClF_4P$ requires C: 55.8, H: 4.7, N: 6.5, Cl: 8.2, P: 7.2%. *m*/*z* (EI): 430 $[M]^+$, 395 $[M - Cl]^+$, 127 $[F_2C_6H_3CH_2]^+$. ^{1}H-NMR ($CDCl_3$): 7.24 (m, 2H, C^8H), 6.88 (m, 4H, C^7H), 4.44 (m, 1H, C^4H), 4.31 (m, 2H, C^4H), 4.02 (m, 1H, C^4H), 3.13 (m, 1H, C^3H), 2.67 (m, 1H, C^3H), 2.67 (m, 2H, C^2H_{eq}), 2.20 (m, 2H, C^1H_{eq}), 1.31 (m, 2H, C^1H_{ax}), 1.14 (m, 2H, C^2H_{ax}). $^1H\{^{31}P\}$-NMR ($CDCl_3$): as above, except 4.44 (d, 1H, $^2J_{C^4H_a-C^4H_b}$ = 14.6 Hz, C^4H_a), 4.32 (d, 1H, $^2J_{C^4H_a-C^4H_b}$ = 14.8 Hz, C^4H_b), 4.28 (d, 1H, $^2J_{C^4H_a-C^4H_b}$ = 14.3 Hz, C^4H_a), 4.02 (d, 1H, $^2J_{C^4H_a-C^4H_b}$ = 14.1 Hz, C^4H_b), 3.14 (td, 1H, $^3J_{C^3H-C^4H}$ = 8.7, $^3J_{C^3H_a-C^3H_b}$ = 2.2 Hz, C^3H_a), 2.67 (td, 1H, $^3J_{C^3H-C^4H}$ = 8.7, $^3J_{C^3H_a-C^3H_b}$ = 2.2 Hz,

C^3H_b). $^{13}C\{^1H\}$-NMR ($CDCl_3$): 161.7 (dd, 4C, $^1J_{C-F}$ = 249.7, $^3J_{C-F}$ = 8.3 Hz, C^6), 129.7 (m, 2C, C^8), 114.0 (m, 2C, C^5), 111.4 (d, 4C, $^2J_{C-F}$ = 20.4 Hz, C^7), 67.9 (d, 1C, $^2J_{C-P}$ = 8.2 Hz, C^3), 66.4 (d, 1C, $^2J_{C-P}$ = 8.3 Hz, C^3), 36.2 (d, 1C, $^2J_{C-P}$ = 15.5 Hz, C^4), 35.3 (d, 1C, $^2J_{C-P}$ = 31.6 Hz, C^4), 29.1 (s, 1C, C^2), 28.5 (s, 1C, C^2), 25.0 (s, 2C, C^1). $^{31}P\{^1H\}$-NMR ($CDCl_3$, 500 MHz): 181.9 (m, 7 peaks). ^{19}F-NMR ($CDCl_3$): −113.4 (m, 2F), −113.9 (d broad, 2F, J = 38.8 Hz).

Crystallography

Single crystals of **4b** were recrystallised from dichloromethane, mounted in inert oil and transferred to the cold gas stream of the diffractometer.

Crystal data. $C_{22}H_{22}ClN_4P$, M = 408.86, orthorhombic, a = 7.4730(3), b = 15.6217(9), c = 17.9713(9) Å, U = 2097.99(18) Å^3, T = 150 K, space group $P2_12_12_1$ (no. 19), Z = 4, μ(Mo-Kα) = 0.27 mm^{-1}, 9792 reflections measured, 4005 unique (R_{int} = 0.063) which were used in all calculations. The final $wR(F^2)$ was 0.110 (all data).

CCDC reference number 181122.

See http://www.rsc.org/suppdata/dt/b2/b202942c/ for crystallographic data in CIF or other electronic format.

NMR analyses—general

The dynamic studies reported here, have been performed in deuterated dichloromethane, which permits sufficient solubility at the slow exchange limit. The dynamic behaviour of **4a** is slowed considerably in toluene, so that the fast exchange regime cannot be observed, even at 363 K. Higher temperatures might lead to partial decomposition. Precision in controlling and measuring temperature is crucial to obtain accurate activation parameters, so great care was taken in calibrating the NMR spectrometer before carrying out any experiments. When recording the $^{13}C\{^1H\}$-NMR spectra, the time period for each transient was chosen to be approximately three times the measured T_1 to ensure as complete relaxation as possible within the timeframe of the experiment, so that the line-width at half height more accurately represents the exchange process. The T_1 values for C^3 and C^4 are 1 and 0.7 s, respectively. Samples were prepared by dissolving various amounts of compound **4a** in 0.5 cm^3 deuterated dichloromethane (Apollo Scientific Limited, UK), in 5 mm OD tubes with PTFE valves (Aldrich, UK) in a dry, dinitrogen-filled glove box. For both concentration studies, a common solution was prepared and used for every tube. The deuterated solvent was degassed and dried in a PTFE-sealed ampoule over P_2O_5 under vacuum at 30 °C.

All NMR spectra were recorded on a Bruker DRX500 spectrometer (operating frequencies for ^{1}H, ^{13}C and ^{31}P of 500.1, 125.8 and 202.5 MHz, respectively) using a 5 mm Quad probe (^{1}H/^{13}C/^{11}B/^{31}P). Chemical shifts are referenced to residual protons in the solvent (for CH_2Cl_2, residual peak at 5.35 ppm for ^{1}H and 53.8 ppm for the ^{13}C spectra) for ^{1}H and ^{13}C. ^{31}P chemical shifts are reported relative to 85% H_3PO_4 in water as an external reference (0 ppm). The chemical shift values are reported in ppm. Prior to variable temperature experiments, a temperature calibration was performed using a standard sample of 100% methanol (T_{cal} *vs.* T_{set} with R^2 = 0.9997).[18]

$^1H\{^{31}P\}$ spectra were recorded in 32k data points, spectral width 7000 Hz, pre-acquisition delay 3 s, 30° pulse (duration 2 μs), digital resolution 0.2 Hz point^{-1}, over 32 transients. The GARP-sequence was used for ^{31}P decoupling. Prior to recording variable temperature and variable concentration spectra, T_1 relaxation times were measured using the inversion-recovery experiment with proton broad-band decoupling. $^{13}C\{^1H\}$ spectra were recorded in 64k data points, spectral width 30 300 Hz, pre-acquisition delay 1.2 s, acquisition time 1.1 s, 25° pulse (duration 2 μs), digital resolution 0.46 Hz point^{-1}, over between 512–2000 transients. The time period for each transient was approximately 3 times the T_1 measured.

$^{31}P\{^1H\}$ spectra were recorded in 32k data points, spectral width 40 650 Hz, pre-acquisition delay 5 s, 30° pulse (duration 3.3 μs), digital resolution 1.24 Hz point^{-1}, over 32 transients. ^{1}H decoupling was achieved using a Waltz-16 sequence. All FIDs were processed using either XWIN-NMR (version 2.1) or 1D WIN-NMR (version 6.0).

NMR analyses—$^{13}C\{^1H\}$-NMR simulation

Prior to importing data to gNMR (version 4.0, Cherwell Scientific, Oxford, UK, 1997 for PC) for exchange analysis, FIDs were processed in 1D WIN-NMR. An exponential window function with a line broadening of 1 Hz and zero filling to 128k data points were performed before Fourier transformation (digital resolution 0.23 Hz point^{-1}). Resultant spectra were converted in gNMR and regions selected, smoothed and baseline corrected as appropriate.

The input for the exchange calculations included two ^{13}C and one ^{31}P chemical shifts (numbered 1–1, 1–2, 1–3, respectively), two ^{13}C–^{31}P coupling constants and the concentration. The coupling constants and the concentration were fixed and the chemical shifts were allowed to vary during the iterative fitting of calculated to experimental spectra. The rate constants (k) were pre-calculated from the experimental spectra using: $\Delta\nu = k/\pi$ in the slow exchange regime, $\Delta\nu = \pi(\delta\nu)/2^{1/2}$ at coalescence, $\Delta\nu = \pi(\delta\nu)^2/2k$ in the fast exchange regime, with $\Delta\nu$ the line-width at half height and $\delta\nu$ the chemical shift difference at slow exchange.[19] A pseudo-first-order rate was calculated and included as a variable, together with the exchange description (1–1 ⟶ 1–2, 1–2 ⟶ 1–1, 1–3 ⟶ 1–3). An iterative full line-shape analysis was performed.

The validity of the simulated rates was checked with the error analysis of the program and taken into account only if all singular values were comparable in magnitude (within a factor of 100). The current version of gNMR did not allow the determination of the error on the rates obtained after the simulation. A prototype version of gNMR (version 5) was used to obtain errors for the pseudo-first-order rates, these were *ca.* +/−1 mol L^{-1} s^{-1}.[20]

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