Carbonyl Phosphonylation *via* [1^N,3^E]-Bifunctional Reagents. Probing Mechanistic and Reactivity Features through Chemical and Isotopic Labelling

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A range of organophosphorus(III) esters of the general form {DIAM}PX(SiR_3)$_n$ {X = O, n = 1; X = N, n = 2; R_3 = Me_3, Ph_3, $^tBuMe_2$, Et_3; DIAM = *N,N'*-$(CH_2NMe)_2$ and *N,N'*-$CH_2(CH_2NMe)_2$} has been prepared *via* reaction of {DIAM}PCl with R_3SiOH or $LiN(SiMe_3)_2$ respectively. These esters will phosphonylate aldehydes *via* the Abramov reaction to afford α-siloxyphosphonate esters cleanly and in high yields. The mechanism of the Abramov reaction using {DIAM}$POSiR_3$ reagents has been investigated by (i) ^{18}O isotopic labelling experiments which reveal that reaction proceeds with exclusive [O–Si] rather than [P–O] bond cleavage which, in turn, supports a mechanism with overall retention of configuration at phosphorus, (ii) double crossover experiments which support intramolecular silyl-group transfer and (iii) manipulations of the electron-donating properties of the carbonyl substrate which suggest that [P–C] bond formation is rate determining. Further tuning of the phosphonylation reaction is possible by manipulating (a) the nature of the phosphorus-coordinated donor atoms in the chelate ring, (b) the size and rigidity of the chelate ring, (c) the ester residue donor atom X and (d) the silicon substituents R.

Organic and metallo-organic synthetic methodology is replete with heterolytic (1,*n*)-bifunctional reagents of the generic form shown in Fig. 1.

Many of the most familiar and useful reagents are of the (1^E,2^N) type[1] M–X in which the metal/metalloid M fulfils the role of electrophile, *E* and the donor atom X, which is invariably a main-group atom, acts as the nucleophile, *N* (n = 0 in Fig. 1).[2] The many 1,3-dipolar reagents used in organic chemistry[3] ($^-$a–b$^+$=c) also belong to this group where nucleophilic and electrophilic moieties are directly connected. The subsequent reactivity of these reagents is intimately related to a synergy between nucleophilic and electrophilic termini, *i.e.* the more electropositive the metal M, then the more nucleophilic the coordinated ligand. A good example of this is the relative reactivity preferences of low and high oxidation-state metal carbene complexes where the former contain formally electrophilic carbene carbon atoms (a [1^N,2^E] system) and the latter formally nucleophilic carbon atoms (a [1^E,2^N] system).[4] (1^E,n^N)-Reagents where n > 2 (Fig. 1) are somewhat less common but nonetheless some highly desirable and versatile synthetic reagents are of this type, silyl enol ethers, metal enolates and σ-allyl complexes (Fig. 1). As with (1^E,2^N)-reagents, reactivity is frequently influenced by the degree of electronic interaction between the two disparate termini, mediated by the intervening spacer group $(S)_n$. Consequently, a very attractive feature of polyfunctional systems such as these is the potential for *multiple contact sites* between a substrate and the reagent. Since the presence of multiple interaction sites is intimately related to the activity and selectivity of many enzyme systems, it is envisaged that by incorporating such enzymic features within much simpler polyfunctional reagents we may be able to exploit both increased reactivity and selectivity in a wider range of reactions.

We have recently initiated a programme of research[5] to develop new, novel main-group and transition metal multi-functional reagents for use in stoichiometric and catalytic organic and metallo-organic syntheses and here report our studies on a class of novel (1^N,3^E)-bifunctional organophosphorus(III) reagents containing the P–X–Si group (X = O, N; Fig. 1), in which the phosphorus atom acts as the nucleophile, the silicon atom acts as the electrophile and the spacer atom X permits electronic transmission between the two termini (since the phosphorus atom has a higher atomic number and hence a higher priority than silicon we classify the nucleophilic terminus as being at position 1). These compounds are excellent reagents for the phosphonylation of prochiral carbonyl substrates through the Abramov reaction (Scheme 1).[6,7]

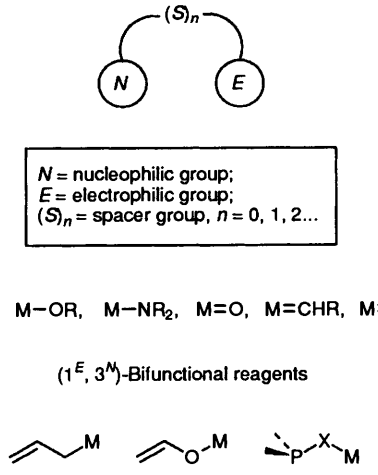
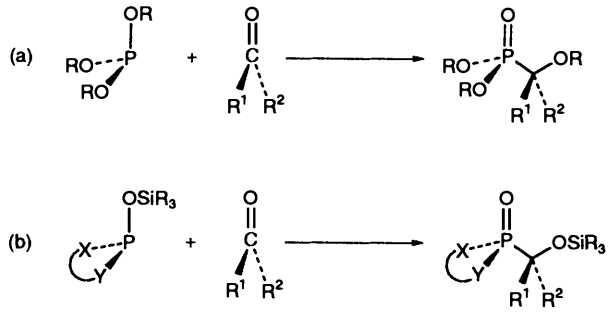


Fig. 1 Examples of (1,*n*)-bifunctional reagents in organic and organometallic synthesis.[1] The nomenclature (1^E,n^N) represents an electrophilic atom at position 1 and a nucleophilic group at position n with respect to the electrophilic atom. The numbering reflects increasing priority order with increasing atomic number. M = main-group or transition metal, R = alkyl, aryl, hydrogen.

The products of the Abramov reaction, α-functionalised phosphonate esters, are highly desirable compounds: they possess a molecular architecture which has been shown to lead to desirable physiological properties such as antibiotics,[8] antiviral properties which have found use in, for example, the treatment of HIV[9] and to the effective modelling of metabolically sensitive biomolecules.[10] Moreover, phosphono isosteres of phosphate biomolecules often differ in biocompatibility from the original phosphate substrates because of (i) differences in the pK_a-values of the parent phosphoric acid and phosphonic acid mimic and (ii) differences in binding abilities due to the replacement of a donor esteric oxygen atom by an isoelectronic but non-donor methylene group. The former

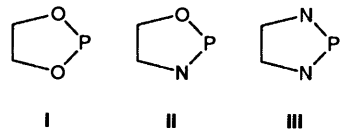


Scheme 1 The Abramov phosphonylation of carbonyls *via* (a) alkylated and (b) silylated organophosphorus(III) esters

problem has been addressed by the incorporation of fluorine atoms in the phosphono methylene group[11] whereas the latter problem may be investigated by the inclusion of donor functionalities such as hydroxo or amino groups coordinated to the α-carbon atom of the phosphono group.[12] It is this latter problem of the binding abilities of phosphonates which makes the Abramov reaction so attractive since it offers a clean, mild and controllable synthetic method for the direct inclusion of either hydroxy or amino functionalities into the α-carbon atom of phosphonic acid derivatives. Furthermore, since it has been shown that the stereochemistry at the functionalised α-carbon atom can radically affect the ability of phosphonic acid analogues of adenosine monophosphate to act as substrates for various kinases,[13] the development of an asymmetric variant of the Abramov reaction would be highly desirable.

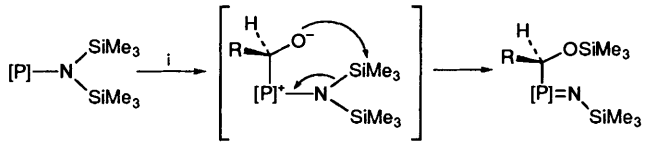
We have recently reported the first example of an asymmetric variant of the Abramov reaction using chiral (1^N,3^E)-bifunctional organophosphorus(III) reagents.[14] This forms the basis of a highly effective methodology for asymmetric phosphonylation as a means of introducing the phosphono [$(RO)_2P(=O)$] moiety into a given environment with control over stereochemistry at the newly created stereogenic carbon and phosphorus centres (Scheme 1b, wherein XY is a chelating chiral auxiliary). Since the objectives of our work are directed towards optimising reactivity and stereoselectivity, we need to consider both the *relative philicities* and *accessibilities* of the nucleophilic (phosphorus) and electrophilic (silicon) functions. We have focussed on the use of chiral auxiliaries as the source of stereoselectivity which can be coordinated to either the nucleophilic or electrophilic function. The former binding site was initially considered more attractive for stoichiometric phosphonylation systems since, being closer to the developing stereogenic centres, it was envisaged that higher stereoselectivities would result.

Previously, we have investigated systems containing chiral auxiliaries with widely differing geometrical profiles such as (+)-dimethyl-L-tartrate,[15] (*rac*)-binaphthol[16] and (1*R*,2*S*)-ephedrine[14,17] where it was observed that amino alcohol auxiliaries promoted Abramov phosphonylation better than did diol auxiliaries. One possible explanation for this trend in reactivity suggests a greater degree of lone pair–lone pair interaction between phosphorus and the α-heteroatoms in the oxazaphospholidine system **II** than in the dioxaphospholidine system **I**. An alternative explanation recognises that the less electronegative amido substituents on phosphorus encourage the phosphorus lone pair to occupy an orbital comprising a greater degree of p-character, which results in the lone pair being (i) more polarisable, and (ii) of a higher valence orbital energy and hence more readily oxidised, as required in the Abramov reaction which is a redox process. Consequently, we reasoned that the chelating diamido ligands in diazaphospholidine systems **III** should result in even greater enhancement of reactivity in Abramov-type phosphonylation reactions.



I **II** **III**

Moreover, previous studies have focused almost exclusively upon systems containing a siloxy ester function (-$OSiR_3$): we envisaged that replacement of this substituent with an isoelectronic but more electron-releasing, and hence activating, bis(trimethylsilyl)amido group [-$N(SiMe_3)_2$] may result in further reactivity enhancement towards the Abramov reaction where the product would now be an imidophosphonate ester (Scheme 2).



Scheme 2 *Reagent:* i, RCHO

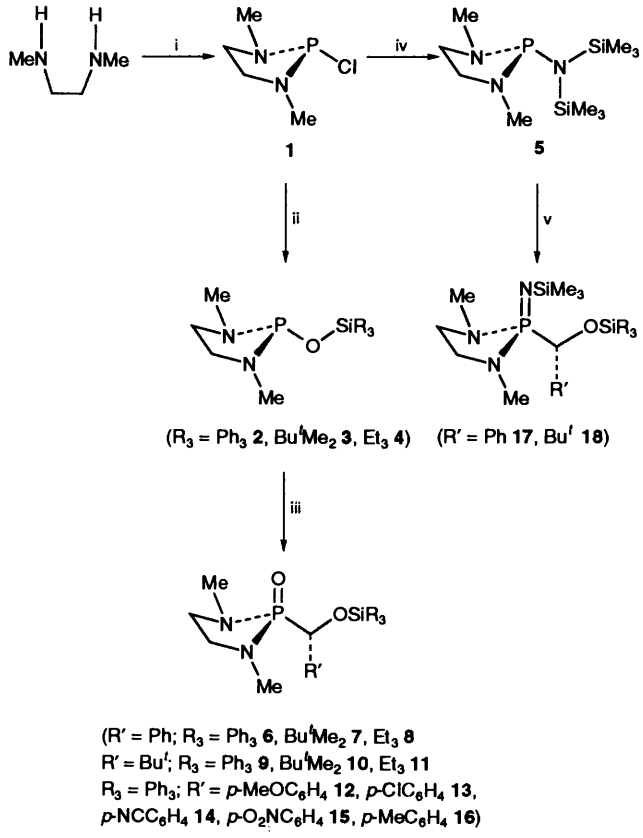
In this paper, we focus on systems which permit an assessment to be made of how modifications at specific sites in both the organophosphorus reagent and the carbonyl substrate affect the phosphonylation reaction and how these modifications can provide information on the mechanism of the Abramov reaction.

Results and Discussion

Syntheses of {*DIAM*}*P-X* {*DIAM* = N,N′-(CH_2NMe)$_2$, N,N′-CH_2(CH_2NMe)$_2$; *X* = *Cl*, *OSiR*$_3$, *N*($SiMe_3$)$_2$}.—Treatment of PCl_3 with an equimolar quantity of $(CH_2NHMe)_2$ as shown in Scheme 3 afforded the previously reported[18] 2-chloro-1,3,2-diazaphospholidine {*N*,*N*′-$(CH_2NMe)_2$}PCl **1** as a liquid in good yield. Spectroscopic and mass spectral data are consistent with a monomeric formulation as shown in Scheme 3. Interestingly, if the configuration of the phosphorus atom is fixed as shown, then the methylene hydrogens would reveal themselves as the A and B parts of a complex AA′BB′X spin system in the ^1H NMR spectrum. However, this is not observed in practice: all four methylene hydrogens are equivalent, implying an averaging process possibly as a result of rapid halide-atom exchange and/or inversion at nitrogen.

Compound **1** is less sensitive to moisture than is either {*O*,*O*-dimethyl-L-tartrato}PCl[15] or {(1*R*,2*S*)-ephedrine}PCl,[17] remaining unchanged after exposure to moist air in $CDCl_3$ solution for over 48 h at room temperature. This presumably reflects the higher energy of P–N σ* orbitals over P–O σ* orbitals due to the higher valence orbital energies of the 2p atomic orbitals of nitrogen over oxygen, which should render the phosphorus atom less susceptible to nucleophilic attack in diazaphospholidine systems than in oxaza- and dioxa-phospholidines. However, treatment of compound **1** with one molar equivalent of water and NEt_3 in toluene solvent did result in hydrolysis.

The 2-triorganosiloxy-1,3,2-diazaphospholidines (phosphorodiamidites) {*N*,*N*′-$(CH_2NMe)_2$}$POSiR_3$ are readily synthesized *via* treatment of chloride **1** with a stoichiometric quantity of R_3SiOH and NEt_3 (2 mol equiv.) in toluene in a similar strategy to that used to prepare other species (XY)-$POSiR_3$.[14–17] The compounds {*N*,*N*′-$(CH_2NMe)_2$}$POSiR_3$, (R_3 = Ph_3 **2**, Bu^tMe_2 **3**, Et_3 **4**) are isolated as crystalline solids (**2**) or liquids (**3** and **4**) in good yield as shown in Scheme 3. NMR spectroscopy reveals that the configuration at phosphorus is not inverting rapidly on the NMR timescale since

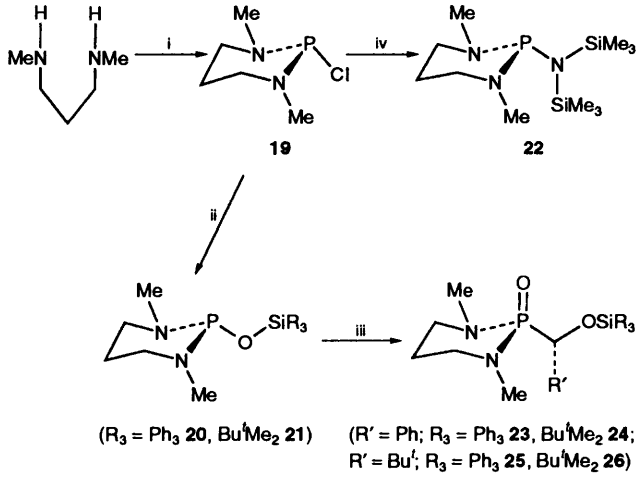


Scheme 3 *Reagents and conditions:* i, PCl_3, NEt_3 (2 mol equiv.), toluene, −78 °C; then 5 h at 25 °C; ii, R_3SiOH, NEt_3 (2 mol equiv.), toluene, 0 °C; then 25 °C for *ca.* 2–4 h; iii, R'CHO (1 mol equiv.), CH_2Cl_2, 25 °C, 1–24 h; iv, $LiN(SiMe_3)_2$, THF, −78 °C; then 1 h at 25 °C; v, R'CHO (1 mol equiv.), pentane, 25 °C

the methylene hydrogens are observed as the A and B parts of a complex AA'BB'X spin system in their ^1H NMR spectra. This result is comparable to that obtained in the corresponding ephedrine system where it was shown that 2-triorganosiloxy-1,3,2-oxazaphospholidines do not undergo any detectable configurational change at phosphorus on the NMR timescale up to 373 K (C_7D_8) but do exchange slowly on the chemical timescale.[17] In a similar manner, variable-temperature $^1H\{^{31}P\}$ NMR studies on compound **2** reveal that inversion of configuration at phosphorus is not significant on the NMR timescale up to 373 K (C_7D_8) since the complex AA'BB' pattern of the methylene hydrogens persists at this temperature. Mass spectrometry suggests products **2–4** to be monomeric as found also for other $\{XY\}POSiR_3$ systems, and high-resolution measurements confirm the expected composition of the parent ion.[14–17]

The novel phosphorus triamide **5**, $\{N,N'\text{-}(CH_2NMe)_2\}PN(SiMe_3)_2$, is isolated in high yield as a yellow liquid as shown in Scheme 3.[19] Spectroscopic and mass spectral data are fully consistent with the composition shown. As found for all $(XY)POSiR_3$ compounds, the configuration at phosphorus is stable on the NMR timescale, with no evidence for inversion up to at least 100 °C (C_7D_8) by $^1H\{^{31}P\}$ NMR spectroscopy. Surprisingly, the $^{31}P\{^1H\}$ NMR resonance for compound **5** is broad at ambient temperature ($\Delta_{1/2}$ 105 Hz at 298 K in C_7D_8) but sharpens significantly upon lowering the temperature ($\Delta_{1/2}$ 16 at 213 K in C_7D_8). This behaviour is characteristic[20] of quadrupolar broadening as a result of the phosphorus atom coupling to an ^{14}N nucleus which is not relaxing sufficiently fast enough to result in complete decoupling and, since we observe this effect only when the $[N(SiMe_3)_2]$ group is present, it is presumably this nitrogen atom that is primarily responsible. Unfortunately, heating of a solution of compound **5** (C_7D_8) to 373 K does not slow quadrupolar relaxation of ^{14}N sufficiently for $^1J_{PN}$ coupling to be resolved.

The compound $\{N,N'\text{-}CH_2(CH_2NMe)_2\}PCl$ **19** is isolated as a liquid as outlined in Scheme 4. Like compound **1**, an



Scheme 4 *Reagents and conditions:* i, PCl_3, NEt_3 (2 mol equiv.), toluene, −78 °C; then 4.5 h at 25 °C; ii, R_3SiOH, NEt_3, toluene, 0 °C; then 25 °C for *ca.* 2–3 h; iii, R'CHO (1 mol equiv.), CH_2Cl_2, 25 °C; iv, $LiN(SiMe_3)_2$, THF, −78 °C; then 1 h at 25 °C

averaging of configuration at phosphorus is implied by the observation of a single pentet resonance for the $\{N,N'\text{-}CH_2(CH_2NMe)_2\}PCl$ hydrogens of compound **19** instead of the ABCC'DD' pattern expected for a configurationally rigid geometry. Compound **19** is converted in high yield into the silylated phosphites $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiR_3$ (R_3 = Ph_3 **20**, Bu^tMe_2 **21**) by reaction with R_3SiOH in the presence of NEt_3 (Scheme 4) whilst treatment with $LiN(SiMe_3)_2$ in tetrahydrofuran (THF) solvent affords $\{N,N'\text{-}CH_2(CH_2NMe)_2\}PN(SiMe_3)_2$ **22**. Spectroscopic data for compounds **19–22** are consistent with their composition.

Reactions of $\{DIAM\}P\text{-}X$ *with Carbonyls* $\{DIAM$ = N,N'-$(CH_2NMe)_2$, N,N,'-$CH_2(CH_2NMe)_2$; $X = OSiR_3$, $N(SiMe_3)_2\}$.—Compounds **2–5** react readily at room temperature with aldehydes such as benzaldehyde and pivalaldehyde to afford racemic α-siloxyphosphonate esters in good yields (see Experimental section and Scheme 3).

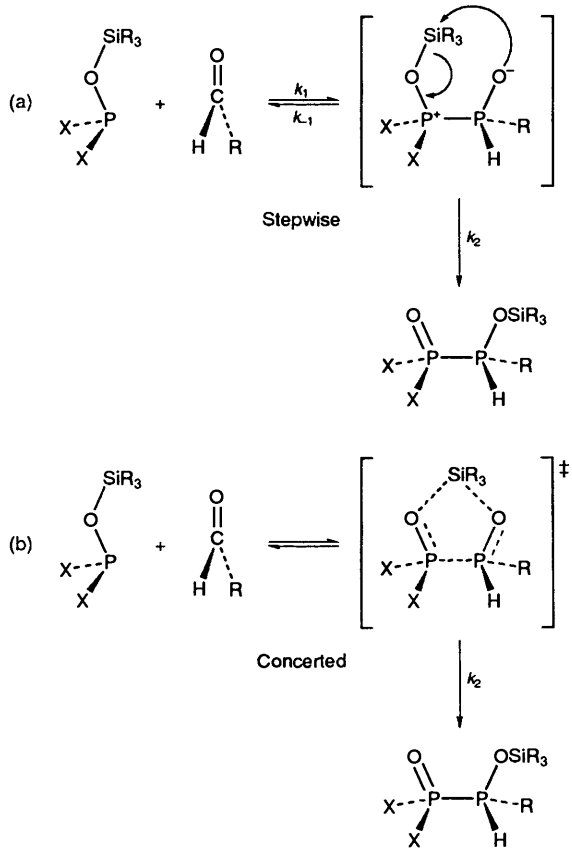
The phosphonate esters **6–16** have been characterised by standard spectroscopic techniques. Solution relative-molecular-mass measurements confirm the monomeric nature of these species and we presume that all other esters will be similarly monomeric. Especially diagnostic of four-coordinate organophosphorus(v) esters is the significantly lower frequency resonance of the ^{31}P nucleus (δ ~ 20–40 ppm) compared with those found in the three-coordinate organophosphorus(III) esters **1–5** (generally δ > 100 ppm).[21] Moreover, the formation of a direct P–C bond in the Abramov reaction is confirmed by the observation of large $^1J_{PC}$ coupling in the $^{13}C\{^1H\}$ NMR spectra of all the esters (within the range 138–160 Hz).[17]

The phosphorotriamidite compound **5** also reacts readily with benzaldehyde and pivaldehyde *via* an Abramov-type reaction to afford the imidophosphonate esters **17** and **18**. Both compounds have been characterised by using spectroscopic techniques and particularly characteristic is the large $^1J_{PC}$ coupling observed for the newly created P–C bonds, 147.2 and 155.5 Hz respectively. Phosphoramidites are currently used extensively in the synthesis of nucleotides[22] and the Abramov reaction reported here represents a new type of reaction mode

for phosphoramidites which may offer a route into a different class of organophosphorus biomolecules.

In a similar manner to compounds **2–5**, compounds **20** and **21** containing the six-membered diamine chelate ring phosphonylate both benzaldehyde and pivaldehyde cleanly to afford the corresponding phosphonate esters **23–26**. Spectroscopic data are consistent with the structures illustrated in Scheme 4.

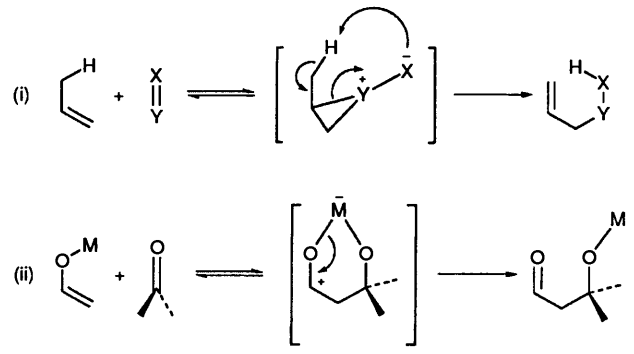
Mechanistic Features of the Abramov Reaction.—The Abramov reaction has long been used in organic synthesis, principally by Russian and Japanese workers.[23] However, when we initiated our studies in early 1992 it was somewhat surprising to find that no asymmetric variants of this phosphonylation reaction existed, especially given its demonstrated ability to generate stereogenic centres in physiologically and biologically relevant organophosphorus architectures. Since our interests are focussed on optimising both reactivity and selectivity in asymmetric phosphonylation reactions, the mechanism of reaction is of prime concern. Evans *et al.* have provided a reasonable mechanistic framework (Scheme 5).[24a]



Scheme 5 Proposed (a) stepwise and (b) concerted mechanisms for the Abramov reaction[24]

Although these workers did not distinguish experimentally between stepwise (Scheme 5a) and concerted (Scheme 5b) processes, they clearly favoured the stepwise process by analogy to the stepwise reaction of $(MeO)_3P$ with aldehydes in the presence of Me_3SiCl.[24a] Moreover, recent studies of the reactions of trialkylphosphines with aldehydes in the presence of hydrohalic acids also suggest a stepwise process.[24b] We are currently probing the question of formation of the intermediate but at the present time we favour stepwise process Scheme 5a as a working mechanism.

We notice the similarity between the stepwise Abramov transformation and some of the most versatile C–C bond-forming reactions in organic chemistry such as the stepwise Ene reaction [Scheme 6(i)], the Aldol condensation [Scheme 6(ii)], especially derivatives such as the Mukaiyama aldol reaction, and closely related reactions involving σ-allyl silanes, stannanes and transition metals.[25] Indeed, the Abramov reaction may be considered to be a phospho-Mukaiyama process. It is not unreasonable that these types of transformation are similar since the ene, metallo-enolate, metallo-σ-allyl and silyl phosphite reagents are each examples of (1,3)-bifunctional reagents containing both nucleophilic and electrophilic reactive functions.[1] A number of important points emerge from the Evans study;[24] (a) silyl-group transfer is an *intramolecular* process, (b) 1 : 1 adducts such as the betaine species shown in Scheme 5 are reasonable intermediates since precedent exists for the stability (*vide supra*)[24b,26] and (c) the small solvent dependence on the rate of reaction of $(MeO)_2POSiMe_3$ with CH_2=CHCHO suggests that the transition state has little charge separation.

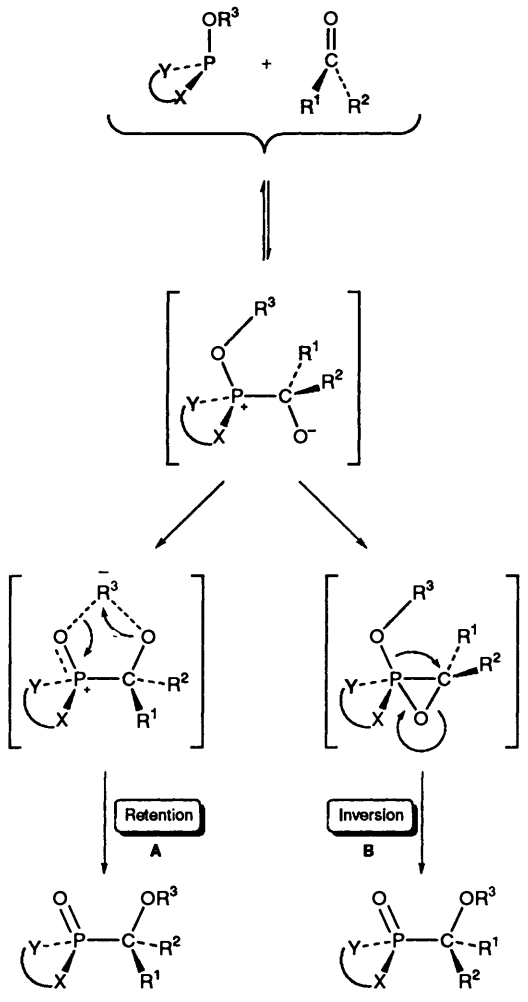


Scheme 6 Common analogues of the Abramov reaction. (i) the Ene reaction; (ii) the Aldol reaction.

We have demonstrated that intramolecular silyl-group transfer is also the case in the diamine systems reported here. Thus, when a mixture of $\{N,N'\text{-}(CH_2NMe)_2\}POSiPh_3$ and $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiBu^tMe_2$ is treated with PhCHO at room temperature in toluene (containing NEt_3 to prevent any trace-acid-catalysed silyl-group scrambling), the only products observed are those resulting from intramolecular silyl-group transfer $\{N,N'\text{-}(CH_2NMe)_2\}P(O)CHPh(OSiPh_3)$ and $\{N,N'\text{-}CH_2(CH_2NMe)_2\}P(O)CHPh(OSiBu^tMe_2)$.

The Evans mechanism results in overall *retention* of configuration at phosphorus. This is an extremely valuable result, if true, for any study of asymmetric Abramov reactions since it permits assignments of configuration of either starting material or product if the configuration of one or the other is known. However, there is another mechanistic possibility to the stepwise Abramov reaction that is also consistent with Evans' findings yet is most likely to result in overall *inversion* of configuration at phosphorus. The two mechanisms are related and are illustrated in Scheme 7. The key intermediate in the alternative mechanism is an epoxy compound which ring opens *via* intramolecular migration of a OR^3 group to afford a product in which the phosphite oxygen atom and the carbonyl oxygen atom have exchanged sites. Epoxy compounds of this nature have been postulated as intermediates in the Perkow reaction[7a] and in the hydrolysis of phosphonoformate triesters.[27] The need to distinguish between the two possibilities led us to examine experiments which could differentiate an oxygen function on phosphorus (Evans mechanism, retention, **A**) from an oxygen function on carbon (alternative mechanism, inversion, **B**).

An intimate probe of the connectivity profile of any reaction involving [P–O] bond formation and/or cleavage exploits the isotopic shift in the ^{31}P NMR resonances of a [P–O] or [P=O] function upon labelling with ^{18}O. By specifically labelling (*) the oxygen atom of $\{N,N'\text{-}(CH_2NMe)_2\}POSiPh_3$ **2** with 10%



R^1, R^2 = alkyl, hydrogen; R^3 = alkyl, SiR_3

Scheme 7 Alternative mechanistic pathways in the Abramov reaction leading to overall retention or inversion of configuration at phosphorus

Table 1 Relative reactivity of $\{N,N'\text{-}(CH_2NMe)_2\}POSiPh_3$ **2** towards various *para*-substituted benzaldehydes in the Abramov reaction

Carbonyl	σ_X	Relative reactivity R^a
p-$O_2NC_6H_4CHO$	+0.78	100
p-NCC_6H_4CHO	+0.66	100
p-ClC_6H_4CHO	+0.23	71
p-MeC_6H_4CHO	−0.17	41
p-$MeOC_6H_4CHO$	−0.27	11

[a] Relative reactivities *R* refer to the percentage reaction in a 1 : 1 mixture of the organophosphorus ester and aldehyde (0.17 mmol scale) in toluene solvent (2 cm^3) after 30 min at 25 °C, as determined by ^{31}P NMR spectroscopy.

^{18}O as outlined in Scheme 3, using Ph_3SiO^*H prepared from Ph_3SiCl and H_2O^*, it is possible to differentiate between the ~90% ^{16}O isotopomer (δ 120.900 ppm) and the ~10% ^{18}O isotopomer (δ 120.854 ppm) by ^{31}P NMR spectroscopy ($CDCl_3$), the ^{18}O species having a slightly lower resonance frequency than the ^{16}O species (Fig. 2) by 7.5 Hz at 161.98 MHz.[27] If the isotopically labelled oxygen were not coordinated directly to phosphorus then no isotopic perturbation of the ^{31}P NMR resonance would be observed.[28]

Compound **2*** undergoes the Abramov reaction with both benzaldehyde and pivalaldehyde to afford $\{N,N'\text{-}(CH_2NMe)_2\}P(=O^*)CHPh(OSiPh_3)$ **6** and $\{N,N'\text{-}(CH_2NMe)_2\}P(=O^*)CHBu^t(OSiPh_3)$ **9** according to Scheme 3. For both compounds **6** and **9**, two ^{31}P resonances are observed; at δ 32.927 ppm and δ 32.880 ppm, corresponding to ^{16}O and ^{18}O of **6** and δ 34.800 ppm and δ 34.752 ppm for ^{16}O and ^{18}O of **9**, respectively (Fig. 2) where the isotopic label (*) has remained coordinated to phosphorus, implying that *the labelled siloxy oxygen atom in labelled compound* **2*** *is transformed into the oxo function in the product esters* **6** *and* **19**, consistent with the retention mechanism **A** in Scheme 7. Integration of the resonances for compound **9** reveals a ratio of ^{16}O : ^{18}O isotopomers of 91 : 9, suggesting that the label has been *completely* retained on phosphorus. This result is supported by high-resolution mass spectrometry (electron-impact mode) which confirms the presence of the label in both compounds **2** and **6**, locating the M^+ parent ion for [**2** − ^{18}O,^{28}Si] at *m*/*z* 393.142 227 (Calc. *m*/*z* 393.143 800) and the $[M - H]^+$ ion for [**6** − ^{18}O,^{16}O,^{28}Si] at δ 500.194 434 (calc. δ 500.193 490). However, since one of the major daughter ions formed from compound **6** is $[PhCHOSiPh_3]^+$ containing the siloxy group, the failure to observe any ^{18}O label (within 20 ppm mass deviation and < 1% relative abundance) in this fragment provides supporting evidence for complete retention of the oxygen label on the phosphorus atom. One further mechanistic possibility that may also be consistent with the observed results involves silyl- rather than siloxy-group transfer from an intermediate epoxy compound similar to that shown in Scheme 7. If this migration were to occur with retention of configuration at phosphorus we would not then be able to differentiate between this mechanism and the Evans-type mechanism on the basis of the ^{18}O-labelling studies reported here.

Retention of configuration at phosphorus *via* preferential N–Si rather than P–N cleavage has also been demonstrated in phosphonylation reactions involving the phosphorodiamidite $\{N,O\text{-}(1R,2S)\text{-ephedrine}\}PN(SiMe_3)_2$ by a combination of spectroscopic and X-ray diffraction experiments.[29]

Table 2 Relative reactivity of various organophosphorus(III) esters towards pivalaldehyde in the Abramov reaction

Organophosphorus(III) ester	Relative reactivity R^a
$\{N,N'\text{-}(CH_2NMe)_2\}POSiPh_3$ **2**	95
$\{N,N'\text{-}(CH_2NMe)_2\}POSiBu^tMe_2$ **3**	86
$\{N,N'\text{-}(CH_2NMe)_2\}POSiEt_3$ **4**	66
$\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiBu^tMe_2$ **21**	43
$\{N,N'\text{-}(CH_2NMe)_2\}PN(SiMe_3)_2$ **5**	37

[a] Relative reactivities *R* refer to the percentage reaction in a 1 : 10 mixture of the organophosphorus ester and aldehyde (0.17 mmol of ester) in toluene solvent (2 cm^3) after 10 min at 25 °C, as determined by ^{31}P NMR spectroscopy.

Assessing Relative Reactivity in the Abramov Reaction.—We originally envisaged that relative reactivity measurements could be obtained through competitive experiments whereby a solution containing *both* a reference compound and the reagent to be measured, in an equimolar ratio, is treated with a fixed molar quantity of aldehyde up to 0.5 molar equivalents of the total phosphorus concentration. However, this protocol was found to be unsuitable due to scrambling of the trialkylsilyl groups between the organophosphorus(III) reagents, which was found to occur on the timescale of this experiment in chlorocarbon solvents. Within 20 min of mixing a $CDCl_3$ solution of $\{N,N'\text{-}(CH_2NMe)_2\}POSiBu^tMe_2$ and $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiPh_3$, ^{31}P NMR spectroscopy revealed the presence of the expected crossover products $\{N,N'\text{-}(CH_2NMe)_2\}POSiPh_3$ and $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiBu^tMe_2$. This process has been examined in more detail and is discussed in a later section. Consequently, an experimental protocol involving a non-competitive procedure has been used

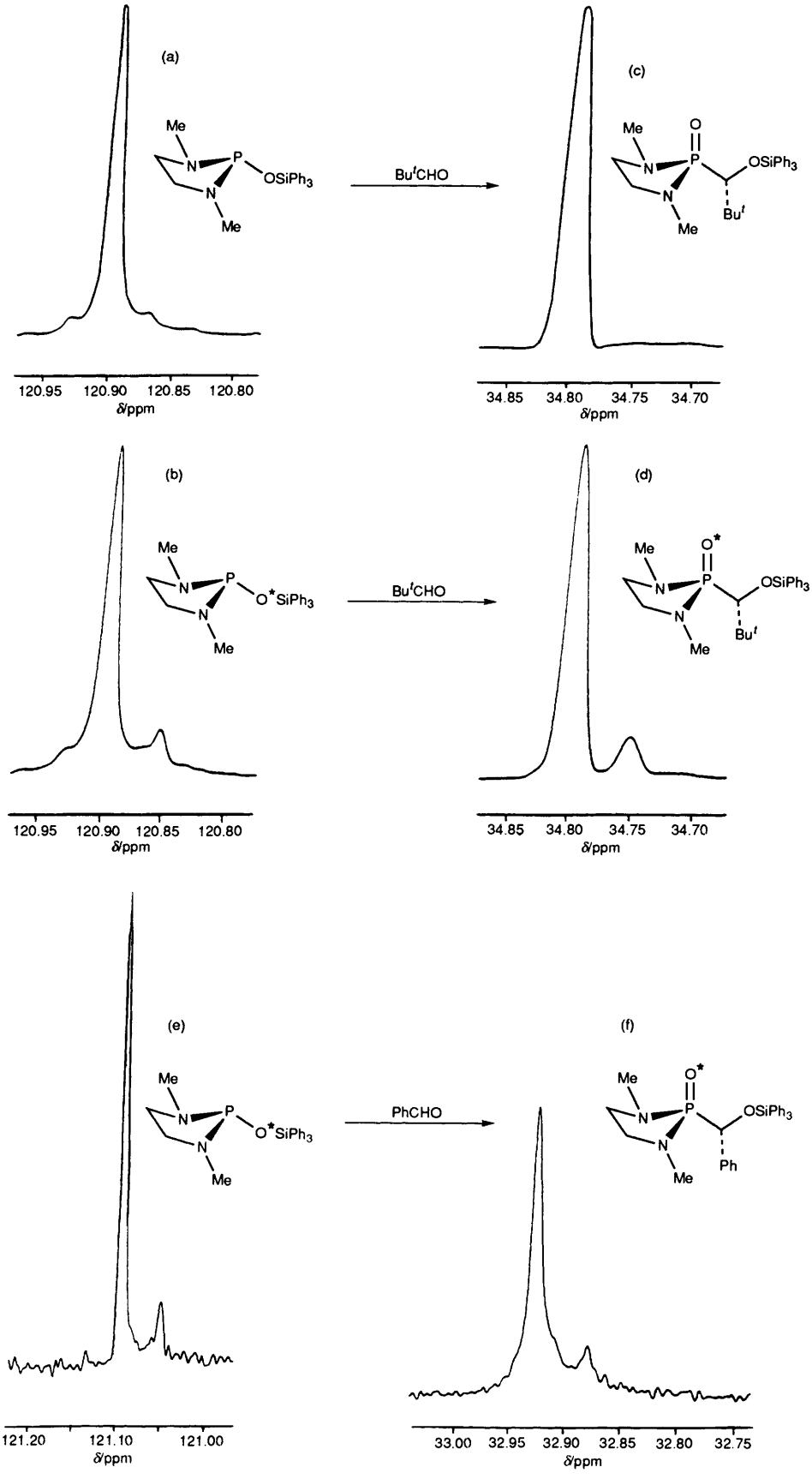


Fig. 2 ^{31}P NMR spectra (161.98 MHz) of (a) unlabelled **2**, (b) labelled **2**, (c) unlabelled **9**, (d) labelled **9**, (e) labelled **2** and (f) labelled **6**. For each labelled compound the ^{18}O isotopomer resonates to lower frequency. The label was purchased as H_2O^* with ^{18}O (10%) and ^{16}O (90%) (Aldrich). Spectra were collected at 233 K ($CDCl_3$ for **9**, C_7D_8 for **6**) to reduce line broadening from the coordinated ^{14}N nuclei. Slight line narrowing has been applied to each spectrum to improve resolution and appearance.

to provide an empirical measure of relative reactivities of various systems under specified conditions (see Experimental section). The data are reproduced in Tables 1 and 2.

Effect of the Carbonyl Substrate.—We have not performed an exhaustive survey of carbonyl-substrate reactivity but we find qualitatively that the reactivity of carbonyls towards silylated organophosphorus(III) esters follows the general order; aldehydes > ketones. The same relative order was observed by Evans.[24a] For aldehydes RCHO we find that the ease of phosphonylation is in the order R = Ph > R = Bu^t. Presumably, the relative reactivity order reflects both steric and electronic factors whereby the carbonyl carbon atom is both more readily accessible to the phosphorus nucleophile and more electrophilic when coordinated to smaller, less electron-donating substituents.[30a]

We have examined the reactivity of several other carbonyl substrates including cyclohexanone, cyclopentanone, pentan-3-one, benzophenone, acetophenone, *N*,*N*-dimethylformamide (DMF) and ethyl acetate with both $\{N,N'\text{-}(CH_2NMe)_2\}PN(SiMe_3)_2$ and $\{N,N'\text{-}CH_2(CH_2NMe)_2\}PN(SiMe_3)_2$ and find that reaction is extremely slow at room temperature and/or leads to several products by ^{31}P NMR spectroscopy, none of which was isolated.

In order to obtain further information on the mechanism of the Abramov phosphonylation, we have investigated the relative reactivities of a representative organophosphorus ester $\{N,N'\text{-}(CH_2NMe)_2\}POSiPh_3$ with a series of *para*-substituted aldehydes XC_6H_4CHO where X is defined by the entries in Table 1. The observation that reaction rates increase dramatically as X becomes more electron-withdrawing (an approximate *ten-fold increase* in rate on going from *p*-methoxybenzaldehyde to *p*-cyano- and *p*-nitro-benzaldehyde) suggests that there is significantly greater [P–C] bond formation in the rate-determining transition state than [O–Si] bond formation.[30b]

Effect of the Silicon Substituents.—Compared with the effects of substituents in the carbonyl residue upon reactivity, changes of substituent at silicon (Table 2) have a slightly smaller influence upon the rate [~1.5-fold rate increase upon going from $SiEt_3$ to $SiPh_3$ (Table 2) whereas a ~10-fold rate increase upon going from *p*-$MeOC_6H_4CHO$ to *p*-$O_2NC_6H_4CHO$ (Table 1)]. We envisage that both steric and electronic properties are important in the relative reactivities of Table 2, controlling both the Lewis acidity of silicon to form a five-membered transition state (Scheme 5) and the facility of pseudorotation in the transition state to afford silyl-group transfer.

Effect of the Phosphorus-coordinated Donor Atoms.—General observations suggest that a nitrogen-rich phosphorus atom coordination sphere results in a more reactive phosphonylating organophosphorus(III) ester than an oxygen-rich phosphorus atom coordination sphere. Indeed, this is supported by the observation that qualitative reactivity of systems of the form $(XY)POSiR_3$ towards aldehydes, where (XY) is either a dioxophospholidine, oxazaphospholidine or diazaphospholidine ring (**I**, **II**, **III** respectively in Fig. 2), decreases in the order **III** ≈ **III** > **I**. Electronically this trend seems reasonable since coordination of phosphorus by less electronegative nitrogen atoms results in the phosphorus lone-pair being more likely to occupy an orbital comprising a greater degree of p-character. This, in turn, results in the lone pair having a higher energy, being more polarisable and presumably more available energetically to an electrophilic reagent. Subsequently, moving to a more nitrogen-substituted coordination sphere by replacing $-OSiR_3$ with the isoelectronic and isolobal[31] $-N(SiMe_3)_2$ function results in a far less pronounced reactivity change than that resulting from changes in the electronic properties of *para*-substituted benzaldehydes above. It was surprising to find that, with pivalaldehyde as substrate, the data in Table 2 suggest that the $-N(SiMe_3)_2$ function is less reactive than the $-OSiR_3$ systems by a factor of approx. 2. We presume that two factors are in competition here, (i) electronic effects which tend to enhance the reactivity of $[P]\text{-}N(SiMe_3)_2$ over $[P]\text{-}OSiR_3$ systems and (ii) steric effects which tend to favour the reverse order of reactivity. Presumably, with pivalaldehyde, steric factors predominate.

Effect of the Size of the Phosphorus-coordinated Chelate Ring.—It has been generally observed that in organophosphorus(III) systems PX_3, the *basicity* of the phosphorus atom lone pair decreases as the phosphorus atom is constrained within a chelate ring.[32]

Our observations show some agreement with the general trend that *increased molecular constraint retards phosphonylating ability*. Thus, $\{O,O'\text{-dimethyl-L-tartrato}\}POSiR_3$ (R_3 = Ph_3, $^tBuMe_2$, Et_3) do not react with PhCHO in refluxing THF[15] and $\{O,O'\text{-binaphtholato}\}POSiR_3$ react only very slowly at 80 °C in toluene solvent[16] in contrast to the silylated organophosphorus(III) esters $(RO)_2POSiMe_3$ (R = Me, Et) which react smoothly with PhCHO over the course of 24 h at room temperature.[24a] Even the phosphoramidite system $\{O,O'\text{-binaphtholato}\}PN(SiMe_3)_2$ does not phosphonylate pivaldehyde at room temperature over at least 18 h.[33]

However, within the closely related series of esters $\{DIAM\}PX[SiR_3]_n$ the derivative containing the six-membered chelate ring $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiBu^tMe_2$ shows *reduced reactivity* compared with the analogue with the five-membered chelate ring by a factor of approx. 2 in their reactions with pivalaldehyde (Table 2). Whilst we do not know whether this order will apply to other aldehydes or to other silyl derivatives, it does indicate that care should be exercised when trying to extrapolate thermodynamic trends to kinetically controlled processes. At the present time we are not able to map the influence of chelate ring size on the Abramov reaction but since it is necessary for the phosphorus atom to undergo major rehybridisation during the reaction, it seems probable that a ground-state phosphorus atom coordination sphere that more closely approximates that of the rate-determining transition state will have the greater reactivity.

Investigation of Silyl-group Exchange in $\{DIAM\}POSiR_3$ systems by the Combination of Isotopic Labelling (*) and Crossover Experiments.—As mentioned above, it appears likely that silyl-group exchange in $\{DIAM\}POSiR_3$ systems is *acid catalysed* since, when a $CDCl_3$ solution containing an equimolar mixture of $\{N,N'\text{-}(CH_2NMe)_2\}POSiBu^tMe_2$ and $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiPh_3$ is treated with NEt_3 prior to mixing, the exchange is inhibited significantly. Moreover, we have found that the cleanliness of exchange is dependent upon the history of the chlorinated solvent used; presumably if too much acidic impurity is present, further reaction may ensue.

We have examined this exchange process further by combining the above crossover experiment with ^{18}O (*) isotopic labelling (10% enrichment). Thus, upon mixing of equimolar quantities of $\{N,N'\text{-}(CH_2NMe)_2\}P^*OSiPh_3$ and $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiBu^tMe_2$, at room temperature in CH_2Cl_2 solvent, the crossover products $\{N,N'\text{-}(CH_2NMe)_2\}P^*OSiBu^tMe_2$ and $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiPh_3$ revealed that the label had been retained completely in the five-membered ring diamine systems and had not been scrambled into the six-membered diamines (Fig. 3) This observation is more supportive of an exchange of *silyl* functions [SiR_3] rather than an exchange of *siloxy* functions [$OSiR_3$], possibly *via* a process such as that illustrated in Scheme 8.

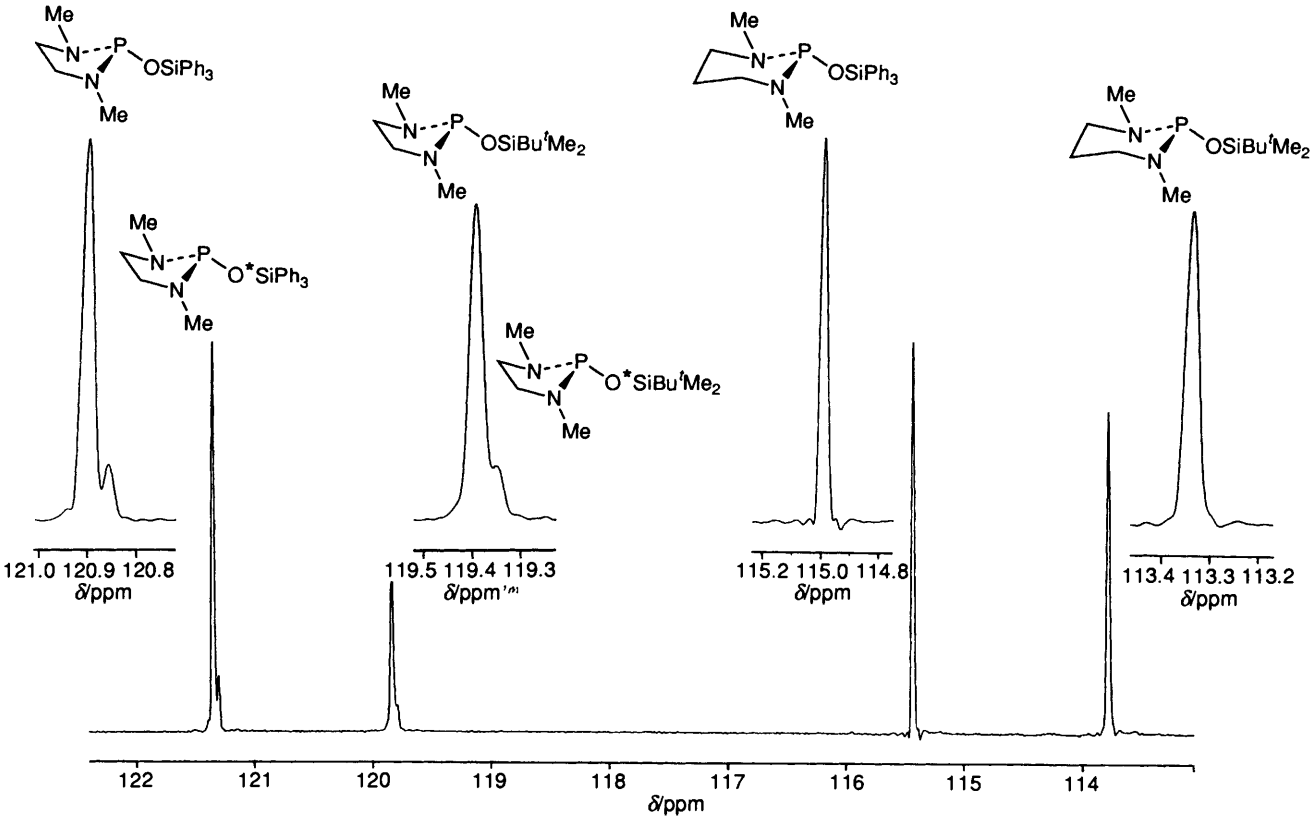


Fig. 3 ^{31}P NMR spectra (161.98 MHz; CH_2Cl_2) of $\{N,N'\text{-}(CH_2NMe)_2\}P(*O)SiPh_3$ (0.5 mmol) and $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiBu^tMe_2$ after 5 days at room temperature. For those compounds with ^{18}O isotopomers, the labelled isotopomer resonates to lower frequency by ~7 Hz. Spectra were collected at 233 K to reduce line broadening from the coordinated ^{14}N nuclei.

The process illustrated in Scheme 8 would involve the intermediacy of $[R_3Si]^+$ and the H-phosphonate esters $\{N,N'\text{-}(CH_2NMe)_2\}P(=O^*)H$ and $\{N,N'\text{-}CH_2(CH_2NMe)_2\}P(=O)H$. Since we do not observe any significant quantities of either of the latter species by ^{31}P NMR spectroscopy, we presume that they are formed in only small amounts (as expected since only trace acid is likely to be present) and silylated rapidly under the conditions of exchange. To test this proposal, equimolar amounts of $\{N,N'\text{-}(CH_2NMe)_2\}POSiPh_3$ and $\{N,N'\text{-}CH_2(CH_2NMe)_2\}P(=O)H$ were mixed in $CDCl_3$ solvent and examined by ^{31}P NMR spectroscopy after 2 days at room temperature. Two new species were observed in the reaction mixture and have been assigned as $\{N,N'\text{-}(CH_2NMe)_2\}P(=O)H$ (δ 19.9) and $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiPh_3$ (δ 115.7), respectively, by comparison with authentic samples. The intermediacy of H-phosphonate esters in silyl group exchange is therefore plausible.

The above results allow us to compose a picture of silyl-group exchange in $\{DIAM\}POSiR_3$ systems in which exchange (i) is acid catalysed, (ii) proceeds with complete retention of isotopically labelled oxygen which, in turn, suggests that (iii) H-phosphonate esters are present as intermediates and (iv) reaction proceeds *via* exclusive O–Si rather than P–O cleavage so that the exchange is indeed of silyl groups rather than siloxy groups.

Conclusions.—(1,3)-Bifunctional organophosphorus(III) esters are excellent reagents for the phosphonylation of aldehydes. They combine within a single molecule the phosphorus (nucleophilic) atom and an intramolecular Lewis acid (electrophilic) site necessary for efficient phosphonylation *via* an Abramov-type reaction. From our studies and the work of others[7,23,24] we may highlight several features that have been shown, or surmised, to be important in influencing the course of the Abramov reaction:

(i) Reaction has been postulated to be stepwise with the intermediacy of a 1:1 adduct species such as that illustrated in Scheme 5.[24] Although not observed directly in the systems reported here, there is precedent for species of this form; related 1:1 betaine adducts have been isolated from reactions of hexamethylphosphorus triamide,[26] monosulfonated triphenylphosphine,[34] or tertiary phosphines[24b] with benzaldehyde in the presence of suitable trapping agents.

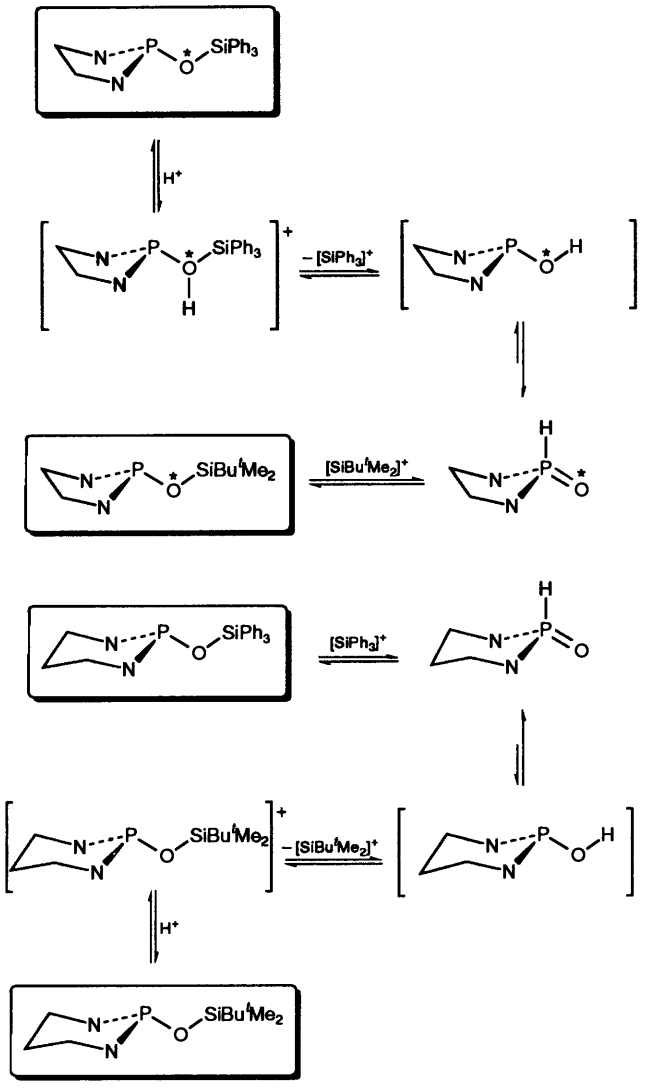
(ii) Reactivity of aldehydes in the Abramov reaction appears to decrease as the carbonyl substituents become more sterically demanding and/or electron releasing (Table 1). The most reactive carbonyls should be those with the most accessible and most electrophilic carbon atom.

(iii) Within organophosphorus(III) esters of the form (XY)P-Z-M, reactivity is a function of the nature of X, Y and Z, generally being greater for X, Y, Z = N over X, Y, Z = O. With pivalaldehyde as substrate, reactivity increases in the order M = $SiPh_3$ > $SiBu^tMe_2$ > $SiEt_3$, whereas systems with five-membered chelate diamine rings are ~twice as reactive as those with six-membered diamine chelate rings (for M = $SiBu^tMe_2$) when phosphonylating the same aldehyde.

(iv) The Abramov reaction involves *intramolecular transfer of the triorganosilyl group.*

(v) Isotopic labelling experiments show that the Abramov reaction proceeds with *complete O–Si rather than P–O bond cleavage* (Fig. 2).

(vi) *Reactivity increases as the phosphorus atom nucleophilicity increases, but decreases as steric congestion within the phosphorus coordination sphere increases.* Thus, within systems containing chelating auxiliaries derived from ephedrine, replacement of the NMe function with NPr^i results in a lowering



Scheme 8 Proposed mechanism for the scrambling of silyl-group functions in {DIAM}POSiR$_3$ systems. The methyl groups on the diamine ligands have been omitted to aid clarity. The asterisks represent ^{18}O labels.

of reactivity.[32] Therefore, in designing reagents for asymmetric phosphonylation, it is necessary to consider both the steric and electronic profile of the auxiliary used since both are important in controlling reactivity and selectivity.[35]

(vii) In the Abramov reaction, the P-O-M function is converted into a P=O function. Consequently, reactivity should increase as the percentage of phosphorus s-character in the P–O bond increases. This should be facilitated by arranging for the P-O-M moiety to approach linearity which, in turn, can be facilitated if M is a strongly *electropositive* function with π-acidic capacity. Thus, the substitution of a trialkysilyl function for a more electropositive main-group or transition metal species may be seen as one way to increase reactivity. Indeed, this has recently been shown to be the case by the excellent studies of Shibuya in Japan and Spilling in USA, which appeared during the course of our asymmetric phosphonylation programme, in which both titanium and lanthanum compounds were shown to catalyse the phosphonylation of aldehydes by secondary phosphites.[36] Moreover, these workers showed that incorporation of a chiral auxiliary within the metal coordination sphere resulted in asymmetric phosphonylation although the enantioselectivities were extremely variable and the active phosphonylating agents were not isolated.

(viii) Since during the course of the Abramov reaction the phosphorus atom undergoes an increase in both its formal oxidation state {(III) to (V)} and its coordination number (from 3 to 4) it may be envisaged that any factors designed to make these transformations occur more readily will increase reactivity. Formal oxidation of the phosphorus atom will be facilitated by having an electron-releasing coordination sphere and a high-energy lone pair of electrons {see point (vii) above}. The change in coordination number from 3 to 4 will be facilitated by arranging for the inter-substituent angles around phosphorus to be either highly flexible (such as when the phosphorus atom is not constrained in a chelate ring) or to resemble closely those angles favoured in a four-coordinate phosphonate ester. Since, in the absence of X-ray or electron-diffraction studies, it is difficult to quantify the structural information necessary it may be prudent to impose as few molecular constraints on the phosphorus atom as possible. Indeed, removing the constraining chelating ligand from phosphorus is a desirable strategy since a more preferable architecture for developing a catalytic asymmetric phosphonylation process may have the chiral auxiliary attached to the electrophilic terminus of the organophosphorus reagent.

We are currently pursuing the latter design strategy in more detail.

Experimental

All manipulations were performed as described previously.[17] Solvents were pre-dried over either sodium wire, calcium chloride or 4 Å molecular sieves before reflux and subsequent distillation from a suitable drying agent (in parentheses); pentane, THF (sodium benzophenone ketyl), toluene (sodium metal) and dichloromethane (calcium hydride). All solvents were deoxygenated before use. Elemental analyses and solution relative molecular-mass measurements were performed by the Microanalytical Laboratory of this department. Mass spectra were collected on a VG Autospec instrument in the electron-impact mode. IR spectra were recorded as either thin films or Nujol mulls between KBr windows using a Perkin-Elmer 257 grating spectrophotometer. NMR spectra were obtained on a JEOL FX90Q, JEOL FX100 and Bruker AM 400 instruments. Deuteriated solvents were dried by flash filtration on a column of basic alumina (Brockmann Grade I) and were deoxygenated before use. All spectra are reported at 298 K and referenced either to solvent resonances or $SiMe_4$ (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P) unless stated otherwise; all the ^{13}C and ^{31}P spectra were run under conditions of broad-band ^1H decoupling, unless noted otherwise. *J* Values are given in Hz. The ^{31}P NMR studies on the ^{18}O isotopomers of compounds **2**, **6** and **9** were performed at 161.98 MHz in either $CDCl_3$ or C_7D_8 at 233 K to prevent excessive line broadening due to coupling to the two quadrupolar ^{14}N nuclei. The compounds PCl_3, NEt_3, $(CH_2NHMe)_2$, R_3SiOH, $CH_2(CH_2NHMe)_2$, and carbonyl compounds were purchased from commercial sources and were either recrystallised (Ph_3SiOH), chromatographed on a short column of Brockmann Grade I basic alumina {liquid carbonyls, NEt_3, Bu^tMe_2SiOH, Et_3SiOH, $(CH_2NHMe)_2$, $CH_2(CH_2NHMe)_2$} or used as received (PCl_3). H_2O^* was purchased from Aldrich, enriched in ^{18}O to a ratio ^{16}O:^{18}O of 9:1.

Synthesis of {N,N'-$(CH_2NMe)_2$}*PCl* **1**.—A solution of $(CH_2NHMe)_2$ in toluene (1.0 g, 11.34 mmol in ~15 cm^3 solvent) was added dropwise over the course of *ca.* 20 min to a stirred solution of PCl_3 (0.99 cm^3, 11.34 mmol) and NEt_3 (3.16 cm^3, 22.68 mmol) in toluene (30 cm^3) at −78 °C. After the addition the mixture was allowed to warm to room temperature and was stirred for *ca.* 5 h. The toluene was removed under reduced pressure to afford a pale yellow amorphous solid. This solid was extracted with pentane (3 × 20 cm^3), the extracts

were combined, and the volatiles were removed under reduced pressure to afford the title compound as a mobile liquid (1.22 g, 71%), $\delta_H(CDCl_3)$ 3.31 (4 H, d, $^3J_{PH}$ 7.3, CH_2) and 2.77 (6 H, d, $^3J_{PH}$ 15.0, Me); $\delta_C(CDCl_3)$ 52.42 (d, $^2J_{PC}$ 10.9, CH_2) and 32.84 (d, $^2J_{PC}$ 18.6, Me); $\delta_P(CDCl_3)$ 171.2 (s) (Found: M^+, 154.023 474. Calc. for $C_4H_{10}{}^{37}ClN_2P$: *M*, 154.024 064).

Syntheses of {N,N'-$(CH_2NMe)_2$}$POSiR_3$ (R_3 = Ph_3 **2**, Bu^tMe_2 **3**, Et_3 **4**).—A solution of Ph_3SiOH in toluene (1.45 g, 5.23 mmol in ~20 cm^3 solvent) was added dropwise to a stirred solution of {*N,N'*-$(CH_2NMe)_2$}PCl **1** (0.80 g, 5.23 mmol) and NEt_3 (1.46 cm^3, 10.46 mmol) in toluene (20 cm^3) which was cooled to 0 °C. After being stirred for 3 h, the volatiles were removed and the solid residue ($NHEt_3Cl$) washed with pentane (2 × 10 cm^3). All extracts were combined and the volatiles were removed under reduced pressure to afford the *title compound* **2**. Subsequent recrystallisation from pentane afforded analytically pure crystals (1.91 g, 93%) (Found: C, 67.45; H, 6.6; N, 6.95%; M^+, 392.147 504. $C_{22}H_{25}N_2POSi$ requires M, 392.147 380; C, 67.32; H, 6.42; N, 7.14%); ν_{max}/cm^{-1} 920s [ν(POSi)]; $\delta_H(CDCl_3)$ 7.5 (15 H, m, Ph), 3.02 (4 H, m, CH_2) and 2.53 (6 H d, $^3J_{PH}$ 13.5 NMe); $\delta_C(CDCl_3)$ 135.47 (s, Ph-C_{ipso}), 135.11 (s, Ph-C_o), 129.65 (s, Ph-C_p), 127.56 (s, Ph-C_m), 52.62 (d, $^2J_{PC}$ 10.3, CH_2) and 34.18 (d, $^2J_{PC}$ 22.4, Me); $\delta_P(CDCl_3)$ 120.9 (s); *m/z* 391 [M − H]$^+$ and 117 [M − $OSiPh_3$]$^+$.

Compounds **3** and **4** were prepared using an analogous procedure but optimum reaction times are 3.5 h (**3**) and 3.0 h (**4**). Both compounds are isolated as liquids. For compound **3** (76%), ν_{max}/cm^{-1} 915s [ν(POSi)]; $\delta_H(CDCl_3)$ 3.04 (4 H, m, CH_2), 2.59 (6 H, d, $^3J_{PH}$ 13.5, NMe), 0.83 (9 H, s, Bu^t) and 0.04 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 52.49 (d, $^2J_{PC}$ 9.4, CH_2), 34.19 (d, $^2J_{PC}$ 22.6, NMe), 25.62 (s, CMe_3), 18.25 (s, CMe_3) and −3.46 (d, $^3J_{PC}$ 2.5, $SiMe_2$); $\delta_P(CDCl_3)$ 119.3 (s); *m/z* 248 [M]$^+$ and 117 [M − $OSiBu^tMe_2$]$^+$ (Found: M^+, 248.146 92. Calc. for $C_{10}H_{25}N_2OPSi$: *M*, 248.147 30).

For compound **4** (72%), ν_{max}/cm^{-1} 915s [ν(POSi)]; $\delta_H(CDCl_3)$ 3.02 (4 H, m, CH_2), 2.58 (6 H, d, $^3J_{PH}$ 13.6, NMe), 0.89 (9 H, t, $^3J_{HH}$ 7.9, CH_2Me) and 0.54 (6 H, q, $^3J_{HH}$ 7.7, CH_2Me); $\delta_C(CDCl_3)$ 52.43 (d, $^2J_{PC}$ 10.7, CH_2), 34.11 (d, $^2J_{PC}$ 22.6, NMe), 6.55 (s, Et) and 5.81 (s, Et); $\delta_P(CDCl_3)$ 119.9 (s); *m/z* 248 [M]$^+$ and 117 [M − $OSiEt_3$]$^+$ (Found: M^+, 248.147 252. Calc. for $C_{10}H_{25}N_2OPSi$: *M*, 248.147 380).

Synthesis of {N,N'-$(CH_2NMe)_2$}$PN(SiMe_3)_2$ **5**.—A solution of Li[$N(SiMe_3)_2$] in THF (5.42 cm^3; 1.0 mol dm^{-3} solution) was added dropwise at −78 °C to a stirred solution of {*N,N'*-$(CH_2NMe_2)_2$ PCl **1** (0.83 g, 5.42 mmol) in THF (~50 cm^3) under dinitrogen. The mixture was allowed to warm to room temperature and was stirred thus for 1 h prior to work-up by removal of the volatiles under reduced pressure and extraction of the desired product into pentane (30 cm^3). Subsequent removal of the pentane under reduced pressure afforded the product as an orange liquid (1.28 g, 85%), ν_{max}/cm^{-1} 1260s [δ(SiMe)]; $\delta_H(C_6D_6)$ 2.63 (4 H, m, CH_2), 2.43 (6 H, d, $^3J_{PH}$ 12.0, NMe) and 0.27 (18 H, d, $^4J_{PH}$ 1.7, $SiMe_3$); $\delta_C(C_6D_6)$ 52.01 (d, $^2J_{PC}$ 8.0, CH_2N), 34.58 (d, $^2J_{PC}$ 29.1, NMe) and 4.85 (d, $^3J_{PC}$ 9.3, $SiMe_3$); $\delta_P(C_6D_6)$ 126.7 (s) (Found: M^+, 277.155 587. Calc. for $C_{10}H_{28}N_3PSi_2$: *M*, 277.155 943).

Synthesis of {N,N'-$CH_2(CH_2NMe)_2$}*PCl* **19**.—A solution of $CH_2(CH_2NHMe)_2$ in toluene (4.1 g, 40.0 mmol in ~30 cm^3 solvent) was added dropwise over the course of *ca.* 20 min to a stirred solution of PCl_3 (3.49 cm^3, 40.0 mmol) and NEt_3 (11.14 cm^3, 80.0 mmol) in toluene (30 cm^3) at −78 °C. The mixture was subsequently allowed to warm to room temperature and was stirred for *ca.* 4.5 h. After this time the volatiles were removed under reduced pressure to afford a pale yellow amorphous solid. This was then washed with pentane (3 × 30 cm^3), filtered, and all the extracts were combined. Removal of the volatiles under reduced pressure afforded the title compound as a liquid (4.6 g, 69%), $\delta_H(CDCl_3)$ 2.80 (4 H, dt, $^3J_{PH}$ 10.5, $^3J_{HH}$ 5.3, NCH_2), 2.59 (6 H, dd, $^3J_{PH}$ 18.6, $^4J_{HH}$ 0.5, Me) and 1.85 (pentet, $^3J_{HH}$ 5.3, CH_2CH_2N); $\delta_C(CDCl_3)$ 44.88 (d, $^2J_{PC}$ 8.0, NCH_2), 39.13 (d, $^2J_{PC}$ 30.6, Me) and 24.79 (s, CH_2CH_2N); $\delta_P(CDCl_3)$ 160.9 (s).

Syntheses of {N,N'-$CH_2(CH_2NMe)_2$}$POSiR_3$ (R_3 = Ph_3 **20**, Bu^tMe_2 **21**).—A solution of Ph_3SiOH in toluene (1.45 g, 5.25 mmol in ~15 cm^3 solvent) was added dropwise to a stirred solution of {*N,N'*-$CH_2(CH_2NMe)_2$}PCl **19** (0.88 g, 5.25 mmol) and NEt_3 (1.46 cm^3, 10.49 mmol) in toluene (20 cm^3) which was cooled to 0 °C. After being stirred for 2 h, the mixture was filtered and the solid residue was washed with pentane (2 × 10 cm^3), all extracts being combined. The volatiles were then removed under reduced pressure to afford a solid. Subsequent recrystallisation from pentane afforded the *title compound* **20** as a crystalline solid (1.80 g, 84%) (Found: C, 67.8; H, 6.85; N, 6.6%; M^+, 406.162 667. $C_{23}H_{27}N_2POSi$ requires C, 67.95; H, 6.69; N, 6.89%; *M*, 406.163 031); ν_{max}/cm^{-1} 910s [ν(POSi)]; $\delta_H(CDCl_3)$ 7.5 (15 H, m, Ph), 3.14 and 2.52 (4 H, 2 m, NCH_2), 2.38 (6 H, d, $^3J_{PH}$ 16.8, NMe) and 2.02 and 1.66 (2 H, 2 m, CH_2CH_2N); $\delta_C(CDCl_3)$ 135–128 (several resonances, Ph-C), 43.87 (d, $^2J_{PC}$ 5.3, NCH_2), 39.69 (d, $^2J_{PC}$ 31.8, NMe) and 25.84 (s, CH_2CH_2N); $\delta_P(CDCl_3)$ 115.8 (s); *m/z* 405 [M − H]$^+$ and 259 [$SiPh_3$]$^+$.

Compound **21** was prepared using an analogous procedure with an optimum reaction time of 2.5 h. Compound **21** was isolated as a liquid, in 84% yield, ν_{max}/cm^{-1} 915s [ν(POSi)]; $\delta_H(CDCl_3)$ 2.95 and 2.45 (4 H, 2 m, NCH_2), 2.45 (6 H, d, $^3J_{PH}$ 16.8, NMe), 1.96 and 1.57 (2 H, 2 m, CH_2CH_2N), 0.85 (9 H, s, Bu^t) and 0.05 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 43.42 (d, $^2J_{PC}$ 6.5, NCH_2) 39.48 (d, $^2J_{PC}$ 31.9, NMe), 25.84 (s, CH_2CH_2N), 25.53 (s, CMe_3), 18.37 (s, CMe_3) and −3.75 (d, $^3J_{PC}$ 2.5, $SiMe_2$); $\delta_P(CDCl_3)$ 114.4 (s); *m/z* 262 [M]$^+$ and 131 [M − $OSiBu^tMe_2$]$^+$(Found: M^+, 262.163 187. Calc. for $C_{11}H_{27}N_2OPSi$: *M*, 262.162 031).

Synthesis of {N,N'-$CH_2(CH_2NMe)_2$}$PN(SiMe_3)_2$ **22**.—This was prepared in an analogous manner to compound **5** but was characterised by ^{31}P NMR spectroscopy only; $\delta_P(CDCl_3)$ 114.4 (s).

Reactions of {N,N'-$(CH_2NMe)_2$}$POSiR_3$ *with Aldehydes: Synthesis of* {N,N'-$(CH_2NMe)_2$}$P(=O)CHR'(OSiR_3)$ (R' = *Ph*, R_3 = Ph_3 **6**, Bu^tMe_2 **7**, Et_3 **8**; R' = Bu^t, R_3 = Ph_3 **9**, Bu^tMe_2 **10**, Et_3 **11**; R_3 = Ph_3, R' = p-$MeOC_6H_4$ **12**, p-ClC_6H_4 **13**, p-NCC_6H_4 **14**, p-$O_2NC_6H_4$ **15**, p-MeC_6H_4 **16**).—The general procedure was the same for all esters. A solution of R'CHO in CH_2Cl_2 or toluene (~10 cm^3) was added dropwise over the course of *ca.* 10 min to a stirred, cooled (0 °C) solution of {*N,N'*-$(CH_2NMe)_2$}$POSiR_3$ **2**–**4** in CH_2Cl_2 or toluene (10 cm^3). The mixture was then stirred at room temperature for the requisite amount of time prior to work-up. The latter consisted of removal of the volatiles under reduced pressure and recrystallisation of the products from pentane.

Product with R' = Ph, R_3 = Ph_3 **6**. PhCHO (146 mm^3, 1.43 mmol) and substrate **2** (0.56 g, 1.43 mmol) in CH_2Cl_2 solvent. Reaction time 2.5 h. Product was isolated as a solid (54%), ν_{max}/cm^{-1} 1240s br [ν(P=O)]; $\delta_H(CDCl_3)$ 7.4 (20 H, m, Ph), 5.23 (1 H, d, $^2J_{PH}$ 10.9, PC*H*Ph), 2.91 (4 H, m, CH_2N), 2.49 (3 H, d, $^3J_{PH}$ 8.4, NMe) and 2.38 (3 H, d, $^3J_{PH}$ 8.6, NMe); $\delta_C(CDCl_3)$ 138–127 (several resonances, Ph-C), 74.67 (d, $^1J_{PC}$ 142.1, P*C*HPh), 47.92 (d, $^2J_{PC}$ 8.0, CH_2N), 47.47 (d, $^2J_{PC}$ 8.0, CH_2N), 32.86 (d, $^2J_{PC}$ 5.3, NMe) and 32.05 (d, $^2J_{PC}$ 5.1, NMe); $\delta_P(CDCl_3)$ 33.0 (s) (Found: M^+, 498.187 87. Calc. for

$C_{29}H_{31}N_2O_2PSi$: M, 498.189 25) (Found: M^+, 480. Calc., *M*, 498).

Product with R′ = Ph, R₃ = Bu^tMe₂ **7**. PhCHO (74 mm³, 0.73 mmol) and substrate **3** (0.18 g, 0.73 mmol) in CH_2Cl solvent. Reaction time 4 h. *Product* was isolated as a solid (80%) (Found: C, 56.45; H, 8.6; N, 7.5%; M^+, 354.187 66. $C_{17}H_{31}N_2O_2PSi$ requires C, 57.60; H, 8.81; N, 7.90%; *M*, 354.189 25); ν_{max}/cm^{-1} 1260s, [ν(P=O)]; $\delta_H(CDCl_3)$ 7.4–7.2 (5 H, m, Ph), 5.09 (1 H, d, $^2J_{PH}$ 11.3, PC*H*Ph), 3.02 (4 H, m, CH_2N), 2.75 (3 H, d, $^3J_{PH}$ 8.8, NMe), 2.31 (3 H, d, $^3J_{PH}$ 8.7, NMe), 0.92 (9 H, s, Bu^t), 0.10 (3 H, s, $SiMe_2$) and −0.18 (3 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 139–127 (several resonances, Ph-C), 73.35 (d, $^1J_{PC}$ 140.6, P*C*HPh), 47.90 (d, $^2J_{PC}$ 7.7, CH_2N), 47.65 (d, $^2J_{PC}$ 8.0, CH_2N), 32.91 (d, $^2J_{PC}$ 4.5, NMe), 32.07 (d, $^2J_{PC}$ 5.3, NMe), 25.89 (s, CMe_3), 18.18 (s, *C*Me₃), −4.63 (s, SiMe) and −4.91 (s, SiMe); $\delta_P(CDCl_3)$ 34.0 (s) *m*/*z*, 340.

Product with R′ = Ph, R₃ = Et₃ **8**. PhCHO (71 mm³, 0.70 mmol) and substrate **4** (0.15 g, 0.70 mmol) in CH_2Cl_2 solvent. Reaction time 1 h. Product was isolated as a liquid (87%); ν_{max}/cm^{-1} 1240s br [ν(P=O)]; $\delta_H(CDCl_3)$ 7.5–7.2 (5 H, m, Ph), 5.12 (1 H, d, $^2J_{PH}$ 11.1, PC*H*Ph), 3.02 (4 H, m, CH_2N), 2.74 (3 H, d, $^3J_{PH}$ 9.0, NMe), 2.31 (3 H, d, $^3J_{PH}$ 8.8, NMe), 0.90 (9 H, t, $^3J_{HH}$ 7.9, $SiCH_2Me$) and 0.55 (6 H, q, $^3J_{HH}$ 7.9, $SiCH_2Me$); $\delta_C(CDCl_3)$ 73.27 (d, $^1J_{PC}$ 140.5, P*C*HPh), 47.66 (d, $^2J_{PC}$ 7.1, CH_2N), 47.59 (d, $^2J_{PC}$ 7.8, CH_2N), 32.64 (d, $^2J_{PC}$ 4.0, NMe), 31.77 (d, $^2J_{PC}$ 5.2, NMe), 6.48 (s, $SiCH_2Me$) and 4.66 (s, $SiCH_2Me$); $\delta_P(CDCl_3)$ 34.0 (s) (Found: *m*/*z*, 346. *M* requires *m*/*z*, 354).

Product with R′ = Bu^t, R₃ = Ph₃ **9**. Bu^tCHO (0.75 ml, 6.9 mmol) and substrate **2** (0.27 g, 0.69 mmol) in CH_2Cl_2 solvent. Reaction time 3 h. Product was isolated as a solid (53%); ν_{max}/cm^{-1} 1240s br [ν(P=O)]; $\delta_H(CDCl_3)$ 7.7–7.2 (15 H, m, Ph), 3.92 (1 H, d, $^2J_{PH}$ 6.9, PC*H*Bu^t), 2.87 (4 H, m, CH_2N), 2.47 (3 H, d, $^3J_{PH}$ 8.8, NMe), 2.45 (3 H, d, $^3J_{PH}$ 7.8, NMe) and 0.96 (9 H, s, Bu^t); $\delta_C(CDCl_3)$ 80.21 (d, $^1J_{PC}$ 141.3, P*C*HBu^t), 47.91 (d, $^2J_{PC}$ 7.9, CH_2N), 47.17 (d, $^2J_{PC}$ 7.3, CH_2N), 35.64 (d, $^2J_{PC}$ 3.7, *C*Me₃), 32.31 (d, $^2J_{PC}$ 4.8, NMe), 32.29 (d, $^2J_{PC}$ 5.9, NMe) and 27.52 (d, $^3J_{PC}$ 5.7, C*Me*₃); $\delta_P(CDCl_3)$ 34.8 (s) (Found: *m*/*z*, 461. *M* requires *m*/*z*, 479).

Product with R′ = Bu^t, R₃ = Bu^tMe₂ **10**. Bu^tCHO (0.53 cm³, 4.9 mmol) and substrate **3** (0.12 g, 0.49 mmol) in CH_2Cl_2 solvent. Reaction time 4 h. Product was isolated as a liquid (78%); ν_{max}/cm^{-1} 1250s br [ν(P=O)]; $\delta_H(CDCl_3)$ 3.71 (1 H, d, $^2J_{PH}$ 5.9, PC*H*Bu^t), 3.06 (4 H, m, CH_2N), 2.65 (3 H, d, $^3J_{PH}$ 8.8, NMe), 2.64 (3 H, d, $^3J_{PH}$ 9.0, NMe), 0.98 (9 H, s, Bu^t), 0.87 (9 H, s, Bu^t), 0.11 (3 H, s, $SiMe_2$) and 0.04 (3 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 80.09 (d, $^1J_{PC}$ 140.6, P*C*HBu^t), 48.30 (d, $^2J_{PC}$ 6.9, CH_2N), 47.51 (d, $^2J_{PC}$ 8.0, CH_2N), 35.74 (d, $^2J_{PC}$ 3.9, *C*Me₃), 32.64 (d, $^2J_{PC}$ 5.7, NMe), 32.49 (d, $^2J_{PC}$ 3.9, NMe), 27.51 (d, $^3J_{PC}$ 5.6, C*Me*₃), 26.45 (s, $SiCMe_3$), 18.83 (s, *C*Me₃), −3.38 (s, SiMe) and −4.89 (s, SiMe); $\delta_P(CDCl_3)$ 34.7 (s) (Found: *m*/*z*, 328. M requires *m*/*z*, 335).

*Product with R′ = Bu^t, R₃ = Et₃***11**. Bu^tCHO (1.98 cm³, 18.2 mmol) and substrate **4** (0.45 g, 1.82 mmol) in CH_2Cl_2 solvent. Reaction time 2 h. Product was isolated as a liquid (88%); ν_{max}/cm^{-1} 1240s br [ν(P=O)]; $\delta_H(CDCl_3)$ 3.82 (1 H, d, $^2J_{PH}$ 6.5, PC*H*Bu^t), 3.13 (4 H, m, CH_2N), 2.67 (3 H, d, $^3J_{PH}$ 8.8, NMe), 2.64 (3 H, d, $^3J_{PH}$ 9.0, NMe), 1.03 (9 H, s, Bu^t), 0.99 (9 H, t, $^3J_{HH}$ 7.9, $SiCH_2Me$) and 0.72 (6 H, q, $^3J_{HH}$ 8.1, $SiCH_2Me$); $\delta_C(CDCl_3)$ 79.99 (d, $^1J_{PC}$ 140.6, P*C*HBu^t), 48.14 (d, $^2J_{PC}$ 6.5, CH_2N), 47.47 (d, $^2J_{PC}$ 6.8, CH_2N), 35.47 (d, $^2J_{PC}$ 3.9, *C*Me₃), 32.58 (d, $^2J_{PC}$ 5.3, NMe), 32.48 (d, $^2J_{PC}$ 4.4, NMe), 27.25 (d, $^3J_{PC}$ 5.9, C*Me*₃), 6.95 (s, $SiCH_2Me$) and 5.04 (s, $SiCH_2Me$); $\delta_P(CDCl_3)$ 34.7 (s) (Found: *m*/*z*, 334. M requires *m*/*z*, 335).

Product with R′ = p-MeOC₆H₄, R₃ = Ph₃ **12**. *p*-$MeOC_6H_4$-CHO (62 mm³, 0.51 mmol) and substrate **2** (0.2 g, 0.51 mmol) in toluene solvent. Reaction time 3 h. Product was isolated as a crystalline solid in quantitative yield by NMR spectroscopy, isolated >90%; $\delta_H(CDCl_3)$ 7.6–6.9 (19 H, m, Ph), 5.18 (1 H, d, $^2J_{PH}$ 10.1, PC*H*Ar), 3.70 (3 H, s, MeO), 290 (4 H, m, CH_2N), 2.50 (3 H, d, $^3J_{PH}$ 8.8, NMe) and 2.40 (3 H, d, $^3J_{PH}$ 8.6, NMe); $\delta_C(CDCl_3)$ 137–125 (several resonances, Ph-C), 74.06 (d, $^1J_{PC}$ 144.4, P*C*HAr), 54.97 (s, MeO), 47.74 (d, $^2J_{PC}$ 7.9, CH_2N), 47.29 (d, $^2J_{PC}$ 7.7, CH_2N), 32.70 (d, $^2J_{PC}$ 4.1, NMe) and 31.89 (d, $^2J_{PC}$ 5.3, NMe); $\delta_P(CDCl_3)$ 33.1 (s).

Product with R′ = p-ClC₆H₄, R₃ = Ph₃ **13**. *p*-ClC_6H_4CHO (72 mg, 0.51 mmol) and substrate **2** (0.2 g, 0.51 mmol) in toluene solvent. Reaction time 3 h. Product was isolated as a crystalline solid. Yield was quantitative by NMR spectroscopy, isolated >90%; $\delta_H(CDCl_3)$ 7.6–7.1 (19 H, m, ArH), 5.21 (1 H, d, $^2J_{PH}$ 11.2, PC*H*Ar), 2.96 (4 H, m, CH_2N), 2.49 (3 H, d, $^3J_{PH}$ 8.9, NMe) and 2.40 (3 H, d, $^3J_{PH}$ 8.7, NMe); $\delta_C(CDCl_3)$ 137–126 (several resonances, Ph-C), 74.00 (d, $^1J_{PC}$ 144.0, P*C*HAr), 47.97 (d, $^2J_{PC}$ 9.1, CH_2N), 47.43 (d, $^2J_{PC}$ 7.9, CH_2N), 32.90 (d, $^2J_{PC}$ 5.2, NMe) and 31.98 (d, $^2J_{PC}$ 5.1, NMe); $\delta_P(CDCl_3)$ 32.6 (s).

Product with R′ = p-NCC₆H₄, R₃ = Ph₃ **14**. *p*-NCC_6H_4-CHO (67 mg, 0.51 mmol) and substrate **2** (0.2 g, 0.51 mmol) in toluene solvent. Reaction time 3 h. Product was isolated as a crystalline solid in quantitative yield by NMR spectroscopy, isolated >90%; $\delta_H(CDCl_3)$ 7.6–7.2 (19 H, m, ArH), 5.30 (1 H, d, $^2J_{PH}$ 12.7, PC*H*Ar), 2.99 (4 H, m, CH_2N), 2.49 (3 H, d, $^3J_{PH}$ 9.1, NMe) and 2.38 (3 H, d, $^3J_{PH}$ 8.8, NMe); $\delta_C(CDCl_3)$ 144–125 (several resonances, Ph-C), 110.83 (d, $^6J_{PC}$ 2.2, N*C*Ar), 74.01 (d, $^1J_{PC}$ 138.9, P*C*HAr), 48.04 (d, $^2J_{PC}$ 7.9, CH_2N), 47.41 (d, $^2J_{PC}$ 8.1, CH_2N), 32.93 (d, $^2J_{PC}$ 5.1, NMe) and 31.88 (d, $^2J_{PC}$ 4.2, NMe); $\delta_P(CDCl_3)$ 32.4 (s).

Product with R′ = p-O₂NC₆H₄, R₃ = Ph₃ **15**. *p*-$O_2NC_6H_4$-CHO (77 mg, 0.51 mmol) and substrate **2** (0.2 g, 0.51 mmol) in toluene solvent. Reaction time 3 h. Product was isolated as a yellow crystalline solid in quantitative yield by NMR spectroscopy, isolated >90%; $\delta_H(CDCl_3)$ 8.0–7.1 (19 H, m, ArH), 5.37 (1 H, d, $^2J_{PH}$ 13.0, PC*H*Ar), 2.97 (4 H, m, CH_2N), 2.49 (3 H, d, $^3J_{PH}$ 9.1, NMe) and 2.39 (3 H, d, $^3J_{PH}$ 8.8, NMe); $\delta_C(CDCl_3)$ 137–122 (several resonances, Ph-C), 73.80 (d, $^1J_{PC}$ 138.1, P*C*HAr), 47.86 (d, $^2J_{PC}$ 8.1, CH_2N), 47.21 (d, $^2J_{PC}$ 8.5, CH_2N), 32.71 (d, $^2J_{PC}$ 5.2, NMe) and 31.71 (d, $^2J_{PC}$ 4.4, NMe); $\delta_P(CDCl_3)$ 32.1 (s).

Product with R′ = p-MeC₆H₄, R₃ = Ph₃ **16**. *p*-MeC_6H_4-CHO (60 mm³, 0.51 mmol) and substrate **2** (0.2 g, 0.51 mmol) in toluene solvent. Reaction time 3 h. Product was isolated as a crystalline solid in quantitative yield by NMR spectroscopy, isolated >90%; $\delta_H(CDCl_3)$ 7.6–6.9 (19 H, m, ArH), 5.18 (1 H, d, $^2J_{PH}$ 10.6, PC*H*Ar), 2.91 (4 H, m, CH_2N), 2.50 (3 H, d, $^3J_{PH}$ 8.7, NMe), 2.40 (3 H, d, $^3J_{PH}$ 8.6, NMe) and 2.26 (3 H, s, MeAr); $\delta_C(CDCl_3)$ 137–125 (several resonances, Ph-C), 74.52 (d, $^1J_{PC}$ 142.1, P*C*HAr), 47.90 (d, $^2J_{PC}$ 7.8, CH_2N), 47.41 (d, $^2J_{PC}$ 8.6, CH_2N), 32.83 (d, $^2J_{PC}$ 4.2, NMe), 32.02 (d, $^2J_{PC}$ 5.1, NMe) and 21.09 (s, *Me*Ar); $\delta_P(CDCl_3)$ 33.0 (s).

Reactions of Compound **5** *with Benzaldehyde and Pivaldehyde: Syntheses of* $\{N,N'\text{-}(CH_2NMe_2)_2\}P(=NSiMe_3)CHR(OSiMe_3)$ (*R = Ph*, **17**; *Bu^t*, **18**).—Benzaldehyde (0.16 cm³, 1.61 mmol) was added dropwise at room temperature to a stirred solution of compound **5** (0.45 g, 1.61 mmol) in pentane solvent (15 cm³). After 80 min, the yellow solution was filtered and removal of the volatile materials under reduced pressure afforded $\{N,N'\text{-}(CH_2NMe_2)_2\}P(=NSiMe_3)CHPh(OSiMe_3)$ **17** as an orange oily solid (0.49 g, 79%); ν_{max}/cm^{-1} 1265s [δ(SiMe)]; $\delta_H(C_6D_6)$ 7.7–7.2 (5 H, m, Ph), 5.05 (1 H, d, $^2J_{PH}$ 11.4, PhC*H*P), 2.84 (2 H, m, CH_2N), 2.70 (2 H, m, CH_2N), 2.58 (3 H, d, $^3J_{PH}$ 9.4, NMe), 2.16 (3 H, d, $^3J_{PH}$ 9.3, NMe), 0.34 (9 H, s, $SiMe_3$) and 0.09 (9 H, s, $SiMe_3$); $\delta_C(C_6D_6)$ 138–126 (Ph-C), 75.54 (d, $^1J_{PC}$ 147.2, PhCHP), 47.94 (d, $^2J_{PC}$ 6.8, CH_2N), 47.87 (d, $^2J_{PC}$ 7.9, CH_2N), 33.36 (d, $^2J_{PC}$ 5.2, NMe), 32.25 (d, $^2J_{PC}$ 5.0, NMe), 4.03 (d, $^3J_{PC}$ 4.0, P=NSiMe₃) and 0.29

(s, $OSiMe_3$); $\delta_P(C_6D_6)$ 19.2 (s) (Found: M^+, 383.197 730. Calc. for $C_{17}H_{34}N_3OPSi_2$: *M*, 383.197 808).

Compound **18** $\{N,N'\text{-}(CH_2NMe_2)_2\}P(=NSiMe_3)CHBu^t(OSiMe_3)$ was prepared and isolated also as an oily orange solid in a similar manner to that described above for compound **17** but by using the following quantities and reaction conditions: substrate **5** (0.57 g, 2.05 mmol) in pentane solvent (15 cm^3) with benzaldehyde (0.32 cm^3, 2.95 mmol). The mixture was stirred at ambient temperature for 7 days prior to work-up in the same manner as for compound **17** to give product **18** (0.58 g, 78%); ν_{max}/cm^{-1} 1270s [δ(SiMe)]; $\delta_H(C_6D_6)$ 3.62 (1 H, d, $^2J_{PH}$ 8.0, Bu^tCHP), 2.86 (2 H, m, CH_2N), 2.62 (2 H, m, CH_2N), 2.38 (6 H, d, $^3J_{PH}$ 8.0, NMe), 1.09 (9 H, s, CMe_3), 0.23 (9 H, s, $SiMe_3$) and 0.17 (9 H, s, $SiMe_3$); $\delta_C(C_6D_6)$ 82.10 (d, $^1J_{PC}$ 155.5, Bu^tCHP), 48.41 (d, $^2J_{PC}$ 6.6, CH_2N), 47.77 (d, $^2J_{PC}$ 6.5, CH_2N), 35.99 (d, $^2J_{PC}$ 4.6, CMe_3), 33.46 (d, $^2J_{PC}$ 6.7, NMe), 32.22 (d, $^2J_{PC}$ 4.7, NMe), 28.34 (d, $^3J_{PC}$ 5.5, CMe_3), 4.15 (d, $^3J_{PC}$ 4.3, $P{=}NSiMe_3$) and 1.16 (s, $OSiMe_3$); $\delta_P(C_6D_6)$ 20.9 (s) (Found: M^+, 363.299 208. Calc. for $C_{15}H_{38}N_3OPSi_2$: *M*, 363.229 108).

Reactions of $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiR_3$ *with Aldehydes: Syntheses of* $\{N,N'\text{-}CH_2(CH_2NMe)_2\}P(=O)CHR'(OSiR_3)$ (*R'* = *Ph*, R_3 = Ph_3 **23**, Bu^tMe_2 **24**; *R'* = Bu^t, R_3 = Ph_3 **25**, Bu^tMe_2 **26**).—*Compound* **23**. A solution of PhCHO (133 mm^3, 1.31 mmol) in CH_2Cl_2 (~15 cm^3) was added dropwise over the course of *ca.* 5 min to a stirred, cooled (0 °C) solution of $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiPh_3$ **20** (0.53 g, 1.31 mmol) in CH_2Cl_2 (15 cm^3). The mixture was then stirred at room temperature for 2.5 h prior to work-up. Removal of the volatiles under reduced pressure and washing of the product with pentane afforded the title compound as crystals (0.35 g, 52%); ν_{max}/cm^{-1} 1275s br [ν(P=O)]; $\delta_H(CDCl_3)$ 7.26 (20 H, m, Ph), 5.04 (1 H, d, $^2J_{PH}$ 10.6, PC*H*Ph), 2.78 (4 H, m, CH_2N), 2.41 (3 H, d, $^3J_{PH}$ 8.3, NMe), 2.29 (3 H, d, $^3J_{PH}$ 8.1, NMe) and 1.55 (2 H, m, CCH_2C); $\delta_C(CDCl_3)$ 135.80–127.10 (several resonances, Ph-C), 75.65 (d, $^1J_{PC}$ 145.0, P*C*HPh), 50.42 (s, CH_2N), 50.14 (s, CH_2N), 35.74 (d, $^2J_{PC}$ 3.3, NMe), 35.10 (d, $^2J_{PC}$ 3.8, NMe) and 24.58 (d, $^3J_{PC}$ 3.6, CCH_2C); $\delta_P(CDCl_3)$ 22.5 (s) (Found: M^+, 512.205 600. Calc. for $C_{30}H_{33}N_2O_2PSi$: *M*, 512.204 895).

Compound **24**. A solution of PhCHO (328 mm^3, 3.23 mmol) in CH_2Cl_2 (~15 cm^3) was added dropwise over the course of *ca.* 5 min to a stirred, cooled (0 °C) solution of $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiBu^tMe_2$ **21** (0.85 g, 3.23 mmol) in CH_2Cl_2 (15 cm^3). The mixture was then allowed to warm to ambient temperature and was stirred for 4 h prior to work-up. Removal of the volatiles under reduced pressure and washing of the product with pentane afforded compound **24** as crystals (1.10 g, 92%); ν_{max}/cm^{-1} 1270s br [ν(P=O)]; $\delta_H(CDCl_3)$ 7.32 (5 H, m, Ph), 5.02 (1 H, d, $^2J_{PH}$ 11.3, PC*H*Ph), 3.07 (2 H, m, CH_2N), 2.94 (1 H, m, CCH_2C), 2.77 (3 H, d, $^3J_{PH}$ 8.5, NMe), 2.28 (3 H, d, $^3J_{PH}$ 7.5, NMe), 1.78 (2 H, m, CH_2N), 1.29 (1 H, m, CCH_2C), 0.92 (9 H, s, CMe), 0.10 (3 H, s, SiMe) and −0.16 (3 H, s, SiMe); $\delta_C(CDCl_3)$ 139.69–126.97 (several resonances, Ph-C), 74.50 (d, $^1J_{PC}$ 142.1, P*C*HPh), 50.89 (s, CH_2N), 50.05 (s, CH_2N), 35.65 (d, $^2J_{PC}$ 3.8, NMe), 35.06 (d, $^2J_{PC}$ 4.0, NMe), 25.82 (s, *CMe*), 24.78 (d, $^3J_{PC}$ 3.5, CCH_2C), 18.09 (s, *C*Me), −4.82 (s, SiMe) and −4.87 (s, SiMe); $\delta_P(CDCl_3)$ 23.5 (s) (Found: *m*/*z*, 383. *M* requires *m*/*z*, 369).

Compound **25**. A solution of Bu^tCHO (2.72 cm^3, 2.50 mmol) in CH_2Cl_2 (~15 cm^3) was added dropwise over the course of *ca.* 5 min to a stirred, cooled (0 °C) solution of compound **20** (1.02 g, 2.50 mmol) in CH_2Cl_2 (15 cm^3). The mixture was then stirred at room temperature for the 3 h prior to work-up using an analogous procedure to that used for compounds **23** and **24**. Removal of the volatiles under reduced pressure and washing of the product with pentane afforded compound **25** as a viscous oil (0.81 g, 66%); ν_{max}/cm^{-1} 1260s br [ν(P=O)]; $\delta_H(CDCl_3)$ 7.52 (15 H, m, Ph), 3.81 (1 H, d, $^2J_{PH}$ 6.1, PC*H*Ph), 2.85 (1 H, m, CCH_2C), 2.72 (2 H, m, CH_2N), 2.65 (1 H, m, CCH_2C), 2.59 (3 H, d, $^3J_{PH}$ 9.0, NMe), 2.29 (3 H, d, $^3J_{PH}$ 9.3, NMe), 1.63 (2 H, m, CH_2N) and 1.00 (9 H, s, CMe_3); $\delta_C(CDCl_3)$ 136.03–127.36 (several resonances, Ph-C), 80.06 (d, $^1J_{PC}$ 124.6, P*C*HPh), 49.53 (s, CH_2N), 49.50 (s, CH_2N), 36.12 (d, $^2J_{PC}$ 2.7, NMe), 35.86 (d, $^2J_{PC}$ 4.1, NMe), 35.08 (s, *C*Me$_3$), 29.57 (d, $^3J_{PC}$ 3.9, CMe) and 23.72 (d, $^3J_{PC}$ 3.9, CCH_2C); $\delta_P(CDCl_3)$ 25.7 (s) (Found: *m*/*z*, 485. *M* requires *m*/*z*, 493).

Compound **26**. A solution of Bu^tCHO (3.06 cm^3, 2.82 mmol) in CH_2Cl_2 (~15 cm^3) was added dropwise over the course of *ca.* 5 min to a stirred, cooled (0 °C) solution of compound **21** (0.74 g, 2.82 mmol) in CH_2Cl_2 (15 cm^3). The mixture was processed as for compound **16** to afford product **26** as a viscous oil (0.95 g, 96%); ν_{max}/cm^{-1} 1265s br [ν(P=O)]; $\delta_H(CDCl_3)$ 3.72 (1 H, d, $^2J_{PH}$ 6.1, PC*H*Ph), 3.02 (4 H, m, CH_2N), 2.68 (3 H, d, $^3J_{PH}$ 9.1, NMe), 2.65 (3 H, d, $^3J_{PH}$ 9.0, NMe), 2.03 (1 H, m, CCH_2C), 1.83 (1 H, m, CCH_2C), 1.05 (9 H, s, CCMe), 0.94 (9 H, s, SiCMe), 0.21 (3 H, s, SiMe) and 0.12 (3 H, s, SiMe); $\delta_C(CDCl_3)$ 79.39 (d, $^1J_{PC}$ 146.0, P*C*HBu^t), 49.77 (s, CH_2N), 49.49 (s, CH_2N), 36.25 (d, $^2J_{PC}$ 2.6, NMe), 35.94 (d, $^2J_{PC}$ 4.1, NMe), 35.89 (s, *C*Me$_3$), 27.44 (d, $^3J_{PC}$ 5.5, SiC*Me*), 26.52 (s, CC*Me*), 24.41 (d, $^3J_{PC}$ 3.0, CCH_2C), 18.96 (s, Si*C*Me), −3.17 (s, SiMe) and −4.84 (s, SiMe); $\delta_P(CDCl_3)$ 25.8 (s) (Found: M^+, 349).

Synthesis and Analysis of ^{18}O*-labelled Organophosphorus Compounds* **2**, **6** *and* **9**.—A solution of H_2O^* (91.8 mm^3; 5.09 mmol) in toluene (15 cm^3) was added over a period of 20 min to a stirred solution of Ph_3SiCl (1.5 g, 5.09 mmol) and *N*-methylmorpholine (0.56 cm^3, 5.09 mmol) at −78 °C. The reaction mixture was then allowed to warm to ambient temperature and was stirred thus for 18 h. The mixture was then filtered and the volatiles were removed under reduced pressure to afford crude Ph_3SiO^*H as crystals. This solid was dissolved in the minimum of CH_2Cl_2 (~10 cm^3) and layered with the same volume of pentane. After several hours at −35 °C, the solvent was decanted from the precipitated crystals which were then dried *in vacuo* (0.52 g, 37%).

A toluene solution (15 cm^3) of this Ph_3SiO^*H (0.51 g, 1.86 mmol) was added dropwise over the course of 15 min at −78 °C to a stirred solution of $\{N,N'\text{-}(CH_2NMe)_2\}PCl$ **1** (0.28 g, 1.86 mmol) and NEt_3 (0.52 cm^3, 3.71 mmol) in toluene (15 cm^3) cooled to −78 °C. Upon warming of the mixture to ambient temperature, the procedure followed was exactly as for compound **2**. This sample of compound **2*** was then treated with PhCHO (1 mol equiv.) and Bu^tCHO (10 mol equiv.) using the same procedures as described above for compounds **6** and **9**. Both samples of **6*** and **9*** were then examined by ^{31}P NMR and mass spectroscopy. Owing to the small ^{31}P NMR shift difference between ^{16}O and ^{18}O isotopomers (7.5–7.8 Hz) and line broadening due to coupling to the two coordinated nitrogen atoms in all three compounds (*e.g.*, compound **2** has a half-height linewidth $\Delta_{1/2}$ of 3.4 Hz at 298 K without artificial line narrowing, whilst compound **6** has $\Delta_{1/2}$ 1.3 Hz under the same conditions) it was necessary to acquire the NMR spectra at low temperatures (223 K) to reduce the effects of coupling to ^{14}N so that reasonable integrations could be obtained. In all cases, the minimum of artificial line narrowing was employed to maintain adequate line shape and achieve accurate integrations (acquisition times were between 1.2 and 5.0 s).

Intra- versus *Inter-molecular Silyl-group Transfer in the Abramov Reaction*.—A solution of $\{N,N'\text{-}(CH_2NMe)_2\}POSiPh_3$ **2** (0.29 g, 0.73 mmol) and $\{N,N'\text{-}CH_2(CH_2NMe)_2\}POSiBu^tMe_2$ **21** (0.19 g, 0.73 mmol) in toluene solvent (15 cm^3) containing NEt_3 (0.1 cm^3, 0.72 mmol), which was added to prevent trace-acid-catalysed silyl-group exchange which may occur in systems of this nature, was left overnight whereupon

analysis by ^{31}P NMR spectroscopy revealed no silyl-group exchange to have occurred. Subsequently, PhCHO (149 mm^3, 1.46 mmol) was added and the mixture was stirred at ambient temperature for 4 h. The volatiles were then removed under reduced pressure and the resulting liquid was examined by ^{31}P NMR spectroscopy in $CDCl_3$. The products of *intramolecular* silyl-group transfer, $\{N,N'$-$(CH_2NMe)_2\}P(O)CHPh(OSiPh_3)$ **6** (33.0 ppm) and $\{N,N'$-$CH_2(CH_2NMe)_2\}P(O)CHPh(OSiBu^tMe_2)$ **24** (23.5 ppm), constitute >95% of the product mixture.

Assessment of Relative Reactivity in the Abramov Phosphonylation Reaction.—(a) *With pivalaldehyde.* Pivalaldehyde (184 cm^3, 1.7 mmol) was added *via* microsyringe through a rubber-septum-sealed 10 mm NMR tube containing the organophosphorus(III) ester (0.17 mmol) in toluene solvent (2.0 cm^3) and a 5 mm NMR tube insert which contained a reference phosphorus compound (0.17 mmol) in C_7D_8 chosen to provide a suitable integration point. The reference compounds used were $(MeO)_3P$ for $\{N,N'$-$(CH_2NMe)_2\}PN(SiMe_3)_2$ **22** and $(PhO)_3P$ for every other ester. The $^{31}P\{^1H\}$ NMR spectra were acquired after 10 min at probe temperature (25 °C) and the percentage of organophosphorus ester that had reacted under these conditions *R* was determined by integration against the standard. The $^{31}P\{^1H\}$ spectra were recorded at 36.2 MHz over a 3 kHz range with 8 K data points, giving a digital resolution of 0.75 Hz. Inverse-gated ^1H decoupling to lessen nuclear Overhauser (NOE) effects and a pulse delay of 1 s were employed for all samples.

(b) *With* para-*substituted benzaldehydes.* The procedure was as described above except that a 1 : 1 molar ratio (0.17 mmol) of the organophosphorus(III) ester used, $\{N,N'$-$(CH_2NMe)_2\}POSiPh_3$ **2**, and aldehyde was used throughout, the samples were shaken vigorously upon addition of the reagents, and $^{31}P\{^1H\}$ NMR spectra were recorded after 35 min at probe temperature.

Investigation of Silyl-group Exchange in $\{DIAM\}POSiR_3$ *Systems.*—A CH_2Cl_2 solution (2 cm^3) containing $\{N,N'$-$(CH_2NMe)_2\}P^*OSiPh_3$ (0.5 mmol) and $\{N,N'$-$CH_2(CH_2NMe)_2\}POSiBu^tMe_2$ (0.5 mmol) was monitored by $^{31}P\{^1H\}$ NMR spectroscopy in a 10 mm NMR tube fitted with a 5 mm insert containing C_6D_6 as external reference. The spectra were recorded at −40 °C to reduce the effects of coupling of phosphorus to the quadrupolar ^{14}N nuclei. After 5 days at ambient temperature it was observed that the crossover products $\{N,N'$-$(CH_2NMe)_2\}POSiBu^tMe_2$ **3** and $\{N,N'$-$(CH_2(CH_2NMe)_2\}POSiPh_3$ **20** were present (by spectral comparison with unlabelled samples) and that the ^{18}O label had been retained only in the five-membered diamine systems $\{N,N'$-$(CH_2NMe)_2\}P^*OSiBu^tMe_2$ and $\{N,N'$-$(CH_2NMe)_2\}P(^*O)SiPh_3$. The same crossover products were observed when reaction was monitored in $CDCl_3$ solvent. However, treatment of the $CDCl_3$ with NEt_3 before addition to a mixture of $\{N,N'$-$(CH_2NMe)_2\}POSiBu^tMe_2$ **3** and $\{N,N'$-$CH_2(CH_2NMe)_2\}POSiPh_3$ **20** resulted in no exchange being observed, suggesting that the exchange process may be catalysed by trace acid.

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