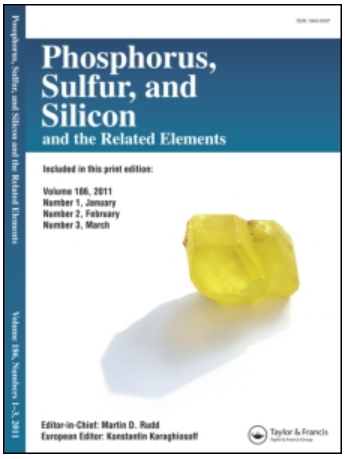

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DIALKYLAMINO GROUP TRANSFER FROM TITANIUM (IV) TO PHOSPHORYL CENTRE. STRUCTURE–REACTIVITY STUDIES

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Reaction between phosphoryl substrates, $(EtO)_2P(O)X$(X = H, R, OR) and dialkylaminoderivatives of Ti(IV), $Ti(NR_2)_nCl_{4-n}$ and $Mn(NEt_2)_2$ leads to the exchange of one or both EtO groups for the NR_2 substituent. The reactivity of the system depends on electronic, as well as steric, effects of both substrates, and approximately correlates with the Lewis acid-base interactions between the substrates, as measured by the i.r. spectroscopy.

Key words: Titanium and manganese dialkylamides; diethylphosphoryl derivatives; group transfer between metal and phosphorus; Lewis acid-base interactions.

In our recent papers[1] we reported on the transfer of functional groups from some metals to the phosphoryl centre, resulting in the exchange of one or two substituents at the phosphorus atom (Equation 1).

$$Z_2P(O)X \xrightarrow{MY_n(2)} ZYP(O)X \text{ and/or } Y_2P(O)X \qquad (1)$$

1 **3** **4**

M = Ti, Mn, Sn;
n = 2 or 4;
Y = NR_2, OR;
Z = OR, OAr;
X = H, OR, OAr, R.

The feasibility and selectivity of such transfer were found to be critically dependent on the nature of metal M, and the substituents Y, X, and Z. For example, titanium tetrakis(diethylamide) (**2a**, M = Ti; Y = NEt_2; n = 4) is capable of displacing both ester functions in dialkyl and diaryl phosphites (**1a**, Z = OR, OAr; X = H) for the NEt_2 groups,[1a] but was found to be unreactive towards phosphate triesters (**1b**, Z = X = OR, OAr). Manganese bis(diethylamide) (**2b**, M = Mn; Y = NEt_2; n = 2), on the other hand, reacts with (**1b**) with a displacement of a single ester function, and with dialkyl phosphites one or both RO groups can be exchanged for the Et_2N substituent.[1b]

In order to acquire more information about the reaction (1), we have now studied the polar and steric effect of substituents in both, phosphorus substrates (**1**) and the reagents (**2**). Substrates (**1**) of the general formula $(EtO)_2P(O)X$ included the following groups: X = H (**1a**); EtO (**1b**); Me (**1c**); CCl_3 (**1d**); CH(OH)Ph (**1e**); and CH(OMe)Ph (**1f**). The last two compounds were chosen

in order to investigate the previously observed anchimeric assistance in reaction (1) of α-hydroxy-substituted phosphonic ester (**1e**).[1c] Structural variations in (**2**) involved both, the size of the alkyl groups in the substituent $Y = NR_2$, and the Lewis acidity of the whole reagent. The following (**2**) were used: $Ti(NEt_2)_4$ (**2a**); $Mn(NEt_2)_2$ (**2b**); $Ti(NEt_2)_3Cl$ (**2c**); $Ti(NEt_2)_2Cl_2$ (**2d**); $Ti(NMe_2)_4$ (**2e**); $Ti(NMe_2)_2Cl_2$ (**2f**), and $Ti(NiPr_2)_4$ (**2g**). Since phosphoryl compounds show ligand properties with respect to a variety of Lewis acids,[2] it seemed reasonable to assume that the first step of reaction (1) involves complexation between substrates (**1**) and (**2**). Such a complexation is known to lower the phosphoryl stretching frequency (e.g. $TiCl_4$ lowers the V_{PO} value of Cl_3PO by 90 cm^{-1} [3]) with the shift related to the electron affinity of the metal centre.[4] We therefore also decided to investigate the effect of reagents (**2**) on the V_{PO} of a selected substrate (**1c**) in order to see whether a correlation exists between the complexation ability and the reactivity in the functional groups transfer from (**2**) to (**1**).

RESULTS AND DISCUSSIONS

(1) *Products identification.* For reactions where high conversion to a single product (**3** or **4**) was obtained, or where no reaction was observed, organophosphorus products or substrates (**1**) were isolated and characterised, as in our previous studies,[1] by n.m.r. (^1H and ^{31}P) spectroscopy, and by comparison with the authentic samples. In cases of the mixtures of both products (**3** and **4**), or for low conversions (hence large quantities of substrates **1**) the separation of individual compounds was not possible. Mixtures of phosphoryl derivatives (**1**), (**3**), (**4**) could not be effectively separated by fractional distillation or chromatographic methods without decomposition. We found that the composition of the mixtures could be best determined by analysing the high resolution ^1H and ^{31}P n.m.r. spectra of reaction products, identifying the individual components, and estimating the relative proportions from the integration data. We have found that the successive substitution of the EtO for the R_2N groups in $(EtO)_2P(O)X$ results in the regular low-field shift of the ^{31}P n.m.r. signal. For example, ^{31}P n.m.r. chemical shift values for (**1a**), $(EtO)(Et_2N)P(O)H$ (**3a**), and $(Et_2N)_2P(O)H$ (**4a**) are 5.0, 11.5, and 17.9 ppm, respectively. Similarly, the ^{31}P chemical shift in the series (**1b**), $(EtO)_2P(O)NEt_2$ (**3b**), $EtOP(O)(NEt_2)_2$, and $(Et_2N)_3PO$ varies in the order: -3.1,[5] $+7.6$,[6] $+13.7$, and $+19.2$[7] ppm, respectively. The exchange of the ester (RO) for the amide (R_2N) group in (**1**) could be also monitored by the ^1H n.m.r. spectroscopy, due to the appearance of the signals characteristics of the P(O)NCH function (δ 2.60–4.0 ppm; $^3J_{HP}$ 7–11 Hz).

Titanium tetrakis (dialkylamides), $Ti(NR_2)_4$. In the series (**2e**), (**2a**), (**2g**) the reactivity decreases with the increasing bulk of the alkyl groups. The N-diisopropyl derivative (**2g**) reacted with none, but the most reactive substrate (**1a**), and even then only the monosubstitution product (**3c**) could be obtained.

$$(EtO)_2P(O)H + Ti(N\text{-}iPr_2)_4 \xrightarrow[57\%]{25°C,\ 24h} (EtO)(iPr_2N)P(O)H \qquad (2)$$

1a **2g** **3c**

The N-diethylderivative (**2a**) shows greater reactivity towards organophosphorus substrates. It reacts smoothly with (**1a**), yielding the disubstituted product, $(Et_2N)_2P(O)H$ (**4a**) in 61% yield after only 1 h at room temperature. It is however unreactive towards triethyl phosphate (**1b**) and methylphosphonate (**1c**); no reaction was observed after 72 h at room temperature, or after 24 h at 40°C. The reaction does take place with the more electrophilic phosphonate, (**1d**), but it leads to a complex mixture of products which we were unable to identify. NMR spectra (^1H, ^{31}P) of this mixture showed that both ester groups have been removed from the molecule of (**1d**), and also suggested substitution of some of the chlorine atom(s) in the CCl_3 substituent by the NR_2 group(s). It seems therefore that for an α-haloposphonic esters, reagents (**2**) may serve as means of displacing both, the phosphorus and the α-carbon substituents.

The least bulky reagent, (**2e**), proved to be the most reactive member of the series; it converted (**1a**) after 1 h at room temperature almost quantitatively into $(Me_2N)_2P(O)H$ (**4b**). Moreover, (**2e**) was found to be the only Ti(IV) reagent capable of displacing albeit in low yields, one ethoxy for the dimethylamino group at the phosphorus atom in (**1b**) and (**1c**).

$$(EtO)_2P(O)X + Ti(NMe_2)_4 \xrightarrow{40°C,\ 24\ h} (EtO)(Me_2N)P(O)X \qquad (3)$$

1 b, X = OEt; **c**, X = Me — **2e** — **3 d**, X = OEt (14%); **e**, X = Me (10%)

For substrate (**1b**) the reaction product could be easily identified as a mixture of unreacted (**1b**) (86%) and (**3d**) by comparison with mixtures of the authentic samples of triethyl phosphate and diethyl *N,N*-dimethylphosphoramidate. In the case of (**1c**), no authentic sample of (**3e**) was available for comparison. The ^{31}P n.m.r. spectrum of the reaction product showed the presence of only two phosphorus-containing compounds (ratio 9:1): one giving rise to a signal at δ 28.1 ppm (**1c**), and the other at δ 32.8 ppm, indicating the exchange of only one OEt group for the Me_2N substituent. This conclusion was confirmed by the ^1H n.m.r. spectrum which showed the appearance of the mono-*N,N*-dimethylphosphoramidate derivative (δ 2.61, d, J_{HP} 9.3 Hz, $PNMe_2$) in a 1:8.5 ratio to the unreacted (**1c**). It is clear that the reactivity of the $Ti(NR_2)_4$ reagents towards phosphoryl substrates is very much a function of the steric hindrance in the exchange reaction. The importance of steric interactions between the ligands of titanium and the substituents in a substrate molecule has been recognized in the titanium-mediated synthesis of 1,3-dienes,[8] and the observed difference in reactivity between phosphite (**1a**) and phosphate (**1c**) substrates is reminiscent of the known[9] preference of titanium (IV) reagents towards aldehydes relative to ketones.

Titanium (dialkylamido)chlorides, $Ti(NR_2)_nCl_{4-n}$. The reagents (**2c**) and (**2d**) are slightly more reactive than the tetrakisamide (**2a**), but show little difference between each other. They both convert (**1a**) into (**4a**) with high yields (93 and 87%, respectively; under the same condition **4a** is obtained from **2a** with only 61%), but they are still unreactive towards (**1b**) and (**1c**). It seems therefore that

the increase in Lewis acidity in the series (**2a**) < (**2c**) < (**2d**) (*vide infra*) is, at least partially, counterbalanced by the decrease in the availability of the diethylamino groups in the exchange reaction.

$Ti(NMe_2)_2Cl_2$ (**2f**) is the only reagent (**2**) solid at room temperature, insoluble in hexane and benzene, and only sparingly soluble in chloroform and dichloromethane. Although it reacts smoothly with (**1a**) (with, or without dichloromethane as a solvent), yielding (**4b**) almost quantitatively, no reaction with (**1b**) would be observed in dichloromethane after 24 h at 40°C; under these conditions (**2e**) (neat) gave *ca* 14% conversion to the monosubstituted product, (**3d**).

Manganese bis-diethylamide, $Mn(NEt_2)_2$ (**2b**). Although (**2b**) shows lower reactivity than Ti(IV) reagents with respect to diethyl phosphite, (the maximum yield of the disubstituted product **4a** obtained from **2b** and **1a** is 52%), it is the most versatile reagent, as it reacts both with phosphate and phosphonic esters (reaction 4).

$$(EtO)_2P(O)X + Mn(NEt_2)_2 \xrightarrow[\text{or } 25°C,\ 96\ h]{0°C,\ 18\ h} (EtO)(Et_2N)P(O)X \qquad (4)$$

1 b, X = OEt; **c**, X = Me

3 b, X = OEt (83%); **f**, X = Me (18%)

The products of reaction (4) were identified in the same way as for the reactions of (**2e**).

Anchimeric assistance. As we have reported before,[1c] (**2a**) is unreactive towards diethyl benzylphosphonate, but reacts smoothly with the α-hydroxybenzyl analoque (**1c**), yielding 65% of the disubstituted product, $(Et_2N)_2P(O)CH(OH)Ph$ (**4c**). We have now confirmed this result (65% of **4c** after 24 at 40°C). We have also found that no reaction can be observed under these conditions when the α-methoxy derivative (**1f**) is used as an organophosphorus substrate. It is most likely therefore that the anchimeric assistance in the exchange of functional groups at phosphorus observed for (**1e**) involves the formation of a covalent α-oxygen—titanium bond in the reactive intermediate (**5**).

$$(\mathbf{1e}) + (\mathbf{2a}) \xrightarrow{-Et_2NH} (EtO)_2P(O) - \underset{\displaystyle OTi(NEt_2)_3}{\overset{\displaystyle |}{CHPh}} \rightarrow (\mathbf{4c}) \qquad (5)$$

5

(2) *IR Measurements.* The relative Lewis acidity of reagents (**2**) was measured in terms of their ability to shift the phosphoryl (ν_{PO}) absorption band of diethyl methylphosphonate (**1c**) occurring in the free ester at 1250 cm^{-1}. The complexation should be expected to decrease the bond order of the phosphoryl group and shift the V_{PO} value towards lower frequencies. While shifts as big as 90 cm^{-1} were reported[3] for the complexes between Ti(IV) and P(IV) substrates, the reported effect of Mn(II) derivatives on dialkyl phosphonic ester involved shifts within the 58–71 cm^{-1} range.[10] Table I lists the effect of reagents (**2**) on the V_{PO} value for (**1c**) in *n*-hexane or *n*-hexane/dichloromethane solutions.

TABLE I

The effect of Lewis acids (**2**) on the phosphoryl stretching frequency (V_{PO}) in diethyl methylphosphonate (**1c**)

Lewis acid (**2**)	(**2**)/(**1c**) molar ratio	V_{PO} free cm^{-1}	V_{PO} complexed cm^{-1}
None		1250	
$Ti(NEt_2)_4$ (**2a**)	0.5	1250	a
	1.0	1250	a
	2.0	1250	a
	4.0	1249	a
	8.0	1248	a
	12.0	1246	a
$Ti(NEt_2)_3Cl$ (**2c**)	0.5	1252	1186, 1144
	1.0	1251	1184, 1146
	2.0	1250	1184, 1146
	4.0	1250 (w)	1194, 1170
	8.0	a	1182 (sh), 1170
	12.0	a	1175, 1156
$Ti(NEt_2)_2Cl_2$ (**2d**)	4.0	a	1990, 1170
	8.0	a	1182 (sh), 1170
	12.0	a	1188, 1166
$Ti(NMe_2)_4$ (**2e**)	0.5	1250	1146
	1.0	1250	1146
	2.0	1250	1146
	4.0	1250 (w)	a
	8.0	1248 (w)	a
	12.0	1246 (v. w)	a
$Ti(NMe_2)_2Cl_2$ (**2f**)	2.0	1247 (v. w)	1177
	4.0	a	1177
$Mn(NEt_2)_2$ (**2b**)	4.0	a	1232, 1202 (sh)
	8.0	a	1232, 1202 (sh)
	12.0	a	1232, 1202 (sh)

a: Absorption band not observed, w: weak, v.w: very weak, sh: shoulder

Reagents (**2**) are weak Lewis acids with respect to (**1c**); the complete disappearance of the "free" P=O absorption band could be obtained only at the four-fold excess of the Lewis acid for (**2d**), (**2f**), and (**2b**); at the eight-fold excess for (**2c**); and could not be achieved for (**2a**) and (**2e**) even at the twelve-fold excess of the titanium reagent. Tetrakisdialkylamides are the weakest Lewis acids among reagents (**2**). (**2a**), even in large excess, yields only small (4 cm^{-1}) shift of the P=O band, with no new absorption, due to the fully complexed species, being observed. This indicates weak interactions with the phosphoryl group, and corresponds to the low reactivity observed for (**2a**) with respect to substrates (**1**). For (**2e**), the gradual decrease in the intensity of the "free" P=O absorption band is observed, together with the appearance of the new band (1146 cm^{-1}) corresponding to the complexed form. This new band disappears at higher (**2e**)/(**1c**) ratios, indicating relatively fast exchange of the functional groups in the intermediate complex. This result corresponds to the reactivity studies which

showed that in the reaction between (**1c**) and (**2e**) (**2e**/**1c** = 2), most of (**1c**) remained unchanged after 24 h, with only *ca* 10% of the monosubstitution. The dialkylamido chlorides (**2c**), (**2d**), and (**2f**) show increased Lewis acidity, and give rise to the new bands, corresponding to the respective (**2**), (**1c**) complexes, even at relatively low concentrations of (**2**). As expected, the effect of the dichloro derivatives is stronger than that of the monochloro compounds; the reactivity studies indicate that this effect is counterbalanced by the decrease in the number of NR_2 groups available for the exchange. The average difference between the V_{PO} values for the "free" (**1c**) and its complexes with titanium-containing reagents (**2**) is $\Delta V = 81\ cm^{-1}$; comparable with the values observed for other Ti(IV), O=PY_3 complexes. The manganese compound (**2b**) shows strong binding properties (no "free" V_{PO} observed for **2b**/**1c** = 4), but the resulting shift (av. $\Delta V = 33\ cm^{-1}$) is significantly smaller.

In conclusion, the net reactivity of reagents (**2**) with respect to substrates (**1**) in the exchange of functional groups (Equation 1) is a function of the electronic effects (electrophilicity of phosphorus atom and Lewis acidity of the metal), and steric requirements of both substrates. The qualitative order of decreasing reactivity of (**2**) towards the phosphoryl centre is as follows: (**2b**) > (**2e**) > (**2f**) > (**2d**) ≈ (**2c**) > (**2a**) > (**2g**). The i.r. measurements indicate that the complexing ability of (**2**) with respect to phosphonate substrate (**1c**) decrease in the order: (**2b**) ≈ (**2f**) ≈ (**2d**) > (**2c**) > (**2e**) > (**2a**). Although both sequences show considerable analogy, there are however some differences with respect to individual reagents. We ascribe the high position of (**2e**) on the reactivity scale to the lower steric bulk of the NMe_2 groups (as compared with NEt_2 or $NiPr_2$ groups), more important in the substitution than in the Lewis acid-base interactions. The manganese reagent (**2b**) is probably the most reactive among the compounds (**2**) studied. We believe that this results from both, greater Lewis acidity of Mn(II) than Ti(IV) derivatives,[11] and from steric factors, more favourable in the case of a disubstituted than a tetrasubstituted reagent (**2**).

As far as the phosphoryl substrates are concerned, we confirmed much greater reactivity of dialkyl phosphites, as compared with other phosphoryl compounds (trialkyl phosphates, phosphonic esters). This marked difference in reactivity suggests that the group transfer from metal to phosphorus is strongly favoured when at least one substituent at the phosphoryl centre (hydrogen atom) has low steric requirements.

EXPERIMENTAL

N.M.R. spectra were recorded on a superconducting FT Bruker AC300 spectrometer, and the chemical shift values are given relative to TMS (^1H, ^{13}C) or trimethyl phosphate (^{31}P). I.r. spectra were recorded on a Beckman 4250 spectrophotometer. Solvents, reagents, and substrates were dried and purified in the conventional manner. Substrates (**1**) were either commercially available, or prepared according to the literature procedures. All reactions were carried out under dry N_2.

Diethyl methylphosphonate (**1c**) was prepared from triethyl phosphite and iodomethane.[12] Bp 114–116°C (9.5 mm); lit.[12] bp 64–65°C (2 mm). ^1H n.m.r. ($CDCl_3$): δ 1.06 (6H, t, J_{HH} 7.1 Hz, 2 × CH_3 of Et); 1.19 (3H, d, J_{HP} 17.5 Hz, PCH_3); 3.82 (4H, m, 2 × OCH_2). $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$): δ 27.95. I.r. (neat): 1250 (V_{PO}), 1052, 1026 (V_{POC}) cm^{-1}.

Diethyl trichloromethylphosphonate (**1d**) was prepared from triethyl phosphite and CCl_4.[13] Bp 124–126°C (10 mm); lit.[13] bp 135–137°C (16 mm). ^1H n.m.r. ($CDCl_3$): δ 1.35 (6H, t, J_{HH} 7.0 Hz, $2 \times CH_3$ of Et); 4.35 (4H, d of quart., J_{HH} 7.0 Hz, J_{HP} 7.6 Hz, $2 \times OCH_2$). $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$): δ 16.10, 16.16 ($2 \times CH_3$); 66.78 (d, J_{CP} 7.0 Hz, $2 \times OCH_2$); 88.5 (d, J_{CP} 188.6 Hz, Cl_3C). $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$): δ 3.04.

Diethyl α-hydroxybenxylphosphonate (**1e**) was prepared as described before.[1c]

Preparation of α-methoxybenzylphosphonate (**1f**). Sodium (0.33 g) was dissolved in the solution of diethyl phosphite (2.0 g) in benzene (20 ml), and benzaldehyde (1.5 g) was added to this solution with stirring. The mixture was stirred for 10 min. Iodomethane (2.1 g) was added and the mixture was stirred at room temperature overnight. After aqueous work-up and extraction with benzene, the benzene solution was evaporated under reduced pressure, and the residue was purified by column chromatography (silica gel 60, 70 to 230 mesh ASTM, ether). The fraction of R_f 0.44 was further purified by distillation ("bulb to bulb") at oven temp. 140°C (1 mm). Yield 1.76 g (47%). ^1H n.m.r. ($CDCl_3$): δ 1.18, 1.21 (6H, two triplets, J_{HH} 7.0 Hz, $2 \times CH_3$ of Et); 3.35 (3H, s, OCH_3); 4.01 (4H, m, $2 \times CH_2$ of Et); 4.46 (1H, d, J_{HP} 15.5 Hz, PCH); 7.33 (3H, m, meta and para H's of Ph); 7.40 (2H, d, J_{HH} 7.8 Hz, ortho H's of Ph). ^{13}C $\{^1H\}$ n.m.r. ($CDCl_3$): 16.23 ($2 \times CH_3$); 58.52 (d, J_{CP} 14.9 Hz, $2 \times OCH_2$); 62.90 (OCH_3); 80.39 (d, J_{CP} 169.2 Hz, PCH); 127.9, 128.2 (o,m,p-aromatic H's); 134.3 (aromatic C-1). $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$): δ 16.78. M.S.: m/z 258(5.3%)(M^+), 153(7.7%)(M-PhCO), 121(100%)(PhCHOMe).

Ethyl N,N'-bisdiethylphosphordiamidate, $EtOP(O)(NEt_2)_2$. Prepared from ethyl phosphorodichloridate and diethylamine.[14] 90%, bp 80–81°C (0.5 mm). ^1H n.m.r. ($CDCl_3$): δ 1.11 (12H, t, J_{HH} 7.2 Hz, $4 \times CH_3$ of NEt); 1.33 (3H, t, J_{HH} 7.0 Hz, CH_3 of OEt); 3.11 (8H, m, $4 \times NCH_2$); 4.15 (2H, m, OCH_2). $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$): δ 13.7.

Preparation of (**2a**), (**2c**), *and* (**2d**).[15] Diethylamine, lithium wire and styrene (molar ratio 1:1:0.5) in ether were heated under reflux in the atmosphere of nitrogen for 4 h, cooled to −60°C, and the required stoichiometric quantity of $TiCl_4$ dissolved in toluene was added to the mixture. The mixture was then stirred for 18 h, volatile compounds were removed under reduced pressure, and the products (**2**) were purified by distillation. (**2a**) (68%), light orange liquid, bp 110–120°C (0.5 mm). ^1H n.m.r. (C_6D_6): δ 1.09 (t, J_{HH} 7.0 Hz, CH_3), 3.56 (q, J_{HH} 7.0 Hz, NCH_2) (signals ratio 1.5:1). $^{13}C\{^1H\}$ n.m.r. (C_6D_6). δ 15.6 (CH_3), 45.4 (NCH_2). (**2c**) (53%), dark-orange liquid, bp 100–110°C (0.2 mm). ^1H n.m.r. (C_6D_6): δ 1.03 (t, J_{HH} 7.1 Hz, CH_3), 3.51 (q, J_{HH} 7.1 Hz, NCH_2) (signals ratio 1.5:1), $^{13}C\{^1H\}$ n.m.r. (C_6D_6): δ 14.9 (CH_3), 45.6 (NCH_3). (**2d**) (48%), red liquid, bp 95–97°C (0.2 mm). ^1H n.m.r. (C_6D_6): δ 0.91 (t, J_{HH} 7.0 Hz, CH_3), 3.59 (q, J_{HH} 7.0 Hz, NCH_2) (signals ratio 1.5:1). $^{13}C\{^1H\}$ n.m.r. (C_6D_6): δ 14.2 (CH_2), 47.3 (NCH_2).

Preparation of (**2e**) *and* (**2f**).[16] A stoichiometric quantity of BuLi (1.6 M solution in hexane) was added to the solution of dimethylamine in ether (2.5 M) at −60°C, the mixture was allowed to warm up to room temperature, and was then stirred for 1 h. After cooling to −60°C, the required stoichiometric quantity of $TiCl_4$ dissolved in toluene was added dropwise to the reaction mixture, which was then stirred at room temperature overnight. Volatile compounds were removed under reduced pressure, and the products were purified by distillation. (**2e**) (57%), orange liquid, bp 52–55°C (0.4 mm) ^1H n.m.r. (C_6D_6): δ 3.09 (s, CH_3). (**2f**) (32%), red liquid, solidifying at 5°C; bp 94–97°C (1.5 mm). ^1H n.m.r. (C_6D_6): δ 3.15 (s, CH_3). $^{13}C\{^1H\}$ n.m.r. (C_6D_6): δ 46.41 (CH_3).

Preparation of **2g**. (**2g**) was prepared[15] as described for (**2a**), from the required quantities of diisopropylamine, lithium, styrene, and $TiCl_4$. Yield 20%; red oil (solidifying at 5°C), bp 113–117°C (0.3 mm). ^1H n.m.r. ($CDCl_3$): δ 1.36 (d, J_{HH} 7.0 Hz, CH_3), 3.92 (m, CH) (signals ratio 6:1). $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$): δ 25.4 (CH_3), 50.0 (CH).

Preparation of (**2b**).[1b] Diethylamine (1.4 g, 19.0 mmol) was added to 1.6 M solution of BuLi in hexane (11.2 ml, 17.9 mmol), and the mixture was stirred at 0°C for 1 h. $MnCl_2$ (1.09 g, 8.7 mmol; dried overnight at 100°C and 0.2 mm vacuum) was added portionwise to this solution at −20°C with stirring under nitrogen. THF (6 ml) was added, and the mixture was stirred at room temperature for 2 h. During this time a white precipitate of LiCl has formed, and the solution has changed its color to deep red. These solutions were used immediately for reactions with substrates (**1**).

Reactions of reagents (**2**) *with organophosphorus substrates* (**1**). *General procedure.* Substrate (**1**) was added to two mole-equivalents of (**2**) (neat, or, in the case of **2f** and **2g**, dissolved in a minimum

volume of CH_2Cl_2), sealed, and the sealed tube was left at the required temperature for the chosen period. After opening the tube, the mixture was quenched with water, extracted with CH_2Cl_2, the organic solution dried ($MgSO_4$), and the solvent removed under reduced pressure. The n.m.r. (^1H and ^{31}P) spectra of the residue were recorded and, depending on the composition of the reaction product, the components were either purified by distillation, or identified in the mixture from their spectroscopic data by comparison with those of the independently prepared samples, or described in the literature.

Unreacted (**1b**), (**1c**), and (**1f**) were recovered by distillation. (**1b**); bp 75–77°C (5 mm); ^1H n.m.r. ($CDCl_3$): δ 1.35 (t, J_{HH} 7.0 Hz, CH_3), 4.09 (quint., $J_{HH} = J_{HP} = 7.0$ Hz, CH_2) (signals ratio 1.5:1); ^{31}P n.m.r. ($CDCl_3$): δ −3.2. (**1c**), (**1f**): as described in the preparation. (**3c**) was obtained in the reaction between (**1a**) and (**2g**) at 25°C for 24 h; 57%, distilled ("bulb to bulb"), oven temp. 110°C (0.6 mm); ^1H n.m.r. ($CDCl_3$): δ 1.18 (12H, d, J_{HH} 6.9 Hz, 4 × CH_3 of $NiPr_2$), 1.26 (3H, t, J_{HH} 6.9 Hz, CH_3 of Et), 3.46 (2H, d of hept., J_{HH} 6.9 Hz, J_{HP} 11.2 Hz, 2 × NCH), 3.98 (2H, d of q, J_{HH} 6.9 Hz, J_{HP} 9.0 Hz, OCH_2), 6.82 (1H, d, J_{HP} 635.2 Hz, PH). $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$): δ 10.4. $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$): δ 16.5 (CH_3 of Et), 22.8 (CH_3 of iPr), 45.1 (d, J_{CP} 6.2 Hz, NCH), 59.3 (d, J_{CP} 4.7 Hz, OCH_2). (**4a**) was obtained in the reaction between (**1a**) and (**2a**) (25°C, 1 h); 61%, distilled, bp 80–82°C (1 mm). ^1H n.m.r. ($CDCl_3$): identical to that given in Reference 1a. ^{31}P n.m.r. ($CDCl_3$): δ 17.9.

Reaction of (**1d**) with (**2a**) (24°C, 48 h) yielded a mixture which could not be separated to individual compounds. ^{31}P n.m.r. spectrum of the product indicated complete disappearance of (**1d**), and the formation of one major, and two minor phosphorus-containing products (δ, 2.50, −0.25, and −3.79 ppm, respectively). ^1H n.m.r. spectrum showed the absence of the ethyl ester groups (no signals in the 4.0–5.0 ppm range), and the presence of three groups of the $PNCH_2CH_3$ signals (major: δ 3.98, quintet, J_{HP} 7.2 Hz; minor: δ 3.60, m, and δ 3.45, quintet $J_{HH} = J_{HP}$ 7.1 Hz), three groups of the $PCHCH_2CH_3$ signals (major: δ 2.52, q, J_{HH} 7.2 Hz; minor: δ 2.71, q, J_{HH} 7.1 Hz, and 2.28, q, J_{HH} 7.1 Hz), and the corresponding signals of the $PNCH_2CH_3$, and $PCNCH_2CH_3$ protons. On this basis the product was tentatively identified as the mixture of tetrakisethyl phosphonic diamides, $(Et_2N)_nCCl_{3-n}P(O)(NEt_2)_2$.

(**4b**) was prepared from (**1a**) and (**2e**) after 1 h at 15°C; 95%. Due to the known[17b] thermal instability of (**4b**), this product was not distilled. The n.m.r. spectrum of crude reaction product showed however the presence of only one component: ^1H n.m.r. ($CDCl_3$): δ 2.62 (12H, d, J_{HP} 10.0 Hz, 4 × NMe); 6.73 (1H, d, J_{HP} 570.0 Hz, PH), $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$): δ 18.1. These spectroscopic data were in full agreement with those given for (**4b**) in the literature.[17]

Reaction between (**1b**) and (**2e**). After the incubation period of 24 h at 40°C and the work-up, the n.m.r. spectra of the reaction product were recorded. It was found that the product consisted of unreacted (**1b**) (ca. 86%); $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$): δ −3.19, and of (**3d**) (ca. 14%). $^{31}P\{^1H\}$ n.m.r. ($CDCl_3$): δ 8.59. ^1H n.m.r. ($CDCl_3$): δ 1.29 (6H, t, partially overlapping with that of **1b**, J_{HH} 7.2 Hz, 2 × CH_3 of OEt), 2.64 (6H, d, J_{HP} 10.0 Hz, 2 × CH_3 of $PNMe_2$: lit.[18]: $PNMe_2$ of **3d**: δ 2.68, d, J_{HP} 10.0 Hz), 3.85 (4H, m, overlapping with that of **1b**, 2 × OCH_2).

Reaction between (**1c**) and (**2e**). The reaction was carried out at 40°C for 24 h. The ^{31}P n.m.r. spectrum of the reaction product revealed the presence of two phosphorus-containing compounds: unreacted (**1c**) ($CDCl_3$, δ 28.10) and another product (δ 32.76); signals ratio 11.5:1. ^1H n.m.r. spectrum ($CDCl_3$) also demonstrated the presence of two components. The major was identified as unreacted (**1c**): δ 1.05 (6H, t, J 7.1 Hz), 1.21 (3H, d, J 17.5 Hz), 3.80–4.00 (4H, m). In addition, the mixture contained the minor product which was identified as (**3e**): δ ca. 1.04 (t, overlapping with that of **1c**, CH_3 of OEt), ca. 1.18 (d, partially overlapping with that of **1c**, CH_3P), 2.61 (d, J_{HP} 9.3 Hz, CH_3 of $PNMe_2$), ca. 3.8 (m, overlapping with that of **1c**, OCH_2). Integration indicated that the two products existed in the 10:1 ratio.

Reactions of (**1a**) with (**2c**) and (**2d**). Both reactions were carried out for 1 h at 25°C, and in both cases (**4a**) was the only product observed. It was isolated by distillation in 93% and 87% in case of (**2c**) and (**2d**), respectively, and the n.m.r. data (^1H and ^{31}P) were identical to those given above for (**4a**) prepared from (**1a**) and (**2a**).

Reaction of (**1a**) with (**2f**). After 1 h at 25°C the reaction gave (**4b**) as the only product in almost quantitative yield. (**4b**) was identified by its ^1H and ^{31}P n.m.r. spectra which were identical to those obtained for (**4b**) prepared from (**1a**) and (**2e**) (see above).

Reaction of (**1a**) with (**2b**). (i) After 24 h at 25°C the reaction product consisted, in agreement with our earlier report,[1b] of unreacted (**1a**) (39%), $(EtO)(Et_2N)P(O)H$ (**3a**) (20%), and (**4a**) (41%). The products were identified and determined by n.m.r. spectroscopy.[1b] (ii) When the reaction time was doubled (48 h), (**3a**) was absent in the reaction product, which consisted of unreacted (**1a**) (48%) and (**4a**) (52%).

Reaction of (**1b**) with (**2b**). As reported before,[1b] when (**1b**) was treated with two mole-equivalents of (**2b**) at 0°C for 18 h, N,N-diethylphosphoroamidate, $(EtO)_2P(O)NEt_2$ (**3b**) was formed in 83%

yield. The product was purified by distillation [bp 90–92°C (0.3 mm)] and identified by its ^1H and ^{31}P n.m.r. (δ 7.60) spectra.[1b]

Reaction of (**1c**) with (**2b**). The reaction mixture was kept at 25°C for 96 h and worked-up in the usual way. $^{31}P\{^1H\}$ n.m.r. spectrum of the reaction product revealed the presence of two phosphorus-containing compounds: unreacted (**1c**) (δ 27.96) (82%) and another product (18%), δ 31.06. This product was identified as N,N-diethyl ethyl methylphosphonoamidate, $MeP(O)(OEt)(NEt_2)$ (**3f**). ^1H n.m.r. ($CDCl_3$): δ 0.92 (6H, t, J_{HH} 7.0 Hz, 2 × CH_3 of NEt), ca. 1.10 (t, partially overlapping with that of **1c**, CH_3 of OEt), ca. 1.17 (d, partially overlapping with the CH_3 signal of the OEt groups in **1c**, CH_3P), 2.90 (4H, d of q, J_{HH} 7.1 Hz, J_{HP} 10.4 Hz, 2 × NCH_2), ca. 3.9 (m, overlapping with that of **1c**, OCH_2). Integration data indicate that the mixture contains 83% of (**1c**) and 17% of (**3f**).

Reaction of (**1e**) with (**2a**). In agreement with our earlier report,[1c] (**1e**) was converted after 24 h at 40°C into (**4c**) in 65% yield. (**4c**) was purified and identified as described in Reference 1c.

I.r. measurements. A required volume of the solution of (**2**) in hexane or dichloromethane of known concentration was added to the required volume of the stock solution of (**1c**) in *n*-hexane to obtain the required (**2**):(**1c**) molar ratio. The concentration of (**1c**) in the final solution was ca. 0.1 M. After good mixing, the solution was transferred to an i.r. cell, and the i.r. spectrum was recorded against the reference cell containing the solution of a given reagent (**2**) in the same solvent and of the same concentration as in the sample cell.

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