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PAPER

Phosphorus containing mixed anhydrides—their preparation, labile behaviour and potential routes to their stabilisation†

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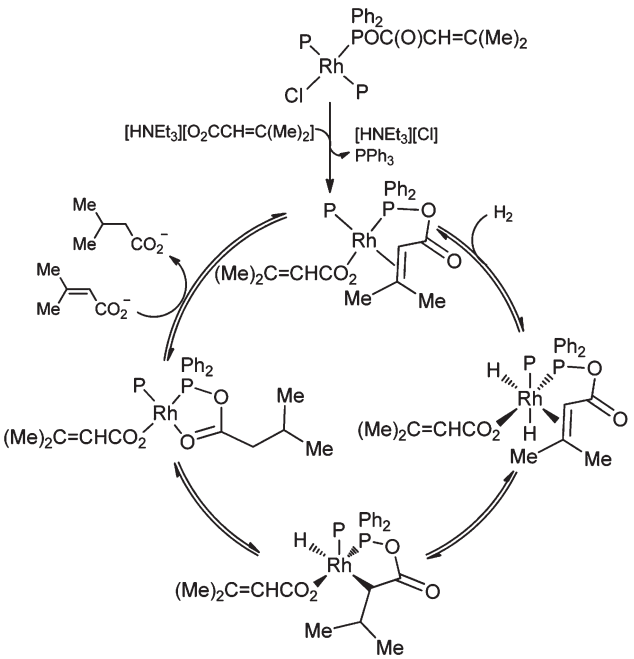
Simple mixed anhydrides are known to pose synthetic difficulties relating to their thermal lability and ways to stabilise such mixed anhydride systems by relying on either electronic or steric effects were therefore explored. Thus, a series of acyloxyphosphines and acylphosphites derived from either propanoic acid or phenylacetic acid were prepared and their in solution stability assessed. These compounds were, where stability allowed, fully characterised using standard analytical techniques. NMR studies, in particular, unearthed interesting coupling behaviour for a number of the acyloxyphosphines and acylphosphites as well as their rearrangement products which could be linked to their chiral nature. Furthermore, the crystal structures for three of the prepared mixed anhydrides were determined using X-ray crystallography and are reported herein.

Introduction

We have previously reported that mixed anhydrides or (acyloxy) diorganylphosphines of the general form $Ph_2POC(O)R^1$[1], where R^1 contains 2,3-unsaturation can be used for the hydrogenation of the parent acrylic acid when reacted with hydrogen in the presence of rhodium complexes such as Wilkinson's catalyst.[1] The mechanism by which these reactions occur involves important steps at the metal centre and at P (Scheme 1).[1] Based on the principle of microscopic reversibility the reverse reactions, dehydrogenations of saturated mixed anhydrides, should in theory also be possible and should occur through C–H activation promoted by binding of the P atom, providing a potential new route to their functionalisation.

Saturated mixed anhydrides are accessible *via* a number of synthetic routes. They can be prepared readily either by the treatment of chlorophosphines with sodium carboxylates or carboxylic anhydrides or by reaction with carboxylic acids in the presence of an amine base.[2] However, their propensity to undergo spontaneous and irreversible condensation and rearrangement reactions, even at low temperatures, is known to complicate both the synthesis and in particular the purification of these compounds.[2–4]



Scheme 1 Mechanism for the hydrogenation of 3-methylbut-2-enoic acid using Rh complexes of mixed anhydrides of diphenylphosphinous acid and acrylic acids.[1] P = PPh_3.

Surprisingly, unsaturated mixed anhydrides derived from acrylic acids such as but-2-enoic acid {$CH_3CH{=}CHCO_2H$}, 3-methylbut-2-enoic acid {$(CH_3)_2C{=}CHCO_2H$}, pent-3-enoic acid {$(CH_3)_2C{=}CHCH_2CO_2H$)}, and 2-methyl-3-phenylacrylic

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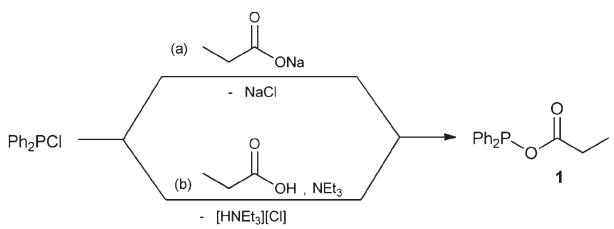
acid {PhCH=C(Me)CO_2H} prove to be remarkably stable in solution at room temperature and indefinitely stable in the solid state under an inert atmosphere.[5] At the other extreme, unsaturated mixed anhydrides derived from the less substituted acrylic acid {CH_2=CHCO_2H} and but-3-enoic acid {CH_2=$CHCH_2CO_2$H}, rearrange rapidly in solution to yield tetraphenyldiphosphine monoxide {$Ph_2PP(O)Ph_2$} together with carboxylic anhydrides as the major products.[6,7] Although no mechanistic studies for this dimerisation have been performed, the formation of $Ph_2PP(O)Ph_2$ is postulated to occur *via* an intermolecular disproportionation reaction.[6]

In a number of more recent reports, changing from chlorophosphines to chlorophosphites as precursors to mixed anhydrides was shown to afford (acyl)phosphites with enhanced thermodynamic stability.[8–11] However, despite this general improved stability of these compounds, the formation of byproducts during the synthesis of more simple (acyl)phosphites was still noted.[10] Stable (acyl)phosphites have shown promise as ligands in catalysts for both isomerisation[8] and asymmetric hydroformylation[11] as well as asymmetric hydrogenation reactions[10] and have also been employed as precursors in the preparation of complex diaryl phosphonates of medicinal importance.[9]

Considering the discussed challenges surrounding the preparation and isolation of stable mixed anhydrides, an investigation into possible ways to stabilise such compounds was launched and the outcome of this study is reported herein. A series of new (except one) mixed anhydrides derived from chlorophosphines or chlorophosphites and propanoic acid were prepared and fully characterised where their stability allowed. In later work, we shall report the coordination chemistry and catalytic potential of these interesting ligands.

Results and discussion

The incentive for this study came from difficulties experienced during the preparation of the simple mixed anhydride, (propanoyloxy)diphenylphosphine, **1**. The synthesis of this compound has been reported before by Bollmacher and Sartori[12] in a study directed towards the synthesis of Cu(I) and Ag(I) complexes of this ligand. During their studies, the desired mixed anhydride could be prepared in yields of 86–90% by the treatment of chlorodiphenylphosphine with sodium propanoate. Following a similar approach, **1** could be prepared by treatment of a suspension of sodium propanoate in tetrahydrofuran with an equimolar amount of chlorodiphenylphosphine at 0 °C for 1 h and then a further 2 h at room temperature [Scheme 2(a)]. Alternatively, this



Scheme 2 Reaction scheme for the preparation of (propanoyloxy)-diphenylphosphine (**1**) *via* (a) a route reported by Bollmacher and Sartori[12] and (b) an adaptation of the procedure reported by Cupertino and Cole-Hamilton.[5]

compound could also be prepared, using an adaptation of a procedure proposed by Cupertino and Cole-Hamilton,[5] by treatment of a propanoic acid solution in thf at −10 °C with chlorodiphenylphosphine and triethylamine for 10 min [Scheme 2(b)].

However, although **1** could be prepared in high purity using either one of the described methods, reactions were on occasions complicated by the facile rearrangement of **1** in solution to tetraphenyldiphosphine monoxide, $Ph_2P(O)PPh_2$. Moreover, following successful preparation of this compound, rearrangement would generally take place during storage, even at temperatures as low as −22 °C, to afford large amounts of $Ph_2P(O)PPh_2$ as a white solid. This rearrangement has also been observed by Bollmacher and Sartori[12] during attempts to purify the ligand by fractional distillation. Similarly, rearrangements of this type have also been described by Irvine and co-workers[6] for simple unsaturated mixed anhydrides derived from chlorodiphenylphosphine and acrylic or vinylacetic acid.

In view of the difficulties associated with the thermal stability of **1**, an investigation into potential ways to stabilise mixed anhydrides of this kind was launched. Encouraged by literature reports on more stabile (acyl)phosphites,[8–11] we envisaged two possible approaches to achieving more stable ligands and preventing unwanted side reactions—approach **A**: by decreasing the nucleophilicity of the phosphorus atom through the incorporation of electron withdrawing heteroatoms directly bonded to phosphorus, or approach **B**: by increasing the steric requirements of the groups attached to phosphorus so as to inhibit neighbouring molecules from participating in intermolecular disproportionation reactions.

With the proposed strategies in mind, a collection of compounds was prepared and their stability in solution as well as under solvent free conditions assessed mainly by ^{31}P NMR spectroscopy. This collection of compounds can be divided into three series (Fig. 1), where ***series I*** comprises of mixed anhydrides **1–3** which contain neither electron withdrawing groups bonded directly to phosphorus (with the exception of the acyloxy moiety) nor bulky substituents on the phenyl rings, while ***series II*** includes mixed anhydrides **8–9** which do possess electron withdrawing atoms directly bonded to the phosphorus atom, but no bulky substituents on the rings. Finally, ***series III*** comprises of mixed anhydrides **10–13** that bear both electron withdrawing groups attached to phosphorus and bulky ring substituents.

It is worth mentioning, however, that together with a gain in stability, approach **A** would also bring about a loss in the overall electron richness of the ligand, which might prove detrimental to their later application in C–H activation. A fine balance will, therefore, need to be reached between their stability and donor abilities. For this reason, diols containing electron donating alkyl groups as ring substituents were chosen for the preparation of the chlorophosphite precursors to compounds **10–13** of ***series III*** in an attempt to counterbalance the electron withdrawing effects of the oxygen atoms to some extent with inductive effects. The function of the alkyl substituents in the 3 and 3′-positions of the rings is dual in this series, acting both as donors of electron density and sterically demanding groups.

Within ***series I***, the preparation and unstable nature of (propanoyloxy)diphenylphosphine, **1**, has already been described. To make this series more comprehensive, the related (phenylacetyloxy)diphenylphosphine (**2**) was prepared from

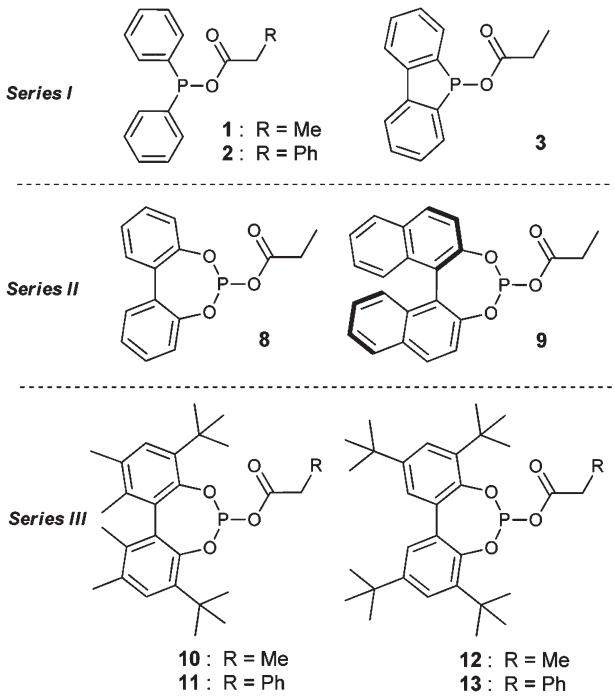
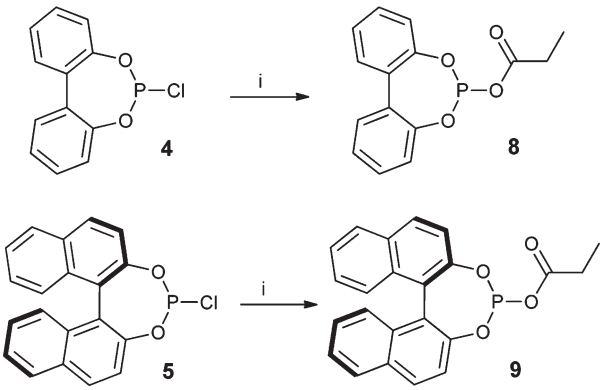


Fig. 1 ***Series I***—mixed anhydrides **1–3** containing neither electron withdrawing groups bonded to the phosphorus (with the exception of the acyloxy moiety) nor bulky substituents on the phenyl rings; ***Series II*** —mixed anhydrides **8–9** with electron withdrawing atoms directly bonded to the phosphorus atom, but no bulky ring substituents and ***Series III***—mixed anhydrides **10–13** bearing both electron withdrawing groups directly attached to phosphorus and bulky ring substituents.

phenylacetic acid using a similar procedure to that used for **1**. Not surprisingly, the behaviour of this compound in solution as well as in the solid state was similar to that of **1**. In addition, an attempt to prepare the related mixed anhydride 5-(propanoyloxy)dibenzophosphole, **3**, where the phosphorus atom forms part of a phosphole ring, was made. We expected this compound to be even more prone to rearrangement reactions, since the greater C–P–O angles (brought about by ring constraints) make the phosphorus atom even more accessible to neighbouring molecules. A suspension of sodium propanoate in thf was therefore treated with 5-chlorodibenzophosphole at room temperature for 2 h, after which the formed NaCl was removed by filtration and all volatiles evaporated under reduced pressure to furnish the crude product as a white solid. However, as anticipated, this solid solely consisted of rearrangement products of which the $Ph_2P(O)PPh_2$ analogue [5,5′-bibenzo[*b*]phosphindole] 5-oxide, constituted the major component. Although it is probable that the lifetime of **3** can be prolonged by lowering the reaction temperature, no further efforts to synthesise and isolate this compound were made.

Next, the effects of electron withdrawing atoms (approach **A**) were explored by constructing ***series II***. Following a literature based procedure,[13,14] chlorophosphites **4** and **5** were reacted with a suspension of sodium propanoate in thf at 45 °C for 2 h to afford (propanoyl)phosphites **8** and **9**, respectively, upon work-up (Scheme 3). Overall, **8** and **9** displayed much greater stability than the (acyloxy)phosphines and no rearrangement products of



Scheme 3 Reaction scheme for the preparation of compounds **8** and **9** from chlorophosphites **4** and **5**, respectively. (i) Sodium propanoate, thf, 45 °C, 2 h.

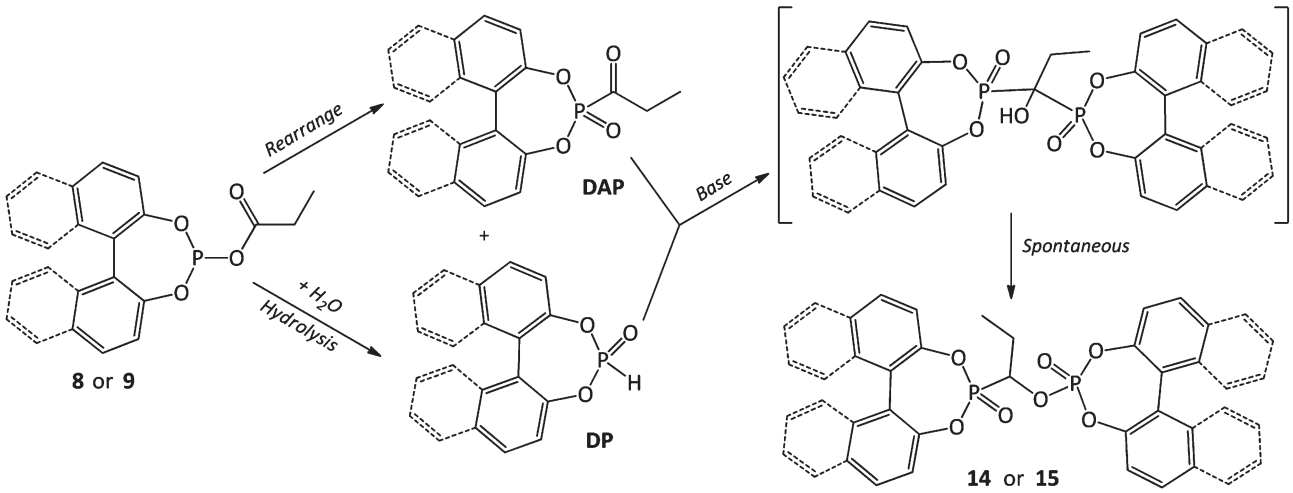
the general formula $(RO)_2P(O)P(OR)_2$ were observed for these compounds.

^{31}P NMR spectra, however, did reveal the presence of minor amounts of by-products **14** and **15** (for **8** and **9**, respectively; Scheme 4). These by-products most likely originated from the base catalysed reaction of dialkylphosphonates (**DP**) with dialkyl acylphosphonates (**DAP**) (Scheme 4), and similar reaction pathways have been reported in the literature for the preparation of tetraethyl 1-hydroxyalkylidenediphosphonates and their isomeric phosphates.[15] These reactions initially generate 1-hydroxyalkylidenediphosphonate esters as intermediates which then undergo spontaneous rearrangement to the more stable phosphates, **14** and **15**. The dialkylphosphonate (**DP**) precursors are generated by hydrolysis of the mixed anhydrides in the presence of trace amounts of water, while the dialkyl acylphosphonates (**DAP**) are formed by the Arbuzov rearrangement of the ligands **8** and **9**. Rearrangements of this type are not uncommon for mixed anhydride ligands and similar rearrangements have been noted before by Lindner and Wuhrmann for (perfluoracyloxy)-diorganylphosphines.[2]

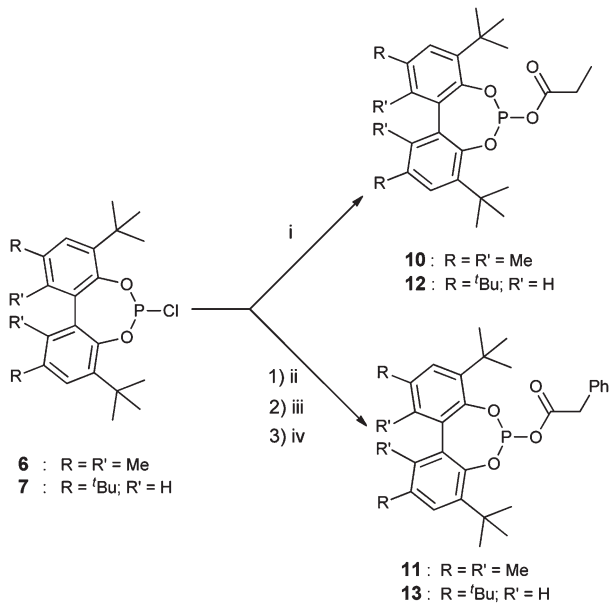
Compounds **8–9** are air and moisture sensitive white solids which are soluble in most aprotic organic solvents such as chloroform, dichloromethane, thf, diethyl ether, toluene, hexane and pentane (sparingly). Furthermore, compounds **8–9** are indefinitely stable both in solution and the solid state at room temperature, provided that a dry, base-free and inert atmosphere is maintained. These findings are in good agreement with literature reports on the general stability of (acyl)phosphites and therefore indicate that a moderate increase in stability can be achieved by the use of electron withdrawing groups on phosphorus.[9,10]

Finally, to complete the collection, mixed anhydrides **10–13** (constituting ***series III***) were prepared from their corresponding chlorophosphites **6–7**[14] (Scheme 5) using the same methodologies as described for the preparation of compounds **8** and **9**.

Following approach **B**, sterically demanding *tert*-butyl groups were included as substituents in the 3-positions of both phenyl rings, shielding the phosphorus centre from neighbouring molecules. This stabilisation approach proved very successful with measured NMR spectra providing no evidence for the presence of any disproportionation products. Moreover, the analytically



Scheme 4 Formation of by-products **14** and **15** from ligands **8** and **9** in the presence of water and base.



Scheme 5 Reaction scheme for the preparation of compounds **10–13** from chlorophosphites **6** and **7**. (i) Sodium propanoate, thf, 45 °C, 2 h; (ii) phenylacetic acid, −10 °C; (iii) NEt_3, −10 °C, 20 min; (iv) 20 min, room temperature.

pure compounds **10–13** are fairly air stable white solids that proved remarkably stable towards rearrangement in solution even at temperatures as high as 60 °C. In addition, these compounds are indefinitely stable in the solid state under an inert atmosphere, emphasizing the substantial increase in stability brought about by the incorporation of steric bulk. Although **10–13** are incompatible with protic solvents, they are soluble in most other organic solvents such as chloroform, dichloromethane, tetrahydrofuran, diethyl ether, toluene and even very non-polar solvents such as hexane and pentane. Owing to the superior stability of these compounds, single crystals suitable for crystal structure determination could be obtained for **10**, **11** and **13**, and are discussed in more detail in the crystallographic section.

Spectroscopic analysis

Nuclear magnetic resonance

^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectroscopic data were collected for dichloromethane-d_2 or chloroform-d_1 solutions of **1–13** and are listed in detail under the Experimental section.

In the $^{31}P\{^{1}H\}$ NMR spectrum of **1**, disproportionation to $Ph_2P(O)PPh_2$ is easily recognised, by the appearance of two doublets (at δ 36.9 and δ −22.1, $^{1}J_{P-P}$ = 229.4 Hz) at the expense of **1** (δ 98.9s, Fig. 2) and are in good agreement with the literature values reported for this compound.[16] Similarly, the by-products **14** and **15** show very distinctive spectral profiles in the ^{31}P NMR spectra of ligands **8** and **9**, respectively, and could be identified using standard 1D and 2D NMR spectroscopic techniques (^{13}C-DEPT, COSY, HMQC, HSQC). In the ^{1}H NMR spectrum of **8**, the central –C*H*– group of the by-product **14** gives rise to a very distinctive multiplet at δ 5.41 (Fig. 3) as a result of coupling to phosphorus in addition to the diastereotopic methylene protons. Likewise, the methylene protons give rise to a complex multiplet at δ 2.34, while the methyl group gives rise to a doublet of doublets observed as a broad triplet at δ 1.39.

In the ^{31}P NMR spectrum, the two distinct P-atoms of **14** are observed as doublets at δ 1.9 and δ 26.4 ($^{4}J_{P-P}$ = 24.1 Hz). Furthermore, in the 2D HMQC spectrum these resonances display ^{1}H–^{31}P correlations of different intensities and are therefore consistent with a structure where one of the phosphorus atoms is incorporated in a phosphate group. In contrast, the by-product **15** gives rise to two sets of doublets in the $^{31}P\{^{1}H\}$ NMR spectrum with distinct ^{31}P–^{31}P coupling constants (Fig. 4) owing to the planar chirality of the binol and the chirality at the central carbon atom.

Since the starting diol used during the preparation of **9** was fixed as the (*R*)-isomer, only two possible diastereomers can be formed for this specific by-product; they are (*R*, *S*, *R*) and (*R*, *R*, *R*). The two distinct diastereomers observed in the ^{31}P NMR spectrum of **15**, display slightly different ^{31}P–^{31}P coupling constants of 23.3 Hz and 28.9 Hz, respectively.

In the ^{13}C NMR spectra of **10** and **11** all carbon atoms are chemically inequivalent owing to the rotated disposition of the

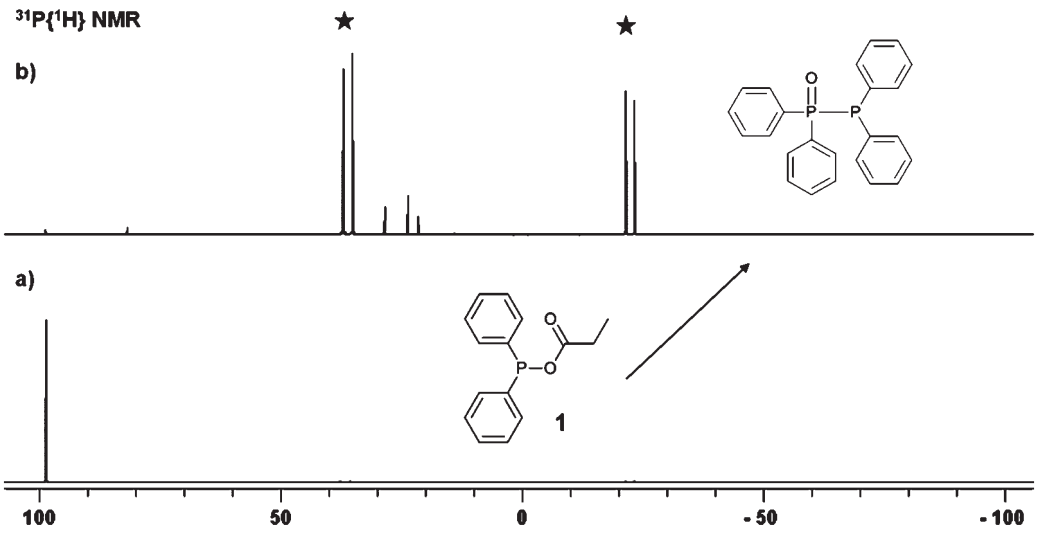


Fig. 2 Examples of typical $^{31}P\{^{1}H\}$ NMR spectra measured for compound **1** (a) following successful preparation thereof and (b) after rearrangement largely to $Ph_2P(O)PPh_2$ has taken place.

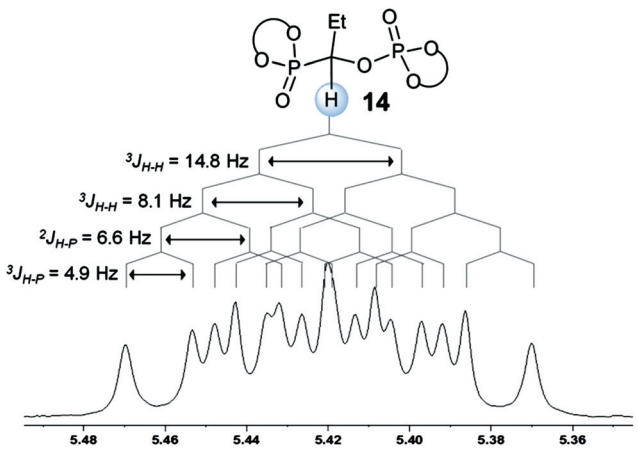


Fig. 3 Multiplicity and coupling constants observed for the complex ^{1}H NMR resonance of the central –C*H*– group in the by-product **14**.

rings (to minimize steric interactions) as well as the chirality of these compounds. Despite this, however, like carbons in compounds **12** and **13** display accidental equivalence giving rise to single resonances in the relevant regions. Furthermore, it is worth mentioning that for **10** and **11** the constants measured for ^{13}C–^{31}P coupling between C^4 to P (0 Hz) and C^{14} to P (4.7–5.0 Hz, see Fig. 5 for numbering scheme) differ significantly. The values of germinal coupling constants are influenced by the angle between the coupled atoms, and variations in the P–O–C angles θ and β (Fig. 5) may therefore be the cause of the observed inconsistencies.

Surprisingly, for compound **12** or **13**, C^4 and C^{14} are only observed as a single resonance signal split into a doublet by equal coupling to phosphorus [4.7 Hz (**12**) and 5.0 Hz (**13**)].

Infrared spectroscopy

Routine FT-IR data were collected for compounds **2** and **8**, **9** and **10–13**, with all relevant absorption bands listed under the Experimental section. In all cases, mixed anhydrides show strong absorption bands in the region 1740–1729 cm^{-1} attributable to the characteristic C═O stretching vibrations. These values are in good agreement with those reported for the literature examples (*R*)-acetyl-(1,1′-binaphthyl-2,2′-diyl)phosphite (1736 cm^{-1}) and (propanoyloxy)diphenylphosphine (**1**; 1740 cm^{-1}).[10,12]

Mass spectrometry

EI-MS spectrometric data were collected for compounds **8–13** and the relevant peaks are listed in the Experimental section. Very little fragmentation was, however, observed for these compounds with this mild ionization technique and as a result, the only diagnostic peaks can be assigned to the molecular ions $[M]^+$ and peaks originating from the loss of either a propanoyloxy group (for **8–10** and **12**) or of a phenylacetyloxy group (for **11** and **13**).

Crystallography

The crystal and molecular structures of compounds **10**, **11** and **13** were determined by single crystal X-ray diffraction.† Compound **10** crystallises from a concentrated hexane solution as colourless prisms in the orthorhombic space group $Pna2_1$ with 4 molecules in the unit cell. Fig. 6 depicts the molecular structure and numbering scheme of **10** and selected bond lengths and angles are summarised in the figure caption. Within the molecular structure of **10**, the two aromatic ring systems are rotated about the central carbon bond at torsion angles of 61.4(9)° and 60.0(9)° in order to minimise steric interactions between the different ring substituents. Although no crystal structures for free mixed anhydrides ligands of the general formula $(RO)_2POC(O)R'$ have been reported to date, the measured P(1)–O(1) bond length of 1.654(5) Å is in close agreement with that reported for the phosphorus ester bond in 2-(methylamino)benzoate-1,4-dihydro-1-methyl-4-oxo-2*H*-3,1,2-benzoxazaphosphorin-2-yl

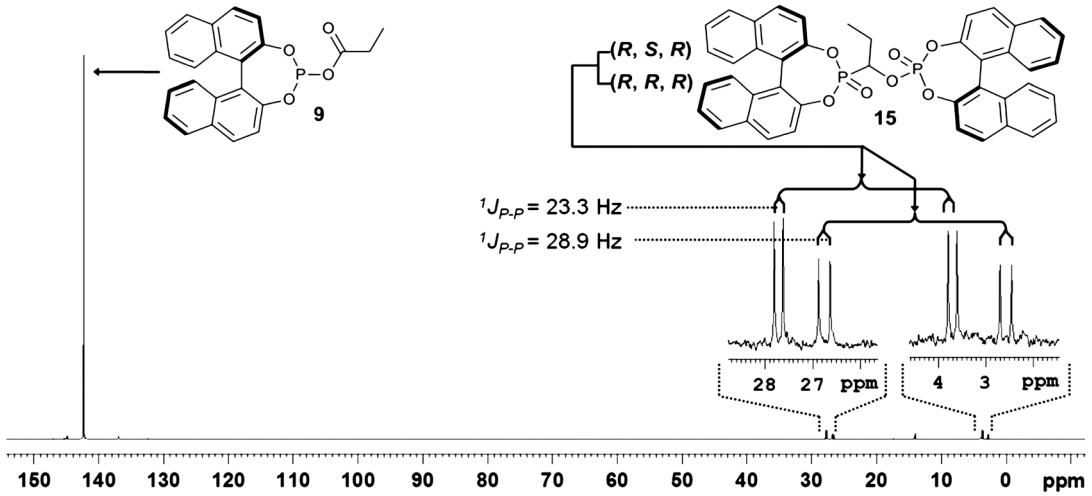


Fig. 4 $^{31}P\{^1H\}$ NMR spectrum measured for compound **9** showing the presence of minor amounts of the two diastereomers of by-product **15**.

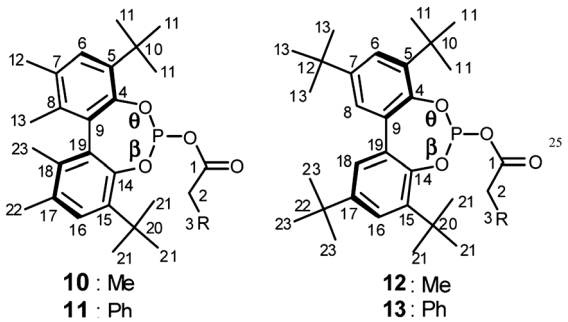


Fig. 5 Numbering scheme for NMR assignments and discussions relating to compounds **10–13**, where θ and β represents the C^4–O–P and C^{14}–O–P angles, respectively.

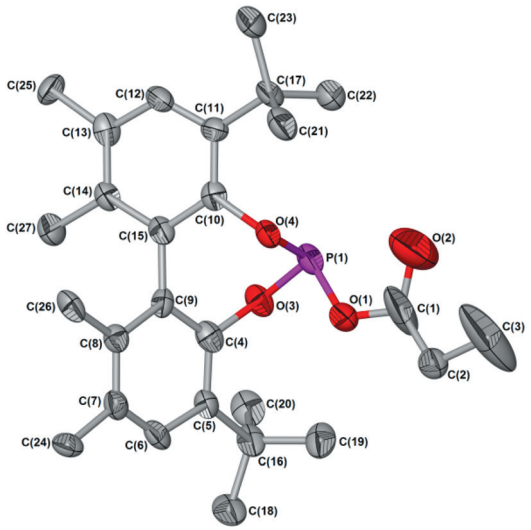


Fig. 6 Molecular structure of **10** showing the numbering scheme. Thermal ellipsoids are set at 50% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–O(1) 1.654(5), P(1)–O(3) 1.614(5), P(1)–O(4) 1.645(5), O(1)–C(1) 1.285(10), O(3)–C(4) 1.415(8), O(4)–C(10) 1.418(8), O(2)–C(1) 1.342 (14), C(1)–C(2) 1.452(12), O(3)–P(1)–O(1) 99.5(3), O(4)–P(1)–O(1) 92.3(3), O(3)–P(1)–O(4) 103.6(2), C(1)–O(1)–P(1) 120.5(6), C(4)–O(3)–P(1) 123.0(4), C(10)–O(4)–P(1) 114.5(4), O(1)–C(1)–O(2) 111.5 (10), O(4)–C(10)–C(15) 114.6(6), O(4)–C(10)–C(11) 121.4(6), C(4)–C(9)–C(15) 120.5(6), C(10)–C(15)–C(9) 120.0(6).

ester [1.6462(13) Å].[17] A very slight variation is observed between the distances for the two analogous P(1)–O(3) and P(1)–O(4) bonds [1.614(5) Å and 1.645(5) Å], and observed bond lengths are comparable to those of the related literature example, 1,1′-biphenyl-2,2′-diyl-bis[(5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite] [1.617(2) Å and 1.639(2)].[18] Interestingly, the P(1)–O(3)–C(4) and P(1)–O(4)–C(10) angles of 123.0(4)° and 114.5(4)°, respectively, differ significantly. This is therefore in good agreement with earlier ^{13}C NMR spectroscopic observations concerning ^{13}C–^{31}P coupling constants, where large differences observed in the coupling behaviour of C(4) to P(1) and C(10) to P(1) were tentatively ascribed to variations in the relevant P–O–C angles. However, it is noted that the structures in solution and in the solid may be different because of crystal packing effects and correlation of such connectivity data with other analytical results should therefore be interpreted with caution.

Compound **11** crystallises at room temperature from a hexane layered toluene solution as colourless prisms in the monoclinic space group $P2_1/n$, while **13** crystallises from chloroform also as colourless prisms in the triclinic space group $P\bar{1}$. Fig. 7 and 8 depict ellipsoid representations of the molecular structures of **11** and **13**, showing the numbering schemes with selected bond lengths and angles listed in the figure captions. The dihedral angles of 61.2(7)° and 56.7(8)° measured between the aryl rings of **11** are analogous to those observed for **10** and the literature example 1,1′-biphenyl-2,2′-diyl-bis[(5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite].[18]

In contrast, the corresponding torsion angles in **13** are significantly smaller [49.5(4)° and 42.7(4)°], suggesting that steric repulsions between the methyl ring substituents contribute to the widening of this angle in **10** and **11**. From a comparison of the bond lengths and angles of **10**, **11** and **13** it is evident that

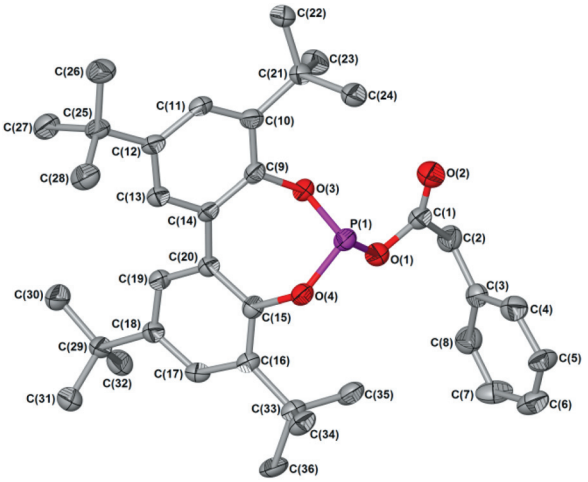


Fig. 7 Molecular structure of **11** showing the numbering scheme. Thermal ellipsoids are set at 50% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–O(1) 1.682(4), P(1)–O(3) 1.629(4), P(1)–O(4) 1.607(5), O(1)–C(1) 1.345(9), O(3)–C(9) 1.441(7), O(4)–C(15) 1.406(8), O(2)–C(1) 1.203 (9), C(1)–C(2) 1.515(8), O(3)–P(1)–O(1) 92.92(19), O(4)–P(1)–O(1) 89.7(2), O(3)–P(1)–O(4) 102.4(2), C(1)–O(1)–P(1) 116.8(4), C(9)–O(3)–P(1) 113.3(3), C(15)–O(4)–P(1) 123.8(3), O(1)–C(1)–O(2) 121.8 (6), O(4)–C(15)–C(20) 117.0(6), O(4)–C(15)–C(16) 120.0(5), C(9)–C(14)–C(20) 119.5(5), C(14)–C(20)–C(15) 119.9(6).

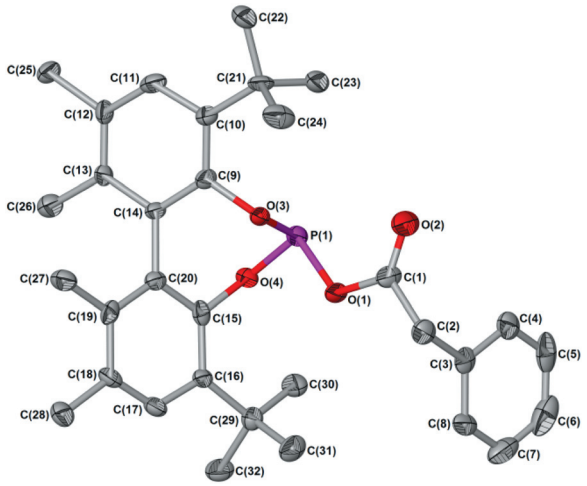


Fig. 8 Molecular structure of **13** showing the numbering scheme. Thermal ellipsoids are set at 50% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–O(1) 1.671(2), P(1)–O(3) 1.635(2), P(1)–O(4) 1.615(2), O(1)–C(1) 1.370(4), O(3)–C(9) 1.404(3), O(4)–C(15) 1.421(4), O(2)–C(1) 1.203 (4), C(1)–C(2) 1.499(5), O(3)–P(1)–O(1) 93.28(11), O(4)–P(1)–O(1) 100.39(12), O(3)–P(1)–O(4) 102.74(11), C(1)–O(1)–P(1) 117.4(2), C(9)–O(3)–P(1) 117.60(18), C(15)–O(4)–P(1) 127.87(19), O(1)–C(1)–O(2) 121.5(3), O(4)–C(15)–C(20) 117.7(3), O(4)–C(15)–C(16) 118.6 (3), C(9)–C(14)–C(20) 123.5(2), C(14)–C(20)–C(15) 124.6(3).

variations amongst like bonds are small, nevertheless, a few observations are in order. On average, the P–O bond lengths in **10** are somewhat longer than those in **11** and **13**, while the P(1)–O(4) bond in **11** is slightly shorter than the equivalent bond in **13**. The latter may too be the result of steric repulsions among methyl substituents on the phenyl backbone. In line with these observations, the P(1)–O(3)–C(9) and P(1)–O(4)–C(15) angles in **13** are significantly greater than the related angles in **10** and **11**. In all cases P(1)–O(3)–C(9) and P(1)–O(4)–C(15) are significantly different so they do not provide an explanation for the apparent equivalence of C(9) and C(15) in the ^{13}C NMR spectra of **12** and **13**.

Experimental

General procedures and instruments

Reactions were carried out under dinitrogen gas (N_2, passed through a column of Cr(II) adsorbed on silica) using standard Schlenk, vacuum-line and cannula techniques. All glassware was flame-dried under vacuum. Triethylamine (NEt_3), chlorodiphenylphosphine (Ph_2Cl) and phosphorus trichloride (PCl_3) were purchased from Aldrich and distilled under N_2 prior to use. Before distilling, the NEt_3 was dried over potassium hydroxide (KOH) pellets while PCl_3 was refluxed for 3 h to remove any free hydrochloric acid (HCl). 5,5′,6,6′-Tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diol, sodium propanoate and phenylacetic acid, were purchased from Aldrich and dried azeotropically with toluene. 2,2′-Biphenyldiol (purified by sublimation), (*R*)-(+)-1,1′-bi(2-naphthol) (dried azeotropically with toluene), 2,2′-dibromobiphenyl and 2,4-di-*tert*-butylphenol were purchased from Alfa Aesar. *N*,*N*′-Tetramethyl-1,2-diaminoethane (TMEDA) and anhydrous copper(II) chloride ($CuCl_2$), purchased from Aldrich, were used as received unless otherwise stated. Propanoic acid, purchased from BDH laboratories, was dried over KOH pellets and distilled under N_2 prior to use. 3,3′,5,5′-Tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diol was prepared using a standard literature procedure.[19] 5-Chlorodibenzophosphole was prepared from 2,2′-dibromobiphenyl following a reported literature procedure.[13]

Toluene, tetrahydrofuran (thf), diethyl ether and hexane were dried using a Braun Solvent Purification System and degassed by additional freeze–pump–thaw cycles when deemed necessary. Methanol was distilled under nitrogen from calcium hydride (CaH_2). Deuterated dichloromethane and chloroform were purchased from Aldrich and dried over phosphorus pentoxide (P_2O_5), degassed *via* three freeze–pump–thaw cycles and trap-to-trap distilled prior to use.

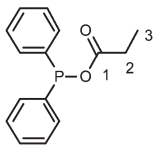
NMR spectra were recorded on a Bruker Avance 300 FT or Bruker Avance II 400 MHz spectrometer (^1H NMR at 300/400 MHz, ^{13}C NMR at 75/100 MHz and ^{31}P NMR at 121/162 MHz) with chemical shifts reported relative to TMS (^1H, ^{13}C) or 85% H_3PO_4 (^{31}P) as external reference. ^1H and ^{13}C NMR spectra were measured internally relative to deuterated solvent resonances which were referenced relative to TMS.

Solid state IR spectra were recorded using pressed KBr pellets on a Perkin Elmer Spectrum GX IR spectrometer. Elemental analysis was performed by the University of St. Andrews microanalytic service using a Carlo Erba CHNS/O microanalyser. Melting points were determined on a Gallenkamp apparatus and are uncorrected. Mass spectra were recorded by the Mass Spectrometry Service Centre at the University of St. Andrews on

either a Micromass GCT EI/CI or a Micromass LCT ES instrument.

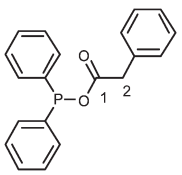
Synthesis

(Propanoyloxy)diphenylphosphine (1).



Compound **1** was prepared following either the known procedure[12] or the adapted literature procedure[5] as described here: Ph_2PCl (1.32 g, 6.0 mmol, 1.08 ml) was added dropwise to a solution of propanoic acid (0.44 g, 6.0 mmol, 0.48 ml) in thf (30 ml) at −10 °C. NEt_3 (0.61 g, 6.0 mmol, 0.836 ml) was added to the stirring mixture, leading to the immediate formation of $[HNEt_3][Cl]$ in the form of a white precipitate. After having been stirred at −10 °C for 10 min, the mixture was filtered over a plug of anhydrous $MgSO_4$ and all volatiles removed under reduced pressure to furnish compound **1** as a colourless oil (yield: 1.43 g, 93%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ_H = 1.18 (t, 3H, ^3J = 7.5 Hz; H^3), 2.53 (m, 2H, ^3J = 7.5 Hz; H^2), 7.40–7.59 (m, 10H, Ph). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ_P = 98.9 (s). The spectra are consistent with those reported in the literature.[12]

(Phenylacetyloxy)diphenylphosphine (2).

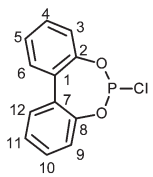


A solution of phenylacetic acid (1.36 g, 10.00 mmol) in thf (30 ml) at −10 °C was treated with Ph_2PCl (2.21 g, 10.00 mmol). NEt_3 (1.01 g, 1.39 ml, 10.00 mmol) was then added dropwise *via* a syringe leading to the immediate precipitation of $[HNEt_3][Cl]$. The resulting mixture was allowed to stir for 10 min at −10 °C and subsequently filtered through a plug of $MgSO_4$ in a filter column. The filtrate was then reduced to dryness to furnish the product as a white microcrystalline solid (yield: 1.37 g, 72%). Mp 22–24 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ_H = 3.91 (d, 2H, ^4J = 1.0 Hz; H^2), 7.42–7.65 (m, 15H, Ph). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ_C = 42.6 (d, $^3J_{C-P}$ = 2.1 Hz; C^2), 127.6 (s; Ph–C^{para}), 128.9 (d, $^4J_{C-P}$ = 7.03 Hz; PPh–C^{meta}), 129.0 (s; PPh–C^{para}), 129.8 (s; Ph–C^{meta}), 130.5 (s; Ph–C^{ortho}), 131.2 (d, $^2J_{C-P}$ = 23.8 Hz, PPh–C^{ortho}), 134.2 (s; P–C^{ipso}), 139.4 (d, $^1J_{C-P}$ = 19.4 Hz; PPh–C^{ipso}). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ_P = 100.2 (s). IR (KBr): $\tilde{\nu}$ = 3058 [w, sp^2 ν(C–H)], 3027–2860 [w, sp^3 ν(C–H)], 1720 [st, ν(C═O)], 1497–1439 [st, Ar ν(C═C)], 738 [st, ν(P–O)].

5-(Propanoyloxy)dibenzophosphole (3). A solution of 5-chloro-dibenzophosphole (0.97 g, 4.45 mmol) in thf (10 ml) was added to a suspension of sodium propanoate (0.43 g, 4.45 mmol) in thf (10 ml) at room temperature. The resulting mixture was allowed to stir at this temperature for 2 h, during which time the white sodium propanoate suspension cleared and sodium chloride (NaCl) precipitated from solution. After the 2 h stirring period, the formed NaCl was removed by filtration (cannula fitted with a membrane filter) and the colourless filtrate reduced to dryness *in vacuo* to yield the product as a colourless viscous oil which analysed to consist solely of disproportionation products.

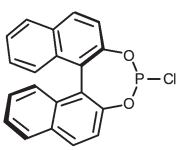
General procedure for the preparation of bisphenoxyphosphoruschlorides (4–7). These compounds were prepared according to a modified literature procedure.[14] A solution of the appropriate diol (9.22 mmol) in thf (20 ml) was added to a solution of PCl_3 (1.27 g, 9.22 mmol, 0.81 ml) in thf (10 ml) at −40 °C. NEt_3 (1.87g, 18.45 mmol, 2.57 ml) was then added dropwise *via* a syringe to the colourless solution. This led to the immediate precipitation of the formed $[HNEt_3][Cl]$ as a white solid. The resulting mixture was stirred at −40 °C for 1 h and then for a further hour at room temperature. After this stirring period, the mixture was filtered and reduced to dryness *in vacuo* to obtain the pure products.

*(a) (1,1′-Biphenyl-2,2′-dioxy)chlorophosphine (**4**). Prepared according to the general procedure described.*



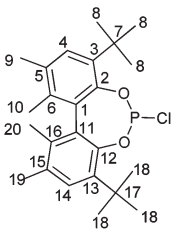
Starting diol: 2,2′-Biphenyldiol (1.72 g, 9.22 mmol). Title product obtained as a viscous colourless oil (yield: 1.92 g, 83%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ_H = 7.29 (dm, 2H, ^3J = 7.5 Hz; H^3/H^9), 7.47 (td, 2H, ^3J = 7.5 Hz, ^4J = 2.0 Hz; H^4/H^{10}), 7.40 (tm, 2H, ^3J = 7.5 Hz; H^5/H^{11}), 7.56 (dd, 2H, ^3J = 7.5 Hz, ^4J = 2.0 Hz; H^6/H^{12}). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ_C = 122.6 (d, $^3J_{C-P}$ = 1.9 Hz; C^3/C^9), 126.9 (s; C^5/C^{11}), 130.0 (s, C^4/C^{10}), 130.3 (d, $^3J_{C-P}$ = 3.3 Hz; C^1/C^7), 130.7 (s; C^6/C^{12}), 149.7 (d, $^2J_{C-P}$ = 5.6 Hz; C^2/C^8). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ_P = 179.7 (s).

*(b) (R)-(1,1′-Binaphthalen-2,2′-dioxy)chlorophosphine (**5**). Prepared according to the general procedure described.*



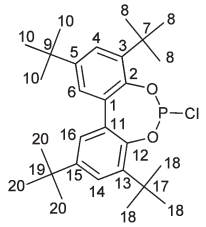
Starting diol: (*R*)-(+)-1,1′-Bi(2-naphthol) (2.64 g, 9.22 mmol). Title product obtained as a white solid (yield: 2.23 g, 69%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ_H = 7.26–7.33 (m, 2H), 7.38 (dd, 2H, ^3J = 8.1 Hz, ^4J = 3.4 Hz), 7.49–7.52 (m, 3H), 7.55 (dd, 1H, ^3J = 8.8 Hz, ^4J = 0.9 Hz), 8.0 (dd, 2H, ^3J = 8.2 Hz, ^4J = 2.8 Hz), 8.05 (dd, 2H, ^3J = 8.8 Hz, ^4J = 2.8 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ_C = 121.5 (s), 121.9 (s), 123.5 (d, $^3J_{C-P}$ = 2.8 Hz), 124.7 (d, $^3J_{C-P}$ = 5.8 Hz), 125.9 (s), 126.1 (s), 126.9 (s), 127.0 (s), 127.1 (s), 127.2 (s), 128.9 (s), 130.5 (s), 131.5 (s), 131.8 (s), 132.0 (s), 132.5 (s), 132.8 (s), 133.1 (s), 147.2 (d, $^2J_{C-P}$ = 3.0 Hz), 148.6 (d, $^2J_{C-P}$ = 4.86 Hz). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): 178.3 (s).

*(c) (5,5′,6,6′-Tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-dioxy)chlorophosphine (**6**). Prepared according to the general procedure described.*



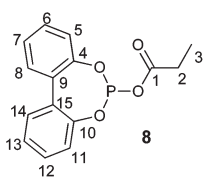
Starting diol: 5,5′,6,6′-Tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diol (3.27 g, 9.22 mmol). Title product obtained as a white solid (yield: 3.17 g, 82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 1.56 (s, 18H; H^8/H^{18}), 1.93 (s, 3H; H^9), 1.99 (s, 3H; H^{19}), 2.39 (s, 6H; H^{10}/H^{20}), 7.32 (s, 1H; H^4), 7.33 (s, 1H; H^{14}). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ_C = 16.6 (s; C^{10}), 16.9 (s; C^{20}), 20.1 (s, C^9/C^{19}), 31.2 (s; C^8), 32.3 (d, $^{5}J_{C-P}$ = 5.0 Hz; C^{18}), 34.7 (s; C^7), 35.1 (s; C^{17}),128.3 (s; C^4), 129.0 (s; C^{14}), 130.4 (d, $^{3}J_{C-P}$ = 2.8 Hz; C^1), 131.9 (d, $^{3}J_{C-P}$ = 5.7 Hz; C^{11}), 132.9 (s; C^5), 133.9 (s; C^{15}), 137.6 (d, $^{3}J_{C-P}$ = 1.8 Hz; C^3), 138.5 (d, $^{3}J_{C-P}$ = 3.5 Hz; C^{13}), 143.9 (d, $^{2}J_{C-P}$ = 5.7 Hz; C^2), 145.5 (s; C^{12}). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ_P = 164.3 (s).

*(d) (3,3′,5,5′-Tetra-*tert*-butyl-1,1′-biphenyl-2,2′-dioxy)-chlorophosphine (**7**). Prepared according to the general procedure described.*

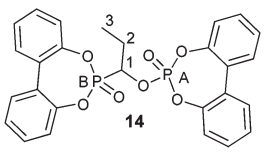


Starting diol: 3,3′,5,5′-Tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diol (3.79 g, 9.22 mmol). Title product obtained as a white solid (yield: 3.24 g, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 1.39 (s, 18H; H^8/H^{18}), 1.51 (s, 18H; H^{10}/H^{20}), 7.21 (d, 2H, ^{4}J = 2.5 Hz; H^4/H^{14}), 7.50 (d, 2H, ^{4}J = 2.5 Hz; H^6/H^{16}). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ_C = 31.5 (s; C^8/C^{18}), 31.5 (s; C^{10}/C^{20}), 34.8 (s; C^9/C^{19}), 35.6 (s; C^7/C^{17}), 124.9 (s, C^4/C^{14}), 126.8 (s; C^6/C^{16}), 132.7 (d, $^{3}J_{C-P}$ = 4.2 Hz; C^1/C^{11}), 140.5 (d, $^{3}J_{C-P}$ = 2.2 Hz; C^3/C^{13}), 145.6 (d, $^{2}J_{C-P}$ = 6.2 Hz; C^2/C^{12}). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ_P = 171.6 (s).

Propanoyl-(1,1′-biphenyl-2,2′-diyl)phosphite (8).



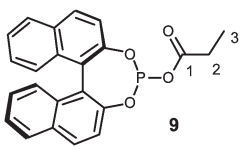
Adapted from a literature procedure for the preparation of (*R*)-acetyl-(1,1′-binaphthyl-2,2′-diyl)phosphite.[10] A solution of **4** (1.45 g, 5.80 mmol) in thf (20 ml) was added to a suspension of sodium propanoate (0.557 g, 5.80 mmol) in thf (15 ml) at 45 °C. The resulting mixture was allowed to stir at this temperature for 2 h, during which time the white sodium propanoate suspension cleared and sodium chloride (NaCl) precipitated from solution. After the 2 h stirring period, the formed NaCl was removed by filtration (either over a $MgSO_4$ plug or by using a cannula fitted with a membrane filter) and the colourless filtrate reduced to dryness *in vacuo* to yield the product as a colourless viscous oil contaminated with *ca.* 8% (based on NMR integration) of the by-product **14** (crude yield: 1.54 g, 93%). This impurity could not be separated from the title compound, using standard purification techniques. ^{1}H NMR (300 MHz, CD_2Cl_2): δ_H = 1.18 (t, 3H, ^{3}J = 7.4 Hz; H^3), 2.46 (q, 2H, ^{3}J = 7.4 Hz; H^2), 7.27 (dd, 2H, ^{3}J = 7.6 Hz, ^{4}J = 1.2 Hz; H^5/H^{11}), 7.37 (td, 2H, ^{3}J = 7.6 Hz, ^{4}J = 1.2 Hz; H^7/H^{13}), 7.45 (td, 2H, ^{3}J = 7.6 Hz, ^{4}J = 2.0 Hz; H^6/H^{12}), 7.54 (dd, 2H, ^{3}J = 7.6 Hz, ^{4}J = 2.0 Hz; H^8/H^{14}). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ_C = 9.0 (s; C^3), 28.9 (s; C^2), 122.4 (s; C^5/C^{11}), 126.3 (s; C^7/C^{13}), 129.9 (s; C^6/C^{12}), 130.6 (s; C^8/C^{14}), 131.5 (d, $^{3}J_{C-P}$ = 3.4 Hz; C^9/C^{15}), 149.3 (d, $^{2}J_{C-P}$ = 4.9 Hz; C^4/C^{10}), 173.6 (d; $^{2}J_{C-P}$ = 5.1 Hz; C^1). ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ_P = 142.5 (s). IR (solution in CH_2Cl_2): $\tilde{\nu}$ = 3066 [w, sp^2 ν(C–H)], 2970–2877 [w, sp^3 ν(C–H)], 1740 [st, ν(C═O)], 1499–1436 [st, Ar ν(C═C)], 769 [st, ν(P–O)]. ES-MS: *m*/*z* (%) = 289 (8) $[M]^+$, 215 (100) $[M - OC(O)CH_2CH_3]^+$. For by-product **14**:



14

^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 1.39 (dd, 3H, ^{3}J = 7.5 Hz; H^3), 2.34 (m, 2H; H^2), 5.41 (m, 1H, $^{3}J_{H-H}$ = 14.8 Hz, $^{3}J_{H-H}$ = 8.1 Hz, $^{2}J_{H-P}$ = 6.6 Hz, $^{2}J_{H-P}$ = 4.9 Hz; H^1), 7.20–7.54 (m, 16H; Ph). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ_C = 8.5 (s; C^3), 25.7 (s; C^2), 74.4 (d, $^{2}J_{C-P}$ = 7.5 Hz; C^1). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ_P = 1.9 (d, $^{3}J_{PA-PB}$ = 24.1 Hz; P_A), 26.4 (d, $^{3}J_{PB-PA}$ = 24.1 Hz; P_B).

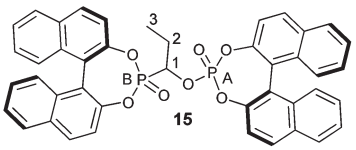
(*R*)-Propanoyl-(1,1′-binaphthyl-2,2′-diyl)phosphite (9).



9

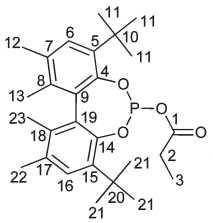
Compound **9** was prepared using the same method as was described for **8**, by treating a solution of **5** (1.28 g, 3.64 mmol) in thf (15 ml) with a suspension of sodium propanoate (0.35 g, 3.64 mmol) in thf (20 ml) at 45 °C for 2 h. The title product was obtained as a white solid contaminated by small amounts of rearrangement products (8%, based on NMR integrals), which could not be separated from **9** using standard purification techniques without effecting further rearrangement. ^{1}H NMR (300 MHz, CD_2Cl_2): δ_H = 1.15 (t, 3H, ^{3}J = 7.5 Hz; H^3), 2.40 (qd, 2H, ^{3}J = 7.5 Hz, $^{4}J_{H-P}$ = 0.8 Hz; H^2), 7.26–7.33 (m, 2H), 7.38 (m, 2H), 7.45–7.52 (m, 3H), 7.58 (dd, 1H, ^{3}J = 8.8 Hz, ^{4}J = 0.9 Hz), 8.0 (d, 2H, ^{3}J = 8.2 Hz), 8.05 (m, 2H). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): δ_C = 8.9 (s; C^3), 28.9 (d, $^{3}J_{C-P}$ = 2.2 Hz; C^2), 121.6 (s), 121.9 (s), 123.3 (d, $^{3}J_{C-P}$ = 2.5 Hz), 124.7 (d, $^{3}J_{C-P}$ = 5.6 Hz), 125.7 (s), 125.9 (s), 126.9 (s), 127.0 (s),

127.1 (s), 127.2 (s), 128.8 (s), 128.9 (s), 130.5 (s), 131.2 (s), 131.8 (s), 132.3 (s), 132.8 (s), 133.1 (s), 147.1 (d, $^{2}J_{C-P}$ = 2.2 Hz), 147.9 (d, $^{2}J_{C-P}$ = 4.1 Hz), 173.6 (d, $^{2}J_{C-P}$ = 5.0 Hz; C^{1}). $^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2): δ_P = 141.8 (s). IR (KBr): $\tilde{\nu}$ = 3059 [w, sp^2 ν(C–H)], 2980–2940 [w, sp^3 ν(C–H)], 1739 [st, ν(C═O)], 1508–1407 [m, Ar ν(C═C)], 746 [st, ν(P–O)]. For by-product **15**:



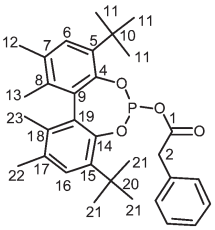
Diastereomer 1: ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 1.23 (dd, 3H, ^{3}J = 7.5 Hz; H^3), 2.18 (m, 2H; H^2), 5.26 (m, 1H; H^1), 7.25–8.10 (m, 24H; Ph). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ_P = 3.57 (d, $^{3}J_{PA-PB}$ = 23.3 Hz; P_A), 27.6 (d, $^{3}J_{PB-PA}$ = 23.3 Hz; P_B). *Diastereomer 2*: ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 1.43 (dd, 3H, ^{3}J = 7.5 Hz; H^3), 2.35 (m, 2H; H^2), 5.27 (m, 1H; H^1), 7.25–8.10 (m, 24H; Ph). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ_P = 2.67 (d, $^{3}J_{PA-PB}$ = 28.9 Hz; P_A), 26.6 (d, $^{3}J_{PB-PA}$ = 28.9 Hz; P_B).

Propanoyl-(5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite (10).



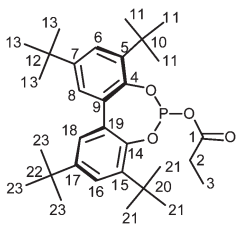
Compound **10** was prepared using a similar methodology to that which was described for the preparation of **8**. A solution of **6** (1.17 g, 2.79 mmol) in thf was added to a suspension of sodium propanoate (0.26 g, 2.79 mmol) in thf (10 ml) at 45 °C. After a 2 h stirring period, the formed NaCl was removed by filtration (cannula fitted with a membrane filter) and the colourless filtrate reduced to dryness *in vacuo*. The resulting white residue was extracted with hexane (40 ml), filtered and subsequently stripped of solvent under reduced pressure to furnish the analytically pure product as a white solid (yield: 1.20 g, 94%). Crystals (colourless prisms) suitable for single crystal X-ray diffraction determination could be obtained by slowly cooling a saturated solution of **10** in warm hexane (40 °C) to −22 °C. Mp 151–153 °C. Anal.: Found C 71.07, H 8.59; $C_{27}H_{37}O_4P$ requires: C 71.03, H 8.17%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ_H = 1.09 (t, 3H, ^{3}J = 7.5 Hz; H^3), 1.45 (s, 9H; H^{11}), 1.49 (s, 9H; H^{21}), 1.83 (s, 3H; H^{12}), 1.86 (s, 3H; H^{22}), 2.29 (s, 6H; H^{13}/H^{23}), 2.36 (q, 2H, ^{3}J = 7.5 Hz; H^2), 7.23 (s, 1H; H^6), 7.24 (s, 1H, H^{16}). $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2): δ_C = 8.6 (s; C^3), 16.6 (s; C^{13}), 16.8 (s; C^{23}), 20.5 (s; C^{12}/C^{22}), 28.8 (d, $^{3}J_{C-P}$ = 2.5 Hz; C^2), 31.1 (d, $^{5}J_{C-P}$ = 4.6 Hz; C^{11}), 31.7 (s; C^{21}), 34.9 (s; C^{10}), 35.1 (s; C^{20}), 128.5 (s; C^6), 128.8 (s; C^{16}), 130.7 (d, $^{3}J_{C-P}$ = 2.9 Hz; C^9), 132.2 (d, $^{3}J_{C-P}$ = 5.5 Hz; C^{19}), 132.8 (s; C^7), 133.9 (s; C^{17}), 134.7 (s; C^8), 135.6 (s; C^{18}), 137.7 (s; C^5), 139.1 (d, $^{3}J_{C-P}$ = 3.2 Hz; C^{15}), 144.2 (s; C^4), 144.9 (d, $^{2}J_{C-P}$ = 5.0 Hz; C^{14}), 173.5 (d, $^{2}J_{C-P}$ = 5.6 Hz; C^1). $^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2): δ_P = 129.6 (s). IR (KBr): $\tilde{\nu}$ = 3036 [w, sp^2 ν(C–H)], 2952–2868 [st, sp^3 ν(C–H)], 1740 [st, ν(C═O)], 1480–1393 [m, Ar ν(C═C)], 738 [m, ν(P–O)]. ES-MS: *m/z* (%) = 456 (20) $[M]^+$, 383 (100) $[M - OC(O)CH_2CH_3]^+$.

Phenylacetyl-(5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)phosphite (11).



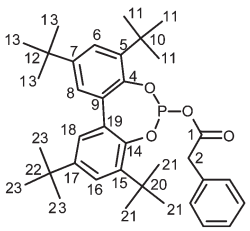
Phenylacetic acid (0.53 g, 3.86 mmol) was dissolved in thf (15 ml) and cooled to −10 °C. NEt_3 (0.39 g, 0.54 ml, 3.86 mmol) was added dropwise *via* syringe to this solution and the resulting mixture allowed to stir for 5 min. A solution of **6** (1.62 g, 3.86 mmol) in thf (20 ml) was then cannulated into the mixture, while maintaining the external temperature at −10 °C. The reaction solution was allowed to stir for 20 min at this temperature and then for another 20 min at room temperature. The formed $[HNEt_3][Cl]$ was subsequently removed by filtration (cannula fitted with a membrane filter) and the colourless filtrate stripped of all volatiles under reduced pressure to obtain the crude product as a white foam. This foam was washed with copious amounts of hexane (3 × 30 ml) and dried *in vacuo* to yield the analytically pure product as a white solid (1.84 g, 92%). Colourless prisms suitable for single crystal X-ray analysis could be obtained by slow diffusion of a hexane into a solution of **11** in toluene at room temperature. Mp 164–166 °C. Anal.: Found C 73.27, H 7.58; $C_{32}H_{39}O_4P$ requires C 74.11, H 7.58%. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H = 1.44 (s, 9H; H^{11}), 1.45 (s, 9H; H^{21}), 1.82 (s, 3H; H^{12}), 1.86 (s, 3H; H^{22}), 2.28 (s, 3H; H^{13}), 2.30 (s, 3H; H^{23}), 3.66 (s, 2H; H^2), 7.23 (s, 1H; H^6), 7.24 (s, 1H; H^{16}), 7.18–7.34 (m, 5H, Ph). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$): δ_C = 16.6 (s; C^{13}), 16.9 (s; C^{23}), 20.5 (s; C^{12}/C^{22}), 31.0 (d, $^{5}J_{C-P}$ = 4.5 Hz; C^{11}), 31.5 (s; C^{21}), 34.7 (s; C^{10}), 34.9 (s; C^{20}), 41.8 (s; C^2), 127.3 (s; Ph–C^{para}), 128.1 (s; Ph–C^{meta}), 128.3 (s; Ph–C^{ortho}), 129.5 (s; C^6), 130.2 (s; C^{16}), 130.2 (s; C^9), 132.0 (s; Ph–C^{ipso}), 132.8 (s; C^{19}), 132.4 (s; C^7), 133.4 (s; C^{17}), 134.4 (s; C^8), 135.2 (s; C^{18}), 137.2 (s; C^5), 138.9 (s, C^{15}), 143.9 (s; C^4), 144.6 (d, $^{2}J_{C-P}$ = 4.7 Hz; C^{14}), 170.5 (d, $^{2}J_{C-P}$ = 5.3 Hz; C^1). $^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2): δ_P = 129.3 (s). IR (KBr): $\tilde{\nu}$ = 3042 [w, sp^2 ν(C–H)], 2952–2863 [st, sp^3 ν(C–H)], 1729 [st, ν(C═O)], 1493–1359 [m, Ar ν(C═C)], 735 [st, ν(P–O)]. ES-MS: *m/z* (%) = 518 (48) $[M]^+$, 383 (100) $[M - OC(O)CH_2(C_6H_5)]^+$.

Propanoyl-(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)-phosphite (12).



Employing a similar procedure to that followed during the preparation of compound **8**, a solution of **7** (2.34 g, 4.93 mmol) in thf (20 ml) was reacted with a suspension of sodium propanoate (0.47 g, 4.93 mmol) in thf (15 ml) at 45 °C for 2 h. After work-up (as described for **8**), the product was extracted with hexane, filtered and reduced to dryness *in vacuo* to yield the analytically pure product as a white solid (yield: 2.34 g, 92%). Mp 139–143 °C. Anal.: Found C 72.77, H 9.31; $C_{31}H_{45}O_4P$ requires C 72.63, H 8.85%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ_H = 1.13 (t, 3H, ^3J = 7.4 Hz; H^3), 1.38 (s, 18H; H^{11}/H^{21}), 1.50 (s, 18H; H^{13}/H^{23}), 2.44 (m, 2H, ^3J = 7.4 Hz; H^2), 7.23 (d, 2H, ^4J = 2.5 Hz; H^6/H^{16}), 7.51 (d, 2H, ^4J = 2.5 Hz; H^8/H^{18}). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ_C = 8.5 (s; C^3), 28.5 (d, $^3J_{C-P}$ = 2.5 Hz; C^2), 31.1 (d, $^5J_{C-P}$ = 1.9 Hz; C^{11}/C^{21}), 31.6 (s; C^{13}/C^{23}), 35.5 (s; C^{12}/C^{22}), 34.7 (s; C^{10}/C^{20}), 124.6 (s; C^6/C^{16}), 126.6 (s; C^8/C^{18}), 132.7 (s; C^9/C^{19}), 140.5 (s; C^5/C^{15}), 145.0 (d, $^2J_{C-P}$ = 4.7 Hz; C^4/C^{14}), 147.1 (s; C^7/C^{17}), 173.3 (d, $^2J_{C-P}$ = 5.1 Hz; C^1). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ_P = 135.9 (s). IR (KBr): $\tilde{\nu}$ = 3054 [w, sp^2 ν(C–H)], 2962–2871 [st, sp^3 ν(C–H)], 1743 [st, ν(C═O)], 1459–1397 [m, Ar ν(C═C)], 748 [m, ν(P–O)]. ES-MS: *m*/*z* (%) = 512 (31) $[M]^+$, 493 (100) $[M - OC(O)CH_2CH_3]^+$.

Phenylacetyl(3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diyl)-phosphite (13).



Compound **13** was prepared according to the procedure described for **11**, employing phenylacetic acid (0.82 g, 6.04 mmol), NEt_3 (0.61 g, 0.84 ml, 6.04 mmol) and **7** (2.87 g, 6.04 mmol). The analytically pure product was obtained as a white solid (yield: 3.12 g, 95%) and colourless prisms suitable for analysis by single crystal X-ray diffraction could be obtained by slow evaporation of a dichloromethane solution of **13** at room temperature. Mp 165–167 °C. Anal.: Found C 75.11, H 8.50; $C_{36}H_{47}O_4P$ requires C 75.23, H 8.24%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ_H = 1.37 (s, 18H; H^{11}/H^{21}), 1.46 (s, 18H; H^{13}/H^{23}), 3.71 (s, 2H; H^2), 7.19 (d, 2H, ^4J = 2.5 Hz; H^6/H^{16}), 7.20–7.35 (m, 5H, Ph), 7.46 (d, 2H, ^4J = 2.5 Hz; H^8/H^{18}). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ_C = 31.0 (s; C^{13}), 31.1 (s; C^{23}), 31.6 (s; C^{11}/C^{21}), 35.5 (s; C^{12}/C^{22}), 34.8 (s; C^{10}/C^{20}), 42.0 (d, $^3J_{C-P}$ = 2.6 Hz; C^2), 124.6 (s; C^6/C^{16}), 126.6 (s; C^8/C^{18}), 127.3 (s; Ph–C^{para}), 128.6 (s; Ph–C^{meta}), 129.5 (s; Ph–C^{ortho}), 132.7 (d, $^3J_{C-P}$ = 3.7 Hz; C^9/C^{19}), 132.8 (s; Ph–C^{ipso}), 140.5 (s; C^5/C^{15}), 145.0 (d, $^2J_{C-P}$ = 5.0 Hz; C^4/C^{14}), 147.2 (s; C^7/C^{17}), 170.4 (d, $^2J_{C-P}$ = 5.0 Hz; C^1). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ_P = 135.7 (s). IR (KBr): $\tilde{\nu}$ = 3044 [w, sp^2 ν(C–H)], 2955–2865 [st, sp^3 ν(C–H)], 1730 [st, ν(C═O)], 1474–1394 [m, Ar ν(C═C)], 733 [m, ν(P–O)]. ES-MS: *m*/*z* (%) = 574 (9) $[M]^+$, 439 (100) $[M - OC(O)CH_2(C_6H_5)]^+$.

X-ray crystal structure determinations

A table containing a summary of the crystal data collection and refinement parameters of compounds **9**, **11** and **13** can be found in the ESI.† Data sets were collected on a Rigaku Mo MM007 (dual port) high brilliance diffractometer with graphite monochromated MoKα radiation (λ = 0.71075 Å). The diffractometer is fitted with Saturn 70 and Mercury CCD detectors and two XStream LT accessories. Data reduction was carried out with standard methods using the software package Bruker SAINT,[20] SMART,[21] SHELXTL[22] and Rigaku CrystalClear, CrystalStructure, HKL2000. All the structures were solved using direct methods and conventional difference Fourier methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares calculations on F^2 using SHELX-97[23] within an X-seed[24,25] environment. The hydrogen atoms were fixed in calculated positions. Figures were generated with X-seed and POV Ray for Windows, with the displacement ellipsoids at 50% probability level unless stated otherwise.

Conclusions

Slight stabilisation of mixed anhydride systems could be achieved by the incorporation of electron withdrawing oxygen atoms directly bonded to the phosphorus atom. Further stabilisation could be realised by increasing the steric bulk surrounding the phosphorus atoms, thus preventing neighbouring molecules from reaching close proximity. The latter approach proved most successful, with the resultant compounds being very stable both in solution and in the solid state. Acylphosphites derived from 5,5′,6,6′-tetramethyl-3,3′-di-*tert*-butyl-1,1′-biphenyl-2,2′-diol and 3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diol represent the most stable of all the mixed anhydrides prepared during this study. The solid state molecular structures could be determined for three of these stable mixed anhydrides using single crystal X-ray diffraction.

Acknowledgements

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