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ARTICLE

Synthetic Strategies to Further-Functionalised Monoaryl Phosphate Primary Building Units: Crystal Structures and Solid-state Aggregation Behavior

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New 4-halo functionalized 2,6-diisopropyl phenyl phosphates, X-dippH$_2$ [(RO)P(O)(OH)$_2$] (R = 4-X-2,6-^{i}Pr$_2$C$_6$H$_3$; X = Cl **1**, Br **2**, I **3**) have been synthesized in two steps starting from the corresponding 4-halophenols and characterized by analytical, spectroscopic, and single crystal X-ray diffraction studies. Isomorphous organophosphates **1-3** form a *tubular* structure in the solid-state through extensive hydrogen bonding interactions between adjacent –PO$_3$H$_2$ groups, an aggregation previously unknown among organophosphates and phosphonic acids. The methyl ester of **2**, [(RO)P(O)(OMe)$_2$] (R = 4-Br-2,6-^{i}Pr$_2$C$_6$H$_3$) (**4**), was reacted with a series of boronic acids under Suzuki coupling conditions to yield the corresponding C-C bond coupled products, 3,5-di*iso*propylbiphenyl-4-yl dimethyl phosphate (**5**), 4'-formyl-3,5-di*iso*propyl-biphenyl-4-yl dimethyl phosphate (**6**) and 4'-(diphenylmethyleneamino)-3,3',5,5'-tetra*iso*propyl-biphenyl-4-yl dimethyl phosphate (**7**). The possible reaction conditions for the selective deprotection of phosphate triesters have been established, under which conditions **6** yields 4'-formyl-3,5-di*iso*propyl-biphenyl-4-yl dihydrogenphosphate (**8**). Compound **8** is formyl group functionalized phosphate and shows hydrogen bonding similar to **1-3** forming tubular channels surrounded by peripheral organic groups. The dangling formyl groups in phosphates **6** and **8** undergo intermolecular tail-to-tail hydrogen bonding forming 1-dimensional assemblies in former and 3-dimensional supramolecules in later. Amino and formyl functionalized phosphates may serve as ideal primary building units for building suitably functionalized metal phosphate secondary building units.

1. Introduction

Main group compounds of the general formula, RE(O)$_x$(OH)$_y$, are versatile starting materials in materials chemistry owing to the presence of multiple hydroxyl groups on the central main group element 'E' which can embrace multiple metal centres and lead to formation of discrete and soluble polyhedral clusters and polymeric solids,[1-6] An appropriate choice of placing a bulky lipophilic 'R' group on the central atom on these hydroxy and oxy-hydroxy acids decree them highly soluble in organic as well as protic solvents, and render them useful synthons in materials chemistry of metal silicates, borates, and phosphates. In this regard, silanetriols RSi(OH)$_3$,[1] boronic acids RB(OH)$_2$,[2] phosphonic acids RP(O)(OH)$_2$,[3-4] and mono-organophosphate esters (RO)P(O)(OH)$_2$[5,6] are investigated during the last two decades as tetrahedral primary primary building units (T-PBUs) to build one or more zeolite secondary building units (SBUs),[7] through their reaction with appropriate metal precursors.

Organophosphates and organo phosphonic acids bearing simple alkyl to very bulky aryl substitutents have been employed for the synthesis of several types of polyhedral metallophosphates[5,6] and phosphonates.[3,4] There are, however, not many reports in the literature on phosphate ligands possessing additional functional groups being utilized as PBUs to construct functionalized SBUs. Amongst the organophosphate PBUs studied till date, 2,6-diisopropylphenyl phosphate (dippH$_2$) has emerged as most successful and versatile precursor, which in the presence of appropriate metal precursors and ancillary ligands forms structurally diverse discrete metal phosphates consisting inorganic cores with organic fringes.[8,9] Post synthetic modifications of such dippH$_2$ derived metal phosphate clusters have been limited so far to exchange of ancillary ligands present on the metal centres, however, producing porous solids,[8e] catalysts,[9k] and fluoride ion scavengers.[9l]

The present study is aimed at addressing the synthetic approaches for functionalized organophosphate esters by introduction of functional groups in the PBU dippH$_2$ through appropriate modifications as envisaged in Scheme 1. Nucleophilic substitution of 2,6-dialkylphenol can take place only at the 4-position, which has been recently been exploited by us to prepare 4-amino-2,6-diisopropyl phenyl phosphate (through the nitration route shown in Scheme 1).[10] This compound exhibits pseudo-polymorphism apart from displaying interesting H-bonded supramolecular one-dimensional porous structures that undergo SC-SC transformation. In a similar vein, in the present study, halogenation pathway of 2,6-dialkylphenol has been investigated to prepare a series of 4-halo-substituted 2,6-diisopropyl phenols. These halo-derivatives can serve as ideal starting point for the preparation of further functionalized phosphates by C-C coupling with suitable boronic acids under appropriate reaction conditions.
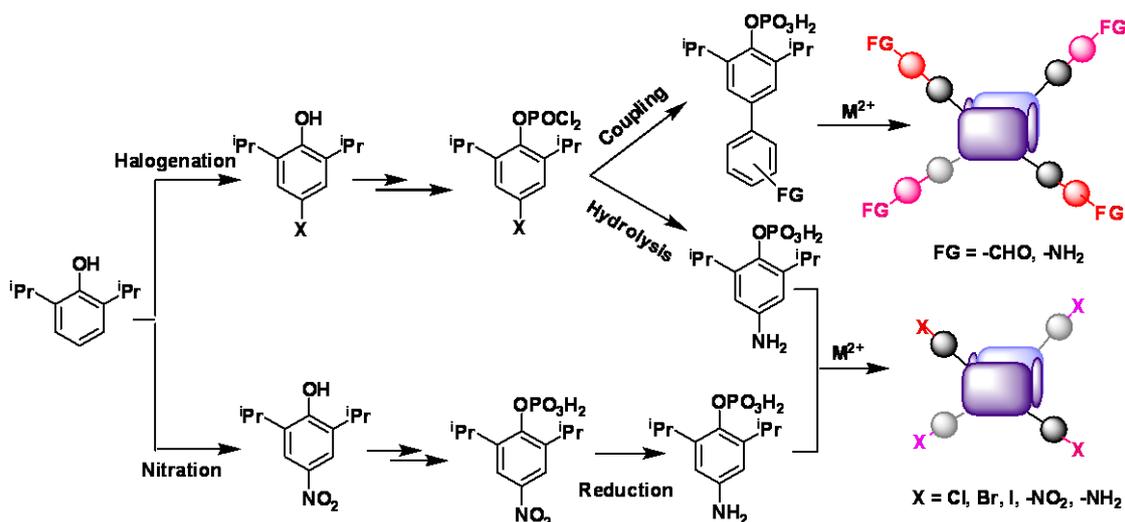
Scheme 1. Envisaged synthetic routes to different types of 4-functionalized monoaryl phosphates

Results and discussion

Synthesis and characterization of 4-halo-arylphosphates [(4-X-2,6-^{i}PrC$_6$H$_2$O)P(O)(OH)$_2$] (1-3)

The impetus for the synthesis of new 4-halo-2,6-diisopropylphenyl phosphates **1-3** in the present study has been two fold. Firstly, it has been envisaged that the presence of Cl, Br, or I functionalities would allow further organic transformations at the aryl ring. Secondly, the presence of halides along with P-OH group within the same molecule can lead to interesting O-H···X hydrogen bonding interactions resulting in supramolecular aggregation of phosphate molecules in solid state similar to those reported by us for the different polymorphs of 4-amino-2,6-diisopropyl phenyl phosphate.[10]

Monoaryl phosphates **1-3** have been synthesized by phosphorylation of the corresponding 4-halo-2,6-diisopropyl phenol with POCl$_3$ in presence of catalytic amount of anhydrous LiCl followed by hydrolysis of dichloridate compound by stoichiometric amount of water dissolved in acetone (Scheme 2). The isolated phosphates **1-3** have been found to be analytically pure and further characterized by a variety of spectroscopic techniques. The solid-state structures of all the three compounds have been determined by single crystal X-ray diffraction studies.

The presence of strong absorption at around 2350 cm^{-1} in the FT-IR spectrum of **1-3** clearly indicates the presence of P-OH groups in these molecules, apart from the presence of corresponding IR spectral signatures for P=O and C-X vibrations. The ^{1}H NMR spectral data for all the three compounds have been found to be consistent with the formulation [(4-X-2,6-^{i}Pr$_2$C$_6$H$_2$O)P(O)(OH)$_2$] both in terms of the observed chemical shifts for various protons in the molecule as well as the integrated intensities of the individual resonances (see experimental section for details). The most convincing evidence for the formation of the monoaryl phosphate
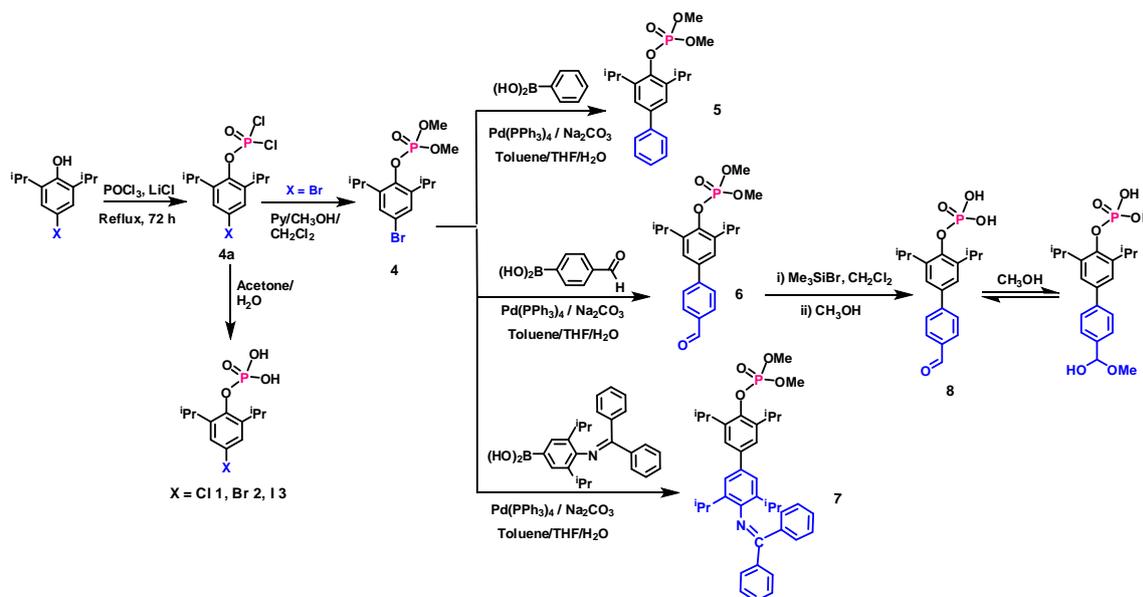
Scheme 2. Synthesis of monoaryl phosphate esters **1-8**.

esters comes from the observance of single sharp ^{31}P NMR resonance at δ_P= -3.0, -4.1 and -4.2 ppm for **1-3**, respectively. For comparison, earlier isolated alkyl substituted aryl phosphates such as $(2,6\text{-}Me_2C_6H_3O)P(O)(OH)_2$ (δ = 4.0 ppm) and $(2,6\text{-}^iPr_2C_6H_3O)P(O)(OH)_2$ (δ = 5.0 ppm)[11] also show a single phosphorus resonance in the same spectral region. The positive ion mode ESI-MS studies yielded signals corresponding to the molecular ions at *m/z* 292.93, 337.05 and 385.03 for compounds **1-3**, respectively, as the base peak in each case.

Molecular structures of 1-3
In view of the capricious solid-state aggregation behavior that has been observed in several multiple-hydroxyl compounds such as silanetriols $RSi(OH)_3$ and phosphonic acids $RP(O)(OH)_2$,[12,13] the solid-state structures of monoaryl phosphates **1-3** have been determined by single crystal X-ray diffraction studies to ascertain their definitive solid-state structures and aggregation characteristics. Crystals suitable for diffraction studies were directly grown from the reaction mixture by slow evaporation of the solvent. Phosphates **1-3** are isomorphous and crystallize in the monoclinic *C*2/c space group. A perspective view of the crystal structure of each of these phosphate molecules along with selected bond lengths and angles are presented in Figure 1. The central prochiral phosphorus in **1-3** adopts tetrahedral geometry; the P-O bond lengths and O-P-O angles are similar to those found in earlier reported monoaryl phosphates.[10,14] In all the three compounds, the P-O(Ar) distance is the longest while the P=O distance is the shortest; the two P-O(H) distances fall in between. No significant distortions from ideal tetrahedral angles have been observed for the O-P-O angles in any of the three compounds.

It is of interest to further probe into the hydrogen bonding assisted association behaviour of **1-3** vis-à-vis the aggregation patterns which have already been described in the case of mono-organo phosphates, phosphonic acids, and silanetriols which can simultaneously act as H-bond donors and acceptors by the virtue of presence of Si-OH, P-OH, and P=O groups (Table S1†). Silanetriols for example are known to show diverse H-bonding behaviour, ranging from formation of close-shell polyhedral cages, tubular wells to double sheet assemblies.[12] Phosphate monoesters and phosphonic acids, on the other hand show preference for the

formation of one-dimensional chains with double P-OH⋯O=P hydrogen bonds, as it has been observed in the case of mesityl-1-methylenephosphonic acid[13b] and 2,6-diisopropylphenylphosphonic acid,[14b] as depicted in Figure 2.

Compounds **1-3** show a solid-state aggregation behaviour, which emanates from a series of P-OH⋯O=P hydrogen bonds as shown in Figure 3 for the chloro derivative **1**. Each of the phosphate monoester molecules in the lattice of **1-3** is involved in four hydrogen bonds; while O2 acts as hydrogen bond acceptor to two P-OH groups present on two different neighbours, the two O-H groups (O3-H3A and O4-H4A) act as hydrogen bond donors.

This double P-OH⋯O=P hydrogen bonding originating from each of the phosphate molecules in the lattice, results in the formation of a one dimensional chain-like structure, as it can be clearly seen from Figure 3 (top) (viewed down b axis). It is further seen from a perpendicular view (Figure 3-bottom; viewed down c axis) that the adjacent molecules along this chain / tape are displaced by a rotation angle of 90° with respect to their neighbours. Hence this 1-D chain structure is indeed a tubular-well rather than a hydrogen-bonded tape as it has been reported in the literature for most phosphonic acids and phosphate esters. The formation of such a tubular well has earlier been observed in the case of silanetriols $RR'NSi(OH)_3$ (R = SiMe_3; R'-2,4,6-Me_3C_6H_2).[12d]

Reactivity of the C-Br bond and C-C coupling involving 4-bromo-2,6-diisopropylphenyl phosphate
With the aim to explore the reactivity and possibility of further functionalization of halo-monoaryl phosphates **1-3**, we have investigated representative Suzuki coupling reactions of these ligands with the functionalized phenyl boronic acid precursors. As all the three phosphate ligands **1-3** will essentially yield same type of Suzuki coupled products, the coupling reactions were carried out only with **4**, which is the dimethyl ester of compound **2** (Scheme 2).

4-Bromo-2,6-diisopropylphenyl dimethyl phosphate (**4**) has been obtained as a viscous colourless oil, in a quantitative yield by reacting dichloridate (**4a**) with anhydrous methanol under basic conditions (added pyridine) in methylene dichloride. The reaction of phosphate triester **4** with an excess of boronic acids (viz. phenyl boronic acid, 4-formylphenyl boronic acid, and 4-
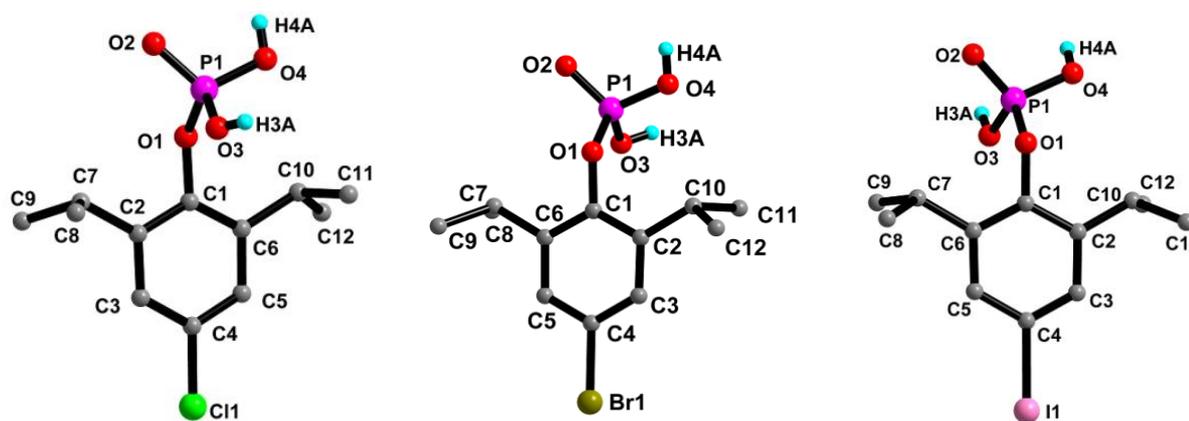

Figure 1. Molecular structure of **1-3**. Selected bond lengths [Å] and angles [°] for **1**: P1-O1 1.561(3), P1-O2 1.474(3), P1-O3 1.534(4), P1-O4 1.538(4), C4-Cl1 1.746(6), O4⋯O2 2.606(2), O3⋯O2 2.563(4), O1-P1-O2 108.7(2), O1-P1-O3 105.89(18), O1-P1-O4 106.7(2), O2-P1-O3 114.6(2), O2-P1-O4 112.1(2), O3-P1-O4 108.5(2), O4-H4A⋯O2 163.8, O3-H3A⋯O2 175.7; for **2**: P1-O1 1.5659(17), P1-O2 1.4926(17, P1-O3 1.5344(17), P1-O4 1.5462(16), C4-Br1 1.901(3), O4⋯O2 2.588(2) , O3⋯O2 2.542(2) , O1-P1-O2 108.14(9), O1-P1-O3 106.26(9), O1-P1-O4 106.62(9), O2-P1-O3 114.54(10), O2-P1-O4 111.49(10), O3-P1-O4 109.35(10), O4-H4A⋯O2 171.1, O3-H3A⋯O2 172.2; for **3**: P1-O1 1.572(5), P1-O2 1.500(5), P1-O3 1.531(5), P1-O4 1.548(4), C4-I1 2.099(7), O4⋯O2 2.593(5), O3⋯O2 2.538(4) O1-P1-O2 108.2(3), O1-P1-O3 106.6(3), O1-P1-O4 106.5(3), O2-P1-O3 114.4(3), O2-P1-O4 111.2(3), O3-P1-O4 109.6(3), O4-H4A⋯O2 116.2, O3-

(diphenylmethyleneamino)-3,5-diisopropylphenyl boronic acid) catalyzed by Na_2CO_3/Pd(PPh$_3$)$_4$, in toluene/THF/H$_2$O (1:1:1 v/v/v, under strict anaerobic conditions), yielded the C-C coupled products 3,5-di*iso*propylbiphenyl-4-yl dimethyl phosphate (**5**), 4'-formyl-3,5-diisopropylbiphenyl-4-yl dimethyl phosphate (**6**), and 4'-(diphenylmethyleneamino)-3,3',5,5'-tetra*iso*propylbiphenyl-4-yl dimethyl phosphate (**7**), respectively, (Scheme 2). Compounds **4-7** have been characterized by analytical and spectroscopic methods.

Strong absorption band observed at 1250, 1289, 1269 or 1289 cm^{-1}(for **4-7**, respectively) correspond to O-C stretch of the P-$\underline{OCH_3}$ groups. Similarly, the strong IR spectral band observed appear at 1699 cm^{-1} in **6** is due to the C=O vibration of the formyl group at the para-position of the second phenyl group, while a similar band appearing at 1623 cm^{-1} in **7** is due the C=N vibration of the C=NPh$_2$ para-substituent. The characteristic Fermi doublet for aldehyde functionality appears at 2721 and 2810 cm^{-1} in **6**. The presence of single resonance in the ^{31}P NMR spectrum at δ -6.3 ppm for **4**, and at around δ -3.8 ppm for **5-7** indicates no major structural change around central phosphorus in these compounds. The ^{1}H NMR spectral data supports the formulation for these compounds both in terms of observed chemical shifts and the intensity ratio of the signals. In addition to other characteristic signals, two close singlet resonances at around δ 3.8 ppm in **4-7**, corresponding
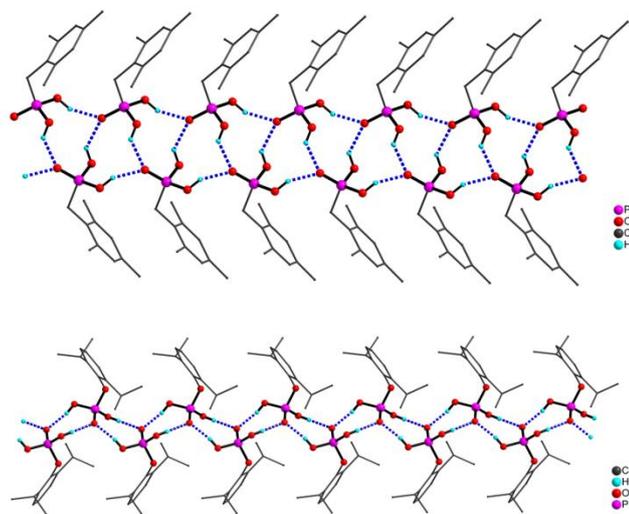

Figure 2. Hydrogen bonding pattern in a) mesityl-1-methylenephosphonic acid, b) 2,6-diisopropylphenyl phosphate resulting in the formation of tape-line one-dimensional chain structures.

to two methoxy groups further confirm methyl protection of P-OH groups in these compounds. The chemical composition of **4-7** has further been confirmed by HR-MS and / or microanalyses (see Experimental).

Molecular structures of 5-7

X-ray quality single crystals of **5-7** have been obtained by recrystallization of the crude samples from a solution of dichloromethane and hexanes (1:1 v/v) at room temperature. Compound **5** crystallizes in the monoclinic crystal system with *C*2/c space group, **6** crystallizes in triclinic crystal system with *P*-1 space groupand **7** crystallizes in the monoclinic crystal system with *P*2/c space group. Molecular structure diagrams of these compounds are shown in Figure 4. Crystals of **7** were found to be extremely

unstable and hence its structure has been deduced from a rapidly collected poor quality incomplete diffraction data set.
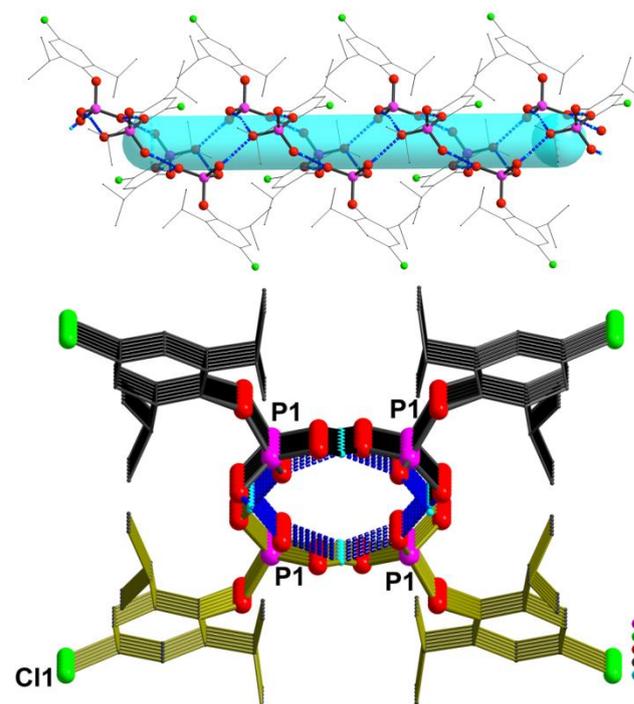

Figure 3. Hydrogen bonding pattern in **1**. (above) view down a-axis where the tube represents the shape of channels formed by hydrogen bonding of –OPO$_3$H$_2$ units; (below) view down c-axis showing the formation of cooperative H-bonding leading to formation of tubular wells.

Compounds **5-7** are phosphate triesters with tetrahedral phosphorus centre bound to two methoxy and one extended-aryloxy substituent apart from the phosphoryl oxygen atom. The phosphorus centre in **5-7** displays tetrahedral geometry with an average O-P-O bond angle of 109.23°, 109.10° and 109.23°, respectively. In all these three compounds the two aryl rings of the biphenyl moiety display a twist with respect to each other (torsion angle of 35.45(4), -36.60(3)° and 53.46(8)°, respectively, for **5-7**). Compound **7** consists of four phenyl rings (biphenyl and CPh$_2$, which are bridged by the imine functionality), in a highly conjugated form. Compound **6** is an example of a bifunctional molecule, where the two functional moieties, –OPO$_3$Me$_2$ and –CHO, separated by the central biphenyl spacer.

The phosphate triesters other than **6** do not show any significant secondary interactions between the adjacent molecules in the solid-state. While the –OMe protected phosphate terminals of **6** are not involved in any secondary interactions as expected, the –CHO terminal acts as hydrogen bond acceptor for hydrogen atom ortho- or meta- to formyl group of adjacent molecules which are placed tail to tail in the lattice, thus forming a phosphate bilayer structure, similar to the arrangement of phospholipids bilayers in biological cell membranes.[15] The less polar biphenyl tails sandwich themselves between polar phosphate groups, which occupy the periphery. In addition there are additional π-π interactions between aryl rings of **6**, at a distance of 4.232 Å and a slip angle of 15°, further stabilizing the phosphate bilayer as depicted in Figure 5.
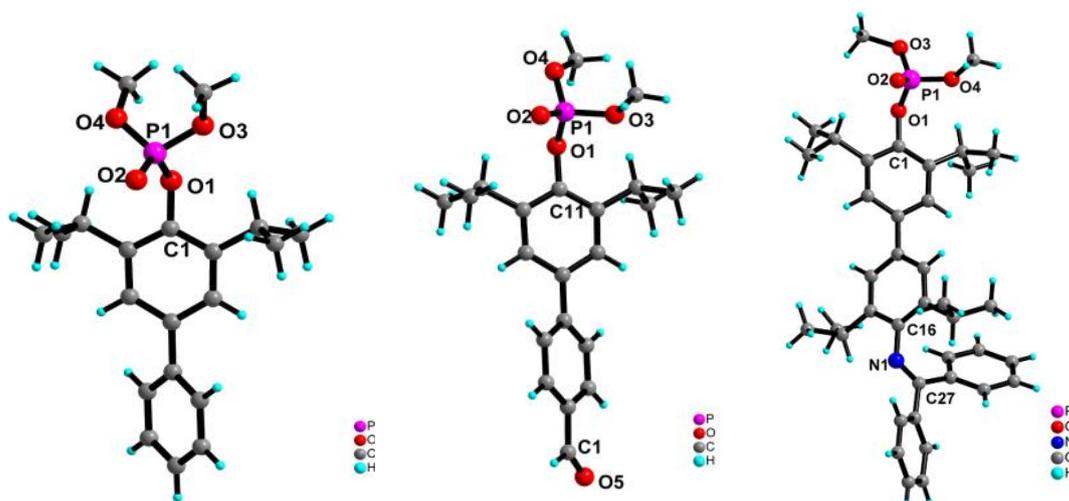
Figure 4. Molecular structures of **5-7** and selected bond lengths [Å] and angles [°], **5**: P1-O2 1.448(2), P1-O4 1.561(2), P1-O3 1.570(2), P1-O1 1.580(2), O1-C1 1.413(3), O2-P1-O4 111.60(12), O2-P1-O3 117.32(13), O4-P1-O3 105.50(11), O2-P1-O1 115.71(11), O4-P1-O1 104.94(11), O3-P1-O1 99.36(10), C1-O1-P1 123.51(16). **6**: P1-O2 1.4543(14), P1-O4 1.5583(13), P1-O3 1.5729(13), P1-O1 1.5912(12), O5-C1 1.205(2), O2-P1-O4 112.20(8), O2-P1-O3 115.15(8), O4-P1-O3 108.12(7), O2-P1-O1 117.20(7), O4-P1-O1 101.18(6), O3-P1-O1 101.53(7), C11-O1-P1 23.89(10). **7**: P1-O2 1.449(7), P1-O4 1.556(7), P1-O3 1.554(6), P1-O1 1.595(6), N1-C27 1.262(14), O2-P1-O4 114.7(4), O2-P1-O3 117.5(5), O4-P1-O3 101.6(4), O2-P1-O1 116.2(3), O4-P1-O1 104.0(4), O3-P1-O1 100.6(3), C1-O1-P1 124.0(4), C16-N1-C27 124.6(8), C28-C27-C34 125.74(7)
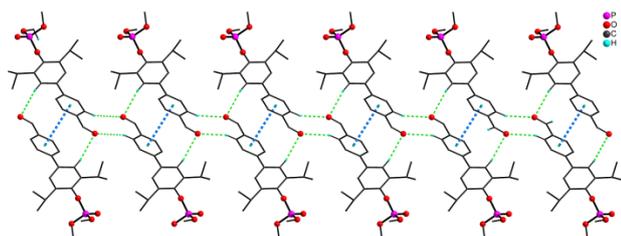

Figure 5. Hydrogen bonding interactions in **6**, showing it's association to organo-phosphate bilayer (O5⋯H3-C3, 2.591(2) Å, 159.83(2)°, O5⋯H13-C13, 2.708 Å, 157.87(2)° and π-π 4.232 Å).

Synthesis and Characterization of bi-functional biphenyl phosphate 8

Phosphate esters **5-7** have limited scope for being used as building blocks owing to the presence of reluctant -OMe binding groups. The selective deprotection of these –OMe groups in **5-7** has been particularly challenging as most of the commonly used deprotecting agents and protocols do not unfortunately differentiate the O-C(Me) from O-C(Ar) groups, thus yielding inorganic phosphate instead of the desired monoaryl dihydrogen phosphates. To achieve selective deprotection of the P-OMe groups, compound **6** has been investigated as a representative case to yield the formyl functionalized monoaryl dihydrogenphosphate by treating it with trimethylsilyl bromide (Me₃SiBr) under appropriate reaction conditions.[16]

In the present case, 4'-formyl-3,5-diisopropylbiphenyl-4-yldimethyl phosphate (**6**), was reacted with an excess of Me₃SiBr in dichloromethane under inert atmosphere at room temperature over period of 2 days, followed by treatment with methanol to obtain 4'-formyl-3,5-diisopropylbiphenyl-4-yldihydrogen phosphate (**8**) as yellow solid in a quantitative yield (Scheme 2). Broad and strong infrared absorption band at around 2230 cm⁻¹ in the FT-IR spectrum of **8** is suggestive of the successful deprotection of P-OMe group by SiMe₃Br to produce free P-$\underline{OH}$ groups. Similarly, the strong absorption band appearing at 1703 cm⁻¹

corresponds to the C=O stretching of formyl group, which is complemented by the Fermi doublet at 2807 and 2272 cm⁻¹. The ¹H NMR spectrum of **8** in DMSO-d_6 is different from that recorded in CD₃OD, suggesting the transformation of **8** to the corresponding hemiacetal in the later solvent.[17] ¹H NMR spectrum recorded in DMSO-d_6 shows well-separated peaks for all the protons of **8**. A singlet appearing at δ 10.02 ppm corresponds to the –C$\underline{H}$O proton, and the two sets of doublets and a singlet in the aromatic region correspond to the three types of aryl protons. The isopropyl –CH- and –CH₃ protons resonate at δ 3.65 and 1.19 ppm, as a septet and doublet, respectively. However, when the spectrum is recorded in CD₃OD the –C$\underline{H}$O resonance (at around δ 10 ppm) disappears and new singlets appear at δ 5.43 and 4.90 ppm, which can be assigned to –CH- and –OCH₃ protons of the hemiacetal form of **8** (Figure SI). The transformation of **8** to hemiacetal form in methanol is further supported by ¹³C NMR study (Figure SI). In the ³¹P NMR spectrum, compound **8** displays a single resonance at around δ -3.9 pm, in both the solvents. The negative ion mode ESI-MS study of **8** in acetonitrile solvent reveals an interesting association behavior of the compound in solution. The most predominant peaks appearing at *m/z* 361.2368, 723.4764, 1085.7156 and 1447.9559 correspond to the monomeric, dimeric, trimeric and tetrameric forms of the compound, respectively, Figure 6.

Molecular structure of 8

Single crystals of **8** for X-ray diffraction study have been obtained by recrystallization from acetonitrile solution at room temperature. Compound **8** crystallizes in the monoclinic space group *C*2/c. A perspective view of the molecular structure of **8** is shown in Figure 7. Compound **8** is a truly bi-functional molecule with a formyl and a -OPO₃H₂ functionalities separated by a central biphenyl group. The prochiral phosphorus centre in **8** is in tetrahedral geometry and bound to two –OH, one oxygen and one functionalized phenoxy groups, with an average O-P-O bond angle of 109.39°. The P-O bond lengths are in the order P-O(Ar) > P-O(H) > P=O, which is comparable to those found in **1-3** and other reported organo
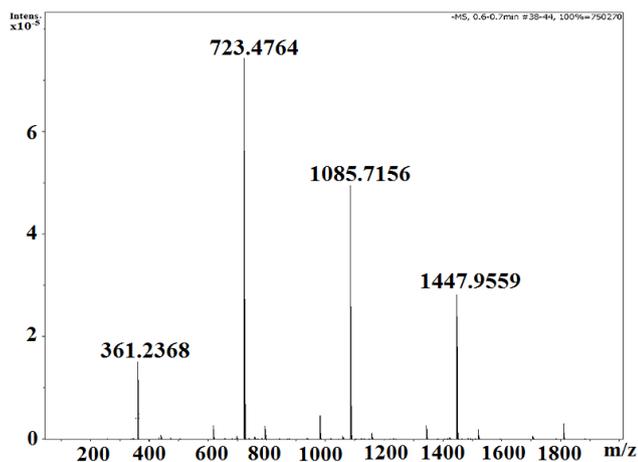
Figure 6. ESI-MS (negative ion mode) spectrum of **8** showing association behaviour in methanol solution; peaks at m/z 361.23, 723.47, 1085.71 and 1447.95 correspond to monomer, dimer, trimer and tetramer of **8**, respectively.

dihydrogen phosphates as well.[11] The two aryl rings of biphenyl moiety display a slight twist with a torsion angle of 32.26(3)°.

The -OPO_3H_2 group in **8** exhibits a hydrogen bonding behavior which is similar to those found for **1-3**, forming tubular channels with peripheral formyl functionalized organo groups as shown in Figure 8. The -OPO_3H_2 group in **8** is involved in the formation of four unique hydrogen bonds. While the phosphoryl oxygen O2 acts as a hydrogen bond acceptor for two different adjacent molecules of **8**, the two P–OH groups (O3-H3 and O4-H4) act as hydrogen bond donors. The O5 of the formyl group of **8** further acts as a hydrogen bond acceptor through C-H…O bonding to the aryl ring (O5…H14-C14) of the adjacent molecules, leading to a H-bonded 3-D structure as depicted in Figure 9 and in SI. However, unlike **6**, the aryl rings of **8** do not stack close enough to each other for any π-π interactions.
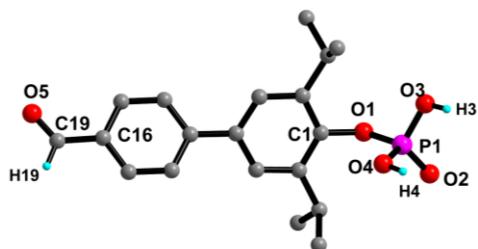

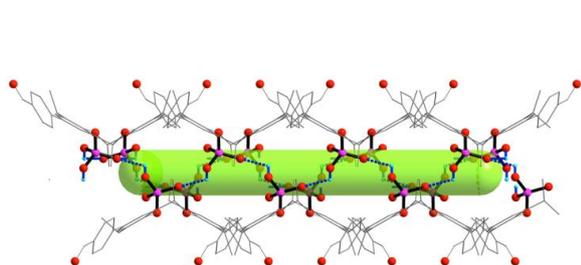**Figure 7**. Molecular strucuture diagram of **8**.

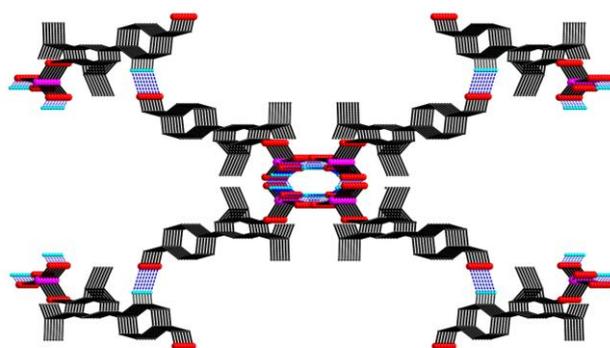**Figure 9.** Association of 1-dimensional chains of **8** formed by H-bonding between –OPO_3H_2 units into 3-dimensional networks by tail to tail H-bonding of –CHO groups.

Conclusions

The new halo-aryl phosphates **1-3** reported in this study form a rare class of organophosphate esters which are not only sterically encumbered around the phosphate group but also bear halo functionality on the para position of the aryl ring. C-C bond coupling reactions involving these halo phosphate ligands have been demonstrated with a series of boronic acid precursors, leading to the isolation of interesting C-C coupled functionalized phosphate triesters **5-7**. Selective deprotection carried out for **6**, yielded bifunctional phosphate **8** bearing formyl functionality, separated by a biphenyl spacer. These compounds offer new possibilities for the synthesis of molecular phosphate clusters with –NH_2 or -CHO functionalities on the cluster periphery. Such clusters will serve as ideal starting points for the synthesis of hybrid MOF-COF materials. We are currently investigating these possibilities.

Experimental section

Methods and materials

The syntheses of compounds **1-8** were carried out under nitrogen atmosphere using standard Schlenk line techniques. All the compounds reported in the present study are stable under ambient conditions. The melting points were measured in glass capillaries and are reported uncorrected. Infrared spectra were obtained using a Perkin–Elmer Spectrum One FT-IR spectrometer as KBr diluted discs. Microanalyses were performed on a Thermo Finnigan (FLASH EA 1112) microanalyzer. The ^1H (Me$_4$Si internal standard) and ^{31}P (85 % H$_3$PO$_4$ external standard) NMR spectra were recorded using a Bruker 500 MHz spectrometer. The ESI MS studies were

Figure 8. Hydrogen bonding diagrams of **8**, as seen along a-axis, tube represents the shape of channels formed by hydrogen bonding of –OPO_3H_2 units and c axis, showing the formation of cooperative H-bonding leading to formation of tubular wells. (H-atoms other than hydroxy protons are omitted for clearity). [H-bonding parameters: O2···H3-O3, 2.072(3) Å, 118.28(2)°, O2···H4-O4, 2.097(4) Å, 113.66(2)° and O5···H14-C14, D···H-A = 2.462(2) Å, 160.27(1)°]

carried out on Bruker MaXis impact mass spectrometer.

Solvents were purified according to standard procedures prior to use.[18] Commercially available starting materials such as 2,6-di*iso*propylphenol (Sigma Aldrich), phenylboronic acid (Sigma Aldrich), 4-formyl phenylboronic acid (Sigma Aldrich), Iodine monochloride (Alfa Aesar), Sulfuryl chloride (Spectrochem)and trimethylsilylbromide (Sigma Aldrich) were used as procured. The syntheses of 4-chloro-2,6-diisopropylphenol, 4-bromo-2,6-diisopropylphenol, 4-iodo-2,6-diisopropylphenol[19] and 4-(diphenylmethyleneamino)-3,5-diisopropylphenyl boronic acid[20] were carried out by as described previously in the literature.

Synthesis of 1-3. To 4-halo-2,6-diisopropylphenol (43.4 mmol), catalytic amount of anhydrous LiCl and phosphrousoxychloride (130 mmol) were added under nitrogen. The reaction mixture was heated under reflux (150 °C) for 72 hours. The resulting solution was filtered, concentrated and distilled under reduced pressure to give 4-halo-2,6-di*iso*propylphenyl phosphoro-dichloridate which was hydrolyzed with water in acetone at room temperature by stirring for 36 hours. The resulting dark solution was concentrated to yield black residue which on washing with hexanes yielded **1-3** as crystalline off-white powder.

1. Yield: 7.5 g (59%). Mp: 175 °C. Anal. Calcd for $C_{12}H_{18}ClO_4P$ (%): C, 49.25; H, 6.20. Found: C, 49.26; H, 6.07. FT-IR (KBr, cm^{-1}): 2971(s), 2929(w), 2871(w), 2346(br), 1579(w), 1467(m), 1328(s), 1159(m), 1098(m), 1046(s), 996(s), 837(s), 492(m).^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.29 (s, 1H, -OH), 7.05 (s, 2H, Ar-H), 3.25 (septet, 2H, ^{i}Pr-CH, $^3J_{HH}$ = 6.8 Hz), 1.12 (d, 12H, ^{i}Pr-CH$_3$, $^3J_{HH}$ = 6.8 Hz) ppm.^{31}P NMR (CDCl$_3$, 161 MHz): δ-3.0 ppm. ESI-MS: m/z calc. for $C_{12}H_{18}ClO_4P$ 292.0631; Found 292.9378 [M+H]$^+$.

2. Yield: 8.5 g (58%).Mp: 185 °C. Anal. Calcd for$C_{12}H_{18}BrO_4P$ (%): C, 42.75; H, 5.38. Found: C, 42.49; H, 5.38. FT-IR (KBr, cm^{-1}): 2974(s), 2930(m), 2871(m), 2360 (b), 1572 (w), 1466(m), 1324(s), 1161(s), 1099(m), 1046(s), 996(s), 812(s), 556(w), 487(m). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.05 (s, 2H, Ar-H), 5.10 (s, 1H, -OH), 3.18 (septet, 2H, ^{i}Pr-CH, $^3J_{HH}$ = 7.0 Hz), 1.01 (d, 12H, -CH$_3$, $^3J_{HH}$ = 6.6 Hz) ppm. ^{31}P NMR (CDCl$_3$, 161 MHz): δ-4.1 ppm. ESI-MS: m/z calc. for $C_{12}H_{18}BrO_4P$ 336.0126; Found 337.0583 [M+H]$^+$.

3. Yield: 7.8 g (47%).Mp: 175 °C. Anal. Calcd for$C_{12}H_{18}IO_4P$ (%): C, 37.52; H, 4.72. Found: C, 38.06; H, 4.48. FT-IR (KBr, cm^{-1}): 2974(s), 2870(w), 2348(br), 1566(w), 1465(s), 1446(s), 1325(s), 1045(s), 995(s), 899(s), 799(s), 763(s), 685(s), 575(w), 550(m), 507(m). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.38 (s, 2H, Ar-H), 5.08 (s, 2H, -OH), 3.32 (septet, 2H, ^{i}Pr-CH, $^3J_{HH}$ = 6.8 Hz), 1.10 (d, 12H, CH$_3$, $^3J_{HH}$ = 6.8 Hz) ppm. ^{31}P NMR (CDCl$_3$, 161 MHz): δ-4.2 ppm. ESI-MS: m/z calc. for $C_{12}H_{18}IO_4P$ 383.9987; Found 385.0386 [M+H]$^+$.

Synthesis of 4. Freshly distilled 4-bromo-2,6-diisopropylphenyl phosphorodichloridate (6.20 g, 16.5 mmol) was dissolved in dichloromethane and 2.5 equivalents each of methanol and pyridine were added to this solution at 0 °C. The reaction contents were stirred for 24 hours at room temperature. The product was extracted with diethyl ether and washed multiple times with 10 % HCl, saturated sodium bicarbonate, and brine solutions, respectively. The organic part was dried over anhydrous sodium sulphate, filtered and concentrated to give viscous colourless oil. Yield: 5.50 g (91.5%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.22 (s, 1H, Ar-H), 3.86 (s, 3H, Me), 3.84 (s, 3H, OMe), 3.42 (septet, 2H, ^{i}Pr-CH, $^3J_{HH}$ = 6.8 Hz), 1.22 (d, 12H, ^{i}Pr-CH$_3$, $^3J_{HH}$ = 6.8 Hz) ppm.^{31}P NMR (CDCl$_3$, 161 MHz): δ -6.3 ppm. HR-MS (ESI): m/z calc. for $C_{14}H_{22}BrO_4P$ 364.2021; Found 365.2018 [M+H]$^+$.

Synthesis of 5. 4-bromo-2,6-diisopropylphenyl dimethyl phosphate (0.80 g, 2.19 mmol), phenyl boronic acid (0.36 g, 3 mmol) and sodium bicarbonate (0.52 g, 5 mmol) were taken in 1:1:1 v/v/v solution of toluene/THF/water (15 mL) in a Schlenck flask. The mixture was frozen at liquid nitrogen/acetone temperature and evacuated for 10-15 min. Catalytic amount of Pd(PPh$_3$)$_4$ (0.04 g, ~ 5-10 mol %) was added under nitrogen at room temperature and the reaction mixture was heated at 80 °C for 4-6 hours. The completion of reaction was judged by TLC analysis, and the reaction mixture was diluted with water and extracted with diethyl ether. The combined organic layers were washed with brine and dried over sodium sulfate. The solvent was evaporated and crude product was purified by column chromatography, using petroleum ether/ethyl acetate (90:10 v/v) as eluent to afford **5**. Yield: 0.60 g (75%). Mp: 65 °C. Anal. Calcd for $C_{20}H_{27}O_4P$ (%): C, 66.28; H, 7.51. Found: C, 65.59; H, 7.71. FT-IR (KBr, cm^{-1}): 3031(m), 2964(s), 2870(w), 1597(w), 1457(s), 1347(w), 1289(s), 1172(s), 1034(s), 952(s), 881(w), 884(s), 760(s), 534(s), 499(m).^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.55 (d, 2H, Ar-H, $^3J_{HH}$ = 7.0 Hz), 7.43 (t, 2H, Ar-H, $^3J_{HH}$ = 7.3 Hz), 7.34 (t, 1H, Ar-H, $^3J_{HH}$ = 7.3 Hz), 7.05 (s, 2H, Ar-H), 3.89 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.50 (septet, 2H, ^{i}Pr-CH, $^3J_{HH}$ = 6.8 Hz), 1.28 (d, 12H, ^{i}Pr-CH$_3$, $^3J_{HH}$ = 6.8 Hz) ppm.^{31}P NMR (CDCl$_3$, 161 MHz): δ-3.88 ppm. HR-MS (ESI): m/z calc. for $C_{20}H_{27}O_4P$ 362.1747; Found 385.1539 : [M+Na]$^+$.

Synthesis of 6. Compound **6** was synthesized by using a similar protocol as above by reacting 4-bromo-2,6-diisopropylphenyl dimethyl phosphate (1.10 g, 3.00 mmol), 4-formylphenyl boronic acid (0.52 g, 3.5 mmol), sodium bicarbonate (0.52 mg, 5.0 mmol), and catalytic amount of Pd(PPh$_3$)$_4$ (0.04 g, ~ 5-10 mol %). Yield: 0.410 g (58.5%). Mp: 115 °C. Anal. Calcd for $C_{21}H_{27}O_5P$ (%): C, 64.61; H, 6.97. Found: C, 61.05; H, 7.78. FT-IR (KBr, cm^{-1}): 2963(s), 2929(w), 2869(w), 1699(s), 1605(w), 1454(s), 1386(w), 1289(s), 1169(s), 1054(m), 949(s), 853(s), 529(m).^{1}H NMR (CDCl$_3$, 400 MHz): δ 10.54 (s, 1H, -CHO), 7.95 (d, 2H, Ar-H, $^3J_{HH}$ = 7.3 Hz), 7.72 (d, 2H, Ar-H, $^3J_{HH}$ = 7.3 Hz), 7.36(s, 2H, Ar-H), 3.91 (s, 3H, OMe), 3.88 (s, 3H, OMe), 3.51 (septet, 2H, ^{i}Pr-CH, $^3J_{HH}$ = 6.8 Hz), 1.29 (d, 12H, ^{i}Pr-CH$_3$, $^3J_{HH}$ = 6.8 Hz) ppm. ^{31}P NMR (CDCl$_3$, 161 MHz): δ-3.9 ppm. HRMS (ESI): m/z calc. for $C_{21}H_{27}O_5P$ 390.1596; Found 413.1489 : [M+Na]$^+$.

Synthesis of 7. Compound **7** was synthesized by a similar protocol as described above by reacting 4-bromo-2,6-diisopropylphenyl dimethyl phosphate (0.80 g, 2.37 mmol), 4-(diphenylmethyleneamino)-3,5-diisopropylphenylboronic acid (1.15 g, 3.0 mmol), sodium bicarbonate (525 mg, 5.0 mmol), and catalytic amount of Pd(PPh$_3$)$_4$ (0.040 g, ~ 5-10 mol %). Yield: 0.85 g (57%). Mp: 115 °C. Anal. Calcd for $C_{39}H_{48}NO_4P$ (%): C, 74.85; H, 7.73; N, 2.24. Found: C, 74.75; H, 7.78; N, 2.24. FT-IR (KBr, cm^{-1}): 2971(s), 2929(w), 2871(w), 2346(br), 1579(w), 1467(m), 1328(s), 1159(m), 1098(m), 1046(s), 996(s), 837(s), 492(m).^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.73 (d, 4H, Ar-H, $^3J_{HH}$ = 6.2 Hz), 7.36 (m, 4H, Ar-H, $^3J_{HH}$ = 7.3 Hz), 7.22 (s, 2H, Ar-H), 7.16 (m, 2H, Ar-H, $^3J_{HH}$ = 10.2 Hz), 7.04 (s, 2H, Ar-H), 3.81 (s, 3H, OMe), 3.78 (s, 3H, OMe) 3.40 (septet, 2H, ^{i}Pr-CH, $^3J_{HH}$ = 6.8 Hz), 2.81 (septet, 2H, ^{i}Pr-CH, $^3J_{HH}$ = 6.8 Hz), 1.21 (d, 12H, ^{i}Pr-CH$_3$, $^3J_{HH}$ = 6.8 Hz), 1.18 (d, 12H, ^{i}Pr-CH$_3$, $^3J_{HH}$ = 6.8 Hz) ppm.^{31}P NMR (CDCl$_3$, 161 MHz): δ-3.8 ppm. HRMS (ESI): m/z: [M+H]$^+$ calc. for $C_{39}H_{48}NO_4P$, 625.3321; Found 626.3390: [M+H]$^+$.

Synthesis of 8. To compound **6** (0.585 g, 1.5mmol), trimethylsilyl bromide (1.5 mL, 8 mmol) was added under nitrogen atmosphere in freshly distilled dichloromethane (25 mL) and the reaction mixture was stirred for 3 days at room temperature. The excess solvent was removed under vacuum to yield a dark brown residue, which was readily treated with methanol (40 mL) and stirred for 2 more days at room temperature. The solvent was removed under vacuum to yield a yellow residue which was triturated with hexanes to yield **8** as yellow solid. Compound **8** was

further purified by washing with dichlormethane. Yield: 0.40 g (73%). Mp: 175 ^{o}C. Anal. Calcd for $C_{19}H_{23}ClO_5P$ (M = 362): C, 62.98; H, 6.40. Found: C, 62.31; H, 6.14.FT-IR (KBr, cm^{-1}): 2970(s), 2930(w), 2807(w), 2722(w), 2276(br), 1703(s), 1604(s), 1459(s), 1305(s), 1169(s), 1119(m), 1050(s), 993(s), 816(s), 508(m).^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.02 (s, 1H, -CHO), 7.98 (d, 2H, $^3J_{HH}$ = 8.3, Ar-H), 7.88 (d, 2H, $^3J_{HH}$ = 8.3, Ar-H) 7.43 (s, 2H, Ar-H), 3.65 (septet, 2H, ^{i}Pr-CH, $^3J_{HH}$ = 6.8 Hz), 3.15 (s, 2H, P-OH), 1.20 (d, 12H, ^{i}Pr-CH$_3$, $^3J_{HH}$ $_=$ 6.8 Hz) ppm.(CD$_3$OD, 500 MHz): δ 7.55 (d, 2H, $^3J_{HH}$ = 8.3, Ar-H), 7.50 (d, 2H, $^3J_{HH}$ = 8.3, Ar-H) 7.34 (s, 2H, Ar-H), 5.43 (s, 1H, -CH-), 4.87 (s, 3H, -OCH$_3$), 3.63 (septet, 2H, ^{i}Pr-CH, $^3J_{HH}$ = 6.8 Hz), 3.15 (s, 2H, P-OH), 1.28 (d, 12H, ^{i}Pr-CH$_3$, $^3J_{HH}$ $_=$ 6.8 Hz) ppm.^{31}P NMR (DMSO-d_6, 202 MHz): δ-3.9 ppm.^{31}P NMR (CD$_3$OD, 202 MHz): δ-3.9 ppm. ESI-MS *m/z*: [M-H]$^-$ Calc. for $C_{19}H_{23}ClO_5P$ 361.12; Found [M-H]$^-$ 361.23, [2M-H]$^-$ 723.47, [3M-H]$^-$ 1085.71, [4M-H]$^-$ 1447.95.

Single crystal X-ray diffraction studies. Single crystals of compounds **1-3** and **5-7** were obtained by recrystallization from dichloromethane and hexane solution (1:1 v/v). Compound **8** was recrystallized from an acetonitrile solution. The crystals were mounted using paratone oil on a Rigaku Saturn 724+ CCD diffractometer for unit cell determination and three dimensional intensity data collection. Data integration and indexing was carried out using CrystalClear. The structures were solved using direct methods (*SIR*-92)[21]. The complete structure refinement and other calculations were carried out using programs in WinGX module.[22] The final structure refinement was carried out using full least square methods on F^2 using SHELXL-97.[23] Details of crystal data and structure refinement are given in Table 1.

Acknowledgments

Notes and references

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†Electronic Supplementary Information (ESI) available: Synthesis, crystallographic details, additional figures, and spectral characterization. Crystallographic data of **1** (CCDC 1009218), **2** (CCDC 1009219), **3** (CCDC 1009220), **5** (CCDC 1009227), **6** (CCDC 1009229), **7** (CCDC 1009228) and **8** (CCDC 1023021).

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Table 1. Crystal data and refinement details for compounds **1**-**8**.

Compound	1	2	3	5	6	7*	8
CCDC number	1009218	1009219	1009220	1009227	1009229	1009228	1023021
Empirical formula	$C_{12}H_{18}ClO_4P$	$C_{12}H_{18}BrO_4P$	$C_{12}H_{18}IO_4P$	$C_{20}H_{27}O_4P$	$C_{21}H_{27}O_5P$	$C_{39}H_{48}NO_4P$	$C_{19}H_{23}O_5P$
Fw	292.68	337.14	384.13	362.39	390.40	625.75	362.34
Temp, [K]	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$	P-1	$P2_1/c$	$C2/c$
a, [Å]	33.100(5)	33.434(1)	34.091(2)	33.710(2)	6.690(2)	13.664(9)	41.181(13)
b, [Å]	11.236(5)	11.241(5)	11.245(6)	6.824(3)	9.064(3)	10.956(6)	11.010(3)
c, [Å]	8.061(5)	7.946(3)	8.001(4)	17.253(8)	17.502(5)	23.642(1)	8.186(3)
α, [°]					79.175(12)		
β, [°]	97.578(5)	97.374(5)	97.511(1)	90.834(8)	89.610(1)	98.563(1)	92.162(6)
γ, [°]					82.167(1)		
V, [Å^3]	2971.9(1)	2962.0(2)	3040.8(9)	3968(3)	1032.5(5)	3500(4)	3709(2)
Z	8	8	8	8	2	4	8
D(calcd), [Mg/cm^3]	1.308	1.512	1.678	1.213	1.256	1.188	1.215
μ [mm^{-1}]	0.368	2.887	2.215	0.159	1.256	0.119	0.174
Θ range, [°]	3.46 to 25.00	3.15 to 25.49	3.14 to 25.00	2.64 to 25.50	2.79 to 25.50	2.62 to 25.50	2.97 to 25.00°.
No. of reflns collected	10070	9304	10903	14827	7604	5027	13678
Independent reflections	2622	2749	2689	3692	3773	3909	3259
GOF	1.082	1.074	1.077	1.143	1.078	1.211	1.104
R1(I$_0$>2σ(I$_0$))	0.0858	0.0360	0.067	0.0667	0.0398	0.1244	0.0488
wR2 (all data)	0.2375	0.0922	0.2019	0.1702	0.0997	0.2577	0.1165

*data refined using just 200 frames; crystal decomposes too quickly to complete the data collection (800 frames).

ARTICLE

Graphical Abstract
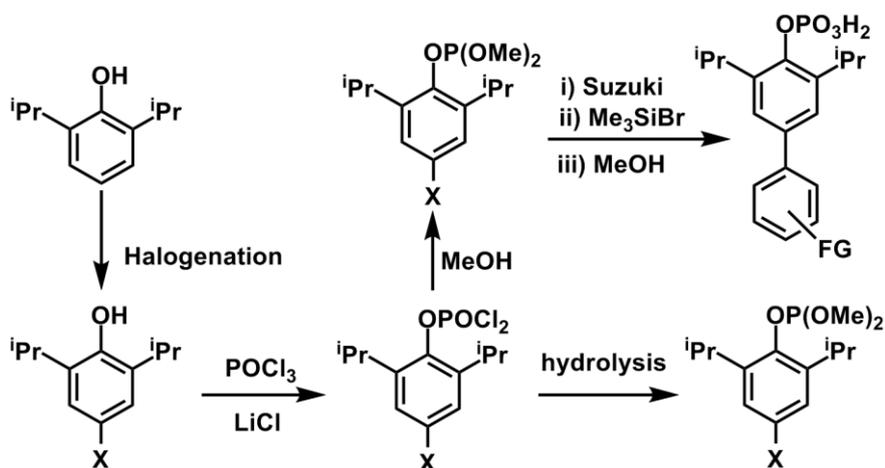
A new class of functionalized organophosphates, potential building units in materials and zeolite chemistry, is reported.