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An unusually unstable *ortho*-phosphinophenol and its use to prepare benzoxaphospholes having enhanced air-stability†

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The primary phosphine 3,5-di-*tert*-butyl-2-phosphinophenol has been prepared and characterized. Oddly, the presence of a sterically demanding *tert*-butyl group adjacent to the PH_2 centre renders the molecule very sensitive to loss of PH_3 and formation of 3,5-di-*tert*-butyl-phenol in chloroform solutions in the presence of air. The process was catalyzed by HCl and dependent on the purity of $CDCl_3$. Despite the instability of 3,5-di-*tert*-butyl-2-phosphinophenol, this material could be employed to produce a series of luminescent 2-*R*-4,6-di-*tert*-butyl-1,3-benzoxaphospholes having greater air stability than corresponding less bulky 2-*R*-1,3-benzoxaphospholes.

Introduction

Within the realm of multiply bonded main group compounds, a key paradigm has been the understanding that compounds bearing sterically demanding ligands shall possess enhanced kinetic stability. Thus over the years much effort has been given to the design and synthesis of bulky aryl and alkyl ligands that have been employed in the successful isolation of new types of element–element bonds.[1–5] In particular, compounds having P═C (phosphaalkene) and P═P (diphosphene) functionalities have become readily characterized when suitably decorated with sterically demanding groups. It was this approach that led to the first successful isolation of the diphosphene Mes*P═PMes*.[6]

At the same time that sterically demanding ligands can provide kinetic stabilization of inter-element multiple bonds, such groups can also inhibit the ability of P═E (E = C or P) bonds to participate in π-conjugation with C═C bonds. Specifically, large *ortho*-substituents (R′) will exert steric pressures to move attached P═C units out of alignment for maximal π-conjugation (Fig. 1).

Our group[7–16] and the Gates group[17–20] have been very interested in conjugated materials featuring P═C bonds. Many of these materials, however, display molecular distortions that diminish pπ overlaps necessary for π-conjugation.

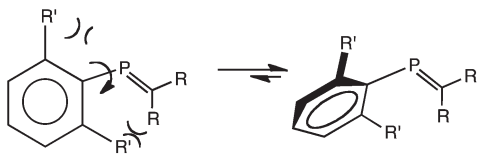

Fig. 1 Structural distortions induced by steric interactions of bulky groups.

One strategy to enforce coplanarity of P═C units with attached aryl frameworks involves incorporation of the phosphaalkene residue into a fused ring. Several examples of such materials are shown in Chart 1.[21–39] The chemistry of the 1,3-benzazaphospholes (**BAP-R**) in particular is quite extensive.[25,33] Our group has become interested in the 1,3-benzoxaphospholes (**BOP-R**) due to their highly fluorescent nature when R = aryl.[9,10]

We have also created new benzoxaphosphole analogues with expanded conjugation, as shown in Chart 2.[8,10] All of

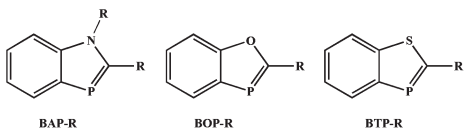

Chart 1

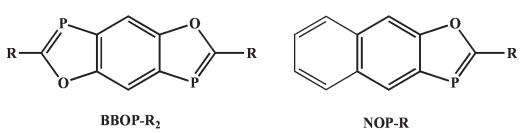

Chart 2

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these cyclic phosphaalkenes offer in comparison to acyclic phosphaalkenes (a) enforced coplanarity of P=C bonds with attached aromatic residues (b) enhanced air and water stability compared to many other phosphaalkenes and (c) unique fluorescent properties. We have found that while many of these benzoxaphospholes are air-stable as solids, they will slowly degrade in solution (days).

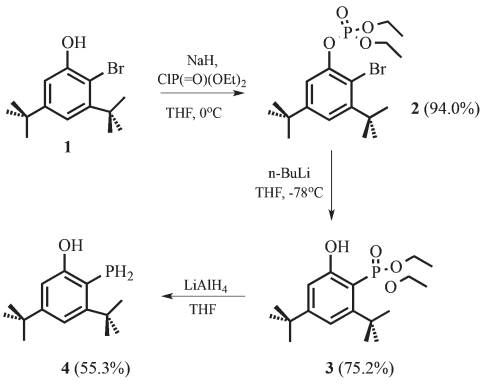
In order to facilitate employment of these types of materials into devices, we sought to increase the stability and solubility of benzoxaphospholes by introduction of a sterically demanding *tert*-butyl group *ortho* to the low coordinate phosphorus center. This article communicates the results of this strategy.

Results and discussion

Synthesis & stability of *ortho*-phosphinophenol 4

The synthesis of 1,3-benzoxaphospholes begins the appropriate *ortho*-phosphinophenol. We chose 3,5-di-*tert*-butyl-phenol (**i**) as a convenient starting point towards this target (Scheme 1). Phosphorylation of **i** by diethyl chlorophosphate readily affords 3,5-di-*tert*-butylphenylphosphate (**ii**). We were not able, however, to find conditions to effect the selective *ortho*-deprotonation of **ii** to generate **iii**. Intermediate **iii** is expected to undergo the anionic *phospha*-Fries rearrangement to yield **iv**. Attempts to access **iv** from **ii** using ^{n}BuLi, $^{i}Pr_2NLi$, or LiTMP (TMP = 2,2,5,5-tetramethylpiperidinyl) as bases led instead to mixtures of products (as ascertained by ^{31}P NMR spectroscopy). Some of the signals observed in the ^{31}P NMR spectra were consistent suggested that the bases were effecting dephosphorylation instead of deprotonation.

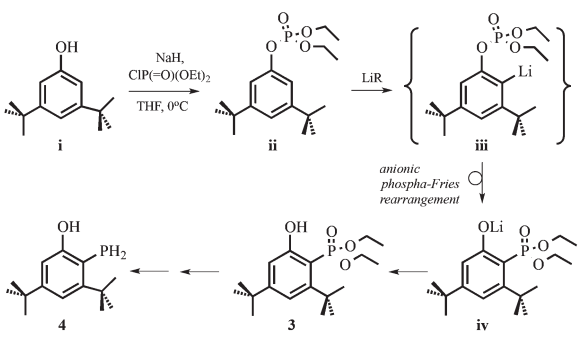
Access to key intermediate **iii** was achieved by an alternative strategy. Bromination of 3,5-di-*tert*-butyl-phenol (**i**) using Br_2 affords 3,5-di-*tert*-butyl-2-bromophenol (**1**).[40–42] Reaction with diethyl chlorophosphate and NaH leads to diethyl (2-bromo-3,5-di-*tert*-butylphenyl)phosphate (**2**) in excellent yield. Addition of *n*-butyllithium initiates lithium–bromine exchange (generating intermediate **iii**), and rapid migration of the phosphorus to the phenyl ring *via* the anionic *phospha*-Fries rearrangement[43,44] to produce **3**. Reduction of **3** using $LiAlH_4$ affords the *ortho*-phosphinophenol **4** in good yield (Scheme 2).



Scheme 2

Compound **4** is readily characterized by its signature ^{31}P NMR signal at −169.7 ppm (t, J_{HP} = 198 Hz). Unfortunately, the isolation of **4** is also accompanied by small amounts of 3,5-di-*tert*-butyl-phenol (*ca*. 2–5%). Oddly, solutions of **4** in $CDCl_3$ open to air quickly begin to decompose, and is completely consumed in 6 days. By contrast, the less hindered *ortho*-phosphinophenol **PP1** (Chart 3) shows no evidence of decomposition under the same conditions and time frame. Another surprising fact is that the major product (>90% ^{1}H NMR) of aerobic oxidation in $CDCl_3$ is 3,5-di-*tert*-butyl-phenol (**i**). The final ^{31}P NMR spectra are uninformative due to the presence of numerous signals of low intensity.

Similar observations have been made by Heinicke during isolation of certain substituted *ortho*-phosphinophenols, such as **PP2**[45] and **PP3**[46] (Chart 3).[47] The presence of traces HX (from the acid hydrolysis workup after the $LiAlH_4$ reduction of corresponding hydroxyphenylphosphonates) was suspected as catalysts for the decomposition process. This hypothesis was corroborated by the finding that replacing HCl with acetic acid during the workup produced less phenol. Attempts to further purify **PP3** and remove contaminating 2,4-di-*tert*-butylphenol by distillation led to further formation of 2,4-di-*tert*-butyl-phenol as well as formation of dihydro-1,2,3-benzoxadiphosphole **DBDP** (Chart 3). The fate of the phosphorus atoms in these reactions was presumed to be PH_3. The presence of sterically demanding groups, especially *ortho* to the OH group, was



Scheme 1

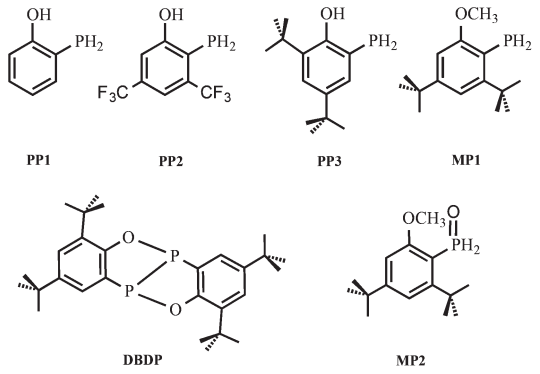


Chart 3

suggested to induce destabilizing OH···P interactions and makes these systems susceptible to carbon–phosphorus bond cleavage. Carbon–phosphorus bond cleavage is well established for organophosphorus compounds having the bulky Mes* (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) group.[48] The primary phosphine Mes*PH$_2$, however, is a rare example of an air-stable primary phosphine.

We were thus interested in determining why compound **4** is unstable. Early investigations of the air stability of **4** showed that solutions of **4** in C_6D_6 and DMSO-d_6 were more stable than solutions in $CDCl_3$ (compound **4** was found to persist up to 120 days in DMSO-d_6 solvent). Upon further investigations, however, the air stability of **4** varied somewhat depending on the specific bottle of $CDCl_3$ and/or the means used to purify the $CDCl_3$ used to prepare solutions.

Among the suspected impurities that can arise from the decomposition of $CDCl_3$ are HCl and phosgene.[49,50] Phosgene would be expected to hydrolyse in moist air to produce HCl. HCl could also be present as a trace contaminant from the synthesis of **4** (aqueous NH_4Cl was used to quench reaction mixture from the reduction of **3** by $LiAlH_4$).

We thus tested the impact of HCl on solutions of **4**. Addition of 5% HCl (in Et_2O) to a solution of **4** in $CDCl_3$ exposed to air does promote the decomposition of **4**. Within 30 minutes **4** is completely consumed and 3,5-di-*tert*-butylphenol is formed in >90% yield (^{1}H NMR, Fig. S1, ESI†). Analysis of the ^{31}P NMR spectra reveals PH_3 as the major product, as identified by a characteristic quartet (J_{HP} = 189 Hz) at δ −237.3. Repeating this experiment after treating the $CDCl_3$ with molecular sieves (Sigma-Aldrich 3 Å, 4–8 mesh, dried at 110 °C) slowed the decomposition of **4** (and production of PH_3) to 7 hours. Under the same conditions but under either nitrogen or dried air instead of air showed little or no decomposition of **4**. A solution of **4** in dry $CDCl_3$ under nitrogen with 5% HCl, in the presence of 1 equiv. of degassed water, slowly produces PH_3 (days–weeks). In addition, the presence of a new species identified by a doublet in the ^{31}P NMR spectra at δ 34.4 ppm with a J_{PH} coupling constant of 490 Hz is noted. This signal is consistent with the presence of 2-hydroxyphenylphosphinic acid.[51]

These observations might suggest the presence of an unknown contaminant in unpurified $CDCl_3$ is responsible for catalyzing the decomposition of **4**. This hypothesis can only be partly true, for addition of 1 equiv. of HCl (in Et_2O) to **4** in dry $CDCl_3$ induces the immediate decomposition of **4** to **i** and PH_3, in either air or under nitrogen.

In order to ascertain the impact of choice of acid, the impact of acetic acid and *p*-toluenesulfonic acid on **4** was examined. Solutions of **4** and 5% acetic acid-d_1 in unpurified $CDCl_3$ produce PH_3 over the period of a couple of days. Oddly, a solution of **4** and 1 equiv. of CH_3COOD in unpurified $CDCl_3$ does not produce any PH_3 in over 20 days open to air (some slight oxidation is noted). In fact, a solution of compound **4** in neat CH_3COOD (Sigma-Aldrich, 99 atom% D) open to the air is remarkably stable. The ^{31}P{^{1}H} NMR analysis of such solutions reveals a facile PH/PD exchange process (Fig. 2). For each successive deuterium added to compound **4**, a shift of 0.86 ppm in the ^{31}P NMR spectrum is observed.

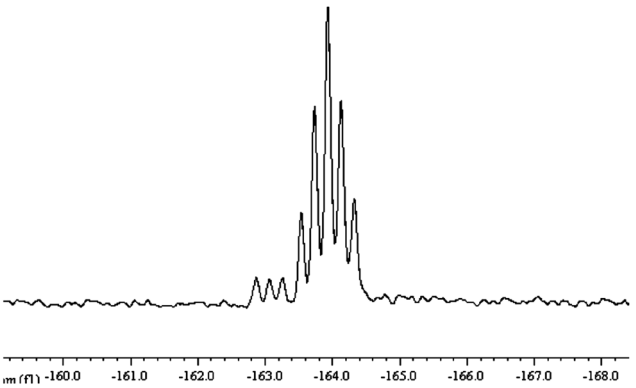
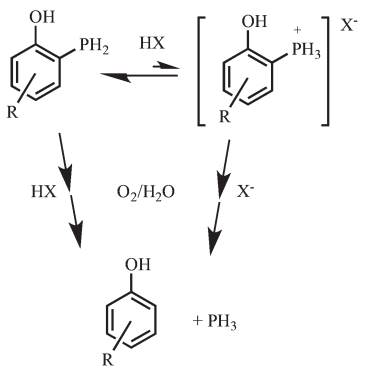


Fig. 2 ^{31}P{^{1}H} NMR spectrum of **4** in CH_3COOD showing **4**-d_1 (minor) and **4**-d_2 (major).

Reaction of **4** with 5% HOTs in unpurified $CDCl_3$ was also slow and produced **i** and PH_3 (5 days). Unlike the case with acetic acid, the reaction of **4** with 1 equivalent of HOTs occurs over 5 hours and shows the formation of 3,5-di-*tert*-butylphenol, and PH_3 as the main phosphorus containing species (Fig. S6, ESI†).

For comparison, we find that **PP1** is stable to acid in all cases. The ^{1}H NMR spectra of mixtures of **PP1** and HCl show broadening of both PH and OH resonances suggesting rapid proton transfer.

These collective experimental data present a challenge for a single clear mechanistic interpretation. The role of HX is further complicated by the uncertainty in the aggregation and dissociation of ionic species in $CDCl_3$. One simple starting point for discussion is depicted in Scheme 3. If the added HX protonates the phosphorus atom, the resulting phosphonium salt might be considered "protected" towards oxidation.[52] This hypothesis would be consistent with the fact that compound **4** is relatively air-stable in neat acetic acid. We have not been able to observe such phosphonium salts by ^{31}P NMR spectroscopy, however. The role of the anion might be critical in initiating carbon–phosphorus bond cleavage from [**4**]$^+$ (Scheme 3, right). Alternatively, the role of the acid might lie with steps occurring after oxidation by O_2/H_2O of **4** (Scheme 3, left).



Scheme 3

While the specific details of the carbon–phosphorus bond cleavage in **4** remain unknown, it is interesting to note that the very closely related *ortho*-phosphinoanisole **MP1** (Chart 3) undergoes aerobic oxidation retaining its phosphorus center to produce **MP2**.[40]

Another means to assess the air stability of primary phosphines has been reported by Higham and coworkers.[53,54] In this model two electronic factors were identified as critical to predict the air stability of a primary phosphine. Primary phosphines that have HOMOs that contained little phosphorus lone pair character displayed enhanced air-stability. In addition, if calculations on $[RPH_2]^{\cdot+}$ revealed SOMO energies above −10.0 eV, then enhanced air-stability was predicted.

We thus undertook similar calculations on phosphinophenols **PP1** and **4**. Minimization of the structure of **PP1** revealed the presence of two low energy conformations (Fig. S1, ESI†) that differ by only 1.0 kcal mol^{-1}. The HOMO for lowest energy isomer has little contribution from the phosphorus lone pair (Fig. 3, left). The OH group projects a hydrogen atom towards the phosphorus lone pair, suggesting OH···P hydrogen bonding. Previous studies, however, suggest limited stability is gained for EH···P hydrogen bonding interactions.[55–57]

The lowest energy isomer of **4** is shown in Fig. 3 (right). Like **PP1**, little phosphorus lone pair contribution is found for the HOMO. The *ortho*-*tert*-butyl group directs the hydrogen atoms on the phosphorus atom away from the bulky group. The hydroxyl hydrogen atom, in response, now directed away from the phosphorus atom and not available for any possible OH···P hydrogen bonding interaction. These results thus meet the first of the two criteria for enhanced air stability for a primary phosphine.

Calculations on $[\mathbf{PP1}]^{\cdot+}$ and $[\mathbf{4}]^{\cdot+}$ produced the results shown in Fig. 4. The lowest energy isomer of $[\mathbf{PP1}]^{\cdot+}$ shows a SOMO energy level at −11.3 eV, while the lowest energy isomer

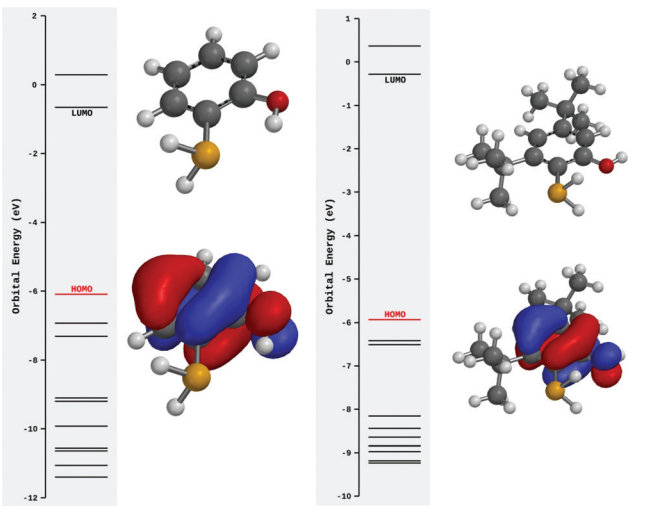


Fig. 3 Calculations results for *ortho*-phosphinophenol (left) and 3,5-di-*tert*-butyl-2-phosphinophenol **4** (right DFT B3LYP/6-31G*). Upper structure in each panel displays lowest energy conformation and lower structure shows HOMO orbital.

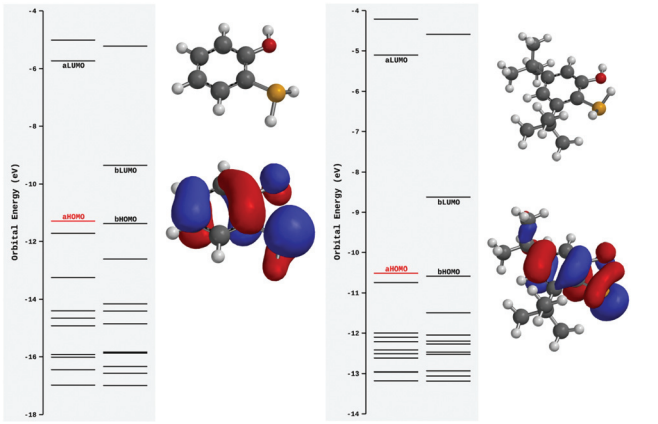
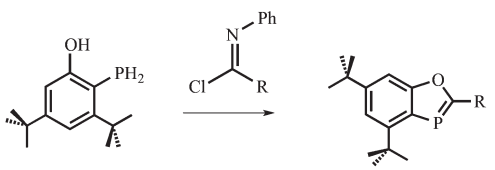


Fig. 4 Calculations results for the radical cations of *ortho*-phosphinophenol (left) and 3,5-di-*tert*-butyl-2-phosphinophenol **4** (right, DFT B3LYP/6-31G*). Upper structure in each panel displays lowest energy conformation and lower structure shows SOMO orbital.

of $[\mathbf{4}]^{\cdot+}$ shows a SOMO energy level at −10.5 eV. Both SOMOs are lower in energy than the −10.0 eV threshold that predicts enhanced air-stability. These criteria alone thus do not illuminate any special electronic reasons for the differences in the air-stability between **PP1** and **4**, and argue that the importance lies more in their special reactivity with acid. The underlying factors dictating stability of primary phosphines can be very subtle. For example, we recently reported on 3-phosphino-2-naphthol which shows no signs of decomposition in $CDCl_3$ open to air for over a month.[8] On the other hand, attempts to produce isomeric 1-phosphino-2-naphthol by analogous reduction of 1-(diethylphosphonate)-2-naphthol led only to 2-naphthol and loss of phosphorus.[47]

Synthesis and characterization of new 1,3-benzoxaphospholes

A series of bulky *tert*-butyl substituted 1,3-benzoxaphospholes (**5a–e**) were synthesized by refluxing solutions of *ortho*-phosphinophenol **4** with imidoyl chlorides (Scheme 4) in THF.[10] Compounds **5a–e** were isolated as colorless or yellow crystalline solids. Each compound displays a $^{31}P\{^1H\}$ diagnostic resonance between δ 77.2–92.2 ppm that is consistent with the reported values for other benzoxaphospholes. The isolated yields are modest, ranging from 20.9% to 46.4%. Under the reaction conditions that generate HX, some additional 3,5-di-



4 **5**

R= 4-MeC_6H_4 (**5a**, 20.9%),
4-MeOC_6H_4 (**5b**, 36.8%)
C_6H_5 (**5c**, 46.2%)
4-BrC_6H_4 (**5d**, 43.1%)
Ad (**5e**, 46.4%)

Scheme 4

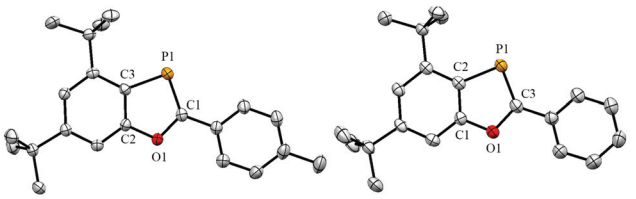


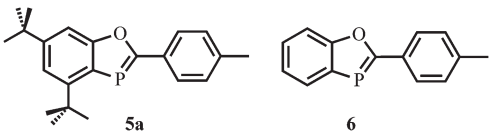
Fig. 5 ORTEP representations of the molecular structure of **5a** (left) and **5c** (right). Selected bond lengths (Å) and angles (°) for **5a**: P(1)–C(1), 1.708(1); P(1)–C(3) 1.795(1); O(1)–C(1), 1.368(1); O(1)–C(2), 1.376(1); C(1)–P(1)–C(3), 88.64(5); C(1)–O(1)–C(2), 110.40(9). Selected bond lengths (Å) and angles (°) for **5c**: P(1)–C(3), 1.703(2); P(1)–C(2) 1.799(2); O(1)–C(1), 1.377(2); O(1)–C(3), 1.374(2); C(2)–P(1)–C(3), 88.68(8); C(1)–O(1)–C(3), 110.4(1).

tert-butylphenol is formed, which not only decreases yields but added challenges in purification of the benzoxaphospholes.

The single-crystal structures of **5a** and **5c** are very similar and are shown in Fig. 5. The P═C bond lengths in **5a** and **5c** are 1.708(1) and 1.703(2) Å, respectively. These distances are slightly shorter than the P═C bond distance of 1.712(1) Å determined for 2-(*p*-chlorophenyl)-1,3-benzoxaphosphole.[58] Neither of these two structures shows evidence for π-stacking in the crystal lattice. Within each structure the 2-aryl group is rotated from the plane of the benzoxaphosphole by 24.3° and 17.6° for **5a** and **5c**, respectively. By contrast, the structures of 2-(*p*-chlorophenyl)-1,3-benzoxaphosphole is completely planar.[58] The *tert*-butyl-groups in **5a** and **5c** are rather remote to the 2-aryl substituents, thus subtle packing forces in the crystals are likely responsible for deviations from planarity in the conjugated backbones of these molecules (Fig. 4).

The *tert*-butyl groups, however, were predicted to increase the air stability of the benzoxaphospholes in solution. Solutions of **5a** and compound **6** (Chart 4), the direct analogue of **5a** bearing no *tert*-butyl groups in $CDCl_3$ (0.71 g mL^{-1}) were left exposed to the atmosphere at room temperature and the decomposition processes were monitored by ^{31}P and ^{1}H NMR spectroscopy (as $CDCl_3$ evaporated more $CDCl_3$ was added). It was found that **6** started to decompose after only 1 hour. After 3 days little **6** remains. Sterically encumbered **5a**, however, exhibits much greater air-stability. The solution of **5a** required 33 days to decompose to the same extent that **6** does in 3 days.

1,3-Benzoxaphospholes are one of a small class of compounds that having phosphaalkene units that display significant fluorescence.[10] The presence of the added *tert*-butyl groups was not expected to greatly influence this key property. Indeed, the new benzoxaphospholes **5**, like previous examples, are blue when irradiated with UV light. The specific absorption and fluorescence spectral data for **5a–e** in CH_2Cl_2 are presented in Table 1. As found for non-hindered BOP-R (Chart 1),



5a **6**

Chart 4

Table 1 Absorption and fluorescence data for **5a–e** in CH_2Cl_2

	R	λ_{max} (nm)	ε (M^{-1} cm^{-1})	$\lambda_{F,max}$ (nm)	Φ_F
5a	4-MeC_6H_4	348	23 650	430	0.13
5b	4-$MeOC_6H_4$	354	12 190	438	0.12
5c	C_6H_5	345	12 110	425	0.12
5d	4-BrC_6H_4	353	21 680	427	0.07
5e	Ad	289	14 440	424	0.04
6[a]	4-MeC_6H_4	343	20 000	426	0.69

[a] Data from ref. 10.

the optical properties depend on the nature of the R group. The data reveal π–π* transitions for the compounds **5a–d** varied from 348 to 354 nm, and at 289 nm for compound **5e**. Aryl substituted compounds **5a–d** displayed λ_{em} from 425 to 438 nm, while alkyl substituted compound **5e** showed λ_{em} at 424 nm. While compounds **5** display comparable absorption and fluorescence properties to previously reported BOP-Rs, the quantum yields (Φ_F) were noticeably lower, possibly due to extra degrees of vibrational energy relaxation provided by additional *tert*-butyl groups. Unlike the compounds such as **6**, compounds **5** show appreciable fluorescence in the solid state. This fact is attributable to the presence of the *tert*-butyl groups which prevent π-stacking and fluorescence quenching in the solid state.

Conclusion

The bulky *ortho*-phosphinophenol 3,5-di-*tert*-butyl-2-phosphinophenol **4** has been prepared and characterized. Compound **4** is unusually susceptible to an acid catalysed carbon–phosphorus bond cleavage reaction that produces 3,5-di-*tert*-butyl-phenol and PH_3. Despite the sensitive nature of **4**, it has been successfully utilized to produce a series of highly luminescent 2-*R*-4,6-di-*tert*-butyl-1,3-benzoxaphospholes. Two of these new benzoxaphospholes have been structurally characterized. Examination of the air stability of the benzoxaphospholes shows that they are more stable than derivatives not possessing *tert*-butyl groups adjacent to the phosphorus atoms.

Experimental

General information

All air-sensitive operations were performed under nitrogen atmosphere, using Schlenk line techniques or within a Vacuum Atmospheres MBraun glove box unless otherwise stated. Tetrahydrofuran, hexanes and toluene were dried by distillation from sodium benzophenone ketyl. Dichloromethane was dried by distillation from CaH_2 prior to use for UV-vis and fluorescence measurements. Benzimidoyl chlorides were prepared according to literature procedures.[59] 2-Bromo-3,5-di-*tert*-butylphenol was prepared by the reaction of 3,5-di-*tert*-butylphenol with Br_2.[41] ^{1}H, $^{13}C\{^{1}H\}$ and ^{31}P NMR spectra were recorded on a Varian INOVA AS-400 or 600 spectrometers, and all chemical shifts are referred to residual $CHCl_3$ signals (for ^{1}H NMR

spectra) or to an external sample of 85% H_3PO_4 (for ^{31}P NMR spectra). Melting points were measured on a Mel-temp melting point apparatus. Elemental analyses were performed by Robertson Microlit Laboratories (Madison, NJ). High resolution mass spectrometry was performed by the University of Michigan Mass Spectrometry facility using a VG (Micromass) 70-250-S magnetic sector spectrometer. UV-vis and fluorescence data were recorded using a Cary 50 Bio UV-Visible spectrophotometer and a Cary Eclipse spectrometer, respectively. Anthracene in ethanol was used as the quantum yield standard.[60]

Experimental procedures

Diethyl (2-bromo-3,5-di-*tert*-butylphenyl)phosphate (2). To a suspension of NaH (60% in mineral oil, 1.47 g, 36.8 mmol) in THF (50 mL) was slowly added a solution of 2-bromo-3,5-di-*tert*-butylphenol (10.0 g, 35.1 mmol) in THF (50 mL) at 0 °C. The yellow mixture was stirred at 0 °C for 30 min, and then diethylchlorophosphate (5.40 mL, 36.8 mmol) was added. The mixture was stirred at room temperature for 1 hour to yield a brown solution. To the reaction mixture was slowly added saturated NH_4Cl solution (~5 mL), followed by the addition of 100 mL of diethylether, then by addition of 100 mL of a saturated brine solution. The organic layer was separated and then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum to yield a brown oil. Yield: 13.9 g (94.0%). ^1H NMR (399.7 Hz): δ 7.34 (m, 1H), 7.27 (m, 1H), 4.27 (m, 4H), 1.52 (s, 9H), 1.35 (td, 6H, $^4J_{PH}$ = 1.2 Hz, $^3J_{HH}$ = 7.2 Hz), 1.29 (s, 9H). $^{31}P\{^1H\}$ NMR (161.8 Hz): δ −6.3 (s). $^{13}C\{^1H\}$ NMR (100.5 Hz): δ 150.7, 148.8, 148.2 (d, J_{pc} = 5.6 Hz), 121.1, 115.7 (d, J_{pc} = 2.1 Hz), 112.0 (d, J_{pc} = 7.9 Hz), 64.6 (d, J_{pc} = 6.3 Hz), 37.3, 34.7, 31.0, 29.7, 16.0 (d, J_{pc} = 6.8 Hz). HRMS ($[M + H]^+$): *m*/*z* 421.1138 (calc. 421.1138).

Diethyl (2-hydroxy-4,6-di-*tert*-butylphenyl)phosphonate (3). To a solution of diethyl (2-bromo-3,5-di-*tert*-butylphenyl)-phosphate (2.53 g, 6.01 mmol) in THF (75 mL) was added 3.40 mL *n*-BuLi (2.5 M in hexane, 8.41 mmol) at −78 °C. The mixture was stirred at −78 °C for 30 minutes, and then was poured into a room temperature mixture of saturated NH_4Cl solution (50 mL) and diethylether (50 mL). The organic layer was separated and then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum to yield a yellow oil. The material was further purified by distillation using Buchi glass oven (B-585 kugelrohr, 190 °C, 0.05 mm Hg) to initially afford a colorless oil, which after cooling to room temperature, yielded a colorless crystalline solid. Yield: 1.55 g (75.2%). Mp: 39–40 °C. ^1H NMR (399.7 Hz): δ 11.9 (br s, 1H, $^4J_{PH}$ = 0.8), 7.14 (dd, 1H, $^4J_{HH}$ = 2.0 Hz, $^4J_{PH}$ = 6.0 Hz), 6.85 (dd, 1H, $^4J_{HH}$ = 2.0 Hz, $^4J_{PH}$ = 4.8 Hz), 4.19 (m, 4H), 1.46 (s, 9H), 1.35 (td, 6H, $^4J_{PH}$ = 0.4 Hz, $^4J_{HH}$ = 6.8 Hz), 1.28 (s, 9H). $^{31}P\{^1H\}$ NMR (161.8 Hz): δ 27.6 (s). $^{13}C\{^1H\}$ NMR (100.5 Hz): δ 164.6 (d, J_{pc} = 7.9 Hz), 157.1 (d, J_{pc} = 2.8 Hz), 154.3 (d, J_{pc} = 8.2 Hz), 117.1 (d, J_{pc} = 14.2 Hz), 114.0 (d, J_{pc} = 12.1 Hz), 103.6 (d, J_{pc} = 177.1 Hz), 62.4 (d, J_{pc} = 5.8 Hz), 38.2 (d, J_{pc} = 3.1 Hz), 35.0, 32.6, 30.7, 16.1 (d, J_{pc} = 6.9 Hz). Elemental Analyses Calc. for $C_{18}H_{31}O_4P$, C 63.14%, H 9.13%; found: C 63.02%, H 8.88%.

3,5-Di-*tert*-butyl-2-phosphinophenol (4). To a solution of $LiAlH_4$ (1.03 g, 27.0 mmol) in 150 mL THF was slowly added a solution of diethyl (2-hydroxy-4,6-di-*tert*-butylphenyl)phosphonate (3.70 g, 10.8 mmol) in 50 mL THF at 0 °C. The mixture was stirred at room temperature overnight. To the reaction mixture was slowly added a degassed saturated NH_4Cl solution (~5 mL). The mixture was then extracted with degassed diethylether (~100 mL) and the organic layer was separated and dried over $MgSO_4$. The solvent was removed *in vacuo* to yield a colorless oil. Yield: 1.42 g (55.3%). ^1H NMR (399.7 Hz): δ 7.11 (m, 1H), 6.86 (d, 1H, $^4J_{HH}$ = 1.6 Hz), 5.53 (br s, 1H), 3.68 (d, 2H, $^1J_{PH}$ = 198.4 Hz), 1.55 (s, 9H), 1.30 (s, 9H). $^{31}P\{^1H\}$ NMR (161.8 Hz): δ −169.7 (s). $^{13}C\{^1H\}$ NMR (100.5 Hz): δ 158.2, 155.6 (d, J_{pc} = 16.7 Hz), 153.1, 116.0 (d, J_{pc} = 6.3 Hz), 109.8, 107.4 (d, J_{pc} = 22.2 Hz), 37.3, 34.8, 31.7 (d, J_{pc} = 11.9 Hz), 31.1. HRMS (EI, 70 eV): *m*/*z* 238.1487 (calc. 238.1487).

4,6-Di-*tert*-butyl-2-(4-methylphenyl)-1,3-benzoxaphosphole (5a). To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (0.562 g, 2.36 mmol) in 10 mL THF was added a solution of 4-methyl-*N*-phenylbenzimidoyl chloride (1.08 g, 4.68 mmol) in 20 mL THF. The reaction was refluxed for 96 hours to produce a yellow cloudy solution. After the reaction was cooled to room temperature, the mixture was filtered to remove a white precipitate. The solvent was removed under vacuum from the filtrate to yield a yellow solid. The solid was extracted with hexanes and filtered through Celite, and then passed through basic alumina to yield a colorless solution. The solvent was removed *in vacuo* to yield a colorless crystalline **5a**. Yield: 0.167 g (20.9%). Mp: 92–94 °C. ^1H NMR (399.7 Hz): δ 7.92 (m, 2H), 7.62 (m, 1H), 7.31 (m, 1H), 7.23 (d, 2H, $^3J_{HH}$ = 8 Hz), 2.39 (s, 3H), 1.59 (s, 9H), 1.41 (s, 9H). $^{31}P\{^1H\}$ NMR (161.8 Hz): δ 85.8 (s). $^{13}C\{^1H\}$ NMR (100.5 Hz): δ 193.9 (d, J_{pc} = 54.1 Hz), 161.2 (d, J_{pc} = 4.0 Hz), 151.1 (d, J_{pc} = 9.7 Hz), 150.7 (d, J_{pc} = 3.1 Hz), 139.6 (d, J_{pc} = 4.7 Hz), 132.0 (d, J_{pc} = 13.6 Hz), 130.6 (d, J_{pc} = 44.3 Hz), 129.5, 124.6 (d, J_{pc} = 14.2 Hz), 117.2 (d, J_{pc} = 7.5 Hz), 108.0, 36.9 (d, J_{pc} = 2.3 Hz), 35.2, 31.5, 31.0 (d, J_{pc} = 8.8 Hz), 21.5. HRMS (EI, 70 eV): *m*/*z* 338.1806 (calc. 338.1800). UV(CH_2Cl_2): λ_{max}, nm (ε, M^{-1} cm^{-1}) 348 (23 650). Fluorescence (CH_2Cl_2): λ_{ex}, 430 nm. Quantum yield (CH_2Cl_2): Φ 0.13.

4,6-Di-*tert*-butyl-2-(4-methoxyphenyl)-1,3-benzoxaphosphole (5b). To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (0.458 g, 1.92 mmol) in 10 mL THF was added a solution of 4-methoxy-*N*-phenylbenzimidoyl chloride (0.519 g, 2.11 mmol) in 20 mL THF. The reaction was refluxed for 38 hours to produce a yellow cloudy solution. After the reaction was cooled to room temperature, the mixture was filtered to remove a white precipitate. The solvent was removed by vacuum to yield a yellow solid. The solid was extracted with hexanes and filtered through Celite and then passed through basic alumina to give a yellow solution. The solvent was removed *in vacuo* to yield a yellow solid. Recrystallization from toluene afforded a yellow crystalline **5b**. Yield: 0.250 g (36.8%). Mp: 99–100 °C. ^1H NMR (399.7 Hz): δ 7.96 (m, 2H), 7.59 (m, 1H), 7.29 (m, 1H), 6.94 (m, 2H), 3.87 (s, 3H), 1.59 (s, 9H), 1.40 (s, 9H). $^{31}P\{^1H\}$ NMR (161.8 Hz): δ 80.9 (s). $^{13}C\{^1H\}$ NMR (150.0 Hz): δ 193.8 (d, J_{pc} = 54 Hz), 161.1 (d, J_{pc} = 3.8 Hz), 160.7 (d, J_{pc} = 4.5 Hz), 151.0

(d, J_{pc} = 9.8 Hz), 150.5 (d, J_{pc} = 3.0 Hz), 130.6 (d, J_{pc} = 44.1 Hz), 127.8 (d, J_{pc} = 13.4 Hz), 126.2 (d, J_{pc} = 14.0 Hz), 117.1 (d, J_{pc} = 7.4 Hz), 114.1, 107.9, 55.4, 36.9 (d, J_{PC} = 2.1 Hz), 35.2, 31.5, 31.0 (d, J_{PC} = 8.9 Hz). HRMS (EI, 70 eV): *m*/*z* 354.1735 (calc. 354.1749). UV(CH_2Cl_2): λ_{max}, nm (ε, M^{-1} cm^{-1}) 354 (12 190). Fluorescence (CH_2Cl_2): λ_{ex}, 438 nm. Quantum yield (CH_2Cl_2): Φ 0.12.

4,6-Di-*tert*-butyl-2-phenyl-1,3-benzoxaphosphole (5c). To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (1.00 g, 4.21 mmol) in 20 mL THF was added a solution of *N*-phenyl-benzimidoyl chloride (0.998 g, 4.63 mmol) in 20 mL THF. The reaction was refluxed for 13 hours to produce a yellow cloudy solution. After the reaction was cooled to room temperature, a white precipitate was removed by filtration, and the solvent was removed by vacuum to yield a yellow solid. The solid was extracted with hexanes and filtered through Celite and then passed through basic alumina to yield a colorless solution. The solvent was removed *in vacuo* to yield a colorless crystalline solid **5c**. Yield: 0.630 g (46.2%). Mp: 98–100 °C. ^{1}H NMR (399.7 Hz): δ 8.03 (m, 2H), 7.63 (m, 1H), 7.43 (m, 2H), 7.38 (m, 1H), 7.32 (m, 1H), 1.60 (s, 9H), 1.41 (s, 9H). $^{31}P\{^1H\}$ NMR (161.8 Hz): δ 89.4 (s). $^{13}C\{^1H\}$ NMR (100.5 Hz): δ 193.5 (d, J_{pc} = 54.0 Hz), 161.4 (d, J_{pc} = 4.0 Hz), 151.3 (d, J_{pc} = 9.8 Hz), 150.9 (d, J_{pc} = 3.0 Hz), 134.7 (d, J_{pc} = 13.2 Hz), 130.6 (d, J_{pc} = 44.5 Hz), 129.3 (d, J_{pc} = 4.6 Hz), 128.7, 124.6 (d, J_{pc} = 14.4 Hz), 117.2 (d, J_{pc} = 7.6 Hz), 108.1, 36.9 (d, J_{pc} = 2.1 Hz), 35.2, 31.5, 31.0 (d, J_{pc} = 8.8 Hz). HRMS (EI, 70 eV): *m*/*z* 324.1644 (calc. 324.1643). UV(CH_2Cl_2): λ_{max}, nm (ε, M^{-1} cm^{-1}) 345 (12 110). Fluorescence (CH_2Cl_2): λ_{ex}, 425 nm. Quantum yield (CH_2Cl_2): Φ 0.12.

4,6-Di-*tert*-butyl-2-(4-bromophenyl)-1,3-benzoxaphosphole (5d). To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (1.00 g, 4.20 mmol) in 20 mL THF was added a solution of 4-bromo-*N*-phenyl-benzimidoyl chloride (1.36 g, 4.62 mmol) in 20 mL THF. The reaction was refluxed for 13 hours to produce a yellow cloudy solution. After the reaction was cooled down to room temperature a white precipitate was removed by filtration, and the solvent was removed under vacuum to yield a yellow solid. The solid was extracted with hexanes and the solution was filtered through Celite and then passed through basic alumina to yield a yellow solution. The solvent was removed *in vacuo* to yield a yellow solid. Recrystallization from hexanes provided a yellow crystalline **5d**. Yield: 0.730 g (43.1%). Mp: 102–103 °C. ^{1}H NMR (399.7 Hz): δ 7.88 (m, 2H), 7.61 (m, 1H), 7.54 (m, 2H), 7.32 (m, 1H), 1.59 (s, 9H), 1.40 (s, 9H). $^{31}P\{^1H\}$ NMR (161.8 Hz): δ 92.2 (s). $^{13}C\{^1H\}$ NMR (150.0 Hz): δ 191.8 (d, J_{pc} = 53.3 Hz), 161.4 (d, J_{pc} = 4.1 Hz), 151.5, 151.4 (d, J_{pc} = 2.3 Hz), 133.6 (d, J_{pc} = 13.4 Hz), 131.9 (d, J_{pc} = 1.1 Hz), 130.4 (d, J_{PC} = 44.3 Hz), 126.0 (d, J_{pc} = 14.4 Hz), 123.2 (d, J_{pc} = 5.9 Hz), 117.4 (d, J_{pc} = 7.8 Hz), 108.1, 36.9 (d, J_{pc} = 2.1 Hz), 35.2, 31.5, 31.1 (d, J_{pc} = 8.7 Hz). HRMS (EI, 70 eV): *m*/*z* 402.0741 (calc. 402.0748). UV(CH_2Cl_2): λ_{max}, nm (ε, M^{-1} cm^{-1}) 353 (21 680). Fluorescence (CH_2Cl_2): λ_{ex}, 427 nm. Quantum yield (CH_2Cl_2): Φ 0.07.

4,6-Di-*tert*-butyl-2-adamantyl-1,3-benzoxaphosphole (5e). To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (1.04 g, 4.37 mmol) in 20 mL THF was added a solution of 1-adamantane-benzimidoyl chloride (1.32 g, 4.82 mmol) in 20 mL THF. The reaction was refluxed for 17 hours to produce a yellow cloudy solution. After the reaction was cooled down to room temperature a white precipitate was removed by filtration, and the solvent was removed under vacuum to yield a yellow solid. The solid was extracted with hexanes and the solution was filtered through Celite and then passed through basic alumina to give a colorless solution. The solvent was removed *in vacuo* to yield white solid **5e**. Yield: 0.776 g (46.4%). Mp: 103–104 °C. ^{1}H NMR (399.7 Hz): δ 7.54 (m, 1H), 7.27 (m, 1H), 2.11 (m, 3H), 2.09 (m, 6H), 1.80 (m, 6H), 1.56 (s, 9H), 1.38 (s, 9H). $^{31}P\{^1H\}$ NMR (161.8 Hz): δ 77.2 (s). $^{13}C\{^1H\}$ NMR (100.5 Hz): δ 210.8 (d, J_{pc} = 61.3 Hz), 161.4 (d, J_{pc} = 3.1 Hz), 151.2 (d, J_{pc} = 9.7 Hz), 149.9 (d, J_{pc} = 2.5 Hz), 129.5 (d, J_{pc} = 45.1 Hz), 116.7 (d, J_{pc} = 6.9 Hz), 107.8, 42.0 (d, J_{pc} = 9.3 Hz), 39.6 (d, J_{pc} = 10.8 Hz), 36.9 (d, J_{pc} = 2.4 Hz), 36.7, 35.1, 31.5, 31.0 (d, J_{pc} = 9.0 Hz), 28.4. HRMS (EI, 70 eV): *m*/*z* 382.2422 (calc. 383.2455). UV(CH_2Cl_2): λ_{max}, nm (ε, M^{-1} cm^{-1}) 289 (14 440). Fluorescence (CH_2Cl_2): λ_{ex}, 424 nm. Quantum yield (CH_2Cl_2): Φ 0.04.

Stability studies. Air-stability tests were performed in NMR tubes with deuterated solvent and opened to air at room temperature. As $CDCl_3$ evaporated, more $CDCl_3$ was added to replenish the solution. For solutions studied under nitrogen, the samples were prepared in glove bags and transferred to J-Young NMR tubes. Samples were monitored by ^{1}H NMR and ^{31}P NMR spectroscopy.

Computational studies. Calculations were undertaken using DFT (6-31G*) level of theory as implemented in the program SPARTAN'10 (Wavefunction, Inc., Irvine, CA) and as previously described.[53]

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