Novel N-phosphorylated iminophosphoranes based on 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide

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Abstract

A series of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-based N-phosphorylated iminophosphoranes was synthesized utilizing Atherton-Todd and subsequently Staudinger reactions. The structures of these iminophosphoranes were revealed by nuclear magnetic resonance spectroscopy and X-ray crystallography. The decomposition properties were determined by thermogravimetric analysis and indicate a relationship between the chemical environment around the phosphorus atom and the thermostability of the corresponding compound.

Keywords: 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, phosphorus, iminophosphorane, Staudinger reaction, Atherton-Todd reaction
**Introduction**

Iminophosphoranes are organophosphorus compounds with a general structural unit $R_3P=NR'$. They are principally known as ligands for homogeneous catalysis.\(^1\) N-Thiophosphorylated ($R' = -P(S)R''_2$) and N-phosphorylated iminophosphoranes ($R = -P(O)R''_2$) are described as intermediates in the synthesis of phosphorus-containing dendrimers.\(^2\) Also limited examples of their use as flame retardants for polymeric materials are described, e.g. the N-(thio)phosphorylated iminophosphoranes with $R = R''_2 = C_6H_5$\(^3\) and some heterocyclic iminophosphoranes.\(^4-6\)

Due to its versatility and effectiveness for use in flame retardants phosphorus is a promising element to displace the widespread halogenated versions.\(^7,8\) A building block of great importance not only for flame retardancy but also as complexing ligand in homogenous catalysis are derivatives of dibenzo[c.e][1,2]oxaphosphorine.\(^9-12\)

Novel derivatives of the commercially available 9,10-dihydro-9-oxa-10-phenaphenanthrene-10-oxide (DOPO) with tailored chemical structures are highly pursued as flame retardants due to their superior flame retardant efficiency, low environmental impact and enhanced mechanical properties when incorporated into polymers, particularly in epoxy resins and engineering plastics.\(^13-15\) Most recently a novel DOPO-containing halogen-free ionic liquid showed promising results in improving the fire safety of an epoxy resin.\(^16\)

From the synthetic point of view, the Staudinger reaction is known to be a very efficient and convenient reaction to synthesize iminophosphoranes from organic azides and trivalent organophosphorus compounds.\(^17\) In recent years various organic azides including phosphoryl azides have been employed in this reaction.\(^18-21\) They can be easily obtained from the corresponding phosphorochloridates. Modern synthetic routes make use of solvent- and catalyst-free microwave techniques\(^22\) as well as phase transfer catalysis.\(^23\) Recently Shi *et al.* described the direct azidation of phosphites under modified Atherton-Todd conditions in which the chlorides occur as intermediates.\(^24\) Riesel *et al.* combined the Atherton-Todd and the Staudinger reaction in a one-pot synthesis.\(^25\) Iminophosphoranes can also be obtained via azayldiides (e.g. Ph$_3$PNLi).\(^26\)

In this study, novel DOPO-containing iminophosphoranes were synthesized, starting from the intermediate 6-azidodibenzo[c.e][1,2]oxaphosphinine-6-oxide (DOPO-N$_3$), and subsequently using the Staudinger reaction.

**Results and Discussion**

The new DOPO-based N-phosphorylated iminophosphoranes were prepared as shown in Scheme 1.\(^17,24\) DOPO-N$_3$ was initially prepared by azidation of DOPO under Atherton-Todd conditions in 92% yield as a pale yellow oil.\(^24\) Column chromatography with EE/hexane (60:40) on silica gel yielded the spectroscopically pure product as a colorless oil ($R_f = 0.66$). For consecutive reactions filtration of the crude product over silica gel and further extraction with NaHCO$_3$/H$_2$O was sufficient.

In the Staudinger reaction the trivalent phosphorus compounds trimethyl phosphite, triphenyl phosphite, triphenylphosphine, 6-ethoxy-6H-dibenzo[c.e][1,2]oxaphosphinine (DOP-OEt)\(^28\) and the bifunctional 1,2-bis(diphenylphosphino)ethane (Diphos) were converted into the DOPO-based N-phosphorylated iminophosphoranes (Scheme 2).
Scheme 1. General synthetic strategy of the DOPO-based iminophosphoranes via the Atherton-Todd and Staudinger reactions. \(^{24,27}\)

Scheme 2. Synthesis of the DOPO-based iminophosphoranes via Staudinger reactions.

For comparative analysis, diphenylphosphoryl azide (DPPA) and DOP-OEt were also transformed into the corresponding N-phosphorylated iminophosphorane (Scheme 3).

Scheme 3. Synthesis of (Ph)\(_2\)(O)P-N=DOP-OEt from DPPA and DOP-OEt via the Staudinger reaction.
DOPO-N=P(OMe)₃ was also obtained directly from DOPO and trimethyl phosphite in a one-pot synthesis as shown in Scheme 4 following an earlier published procedure of Riesel et al.²⁵ Due to the combination of the Atherton-Todd and the Staudinger reactions, DOPO-N₃ is formed only in situ and azide concentration during work sequence is kept very low. The yield referred to DOPO was merely 76 % though.

Scheme 4. One-pot synthesis of DOPO-N=P(OMe)₃.²⁵

The transformation of the starting materials was confirmed using ³¹P and ¹H-NMR. The ¹H-NMR spectra show the characteristic signal pattern of the DOPO moiety in the aromatic region while the ³¹P-NMR spectra indicate the ²Jpp coupling of N-phosphorylated iminophosphoranes except for DOPO-N=P(OPh)₃ which shows a singlet due to coincidence.² If applicable, assignments of ¹³C-NMR signals could be made in accordance with previous published results by our group based on DOPO itself and can be found in the supplementary information.¹²

The N-phosphorylated iminophosphoranes DOPO-N=P(OPh)₃, DOPO-N=P(Ph)₃ and [DOPO-N=P(Ph)₂CH₂]₂ were recrystallized from isopropyl alcohol. Single-crystal X-ray diffraction studies of those compounds led to comparable results on molecular parameters such as bond angles and bond lengths (Table 1). Crystallographic data and structure refinement details are shown in the supplementary information.

The molecular structure of DOPO-N=P(OPh)₃ is shown in Figure 1. It contains an iminophosphorane unit that consists of two phosphorus atoms bonded to a connecting nitrogen atom spanning an angle of 131.0(3)°. Atom P₁ is part of the chiral DOPO unit that is statistically disordered whereas P₂ is connected to three phenoxy groups through P-O-C linkages. The distance P₁-N is 1.604(4) Å and P₂-N is 1.528(4) Å.

The molecular structure of DOPO-N=P(Ph)₃ (Figure 2) contains the same basic iminophosphorane skeletal unit as DOPO-N=P(OPh)₃. Compared to the reference compound (PhO)₂(O)P-N=P(OPh)₃ and DOPO-N=P(Ph)₃, the P-N-P angle of DOPO-N=P(Ph)₃ is spread by roughly 10° to 142.50(15)°. The P-N bonds converge to 1.581(2) Å for P₁-N in the DOPO-containing unit and 1.558(2) Å for P₂-N in the phenyl unit.

Table 1. Structural comparison of new N-phosphorylated iminophosphoranes, Ph-N=P(Ph)₃, (PhO)₂(O)P-N=P(OPh)₃ and [(PhO)₂(O)P-N=P(Ph)₂cp]₂Fe

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<th>Bond angles (°)</th>
<th>Bond lengths (Å)</th>
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<td>P-N-C</td>
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<tr>
<td>Compound</td>
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<tr>
<td>Ph-N=P(Ph)₃</td>
<td>130.4(3)</td>
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<tr>
<td>DOIPO-N=P(OPh)₃</td>
<td>131.0(3)</td>
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Table 1. Continued

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<th>Bond angles (°)</th>
<th>Bond lengths (Å)</th>
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<td>P-N-C</td>
<td>P1-N-P2</td>
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<tr>
<td>(PhO)₂(O)P=N=P(OPh)₃</td>
<td>133.9(3)</td>
<td>1.596(4)</td>
</tr>
<tr>
<td>[(PhO)₂(O)P-N=P(Ph)₂cp]₂Fe²</td>
<td>134.4(1)</td>
<td>1.624(2)</td>
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<tr>
<td>DOPO-N=P(Ph)₃</td>
<td>142.50(15)</td>
<td>1.581(2)</td>
</tr>
<tr>
<td>[DOPO-N=P(Ph)₂CH₂]₂</td>
<td>145.7(3)</td>
<td>1.560(3)</td>
</tr>
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</table>

Figure 1. Molecular structure of DOPO-N=P(OPh)₃ in solid state. For clarity, second disordered DOPO unit and H-atoms are omitted.
Figure 2. Molecular structure of DOPO-N=P(Ph)$_3$ in solid state. For clarity, H-atoms are omitted.

[DOPO-N=P(Ph)$_2$-CH$_2$)$_2$ crystallizes with half an iminophosphorane molecule and one molecule of isopropyl alcohol per asymmetric unit (Figure 3). The P-N-P angle is 145.7(3)$^\circ$ and shows the greatest spread of all investigated compounds. The distance P1-N is even shorter and almost equal to P2-N, in particular 1.560(3) Å and 1.555(3) Å.

Figure 3. Molecular structure of [DOPO-N=P(Ph)$_2$-CH$_2$]$_2$ and isopropyl alcohol in solid state. For clarity, H-atoms are omitted.
These results show a close coherence between the P-N-P angle and the bond length of P-N, as already revealed for derivatives of hexaphenoxytricyclopentaphosphazene [NP(OPh)₂]₃ and Ph-N=P(Ph)₃ where larger P-N-P angles are accompanied by shorter P-N bonds.²⁹,³¹

Regarding both phosphorus-nitrogen bonds in one molecule it is apparent that the phenoxy moiety in DOPO-N=P(OPh)₃ and (PhO)₂(O)P-N=P(OPh)₃ leads to smaller P₁-N-P₂ angles and clearly distinguishable bond lengths among the phosphorus and each nitrogen atom, whereas carbon-connected moieties (as present in DOPO-N=P(Ph)₃ and [DOPO-N=P(Ph)₂CH₂]₂) implicate almost equal bond lengths and larger P₁-N-P₂ angles. Furthermore, P₂-C bonds between the phosphorus atom and phenyllic groups as well as the methylene unit in [DOPO-N=P(Ph)₂CH₂]₂ appear unaffected by the substitution pattern. The bond lengths are uniformly about 1.800 Å. On the other hand, in [(PhO)₂(O)P-N=P(Ph)₂cp]₂Fe the ferrocene moiety leads to various P₂-C bond lengths ranging from 1.797(2) Å to 1.949(2) Å, the bond to ferrocene being the shortest.²

**Behavior against hydrolysis.** Due to their highly nucleophilic negatively charged nitrogen atom iminophosphoranes are known to readily undergo hydrolysis delivering primary amines and a phosphine (V) oxide, which is commonly known from Staudinger reduction.³² The susceptibility to hydrolysis is related to the basicity of the phosphorane.³³

Thus the stability of the new N-phosphorylated iminophosphoranes towards hydrolysis was tested in a simple NMR experiment exemplary for DOPO-N=P(OPh)₃ and DOPO-N=P(Ph)₃. Therefore both compounds were dissolved in methanol-d₄ and treated with water and 0.1 M hydrochloric acid. Even when heated for two hours at 60 °C no hydrolysis products could be observed (Figure 4). These results are consistent with previous studies conducted with N-phosphorylated iminophosphoranes of the general structure Ar₂P(O)N=PR₃ which are also stable against hydrolysis.²¹

![Figure 4. ³¹P{¹H}-NMR spectra of DOPO-N=(OPh)₃ (left) and DOPO-N=P(Ph)₃ (right) during hydrolysis experiments recorded in methanol-d₄.](image-url)

**Thermal properties of the new iminophosphoranes.** In order to process a FR into the target resin or a thermoplastic polymer, the FR must not decompose at temperatures below the resin’s curing or compounding temperature. The thermal decomposition of the iminophosphoranes was therefore investigated using thermogravimetric analysis (TGA).

The TGA curves of the novel iminophosphoranes are displayed in...
Figure 5 and compared to the known flame retardant polyphosphazene \([\text{NP}(\text{OPh})_2]_x\). All the novel iminophosphoranes show likewise significantly different degradation temperatures, determined by the phosphorus moieties.

**Figure 5.** TGA curves of the new DOPO-based iminophosphoranes compared to \([\text{NP}(\text{OPh})_2]_x\) under nitrogen atmosphere (left) and air (right).

**DOPO-N=P(OMe)_3** and **DOPO-N=P(OPh)_3** arising from phosphites are the least stable of all investigated potential flame retardants. In Table 2 decomposition temperatures at 2% weight loss (\(T_{98}\)) as well as the temperatures corresponding to the maximum weight loss rate (\(T_{\text{max}}\)) are listed. Under nitrogen atmosphere DOPO-N=P(OMe)_3 is the least stable compound of this investigated array starting to decompose at 200 °C. DOPO-N=DOP-OEt, (Ph_2O)(O)P-N=DOP-OEt and DOPO-N=P(OPh)_3 exhibit nearly the same stability starting to decompose at around 245 °C. The polyphosphazene \([\text{NP}(\text{OPh})_2]_x\) starts to decompose at 278 °C. DOPO-N=P(Ph)_3 and \([\text{DOPO-N}=\text{P(Ph)}_2\text{CH}_2]_2\) derived from phosphine oxides are even more stable. The decomposition of DOPO-N=P(Ph)_3 starts at 311 °C and \([\text{DOPO-N}=\text{P(Ph)}_2\text{CH}_2]_2\) at 316 °C. Thermal degradation of these compounds conducted under air shows a very similar behavior.

These results indicate a close relationship between the chemical environment of the phosphorus and the thermal stability of the molecule, in fact the \(N\)-phosphorylated iminophosphorane with P-C moieties (e.g. Ph) are apparently more stable than those with P-O moieties (e.g. OPh). These results are consistent with the thermal degradation of triphenyl phosphate and triphenylphosphine oxide.\(^{34}\) As compared with the molecular parameters revealed by single-crystal x-ray diffraction (see Table 1) thermal stability correlates with larger P1-N-P2 angles and mounting equilibrated P-N bond lengths.
Table 2. Thermal decomposition data of the additives based on TGA analysis recorded under nitrogen atmosphere and air

<table>
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<th>Compound</th>
<th>Nitrogen atmosphere</th>
<th>Air</th>
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<tr>
<td></td>
<td>$T_{98}$</td>
<td>$T_{\text{max}}$</td>
</tr>
<tr>
<td></td>
<td>[°C]</td>
<td>[°C]</td>
</tr>
<tr>
<td>DOPO-$N=$P(OMe)$_3$</td>
<td>200</td>
<td>267</td>
</tr>
<tr>
<td>DOPO-$N=$P(OPh)$_3$</td>
<td>246</td>
<td>333</td>
</tr>
<tr>
<td>DOPO-$N=$P(Ph)$_3$</td>
<td>311</td>
<td>403</td>
</tr>
<tr>
<td>[DOPO-NP(Ph)$_2$CH$_2$]$_2$</td>
<td>316</td>
<td>370</td>
</tr>
<tr>
<td>DOPO-$N=$DOP-OEt</td>
<td>241</td>
<td>325</td>
</tr>
<tr>
<td>(Ph$_2$O)(O)P-N=DOP-OEt</td>
<td>244</td>
<td>321</td>
</tr>
<tr>
<td>[NP(OPh)$_2$]$_x$</td>
<td>278</td>
<td>362</td>
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The very low residues at 700 °C (residue$_{700 \degree \text{C}}$) of the N-phosphorylated iminophosphoranes presented in this study indicate a ready transition into the vapor phase which is crucial for flame retardants to perform an enhanced gas-phase activity. They range from 0.2 to 7.0 wt% in air and from 0.2 to 4.6 wt% in nitrogen atmosphere (Table 2).

Conclusions

The Staudinger reaction proves to be a versatile reaction pathway in the synthesis of N-phosphorylated iminophosphoranes, leading to a finely tunable array of molecules with mixed phosphorus moieties. This may allow an on-demand synthesis of tailored additives according to the requirements of a specific polymeric material.

Thus, six new N-phosphorylated iminophosphoranes, each with a different chemical environment around the phosphorus atom, were synthesized using the Staudinger reaction. As a DOPO source the phosphoryl azide DOPO-$N_3$ was previously obtained via the Atherton-Todd reaction.

Single-crystal X-ray diffraction studies led to comparable results on molecular parameters showing that larger P1-N-P2 angles result in assimilation of the involved P-N bond lengths.

A relationship between the chemical environment around the phosphorus atom and the thermal stability of the corresponding compound was confirmed by TGA measurements. N-phosphorylated iminophosphoranes with P-C moieties (e.g. Ph) are thermally more stable than those with P-O moieties (e.g. OPh) which correlates with larger P1-N-P2 angles and mounting equilibrated P-N bond lengths resulting in a higher degree of delocalization of the electrons.
**Experimental Section**

**General.** Unless stated otherwise, solvents and chemicals were obtained from Sigma Aldrich and used as received without further purification. DOPO and DOPO-O-PEPA were supplied by Metadyne Austria GmbH. Polyphosphazene [NP(OPh)₂]₄ (SPB®-100) was supplied by Hebron S.A. 6-Ethoxy-6H-dibenzo[c, e][1,2]-oxaphosphinine (DOP-OEt) was synthesized according to the literature.orthy NMR spectra were recorded with a Bruker ARX 300 (300 MHz). Chemical shifts are reported as δ values relative to the solvent peak. For all 31P NMR spectra proton decoupled measurement was used. For all 13C-NMR spectra proton decoupled and phosphorus coupled measurement was used. For 1H-NMR spectra phosphorus coupled measurement was used. FT-IR spectra were recorded with a Nicolet SX™ 5 spectrometer (Diamond ATR cell). High-resolution mass spectrometry (HR-MS) analyses were performed using an ApexQe FT-ICR mass spectrometer and the ionization method DART. Elemental analysis was performed using a Thermo Flash EA from Thermo Fisher Scientific. Diffraction data of DOPO-N=P(OPh)₃, DOPO-N=P(Ph)₃ and [DOPO-N=P(Ph)₂CH₂]₂ were collected on a STOE IPDS 2T diffractometer using Mo-Kα radiation (λ = 0.71073 Å) equipped with a low-temperature device (T = 180.2 K). Using Olex2, the structure was solved with the ShelXS structure solution program using direct methods and refined with the ShelXL refinement package using least squares minimization. Non-hydrogen atoms were refined with anisotropic displacement parameters (disordered atoms were refined isotropically). Hydrogen atoms were modelled on idealized positions. Visualizations of crystal structures were created with Mercury 3.10 from CCDC. The thermogravimetric analysis (TGA) of the FR additives was performed with a TA Instrument Q5000 in a nitrogen or air environment, keeping a gas flow of 25 mL min⁻¹. The samples were heated between 40 °C and 700 °C with a rate of 10 °C min⁻¹. The weight of the examined samples was within the range of 1-2 mg.

6-Azidodibenzo[c,e][1,2]oxaphosphinine-6-oxide (DOPO-N₃). Under argon atmosphere, DOPO (86.5 g, 0.4 mol), NaN₃ (39.0 g, 0.6 mol), CCl₄ (92.3 g, 0.6 mol) and 1000 mL acetonitrile were introduced into a flame-dried three-necked round-bottom flask fitted with a condenser, KPG stirrer, septum and a thermometer. Triethylamine was added slowly under vigorous stirring. The temperature was maintained below 25 °C. When thin layer chromatography showed complete conversion of DOPO, the suspension was filtered and the filtrate was concentrated in vacuo. The concentrate was diluted with CHCl₃ and washed three times with saturated aqueous NaHCO₃ solution and three times with water. After removal of the solvent, column chromatography gave the pure azide as a pale yellow oil. Yield: 92%. 31P-NMR (CDCl₃, 101.22 MHz): δ 10.38 (s); 1H-NMR (300.38 MHz, CDCl₃): δ 7.65 (ddd, J 15.3 Hz, J 7.5 Hz, J 1.2 Hz, 1H), 7.55-7.64 (m, 2H), 7.30 (t, J 7.8 Hz, 1H), 7.13 (ddt, J 7.5 Hz, J 3.6 Hz, J 0.3 Hz, 1H), 6.98 (tt, J 7.8 Hz, J 1.2 Hz, 1H), 6.87-6.83 (m, 2H) ppm. 13C-NMR (75.53 MHz, CDCl₃): δ 148.0 (d, 3J 9.1 Hz, C₁), 135.5 (d, 3J 6.8 Hz, C₇), 133.6 (d, 3J 2.3 Hz, C₁₀), 130.1 (s, C₃), 129.1 (d, 3J 9.8 Hz, C₈), 127.8 (d, 3J 15.9 Hz, C₉), 124.6 (s, C₄), 124.5 (s, C₅), 123.4 (d, 3J 12.1 Hz, C₁₁), 120.8 (d, 3J 12.1 Hz, C₆), 120.7 (d, 3J 1679.9 Hz, C₁₂), 119.2 (d, 3J 6.8 Hz, C₂) ppm. HR-MS (DART pos.) calc. for [C₆H₄NO₃O₃P + H]⁺ 258.0427, found 258.0427 [M+H]⁺. IR (ATR): v = 3068 (w, Caryl-H), 2146 (vs, N₃), 1608 (m, Caryl-Caryl), 1595 (m, Caryl-Caryl), 1583 (m, Caryl-Caryl), 1561 (m, Caryl-Caryl), 1476 (m, Caryl-Caryl), 1449 (Caryl-Caryl), 1431 (P-Caryl), 1258 (s, P=O), 1193 (s, N₃), 1151 (m, Caryl-H), 1117 (m, Caryl-H), 924 (s, Caryl-H), 792 (m, Caryl-H), 746 (vs, Caryl-H), 731 (vs, Caryl-H), 714 (s, Caryl-H).

Trimethyl-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl) phosphorimidate (DOPO-N=P(OMe)₃). Via 6-azidodibenzo[c,e][1,2]oxaphosphinine-6-oxide (DOPO-N₃). A flame-dried three-necked round-bottom flask filled with a thermometer and a septum was filled with a solution of trimethylphosphite (2.5 g, 20.0 mmol) in 30 mL CH₂Cl₂, and DOPO-N₃ (5.1 g, 20.0 mmol) in 100 mL CH₂Cl₂ was added dropwise at 2 °C.
Upon completion the reaction mixture was heated to RT for 24 h. The solvent was subsequently removed in vacuum. Column chromatography through silica gel (EtOAc/MeOH 90:10) on silica gel yielded the pure product as a colorless oil. Yield: 99%.

One-pot synthesis. In a flame-dried three-necked round-bottom flask fitted with a condenser, KPG stirrer, septum and a thermometer DOPO (64.8 g, 0.3 mol), trimethylphosphate (37.2 g, 0.3 mol) and NaN₃ (29.3 g, 0.45 mol) were suspended in acetonitrile (100 mL). At a temperature of 80 °C CCl₄ (46.14 g, 0.30 mol) was added dropwise over 60 minutes. When the N₂ formation stopped, 1 mL of trimethylphosphate was added and IR spectroscopy was used to determine whether the azide was entirely converted (vₐžide = 2146 cm⁻¹). The solvent and CHCl₃ were then removed. The crude product was dissolved in CHCl₃ and the solution was washed with water three times and dried over MgSO₄ before the solvent was removed once again. Yield: 76%. ³¹P-NMR (121.60 MHz, CDCl₃): δ -0.25 ppm. ¹H-NMR (300.38 MHz, CDCl₃): δ 7.45 (ddd, J 14.2, 7.3, 1.1 Hz, 1H), 7.37-7.24 (m, J 14.4, 9.5, 5.1 Hz, 2H), 7.00 (t, J 7.2 Hz, 1H), 6.90 (t, J 6.9 Hz, 1H), 6.77 (t, J 7.2 Hz, 1H), 6.70-6.54 (m, 2H), 3.15-3.03 (m, 9H) ppm. ¹³C-NMR (75.53 MHz, CDCl₃): δ 149.89-149.52 (m, C₁), 134.44-133.89 (dd, J 3.5, 3.5 Hz, C₇), 130.33 (s, C₁₀), 128.69 (dd, J 185.5, 3.6 Hz, C₁₂), 128.56 (s, C₈), 127.33 (dd, J 4.6, 4.6 Hz, C₈), 126.61 (dd, J 8.5, 6.3 Hz, C₉), 124.00 (s, C₁₂), 127.75-122.60 (m, C₄, C₆, C₁₁), 119.07 (dd, J 3.0, 3.0 Hz, C₂), 53.74 (dd, J 3.0, 3.0 Hz, C₁₃) ppm. IR (ATR): v = 2957 (w, Caryl-H), 2855 (w, Caryl⁻Caryl), 1606 (w, Caryl⁻Caryl), 1596 (w, Caryl⁻Caryl), 1581 (w, Caryl⁻Caryl), 1561 (w, Caryl⁻Caryl), 1476 (m, P=N), 1431 (m, P-Caryl), 1201 (s, P=O), 1027 (vs, P-O-Me), 899 (s, Caryl⁻H), 781 (s, Caryl⁻H), 753 (s, Caryl⁻H), 719 (s, Caryl⁻H), 692 (s, Caryl⁻H) cm⁻¹. EA calc. for C₁₅H₁₇NO₅P₂: C 51.00, H 4.85, N 3.97, O 22.65. Found: C 51.21, H 4.75, N 4.09, O 22.1. HR-MS (DART pos.) calc. for [C₁₅H₁₇NO₅P₂⁺]⁺ 354.0655, found 354.0652 [M+H]⁺.

Triphenyl (6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)phosphorimidate (DOPO-N=P(OPh)₃). A flame-dried three-necked round-bottom flask fitted with a thermometer and a pressure-equalizing dropping funnel was filled under argon counterflow with a solution of DOPO-N₃ (5.1 g, 20.7 mmol) in 40 mL acetonitrile, and triphenylphosphine (6.4 g, 20.7 mmol) was added. The reaction mixture was heated for 27 h at 80 °C. The solvent was subsequently removed in vacuum. In parallel the crude product solidified as a colorless amorphous substance (11.24 g) which was recrystallized from isopropyl alcohol. Yield: 60%. mp 99 °C. ³¹P-NMR (CDCl₃, 121.60 MHz): δ -1.96 (d, J 45.0 Hz, 1P), -25.20 (d, J 45.0 Hz, 1P); ¹H-NMR (300.38 MHz, CDCl₃): δ 7.76-7.71 (m, 2H), 7.58 (dd, J 15.0 Hz, J 9.0 Hz, 1H), 7.48 (t, J 6.0 Hz, 1H), 7.28-7.06 (m, 18H), 6.97 (d, J 9.0 Hz, 1H) ppm; ¹³C-NMR (75.53 MHz, CDCl₃): δ 150.51 (d, J 7.6 Hz, C₁), 149.99 (d, J 8.8 Hz, C₁₃), 135.41 (d, J 6.7 Hz, C₁), 131.29 (d, J 2.5 Hz, C₁₀), 129.75 (d, J 1.0 Hz, C₁₅), 129.50 (s, C₃), 128.93 (dd, J 175.5, 6.8 Hz, C₁₂), 128.74 (d, J 9.4 Hz, C₈), 127.53 (d, J 15.0 Hz, C₉), 125.81 (d, J 1.5 Hz, C₁₆), 124.87 (d, J 1.2 Hz, C₅), 123.91-123.19 (m, C₄, C₆, C₁₁), 120.41-120.21 (m, C₂), 120.26 (d, J 5.1 Hz, C₁₄) ppm. EA calc. for C₃₀H₂₃NO₅P₂: C 66.79, H 4.30, N 2.60, O 14.83; found: C 66.81, H 3.95, N 2.51, O 14.85. HR-MS (DART pos.) calc. for [C₃₀H₂₃NO₅P₂⁺]⁺ 540.1124; found: 540.1129 [M+H]⁺. IR (ATR): v = 3074 (w, Caryl-H), 1586 (m, Caryl⁻Caryl), 1485 (m, P=N), 1300 (m, P=O), 1173 (O-Caryl), 1117 (P-DOPO), 957 (s, P-O-Caryl), 835 (P-O-Caryl), 783 (m, Caryl⁻H), 767 (m, Caryl⁻H), 750 (vs, Caryl-H), 715 (m, Caryl⁻H).

6-((Triphenyl-λ⁵-phosphanylidene)amino) dibenzo[c,e][1,2]oxaphosphininine 6-oxide (DOPO-N=P(Ph)₃). A flame-dried three-necked round-bottom flask fitted with a thermometer and a pressure-equalizing dropping funnel was filled under argon counterflow with triphenylphosphane (15.7 g, 60 mmol) in 100 mL diethyl ether. A solution of DOPO-N₃ (15.4 g, 60 mmol) in 100 mL diethyl ether was added slowly under vigorous stirring while maintaining a temperature of 5 °C. The temperature was then allowed to rise to RT. After 2 h the colorless precipitate was filtered and washed with diethyl ether before it was dried in vacuo. The crude product was recrystallized from isopropyl alcohol. Yield: 96%. mp 228 °C. ³¹P-NMR (CDCl₃, 121.60 MHz): δ 10.23 (d, J 17.2 Hz), 3.43 (d, J 17.2 Hz); ¹H-NMR (300.38 MHz, CDCl₃): δ 7.77-7.60 (m, 3H), 7.59-7.25 (m, 16H), 7.15 (s, Caryl⁻H).
aryl + C

\[ \text{calc. for } [\text{C}(75.53) \text{H}(75.53) \text{O}(16) \text{N}(4)]^+ \]

IR (ATR): \( \nu = 3081 \text{ (w, C=H-H)}, 3051 \text{ (w, C=H-H)}, 3033 \text{ (w, C=H-H)}, 2994 \text{ (w, C=H-H)}, 1927 \text{ (w, C=H-H)}, 1889 \text{ (w, C=H-H)}, 1810 \text{ (w, C=H-H)}, 1601 \text{ (m, C=H=C}), 1593 \text{ (m, C=H=C)}, 1577 \text{ (m, C=H=C)}, 1559 \text{ (m, C=H=C)}, 1471 \text{ (m, P=N)}, 1437 \text{ (m, P-C=C}), 1427 \text{ (m, P-C=C)}, 1308 \text{ (m, P=O)}, 1114 \text{ (s, P-Ph), 1077 (m, C=H-H), 1039 (m, P-N), 877 (C=H-H), 742 (vs, C=H-H), 736 (vs, C=H-H), 718 (vs, C=H-H), 686 (vs, C=H-H).}

6,6′-[((Ethane-1,2-diylbis(diphenyl-\( \lambda^2 \)-phosphanylidene))bis(azanylylidene))bis(dibenzo[c,e][1,2]oxaphosphinophen-6-oxide)](DOPO-N=P(Ph)_2CH_2)_2. A flame-dried three-necked round-bottom flask fitted with a thermometer septum and a condenser was filled under argon counterflow with 1,2-bis(diphenylphosphino)ethane (19.9 g, 0.1 mol) in 75 mL CHCl_3. A solution of DOPO-N_3 (25.7 g, 0.05 mol) in 50 mL CHCl_3 was added slowly under vigorous stirring while maintaining a temperature below 15 °C. The temperature was then allowed to rise to RT. After 2 h the colorless precipitate was filtered and digested with isopropyl alcohol to yield the spectroscopically pure product. Yield: 91%. mp 274 °C. \( ^1^\text{H}-\text{NMR (300.38 MHz, CDCl}_3\): \delta 7.95-7.67 (m, 14H), 7.61-7.51 (m, 2H), 7.50-7.27 (m, 14H), 7.25-7.11 (m, 4H), 6.90 (ddd, J 10.6, 7.8, 1.3 Hz, 1H), 3.32-3.03 (m, 2H) ppm. \( ^{13}\text{C}-\text{NMR (75.53 MHz, CDCl}_3\): \delta 151.41 (d, J 7.4 Hz, C\_1), 135.72 (d, J 6.8 Hz, C\_7), 132.34 (d, J 6.2 Hz, C\_15), 131.65-130.94 (m, C\_14), 129.58 (s, C\_3), 129.34-128.89 (m, C\_15), 128.74 (d, J 9.0 Hz, C\_9), 127.79 (d, J 14.7 Hz, C\_9), 125.27 (s, C\_5), 124.32 (dd, J 12.2, 2.6 Hz, C\_6), 123.90 (d, J 11.9 Hz, C\_11), 123.55 (s, C\_4), 120.46 (dd, J 5.8, 2.0 Hz, C\_2), 23.36-22.25 (m, C\_7) ppm. EA calc. for \( [\text{C}_5\text{H}_4\text{O}_2\text{N}_2\text{O}_4\text{P}_4]^+ \): C 70.09, H 4.71, N 3.27, O 7.47. Found: C 69.83, H 4.53, N 3.27, O 6.96. HR-MS (DART pos) calc. for \( [\text{C}_5\text{H}_4\text{O}_2\text{N}_2\text{O}_4\text{P}_4]^+ \): 857.2011, found 857.1981 [M+H]^+. IR (ATR): \( \tilde{\nu} = 3053 \text{ (w, C=H-H), 2950 (w, C=H-Ph), 2909 (w, C=H-Ph), 1606, 1594, 1582, 1560 (w, C=H=C), 1475 (m, CH_2, scissor vib.), 1438, 1429 (m, =C=H-Ph and C=H=C str.), 1292 (s, P=N), 1194 (vs, P=O), 1117, 1080, 1045, 1026, 1005, 997 (m, =C=H-in plane def.), 885 (s, P-C), 814, 777, 751, 743, 719, 692 (s, C=H-out of plane) cm\(^{-1}\).}

Diphenyl (6-ethoxy-6H-6\( \lambda^5 \)-dibenzo[c,e][1,2]oxaphosphinophen-6-ylidene)phosphoramidate (PhO)=P-N=DOPOEt. In a flame-dried three-necked round-bottom flask fitted with a condenser, septum and a thermometer, 6-ethoxy-6H-dibenzo[c,e][1,2]oxaphosphine (11.4 g, 46.5 mmol) was dissolved in dry CHCl_2 (24 mL) under argon atmosphere. Diphenylphosphoryl azide (12.8 g, 46.5 mmol) was subsequently added under vigorous stirring at room temperature. When no further N_2 evolution the solvent was removed in vacuo to yield 22.9 g of the desired crude product. Purification was performed by column chromatography on silica gel (EtOAc/petroleum ether 80:20) to yield the spectroscopically pure compound as a colorless oil. Yield: 98%. \( ^1\text{H}-\text{NMR (121.60 MHz, CDCl}_3\): \delta 6.33 (d, J 61.7 Hz, 1P), -12.83 (d, J 61.9 Hz, 1P) ppm. \( ^1\text{C}-\text{NMR (75.53 MHz, CDCl}_3\): \delta 151.52 (dd, J 7.6, 1.3 Hz, C\_15), 148.51 (d, J 7.7 Hz, C\_13), 135.90 (d, J 7.6 Hz, C\_7), 133.55 (d, J 2.5 Hz, C\_10), 130.14 (s, C\_3), 129.97 (d, J 10.5 Hz, C\_8), 128.86 (d, J 1.8 Hz, C\_17), 127.86 (d, J 16.2 Hz, C\_9), 124.86 (s, C\_4), 124.68 (s, C\_5), 123.69-123.49 (m, C\_11, C\_18), 121.54 (d, J 12.5 Hz, C\_6), 120.44 (dd, J 182.3, 2.4 Hz, C\_12), 120.12 (dd, J 5.1, 1.6 Hz, C\_6), 119.39 (d, J 7.0 Hz, C\_2), 63.81 (d, J 7.6 Hz, C\_13), 15.42 (d, J 6.4 Hz, C\_14) ppm. HR-MS (DART pos) calc. for \( [\text{C}_2\text{H}_2\text{N}_2\text{O}_2\text{P}_2]^+ \): 492.1244, found 492.1166 [M+H]^+. EA calc. for \( [\text{C}_2\text{H}_2\text{N}_2\text{O}_2\text{P}_2]^+ \): C 63.55, H 4.72, N 2.85, O 16.28. Found: C 63.88, H 4.43, N 2.71, O 15.82. IR (ATR): \( \tilde{\nu} = 3066 \text{ (w, C=H-H), 2983 (w, C=H-Ph), 2929 (w, C=H-Ph), 1594 (m, C=H-H/C=H=C), 1488 (m, P=N, str.), 1449, 1431, 1373, 1339 (m, C=H-H/C=H-H), 1254 (m, C=H-H/C=H-H), 1253 (vs, C=H-H/cm\(^{-1}\).}
6-((6-Ethoxy-6H-6λ5-dibenzo[c,e][1,2]oxaphosphinin-6-ylidene)amino)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-N=DOP-OEt). In a flame dried three necked round bottom flask fitted with a condenser, septum and a thermometer 6-ethoxy-6H-dibenzo[c,e][1,2]oxaphosphinine (10.8 g, 44.2 mmol) was dissolved in dry CH₂Cl₂ (24 ml) under argon atmosphere. DOPO-N₃ (11.4 g, 44.2 mmol) was added subsequently under vigorous stirring at room temperature. When no further N₂ evolved the solvent was removed in vacuo to yield 20.8 g of the desired crude product. Purification was performed by column chromatography EE/MeOH 20:1 on silicagel to yield the spectroscopically pure compound as a colorless solid. Yield: 99%. ³¹P-NMR (121.60 MHz, CDCl₃): δ 4.47 (d, J 37.2 Hz, 1P), 0.06 (dd, J 37.2, 13.6 Hz, 1P) ppm. ¹H-NMR (300.38 MHz, CDCl₃): δ 7.83 (dddd, J 13.7, 11.8, 7.5, 1.5 Hz, 1H), 7.70-7.48 (m, 5H), 7.40 (td, J 7.7, 1.4 Hz, 1H), 7.36-7.29 (m, 1H), 7.25-7.08 (m, 3H), 7.07-6.79 (m, 5H), 4.13-3.89 (m, 2H), 0.97 (t, J 7.1 Hz, 3H) ppm, ¹³C-NMR (75.53 MHz, CDCl₃): δ 150.31 (dd, J 7.4, 4.5 Hz, C₁₃a), 148.55 (dd, J 7.8, 2.7 Hz, C₁b), 135.82 (d, J 7.7 Hz, C₇a), 135.07 (d, J 6.7 Hz, C₇b), 133.38 (dd, J 2.8, 2.8 Hz, C₁₀a), 131.00 (dd, J 2.2, 2.2 Hz, C₁₀b), 130.09 (s, C₃a), 129.95 (dd, J 10.6, 4.1 Hz C₁₁a), 129.16 (s, C₃b), 128.74 (dd, J 9.2, 2.5 Hz, C₁₁b), 127.85 (dd, J 16.2, 3.6 Hz, C₉a), 127.32 (d, J 14.7 Hz, C₉b), 124.79-124.54 (m, C₄a, C₅a, C₆a), 123.57-123.12 (m, C₄b, C₅b, C₆b), 121.81 (dd, J 15.0, 1.8 Hz, C₆a), 121.44 (dd, J 12.5, 2.6 Hz, C₆b), 120.00 (dd, J 7.8, 6.1 Hz, C₂a), 119.44 (dd, J 6.9, 2.9 Hz, C₂b), 64.11 (dd, J 7.7, 7.7 Hz, C₁₃), 15.54 (d, J 6.6 Hz, C₁₄) ppm. IR (ATR): v = 3064 (w, Caryl-H), 2983 (w, Calkyl-H), 2928 (w, Calkyl-H), 1607, 1596, 1582, 1561 (w, Caryl-H/Caryl=HCaryl=HCaryl), 1476 (m, P=N, str.), 1447, 1431, 1371, 1314 (m, Calkyl-H), 1228 (m, Calkyl-Calkyl), 1190 (vs, P=O), 1117 (m, Caryl-O), 1023 (s, P-O-C), 938 (m), 891 (m), 828 (m), 799 (m), 750 (vs, Caryl-H) cm⁻¹. HR-MS (DART pos) calc. for [C₂₆H₂₃NO₃P₂⁺H⁺] 474.1019, found 474.1017 [M+H]⁺. EA calc. for C₂₆H₂₁NO₄P₂: C 65.97, H 4.47, N 2.96, O 13.52. Found: C 66.36, H 4.22, N 2.88, O 12.59.

**Supplementary Material**

³¹P-NMR spectra of the new compounds as well as crystallographic data and structure refinement details of DOPO-N=P(OPh)₃, DOPO-N=P(Ph)₃ and [DOPO-N=P(Ph)₂CH₂]₂ are shown in the supplementary information.

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