Isolation and Characterization of a Two-coordinate Phosphinidene Oxide

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Abstract. Nitroso compounds, R–N=O, are common intermediates in organic synthesis, and are typically amenable to storage and manipulation at ambient temperature under aerobic conditions. By contrast, phosphorus-containing analogues, such as R–P=O (R = OH, CH_3, OCH_3, Ph), are extremely reactive and can only be studied in inert gas matrices at ultralow temperatures (3–15 K). These species are believed to be key intermediates in the degradation/combustion of organic phosphorus compounds (a class of chemicals that includes chemical warfare agents and flame retardants). Here we describe the use of an extremely bulky amine ligand to isolate a two-coordinate phosphorus(III) oxide. Reactivity studies on this and other related compounds reveals that phosphorus center can be readily oxidized, and that in doing so, the P–O bond remains intact, an observation that is of interest to the proposed reactivity of transient phosphorus(III) oxides.

1. Introduction

Nitroso compounds, R–N=O, are nitrogen(III) oxides with a bent geometry and a stereochemically active lone pair on the nitrogen atom. They are key intermediates in several important organic transformations such as the hetero Diels-Alder (HDA) and nitroso-aldol reactions.[1,2] Despite the propensity of nitrosoarenes to dimerize, many monomeric *C*- and *N*-nitroso compounds are stable at ambient temperature and commercially available. By contrast, analogous phosphorus(III) oxides, R–P=O (phosphanones or phosphinidene oxides), are highly unstable. Compounds such as CH_3PO,[3] CH_3OPO,[4] and PhPO[5] can only be observed at extremely low temperatures (3–15 K) in inert gas matrices. Despite their highly reactive nature, these compounds are of enormous fundamental importance. For example, metaphosphorous acid (*cis*-HOPO) is proposed to be a key intermediate in the oxidation of organic phosphorus compounds such as phosphines.[6–9] The aforementioned studies point at the difficulties associated with the isolation of phosphorus(III) oxides, which are prone to intermolecular polymerization pathways on account of their diminished π-bond energies when compared to their nitrogen analogs.

A common strategy for the isolation of highly reactive molecules is to trap these in the coordination sphere of metals. For example, Cummins has shown that phosphorus monoxide can be employed as a terminal ligand for the formation of a molybdenum complex with a terminal Mo–P=O bond (Figure 1, **A**).[10] This species exhibits a short Mo–P bond (2.079(5) Å) and a linear Mo-P-O bond angle (177.6(8)°), both of which imply significant d_π–p_π interactions between the metal center and phosphorus monoxide moiety. To our knowledge, the synthesis of an isolable phosphinidene oxide with a bent structure such as that predicted for R–P=O, (R = OH, CH_3, OCH_3, Ph) has not been achieved to date despite various attempts to characterize such

compounds in the condensed phase.[11–16] The first direct observation of a phosphenite RO–P=O (R = 2,6-di-*tert*-butyl-4-methylphenyl; **B**) was accomplished by pyrolyzing its cyclic trimer. This species was identified by $^{31}P\{^{1}H\}$ NMR spectroscopy (singlet resonance at 238 ppm) and IR spectroscopy ($\nu_{P=O}$ = 1235 cm^{-1}).[17] However, the monomer rapidly reverted to the starting material upon warming up to 272 K. Phosphinidene oxides have been stabilized when coordinated to transition metal centers or through interactions with main group Lewis acid/bases. An isolable phosphinidene oxide complex was stabilized within the coordination sphere of chromium, as reported by Niecke and colleagues in 1980 (**C**), and several group six metal stabilized cases were reported later.[18,19–22] More recently, Stephen and Liu successfully isolated a donor-acceptor stabilized phosphinidene oxide compound (**D**).[23] Compounds stabilized exclusively by an external donor would come several years later with Braunschweig describing an N-heterocyclic carbene adduct of phosphinidene oxide,[24] while Nikonov and co-workers reported a phosphine stabilized congener (**E**).[25]

The availability of phosphinidene oxides stabilized by external Lewis bases prompted us to explore whether the use of an internal π-donor substituent would allow access to an isolable variant. In addition to the electronic stabilization offered by such a ligand, significant steric bulk would be required to circumvent the aforementioned oligomerization pathways. Herein, we describe the synthesis of an anionic imine stabilized phosphinidene oxide $RNPO^{-}$ which can be further functionalized into a neutral amido-functionalized phosphinidene oxide R(R')NPO. These species are two coordinate phosphorus(III) oxides that can be isolated and manipulated at room temperature.

2. Result and Discussion

In contrast to other kinetically stabilized main group species with multiple bonds, phosphinidene oxides R–P=O present a unique challenge. The use of steric protection is only viable at one end of the molecule, thus necessitating the presence of an R group capable of providing long-range steric shielding to prevent oligomerization. Inspired by the work of Goto and co-workers, in which they adopted *meta*-substituted terphenyl group to protect nitroso-selenocysteine (R–SeNO) and selenenic acids (R–SeOH),[26–29] we synthesized compound **1** as an N-terminal protecting group (Figure 2). In addition to the kinetic stabilization offered by steric bulk, the corresponding phosphine oxide precursors $R–NPO^-$ are viable targets for compounds with P^{III}=O double bond character on account of their anionic charge. Electrostatic repulsion can effectively deter oligomerization or polymerization of such species. An exemplary case of this strategy is the isolation of the phosphaethynolate anion PCO^- and its analogs.[30–34] However, it is crucial to note that upon losing the charge (through protonation, for instance), these anions readily oligomerize.[35]

2.1 An anionic imine stabilized phosphinidene oxide $RNPO^-$

To achieve our goal, we reacted the chloro(imino)phosphane **2**, which was synthesized according to a modified literature procedure,[36] with KOTMS (Figure 2). Upon treatment of **2** with 2.5 equivalents of KOTMS in tetrahydrofuran (THF), *in situ* $^{31}P\{^1H\}$ NMR spectroscopy revealed a distinct singlet at 237.2 ppm, corresponding to the formation of **3**. Interestingly, this reaction did not proceed via the expected intermediate R–N=P–OTMS followed by desilylation. Instead, it proceeds via a three-coordinate phosphite $K[R–N–P(OTMS)_2]$, facilitated by the excess KOTMS, ultimately leading to the elimination of hexamethyldisiloxane $OTMS_2$ (see Supplementary Information).

Structural confirmation of compounds **2** and **3** was obtained through single crystal X-ray diffraction analysis (Figure 3). The crystal structure of **3** reveals a bent N-P-O moiety (116.85(11)°) and a P–O bond length of 1.501(2) Å. Notably, this P–O bond length closely resembles those observed in phosphinidene oxides stabilized by either acids or bases.[18,24–25] The P–N bond elongates from 1.497(2) Å in **2** to 1.5822(19) Å. These bond lengths suggest that there is π-bonding character between both P–O and P–N. In fact, the anionic moiety in **3** can be rationalized as a heavier analog of nitrite (NO_2^-), exhibiting phosphorus-centered 3-center-4-electron (3c-4e) bonding. The oxygen atom of the anionic moiety exhibits a short electrostatic interaction with the $[K(18\text{-crown-6})]^+$ counteraction with an O···K interatomic distance of 2.634(2) Å.

DFT calculations were conducted to elucidate the electronic structure of **3**. The optimized geometries of both the free ion ($[ArNPO]^-$) and the ion-paired salt (**3**) were computed at the M06-2X/Def2-svp level of theory (a comparison is provided in the Supplementary Information). The computed structural metrics and are in good agreement with those obtained by X-ray crystallography (e.g. N1–P1: 1.601 Å; O1–P1: 1.522 Å for $[ArNPO]^-_{DFT}$). Natural bond orbital (NBO) analysis revealed the presence of a 3-center-4-electron (3c-4e) bonding interaction, with the N–P double bond contributing 57.3% to the system and the P–O double bond contributing 42.7% (refer to the resonance forms in Figure 4a). This is supported by Wiberg bond indices (WBIs), which indicate similar bond orders for the N–P (1.25) and P–O (1.24) bonds. Mayer bond indices indicate a slightly higher bond order for P–O (1.64) compared to N–P (1.40). Nevertheless, both bond indices collectively confirmed the existence of multiple bonding

character within the N-P-O moiety. Remarkably, in both WBIs and Mayer bond index, N–O showed a non-negligible bond order (0.16 in WBIs and 0.07 in Mayer). This observation underscores the delocalized nature of the N-P-O bonding interaction, with N–O exhibiting some degree of π bonding. Indeed, three molecular orbitals can be located in a simplified model ($MeNPO^-$), representing a classic three-center-four-electron system (Figure 4b). The Natural Population Analysis (NPA) showed that both N (–1.06 a.u.) and O (–1.10 a.u.) carry significant negative charge, indicating both atoms can be used for further functionalization. To gain further insight into the reactive sight, a conceptual DFT calculation was conducted. The dual descriptor iso-surface showed that N1 has a larger negative $\Delta f(r)$ compared O1, which implies that N1 is a more nucleophilic center (Figure 4c).[37–39]

2.2. Functionalization of $RNPO^-$ with electrophiles

To probe the reactivity of **3**, benzyl bromide was selected as an electrophile, and was heated with **3** at 40 °C for 12 h (Figure 5). Monitoring the reaction mixture by *in situ* $^{31}P\{^1H\}$ NMR spectroscopy revealed two new singlet peaks at 284.4 and 286.3 ppm.

The structure of the resulting product, **4**, was confirmed by single crystal X-ray diffraction (Figure 3). Crystallographic analysis confirms functionalization at the nitrogen atom, yielding a neutral amido-phosphinidene oxide. Notably, the P–O bond in **4** shortens significantly (1.447(6) Å), compared to that in compound **3** (1.501(2) Å). Additionally, the N–P bond in **4** elongated to 1.667(6) Å relative to **3** (1.5822(19) Å). This extended N–P bond length, while shorter than the standard N–P single bond predicted by Pyykkö (1.82 Å),[40] indicates strong π donation from the nitrogen atom lone pair to the P–O π* bond. This π donation is further supported by the trigonal planar geometry of nitrogen (Σ°: 360.0°). In the context of the diagonal relationship between

phosphorus and carbon,[41] compound **4** can be regarded as a heavier analogue of an amide, as it exhibits strikingly similar geometric characteristics to such compounds, including shorter N–C bonds and a trigonal planar nitrogen center. An IR band corresponding the $\nu_{P=O}$ stretch for **4** was observed at 1186 cm^{-1} (cf. 1077 cm^{-1} for **3**) suggesting an increase in the multiple bond character of the P–O bond. The blue-shift in the $\nu_{P=O}$ absorption aligns with the observation of a shorter P–O bond in the crystal structure, reinforcing the structural changes brought about by the chemical functionalization. These absorptions are slightly blue-shifted from reported vibrations for the phosphenite **B** (1252.6 and 1292.2 cm^{-1}),[17] in line with the greater electron donating ability of imine and amide groups over an oxyl functionality.

The origin of the two singlets observed in the $^{31}P\{^{1}H\}$ NMR spectrum of **4** was attributed to *cis-trans* isomerization about the N–P bond and was further investigated using Saturation Transfer Differential NMR (STD-NMR). In toluene solution at ambient temperature, **4** exists in two forms in a 1:6 ratio as shown by the ^{31}P NMR spectrum (Figure 6a). To prove that these two species are in exchange and to ascertain the exchange rate, a series of ^{31}P 1D-EXSY experiments (Figure 6b) were performed over a range of temperatures. These results are summarized in the Eyring plot (Figure 6c) from which $\Delta H^* = 19(2)$ kcal mol^{-1}, $\Delta S^* = 3.8(60)$ cal mol^{-1} K^{-1} and $\Delta G^*(298K) = 18(2)$ kcal mol^{-1} can be calculated for the exchange process.

DFT calculations were carried out to gain a deeper understanding of the electronic structure of **4**. Natural bond orbital (NBO) analysis revealed a similar 3-center-4-electron (3c-4e) interaction with the P=O moiety contributing more significantly to the overall electronic structure (65.3%) than the N=P component (34.7%) (see resonance forms in Figure 6d). This observation was

consistent with calculated Wiberg and Mayer bond indices (Supplementary Table 3&4). Notably, both σ-bonding and π-bonding orbitals were identified between phosphorus and oxygen (see Figures 6e and 6f), providing further evidence of the double bond character of the P=O fragment in **4**. Second order perturbation theory analysis, reveals strong donation from the lone pair of nitrogen into the P–O π* orbital (E(2) = 41.12 Kcal mol^{-1}). This donation aligns with the presence of the 3c-4e π bond in the NPO fragment, corroborating the structural evidence from crystallography. Energy calculations using the SMD-M062X/def2-TZVP//M062X/def2-SVP level of theory indicated that the *trans*-isomer represents the ground state, with the *cis*-isomer being 1.2 kcal mol^{-1} higher in energy. The Gibbs free energy barrier for the isomerization process was determined to be 21.8 kcal mol^{-1}. These computational findings are in excellent agreement with the experimental observations obtained through STD-NMR, as the experimental measured energy barrier is 18(2) kcal mol^{-1}. Based on the predicted ground state, as well as the *trans*-geometry observed in crystallography, we can confidently assign the singlet at 284.4 ppm in ^{31}P NMR spectrum to be the *trans*-isomer, while the peak at 286.3 ppm corresponds to the *cis*-isomer.

While the nitrogen atom in compound **3** is identified as the most nucleophilic position based on the dual descriptor analysis, it is noteworthy that the oxygen atom also carries a significant amount of negative charge. Given that the oxygen atom is less sterically hindered, we postulated that bulky electrophiles could be employed to access oxygen functionalized compounds. Treatment of **3** with $^{i}Pr_3SiOTf$ in benzene afforded **5**, which features a singlet in its $^{31}P\{^{1}H\}$ NMR spectrum at 169.0 ppm. The solid-state molecular structure of **5** was determined by single crystal X-ray diffraction (Figure 3). This analysis revealed the presence of a silanolate-substituted N=P double bond with a N–P bond length of 1.544(2) Å. **5** exhibits comparable bond

metrics to related compounds of general formula of R–N=P–OR′.[42–48] Following silylation, the Mayer bond order for N–P increased from 1.40 in **3** to 1.79 in **5**, while P–O bond order decreased from 1.64 to 1.01. This can be reasoned as **5** has a more localized N–P π bond.

2.3 Formal oxidation reactions from P(III) to P(V)

While **3** is stable at ambient or even elevated temperature in both solution and the solid-state under an inert atmosphere, it readily reacts with trace amounts of moisture (Figure 5). Upon exposing to one equivalent of H_2O at –78 °C, **3** undergoes conversion to a phosphorous acid derivative **6**, which exhibits a doublet in ^{31}P NMR at –3.5 ppm ($^1J_{P–H}$ = 572.4 Hz). The connectivity was confirmed by single crystal X-ray diffraction (Extended Data Figure 1). Compound **6** is structurally and electronically related to a carbodiphosphorane-stabilized dioxophosphorane recently reported by Vidović and co-workers.[49] The most intriguing aspect of the structure is the protonation of the nitrogen atom instead of oxygen, with the anionic charge being delocalized solely between two oxygen atoms. This conclusion is supported by several key structural features, including the elongation of the N1–P1 bond length (1.719(2) Å) and the nearly identical P–O bond lengths (P1–O1: 1.473(3) Å and P1–O2: 1.487(3) Å), which fall within the typical range for a P=O double bond.[40] Protonation of N1 was further confirmed by the observation of a resonance at 5.64 ppm in the ^{1}H NMR spectrum, and by NOESY NMR spectroscopy, which revealed correlation between the N–H resonance and the benzylic C–H adjacent to the central phenyl ring (see Supplementary information). This reactivity showcases that **3** represents a novel mononuclear phosphorous acid anhydride, distinguishing it from the previously known tetranuclear phosphorous acid anhydride P_4O_6.[50]

In addition to hydrolysis, as a phosphorus(III) center, **3** can also undergo oxidative processes to form phosphorus(V) compounds. Reaction of a toluene solution of **3** and iodine at –30 °C gave rise to a light-yellow solution. *In situ* $^{31}P\{^{1}H\}$ NMR spectroscopy revealed a broad singlet at –147.8 ppm corresponding to **7**. Single crystals of **7** can be obtained by slow evaporation of a toluene/hexane solution. Single crystal X-ray diffraction allowed for structural authentication of this compound, revealing a di-iodide substituted phosphorus(V) center with short N1–P1 (1.560(5) Å) and O1–P1 bonds (1.457(6) Å). These bond lengths imply that the anionic charge remains delocalized between N1 and O1. Notably, the P–I bond lengths (mean bond length: 2.529 Å) are longer than any reported P(V)–I bond lengths, which typically range from 2.33 to 2.45 Å. The elongated P–I bond and the shortened N–P and O–P bonds can be attributed to strong back donation from the lone pairs of nitrogen and/or oxygen to the P–I σ* orbital, a phenomenon arising from the inherent weakness of the P–I bond (refer to the Supplementary Information for DFT calculations). While the synthesis of OPI_3 was reported in 1973,[51] this compound remains poorly characterized. To date, no crystallographic data are available for OPI_3 or its derivatives. The closest known compound is a Lewis acid-stabilized OPI_3 moiety reported by the Krossing group in 2006.[52] The crystal structure of **7** sheds light on the structural properties of this elusive class of compounds.

The aforementioned oxidative process observed for **3** is not limited to iodine. When treated with one equivalent of diphenyl diselenide Se_2Ph_2, a new species **8** was detected by *in situ* $^{31}P\{^{1}H\}$ NMR spectroscopy. Compound **8** exhibits a singlet at –23.2 ppm in its $^{31}P\{^{1}H\}$ NMR spectrum, with a P–Se coupling constant of 398.7 Hz. The single crystal X-ray structure of **8** reveals a four-coordinate P(V) center. Structurally, **8** closely resembles **7**, with relatively short N–P (1.557(2)

Å) and P–O (1.474(2) Å) bonds. The P–Se bonds in **8** (mean bond length: 2.310 Å) are slightly elongated compared to the standard P–Se single bond (2.27 Å).[40] Again, this elongation can be attributed to the delocalization of the anionic charge and back donation to the P–Se σ * orbital.

3. Conclusions

More than four decades after the first direct observation of phosphinite oxide RO–P=O at low temperature, we have shown that a free two coordinate phosphinidene oxide can be sufficiently stabilized to be isolated at ambient temperature. Electronically and sterically stabilized by a *meta*-substituted terphenyl group, a heavier analog of nitrite (NO_2^-) can be accessed as $ArNPO^-$ (**3**), featuring a phosphorus center containing a three-center-four-electron (3c-4e) π-bond. Due to the delocalization of the anionic charge between nitrogen and oxygen, both atoms can be selectively functionalized depending on the electrophile employed. With small alkyl groups, *N*-functionalization takes place giving rise to the formation of an amido phosphinidene oxide **4**, which can be considered a heavier analog of amide. Alternatively, when reacted with a bulky silyl group, *O*-functionalization occurs, resulting in the generation of a silanolate-substituted N=P double-bonded species. Moreover, compound **3** displays versatility in its reactivity, as it can also undergo functionalization through oxidative transformations, as exemplified by reactions with iodine and diphenyl diselenide. Ongoing research efforts are dedicated to exploring additional reactivities of phosphinidene oxide compounds, further enhancing our understanding of their chemical properties and potential applications.

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5. Contributions

C.H. and J.M.G. conceived of the project. C.H. carried out all of the experimental work including the collection of spectroscopic and X-ray data. N.H.R. carried out the Saturation Transfer Differential NMR (STD-NMR) experiments. M.P. refined all of the single crystal X-ray data. C.H. conducted all of the computational work. C.H. and J.M.G. wrote the manuscript. J.M.G. supervised the project. All authors provided insights and edited the manuscript.

6. Competing interests

The authors declare no competing interests.

7. Figure Legends/Captions

Figure 1. Phosphinidene oxides and their complexes.

Figure 2. Top: Compound **1**, herein abbreviated as $ArNH_2$. Bottom: Synthesis of **3**.

Figure 3. Single crystal X-ray structures of **2** (top left), **3** (top right), **4** (bottom left) and **5** (bottom right). Carbon atoms depicted with an arbitrary radius. Thermal ellipsoids pictured at 50% probability level. Solvent of crystallization and hydrogen atoms are removed for clarity. Nitrogen: blue; Phosphorus: purple; Oxygen: red; Chlorine: green; Silicon: yellow.

Figure 4. a) Resonance forms and NBO analysis of **3**; b) Selected Kohn-Sham molecular orbitals and a simplified MO diagram for the three-center-four-electron bonding interaction present in **3**; c) Dual descriptor iso-surface model.

Figure 5. Synthesis of **4**, **5**, **6**, **7** and **8** from **3**.

Figure 6. a) ^{31}P NMR spectrum of **4** at 298K; b) ^{31}P 1D-EXSY spectrum at 353K; c) Eyring plot; d) Resonance forms and NBO analysis of **4**; e) Natural Bonding Orbital depiction of the σ-bonding orbital interaction between P–O; f) Natural Bonding Orbital depiction of the π-bonding orbital interaction between P–O; g) Computed energy barrier for interconversion of *trans*- and *cis*-isomers of **4**.

Extended data Figure 1. Single crystal X-ray structures of **6**, **7** and **8** (from left to right). Carbon atoms depicted with an arbitrary radius; thermal ellipsoids of heteroatoms pictured at 50% probability level. Counter cations, solvent of crystallization and hydrogen atoms (expect for H1N and H1P in **6**) are removed for clarity. Nitrogen: blue; Phosphorus: purple; Oxygen: red; Iodine: plum; Selenium: grey.

8. References

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9. Methods

General Considerations

All reactions and product manipulations were carried out under an inert atmosphere of argon or dinitrogen using standard Schlenk-line or glovebox techniques (MBraun UNIlab glovebox maintained at < 0.1 ppm H_2O and < 0.1 ppm O_2). Hexane (hex; Sigma Aldrich HPLC grade), pentane (pent; Sigma Aldrich HPLC grade), and toluene (tol; Sigma Aldrich HPLC grade) were purified using an MBraun SPS-800 solvent system. Tetrahydrofuran (THF; Sigma Aldrich, ≥99.9%) and d_8-THF (Eurisotop, >99.5%) were distilled over a sodium metal/benzophenone mixture. C_6D_6 (Sigma Aldrich, 99.5%) was degassed prior to use. d_8-Toluene (Sigma-Aldrich 99%) was stirred over a Na/K alloy and filtered before use. All dry solvents were stored under argon in airtight ampoules over activated 3 Å molecular sieves. Commercial reagents were obtained from Sigma Aldrich, Fluorochem, Alfa Aesar and Santa Cruz Biotechnology. Potassium trimethylsilanolate (KOTMS) was dried under vacuum at 60 ^oC for 3 days before use. Triethylamine (NEt_3) was distilled over CaH_2 and degassed prior to use. Phosphorus trichloride was degassed prior to use. 5′-Bromo-2,2″,4,4″,6,6″-hexakis(1-methylethyl)-1,1′:3′,1″-terphenyl (HIPTBr)[1] and benzylpotassium[2] were synthesized following procedures described in the literature. Detailed experimental procedures for the synthesis of compounds **1** and **2** are listed in the supporting information.

Synthesis of 3

To a solid mixture of **2** (150 mg, 0.134 mmol, 1.0 eq.) and KOTMS (42.5 mg, 0.331 mmol, 2.5 eq.), THF (15 ml) was added. The mixture was stirred vigorously for 5 min before all volatiles were removed *in vacuo*. Hexane (10 ml) was added to the residue, and the solution was filtered

using a filter cannula. To the filtrate, a solution of 18-crown-6 (35 mg, 0.132 mmol; 0.99 eq.) in hexane (10 ml) was added, and the mixture was left standing overnight. **3** precipitated out of solution over the course of 24 h, the suspension was filtered and the resulting solid was washed with hexane (10 ml × 2) then dried *in vacuo* to afford **3** (120 mg, 0.086 mmol; yield: 64%) as a reddish white powder. Single crystals of **3** suitable for X-ray diffraction were obtained by slowly evaporating a concentrated toluene/hexane mixed solution of **3** in a −35 °C freezer for a week. Anal. Calcd for $C_{90}H_{125}KNO_7P$ (M.W. 1403.06 g mol^{-1}): C, 77.05; H, 8.98; N, 1.00; Found: C 75.49; H, 8.78; N, 1.12. ^{1}H NMR (600 MHz, C_6D_6): δ (ppm) 1.29 (d, $^3J_{H–H}$ = 6.8 Hz, 24H; CH(C*H*$_3$)$_2$), 1.30 (d, $^3J_{H–H}$ = 6.8 Hz, 24H; CH(C*H*$_3$)$_2$), 1.33 (d, $^3J_{H–H}$ = 6.8 Hz, 24H; CH(C*H*$_3$)$_2$), 2.88 (sept, $^3J_{H–H}$ = 6.8 Hz, 4H; C*H*(CH$_3$)$_2$), 3.00 (s, 24H; 18-crown-6), 3.42 (sept, $^3J_{H–H}$ = 6.8 Hz, 8H; C*H*(CH$_3$)$_2$), 6.79 (t, $^3J_{H–H}$ = 7.8 Hz, 1H; Ar*H*), 7.12 (t, $^4J_{H–H}$ = 1.6 Hz, 2H; Ar*H*), 7.20 (s, 8H; Ar*H*), 7.44 (d, $^3J_{H–H}$ = 7.8 Hz, 2H; Ar*H*), 7.86 (d, $^4J_{H–H}$ = 1.6 Hz, 4H; Ar*H*). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ (ppm) 24.56, 24.72, 25.11 (s, CH(*C*H$_3$)$_2$), 30.77, 34.89 (s, *C*H(CH$_3$)$_2$), 69.87 (s; 18-crown-6), 117.11 (s), 120.60 (s), 129.15 (s), 129.19 (s), 130.33 (s), 134.75 (d, $^3J_{P–C}$ = 8.6 Hz), 138.97 (s), 139.41 (s), 144.62 (s), 147.41 (s), 147.59 (s), 150.21 (s, d, $^2J_{P–C}$ = 23.7 Hz) (Ar*C*). ^{31}P NMR (162 MHz, C_6D_6): δ (ppm) 237.2 (s). HRMS(*m*/*z*): [Anion+H_2O]$^+$ calcd. For $C_{78}H_{103}NPO_2$, 1116.7721; found 1116.7736. m.p. 204 °C. FTIR (ATR): ν(cm^{-1}) 1077 (s, PO stretch).

Synthesis of 4

A benzene solution (0.2 mL) of BnBr (1.3 mg, 0.0076 mmol, 1.07 eq.) was slowly added to a benzene solution (0.3 mL) of **3** (10 mg, 0.0071 mmol, 1.00 eq.). The mixture was heated for 12 hours in a sealed NMR tube before all volatiles were removed *in vacuo*. Hexane (0.5 ml) was added to the residue, and the mixture was filtered to obtain the filtrate. The solution was

evaporated under vacuum to obtain a colorless oily residue, which was then triturated with MeCN to give **4** (6 mg, 0.0050 mmol; yield: 71%) as a white powder. Single crystals of **4** suitable for X-ray diffraction were obtained by slow evaporation of a concentrated hexane solution of **4** at room temperature. Anal. Calcd. for $C_{85}H_{108}NOP$ (M.W. 1190.78 g mol^{-1}): C, 85.74; H, 9.14; N, 1.18; Found: C 84.32; H, 8.97; N, 1.28. ^{1}H NMR (600 MHz, C_6D_6): δ (ppm) 1.17–1.20 (m, 24H; CH(C*H*$_3$)$_2$), 1.23 (d, $^{3}J_{H–H}$ = 6.8 Hz, 12H; CH(C*H*$_3$)$_2$), 1.27-1.30 (m, 36H; CH(C*H*$_3$)$_2$), 2.86 (sept, $^{3}J_{H–H}$ = 6.8 Hz, 4H; C*H*(CH$_3$)$_2$), 2.99 (sept, $^{3}J_{H–H}$ = 6.8 Hz, 8H; C*H*(CH$_3$)$_2$), 5.03 (s, 2H; NC*H*$_2$Ph), 6.61 (t, $^{3}J_{H–H}$ = 7.4 Hz, 2H; Ar*H*), 6.77 (t, $^{3}J_{H–H}$ = 7.4 Hz, 1H; Ar*H*), 6.89-6.94 (m, 3H; Ar*H*), 7.11 (s, 2H; Ar*H*), 7.17-7.21 (m, 12H; Ar*H*), 7.32 (d, $^{3}J_{H–H}$ = 7.4 Hz, 2H; Ar*H*). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ (ppm) 24.23, 24.42, 24.67, 25.06 (s, CH(*C*H$_3$)$_2$), 30.97, 34.88 (s, *C*H(CH$_3$)$_2$), 47.96 (s; N*C*H$_2$Ph), 120.75, 130.87 , 131.47 , 131.73 , 132.09 , 133.53 , 135.98 , 137.03 , 137.24 , 139.98, 140.44 , 141.17 , 141.80 , 146.88 , 148.63 (s, Ar*C*). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ (ppm) 284.4 (s, *trans*-isomer), 286.3 (s, *cis*-isomer). HRMS(m/z): $[M+H_3O]^+$ calcd. For $C_{85}H_{111}NPO_2$, 1208.8347; found 1208.8295. m.p. 158 °C. FTIR(ATR): ν(cm^{-1}) 1186 (s, PO stretch).

Synthesis of 5

A benzene solution (0.2 mL) of ^{i}Pr$_3$SiOTf (2.4 mg, 0.0078 mmol, 1.10 eq.) was slowly added to a benzene solution (0.3 mL) of **3** (10 mg, 0.0071 mmol, 1.00 eq.). The mixture was stirred for 1 min and filtered to obtain the filtrate. MeCN (5 ml) was added to the filtrate and the mixture was left in a in a –35 °C freezer overnight. The supernatant was removed and the resulting solid was dried *in vacuo* to afford **5** (7 mg, 0.0057 mmol; 78% yield) as a light yellow powder. Single crystals of **5** suitable for X-ray diffraction were obtained by slow evaporation of a concentrated

hexane solution of **5** at room temperature. Anal. Calcd. for $C_{87}H_{122}NOPSi$ (M.W. 1257.00 g mol^{-1}): C, 83.13; H, 9.78; N, 1.11; Found: C 83.13; H, 9.39; N, 1.05. ^{1}H NMR (600 MHz, C_6D_6): δ (ppm) 0.83-0.84 (m, 21H; SiC*H*(CH_3)$_2$), 1.24 (d, $^{3}J_{H–H}$ = 6.8 Hz, 24H; CH(C*H*$_3$)$_2$), 1.27 (d, $^{3}J_{H–H}$ = 6.8 Hz, 24H; CH(C*H*$_3$)$_2$), 1.33 (d, $^{3}J_{H–H}$ = 6.8 Hz, 24H; CH(C*H*$_3$)$_2$), 2.91 (sept, $^{3}J_{H–H}$ = 6.8 Hz, 4H; C*H*(CH_3)$_2$), 3.12 (sept, $^{3}J_{H–H}$ = 6.8 Hz, 8H; C*H*(CH_3)$_2$), 6.94 (t, $^{3}J_{H–H}$ = 7.6 Hz, 1H; Ar*H*), 7.08 (t, $^{4}J_{H–H}$ = 1.6 Hz, 2H; Ar*H*), 7.24 (s, 8H; Ar*H*), 7.49 (d, $^{3}J_{H–H}$ = 7.6 Hz, 2H; Ar*H*), 7.91 (d, $^{4}J_{H–H}$ = 1.6 Hz, 4H; Ar*H*). $^{13}C\{^{1}H\}$ NMR (151 MHz, C_6D_6): δ (ppm) 12.31 (s, Si*C*H(CH_3)$_2$), 17.44 (s, SiCH(*C*H$_3$)$_2$), 24.49, 24.55, 25.13 (s, CH(*C*H$_3$)$_2$), 30.93, 34.94 (s, *C*H(CH_3)$_2$), 120.89 (s), 123.18 (s), 129.48 (s), 130.59 (s), 130.76 (s), 131.96 (d, $^{3}J_{P–C}$ = 9.6 Hz), 137.78 (s), 140.63 (s), 140.73 (s), 141.55 (d, $^{2}J_{P–C}$ = 27.8 Hz), 147.06 (s), 148.39 (s) (Ar*C*). $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6): δ (ppm) 169.0 (s). HRMS(*m*/*z*): $[M+H]^+$ calcd. For $C_{87}H_{123}NPOSi$, 1256.9112; found 1256.9060. m.p. > 240 °C.

Synthesis of 6

To a solid mixture of **2** (30 mg, 0.0268 mmol, 1.0 eq.) and KOTMS (8.5 mg, 0.066 mmol, 2.5 eq.), THF (5 ml) was added. The mixture was stirred vigorously for 5 min before all volatiles were removed *in vacuo*. Hexane (10 ml) was added to the residue, and the solution was filtered using a filter cannula, and the filtrate was dried *in vacuo* again. THF (5 ml) was added to the residue and the solution was cooled to –78 °C before a THF solution of H_2O (5 mg/ml, 0.12 ml, 0.033 mmol, 1.25 eq.) was added dropwise. The mixture was stirred for 20 min at –78 °C then slowly warmed up to room temperature. (PPN)Cl (30.7 mg, 0.0536 mmol, 2 eq.) was then added to the mixture. The mixture was sonicated for 5 min and stirred for another 2 h before filtering to remove insoluble salts. The filtrate was dried under vacuum, and toluene (3 ml) was added to

dissolve the residue. The solution was then stored in a –35 °C freezer for three days to crystallize. The supernatant was removed and the resulting solid was dried *in vacuo* to afford **6** (16 mg, 0.00966 mmol; 36% yield) as a white powder. Single crystals of **6** suitable for X-ray diffraction were obtained by slow diffusion of hexane into a concentrated THF solution of the product at room temperature. Anal. Calcd. for $C_{87}H_{122}NOPSi$ (M.W. 1656.25 g mol^{-1}): C, 82.67; H, 8.09; N, 1.69; Found: C 81.43; H, 7.77; N, 1.71. ^{1}H NMR (500 MHz, C_6D_6): δ (ppm) 1.28–1.31 (m, 72H; CH(C*H*$_3$)$_2$), 2.88 (sept, $^{3}J_{H–H}$ = 6.8 Hz, 4H; C*H*(CH$_3$)$_2$), 3.38 (sept, $^{3}J_{H–H}$ = 6.8 Hz, 8H; C*H*(CH$_3$)$_2$), 5.64 (s, 1H; N*H*), 6.94 (t, $^{3}J_{H–H}$ = 7.4 Hz, 1H; Ar*H*), 7.04-7.08 (m, 12H; Ar*H*), 7.12-7.15 (m, 8H; ArH), 7.14 (d, $^{1}J_{P–H}$ = 572.4 Hz, 1H; P*H*), 7.21 (s, 8H; Ar*H*), 7.39-7.43 (m, 12H; Ar*H*), 7.47 (d, $^{3}J_{H–H}$ = 7.4 Hz, 2H; Ar*H*), 7.82 (d, $^{4}J_{H–H}$ = 1.1 Hz, 4H; Ar*H*). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6): δ (ppm) 24.56, 24.86, 25.90 (s, CH(*C*H$_3$)$_2$), 30.96, 34.93 (s, *C*H(CH$_3$)$_2$), 119.23 (s), 120.55 (s), 126.54 (d, $J_{P–C}$ = 2.3 Hz), 127.39 (d, $J_{P–C}$ = 2.5 Hz), 129.74-129.89 (m), 130.31 (s), 130.60 (s), 132.68 (s), 132.72 (s), 132.77 (s), 133.60 (s), 135.34 (s), 138.67 (s), 140.53 (s), 143.41 (s), 147.60 (s), 147.63 (s) (Ar*C*). ^{31}P NMR (202 MHz, C_6D_6): δ (ppm) –3.5 (d, $^{1}J_{P–H}$ = 572.4 Hz), 21.2 (s). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ (ppm) –3.5 (s), 21.2 (s, Ph$_3$*P*=N=*P*Ph$_3$). HRMS(*m*/*z*): [Anion]$^{+}$ calcd. For $C_{78}H_{103}NPO_2$, 1116.7732; found 1116.7732. m.p. 210 °C. FTIR (ATR): ν(cm^{-1}) 1063 (s, $PO_{2\ symm}$ stretch), 1114 (s, PNP stretch).

Synthesis of 7

A toluene solution (3 mL) of I_2 (18 mg, 0.07 mmol, 1.00 eq.) was slowly added to a toluene solution (5 mL) of **3** (100 mg, 0.07 mmol, 1.00 eq.) dropwise at –35 °C. The mixture was stirred for 5 min before all volatiles were removed *in vacuo*. The oily yellow residue was then triturated with hexane to give **7** (102 mg, 0.0062 mmol; yield: 87%) as a brown powder. Single crystals of

7 suitable for X-ray diffraction were obtained by slow evaporation of a concentrated hexane/toluene solution of **7** at room temperature. Anal. Calcd. for $C_{90}H_{125}NO_7PI_2$ (M.W. 1641.84 g mol^{-1}): C, 65.11; H, 7.49; N, 0.85; Found: C 61.65; H, 7.24; N, 0.72. ^{1}H NMR (500 MHz, C_6D_6): δ (ppm) 1.30 (d, $^{3}J_{H–H}$ = 6.8 Hz, 24H; CH(C*H*$_3$)$_2$), 1.33 (d, $^{3}J_{H–H}$ = 6.8 Hz, 24H; CH(C*H*$_3$)$_2$), 1.35 (d, $^{3}J_{H–H}$ = 6.8 Hz, 24H; CH(C*H*$_3$)$_2$), 2.95 (sept, $^{3}J_{H–H}$ = 6.8 Hz, 4H; C*H*(CH$_3$)$_2$), 3.26 (s, 24H; 18-crown-6), 3.47 (sept, $^{3}J_{H–H}$ = 6.8 Hz, 8H; C*H*(CH$_3$)$_2$), 7.09 (d, $^{4}J_{H–H}$ = 1.1 Hz, 2H; Ar*H*), 7.21 (t, $^{3}J_{H–H}$ = 7.5 Hz, 1H; Ar*H*), 7.29 (s, 8H; Ar*H*), 7.58 (d, $^{3}J_{H–H}$ = 7.6 Hz, 2H; Ar*H*), 8.07 (d, $^{4}J_{H–H}$ = 1.1 Hz, 4H; Ar*H*). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ (ppm) 24.59, 25.03, 25.59 (s, CH(*C*H$_3$)$_2$), 30.82, 35.01 (s, *C*H(CH$_3$)$_2$), 70.06 (s, 18-crown-6), 120.72 (s), 129.51 (s), 131.43 (s), 132.93 (d, $^{2}J_{P–C}$ = 9.0 Hz), 138.06 (s), 138.87 (s), 139.82 (s), 144.60 (s), 146.98 (s), 147.47 (s), 147.75 (s), 148.55 (s) (Ar*C*). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ (ppm) –147.8 (br). HRMS(*m*/*z*): $[M+H]^+$ calcd. For $C_{78}H_{101}NPOI_2$, 1352.5716; found 1352.5701. m.p. sample decomposes above 166 °C. FTIR (ATR): ν(cm^{-1}) 1105 (s, 18-crown-6 stretch).

Synthesis of 8

A benzene solution (0.2 mL) of Se_2Ph_2 (2.2 mg, 0.007 mmol, 1.00 eq.) was added to a benzene solution (0.3 mL) of **3** (10 mg, 0.007 mmol, 1.00 eq.). The mixture was stirred for 24 h before all volatiles were removed *in vacuo*. THF (0.5 ml) was added to the residue together with (PPN)Cl (8 mg, 0.014 mmol, 2.00 eq.). The mixture was sonicated for 5 min and then stirred for 2 h before filtered to remove insoluble salts. The filtrate was layered with hexane (6 ml) and left for 24 h before removing the supernatant. The remaining crystals were dried *in vacuo* to afford **8** (8 mg, 0.0041 mmol; yield: 59%) as a yellow powder. Single crystals of **8** suitable for X-ray diffraction were obtained by slow diffusion of hexane into a concentrated THF solution of the

product at room temperature. Anal. Calcd. for $C_{126}H_{141}N_2OP_3Se_2$ (M.W. 1950.39 g mol^{-1}): C, 77.59; H, 7.29; N, 1.44; Found: C 77.16; H, 6.96; N, 1.42. ^{1}H NMR (400 MHz, d_8-THF): δ (ppm) 0.98 (d, $^3J_{H–H}$ = 7.0 Hz, 24H; CH(CH_3)$_2$), 1.10 (d, $^3J_{H–H}$ = 7.0 Hz, 24H; CH(CH_3)$_2$), 1.22 (d, $^3J_{H-H}$ = 7.0 Hz, 24H; CH(CH_3)$_2$), 2.83 (sept, $^3J_{H–H}$ = 7.0 Hz, 4H; CH(CH$_3$)$_2$), 3.22 (sept, $^3J_{H–H}$ = 7.0 Hz, 8H; CH(CH$_3$)$_2$), 6.61-6.67 (m, 8H; ArH), 6.95 (s, 8H; ArH), 7.08 (dd, $^3J_{H–H}$ = 7.6 Hz, $^4J_{H–H}$ = 1.5 Hz, 2H; ArH), 7.33 (d, $^3J_{H–H}$ = 7.6 Hz, 4H; ArH), 7.43–7.48 (m, 13H; ArH), 7.54–7.60 (m, 16H; ArH), 7.66 (td, $^3J_{H–H}$ = 7.6 Hz, $^4J_{H–H}$ = 1.5 Hz, 6H; ArH). ^{13}C{^{1}H} NMR (151 MHz, d_8-THF): δ (ppm) 24.47, 24.71, 25.23 (s, CH(*C*H$_3$)$_2$), 30.70, 35.20 (s, *C*H(CH$_3$)$_2$), 118.21 (d, $J_{P–C}$ = 5.5 Hz), 120.43 (d, $J_{P–C}$ = 2.1 Hz), 128.64 (d, $J_{P–C}$ = 11.6 Hz), 128.83 (s), 128.86 (s), 128.94 (s), 129.43 (s), 130.12-130.25 (m), 130.34 (d, $J_{P–C}$ = 4.5 Hz), 130.73 (s), 131.30 (d, $J_{P–C}$ = 2.3 Hz), 132.03 (d, $J_{P–C}$ = 2.7 Hz), 132.47 (s), 132.59 (d, $J_{P–C}$ = 2.6 Hz), 132.65 (d, $J_{P–C}$ = 2.1 Hz), 132.97-133.08 (m), 134.51 (s), 135.57 (d, $J_{P–C}$ = 2.0 Hz), 135.96 (d, $J_{P–C}$ = 5.5 Hz), 138.70 (d, $J_{P–C}$ = 10.7 Hz), 139.52 (d, $J_{P–C}$ = 6.3 Hz), 144.96 (s), 146.97 (d, $J_{P–C}$ = 5.5 Hz), 147.23 (s), 147.88 (s) (Ar*C*). ^{77}Se NMR (95.4 MHz, d_8-THF): δ (ppm) 512.7 (d, $J_{P–Se}$ = 398.7 Hz). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ (ppm) –23.2 with two satellites at –24.5 and –22.0 (s, $J_{P–Se}$ = 398.7 Hz), 21.0 (s, Ph$_3$*P*=N=*P*Ph$_3$). HRMS(*m*/*z*): [Anion]$^+$ calcd. For $C_{90}H_{111}NPOSe_2$, 1412.6739; found 1412.6758. m.p. 199 °C. FTIR (ATR): ν(cm^{-1}) 1115 (s, PNP stretch).

10. Data availability

All data are available in the main text or the supplementary Information. Crystallographic data for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 2339506 (**S2**·hex), 2339507 (**2**·hex), 2339508 (**S3**), 2339509 (**3**·2tol), 2339510 (**4**), 2339511 (**5**·hex), 2339512 (**6**), 2339513 (**7**·hex), and 2339514

(**8**·3THF). Copies of the data can be obtained free of charge from http://www.ccdc.cam.ac.uk/structures/. Cartesian coordinates of optimized structures are available as a Supplementary Information file.

11. Methods-only References

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