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# Isolation of arylhalodiphosphenes: periodic trends in R–P=P–X bonding (X = Cl, Br, I)

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For over a century, aryldiazonium halides have served as widely used building blocks within synthetic chemistry. They are vital intermediates in converting simple anilines to high-value products, including those needed to prepare pharmaceuticals, dyes, and functional materials. Despite the prevalence of these nitrogen-based organic salts in laboratories, structurally related phosphorus-based salts remain scarce. Herein, we report the isolation and structural characterization of a monomeric arylchlorodiphosphene, (M<sup>5</sup>FluInd\*)P=P(Cl)(Et<sub>2</sub>O)<sub>2</sub> (where M<sup>5</sup>FluInd\* is a sterically demanding hydrindacene substituent), for the first time. The structure and reactivity of (M<sup>5</sup>FluInd\*)P=P(Cl) were explored to compare the novel arylhalodiphosphene with compositionally related aryldiazonium chlorides, [RNN][Cl], and chloroiminophosphanes, RN=P(Cl). The P–P bond of (M<sup>5</sup>FluInd\*)P=P(Cl) was cleaved *via* protonolysis to afford the parent phosphine, (M<sup>5</sup>FluInd\*)PH<sub>2</sub>. Halogen-exchange reactions between (M<sup>5</sup>FluInd\*)P=P(Cl) and TMSX (TMS = trimethylsilyl, X = Br, I) afforded the related monomeric arylhalodiphosphenes, (M<sup>5</sup>FluInd\*)P=P(X) (X = Br, I). Finally, the coordination complex, [(M<sup>5</sup>FluInd\*)P=P(Cl)·Ag][CF<sub>3</sub>SO<sub>3</sub>], was isolated by treatment of (M<sup>5</sup>FluInd\*)P=P(Cl) with AgCF<sub>3</sub>SO<sub>3</sub>. Periodic trends in the structure and bonding of (M<sup>5</sup>FluInd\*)P=P(X) (X = Cl, Br, I) were investigated with spectroscopic, crystallographic, and computational methods. These studies confirm that the {PPX} moiety consists of a formal P–P double bond, and polar covalent P–X (X = Cl, Br, I) single bonds. (M<sup>5</sup>FluInd\*)P=P(X) (X = Cl, Br, I) represent the first fully characterized, crystalline arylhalodiphosphenes and serve to advance the state of low-coordinate phosphorus chemistry.

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## Introduction

The isolation of heavy element analogues of common organic functional groups remains central to advancing our understanding of periodic trends and developing new precursors.<sup>1,2</sup> The inherent challenges in stabilizing molecular species bearing multiple bonds between main-group elements heavier than those of the second period of the periodic table is encapsulated by the so-called “double bond rule”.<sup>3–5</sup> Such molecules often form self-associated oligomers rather than retaining the heavy element–element multiple bond.<sup>6</sup> Chemists may overcome this challenge by invoking thermodynamic stabilization whereby a Lewis acid and/or base is used to perturb the frontier molecular orbitals of the reactive unsaturated fragment,<sup>7</sup> and/or *via* kinetic stabilization where the reactive fragment is sterically protected.<sup>8,9</sup>

Initially reported in 1858, aryldiazonium chlorides are conveniently prepared by treatment of anilines with HCl and

NaNO<sub>2</sub> (Fig. 1).<sup>10</sup> Aryldiazonium salts have served as important reagents and intermediates in numerous key named reactions, including the Sandmeyer reaction,<sup>11</sup> Pschorr reaction,<sup>12</sup> Gomberg–Bachmann reaction,<sup>13</sup> Balz–Schiemann reaction,<sup>14</sup> and Meerwein arylations.<sup>15</sup> These reagents continue to be under intense investigation for their powerful utility in converting simple anilines to value-added products *via* diverse synthetic pathways.<sup>16</sup> Despite the prevalence of diazonium salts across synthetic chemistry, analogous species in which one or both of the diazonium N atoms are replaced by a heavier pnictogen remains rare. In an early report, (Mes\*)N=P(Cl) (Mes\* = 2,4,6-*tert*-butylphenyl) was isolated by treating the corresponding aniline with an excess of PCl<sub>3</sub> and Et<sub>3</sub>N (Fig. 1).<sup>17</sup> (Mes\*)N=P(Cl) may be viewed as a “monophosphadiazonium chloride” in which the Cl atom directly binds the terminal P atom, in contrast to diazonium chlorides which do not feature a similar N–Cl bond and instead exist as separated ion pairs even in the solid-state.<sup>18</sup> Coordination of the Cl anion to the terminal P-atom disrupts multiple-bonding between the N and P atoms, and (Mes\*)N=P(Cl) features an N–P double bond. (Mes\*)N=P(Cl) may undergo halogen-exchange reactions to form (Mes\*)N=P(X) (X = Br, I) by treating (Mes\*)N=P(Cl) with the corresponding trimethylsilyl (TMS) halide (Fig. 1).

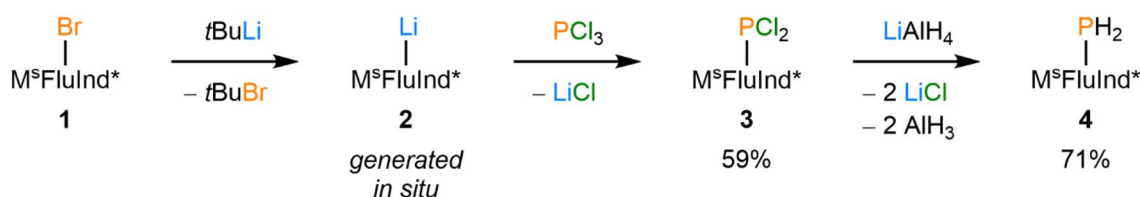
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Fig. 1 General synthesis of  $[\text{RNN}][\text{Cl}]$  ( $i = \text{excess HCl}$ ,  $\text{excess NaNO}_2$ ). Synthesis of  $(\text{Mes}^*)\text{N}=\text{P}=\text{Cl}$  and  $[\text{ClP}(\mu\text{-PMes}^*)_2]$  ( $ii = \text{excess PCl}_3$ ,  $\text{excess Et}_3\text{N}$ ). Synthesis of  $[(\text{Mes}^*)\text{NP}][\text{AlCl}_4]$  ( $iii = \text{AlCl}_3$ ). Synthesis of  $(\text{Mes}^*)\text{NPX}$  ( $iv = \text{TMSX}$ ;  $\text{X} = \text{Br}, \text{I}$ ) reported herein. Structural diagrams of ligands  $\text{M}^s\text{FluInd}^*$  and  $\text{Mes}^*$ .



Scheme 1 Synthesis of compounds 2, 3, and 4.

$(\text{Mes}^*)\text{N}=\text{P}=\text{Cl}$  has served as a seminal precursor to phosphadiazonium compounds. For example, treatment of  $(\text{Mes}^*)\text{N}=\text{P}=\text{Cl}$  with  $\text{AlCl}_3$  resulted in chloride abstraction to form the iminophosphenium tetrachloroaluminate,  $[(\text{Mes}^*)\text{NP}][\text{AlCl}_4]$  (Fig. 1). The same group later isolated a range of oxy-substituted iminophosphanes by treatment of  $(\text{Mes}^*)\text{N}=\text{P}=\text{Cl}$  with silver or lithium salts.<sup>19</sup> Further, iminophosphenium species may also be generated *in situ* by reacting with  $\text{GaCl}_3$ .<sup>20</sup> Recently, the chloroiminophosphane,  $(\text{Ter}^*)\text{N}=\text{P}=\text{Cl}$  [ $\text{Ter}^* = \text{bis}(\text{ortho-}m\text{-hexaisopropylterphenyl})\text{phenyl}$ ] was prepared from the bulky aniline  $(\text{Ter}^*)\text{NH}_2$  and employed as a precursor in the isolation of a two-coordinate phosphindene oxide,  $(\text{Ter}^*)\text{NBnPO}$ .<sup>21</sup> Further,  $(\text{M}^s\text{FluInd}^*)\text{N}=\text{P}=\text{Cl}$  was recently prepared from  $(\text{M}^s\text{FluInd}^*)\text{NH}_2$  and served as a precursor for an aryliminophosphinyl radical,  $(\text{M}^s\text{FluInd}^*)\text{NP}$ .<sup>22</sup>

Numerous diphosphenes of the form  $\text{RP}=\text{P}'\text{R}'$  have been reported since the seminal discovery of the diaryldiphosphene,  $(\text{Mes}^*)\text{P}=\text{P}(\text{Mes}^*)$ .<sup>23</sup> The stability of diphosphenes is largely attributed to the presence of bulky substituents at each P atom that form a sterically protected cavity for the P–P double-bonded core to reside.<sup>24</sup> Compounds featuring  $\{\text{P}_2\}$  fragments stabilized by either carbene ligands or transition metals have also been isolated.<sup>25–30</sup>

Asymmetric diphosphenes that feature an alkyl, alkoxy, or amino group in addition to an aryl substituent have also been reported and, in some cases, have served as precursors to donor-stabilized diphosphadiazonium species.<sup>31–34</sup> Treatment of the aminoaryldiphosphenes,  $(\text{Mes}^*)\text{P}=\text{PNR}_2$  ( $\text{NR}_2 = \text{N}(\text{Pr})_2$ ,  $\text{N}(\text{cyclohexyl})_2$ , or 2,2,6,6-tetramethylpiperidine) with one equivalent of  $\text{HCF}_3\text{SO}_3$  affords ammonium salts,  $[(\text{Mes}^*)\text{P}=\text{PNHR}_2][\text{CF}_3\text{SO}_3]$ , which are stable in solution at  $-50^\circ\text{C}$ .<sup>35</sup> Remarkably, treatment of a 1 : 1 mixture of  $(\text{Mes}^*)\text{P}=\text{PNR}_2$  and  $\text{Ph}_3\text{P}$  with two equivalents of  $\text{HCF}_3\text{SO}_3$  affords  $[(\text{Mes}^*)\text{P}=\text{P}(\text{PPh}_3)][\text{CF}_3\text{SO}_3]$ , which was initially reported as a donor-stabilized diphosphadiazonium cation. However, crystallographic and computational data indicate that  $[(\text{Mes}^*)\text{P}=\text{P}(\text{PPh}_3)][\text{CF}_3\text{SO}_3]$  is best described as a diphosphene with an adjacent triphenylphosphonium center.<sup>36</sup>

Treatment of  $(\text{Mes}^*)\text{P}=\text{PN}^i\text{Pr}_2$  with  $\text{HCl}$  was reported to form monomeric  $(\text{Mes}^*)\text{P}=\text{P}=\text{Cl}$  *via* the loss of  $\text{HN}^i\text{Pr}_2$ .<sup>37</sup> However,  $(\text{Mes}^*)\text{P}=\text{P}=\text{Cl}$  was reported to exist only transiently at  $-50^\circ\text{C}$  in solution, and its structure has only been inferred by  $^{31}\text{P}$  NMR analysis and follow-on reactivity studies with organolithium reagents to form asymmetric diphosphenes.<sup>38</sup> Monomeric  $(\text{Mes}^*)\text{P}=\text{PX}$  ( $\text{X} = \text{Br}, \text{I}$ ) were reported to be prepared by treatment of  $(\text{Mes}^*)\text{P}=\text{PN}^i\text{Pr}_2$  with  $\text{HX}$  ( $\text{X} = \text{Br}, \text{I}$ ), or by treatment of  $[(\text{Mes}^*)\text{P}=\text{P}(\text{PPh}_3)][\text{CF}_3\text{SO}_3]$  with  $[\text{Et}_3\text{NH}][\text{X}]$  ( $\text{X} = \text{Br}, \text{I}$ )



at  $-78\text{ }^{\circ}\text{C}$ , but again these compounds were only characterized by  $^{31}\text{P}$  NMR spectroscopy and it is unclear at which temperature these spectra were collected.<sup>35,39</sup> The existence of monomeric  $(\text{Mes}^*)\text{P}=\text{PX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) as isolable reagents has recently been called into question in the absence of conclusive analytical evidence and crystallographic characterization; treatment of the primary phosphine,  $(\text{Mes}^*)\text{PH}_2$  with an excess of  $\text{PCl}_3$  and  $\text{NET}_3$ , does not afford monomeric  $(\text{Mes}^*)\text{P}=\text{PCL}$ , but rather affords the dimeric form  $[\text{ClP}(\mu\text{-PMes}^*)]_2$ , which was characterized in both solution and solid-state (Fig. 1).<sup>36,40,41</sup>

Herein, we report the isolation of a crystalline, monomeric arylchlorodiphosphene,  $(\text{M}^{\text{s}}\text{FluInd}^*)\text{P}=\text{PCL}$  (**8**) (Fig. 1). Spectroscopic, crystallographic, and computational characterization of compound **8** confirms the presence of a formal P–P double bond and a polar, covalent P–Cl single bond, in contrast to compositionally analogous aryldiazonium chlorides of the form  $[\text{RNN}][\text{Cl}]$ . The terminal  $\{\text{PPCl}\}$  unit in **8** is kinetically stabilized by the sterically demanding hydrindacene substituent,  $\text{M}^{\text{s}}\text{FluInd}^*$ .<sup>42</sup> The unsaturated P–P bond in **8** may be cleaved *via* protonolysis to form the primary phosphine,  $(\text{M}^{\text{s}}\text{FluInd}^*)\text{PH}_2$  (**4**). Treatment of compound **8** with  $\text{TMSBr}$  or  $\text{TMSI}$  affords  $(\text{M}^{\text{s}}\text{FluInd}^*)\text{PPBr}$  (**9**), and  $(\text{M}^{\text{s}}\text{FluInd}^*)\text{PPI}$  (**10**), respectively, highlighting the synthetic

utility of the terminal P–Cl bond in **8**. Attempts to abstract the Cl atom from **8** with  $\text{AlCl}_3$  or  $\text{GaCl}_3$  afforded complex reaction mixtures, while treatment of **8** with  $\text{AgCF}_3\text{SO}_3$  afforded the coordination complex,  $[(\text{M}^{\text{s}}\text{FluInd}^*)\text{PPCl}\cdot\text{Ag}][\text{CF}_3\text{SO}_3]$  (**11**). Periodic trends in structure and bonding between the novel catalogue of isolable arylhalodiphosphenes **8**, **9**, and **10** were explored with spectroscopic, crystallographic, and computational methods.

## Results and discussion

### Synthesis of novel phosphine precursors

Inspired by the success of bulky hydrindacene-based ligands in stabilizing reactive molecular fragments,<sup>22,42–59</sup> literature known  $(\text{M}^{\text{s}}\text{FluInd}^*)\text{Br}$  (**1**) was treated with an excess of *tert*-butyl lithium to form  $(\text{M}^{\text{s}}\text{FluInd}^*)\text{Li}$  (**2**) *in situ*,<sup>42</sup> which was subsequently treated with  $\text{PCl}_3$  to afford  $(\text{M}^{\text{s}}\text{FluInd}^*)\text{PCl}_2$  (**3**), characterized as the hexane solvate (Scheme 1). Compound **3** was then reduced with an excess of  $\text{LiAlH}_4$  to afford  $(\text{M}^{\text{s}}\text{FluInd}^*)\text{PH}_2$  (**4**) (Scheme 1). However, we found it was most efficient to synthesize **4** directly from **1** without fully isolating **3**. Like other primary phosphines bearing bulky aryl substituents, **4** is air-stable in both the solid-state and in solution.<sup>60,61</sup> Compound **4**



Fig. 2 Thermal ellipsoid plot (50% probability) of (A) **4**·(hexane), (B) **5**·(toluene)<sub>2.5</sub>, (C) **6**·(Et<sub>2</sub>O)<sub>2</sub>, and (D) **7**·(Et<sub>2</sub>O)<sub>2</sub>. Solvent molecules, C-bound H atoms, and disordered components are omitted for clarity. Only the major component of disorder is displayed in all cases. Select C atoms and H atoms are shown as spheres of arbitrary radius for clarity. Color code: P orange, Cl dark green, Si dark yellow, K sky blue, C black, H grey.



could be crystallized from a  $-30\text{ }^{\circ}\text{C}$  solution of hexane to afford colorless blocks of  $4\cdot(\text{hexane})$ . Structural characterization of  $4\cdot(\text{hexane})$  by single-crystal X-ray diffraction (SC-XRD) confirms the presence of a terminal  $\{\text{PH}_2\}$  group within the sterically protected environment created by the flanking fluorenyl substituents of the  $\text{M}^{\text{s}}\text{FluInd}^*$  ligand (Fig. 2A).

Compound  $4\cdot(\text{hexane})$  was reacted with potassium benzylate (KBz) in benzene to form intensely red solutions of  $(\text{M}^{\text{s}}\text{FluInd}^*)\text{PHK}$  (**5**) *in situ* (Scheme 2), which was structurally characterized as a toluene solvate (Fig. 2B). In the solid-state,  $5\cdot(\text{toluene})_{2.5}$  exists as a centrosymmetric dimer in which a disordered toluene molecule resides on the crystallographic inversion center and coordinates the potassium ions. Each potassium ion is further coordinated by a 6-membered ring within the fluorenyl groups and by the anionic P-donor.

We hypothesized that a silylated phosphine substituted with the sterically demanding  $\text{M}^{\text{s}}\text{FluInd}^*$  substituent could serve as an effective precursor for the synthesis of unsaturated main-group species.  $(\text{M}^{\text{s}}\text{FluInd}^*)\text{PTMSH}$  (**6**) was isolated *via* sequential treatment of  $4\cdot(\text{hexane})$  with KBz followed by TMSCl (Scheme 2). Colorless blocks of analytically pure  $6\cdot(\text{Et}_2\text{O})_2$  were isolated by crystallization from  $\text{Et}_2\text{O}$  solutions at  $-30\text{ }^{\circ}\text{C}$ .  $6\cdot(\text{Et}_2\text{O})_2$  crystallizes in the  $P4_21m$  space-group on a special position distinguished by a two-fold rotation axis and two mirror planes, such that 0.25 of the  $\text{M}^{\text{s}}\text{FluInd}^*$  ligand resides in the asymmetric unit and the central  $\{\text{PTMSH}\}$  unit is disordered about these symmetry elements (Fig. 2C).

Sequential treatment of  $4\cdot(\text{hexane})$  with KBz followed by  $\text{PCl}_3$  successfully afforded  $(\text{M}^{\text{s}}\text{FluInd}^*)\text{PHPCl}_2$  (**7**) which was obtained as the  $\text{Et}_2\text{O}$  disolvate from solutions of **7** in  $\text{Et}_2\text{O}$  at  $-30\text{ }^{\circ}\text{C}$  (Scheme 2). The  $^{31}\text{P}\{^1\text{H}\}$  nuclear magnetic resonance (NMR) spectrum of  $7\cdot(\text{Et}_2\text{O})_2$  exhibits a prominent pair of doublets at  $-41\text{ ppm}$  and  $209\text{ ppm}$  with a  $^1J_{\text{PP}}$  value of  $247\text{ Hz}$ , consistent with the presence of a P–P single bond in **7**.<sup>62</sup> Additionally, the  $^{31}\text{P}$  and  $^1\text{H}$  NMR spectra confirm a P-bound proton in **7** with  $^1J_{\text{PH}} = 219\text{ Hz}$  and  $^2J_{\text{PH}} = 14.5\text{ Hz}$ . Crystals of  $7\cdot(\text{Et}_2\text{O})_2$  are crystallographically isomorphic with  $6\cdot(\text{Et}_2\text{O})_2$  and feature

a terminal  $\{\text{PHPCl}_2\}$  motif disordered about multiple positions (Fig. 2D). Unfortunately, we were unable to isolate  $7\cdot(\text{Et}_2\text{O})_2$  as an analytically pure material; we attribute our inability to purify **7** to the high crystallinity and similar solubility of  $\text{M}^{\text{s}}\text{FluInd}^*$ -containing impurities, a common challenge associated with the use of such sterically demanding substituents.<sup>21,42,63</sup>

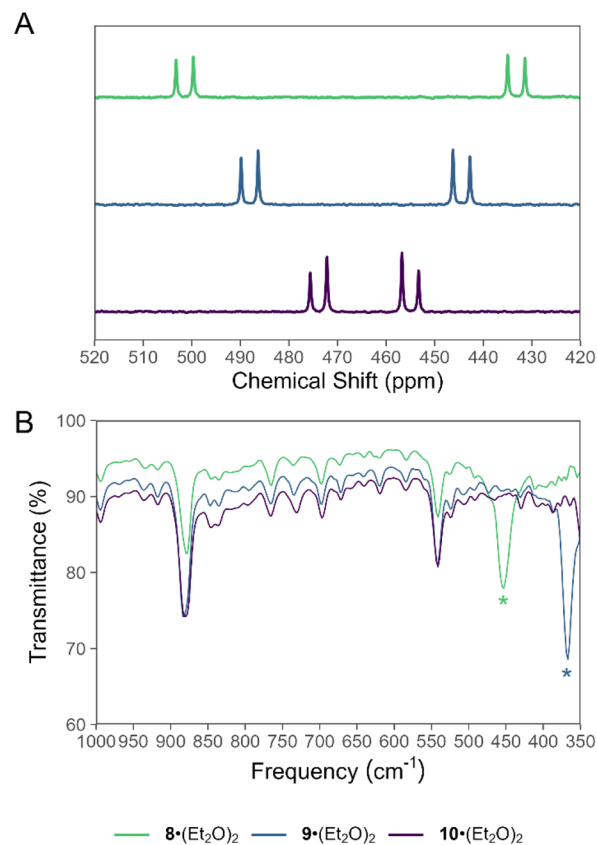


Fig. 3 Stacked (A)  $^{31}\text{P}$  NMR spectra and (B) IR spectra of  $8\cdot(\text{Et}_2\text{O})_2$ ,  $9\cdot(\text{Et}_2\text{O})_2$ , and  $10\cdot(\text{Et}_2\text{O})_2$ . Signals in the IR spectrum assigned to a P–X bond stretching mode are denoted with an asterisk.



Scheme 2 Synthesis of compounds **5**, **6**, **7**, and **8**.



### Synthesis and reactivity of a monomeric arylchlorodiphosphene

Treatment of a hexane solution of  $7 \cdot (\text{Et}_2\text{O})_2$  with triethylamine resulted in the formation of a yellow suspension (Scheme 2). Removal of the solid by-product  $[\text{Et}_3\text{NH}][\text{Cl}]$  and volatiles, followed by recrystallization of the residue from  $\text{Et}_2\text{O}$  resulted in the isolation of yellow crystals. Analysis of the crystalline product by  $^{31}\text{P}$  NMR spectroscopy revealed two new doublets in the spectrum, which do not exhibit any  $^1\text{H}$  coupling (Fig. 3A). The  $^{31}\text{P}$  NMR resonances of the product are shifted strongly downfield with respect to the precursor at 433 ppm and 502 ppm and exhibit a larger  $^1J_{\text{PP}}$  coupling constant of 574 Hz, consistent with an asymmetric diphosphene species with a P–P double bond.<sup>31,36,64–66</sup> Furthermore, the infrared (IR) spectrum of the product features a strong band assigned to the P–Cl stretch that appears at a lower wavenumber ( $\nu_{\text{P-Cl}} = 451 \text{ cm}^{-1}$ ) relative to that of  $7 \cdot (\text{Et}_2\text{O})_2$  ( $\nu_{\text{P-Cl}} = 461 \text{ cm}^{-1}$ ) (Fig. 3B, SI Fig. S34).

Analysis of the yellow crystals by SC-XRD reveals the sample to be crystallographically isomorphous with those of  $6 \cdot (\text{Et}_2\text{O})_2$  and  $7 \cdot (\text{Et}_2\text{O})_2$ ; the product also crystallizes in the  $P\bar{4}2_1m$  space

group with nearly identical unit cell parameters. However, solution of the solid-state structure confirms a distinct Fourier difference map within the cavity created by the  $\text{M}^{\text{FluInd}^*}$  ligand. Indeed, the crystallographic data are fit excellently by  $8 \cdot (\text{Et}_2\text{O})_2$  ( $R_1 = 4.62\%$ ). Our model features disorder between a major *E*-isomer with an occupancy of 85% (Fig. 4A) and a minor *Z*-isomer with an occupancy of 15% with respect to the asymmetric diphosphene unit. The major *E*-isomer is further disordered about two positions, and the entire  $\{\text{PPCl}\}$  motif is disordered about a special position. We note that the connectivity of  $8 \cdot (\text{Et}_2\text{O})_2$  is unambiguous, but meaningful discussion of structural parameters is precluded by this disorder. Remarkably, compound **8** may also be synthesized by treatment of  $6 \cdot (\text{Et}_2\text{O})_2$  with  $\text{KBz}$  followed by  $\text{PCl}_3$  *via* the formal elimination of  $\text{KCl}$  and  $\text{TMSCl}$  (Scheme 2).

For most monomeric diphosphenes, the synthesis of *Z*-isomers from *E*-isomers requires photolytic conditions and low temperatures, and warming solutions of the resulting *Z*-isomer to room-temperature results in the formation of the more stable *E*-isomer.<sup>31,67,68</sup> The observed isomerism in the solid-state structure may be the result of a photoisomerization reaction



Fig. 4 Thermal ellipsoid plots (50% probability) depicting the major *E*-isomer for (A)  $8 \cdot (\text{Et}_2\text{O})_2$ , (B)  $9 \cdot (\text{Et}_2\text{O})_2$ , (C)  $10 \cdot (\text{Et}_2\text{O})_2$ , and (D) **11**. The refined *E* : *Z* occupancy ratios in our models are 85 : 15, 78 : 22, 60 : 40, and 67 : 33 for  $8 \cdot (\text{Et}_2\text{O})_2$ ,  $9 \cdot (\text{Et}_2\text{O})_2$ ,  $10 \cdot (\text{Et}_2\text{O})_2$ , and **11**, respectively. Only the major component of disorder for the *E*-isomer of  $8 \cdot (\text{Et}_2\text{O})_2$  and  $9 \cdot (\text{Et}_2\text{O})_2$  are depicted. Solvent molecules, H atoms, and disordered components are omitted for clarity. Select C atoms are shown as spheres of arbitrary radius for clarity. Color code: P orange, Cl dark green, Br blue, I purple, Ag navy, F pink, S yellow, O red, C black.





to  $\text{Ag}^+$  (Fig. 4D).<sup>31</sup> Remarkably, the solid-state structure of **11** features a two-component disorder arising from the presence of the *E* and the *Z* isomer of the coordinated diphosphene, **8**, in a 68 : 32 occupancy ratio, respectively. These results ultimately highlight the divergent reactivity between the chloroiminophosphane,  $(\text{Mes}^*)\text{N}=\text{PCL}$ , and compound **8**.

### Theoretical analysis of monomeric arylhalodiphosphenes

Curious to investigate periodic trends in structure and bonding amongst this newly discovered class of monomeric arylhalodiphosphenes, the theoretical molecules *E-8\**, *E-9\**, *E-10\**, *Z-8\**, *Z-9\**, and *Z-10\** (pictured in the SI Fig. S73–S75) were optimized at the PBE0-D3/def2-TZVPP level of theory. Selected bond metrics are provided in SI Tables S5 and S6.

Frequency calculations predict the enthalpy of formation of *E-8\** to be 2.96 kcal mol<sup>-1</sup> more favorable than that of *Z-8\**. Similarly, *E-9\** and *E-10\** are predicted to be more stable than *Z-9\** and *Z-10\** by 3.48 kcal mol<sup>-1</sup> and 3.83 kcal mol<sup>-1</sup>, respectively. Calculated gas-phase <sup>31</sup>P NMR spectroscopic data (PBE0-D4/pcseg-2//PBE0-D3/def2-TZVPP) found the <sup>1</sup>*J*<sub>PP</sub> coupling

constant for *E-8\** to be more consistent with our experimental value than that calculated for *Z-8\** (SI Table S21). Subsequent discussions are limited to the more stable theoretical *E*-isomers. The P–X bond stretching frequencies for *E-8\**, *E-9\**, and *E-10\** were calculated to be 481, 392, and 357 cm<sup>-1</sup>. The associated P–X stretching force constants are 2.10, 1.73, and 1.45 mdyne/Å, respectively, showing the weakening of the P–X bond from *E-8\** > *E-9\** > *E-10\**. The P–P bond stretching frequencies for *E-8\**, *E-9\**, and *E-10\** are 656, 653, and 649 cm<sup>-1</sup> and predicted to have negligible intensity.

A single point energy calculation at the DKH-PBE0/old-DKH-TZVPP level of theory was performed on the optimized coordinates of *E-8\**, *E-9\**, and *E-10\** for a detailed computational analysis (SI Tables S10–S17), and the summarized results are discussed. Topological analysis of the electron density ( $\rho$ )<sup>73</sup> of *E-8\**, *E-9\**, and *E-10\** along the P–P interatomic vector reveals bond critical points, at which  $\rho = 0.156$ , 0.155, and 0.154 e<sup>-</sup> Bohr<sup>-3</sup>, respectively (Fig. 5A). The negative Laplacian of  $\rho$  ( $\nabla^2\rho$ ) in the P–P valence region signifies significant charge concentration and covalency of the dipnictene bond of *E-8\**, *E-9\**, and *E-10\** (Fig. 5B).<sup>74</sup> We also calculate significant ellipticity of  $\rho$  ( $\epsilon$ )

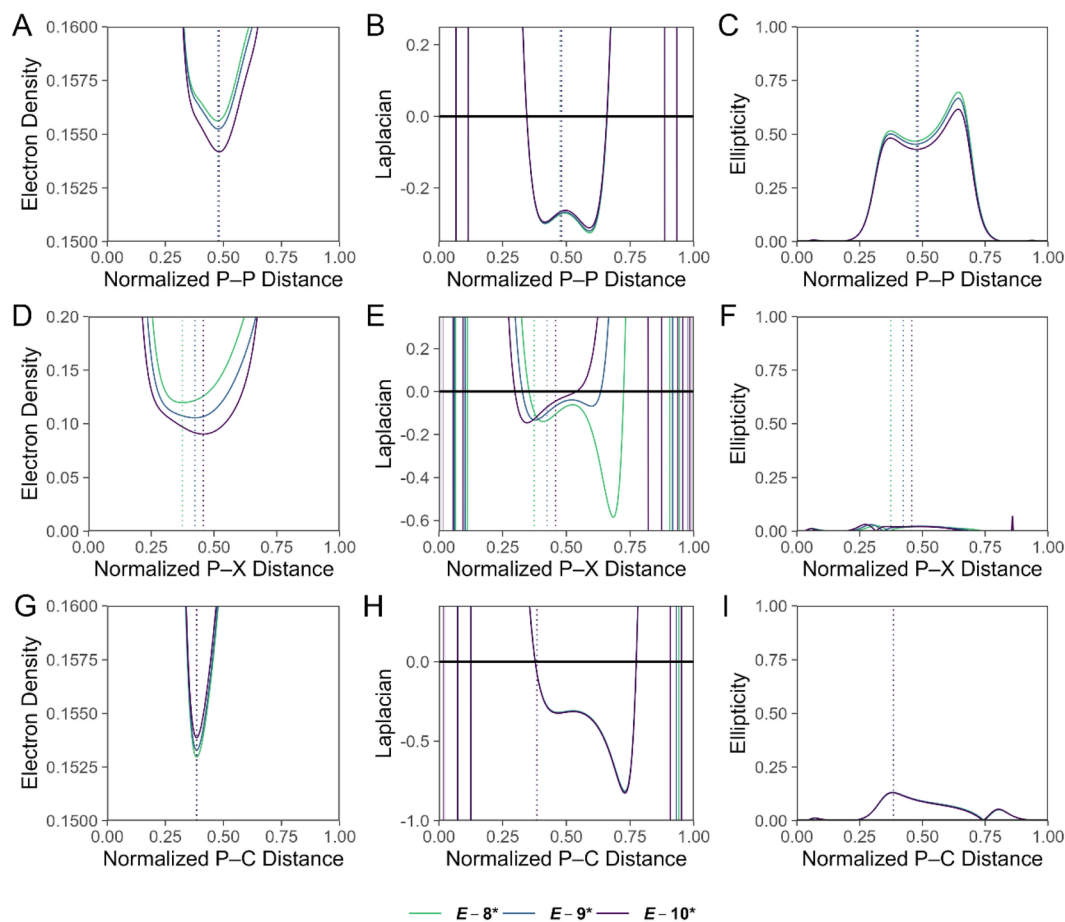


Fig. 5 Values of (A)  $\rho$  (e<sup>-</sup> Bohr<sup>-3</sup>), (B)  $\nabla^2\rho$  (e<sup>-</sup> Bohr<sup>-5</sup>), and (C)  $\epsilon$  for *E-8\**, *E-9\**, and *E-10\** along the P–P interatomic vector, with the C-bound P atom at 0.00 and the X-bound P atom (X = Cl, Br, I) at 1.00 along the horizontal axis. Values of (D)  $\rho$  (e<sup>-</sup> Bohr<sup>-3</sup>), (E)  $\nabla^2\rho$  (e<sup>-</sup> Bohr<sup>-5</sup>), and (F)  $\epsilon$  for *E-8\**, *E-9\**, and *E-10\** along the P–X (X = Cl, Br, I) interatomic vector. Values of (G)  $\rho$  (e<sup>-</sup> Bohr<sup>-3</sup>), (H)  $\nabla^2\rho$  (e<sup>-</sup> Bohr<sup>-5</sup>), and (I)  $\epsilon$  for *E-8\**, *E-9\**, and *E-10\** along the P–C interatomic vector. The bond lengths are normalized to 1.00. The location of the (3, -1) critical point is shown with a dashed vertical line. Calculations were performed at the (DKH-PBE0/old-DKH-TZVPP//PBE0-D3/TZVPP) level of theory.



in the P–P valence region, consistent with formal double bond character of the interaction (Fig. 5C). Along the P–X (X = Cl, Br, I) interatomic vector,  $\rho = 0.120, 0.106,$  and  $0.090 \text{ e}^- \text{ Bohr}^{-3}$  at the bond critical point for *E-8\**, *E-9\**, and *E-10\**, respectively, reflecting the weakening of the P–X bond from *E-8\** > *E-9\** > *E-10\** (Fig. 5D). The  $\nabla^2\rho$  function in the P–Cl bonding region in *E-8\** is highly asymmetric and signifies a polarization of charge towards the more electronegative Cl atom, reflecting the ionic character of the bond (Fig. 5E). For *E-9\** and *E-10\**, the  $\nabla^2\rho$  function in the P–X (Br, I) bonding region is dramatically less polarized (Fig. 5E). Topological analysis along the P–C bond path in *E-8\**, *E-9\**, and *E-10\** is reminiscent of that of the P–Cl bond in *E-8\**, but features higher values of  $\rho$  at the bond critical point, and values of the  $\nabla^2\rho$  function in the bonding region are less polarized and more negative, consistent with a stronger, more covalent bonding interaction (Fig. 5G and H). Values for  $\epsilon$  along the P–X (X = Cl, Br, I) and P–C bond paths in *E-8\**, *E-9\**, and *E-10\** are low, but not negligible and likely signify  $\pi$ -type donor–acceptor interactions (Fig. 5F and I).

The highest occupied molecular orbital (HOMO) of *E-8\** is highly delocalized and largely comprised of contribution by the P–P  $\pi$  bond and a Cl-centered lone pair (Fig. 6A). The lowest unoccupied molecular orbital (LUMO) of *E-8\** is largely defined

by P–P  $\pi^*$  contribution and the LUMO+2 of *E-8\** is largely defined by P–Cl  $\sigma^*$  contribution (Fig. 6B and C). Similar results were obtained for *E-9\** and *E-10\**; however, the LUMO+1 is largely comprised of the P–X  $\sigma^*$  (X = Br, I) contribution in these cases (SI Fig. S77–S82).

Energetic analysis of the canonical molecular orbitals (CMO) reveals the HOMO increases in energy from *E-8\** < *E-9\** < *E-10\** while the LUMO and LUMO+1 decrease in energy from *E-8\** > *E-9\** > *E-10\** (Fig. 7). These data are consistent with the weakening of the P–P and P–X (X = Cl, Br, I) bonds as the terminal halide becomes heavier. We performed a similar energetic analysis of the simple, theoretical diaryldiphosphene, *E*-MesP=PMes (*E-12\**), for comparison, and *E-12\** features a significantly lower LUMO than the theoretical arylhalodiphosphenes (Fig. 7).

Experimental ultraviolet-visible (UV-Vis) spectra of **8**·(Et<sub>2</sub>O)<sub>2</sub>, **9**·(Et<sub>2</sub>O)<sub>2</sub>, and **10**·(Et<sub>2</sub>O)<sub>2</sub> feature  $\lambda_{\text{max}}$  values of 349 nm, 355 nm, and 370 nm, respectively, reflecting the lowering of the LUMO from *E-8\** > *E-9\** > *E-10\**. Time-dependent density functional theory (TD-DFT) calculations suggest that the observed yellow color in these species is predicted to arise from electronic transitions between the HOMO–3/HOMO–2/HOMO–1/HOMO and the LUMO in each case (SI Tables S12–S14).



Fig. 6 (A) HOMO, (B) LUMO, and (C) LUMO+2 of *E-8\** (isovalue = 0.015). Surface plots (isovalue = 0.06) for *E-8\**, depicting the (D) P–P  $\pi$  bonding NLMO, (E) P–P  $\pi^*$  antibonding NLMO, (F) P–Cl  $\sigma^*$  antibonding NLMO, (G) a Cl-centered lone pair, (H) overlap between a Cl-centered lone pair and the P–P  $\pi^*$  antibonding NLMO, and (I) overlap between the P–C  $\sigma$  bonding NLMO and the P–Cl  $\sigma^*$  antibonding NLMO. In Fig. 6A–H, the molecule is viewed down the plane defined by the {PPCl} unit. In Fig. 6I, the molecule is oriented differently for clarity of the displayed NLMOs. Color code: P orange, Cl dark green, C black, H grey. Displayed NLMOs are pre-orthogonalized. Calculations were performed at the (DKH-PBE0/old-DKH-TZVPP//PBE0-D3/TZVPP) level of theory.



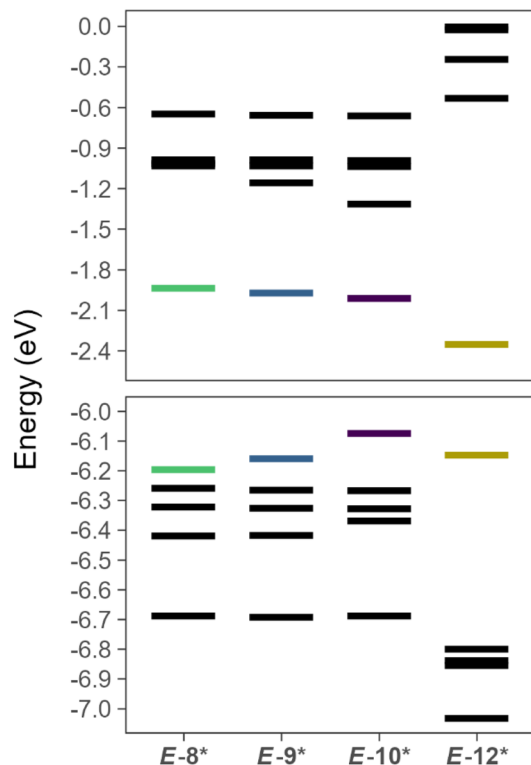


Fig. 7 Calculated orbital energies (DKH-PBE0/old-DKH-TZVPP//PBE0/def2-TZVPP) for *E-8\**, *E-9\**, *E-10\**, and *E-12\** with frontier molecular orbitals shown in color. The upper panel contains the values for the LUMO, LUMO+1, LUMO+2, LUMO+3, and LUMO+4. The lower panel contains values for the HOMO, HOMO-1, HOMO-2, HOMO-3, and HOMO-4.

Natural Population Analysis (NPA) reveals a systematic decrease in negative charge on the halide from *E-8\** > *E-9\** > *E-10\** (SI Fig. S84). Similarly, a decrease in positive charge is calculated for the X-bound P atom from *E-8\** > *E-9\** > *E-10\**. These results are consistent with a less polarized P-X bond as the halide increases in size. The theoretical asymmetric diphosphenes, *E-MesP=P*(<sup>t</sup>Bu) (*E-13\**), *E-MesP=P*(SiMe<sub>3</sub>) (*E-14\**), *E-MesP=P*(OMe) (*E-15\**), *E-MesP=P*(NMe<sub>2</sub>) (*E-16\**), [*E-MesP=P*(NMe<sub>3</sub>)]<sup>+</sup> (*E-17\**), and [*E-MesP=P*(PMe<sub>3</sub>)]<sup>+</sup> (*E-18\**) were investigated at the same level of theory to compare polarization of the P-P bond in arylhalodiphosphenes with other asymmetric diphosphenes (pictured in the SI Fig. S83). NPA analysis suggests that among the arylhalodiphosphenes, the P-P bond becomes increasingly polarized from *E-8\** < *E-9\** < *E-10\**, as the positive charge on the X-bound (X = Cl, Br, I) P atom decreases. The alkyl-substituted diphosphene, *E-13\** features a relatively unpolarized P-P bond, similar to *E-8\** and *E-9\**. However, the heteroatom-substituted aryldiphosphenes feature relatively large polarization of the P-P bond, which is more akin to *E-10\**, with the exception of the ammonium cation, *E-17\**.

Natural Localized Molecular Orbital (NLMO) analysis of *E-8\** reveals the presence of a P-P π NLMO and a P-P π\* NLMO, which closely resemble the nodal structure calculated for the HOMO and LUMO, respectively (Fig. 6D and E). The NLMO analysis further identified a P-Cl σ\* NLMO which resembles the

LUMO+2 and a filled Cl-centered 3p orbital, which appears prominently in both the HOMO and LUMO (Fig. 6F and G).

Intriguingly, second-order perturbation theory analysis of *E-8\**, *E-9\**, and *E-10\** reveals delocalization from an X-centered (X = Cl, Br, I) lone pair to the P-P π\* orbital to afford an energy of stabilization of 9.39, 7.82, and 6.30 kcal mol<sup>-1</sup>, respectively (Fig. 6H). Furthermore, delocalization of electron density from the P-C σ orbital and the lone pair of the C-bound P atom to the terminal P-X σ\* orbital (X = Cl, Br, I) afford a total energy of stabilization of 4.73, 4.92, and 4.53 kcal mol<sup>-1</sup> for *E-8\**, *E-9\**, and *E-10\**, respectively (Fig. 6I). In order to more broadly assess the relative strengths of the non-covalent donor-acceptor interactions present in *E-8\**, *E-9\**, and *E-10\**, we performed deletion calculations, in which all non-covalent interactions from the halide to the {P<sub>2</sub>} unit and *vice versa* were deleted. The removal of these non-covalent interactions resulted in the destabilization of *E-8\**, *E-9\**, and *E-10\** by 30.73, 25.73, and 19.96 kcal mol<sup>-1</sup>, respectively. The results of these deletion calculations are in line with the general trend that non-covalent interactions between the halide and the {P<sub>2</sub>} unit become less efficient from *E-8\** > *E-9\** > *E-10\**.

Natural Resonance Theory (NRT) analysis identified leading resonance structures featuring a P-P double bond and a polar, covalent P-X (X = Cl, Br, I) single bond for the simple theoretical molecules *E-MePPCl*, *E-MePPBr*, and *E-MePPI*, respectively (SI Tables S18-S20). The NRT analysis is consistent with increasing ionicity of the P-X bond from *E-MePPI* < *E-MePPBr* < *E-MePPCl*.

## Conclusions

In conclusion, we report the isolation of **8**·(Et<sub>2</sub>O)<sub>2</sub>, a thermally robust, monomeric arylhalodiphosphene. Compound **8** features a terminal {PPCl} unit and can thus be regarded as a 'masked' aryldiphosphadiazonium chloride, marking a significant advancement in the context of decades of diphosphene chemistry. The P-P bond of **8** could be cleaved *via* protonolysis by aqueous hydrobromic acid, and the synthetic utility of the P-Cl bond in **8** was demonstrated in halogen-exchange reactions with TMSBr and TMSI to form the monomeric arylhalodiphosphenes, **9** and **10**, respectively. Treatment of **8** with GaCl<sub>3</sub> or AlCl<sub>3</sub> resulted in rapid decomposition to form complex reaction mixtures. However, **8** participates in coordination chemistry that is typical of diphosphenes; treatment of **8** with AgCF<sub>3</sub>SO<sub>3</sub> forms, **11**. In **8**, **9**, **10**, and **11**, SC-XRD experiments clearly identified the presence of both the *E* and the *Z* isomer with respect to the diphosphene motif in solid state. Our theoretical investigation elucidated trends in bonding amongst the theoretical arylhalodiphosphenes *E-8\**, *E-9\**, and *E-10\**. Notably, the HOMO increases in energy, the LUMO and LUMO+1 decrease in energy, and the P-X (X = Cl, Br, I) bond weakens as the terminal halide increases in size. Further investigations into the reactivity of monomeric arylhalodiphosphenes are currently underway, as are efforts to isolate a genuine diphosphadiazonium salt.

## Author contributions

J. S. W.: conceptualization, data curation, funding acquisition, investigation (chemical synthesis, data acquisition, X-ray



crystallography, DFT methods), methodology, visualization, writing – original draft, writing – review and editing. N. G.: investigation (chemical synthesis). W. J. R.: investigation (chemical synthesis). A. E. C.: investigation (X-ray crystallography). B. v. I.: investigation (acquisition of VT-NMR data). M. M.: conceptualization, funding acquisition, project administration, resources, supervision, writing – review and editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

CCDC 2501235–2501241, 2512823, 2512824, and 2523752 contain the supplementary crystallographic data for this paper.<sup>75a–j</sup>

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d6sc00723f>.

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