

# Chemical Science

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: J. Fidelius, C. Taube, K. Schwedtmann, F. Hennersdorf, R. M. Gomila, A. Frontera, R. Wolf and J. J. Weigand, *Chem. Sci.*, 2026, DOI: 10.1039/D6SC02577C.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

## ARTICLE

## Imidazoliumyl-Substituted Di- and Iso-Tetraphosphanes and Their Metal-Mediated Fragmentation Reactions

Jannis Fidelius,<sup>a†</sup> Clemens Taube,<sup>a†</sup> Kai Schwedtman,<sup>a</sup> Felix Hennersdorf,<sup>a</sup> Rosa M. Gomila,<sup>c</sup> Antonio Frontera,<sup>c</sup> Robert Wolf,<sup>\*b</sup> and Jan J. Weigand<sup>\*,a</sup>Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Monocationic imidazoliumyl-substituted phosphanes,  $L_cP(R)Cl^+$  ( $L_c=1,3$ -diisopropyl-4,5-dimethylimidazol-2-yl), were synthesized as their respective triflate salts **2a-c**[OTf] (a: R = Cy; b: R = Ph; c: R = Py). These serve as versatile building blocks for the formation of the corresponding imidazoliumyl-substituted diphosphanes ( $(L_cPR)_2$  **5a-c**[OTf]<sub>2</sub>) and *iso*-tetraphosphanes ( $(L_cPR)_3P$ [OTf]<sub>3</sub> **6a,b**[OTf]<sub>3</sub>). The introduction of a cationic (onio) substituent substantially alters the preferred reaction pathways of the P-scaffolds compared to their neutral congeners and electronically predisposes selected P–P bonds toward fragmentation. DFT calculations reveal a strong localization of the LUMO orbitals on the P–P bond, indicating susceptibility to nucleophilic attack. Both **5a,b**[OTf]<sub>2</sub> and **6a**[OTf]<sub>3</sub> undergo metal-mediated fragmentation reactions. Reactions of **5a,b**[OTf]<sub>2</sub> with Pd(PPh<sub>3</sub>)<sub>4</sub> afford two distinct dinuclear complexes, while reactions of **6a**[OTf]<sub>3</sub> with metal chlorides yield triphosphanide complexes ( $(L_cPCy)_2PM$ [OTf]<sub>2</sub> (**9**[OTf]<sub>2</sub>; M = Pd(allyl), **10**[OTf]<sub>2</sub>; M = Au(PPh<sub>3</sub>), accompanied by the formation of **2a**[OTf]. Treatment of **6a**[OTf]<sub>3</sub> with the NHC IPr (1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) provides the free triphosphanide ligand  $(L_cPCy)_2P$ [OTf] (**11**[OTf]).

## Introduction

The importance of tertiary phosphanes ( $R_3P$ ) as ligands in organometallic chemistry, both in fundamental research and in industry, cannot be overstated. In particular, the facile fine-tuning of steric and electronic properties of the P atom through alteration of the substituents has led to the development of neutral and, more recently, cationic (onio)-substituted phosphorus ligand systems.<sup>1,2</sup> Similarly, neutral diphosphanes of type  $R_4P_2$  (R = alkyl, aryl) are potent ligands for mono- and bimetallic complexes,<sup>3,4</sup> comprising various coordination modes while typically preserving the central P–P bond (Figure 1, I).<sup>5</sup> In contrast, despite several synthetic approaches, the coordination chemistry of related triphosphanes  $R_5P_3$  remains far less explored and is mainly limited to transition metal carbonyls (Figure 1, II).<sup>6</sup> The limited availability of *iso*-tetraphosphanes  $R_6P_4$ <sup>7,8,9,10,11</sup> is mainly attributed to scrambling reactions<sup>8,11</sup> which hinder the syntheses of larger catenated and branched structures compared to their cyclic derivatives.

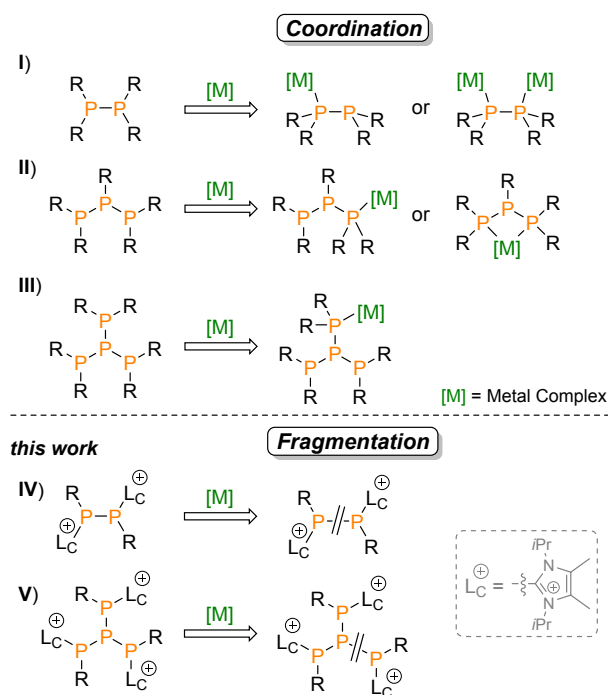


Figure 1. Coordination behaviour of neutral branched and catenated oligophosphanes (top) and fragmentation reactions of cationic derivatives (bottom); ( $L_c=1,3$ -diisopropyl-4,5-dimethylimidazole-2-yl).

As a result, there is a notable lack of detailed studies on the reactivity of these systems towards transition metals. To the best of our knowledge, only one iron carbonyl complex has been structurally characterized (Figure 1, III).<sup>11</sup>

<sup>a</sup> Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany; E-mail: jan.weigand@tu-dresden.de

<sup>b</sup> Institute of Inorganic Chemistry, Universität Regensburg, 93040 Regensburg, Germany

<sup>c</sup> Department of Chemistry, Universitat de Illes Balears, 07122 Palma de Mallorca, Spain

† These authors contributed equally to this work.

Electronic Supplementary Information (ESI) available. CCDC 2524560 - 2524572. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

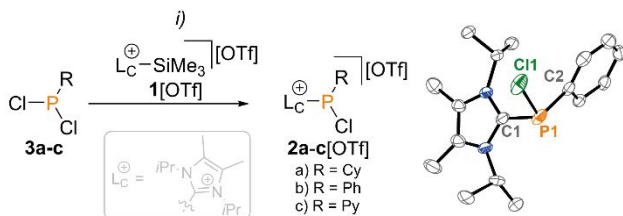


Beyond neutral oligophosphanes, the coordination chemistry of phosphorus-centered cations has garnered considerable interest over the last decade.<sup>12</sup> Recently, we reported the synthesis of various cationic polyphosphanes that exhibit metal-dependent coordination and insertion reactions.<sup>13,14</sup> Key to the formation of stable cationic oligophosphanes is the introduction of imidazoliumyl substituents, which enables precise electronic tuning of the attached phosphorus atoms,<sup>2,15</sup> allowing for the stabilization of a wide range of phosphorus bonding motifs.<sup>16,17</sup> Our access to imidazoliumyl-substituted chlorophosphane salts of the type  $L_cP(R)Cl[OTf]^{17}$  motivated us to explore their potential in constructing imidazoliumyl-substituted oligophosphanes. Building on this platform, we now report the synthesis of cationic diphosphanes and *iso*-tetraphosphanes via controlled coupling of  $L_cP(R)Cl^+$  precursors. Using these chlorophosphanes as a starting point, we highlight in this contribution the generation of the symmetric diphosphanes ( $(L_cPR)_2[OTf]_2$ , **Figure 1, IV**) and *iso*-tetraphosphanes ( $(L_cPR)_3P[OTf]_3$ , **Figure 1, V**). Notably, this is the first report of a successful synthesis of branched oligophosphanes featuring cationic substituents. These substituents substantially alter the preferred reaction pathways of these phosphanes and electronically predispose selected P–P bonds toward fragmentation, leading to distinct products upon reaction with transition metal compounds or nucleophiles. In contrast to literature reports on di- and *iso*-tetraphosphanes, the synthesized compounds do not exhibit classical coordination to transition metals via the free electron pairs on the phosphorus atoms (cf. **Figure 1, I and III**), but rather engage in selective P–P bond cleavage reactions.

## Results and discussion

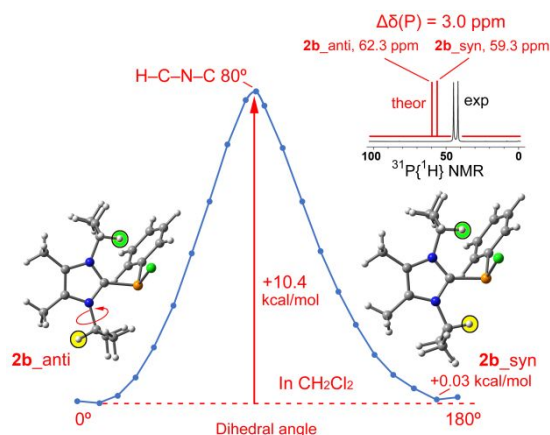
### Syntheses and Characterizations of Imidazoliumyl-Substituted Chlorophosphanes, Diphosphanes, and Iso-Tetraphosphanes.

Our established protocol of using  $L_c-SiMe_3[OTf]$  **1**[OTf] as an “onio-transfer” reagent provides access to chlorophosphane salts **2a-c**[OTf] containing cationic imidazoliumyl substituents.<sup>17,18</sup> Accordingly, treatment of **1**[OTf] with a slight excess of the dichlorophosphane **3a-c** affords **2a-c**[OTf] in excellent to quantitative yield (**Scheme 1**).



**Scheme 1.** Synthesis of imidazoliumyl-substituted chlorophosphanes **2a-c**[OTf] and the molecular structure of **2b**[OTf]· $C_6H_5F$  (hydrogen atoms, solvate molecule, and anion are omitted for clarity, and ellipsoids are displayed at 50% probability). Selected bond lengths [Å] and angles [°]: C1-P1 1.827(3), P1-C2 1.822(2), P1-Cl1 2.0638(8), C1-P1-C2 100.78(9), C1-P1-Cl1 98.86(7), C2-P1-Cl1 102.83(7). i) **2a**[OTf] (R = Cy):  $C_6H_5F$ , 70°C, 3 d, 74%; **2b**[OTf] (R = Ph):  $C_6H_5F$ , 90°C, 16 h, 74%; **2c**[OTf] (R = Py):  $C_6H_5F$ , 70°C, 3 h, 99%<sup>18</sup>.

The  $^{31}P\{^1H\}$  NMR spectra of **2a-c**[OTf] each show a single, broad resonance (**2a**[OTf]:  $\delta(P) = 55.6$  ppm; **2b**[OTf]:  $\delta(P) = 48.8$  ppm; **2c**[OTf]:  $\delta(P) = 24.0$  ppm), which are significantly upfield-shifted compared to **3a-c**. The resonance of **2c**[OTf] is downfield-shifted compared to **2b**[OTf] due to the mesomeric effect of the pyridyl substituent. Upon cooling to 250 K, the resonances of **2a-c**[OTf] each resolve into two singlet resonances. This is attributed to the presence of two rotamers, which originate from hindered rotation of the *i*Pr-groups at the imidazoliumyl substituent. This assumption is supported by the observation of a splitting of the resonances of the *i*Pr-groups in the  $^1H$ -NMR spectra at low temperatures and by a disordered *i*Pr-group in the molecular structure of **2b**[OTf] (see SI, section 2.1.2).

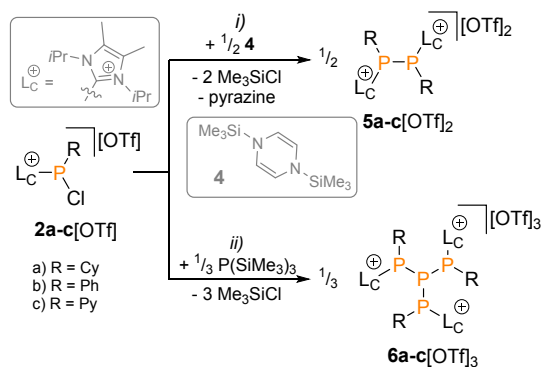


**Figure 2.** Energy profile of the rotation of the lower *iso*-propyl substituent along the C–N bond in **2b**[OTf], with a comparison between calculated and experimental  $^{31}P\{^1H\}$ -NMR spectra of **2b**[OTf] in  $CD_2Cl_2$  (top right insert).

To better understand this behaviour, a conformer search for **2b**<sup>+</sup> was conducted using the Conformer-Rotamer Ensemble Sampling Tool (CREST; see **Figure 2**).<sup>19</sup> After geometry optimization (BP86-D4/def2-TZVP), two isoenergetic isomers were identified. The calculated rotational barrier in  $CH_2Cl_2$  was 10.4 kcal/mol, which agrees well with the NMR-derived barrier (12.3 kcal/mol) at the coalescence temperature. The calculated chemical shift difference  $\Delta\delta(P)$  is 3.0 ppm, which is also consistent with the experimental data ( $\Delta\delta(P_{exp}) = 3.1$  ppm). Both computationally disclosed conformers were also observed in the molecular structure of **2b**<sup>+</sup> in the form of a disordered isopropyl group (see **Scheme 1** and **Figure S2**). As expected, the molecular structures (**2a,c**[OTf]: See SI) show the pyramidal bonding environment at the phosphorus atom, with typical P–Cl bond lengths ranging from 2.064(8) Å to 2.0770(13) Å, and P–C bonds which are comparable to those in known imidazoliumyl-substituted phosphanes.<sup>17</sup>

With larger quantities of **2a-c**[OTf] in hand, we explored the reduction reactions using 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (**4**), a reagent previously shown to be effective for reductive P–P bond formation.<sup>14,20</sup> The 2:1 reaction of **2a-c**[OTf] in  $C_6H_5F$  produced colourless or yellow precipitates over 16 h. After filtration and subsequent drying under vacuum, diphosphane salts **5a-c**[OTf]<sub>2</sub> were isolated in good yields (**5a**[OTf]<sub>2</sub>: 63%; **5b**[OTf]<sub>2</sub>: 78%; **5c**[OTf]<sub>2</sub>: 87%; **Scheme 2**).



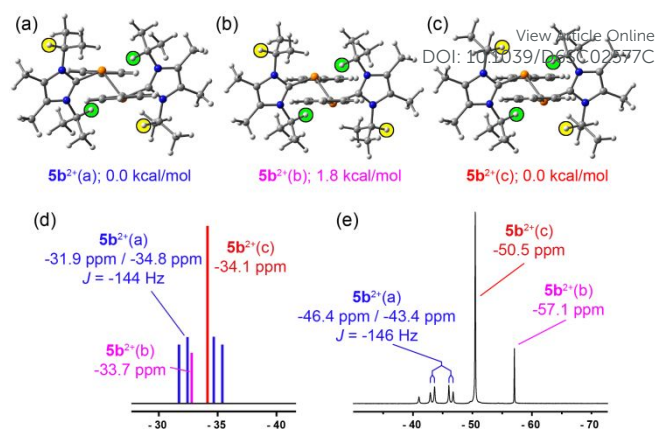


At ambient temperature, the <sup>31</sup>P{<sup>1</sup>H}-NMR spectra show a single broad resonance in each case (**5a[OTf]<sub>2</sub>**: δ(P) = −50.0 to −38.4 ppm; **5b[OTf]<sub>2</sub>**: δ(P) = −47.9 ppm; **5c[OTf]<sub>2</sub>**: δ(P) = −43.0 ppm). The signals are upfield-shifted compared to related neutral diphosphanes (e.g. Cy<sub>2</sub>P−PCy<sub>2</sub>: δ(P) = −21.0 ppm; Ph<sub>2</sub>P−PPh<sub>2</sub>: δ(P) = −14.6 ppm).<sup>21</sup> Upon cooling to 250 K, the broad resonances resolve into singlet resonances (**5b[OTf]<sub>2</sub>**: δ(P) = −57.1 ppm, δ(P) = −50.5 ppm, δ(P) = −41.0 ppm) and an AB spin system (**5b[OTf]<sub>2</sub>**: δ(P<sub>A</sub>) = −46.4 ppm, δ(P<sub>B</sub>) = −43.3 ppm, <sup>1</sup>J(PP) = −146 Hz; **Figure 3e**). This is attributed to the presence of three conformers, arising from hindered rotation around the N−C bond of the *i*Pr groups.

A conformational analysis using CREST was performed on compound **5b<sup>2+</sup>**. The analysis identified three isomers with comparable energies. **Figure 3a-c** presents the optimized geometries and relative energies, alongside the predicted <sup>31</sup>P{<sup>1</sup>H}-NMR spectra for these isomers. Two of the isomers are centrosymmetric, leading to an anticipated singlet resonance in the <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum (labelled as **5b<sup>2+</sup>(b)** and **5b<sup>2+</sup>(c)**; in **Figure 3b,c**). The third isomer, denoted as **5b<sup>2+</sup>(a)**, lacks symmetry and is expected to display an AB spin system in <sup>31</sup>P{<sup>1</sup>H}-NMR (**Figure 3d,e**). These three isomers arise from rotation of the *i*Pr groups marked in yellow in **Figure 3a-c**. In contrast, the rotation of the green-marked groups leads to significantly higher-energy rotamers, resulting in diminished population. The predicted <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum for this isomer mixture is shown in **Figure 3d**. The calculated spectrum aligns with the experimental spectra. The close match of the expected coupling constant for **5b<sup>2+</sup>(a)**; −144 Hz) and the experimental value (−146 Hz) strongly supports the presence of this non-symmetric rotamer in solution.

The molecular structure of **5c[OTf]<sub>2</sub>** evidenced disordered isopropyl groups, confirming the presence of the computationally predicted conformers (see **Figure S8**). The crystal structures of **5a-c[OTf]<sub>2</sub>** show an *anti*-conformation along the P−P bond (**5b[OTf]<sub>2</sub>**: **Figure 4**; **5a,c[OTf]<sub>2</sub>**: see SI, section 2.2.1 and 2.2.3). The P−P bond lengths range from 2.2315(17) Å to 2.2581(7) Å, in line with P−P single bonds in neutral diphosphanes (Cy<sub>2</sub>P−PCy<sub>2</sub> 2.21 Å; Ph<sub>2</sub>P−PPh<sub>2</sub> 2.22 Å).<sup>21,22</sup>

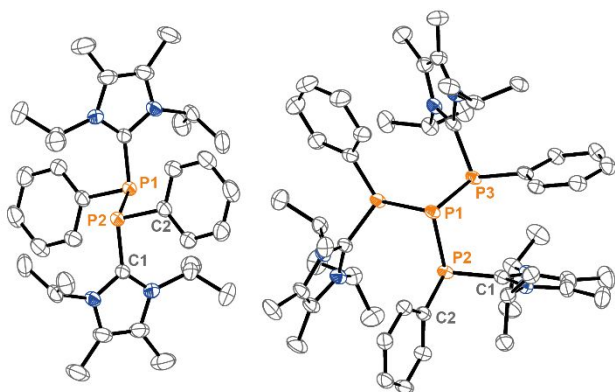
The molecular structure of **5c[OTf]<sub>2</sub>** evidenced disordered isopropyl groups, confirming the presence of the computationally predicted conformers (see **Figure S8**). The crystal structures of **5a-c[OTf]<sub>2</sub>** show an *anti*-conformation along the P−P bond (**5b[OTf]<sub>2</sub>**: **Figure 4**; **5a,c[OTf]<sub>2</sub>**: see SI, section 2.2.1 and 2.2.3). The P−P bond lengths range from 2.2315(17) Å to 2.2581(7) Å, in line with P−P single bonds in neutral diphosphanes (Cy<sub>2</sub>P−PCy<sub>2</sub> 2.21 Å; Ph<sub>2</sub>P−PPh<sub>2</sub> 2.22 Å).<sup>21,22</sup>



**Figure 3.** (a-c): Conformers of **5b<sup>2+</sup>** through rotation of the N−C bond of the *i*Pr-groups obtained from conformer search and geometry optimization; (d) computationally obtained <sup>31</sup>P-NMR spectrum of the isomer mixture of **5b<sup>2+</sup>**; (e): <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum of **5b[OTf]<sub>2</sub>** in CD<sub>2</sub>Cl<sub>2</sub> at 250 K.

Aiming at the construction of larger oligophosphorus scaffolds, we treated the chlorophosphanes **2a-c[OTf]** with an excess of P(SiMe<sub>3</sub>)<sub>3</sub> in C<sub>6</sub>H<sub>5</sub>F. The reaction leads to the formation of colourless precipitates over the course of 1 to 3 days, which, after filtration, could be identified as the desired tricationic *iso*-tetraphosphane salts **6a,b[OTf]<sub>3</sub>** (see **Scheme 2**). **6a,b[OTf]<sub>3</sub>** were isolated in 76 % and 81 %, respectively. In contrast, the pyridyl-substituted derivative **6c[OTf]<sub>3</sub>** was found to decompose in solution, preventing its isolation. **6a,b[OTf]<sub>3</sub>** show AX<sub>3</sub>-type spin systems in the <sup>31</sup>P{<sup>1</sup>H}-NMR spectra (AX<sub>3</sub> spin system: **6a[OTf]<sub>3</sub>** δ(P<sub>A</sub>) = −87.4 ppm, δ(P<sub>X</sub>) = −57.7 ppm, <sup>1</sup>J(PP) = −271 Hz; **6b[OTf]<sub>3</sub>** δ(P<sub>A</sub>) = −47.9 ppm, δ(P<sub>X</sub>) = −41.8 ppm, <sup>1</sup>J(PP) = −130 Hz). **6a<sup>3+</sup>** additionally shows dynamic behaviour at ambient temperature. The observed additional broad resonances resolve into an AX<sub>3</sub> pattern at 240 K (δ(P<sub>A</sub>) = −84.0 ppm, δ(P<sub>X</sub>) = −41.5 ppm, <sup>1</sup>J(PP) = −296 Hz), which is attributed to a similar rotational behaviour of its isopropyl groups, as described above for **2a-c[OTf]**. Additional resonances at ca. −23 ppm are assigned to an unknown isomer formed by an exchange process, which could be monitored via <sup>31</sup>P-<sup>31</sup>P EXSY NMR spectroscopy (see SI, section 2.3.4). The resonances of **6b[OTf]<sub>3</sub>** exhibit second-order effects, as documented for related systems.<sup>7,11</sup> Compared to the neutral *iso*-tetraphosphane (Cy<sub>2</sub>P)<sub>3</sub>P (AX<sub>3</sub>: δ(P<sub>A</sub>) = −108.9 ppm, δ(P<sub>X</sub>) = −5.2 ppm; <sup>1</sup>J(PP) = −361.9 Hz), the cationic analogues **6a,b[OTf]<sub>3</sub>** exhibit upfield shifted P<sub>X</sub> resonances. Additionally, significantly smaller |<sup>1</sup>J(PP)| values are observed for the phenyl-substituted species **6b<sup>3+</sup>** compared to the cyclohexyl-substituted derivative **6a<sup>3+</sup>**. This is attributed to the smaller steric volume of the phenyl substituent. Less steric congestion results in a diminished spatial overlap of the lone pairs on the outer phosphorus atoms, thereby reducing the electronic coupling between the central and terminal phosphorus atoms in **6b<sup>3+</sup>**.<sup>23</sup>





**Figure 4.** Molecular structure cations **5b**<sup>2+</sup> in **5b**[OTf]<sub>2</sub> (left) and **6b**<sup>3+</sup> in **6b**[OTf]<sub>3</sub>·4 CH<sub>2</sub>Cl<sub>2</sub> (right; one of two independent molecules of the asymmetric unit shown). Hydrogen atoms, solvate molecules, and anions are omitted for clarity; ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: **5b**<sup>2+</sup>: P1–C1 1.8256(15), P1–P1 2.2581(7), P1–C2 1.8312(15), C1–P1–P1 98.57(5); **6b**<sup>3+</sup>: P2–C1 1.835(3), P1–P2 2.255(8), P2–C2 1.825(2), P1–P2–C1 101.91(8), P1–P2–C2 107.62(8), P2–P1–P3 89.35(3).

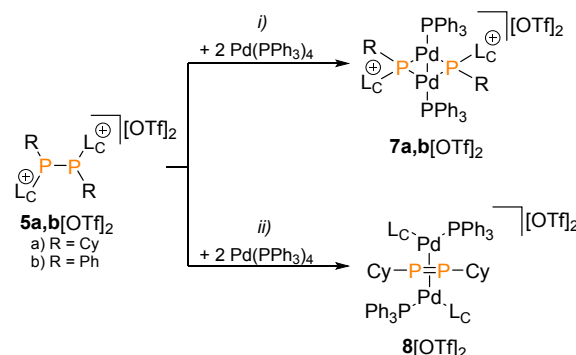
Suitable crystals for X-ray diffraction analysis could be obtained by diffusion of Et<sub>2</sub>O into a saturated CH<sub>3</sub>CN (**6a**[OTf]<sub>3</sub>) or CH<sub>2</sub>Cl<sub>2</sub> (**6b**[OTf]<sub>3</sub>) solution at –30°C. The crystal structure of **6b**[OTf]<sub>3</sub> (**Figure 4**) confirms the expected pyramidal coordination geometry at the central phosphorus atom. Due to the presence of two different substituents at the terminal phosphorus atoms, the cations **6a**<sup>3+</sup> and **6b**<sup>3+</sup> are chiral. The *rac*-diastereomer is observed in the single-crystal X-ray structure, with both enantiomers present in the unit cell. The P–P bond lengths (2.2315(17) Å to 2.2596(7) Å) are slightly elongated compared to neutral *iso*-tetraphosphanes.<sup>10,11</sup> In **6a**<sup>3+</sup>, the imidazoliumyl-substituent and the lone pair of electron pair at the central phosphorus atom adopt an *eclipsed* arrangement. In contrast, cation **6b**<sup>3+</sup> exhibits a staggered conformation along the same axis, wherein the lone pairs on P1 and P2 are arranged in an antiperiplanar fashion.

#### Reactivity of Imidazoliumyl-substituted Diphosphanes **5a,b**[OTf]<sub>2</sub> towards Pd(PPh<sub>3</sub>)<sub>4</sub>

The presence of two lone pairs in the dicationic diphosphanes **5a-c**[OTf]<sub>2</sub> motivated us to explore the coordination chemistry of these compounds towards selected transition metal complexes. Addition of a solution of Pd(PPh<sub>3</sub>)<sub>4</sub> to **5b**[OTf]<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> resulted in an immediate colour change to deep purple. Precipitation and washing of the obtained solid led to the isolation of the Pd-complex **7b**[OTf]<sub>2</sub> in 63 % yield as a deep purple solid (see **Scheme 3**). For the analogous reaction of **5a**[OTf]<sub>2</sub>, elevated temperatures of 120°C and a prolonged reaction time were required. We attribute this to the increased steric bulk of the cyclohexyl substituents, which likely hampers Pd insertion into the P–P bond of **5a**<sup>2+</sup>. Using this procedure, **7a,b**[OTf]<sub>2</sub> was isolated in 30 % yield. It seems likely that **7a,b**[OTf]<sub>2</sub> are formed an oxidative insertion of two Pd atoms into the P–P bond of the diphosphane with concomitant release of six equivalents of PPh<sub>3</sub>.

The Pd atoms in **7a,b**[OTf]<sub>2</sub> are in the formal oxidation state +I. The structural data indicate a Pd–Pd interaction (**7b**<sup>2+</sup>: Pd–Pd 2.584(19) Å). In the <sup>31</sup>P{<sup>1</sup>H}-NMR spectra, the complexes show

two sets of A<sub>2</sub>X<sub>2</sub> spin systems (**7b**[OTf]<sub>2</sub>: δ(P<sub>A</sub>) = 24.5 ppm, δ(P<sub>X</sub>) = 105.33 ppm, <sup>2</sup>J(AX) = 44 Hz; δ(P<sub>A</sub>) = 25.9 ppm, δ(P<sub>X</sub>) = 111.5 ppm, <sup>2</sup>J(AX) = 41 Hz; for **7a**[OTf]<sub>2</sub>, see SI section 2.4), attributed to the *rac* and *meso* stereoisomers resulting from the different orientation of the imidazoliumyl-substituents. The P<sub>A</sub> resonances show the typical chemical shift of PPh<sub>3</sub> ligands at palladium. The P<sub>X</sub> resonances of the bridging phosphanide moieties show a substantial downfield shift compared to chemical shifts of related imidazoliumyl-substituted phosphanides,<sup>15</sup> including bridging phosphanides in three-membered metallacycles.<sup>24</sup> In the case of **7b**[OTf]<sub>2</sub>, the isomer with the more downfield-shifted P<sub>X</sub> resonances is the major isomer (84/16), whereas **7a**[OTf]<sub>2</sub> shows an inverted ratio (10/90). Interestingly, in both cases, no interconversion between isomers was observed, even at elevated temperatures or in highly polar solvents. Although these conditions typically promote isomerization in phosphorus-metal complexes, this does not seem to occur with **7a**[OTf]<sub>2</sub>.<sup>25</sup>



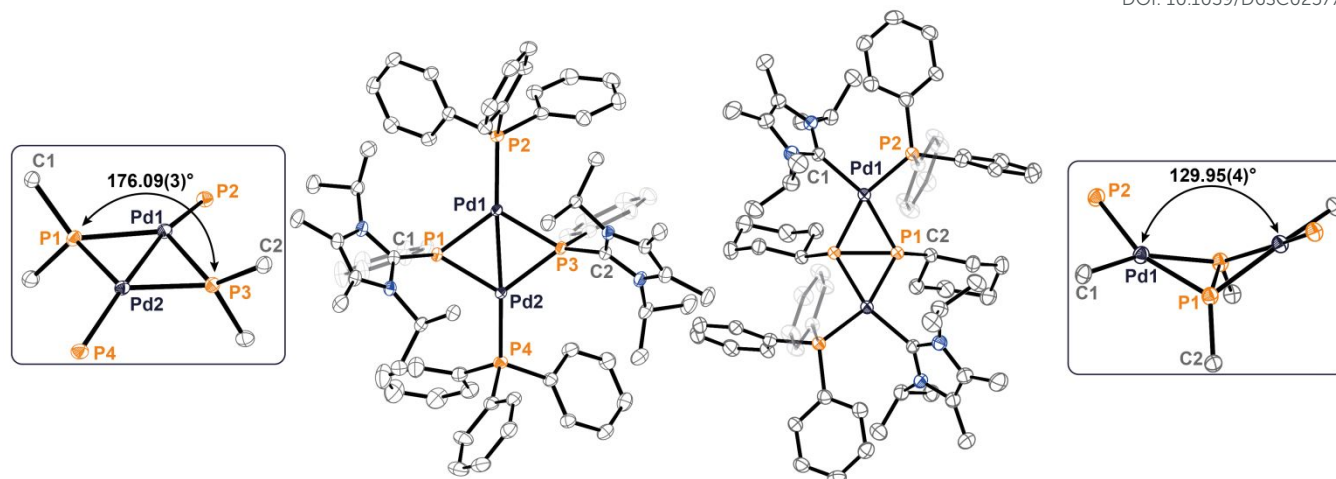
**Scheme 3.** Synthesis of complexes **7a,b**[OTf]<sub>2</sub> and diphosphene complex **8**[OTf]<sub>2</sub> (a: R = Cy; b: R = Ph); i) **7a**[OTf]<sub>2</sub>: toluene, 120°C, 2 d, 30%; **7b**[OTf]<sub>2</sub>: CH<sub>2</sub>Cl<sub>2</sub>, rt, 16 h, 63%; ii) **8**[OTf]<sub>2</sub>: C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>, 40°C, 14d, 54%.

Suitable crystals for X-ray diffraction analysis could be obtained by diffusion of *n*-pentane into a saturated CH<sub>2</sub>Cl<sub>2</sub> solution at –30°C. The molecular structure of the *meso* isomer of **7b**[OTf]<sub>2</sub> is depicted in **Figure 5**. In the bicyclic P<sub>2</sub>Pd<sub>2</sub> core, the two imidazoliumyl-substituted phosphanide units bridge the palladium atoms, which are connected through a short Pd–Pd contact (2.584(19) Å), indicating metal-metal interaction as known from related compounds.<sup>26</sup> Additionally, one remaining PPh<sub>3</sub> ligand is coordinated each of the Pd-atoms.

Although the Pd–Pd bond length is comparably short,<sup>27</sup> the calculated Wiberg Bond Index (WBI) is fairly low (0.24), indicating only a weak interaction of the two palladium atoms (see ESI Section 3.2).

During our attempts to isolate pure **7b**[OTf]<sub>2</sub>, we observed the formation of a side-product at elevated temperatures. <sup>31</sup>P-NMR investigations of the reaction mixture of **5a**[OTf]<sub>2</sub> with Pd(PPh<sub>3</sub>)<sub>4</sub> stirred at 80 °C indicate the formation of dinuclear μ<sub>2</sub>(η<sup>2</sup>:η<sup>2</sup>)-diphosphene complex **8**[OTf]<sub>2</sub>.





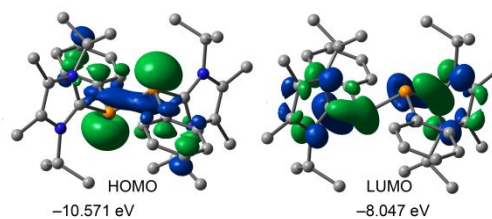
**Figure 5.** Molecular structures of cations  $7b^{2+}$  in  $7b[OTf]_2 \cdot 4 CH_2Cl_2$  (left) and  $8^{2+}$  in  $8[OTf]_2 \cdot 2 C_6H_4F_2 \cdot Et_2O$  (right); insets show detailed coordination environment. Hydrogen atoms, solvate molecules, and anions are omitted for clarity. Ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]:  $7b^{2+}$ : Pd–Pd 2.584(19), P1–C1 1.840(3), P3–C3 1.834(3), P2–Pd1 2.3011(6), P4–Pd2 2.2988(6), Pd1–P1–Pd2 67.78(18), Pd1–P3–Pd2 67.80(18);  $8^{2+}$ : P1–P1 2.1160(12), P2–Pd 2.3213(6), C1–Pd 2.061(2), Pd–Pd 3.8007(8), P1–Pd–P1 53.54(4), P–Pd–P plane fold angle 129.95(4).

The complex is a structural isomer of  $7b[OTf]_2$  and is formed by oxidative addition of the P–C bond of the imidazoliumyl substituent to Pd, rather than the P–P bond. Such P–C activation is rare and typically occurs only as a side reaction with phosphane ligands in organometallic chemistry.<sup>28</sup>

A selective synthesis of  $8[OTf]_2$  was achieved by stirring the reaction mixture of  $5a[OTf]_2$  with two equivalents of  $Pd(PPh_3)_4$  at 40°C for 14 days in *ortho*- $C_6H_4F_2$ . The  $^{31}P$ -NMR spectrum of  $8[OTf]_2$  shows broad resonances at  $\delta(P_A) = -11.7$  ppm and  $\delta(P_X) = 18.2$  ppm, which resolve at higher temperatures to an AA'XX' spin system (fitted iteratively; see SI, section 2.4.3). The resonance of the diphosphene moiety ( $P_A$ ) is shifted downfield compared to the related molybdenum complex  $[(Cp)_2Mo_2(CO)_4(PPh_2)_2]$  ( $\delta(P) = -94$  ppm)<sup>29,30</sup> and the large  $^1J(PP)$  coupling constant of  $-489$  Hz is typical for diphosphene complexes.<sup>31</sup> In the  $^{31}P$ -NMR spectrum, a minor isomer is observed, which is presumed to be the corresponding *meso* isomer.

Single crystals of  $8[OTf]_2$  suitable for X-ray analysis were obtained by slow diffusion of  $Et_2O$  into a saturated *ortho*- $C_6H_4F_2$  solution at  $-30^\circ C$  (see **Figure 5**). The molecular structure revealed the *rac* isomer, with a central *cis*-substituted diphosphene coordinated to two palladium atoms in  $\eta^2$  mode. The palladium atoms are additionally coordinated by one  $L_c$  ligand and one  $PPh_3$  ligand. The P–P bond length of 2.1160(12) Å is in the expected range for diphosphene complexes.<sup>31</sup> The central four-membered  $Pd_2P_2$  ring is puckered, adopting a “butterfly” conformation (fold angle between the P–Pd–P planes = 129.95(4)°; **Figure 5**). The Pd–C bond (2.061(2) Å) aligns well with those in known *N*-heterocyclic carbene palladium complexes.<sup>32</sup> Only a few related complexes have been reported, which feature a similar diphosphene ligand bridging two transition-metal atoms, such as Fe, Mo and Ta.<sup>29,30,33,34</sup> The Pd–Pd distance of 3.8007(8) Å is significantly larger than the sum of

the van der Waals radii (3.26 Å),<sup>35</sup> indicating that there is no significant Pd...Pd interaction in  $8^{2+}$ .



**Figure 6.** Frontier molecular orbitals of  $5b^{2+}$ , resembling the high antibonding character of the LUMO.

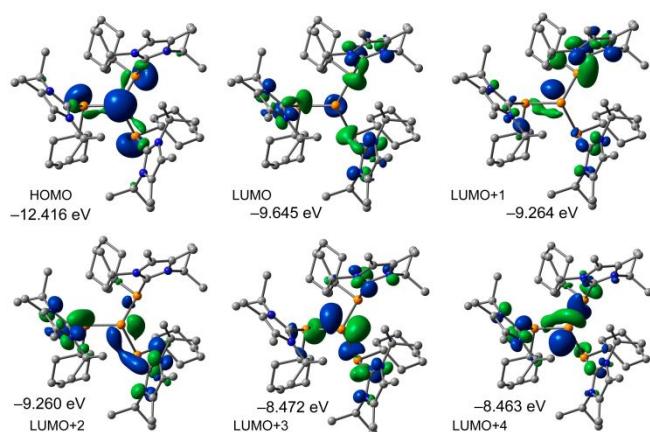
It is noteworthy that the formation of  $8[OTf]_2$  from  $5b[OTf]_2$  is highly selective. The mechanism likely involves a nucleophilic attack by a Pd atom on  $5b^{2+}$ , which ultimately results in the cleavage of two P–P bonds. The DFT-calculated frontier molecular orbitals of  $5b^{2+}$  (RI-BP86-D4/def2-TZVP level, **Figure 6**) show that the PP bonds exhibit strong antibonding behaviour in the LUMO, indicating pronounced electrophilic character. The detailed mechanism presently remains unknown. However, it is noteworthy that  $8[OTf]_2$  could not be generated from the isomeric complex  $7b[OTf]_2$ , which remained stable in solution at elevated temperatures for days. This indicates that  $8[OTf]_2$  does not form via isomerization from  $7b[OTf]_2$ .

#### Reactivity of Imidazoliumyl-substituted *Iso*-Tetraphosphane $6a[OTf]_3$ towards Metal Chlorides and Nucleophiles

We were also keen to investigate the potential follow-up chemistry of the *iso*-tetraphosphanes  $6a[OTf]_3$ . Consistent with the observations for  $5b^{2+}$ , the frontier molecular orbital analysis of  $6a^{3+}$  indicated a rather electrophilic character of the *iso*-tetraphosphane framework (**Figure 7**). The LUMO is notably delocalized, featuring contributions that exhibit antibonding character of the P–P bonds. Across the HOMO through LUMO+4, there is a significant involvement of the *iso*-



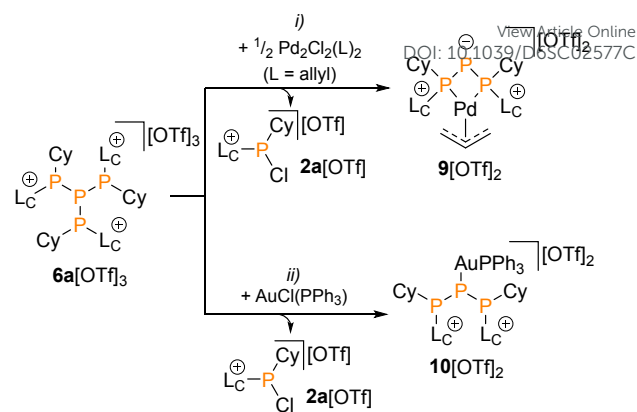
tetraphosphane core. To probe this predicted electrophilicity experimentally, we studied the reactivity of **6a**[OTf]<sub>3</sub> with nucleophiles. Reactions of **6a**[OTf]<sub>3</sub> with Pd(PPh<sub>3</sub>)<sub>4</sub> showed no conversion, even at 60°C. In contrast, Pd<sub>2</sub>Cl<sub>2</sub>(allyl)<sub>2</sub> triggered reactivity (see **Scheme 4**). The initially colourless reaction mixture of **6a**[OTf]<sub>3</sub> with 0.5 equivalents of Pd<sub>2</sub>Cl<sub>2</sub>(allyl)<sub>2</sub> turned orange within 5 min. The <sup>31</sup>P-NMR spectrum of the reaction mixture revealed two new A<sub>2</sub>B spin systems ( $\delta(P_A) = -61.3$  ppm,  $\delta(P_B) = -16.1$  ppm,  $^1J(PP) = -323$  Hz; and  $\delta(P_A) = -57.6$  ppm,  $\delta(P_B) = -25.1$  ppm,  $^1J(PP) = -321$  Hz), displaying higher-order coupling effects.<sup>7,11,36</sup> Additionally, a broad singlet resonance at  $\delta(P) = 55.6$  ppm appeared, which was assigned to the chlorophosphane **2a**<sup>+</sup>. This observation indicates that the palladium complex is formed via a chloride-induced P–P bond cleavage reaction of **6a**[OTf]<sub>3</sub>.



**Figure 7.** Frontier molecular orbitals of **6a**<sup>3+</sup>, resembling the high antibonding character of the LUMO and LUMO+1/+2.

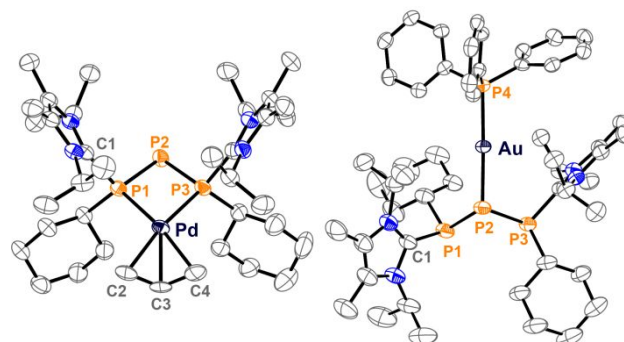
Following solvent removal and toluene extraction of **2a**[OTf], complex **9**[OTf]<sub>2</sub> was obtained as a pure orange solid in 59% yield. The two A<sub>2</sub>X spin systems are observed in the <sup>31</sup>P-NMR spectrum of the isolated compound in a 44:56 ratio. These correspond to the *rac* and *meso* diastereomers, which originate from different configurations of the P atoms in the triphosphanide ligand present in **9**[OTf]<sub>2</sub>.<sup>37</sup>

The susceptibility of *iso*-tetraphosphane **6a**[OTf]<sub>3</sub> towards chloride-induced P–P cleavage motivated further reactions with transition metal chlorides. To this end, we treated **6a**[OTf]<sub>3</sub> with AuCl(PPh<sub>3</sub>), assuming that a similar fragmentation process might occur (**Scheme 4**). As expected, the reaction of **6a**[OTf]<sub>3</sub> with AuCl·PPh<sub>3</sub> (1 equiv.) leads to the formation of **2a**[OTf] and gold complex **10**[OTf]<sub>2</sub>. **10**[OTf]<sub>2</sub> was isolated as an analytically pure, colourless powder (88% yield) after removal of all volatiles and repeated washing with toluene.



**Scheme 4.** Synthesis of palladium complex **9**[OTf]<sub>2</sub> and gold complex **10**[OTf]<sub>2</sub> from **6a**[OTf]<sub>3</sub> via chloride-induced P–P bond cleavage; i) - **2a**[OTf], CH<sub>3</sub>CN, rt, 30 min, 59%; ii) - **2a**[OTf], CH<sub>3</sub>CN, -30°C, 30 min, 88%.

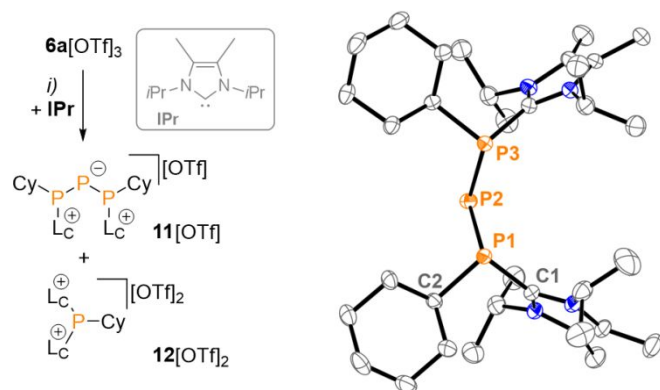
At room temperature, the <sup>31</sup>P NMR spectrum of **10**[OTf]<sub>2</sub> shows broad signals. Upon cooling to 190 K, four distinct spin systems are resolved, corresponding to four isomers: *rac*, *meso*, and the inverted-isopropyl rotamers *rac'* and *meso'* (see SI, Figure S25). Both *rac* isomers exhibit AM<sub>N</sub>X spin systems with comparable features, while the symmetric *meso* isomer displays an AM<sub>2</sub>X spin system. The *meso* isomer also exhibits an AM<sub>2</sub>X spin system, with only slight differences in chemical shift between the P<sub>M</sub> and P<sub>N</sub> atoms ( $\delta(P_M) = -21.6$  ppm,  $\delta(P_N) = -21.3$  ppm). The central phosphorus atom shows a downfield-shifted resonance ( $\delta(P_A) = -78.9$  to  $-84.5$  ppm) compared to the anionic ligand [P(tBu<sub>2</sub>P)<sub>2</sub>]<sup>-</sup> ( $\delta(P_A) = -134$  ppm),<sup>8</sup> suggesting its coordination to the metal center. This assignment is corroborated by the crystal structure of **10**[OTf]<sub>2</sub> (see **Figure 8**), which shows the *rac* isomer with gold coordinated linearly by the PPh<sub>3</sub> ligand and the central P atom of the triphosphanide ligand (P2–Au–P4 angle of 172.38(5)°). The P–P bond lengths (2.210(2) Å and 2.207(2) Å) fall within the range expected for P–P single bonds.<sup>38</sup> A slight elongation of the P–P bond is attributed to reduced negative hyperconjugation from the central phosphorus atom due to the lower electron density upon metal coordination.



**Figure 8.** Molecular structures of **9**[OTf]<sub>2</sub>·C<sub>6</sub>H<sub>5</sub>F·0.5 THF and **10**[OTf]<sub>2</sub>·1.5 CH<sub>2</sub>Cl<sub>2</sub>·2 MeCN. Hydrogen atoms, solvate molecules, and anions are omitted for clarity. Ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: **9**<sup>2+</sup>: P1–P2 2.1527(13), P2–P3 2.1544(13), C1–P1 1.857(4), C2–Pd 2.189(4), C3a–Pd 2.169(6), C3b–Pd 2.169(12), C4–Pd 2.182(5), P1–P2–P3 85.40(5), P1–Pd–P3 74.47(3); **10**<sup>2+</sup>: P1–P2 2.210(2), P2–P3 2.207(2), C1–P1 1.845(6), Au–P2 2.3302(12), P4–Au 2.3028(12), P1–P2–P3 91.21(8), P2–Au–P4 172.38(5).



Based on the successful synthesis of triphosphanide complexes **9**[OTf]<sub>2</sub> and **10**[OTf]<sub>2</sub>, we explored the isolation of the free ligand. At first, we tested the reaction of **6a**[OTf]<sub>3</sub> with Ph<sub>4</sub>P[Cl] as a soluble chloride source. However, the reaction proved unselective, forming several products (see the ESI, section 2.5.5). Using the N-heterocyclic carbene **IPr** instead of chloride resulted in the clean formation of the desired triphosphanide salt **11**[OTf] and bis(imidazoliumyl)phosphane salt **12**[OTf]<sub>2</sub> (Figure 9). **12**[OTf]<sub>2</sub> is formed by nucleophilic attack of **IPr** on a L<sub>c</sub>PCy unit of **6a**<sup>3+</sup>. The formation of **12**[OTf]<sub>2</sub> was confirmed by <sup>31</sup>P-NMR spectroscopy, which showed an identical resonance  $\delta(\text{P}) = -38.2$  ppm as a sample independently synthesized via an alternative route (see SI, section 2.5.4).<sup>39</sup> Triphosphanide salt **11**[OTf] was isolated as a yellow crystalline solid 65% yield after recrystallization from THF. The <sup>31</sup>P-NMR spectrum of **11**[OTf] at room temperature shows two broad AX<sub>2</sub> spin systems, consistent with a *rac*, *meso* mixture (*meso*:  $\delta(\text{P}_A) = -135.2$  ppm,  $\delta(\text{P}_X) = -3.2$  ppm,  $^1J(\text{PP}) = -316$  Hz; *rac*:  $\delta(\text{P}_A) = -130.6$  ppm,  $\delta(\text{P}_X) = -6.9$  ppm,  $^1J(\text{PP}) = -315$  Hz). Upon cooling to 190 K, four spin systems emerge, corresponding to the *rac* and *meso* diastereomers as well as their inverted rotamers *rac'* and *meso'*, analogous to the behaviour for **10**[OTf]<sub>2</sub>.



**Figure 9.** Synthesis of triphosphanide **11**[OTf] (left) and molecular structure of **11**<sup>+</sup> in **11**[OTf]·CH<sub>2</sub>Cl<sub>2</sub> (right); i) C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>, 60 min, 65%. Hydrogen atoms, solvate molecules, and anions are omitted for clarity. Ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: P1–P2 2.1592(7), P2–P3 2.1606(7), C1–P1 1.8561(18), C2–P1 1.8738(18), P1–P2–P3 93.65(7).

Crystals of **11**[OTf] suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-pentane into a saturated solution in CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>H<sub>5</sub>F (v/v = 1:1) at –30°C. The molecular structure is depicted in Figure 9, confirming the presence of the *meso* diastereomer. The structure features the two nearly identical P–P bonds (2.1591(6) Å and 2.1606(6) Å) and a central P1–P2–P3 angle of 93.65(7)°, consistent with a flexible, uncoordinated triphosphanide framework.<sup>40</sup>

## Conclusions

The present work demonstrates that onio substitution not only stabilizes cationic oligophosphorus frameworks, but can also electronically predispose specific P–P bonds toward selective fragmentation pathways. Using the chlorophosphane salts **2a**–**c**[OTf], we have isolated the dicationic diphosphane salts **5a**–

**c**[OTf]<sub>2</sub> and the first cationic *iso*-tetraphosphane salts **6a,b**[OTf]<sub>3</sub>. Reactivity studies of **5a,b**[OTf]<sub>2</sub> towards Pd(PPh<sub>3</sub>)<sub>4</sub> showed competing oxidative additions of either a P–P bond or a P–C bond, yielding **7a,b**[OTf]<sub>2</sub> or the unusual  $\mu_2(\eta^2:\eta^2)$ -diphosphene complex **8a**[OTf]<sub>2</sub>. The significant disparity in reactivity between **5a**[OTf]<sub>2</sub> and **5b**[OTf]<sub>2</sub> raises questions regarding the general stability of imidazoliumyl-substituted phosphanes in transition metal complexes, particularly in catalytic applications.

The use of transition metal chlorides in reactions with the readily accessible **6a**[OTf]<sub>3</sub> enabled the selective generation of cationic triphosphanide complexes. Two distinct coordination motifs were identified: a four-membered metallacycle in the case of palladium (**9**[OTf]<sub>2</sub>) and a linear coordination to the central phosphorus atom in the case of gold (**10**[OTf]<sub>2</sub>), showcasing the versatility of the triphosphanide framework. Motivated by these findings, we developed a direct route to the free, non-coordinated triphosphanide ligand **11**[OTf], whose flexibility and structural integrity suggest a rich coordination chemistry yet to be explored.

## Author Contributions

J.F., K.S., R.W., and J.J.W. conceptualized the topic. J.F. and C.T. conducted the experiments and optimized the syntheses, isolations, and purifications. R.M.G. and A.F. were responsible for computational investigations. J.F., F.H. and J.J.W. were responsible for collecting X-ray data and refinement. K.S. and J.J.W. conceived, oversaw, and directed the project. J.F., K.S. and J.J.W. prepared the initial draft of the paper. A.F., R.W. and J.J.W. acquired funding. All authors discussed and analyzed the results and contributed to the editing of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the German Science Foundation (DFG grant numbers WE 4621/3-2 and WO1496/7-2). A.F. and R.M.G. thank the MICIU/AEI of Spain (project PID2023-148453NB-I00 FEDER funds) for financial support. J.F. and F.H. thank the Graduate Academy of TU Dresden for financial support. Philipp Lange is acknowledged for performing elemental analyses. TU Dresden is also thanked for its financial support.

## Notes and references

- 1 a) M. Alcarazo, *Chem. Eur. J.*, 2014, **20**, 7868; b) L. D. M. Nicholls and M. Alcarazo, *Chem. Lett.*, 2019, **48**, 1;
- 2 K. Schwedtman, G. Zanoni and J. J. Weigand, *Chem. Asian J.*, 2018, **13**, 1388.
- 3 a) W. Hieber and R. Kummer, *Z. Anorg. Allg. Chem.*, 1966, **344**, 292; b) J. A. S. Howell, M. G. Palin, P. McArdle, D.



- Cunningham, Z. Goldschmidt, H. E. Gottlieb and D. Hezroni-Langerman, *Inorg. Chem.*, 1993, **32**, 3493; c) R. Giannandrea, P. Mastrorilli, C. F. Nobile and M. Dilonardo, *Inorg. Chim. Acta*, 1996, **249**, 237; d) S. J. Geier and D. W. Stephan, *Chem. Commun.*, 2010, **46**, 1026;
- 4 a) L. J. Arnold, L. Main and B. K. Nicholson, *Appl. Organomet. Chem.*, 1990, **4**, 503; b) O. Kühl, S. Blaurock and E. Hey-Hawkins, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1517; c) Y. Miyake, Y. Nomaguchi, M. Yuki and Y. Nishibayashi, *Organometallics*, 2007, **26**, 3611; d) D. Tofan and C. C. Cummins, *Chem. Sci.*, 2012, **3**, 2474; e) S. Molitor, C. Mahler and V. H. Gessner, *New J. Chem.*, 2016, **40**, 6467;
- 5 A. M. Caminade, J. P. Majoral and R. Mathieu, *Chem. Rev.*, 1991, **91**, 575.
- 6 a) M. Scheer, S. Gremler, E. Herrmann and P. G. Jones, *J. Organomet. Chem.*, 1991, **414**, 337; b) V. Balema, H. Goesmann, E. Matern and G. Fritz, *Z. Anorg. Allg. Chem.*, 1996, **622**, 35; c) W. S. Sheldrick, *Acta Crystallogr. B*, 1976, 308; d) W. S. Sheldrick, S. Morton and O. Stelzer, *Z. Anorg. Allg. Chem.*, 1981, **475**, 232; e) M. Baacke, S. Morton, G. Johannsen, N. Weferling and O. Stelzer, *Chem. Ber.*, 1980, **113**, 1328; f) R. Schoemaker, K. Schwedtmann, A. Franconetti, A. Frontera, F. Hennersdorf and J. J. Weigand, *Chem. Sci.*, 2019, **10**, 11054;
- 7 G. Fritz, K. Stoll, W. Hönle and H. G. V. Schnering, *Z. Anorg. Allg. Chem.*, 1987, **544**, 127.
- 8 G. Fritz and T. Vaahs, *Z. Anorg. Allg. Chem.*, 1987, **553**, 85.
- 9 a) A. H. Cowley, S. M. Dennis, S. Kamepalli, C. J. Carrano and M. R. Bond, *J. Organomet. Chem.*, 1997, **529**, 75; b) M. Scheer, St. Gremler, E. Herrmann, U. Grünhagen, M. Dargatz and E. Kleinpeter, *Z. Anorg. Allg. Chem.*, 1991, **600**, 203; c) M. Baudler, G. Reuschenbach and J. Hahn, *Z. Anorg. Allg. Chem.*, 1981, **482**, 27;
- 10 G. Fritz, E. Matern, H. Krautscheid, R. Ahlrichs, J. W. Olkowska and J. Pikies, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1604.
- 11 K.-O. Feldmann, R. Fröhlich and J. J. Weigand, *Chem. Commun.*, 2012, **48**, 4296.
- 12 a) C. A. Dyker and N. Burford, *Chem. Asian J.*, 2008, **3**, 28; b) M. Donath, F. Hennersdorf and J. J. Weigand, *Chem. Soc. Rev.*, 2016, **45**, 1145;
- 13 C. Taube, K. Schwedtmann, M. Noikham, E. Somsook, F. Hennersdorf, R. Wolf and J. J. Weigand, *Angew. Chem. Int. Ed.*, 2020, **59**, 3585.
- 14 K. Schwedtmann, J. Haberstroh, S. Roediger, A. Bauzá, A. Frontera, F. Hennersdorf and J. J. Weigand, *Chem. Sci.*, 2019, **10**, 6868.
- 15 T. Krachko and J. C. Slootweg, *Eur. J. Inorg. Chem.*, 2018, **2018**, 2734.
- 16 a) O. Back, B. Donnadieu, P. Parameswaran, G. Frenking and G. Bertrand, *Nat. Chem.*, 2010, **2**, 369; b) A. Hermannsdorfer, D. W. Stephan and M. Driess, *Chem. Commun.*, 2018, **54**, 13523; c) A. M. Tondreau, Z. Benkó, J. R. Harmer and H. Grützmacher, *Chem. Sci.*, 2014, **5**, 1545; d) K. Schwedtmann, M. H. Holthausen, C. H. Sala, F. Hennersdorf, R. Fröhlich and J. J. Weigand, *Chem. Commun.*, 2016, **52**, 1409;
- 17 J. J. Weigand, K.-O. Feldmann and F. D. Henne, *J. Am. Chem. Soc.*, 2010, **132**, 16321.
- 18 J. Fidelius, K. Schwedtmann, S. Schellhammer, J. Haberstroh, S. Schulz, R. Huang, M. C. Klotzsche, A. Bauzá, A. Frontera, S. Reineke and J. J. Weigand, *Chem*, 2024, **10**, 644.
- 19 P. Pracht, F. Bohle and S. Grimme, *Phys. Chem. Chem. Phys.*, 2020, **22**, 7169.
- 20 L. P. Ho, A. Nasr, P. G. Jones, A. Altun, F. Neese, G. Bistoni and M. Tamm, *Chem. Eur. J.*, 2018, **24**, 18922.
- 21 D. L. Dodds, M. F. Haddow, A. G. Orpen, P. G. Pringle and G. Woodward, *Organometallics*, 2006, **25**, 5937.
- 22 A. Dashti-Mommertz and B. Neumüller, *Z. Anorg. Allg. Chem.*, 1999, **625**, 954.
- 23 M. Baudler, G. Reuschenbach, D. Koch and B. Carlsohn, *Chem. Ber.*, 1980, **113**, 1264.
- 24 O. Kühl, *Phosphorus-31 NMR Spectroscopy*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2009.
- 25 C. Taube, J. Fidelius, K. Schwedtmann, C. Ziegler, F. Kreuter, L. Loots, L. J. Barbour, R. Tonner-Zech, R. Wolf and J. J. Weigand, *Angew. Chem. Int. Ed.*, 2023, **62**, e202306706.
- 26 a) A. M. Arif, D. E. Heaton, R. A. Jones and C. M. Nunn, *Inorg. Chem.*, 1987, **26**, 4228; b) M. Sommovigo, M. Pasquali, P. Leoni and U. Englert, *Inorg. Chem.*, 1994, **33**, 2686;
- 27 N. W. J. Scott, M. J. Ford, C. Schotes, R. R. Parker, A. C. Whitwood and I. J. S. Fairlamb, *Chem. Sci.*, 2019, **10**, 7898.
- 28 Y. H. Lee and B. Morandi, *Coord. Chem. Rev.*, 2019, **386**, 96.
- 29 D. Fenske and K. Merzweiler, *Angew. Chem.*, 1986, **98**, 357.
- 30 D. Fenske and K. Merzweiler, *Angew. Chem. Int. Ed.*, 1986, **25**, 338.
- 31 L. Weber, *Chem. Rev.*, 1992, **92**, 1839.
- 32 M. S. Viciu, R. F. Germaneau, O. Navarro-Fernandez, E. D. Stevens and S. P. Nolan, *Organometallics*, 2002, **21**, 5470.
- 33 A. H. Cowley, D. M. Giolando, C. M. Nunn, M. Pakulski, D. Westmoreland and N. C. Norman, *Dalton Trans.*, 1988, 2127.
- 34 S. Blaurock and E. Hey-Hawkins, *Eur. J. Inorg. Chem.*, 2002, **2002**, 2975.
- 35 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
- 36 C. E. Averre, M. P. Coles, I. R. Crossley and I. J. Day, *Dalton Trans.*, 2012, **41**, 278.
- 37 a) L.-M. Frenzel, C. Bruhn and R. Pietschnig, *Inorg. Chim. Acta*, 2021, **516**, 120091; b) R. Franz, D. Gál, C. Bruhn, Z. Kelemen and R. Pietschnig, *Adv. Sci.*, 2024, **11**, e2306805;
- 38 A. F. Holleman, N. Wiberg and E. Wiberg, *Lehrbuch der Anorganischen Chemie*, Walter de Gruyter, 2007.
- 39 a) C. L. B. Macdonald, J. F. Binder, A. Swidan, J. H. Nguyen, S. C. Kosnik and B. D. Ellis, *Inorg. Chem.*, 2016, **55**, 7152; b) M. Azouri, J. Andrieu, M. Picquet and H. Cattet, *Inorg. Chem.*, 2009, **48**, 1236;
- 40 a) G. Fritz, T. Vaahs, W. Hönle and H. G. v. Schnering, *Z. Anorg. Allg. Chem.*, 1987, **552**, 34; b) G. Fritz, J. Härer and K. H. Scheider, *Z. Anorg. Allg. Chem.*, 1982, **487**, 44;



**Data availability.** The data supporting the findings of this study, including CIF files, NMR spectra, and computational details, are available in the ESI. Additional data can be obtained from the corresponding author upon reasonable request. CCDC Deposition numbers 2501246-2501257 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service (<https://www.ccdc.cam.ac.uk/>).

View Article Online

DOI: 10.1039/D6SC02577C

