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The *bis*(Biphenyl)phosphorus Fragment in Trivalent and Tetravalent P-Environments

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Abstract: Diaryl substituted phosphorus (III) compounds are commonly used motifs in synthesis. Although the basic synthetic routes to these molecules starting from PCl_3 are well reported, sterically hindered aryl substituents can be difficult to introduce, especially if the P atom is in *ortho* position to another group. This work explores the chemistry of the *bis*(biphenyl)phosphorus(III) fragment. As third substituents, H, M, Cl, NR_2, two group 14 element substituents and also Li were introduced in high-yielding processes offering a wide chemical variety of the *bis*(biphenyl) phosphine motif. In addition, also a tetravalent phosphine borane adduct was isolated. All structures were thoroughly investigated by heteronuclear NMR spectroscopic analysis. Furthermore, the reaction conditions are discussed in connection with the structures and four crystal structures of the aminophosphine, phosphine, phosphine borane and phosphide are provided. The latter crystallized as a dimer with a unique planar P_2Li_2 ring, which is stabilized by the non-covalent C· · · Li interaction arising from the biphenyl motif and represents a rare example of a donor-free planar P_2Li_2 ring.

Keywords: organophosphorus chemistry; phosphide; phosphine; ligand; phosphine borane; aminophosphine; silylphosphine; stannylphosphine

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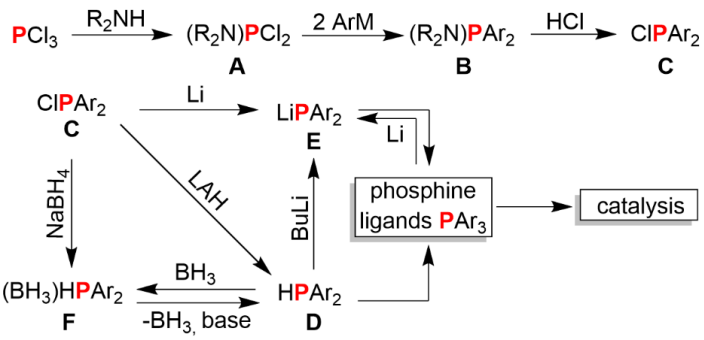
1. Introduction

Phosphorus diaryl fragments are very common motifs in reagents for the preparation of ligands for metal complexes. Their use in catalysis is therefore undisputed. These fragments also occur in inorganic polymers and rings [1–3]. The most common ones among these are trivalent diarylphosphines, Ar_2PH, the corresponding tetravalent phosphine boranes, $R_2PH–BH_3$, the corresponding lithiated species, Ar_2PLi, and the aminospecies Ar_2PNR_2. There are well-established ways in which all these species can be obtained and how they are synthetically connected (Scheme 1).



Scheme 1. Synthesis of diarylphosphine, diarylphosphides and diarylphosphine borane. Abbreviation: Lithium aluminum hydroxide (LAH), butyl lithium (BuLi).

Aminophosphines are classically prepared by the reaction of substituted amines with phosphorous trichloride and potentially followed by the nucleophilic substitution with a carbonucleophile [4]. They represent a special class of phosphines as they behave as ambident reagents due to the presence of a Lewis soft (P) and a Lewis hard (N) basic atom connected to each other. Hence, in combination with soft Lewis acids, the phosphorus will serve as Lewis basic center and consequently, hard Lewis acids will coordinate with the nitrogen atoms [5]. The special bonding nature of aminophosphine is defined by the π-electron transfer from the nitrogen atom to the phosphorus and, therefore, the basicity of aminophosphines is similar or higher to tertiary alkylamines or alkylphosphines. However, aminophosphines are not as reactive as tertiary alkylphosphines, which are very susceptible to oxidation, which indicates that steric hindrance at the phosphorus and/or nitrogen are more important factors to their reactivity than electronic effects [4].

Diarylphosphines are commonly synthesized from triarylphosphines, which are reduced to the respective diarylphosphide and quenched with a protic medium [6,7]. Diarylphosphines often only serve as precursors for further ligand synthesis. However, diphenylphosphine is used in Michael addition reactions for activated alkenes [8], in a radical fashion to ketenes [9] or as precursor for Wittig reagents [10]. Moreover, diarylphosphines can be introduced to an aromatic system by C–P coupling using an aryl halide and palladium [11,12] or nickel [13] catalysis.

As described above diarylphosphides are prepared from reductive C–P bond cleavage of a triaryl phosphine, by reduction of a diarylchlorophosphine with a hydride-based reductant (e.g., LAH) or deprotonation of diarylphosphines with butyllithium (BuLi). They represent precursors for prominent ligands such as 1,2-*bis*(diphenylphosphino)methane (dppm) 1,2-*bis*(diphenylphosphino)ethane (dppe) [1]. Moreover, diarylphosphides can also serve as reagents. In particular, it was shown that lithium diphenylphosphide supports the dihydroxylation of α-hydroxyketones [14] or the dealkylation of alkyl aryl ethers [15,16].

As diarylphosphines quickly undergo oxidation, they are commonly protected with borane to form diarylphosphine boranes [17,18]. As this class of species is more reactive towards substitution, it is widely used in catalyst-free Staudinger ligation [19], as stereogenic precursor for ligand synthesis [20], for the preparation of alkynylphosphine derivatives [21]. Diarylphosphine boranes can be coupled to vinyl triflates or aryl halides to cyclic or acyclic vinyl triflates using palladium catalyst to access the respective tertiary phosphine boranes [22–24].

As all these diaryl fragments are mainly used en route to other compounds, their structure is very important not only for the assessment of their reactivity but also for an understanding of their steric impact on the target molecules. As the structure (chemical and electronic) is key for their function, these reagents deserve in-depth investigations.

The most commonly used aryl group is phenyl, but less is known about other aryl groups. However, one very important aryl motif in the context of phosphine chemistry is the biaryl motif, in which phosphorus is bound *ortho* to the phenyl group. Ligands of this type are for example Buchwald ligands, which facilitate the reductive elimination in the catalytic cycle.

While the synthesis of such ligands is primarily based on the preparation of a carbonucleophile using both Grignard-based [25,26] and organolithium-based [27,28] routes, which are further reacted with chlorodialkylphosphine (catalyzed by CuCl), the isolation of any nucleophilic phosphide with already formed carbon scaffold remains elusive. In particular, the *bis*(biphenyl)phosphine has been successfully deployed as resin-bound ligand in cross coupling reactions [29] but the *bis*(biphenyl)phosphine and its derivatives have not been isolated yet. Various trivalent and tetravalent *bis*(biphenyl)phosphine derivatives could serve as a starting point for the synthesis of a novel ligand class that is based on the *bis*(biphenyl)phosphine motif.

As a *bis*(biphenyl)phosphine motif has great potential as a ligand for catalysis, we present its most common ones among these are trivalent diarylphosphines, Ar_2PH, the

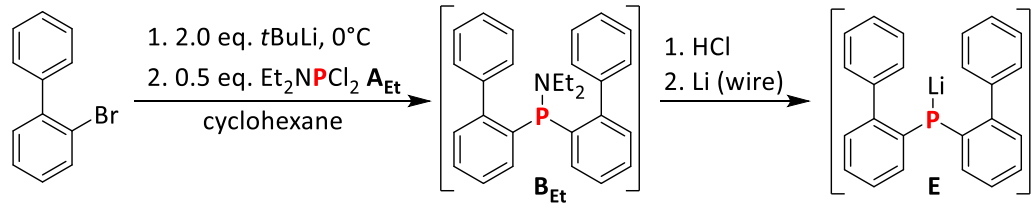
corresponding tetravalent phosphine boranes, $R_2PH\text{-}BH_3$, the corresponding lithiated species, Ar_2PLi, starting from the aminospecies Ar_2PNR_2.

2. Results

2.1. Syntheses

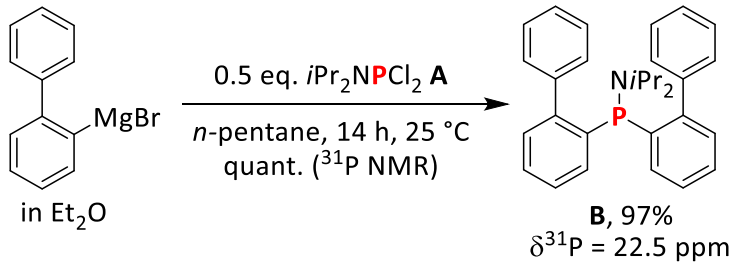
2.1.1. Synthesis of *bis*(Biphenyl)diisopropylamino Phosphine (**A**)

The synthesis of the lithiated *bis*(biphenyl)phosphide (**E**) was already reported as a consecutive reaction [29]. The procedure included a bromide-lithium exchange of 2-bromobiphenyl, followed by the reaction with *N*,*N*-diethylphosphoramidous dichloride (**A**) to form the protected diarylamino phosphine ($\mathbf{B_{Et}}$). This was deprotected with hydrogen chloride to form the diarylchlorophosphine (**C**) followed by reduction with lithium wire to give the lithium *bis*(biphenyl)phosphide (**E**) (Scheme 2) [29].



Scheme 2. The synthetic procedure to lithium diarylphosphide **E** according to Le Drian and coworkers [29].

However, there were no isolated species reported in this reference. Therefore, the steps were investigated in detail. After the initial step could not be reproduced in our hands using these conditions with another P precursor, the formation of the diarylamino phosphine **B** succeeded with the commercially available Grignard reagent in *n*-pentane as a solvent (Scheme 3).

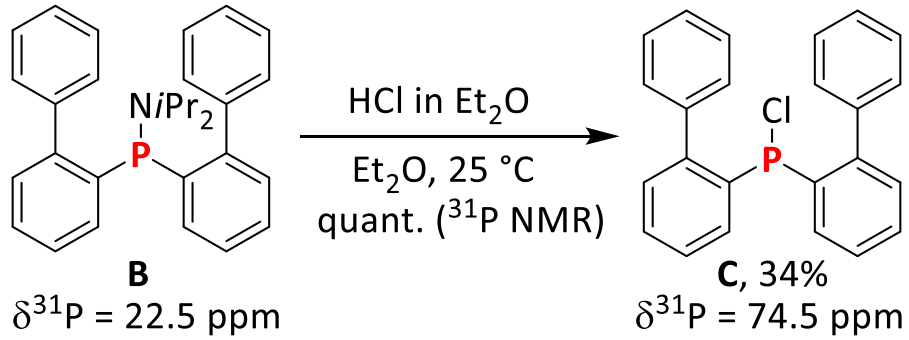


Scheme 3. Synthesis of the *bis*(biphenyl-2-yl)-*N*,*N*-di*iso*propylphosphanamine **B**.

Although the reaction mixture was inhomogeneous, ^{31}P NMR experiments indicated that the disubstituted product **A** (δ = 22.5 ppm) was formed selectively. This was confirmed since we could isolate the product in excellent yield and purity. Product **B** showed stability against moisture and air which was not observed for its phenyl derivative [30]. Therefore, it was concluded that the biphenyl ligands sterically shield the phosphorus atom which was confirmed by single-crystal X-ray analysis (see Section 2.2). The phenyl derivative of *bis*(biphenyl)diisopropylamino phosphine is widely used as ligand for transition-metal catalyzed cross-coupling reactions [31–33] or for coordination chemistry [34,35].

2.1.2. Synthesis of *bis*(Biphenyl)chlorophosphine

The diarylamino phosphine was converted to the respective phosphine chloride **C** by using an excess of hydrogen chloride in an etheric solution (Scheme 4).

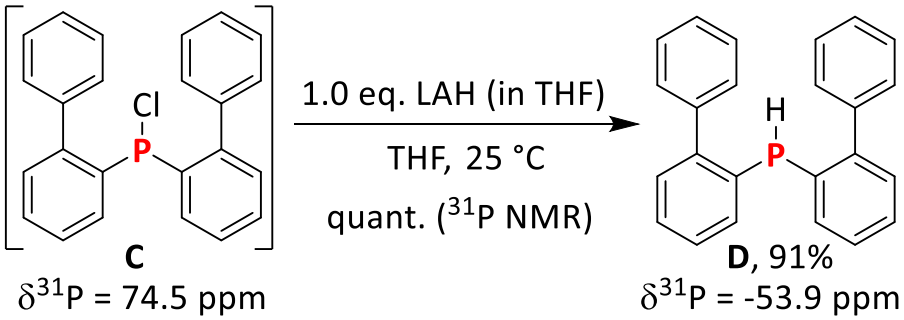


Scheme 4. Synthesis of the *bis*(biphenyl)chlorophosphine (**C**).

The ^{31}P NMR spectrum of the reaction mixture indicated a quantitative conversion to product **C**, which was obtained after filtration from the ammonium salts. The isolation of this molecule succeeded using high temperature, high vacuum Kugelrohr (180 °C, 3.2×10^{-2} mbar) distillation and resulted in the pure compound but in a low yield of 34%. Over the course of this distillation, side products, which are likely to be phosphinic chlorides (δ = 34.0 ppm) and phosphine oxides (δ = 15.9 ($^{1}J_{PH}$ = 503.3 Hz) ppm), occurred. However, the isolation of this product was not pursued further as in situ performed ^{31}P NMR analysis showed quantitative conversion.

2.1.3. Synthesis of *bis*(Biphenyl)phosphine

Because of the quantitative conversion of **B** to **C**, this chlorophosphine could be directly reduced with lithium aluminum hydride in a THF solution to give the diarylphosphine **D** in 91% yield (Scheme 5).

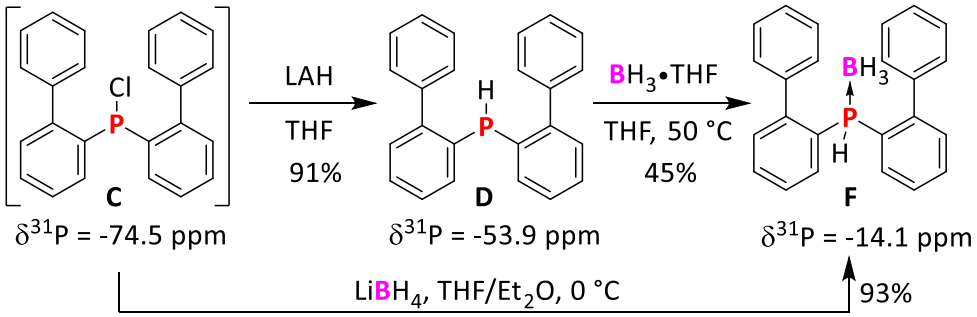


Scheme 5. Reduction of the chlorophosphine **C** with LAH solution gave the phosphine **D** as the pure product after distillation.

The reduction resulted in the full conversion as determined by ^{31}P NMR analysis. Initial attempts to purify the product by column chromatography failed as the phosphine **D** oxidized readily. However, the isolation of the compound **D** succeeded using high temperature (160 °C), high vacuum (10^{-2} mbar) inert Kugelrohr distillation. After cooling the product, it crystallized readily (the crystal structure is discussed in Section 2.2).

2.1.4. Synthesis of *bis*(Biphenyl)phosphine Borane Adduct F

Since the phosphine **D** was not stable against oxidation, it was stabilized by transforming it to the respective phosphine-borane **F**. To access compound **F**, two synthetic routes were successfully developed: First by the successive reduction with lithium aluminum hydride to access the phosphine **D** (*vide supra*) and further protection with the borane THF adduct as a reagent. Secondly, the direct reduction of the chlorophosphine **C** with lithium borohydride succeed in high yields (Scheme 6).

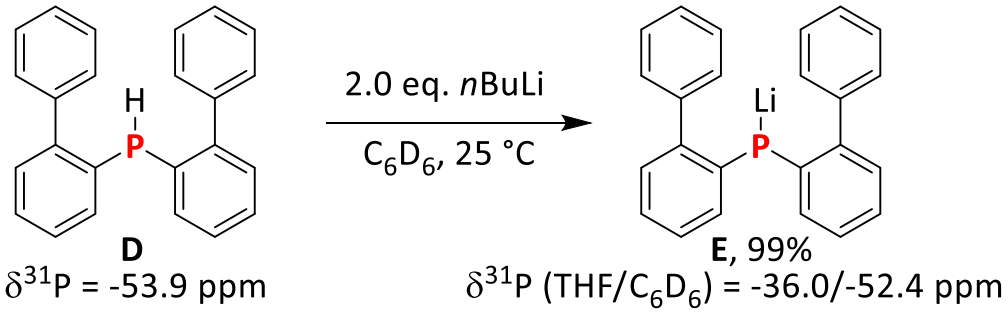


Scheme 6. Synthesis of the *bis*(biphenyl)phosphine borane (**F**) starting from chlorophosphine **C**.

The protection of the phosphine **D** with the borane THF adduct at 25 °C initially showed no conversion. Upon heating to 50 °C, it was possible to obtain nearly quantitative conversion to the phosphine borane **F** as determined by ^{31}P NMR (δ = −14.1 ppm, see Figure S23). The borane adduct **D** could be isolated by crystallization in a 45% yield. However, a direct reduction/borylation procedure using lithium borohydride in THF gave **D** in an excellent yield of 93% after crystallization. The resulting crystals of **D** were suitable for X-ray analysis (see Section 2.2). However, the phosphine borane **D** was moisture-, air- and temperature-sensitive and must be stored under inert conditions at low temperature.

2.1.5. Synthesis and Reactivity of Lithium *bis*(Biphenyl)phosphide

The synthesis of the lithium *bis*(biphenyl)phosphide **E** by reducing the chlorophosphine **C** directly with lithium [29] was unsuccessful initially, because C–P bond cleavage occurred to give biphenylphosphine and biphenyl. Therefore, the formation of phosphide was pursued by deprotonation from the respective phosphine with *n*BuLi (Scheme 7).

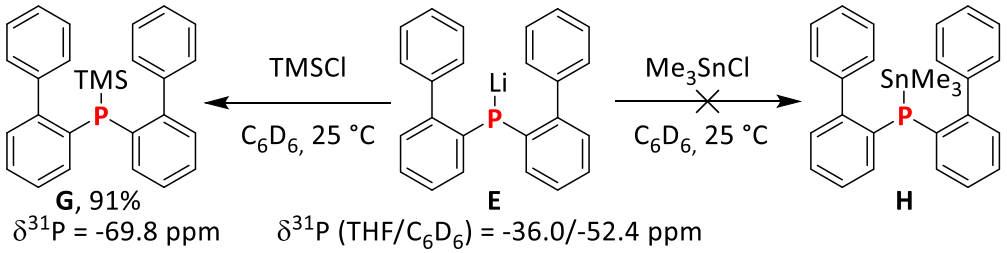


Scheme 7. Metalation of phosphine **D** with *n*BuLi gave the phosphide **E**. The phosphide was only slightly soluble in C_6D_6; therefore, no ^{7}Li NMR signal was found. In THF, the ^{7}Li and ^{31}P NMR species were clearly observable but, in the latter, slightly shifted.

When the reaction was performed in deuterated benzene precipitate formed instantaneously upon the addition of *n*BuLi and an intense orange color was observed. The full conversion to the poorly soluble phosphide **E** was achieved by using two equivalents of *n*BuLi at 25 °C resulting in the formation of the product in excellent yield (99%). The phosphide was stable at 25 °C in the glove box but decomposed rapidly upon mixing with ethers or other solvents except for benzene/toluene or aliphatic solvents.

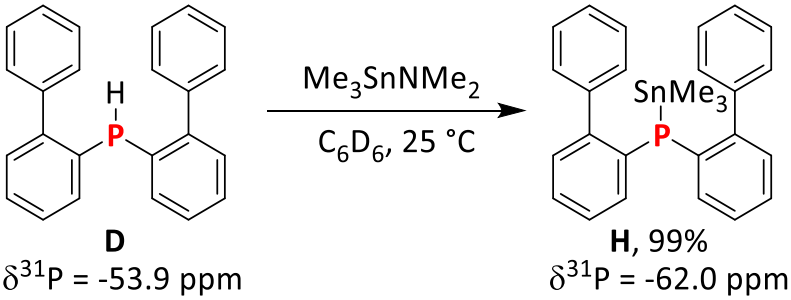
The ^{31}P{^{1}H} NMR shift of **E** was strongly dependent on the solvent and was observed as a broad signal in C_6D_6 (δ = −52.4 ppm). In a mixture with THF, the signal was shifted downfield (δ = −36.0 ppm) due to the coordination of the solvent (see Figures S16 and S17). Crystals of phosphide **E** without any coordinating solvent could be grown and revealed that the product crystallized as a dimer with each phosphorus atom interacting with two lithium atoms forming a P_2Li_2 planar ring (see below).

To highlight the reactive nature of the phosphide, it was reacted with trimethylsilyl chloride to give the respective silyl phosphine but it did not react with its heavier congener trimethyltin chloride (Scheme 8).



Scheme 8. Reaction of phosphide **E** with two trimethyl tetrel chlorides.

The latter reaction did not occur although the reaction mixture was treated at an elevated temperature (80 °C). This clearly indicated that the phosphide **E** had an organometallic 'hard' character and therefore, the reaction with the rather 'soft' trimethyltin chloride did not proceed. With this information in hand, the trimethylstannyl phosphine **H** could be accessed from the 'soft' phosphine **D** using (dimethylamino)trimethyltin as a 'soft' trimethylstannyl transfer reagent [36] (Scheme 9).



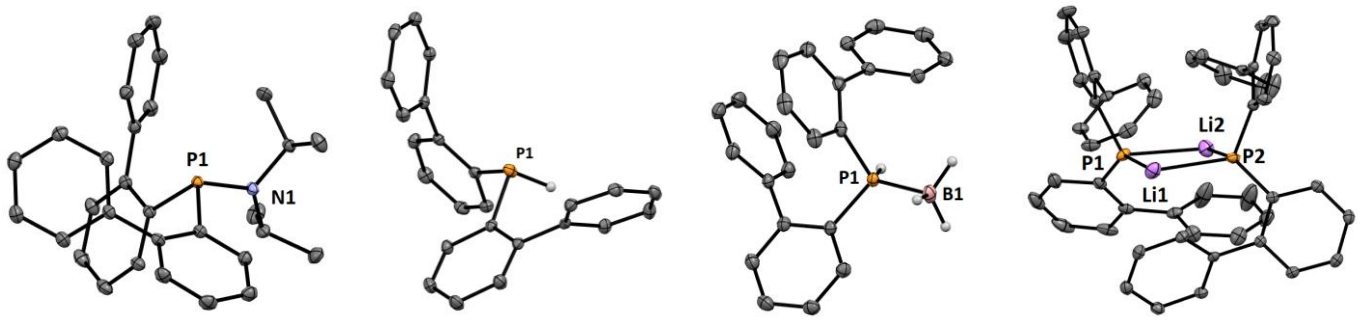
Scheme 9. Stannylation of phosphine **D** with (dimethylamino)trimethyltin.

The sole byproduct formed in this reaction, dimethylamine, could be easily removed by applying a vacuum leaving behind the pure product in an excellent yield. Compared to the silyl phosphine (δ = −69.8 ppm), the stannyl phosphine displayed a deshielded phosphorus atom with a ^{31}P NMR shift of δ = −62.0 ppm. Neither compound could by crystallized.

2.2. Crystal Structures

The crystals of *bis*(biphenyl)di*iso*proylamino phosphine (**B**), *bis*(biphenyl)phosphine (**D**), *bis*(biphenyl)phosphine borane adduct (**F**) and lithium *bis*(biphenyl)phosphide (**E**) could be grown and they were characterized by single-crystal X-ray analysis (Figure 1, Table 1). In the following, the structures will be discussed and a conclusion with respect to their reactivity will be outlined.

While structure **B** crystallized in a triclinic crystal system, the other structures were found in a monoclinic crystal system. Structure **B** has a P–N bond length of 1.6917(7) Å, which is a typical value for P(III)-N bond systems similar to the 1,2-*bis*(diphenylphosphino) (benzyl)aminoethane (1.68(1) Å) [37]. Interestingly, this structure did not oxidize whereas its phenyl-derivative was prone to oxidation. Although the sum of angles at the phosphorus atom (Σ = 307.71°) indicated sufficient space for oxidation events, the similar biphenyl of dialkylbiphenyl phosphines, also referred to as Buchwald ligands, [38], is known to prevent the ligand's oxidation effectively [39]. The C–P–C angle (99.39°), of structure **B** was the lowest value in the here reported quartet. The biphenyl groups of **B** showed internal twisting, as indicated by the respective large torsion angles (−56.2° and −55.6°).



B **D** **F** **E**

Figure 1. Overview of molecule structures. All carbon-bonded hydrogen atoms were removed for clarity.

Table 1. Overview key crystal structure details for **B**, **D**, **F** and **E**.

	B	**D**	**F**	**E**
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	P-1	$P2_1/c$	$P2_1/c$	$P2_1/n$
P–X bond length	1.6917(7) Å	1.32(2) Å	1.30(1) Å/ 1.926(1) Å	2.503(2)/2.490(3) Å 2.507(3)/2.567(2) Å
P–C bond length	1.8491(6) Å	1.837(1) Å	1.817(1) Å	1.820(1)/1.822(1) Å
P–C bond length	1.8546(9) Å	1.847(1) Å	1.812(1) Å	1.821(1)/1.824(1) Å
$\angle_{\textbf{C-P-C}}$	99.39°	102.30°	104.93°	104.33°/103.58°
ΣP	307.71°	297.23°	316.13°	326.29°
ϕbiaryl$_1$	−56.2(1)°	−65.2(2)°	−49.7(1)°	66.2(2)°/−69.3(2)°
ϕbiaryl$_2$	−55.6(1)°	−65.6(2)°	−113.3(1)°	−76.3(2)°/−58.6(2)°

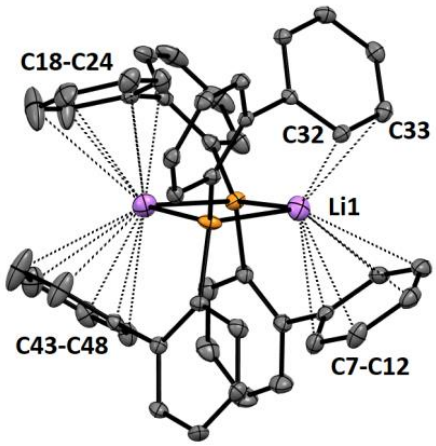
The crystal structure of phosphine **D** had the space group $P2_1/c$. The sum of angles at the phosphorus atom (Σ P = 297.23°) was the lowest from the here presented structures. As visualized, the geometry of the biphenyl ligand was so spacious that still chemical modification at the phosphorus atom was possible and the structure underwent oxidation rapidly. Therefore, it was protected with borane to form structure **F**, which was found in space group $P2_1/c$. The key interest in this system was the P–B bond length, which was determined as 1.926(1) Å. This was similar to a common P–B bond length of 1.915(3) Å in *bis*(*ortho*-*N*,*N*-dimethylaniline)phosphine borane [40].

The lithium *bis*(biphenyl)phosphide (**E**) crystalized as a phosphide-bridged dimer in the space group $P2_1/n$. The central unit of the crystal structure was a quasi-planar four-membered rhombic P_2Li_2 ring with a small dihedral angle (ϕ(P–Li–P–Li) = 4.73°) and nearly orthogonal Li–P–Li angles (∠(Li1–P1–Li2) = 80.60°, ∠(Li1–P2–Li2) = 82.18 °). The biphenyl ligands filled the edges in this ring structure in an orthogonal fashion. The P–Li bond distances (2.503(2)/2.490(3) Å, 2.507(3)/2.567(2) Å) were similar compared to other reported organo arylphosphides [41]. For the carbon atoms of the second biphenyl ring and the lithium cation• • • π interaction, similar to the reported [{Li(2,4,6-*t*$Bu_3C_6H_2$)}{LiP(H)(2,4,6-*t*$Bu_3C_6H_2$)}]$_2$ [42] (η_6 fashion) and {[Ar^{Mes2} P(Ph)]Li(THF)$_2$} (η_2 fashion) [43], was present (Figure 2).

Due to the sterically demand of the biphenyl ligands, the central Li_2P_2 ring appeared to be peripherally shielded and hinders the formation of amorphous polymeric structures. Hence, this allowed the isolation of the dimer. The dimeric motif is common for certain organolithium structures (e.g., see *ortho*-tolyllithium and *para*-tolyllithium) [44]. However, it should be highlighted that this crystal structure is one of the rare examples of a phosphide where the metal is not coordinated by any nitrogen or oxygen. For such an example including a planar P_2Li_2 ring, the lithium *bis*(trimethylsilyl)phosphide THF adduct {Li[P($SiMe_3$)$_2$]$_2$$THF_2$}$_2$ [45] and lithium diphenyl phosphide TMEDA adduct (TMEDA·$LiPPh_2$)$_2$ are reported. In addition, in the latter structure, both the P and Li atoms are found in less distorted tetrahedral environments (mean angles: ∠(P–Li–P) = 91° and

∠(Li–P–Li) = 89°) with a mean Li–P distance of 2.61 Å [46], or with larger distortion of the P_2Li_2 ring in $\{Li[P(SiMe_3)_2]_2THF_2\}_2$ (∠(P–Li–P) = 100.0(8)°, ∠(Li–P–Li) = 80.0(7)°) [45].

Overall, the close interaction of the biphenyl ligands with the lithium atoms might explain the high stability of the phosphides in solid and solution. This was in good agreement with the observation that the phosphide decomposed as it was mixed with coordinating solvents (THF, diethyl ether).



Connection	Li–C distance
Li1–C12	2.673(3) Å
Li1–C7	2.663(3) Å
Li1–C33	2.852(3) Å
Li1–C32	2.567(3) Å
Li2–C19	2.714(3) Å
Li2–C20	2.672(3) Å
Li2–C43	2.694(3) Å
Li2–C48	2.793(3) Å

Figure 2. Overview of isolated crystal structure of the phosphide **E** and close contacts of the lithium atom with various carbon atoms. The hydrogen atoms were omitted for clarity. Inset: Close lithium-carbon distances which indicate non-bonding interactions.

3. Discussion

The preparation of the *bis*(biphenyl)phosphide is commonly performed by a one-pot reaction sequence forming the *bis*(biphenyl)phosphine amide, in-situ formation of the respective chlorophosphine followed by the reduction with elemental lithium [29]. We found that this methodology suffers from the cleavage of any C–P bond due to the use of the strong reductant lithium. Therefore, we report a high yielding process to synthesize the *bis*(biphenyl)phosphide motif. It uses a step-wise synthetic route from the synthesis of the isolatable *bis*(biphenyl)phosphine amide, the respective chlorophosphine, phosphine and after subsequent lithiation, finally the phosphide species. Moreover, we examined the phosphides' reactivity with two trimethyltetrel (Si/Sn) chlorides. As the respective phosphine-trimethyltetrel species could be only accessed for the rather small trimethylsilyl chloride, we conclude that both biphenyls sterically shield the phosphide (see crystal structure) which renders it inaccessible for a reaction with the rather large trimethyltin chloride. This is in contrast to the reactivity of the diphenylphosphide which reacts which trimethyltin chloride [47].

4. Materials and Methods

In general, NMR-tubes and glassware were dried in an oven at 200 °C overnight before use. If not stated otherwise, all reaction vessels were heated to minimum of 200 °C under vacuum (1.3×10^{-2} mbar to 6.2×10^{-2} mbar) and purged with argon at least three times before adding reagents. Syringes were purged with argon three times prior use. In general, a nitrogen filled glovebox (Inert Innovative Technology Inc., Newburyport, MA, USA) (<0.1 ppm O_2 and <0.1 ppm H_2O) was used unless noted otherwise. All dry solvents were taken from the solvent purification system (SPS, Inert Technology or MB-SPS-800, M. Braun Inertgas-Systeme GmbH, Garching, Germany), degassed by three freeze-pump-thaw cycles and stored under a nitrogen or argon atmosphere unless noted otherwise. Kugelrohr distillation was performed with a Büchi B-585 Kugelrohr oven (Büchi, Flawil, Switzerland). All NMR -spectra were carried out at 23 C. ^{1}H NMR (601 MHz) and ^{13}C{^{1}H} NMR (151 MHz) spectra were recorded on a Bruker Avance Neo spectrometer equipped with a TXI probe head. ^{1}H NMR (601 MHz), ^{13}C{^{1}H} NMR (151 MHz), ^{11}B{^{1}H} NMR

(193 MHz), ^{29}Si{^{1}H} NMR (119 MHz), ^{31}P{^{1}H} NMR (243 MHz), ^{119}Sn{^{1}H} NMR (223 MHz) spectra were recorded on a Bruker Avance Neo spectrometer equipped with a BBO probe head. ^{1}H, ^{13}C, ^{29}Si, ^{31}P NMR, ^{119}Sn NMR spectra are reported on the δ scale (ppm) and are referenced against tetramethylsilane respectively Where possible, NMR signals were assigned using ^{1}H COSY, ^{1}H/^{1}H NOESY, ^{1}H/^{13}C HSQC and ^{1}H/^{13}C HMBC experiments. IR spectra were recorded on a Nicolet Thermo iS10 scientific spectrometer (Thermo Fisher SCIENTIFIC, Waltham, MA, USA) with a diamond ATR unit. Electron impact (EI) mass experiments were measured using the direct inlet or indirect inlet methods on a MAT95 XL double-focusing mass spectrometer from Finnigan MAT (Thermo Fisher SCIENTIFIC, Waltham, MA, USA). The ionization energy of the electron impact ionization was 70 eV. Atmospheric pressure chemical ionization (APCI) and electron spray ionization (ESI) experiments were performed on a Bruker Impact II (Bruker Daltonics, Bremen, Germany). Melting points of solids were measured on a Büchi M-5600 Melting Point (Büchi, Flawil, Switzerland) apparatus and are uncorrected.

X-ray measurements were carried out at 100 K on a Bruker Venture D8 diffractometer (Bruker, Karlsruhe, Germany) with Mo-Kα (0.7107 Å) radiation. Air and moisture sensitive compounds were transferred in the glovebox into a cryoproctectant and then mounted on the diffractometer. All structures were solved by intrinsic phasing and refined based on F^2 by use of the SHELX program package, as implemented in Olex2 1.2 [48]. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. Figures were created using Mercury 4.2. [49].

Commercially available compounds were bought from the subsequent suppliers: 2-biphenylmagnesium bromide (0.5 M in Et_2O, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), borane THF adduct (1.0 M in THF, Sigma Aldrich), nBuLi (2.5 M in hexanes, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), (dimethylamino)trimethyltin (>90%, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), trimethylsilyl chloride (Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), lithium borohydride (>95%, Sigma Aldrich), lithium aluminum hydride (1.0 M in THF, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), hydrogen chloride (2.0 M in Et_2O, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany).

The amino-protected dichlorophosphine **A** was synthesized by the reaction of phosphorus trichloride and two equivalents of di*iso*propylamine according to a literature protocol [50].

bis(Biphenyl-2-yl)-*N*,*N*-di*iso*propylphosphanamine (**B**)

Under constant stirring at 0 °C 2-biphenylmagensium bromide (30.0 mL, 15.0 mmol, 0.5 M in diethyl ether) was added to *n*-pentane (100 mL). To this **A** (1.30 mL, 7.07 mmol) was added dropwise and the solution formed a white precipitate. The reaction progress was followed by ^{31}P NMR spectroscopy. After 14 h of stirring at 25 °C, the solids were filtrated off and washed with *n*-pentane (100 mL). All volatiles were removed at reduced pressure and recrystallization of the solid was performed by dissolving the residue in a minimal amount of DCM and adding acetonitrile (100 mL) in an open flask. Using fractional crystallization, the product was obtained in high purity as colorless crystals (**B**, 3.02 g, 6.91 mmol, 97%), which were also suitable for X-ray analysis. **^{1}H NMR** (601 MHz, DCM-d_2): δ = 7.42 (dd, ^{3}J = 7.4 Hz, ^{4}J = 1.5 Hz, 2H, *H*-3), 7.31 (td, ^{3}J = 7.4, ^{4}J = 1.5 Hz, 2H, *H*-5), 7.27 (td, ^{3}J = 7.4 Hz, ^{4}J = 1.5 Hz, 2H, *H*-4), 7.25–7.18 (m, 6H, *H*-9,10,11), 7.06 (ddd, ^{3}J = 7.4, ^{3}J = 4.7, ^{4}J = 1.5 Hz, 2H, *H*-6), 7.04 (d, ^{3}J = 7.5 Hz, 4H, *H*-8,12), 3.24–3.13 (two hept., ^{3}J = 6.7 Hz, 2H, C*H*), 0.68 (d, ^{3}J = 6.7 Hz, 12H, CH_3) ppm. **^{13}C {^{1}H} NMR** (151 MHz, DCM-d_2): δ = 146.79 (d, $^{2}J_{C\text{-}P}$ = 27.8 Hz, *C*-1), 142.78 (d, $^{3}J_{C\text{-}P}$ = 4.2 Hz, *C*-7), 139.98 (d, $^{1}J_{C\text{-}P}$ = 20.0 Hz, *C*-2), 133.81 (s (br), *C*-3), 130.73 (d, $^{4}J_{C\text{-}P}$ = 4.3 Hz, *C*-8,12), 130.61 (d, $^{3}J_{C\text{-}P}$ = 3.4 Hz, *C*-6), 128.43 (s, *C*-5), 127.89 (s, *C*-9,10,11), 127.66 (d, $^{3}J_{C\text{-}P}$ = 5.0 Hz, *C*-4), 47.74 (s (br), CH), 23.50 (s, CH_3) ppm. **^{31}P {^{1}H} NMR** (243 MHz, DCM-d_2): δ = 22.52 (s) ppm. **IR (ATR)**: ν = 3053 (w), 2964 (w), 2925 (w), 1456 (w), 1443 (w), 1424 (w), 1386 (w), 1360 (w), 1191 (w), 1174 (w), 1118 (m), 1071 (s), 1008 (w), 962 (m), 912 (w), 775 (w), 744 (s), 698 (s) cm^{-1}. **HRMS** (EI,

70 eV, MAT95, direct): m/z [M-H]$^+$ Calcd. for $C_{30}H_{31}NP$ 436.21886; Found 436.21914; [M]$^{+\cdot}$ Calcd. for $C_{30}H_{32}NP$ 437.22669; Found 437.22676: **MS** (EI): m/z 437.3 (35%) [M]$^{+\cdot}$, 337.2 (49%) [M-N(*i*Pr)$_2$]$^{+\cdot}$, 183.0 (100%) [M-H,(N(*i*Pr)$_2$),($C_{12}H_9$)]$^+$. **Mp:** 125 °C.

Single crystals were obtained by slow evaporation of an ACN/DCM mixture at 25 °C. Crystal Data for $C_{30}H_{32}NP$ (M = 437.57 g/mol): triclinic, space group P-1, a = 9.4189(3) Å, b = 11.1819(4) Å, c = 12.7140(4) Å, α = 89.0990(10)°, β = 76.1210(10)°, γ = 70.6150(10)°, V = 1223.28(7) Å^3, Z = 2, T = 100.0 K, μ(MoKα) = 0.130 mm^{-1}, D_{calc} = 1.188 g/cm^3, 102866 reflections measured (5.472° ≤ 2Θ ≤ 66.998°), 9585 unique (R_{int} = 0.0282, R_{sigma} = 0.0149), which were used in all calculations. The final R_1 was 0.0333 (I > 2σ(I)) and wR_2 was 0.0960 (all data).

bis(Biphenyl-2-yl)chlorophosphine (**C**)

In a Schlenk flask, **B** (1.00 g, 2.28 mmol) was dissolved in diethyl ether (60 mL). To this a hydrogen chloride solution (8.00 mL, 16.0 mmol, 2.0 M in diethyl ether) was added. The reaction mixture turned directly cloudy and was stirred for 2 h while the reaction progress was monitored by ^{31}P NMR. The reaction mixture was allowed to settle and afterwards transferred into another Schlenk flask using syringe filters. A yellow oil was received after drying (25 °C, 2.2 × 10^{-2} mbar) and used for further steps. For analytical purposes, a part of the reaction mixture (247 mg, 0.67 mmol) was distilled by inert fractional Kugelrohr distillation (180 °C, 3.2 × 10^{-2} mbar) to give the crystalline product (**D**, 86 mg, 0.23 mmol, 34%). Crystals which were suitable for X-ray analysis could be directly taken from the solidified distillate. Due to the high temperature in this process, also oxidation products (phosphinic chloride (^{31}P NMR δ = 34.0 ppm) and phosphine oxides (^{31}P NMR δ = 15.9 ($^1J_{PH}$ = 503.3 Hz) ppm)) were detectable after distillation. **^{1}H NMR** (601 MHz, $CDCl_3$): δ = 7.72 (m, 2H, *H*-3), 7.48–7.40 (m, 4H, *H*-5 and *H*-4), 7.35–7.30 (m, 2H, *H*-10), 7.26 (t, ^3J = 7.6 Hz, 4H, *H*-9,11), 7.22–7.19 (m, 2H, *H*-6), 6.99 (d, ^3J = 7.6 Hz, 4H, *H*-8,12) ppm. **^{13}C {^{1}H} NMR** (151 MHz, $CDCl_3$): δ = 146.79 (d, $^2J_{C\text{-}P}$ = 32.4 Hz, *C*-1), 140.31 (d, $^3J_{C\text{-}P}$ = 6.6 Hz, *C*-7), 137.03 (d, $^1J_{C\text{-}P}$ = 38.9 Hz, *C*-2), 132.52 (d, $^2J_{C\text{-}P}$ = 2.1 Hz, *C*-3), 130.06 (s, *C*-5), 130.01 (d, $^3J_{C\text{-}P}$ = 3.4 Hz, *C*-6), 129.74 (d, $^4J_{C\text{-}P}$ = 4.9 Hz, *C*-8,12), 127.96 (s, *C*-9,11), 127.78 (s, *C*-4), 127.55 (s, *C*-10) ppm. **^{31}P {^{1}H} NMR** (243 MHz, $CDCl_3$): δ = 74.53 (s) ppm. **HRMS** (EI, 70 eV, MAT95, direct): m/z [M-H]$^+$ Calcd. for $C_{24}H_{17}PCl$ 371.07509; Found 371.07512; [M-H,HCl]$^{+\cdot}$ Calcd. for $C_{24}H_{16}P$ 335.09841; Found 355.09838. **MS** (EI): m/z 371.2 (100%) [M-H]$^+$, 335.2 (27%) [M-H,HCl]$^{+\cdot}$, 183.0 (60%) [M-H,HCl),($C_{12}H_9$)]$^+$.

bis(Biphenyl-2-yl)phosphine (**D**)

To a solution of freshly prepared **C** (0.32 mmol) in THF (40 mL), lithium aluminum hydride solution (0.32 mL, 0.32 mmol, 1.0 M in THF) was added at 25 °C. The reaction mixture was stirred for 15 h and the reaction progress was observed via ^{31}P NMR. After completion of the reaction the solvent was removed in vacuo and the residue was dissolved in toluene (2.0 mL) and filtered over Celite. The product was obtained using inert Kugelrohr distillation (130–160 °C, 2.0 × 10^{-3} mbar) and the product was isolated as colorless solid (**D**, 99 mg, 0.29 mmol, 91%). Crystals which were suitable for X-ray analysis were obtained after solidification of the distillate. **^{1}H NMR** (601 MHz, C_6D_6): δ = 7.32 (ddd, ^3J = 7.4, 5.7 Hz, ^4J = 0.9 Hz, 2H, *H*-3), 7.18 (m, 4H, *H*-8,12), 7.16–7.12 (m, 2H, *H*-6), 7.09–7.03 (m, 4H, *H*-5, *H*-9,11 and *H*-10), 7.06 (tt, ^3J = 7.5 Hz, ^4J = 1.1 Hz, 2H, *H*-4), 4.97 (d, $^1J_{P\text{-}H}$ = 223.0 Hz, 1H, P*H*) ppm. **^{13}C {^{1}H} NMR** (151 MHz, C_6D_6): δ = 147.18 (d, $^2J_{C\text{-}P}$ = 16.4 Hz, *C*-1), 142.10 (d, $^3J_{C\text{-}P}$ = 3.3 Hz, *C*-7), 135.55 (d, $^1J_{C\text{-}P}$ = 10.1 Hz, *C*-3), 134.24 (d, $^2J_{C\text{-}P}$ = 15.9 Hz, *C*-2), 129.91 (d, $^3J_{C\text{-}P}$ = 2.7 Hz, *C*-6), 129.91 (d, $^3J_{C\text{-}P}$ = 3.1 Hz, *C*-8,12), 128.27 (s, *C*-5), 127.85 (overlapping with C_6D_6 signal, *C*-9,11, 129.74 (d, $^4J_{C\text{-}P}$ = 3.4 Hz, *C*-4), 127.05 (s, *C*-10) ppm. **^{31}P {^{1}H} NMR** (243 MHz, $CDCl_3$): δ = −53.87 (s) ppm. **^{31}P NMR** (243 MHz, $CDCl_3$): δ = −53.87 (d, $^1J_{P\text{-}H}$ = 223.0 Hz) ppm. **HRMS** (EI, 70 eV, MAT95, direct): m/z [M-H]$^+$ Calcd. for $C_{24}H_{18}P$ 337.11406; Found 337.11412. **MS** (EI, 120 °C): m/z 337.1 (80%) [M-H]$^+$, 335.2 (27%) [M], 183.0 (100%) [M-H),($C_{12}H_9$)]$^+$.

Crystal Data for $C_{24}H_{19}P$ (M = 338.36 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 7.5529(2) Å, b = 20.0280(6) Å, c = 11.7785(3) Å, β = 94.2750(10)°, V = 1776.77(8) Å^3, Z = 4, T = 100.0 K, μ(MoKα) = 0.157 mm^{-1}, D_{calc} = 1.265 g/cm^3, 36505 reflections measured

(5.346° ≤ 2Θ ≤ 57°), 4485 unique (R_{int} = 0.0402, R_{sigma} = 0.0225), which were used in all calculations. The final R_1 was 0.0389 (I > 2σ(I)) and wR_2 was 0.0912 (all data).

bis(Biphenyl-2-yl)phosphine borane (**F**)

Method A: In a Schlenk flask, **D** (169 mg, 0.50 mmol) was dissolved in THF (20 mL). To this the borane solution (0.50 mL, 0.50 mmol, 1.0 M in THF) was slowly added. The reaction was stirred at 50 °C for 2 h. After removal of the solvent the residue was mixed with *n*-hexane (20 mL) and stirred for 30 min. Afterwards, the white cloudy solution was allowed so settle for 14 h. The supernatant was transferred through syringe filters into a another Schlenk flask. The flask was stored at −8 °C giving a cloudy color to the glass surface. After 6 days the solution was decanted, and the white solids were collected. The recrystallization from *n*-hexane (50 mL) gave colorless crystals (**F**, 85 mg, 0.24 mmol, 48%). These crystals were suitable for X-Ray analysis.

Method B: To a solution of $LiBH_4$ (6.5 mg, 0.30 mmol) in diethyl ether (5.0 mL), a solution of **C** (49.4 mg, 0.131 mmol) in THF (5.0 mL) was added dropwise at 0 °C. Reaction progress was monitored with ^{31}P NMR and visible signals for the product were recognized. After 1 h of stirring at 25 °C, the solvent was removed, and the reaction mixture was dissolved in *n*-hexane (10 mL) at 60 °C. This solution was transferred through syringe filters into another Schlenk flask and stored in a freezer (−30 °C) in the glove box to obtain colorless crystals (**F**, 44 mg, 0.125 mmol, 94%). **^{1}H NMR** (601 MHz, C_6D_6): δ = 7.89 (dd, ^3J = 12.8, 7.6 Hz, 2H, *H*-3), 7.12–6.98 (m, 10H, *H*-4,5 and *H*-9,10,11), 6.95 (dd, ^3J = 7.6, ^4J = 3.3 Hz, 2H, *H*-6), 6.84 (s (br), 4H, *H*-8,12), 6.30 (dq, $^1J_{P\text{-}H}$ = 396.4 Hz, $^2J_{PH\text{-}BH3}$ = 6.7 Hz, 1H, P*H*), 2.13 (d, $^1J_{BH}$ = 126.9 Hz, 3H, BH_3) ppm. **^{13}C {^{1}H} NMR** (151 MHz, C_6D_6): δ = 146.79 (d, $^2J_{C\text{-}P}$ = 2.8 Hz, *C*-1), 140.21 (d, $^3J_{C\text{-}P}$ = 3.6 Hz, *C*-7), 134.51 (d, $^3J_{C\text{-}P}$ = 15.2 Hz, *C*-3), 130.87 (d, $^4J_{C\text{-}P}$ = 2.4 Hz, *C*-5), 130.53 (d, $^3J_{C\text{-}P}$ = 6.2 Hz, *C*-6), 129.35 (s, *C*-8,12), 128.21 (overlap with benzene, *C*-9,11), 127.72 (s, *C*-10), 127.66 (within $^3J_{C\text{-}P}$ = 11.8 Hz, *C*-4), 126.96 (d, $^1J_{C\text{-}P}$ = 54.5 Hz, *C*-2) ppm. **^{11}B {^{1}H} NMR** (193 MHz, C_6D_6): δ = −36.69 (s, br) ppm. **^{11}B NMR** (193 MHz, C_6D_6): δ = −36.69 (d, $^1J_{B\text{-}H}$ = 52.7 Hz) ppm. **^{31}P {^{1}H} NMR** (243 MHz, C_6D_6): δ = −14.09 (s) ppm. **^{31}P NMR** (243 MHz, C_6D_6): δ = −14.09 (d, $^1J_{P\text{-}H}$ = 397.9 Hz) ppm. **HRMS** (ESI, Impact II, DCM/acetonitrile): *m*/*z* $[M+K]^+$ Calcd. for $C_{24}H_{22}PBK$ 391.11838; Found 391.11864, $[(M\text{-}BH_3)+K]^+$ Calcd. for $C_{24}H_{18}PK$ 377.08560; Found 377.08567, $[M+Na]^+$ Calcd. for $C_{24}H_{22}PBNa$ 375.14444; Found 375.14472, $[(M\text{-}BH_3)+Na]^+$ Calcd. for $C_{24}H_{19}PNa$ 361.11166; Found 361.11159.

Single crystals were obtained after cooling a saturated hexane/benzene solution to −10 °C for several days. Crystal Data for $C_{24}H_{22}BP$ $(C_6H_6)_{0.5}$ (M = 391.25 g/mol): monoclinic, space group $P2_1/c$, a = 11.8705(5) Å, b = 10.2205(4) Å, c = 17.8670(7) Å, β = 93.7090(10)°, V = 2163.13(15) Å^3, Z = 4, T = 100.0 K, μ(MoKα) = 0.137 mm^{-1}, D_{calc} = 1.201 g/cm^3, 78277 reflections measured (4.594° ≤ 2Θ ≤ 59.996°), 6303 unique (R_{int} = 0.0291, R_{sigma} = 0.0146), which were used in all calculations. The final R_1 was 0.0352 (I > 2σ(I)) and wR_2 was 0.0974 (all data).

Lithium *bis*(biphenyl-2-yl)phosphide (**E**)

In the glove box, phosphine **D** (20.0 mg, 59.7 μmol) was dissolved in benzene (10 mL) and *n*-butyllithium (0.50 mL, 125 μmol, 2.5 M in hexanes) was added at 25 °C. The reaction mixture was stirred for 2 h and the supernatant was filtered through syringe filters. The solution was crystallized by over layering the solution with *n*-hexane to give the product as orange solids (E, 19.7 mg, 58.9 μmol, 99%). **^{1}H NMR** (601 MHz, C_6D_6:THF-d_8 80:20): δ = 7.32 (dd, ^3J = 7.4, 5.7 Hz, ^4J = 1.4 Hz, 2H, *H*-3), 7.18 (^3J = 7.6 Hz, 4H, *H*-8,12), 7.09–7.03 (m, 4H, *H*-6 and *H*-9,11), 6.98 (t, ^3J = 7.0 Hz, 2H, *H*-4), 6.94 (t, ^3J = 7.7 Hz, 2H, *H*-10), 6.85 (t, ^3J = 7.8 Hz, 2H, *H*-5) ppm. **^{13}C {^{1}H} NMR** (151 MHz, C_6D_6:THF-d_8 80:20): δ = 153.92 (d, $^1J_{C\text{-}P}$ = 49.6 Hz, *C*-2), 146.45 (d, $^3J_{C\text{-}P}$ = 3.1 Hz, *C*-7), 142.10 (d, $^3J_{C\text{-}P}$ = 20.6 Hz, *C*-1), 135.55 (s, *C*-3), 129.67 (d, $^3J_{C\text{-}P}$ = 5.8 Hz, *C*-8,12), 129.67 (d, $^3J_{C\text{-}P}$ = 2.1 Hz, *C*-6), 126.96 (s, *C*-9,11), 125.65 (s, *C*-10), 125.06 (s, *C*-4), 120.45 (s, *C*-5) ppm. **^{9}Li NMR** (233 MHz, C_6D_6:THF-d_8 80:20): δ = −0.06 (s) ppm. **^{31}P NMR** (243 MHz, C_6D_6:THF-d_8 80:20): δ = −33.39 (s) ppm. **^{31}P NMR** (243 MHz, C_6D_6): δ = −52.41 (s) ppm.

Single crystals were obtained from evaporation of a sat. benzene solution in the glovebox. Crystal Data for ($C_{24}H_{18}LiP$) (M = 344.29 g/mol): monoclinic, space group $P2_1/n$, a = 12.6051(9) Å, b = 16.0123(12) Å, c =18.4340(12) Å, β = 104.712(2)°, V = 3598.7(4) $Å^3$, Z = 8, T = 100.0 K, μ(MoKα) = 0.156 mm^{-1}, D_{calc} = 1.271 g/cm^3, 108594 reflections measured ($4.2° \leq 2\Theta \leq 61.016°$), 10966 unique ($R_{int}$ = 0.0504, R_{sigma} = 0.0288), which were used in all calculations. The final R_1 was 0.0447 ($I > 2\sigma(I)$) and wR_2 was 0.1170 (all data).

bis(Biphenyl-2-yl)(trimethylsilyl)phosphine (**G**)

To a solution of **D** (63 mg, 59.0 μmol) in benzene (2.0 mL), *n*-butyllithium (47.0 μL, 118 μmol, 2.5 M in hexanes) was added and the reaction mixture was stirred at 25 °C for 2 h, giving an intense orange color. To this solution, trimethylsilyl chloride (100 μL, 786 μmol) was added in one portion. The reaction mixture was allowed to settle and the supernatant solution was transferred to another flask. After removal of all volatiles and drying (25 °C, 2 h, 1×10^{-3} mbar), a white waxy solid was obtained (**G**, 22 mg, 53.8 μmol, 91%). **^{1}H NMR** (601 MHz, C_6D_6): δ = 7.60–7.57 (m, 2H, *H*-3), 7.23–7.20 (m, 4H, *H*-8,12), 7.19–7.16 (m, overlapping with residual benzene signals, 2H, *H*-6), 7.16–7.12 (m, 4H, *H*-9,11), 7.11–7.07 (m, 4H, *H*-5 and *H*-10), 7.05 (td, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 2H, *H*-4), -0.03 (d, $^3J_{P\text{-}Si(CH3)3}$ = 4.50 Hz, 9H, CH_3) ppm. **^{13}C {^{1}H} NMR** (151 MHz, C_6D_6): δ = 148.49 (d, $^2J_{C\text{-}P}$ = 26.0 Hz, *C*-1), 143.28 (d, $^3J_{C\text{-}P}$ = 4.9 Hz, *C*-7), 136.32 (d, $^1J_{C\text{-}P}$ = 10.1 Hz, *C*-3), 135.82 (d, $^2J_{C\text{-}P}$ = 21.0 Hz, *C*-2), 131.31 (d, $^3J_{C\text{-}P}$ = 4.9 Hz, *C*-6), 130.59 (d, $^3J_{C\text{-}P}$ = 3.9 Hz, *C*-8,12), 128.35 (s, *C*-10), 127.99 (s, overlapping with C_6D_6 signal, *C*-9,11 and *C*-5), 127.10 (d, $^4J_{C\text{-}P}$ = 5.3 Hz, *C*-4), −0.48 (d, $^2J_{C\text{-}P}$ = 12.7 Hz, P–Si(CH_3)$_3$ ppm. **^{29}Si {^{1}H} NMR** (243 MHz, C_6D_6): δ = 1.90 (d, $^2J_{P\text{-}Si}$ = 25.4 Hz) ppm. **^{31}P {^{1}H} NMR** (243 MHz, C_6D_6): δ = −69.77 (s) ppm. **^{31}P NMR** (243 MHz, C_6D_6): δ = −69.77 (dec., $^3J_{P\text{-}Si(CH3)3}$ = 4.5 Hz) ppm. **HRMS** (EI, 70 eV, MAT95, indirect in *n*-hexane): *m*/*z* $[M\text{-}H]^+$ Calcd. for $C_{27}H_{27}NPSi$ 409.15359; Found 409.15359. **MS** (EI): *m*/*z* 409.3 (10%) $[M]^{+\cdot}$, 337.2 (14%) [M-TMS]$^+$, 183.0 (45%) [M-H,(TMS),($C_{12}H_9$)]$^+$, 73.1 (100%) [TMS] $^+$.

bis(Biphenyl-2-yl)(trimethyltin)phosphine (**H**)

The synthesis was conducted similar to [36]: In a glovebox, an inert NMR tube was charged with **D** (10.0 mg, 29.6 μmol) and dimethylamino(trimethyl)tin (15.0 mg, 72.0 μmol). To this, C_6D_6 (0.5 mL) was added and the tube was shaken intensively. The reaction progress was followed by ^{31}P NMR spectroscopy. Since the wanted species was not totally formed the tube was rotated for 2 h at a rotary evaporator. Afterwards the reaction mixture was dried *in vacuo* (25 °C,24 h, 10^{-3} mbar) and the resulting wax (**H**, 14.8 mg, 29.5 μmol, 99%) was isolated. **^{1}H NMR** (601 MHz, C_6D_6): δ = 7.59–7.53 (m, 2H, *H*-3), 7.44–7.39 (m, 4H, *H*-8,12), 7.19–7.16 (m, 2H, *H*-6), 7.13–7.09 (m, 4H, *H*-9,11), 7.09–7.02 (m, 4H, *H*-4, *H*-5 and *H*-10), −0.03 (d, $^3J_{P\text{-}SnCH33}$ = 1.70 Hz, 9H, CH_3) ppm. **^{13}C {^{1}H} NMR** (151 MHz, C_6D_6): δ = 147.75 (d, $^2J_{C\text{-}P}$ = 25.6 Hz, *C*-1), 143.00 (d, $^3J_{C\text{-}P}$ = 4.7 Hz, *C*-7), 137.62 (d, $^1J_{C\text{-}P}$ = 10.1 Hz, *C*-2), 136.68 (s, *C*-3), 131.17 (d, $^3J_{C\text{-}P}$ = 3.9 Hz, *C*-6), 130.12 (d, $^3J_{C\text{-}P}$ = 5.0 Hz, *C*-8,12), 128.32 (d, $^3J_{C\text{-}P}$ = 7.7 Hz, *C*-10), 127.78 (s, overlapping with C_6D_6 signal, *C*-9,11 and *C*-5), 127.45 (d, $^4J_{C\text{-}P}$ = 42.4 Hz, *C*-4), −7.78 (d, $^2J_{C\text{-}P}$ = 6.0 Hz, P-Sn(CH_3)$_3$) ppm. **^{31}P {^{1}H} NMR** (243 MHz, C_6D_6): δ = −61.98 (s, $^1J_{P\text{-}Sn}$ satellites: 661 Hz) ppm. **^{119}Sn{^{1}H} NMR** (224 MHz, C_6D_6): δ = 0.67 (d, $^1J_{P\text{-}Sn}$ = 661.8 Hz) ppm. **HRMS** (EI, 70 eV, MAT95, indirect in *n*-hexane): *m*/*z* $[M\text{-}H]^+$ Calcd. for $C_{27}H_{26}P^{116}Sn$ 497.07846; Found 497.07859, [M-CH_3]$^+$ Calcd. for $C_{26}H_{24}P^{116}Sn$ 483.06280; Found 483.06283. **MS** (EI, giving for ^{120}Sn): *m*/*z* 502.2 (35%) $[M]^{+\cdot}$, 487.2 (22%) [M-Me]$^+$, 457.1 (3%) $[M\text{-}Me_3]^{+\cdot}$, 337.2 (30%) [M-H,($SnMe_3$)]$^+$, 183.0 (100%) [M-H,($SnMe_3$),($C_{12}H_9$)]$^{+\cdot}$.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/inorganics9110082/s1, all NMR spectra, Table S1: Overview of essential crystal structure details for B, D, E and F. CCDCs 2106887, 2106888, 2106889 and 2108753 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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