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Traditio et Innovatio

Reactivity of Bhp-PH₂: Phosphines with Flexible Steric Bulk

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Rostock, September 13, 2018

The work presented in this thesis was carried out between May, 2018 and August, 2018 in the research group of Prof. Dr. Axel Schulz, holder of the chair for Inorganic Chemistry at the Institute of Chemistry of the University of Rostock.

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I hereby declare that this thesis and the work presented in it are my own and that this thesis is the result of my own original research. I confirm that I have acknowledged all main sources of help and that I have clearly indicated the presence of all material I have quoted from other sources. This thesis has not been submitted for any other qualification or at any other institution.

Rostock, September 13, 2018

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Tim Suhrbier

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Lastly, I want to thank my family for financial support and always putting trust in my decisions, which made me the person I am today, for better or for worse.

Summary

In this work, the synthesis of the novel phosphine Bhp-PH₂ was approached starting from 4-*tert*-butylaniline instead of 4-methylaniline. Consecutive reactions of the phosphine ^{Me}Bhp-PX₂ (X = Cl, I) with [PCO]⁻ and of the phosphine ^{Me}Bhp-PH₂ with pnictogen trichlorides proved to be quite unselective and gave complex mixtures with products only being partly identified. The attempted synthesis of secondary phosphines resulted in similar outcomes, with isolation being complicated by the presence of a variety of products with similar solubility.

In an empirical investigation of DFT computations, geometric optimizations and NMR calculations could be evaluated in a quantitative manner and specific combinations of functionals and basis sets with the highest accuracy can be recommended for future applications.

Zusammenfassung

Für diese Arbeit wurde das neuartige Phosphin Bhp-PH₂ ausgehend von 4-*tert*-Butylanilin analog zu bereits erarbeiteten Vorschriften synthetisiert. Anschließende Folgereaktionen des Phosphins ^{Me}Bhp-PX₂ (X = Cl, I) mit [PCO]⁻, sowie des Phosphins ^{Me}Bhp-PH₂ mit Pnictogentrichloriden führten zu komplexen Produktgemischen, von denen lediglich einige Komponenten identifiziert werden konnten. Die angestrebte Synthese sekundärer Phosphine führte zu ähnlichen Ergebnissen, weshalb die gewünschten Produkte aufgrund der Anwesenheit mehrerer Verbindungen mit vergleichbaren Löslichkeiten nicht isoliert werden konnten.

In einer auf empirischen Daten beruhenden quantitativen Analyse von DFT-Rechenmethoden wurden verschiedene Funktionale und Basissätze hinsichtlich ihrer Präzision bei der Berechnung von geometrischen und NMR-Daten getestet. Ein Vergleich mit experimentellen Werten gab Aufschluss über geeignete Kombinationen für zukünftige Berechnungen.

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List of Abbreviations

Ad	Adamantyl	exptl.	experimental
ATR	Attenuated Total Reflectance	HF	HARTREE-FOCK
Bbp	2,6-Bis(bis(trimethylsilyl)methylphenyl	Hyp	Tris(trimethylsilyl)silyl
Bhp	2,6-Bis(benzhydryl)phenyl	<i>i</i> Pr	<i>iso</i> -Propyl
BINAP	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl	IR	Infrared
BTMSA	Bis(trimethylsilyl)amide	IUPAC	International Union of Pure and Applied Chemistry
calcd.	calculated	<i>J</i>	Coupling Constant
CAMP	Cyclohexyl- <i>o</i> -anisylmethylphosphane	<i>m</i>	medium (IR), Multiplet (NMR)
Cp*	Pentamethylcyclopentadienyl	<i>m</i>	<i>meta</i>
CPU	Central Processing Unit	Me	Methyl
Cy	Cyclohexyl	^{Me} Bhp	2,6-Benzhydryl-4-methylphenyl
δ	Chemical Shift	Mes	2,4,6-Trimethylphenyl
d	Doublet (NMR)	Mes*	2,4,6-Tris(<i>tert</i> -butyl)phenyl
DBU	1,8-Diazabicyclo(5.4.0)undec-7-ene	NMR	Nuclear Magnetic Resonance
DFT	Density Functional Theory	<i>o</i>	<i>ortho</i>
DIBAL	Diisobutylaluminium hydride	ORTEP	Oak Ridge Thermal Ellipsoid Plot
DIOP	<i>O</i> -Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane	<i>p</i>	<i>para</i>
Dipp	2,6-Bis(isopropyl)phenyl	Ph	Phenyl
Dmp	2,6-Dimethylphenyl	ppm	Parts per Million
Dph	2,6-Diphenylphenyl	<i>s</i>	strong (IR), Singlet (NMR)
Et	Ethyl	<i>t</i>	Triplet (NMR)
<i>et al.</i>	<i>et alii/aliae</i> (and others)	<i>t</i>	tertiary

Tbs	Tris(<i>tert</i> -butyl)silyl
<i>t</i> Bu	<i>tert</i> -Butyl
Ter	2,6-Bis(2,4,6-trimethylphenyl)-phenyl
Ter*	2,6-Bis(2,4,6-tris(<i>tert</i> -butyl)phenyl)phenyl
Ter†	2,6-Bis(2,4,6-tris(<i>iso</i> -propyl)phenyl)phenyl
Tis	Tris(<i>isopropyl</i>)silyl
Tripp	2,4,6-Tris(<i>isopropyl</i>)phenyl
Ttm	Tris(trimethylsilyl)-methyl
$\tilde{\nu}$	Wavenumber

Units of measurement

The International System of Units (SI) is generally used for physical quantities. Deviating units are displayed in the following table, including their unit names and their conversions.

Physical quantity	Unit symbol	Unit name	Conversion
Amount of substance	mmol	millimole	$1 \text{ mmol} = 10^{-3} \text{ mol}$
Energy	eV	electronvolt	$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$
Frequency	MHz	megahertz	$1 \text{ MHz} = 10^6 \text{ s}^{-1}$
	Hz	hertz	$1 \text{ Hz} = 1 \text{ s}^{-1}$
Length	Å	ångström	$1 \text{ Å} = 10^{-10} \text{ m}$
Mass	g	gram	$1 \text{ g} = 10^{-3} \text{ kg}$
Temperature	°C	degrees celsius	$\{\theta\}_{\text{C}} = \{T\}_{\text{K}} - 273.15$
Time	d	day	$1 \text{ d} = 86,400 \text{ s}$
	h	hour	$1 \text{ h} = 3,600 \text{ s}$
Volume	mL	milliliter	$1 \text{ mL} = 10^{-6} \text{ m}^3$
Wavenumber	cm^{-1}	reciprocal centimeter	$1 \text{ cm}^{-1} = 100 \text{ m}^{-1}$

1. Aim and Motivation

The previously synthesized sterically demanding phosphine $^{\text{Me}}\text{Bhp-PH}_2$ (**1**) includes an organic substituent, which exhibits a feature that can be described as flexible bulk.^[1] Due to the rotational freedom within the benzhydryl groups located in *meta*-position, the two phenyl groups can effectively shield the central phosphorus atom from other molecules, while the hydrogen atom is directed towards it (Figure 1).

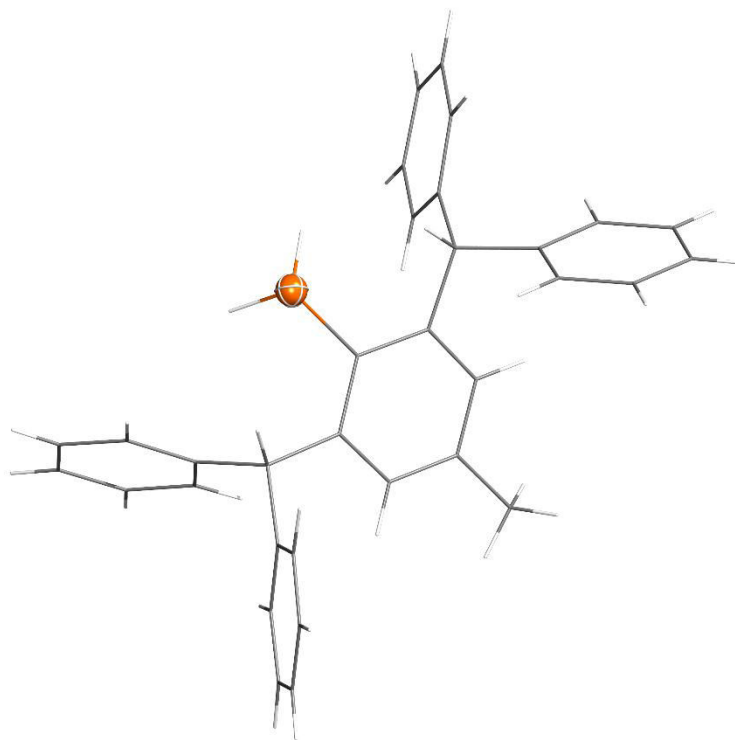


Figure 1. ORTEP depiction of the single-crystal structure of $^{\text{Me}}\text{Bhp-PH}_2$ (**1**). Thermal ellipsoids set at 50 % probability at 150(2) K. The Bhp moiety is displayed as wireframe.^[1]

In the first part of this work, the reactivity of **1** and its halogenated precursor $^{\text{Me}}\text{Bhp-PX}_2$ (**2**) was to be investigated and compared to other sterically demanding primary phosphines. Therefore, reactions with the phosphorus nucleophile $[\text{PCO}]^-$ and pnictogen trichloride compounds of the type ECl_3 ($\text{E} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) were to be carried out.

In the second part, a variety of different secondary phosphines and amines of the type $(^{\text{R}}\text{Bhp})_2\text{EX}$ ($\text{R} = \text{Me}, t\text{Bu}$; $\text{E} = \text{N}, \text{P}$; $\text{X} = \text{H}, \text{Cl}, \text{I}$) were to be prepared and isolated. The future goal of this is to create precursor structures, with respect to activating small molecules.

Due to the increasing size of the molecules bearing two substituents, isolation of the intended products from possible mixtures was to be tried based on differing solubilities.

In the last part of this thesis, a great number of DFT computations with varying methods and basis sets were to be carried out, utilizing a test set of pnictogen systems from our group. A quantitative evaluation was supposed to give an overview of the most suitable combinations for future calculations, especially with respect to NMR spectroscopic data.

2. Introduction

2.1 Nomenclature of Phosphorus Compounds

The nomenclature of phosphorus compounds still remains a highly debated topic and whole book chapters deal with this issue.^[2] A distinction is made by the IUPAC, which defines the two terms as follows:^[3]

- phosphines: *“ PH_3 and compounds derived from it by substituting one, two or three hydrogen atoms by hydrocarbyl groups R_3P , RPH_2 , R_2PH and R_3P ($R \neq H$) are called primary, secondary and tertiary phosphines, respectively. A specific phosphine is preferably named as a substituted phosphane, e.g. CH_3PH_2 methylphosphane.”*
- phosphanes: *“The saturated hydrides of tervalent phosphorus having the general formula P_nH_{n+2} . Individual members having an unbranched phosphorus chain are named phosphane, diphosphane, triphosphane, etc. The name of a saturated hydride of phosphorus wherein one or more phosphorus atoms have a bonding number of 5 is formed by prefixing locants and λ^5 symbols to the name of the corresponding phosphane. Hydrocarbyl derivatives of PH_3 belong to the class phosphines.”*

While “phosphine” should apparently be used for PH_3 derivatives with aliphatic or aromatic substituents, it is simultaneously stated that a specific compound should be dubbed a “phosphane”. “Phosphanes” should only refer to derivatives containing solely phosphorus and hydrogen. The two definitions are still kind of contradictory and do not resolve all issues.

A simple research in SciFinder reveals that the term “phosphane” was not used in publications until mid-20th century. Also, the number of publications using the term “phosphine” today is still 30 times higher than the alternative name (Figure 2).^[4] Obviously, more publications are dealing with these phosphorus compounds in general, rather than specific ones, so these numbers are only moderately representative.

In an attempt to adapt to regulations, compounds of the type R_n-PH_{3-n} ($n = 1-3$) will be called “phosphines” in the following work. Whenever a specific compound is discussed, “phosphane” will be used in the name.

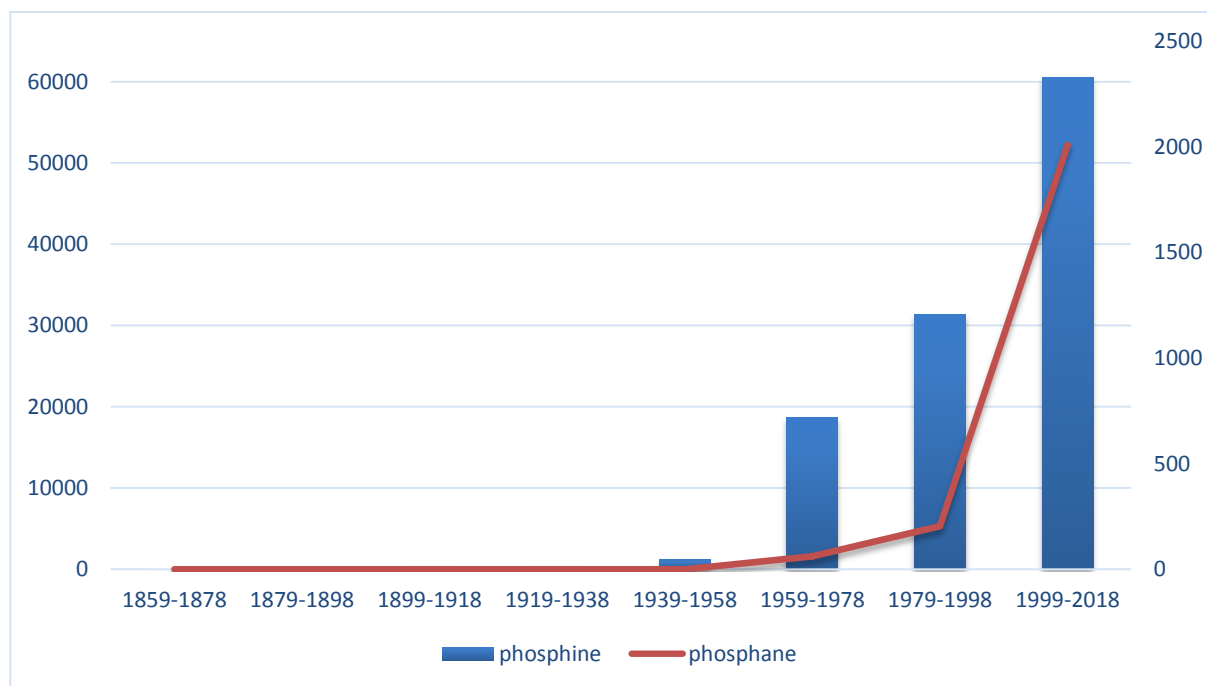


Figure 2. Number of publications using the terms “*phosphine*” (primary Y-axis) and “*phosphane*” (secondary Y-axis).^[4]

2.2 Phosphines Substituted with Sterically Demanding Groups

The terms “*steric hindrance*” and “*steric demand*” are often associated with homogeneous catalysis, where they refer to comparably bulky, mostly organic ligands, bonded to a central transition metal, resulting in selective reactivity.^[5] The IUPAC defines “*steric effect*” as follows:^[3]

“The effect on a chemical or physical property (structure, rate or equilibrium constant) upon introduction of substituents having different steric requirements. The steric effect in a reaction is ascribed to the difference in steric energy between, on the one hand, reactants and, on the other hand, a transition state (or products). A steric effect on a rate process may result in a rate increase ('steric acceleration') or a decrease ('steric retardation'). [...] Steric effects arise from contributions ascribed to strain as the sum of (1) non-bonded repulsions, (2) bond angle strain and (3) bond stretches or compressions. [...]”

Within the field of homogeneous catalysis, trivalent organophosphorus compounds hold an especially important place, as evidenced by the tris(cyclohexyl)phosphane ligand **3** in GRUBBS’

catalysts, earning their eponymous chemist a NOBEL Prize in Chemistry in 2005 (Figure 3). The phosphorus compounds are either used as ligands or they are catalytically active themselves.^[5,6]

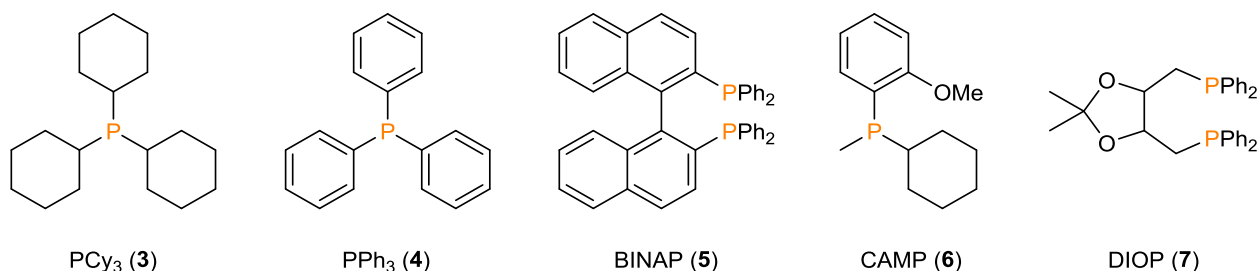


Figure 3. Selection of trivalent organophosphorus compounds used in catalysis (molecules displayed without chirality).

The use in catalysis relies on a higher inversion barrier of phosphines as compared to amines, facilitating asymmetric transformations.^[6] Apart from these applications, bulky organic substituents at pnictogen centers can enable pathways to otherwise unstable compounds. Prominent examples are the isolated salts [Mes*NP][AlCl₄] and [Mes*NA][GaCl₄], which contain terminal triple bonds.^[7,8] A way of comparing sterical demand is represented by the cone angle, which was introduced by TOLMAN in 1977.^[9] He used a monophosphine ligand bonded to a Nickel center (Ni–P distance 2.28 Å) to define an angle as a measure of steric bulk. However, the angle obviously depends on the distance between the two considered atoms and is not really meaningful when used for other bonds. A mathematically improved approach for calculating cone angles was published by ALLEN *et al.* in 2013.^[10] They computed the exact cone angles for more than 275 structures with DFT methods, using a variety of transition metals and phosphine and amine ligands. In 2014, SCHULZ reported on a computational analysis of common bulky substituents and also provided a fitted polynomial equation that can be used to calculate cone angles for any element (Equation 1).^[11]

$$\Theta = ax^4 + bx^3 + cx^2 + dx + e$$

Equation 1. Fitted polynomial for the calculation of the cone angle Θ , where a , b , c , d and e represent substituent-dependent values and x equals the sum of covalent radii of any element E and the atom Z of the substituent, which is attached to E .^[11]

Using this knowledge, the cone angles for a selection of sterically demanding primary phosphines were calculated, which allows for an estimation of monodentate bulk (Figure 4).

2. Introduction

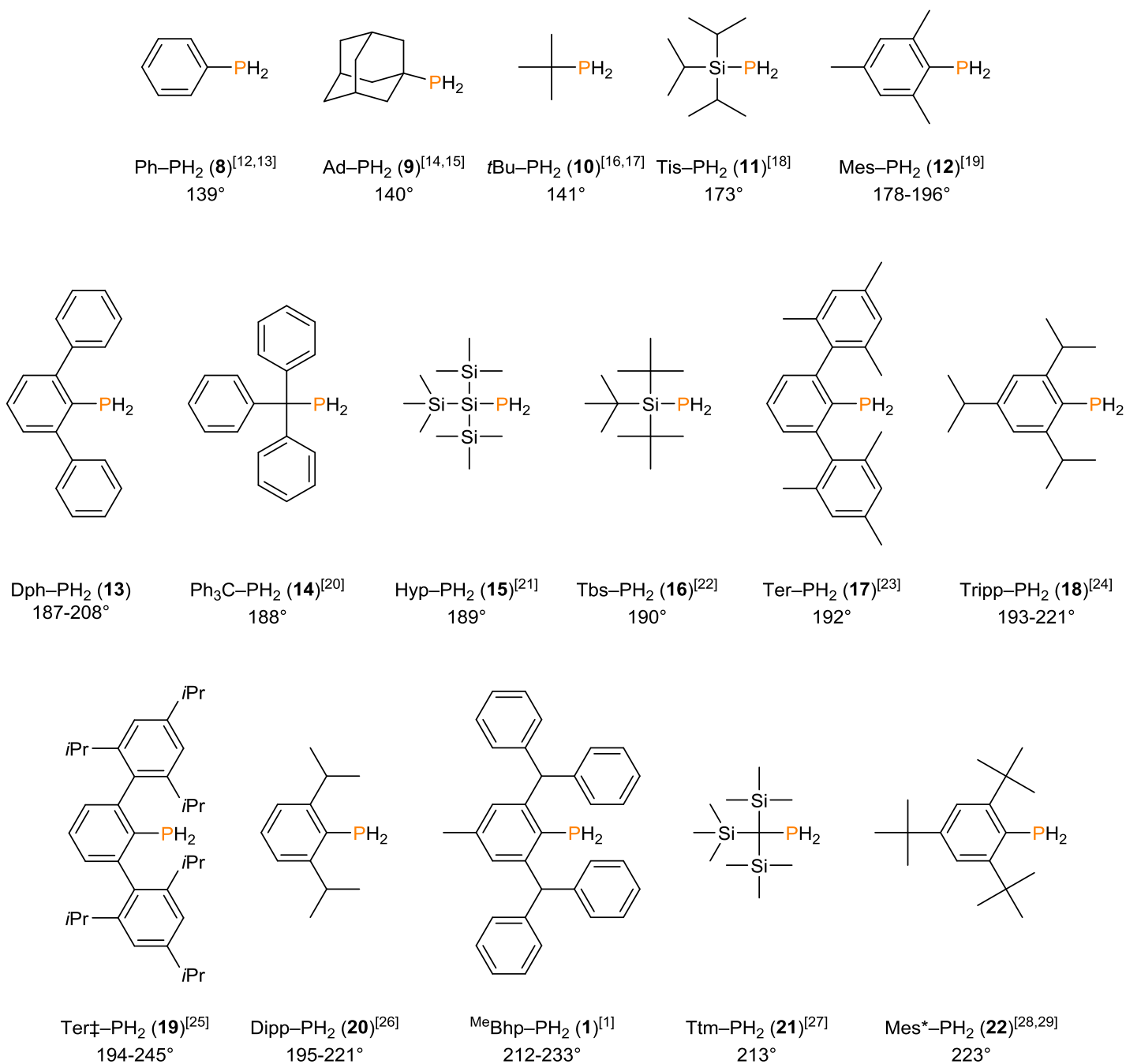
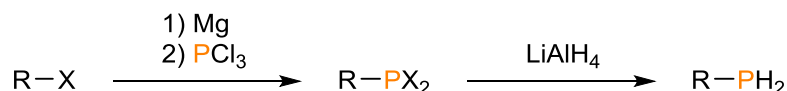
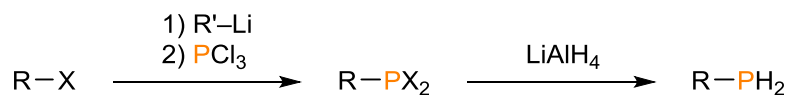


Figure 4. Selected primary phosphines with bulky substituents and their cone angles with respect to the phosphorus atom (a range is given if different conformers were considered).

Since the equation is derived from extrapolation and merely uses the sum of covalent radii, which does not consider the influence of inductive or resonance effects on the bonding situation, the obtained values are only an orientation. Furthermore, the rotational flexibility within the substituent moieties can cause significant differences in solution and lead to different steric effects. As indicated by the references in Figure 4, almost all displayed phosphines are already known to literature. Preparation procedures quite differ, but the most common routes are *via* GRIGNARD intermediates and organolithium salts (Scheme 1 and 2).

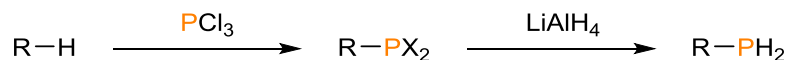


Scheme 1. Synthesis of primary phosphines (R = *t*Bu, Mes, Ph₃C, Tripp, Dipp; X = H, Cl, Br).^[16,17,19,20,24,26]



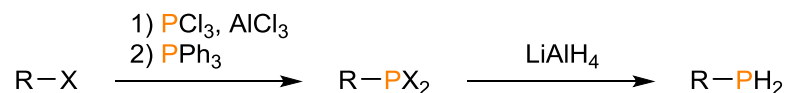
Scheme 2. Synthesis of primary phosphines (R = Ter[‡], ^{Me}Bhp, Mes^{*}; X = Br, I; R' = *n*Bu, *t*Bu).^[25,1,28,29]

Phosphines **8** and **17** can be directly prepared from their unsubstituted precursors, although a LEWIS acid like AlCl₃ has to be added in case of the former reaction (Scheme 3).



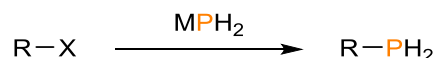
Scheme 3. Synthesis of primary phosphines (R = Ph, Ter; X = Cl, Br).^[12,13,23]

A slight variation of this route can be used for the adamantyl derivate **9**, the only difference being the additional use of triphenylphosphane (Scheme 4).

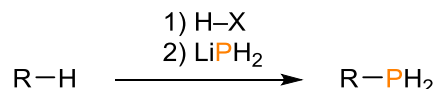


Scheme 4. Synthesis of primary phosphines (R = Ad; X = Cl, Br).^[14,15]

For the majority of silyl-substituted phosphines, alkali phosphides are used to introduce a Si-P bond (Scheme 5 and 6).

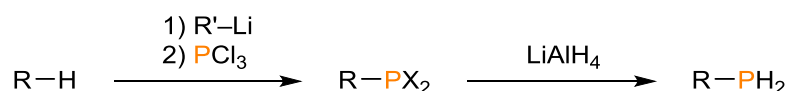


Scheme 5. Synthesis of primary phosphines (R = Tis, Hyp; X = Cl; M = Li, Na).^[18,21]



Scheme 6. Synthesis of primary phosphines (R = Tbs; X = OTf).^[22]

The only exception is tris(trimethylsilyl)methylphosphane (**21**), which is also prepared by using organolithium compounds, but in contrast to Scheme 2, can be carried out with the unsubstituted starting material (Scheme 7).



Scheme 7. Synthesis of primary phosphines (R = Ttm; R' = Me; X = Cl).^[27]

Halogen interchange in the intermediary dihalophosphines is common, but does not pose a problem in subsequent reactions. The final transformation to primary phosphines can always be achieved with LiAlH₄, regardless of the size or structure of the bulky substituent R.

Apart from the discussed phosphines in Figure 4, several other examples may be synthesized according to similar reaction protocols (Figure 5).

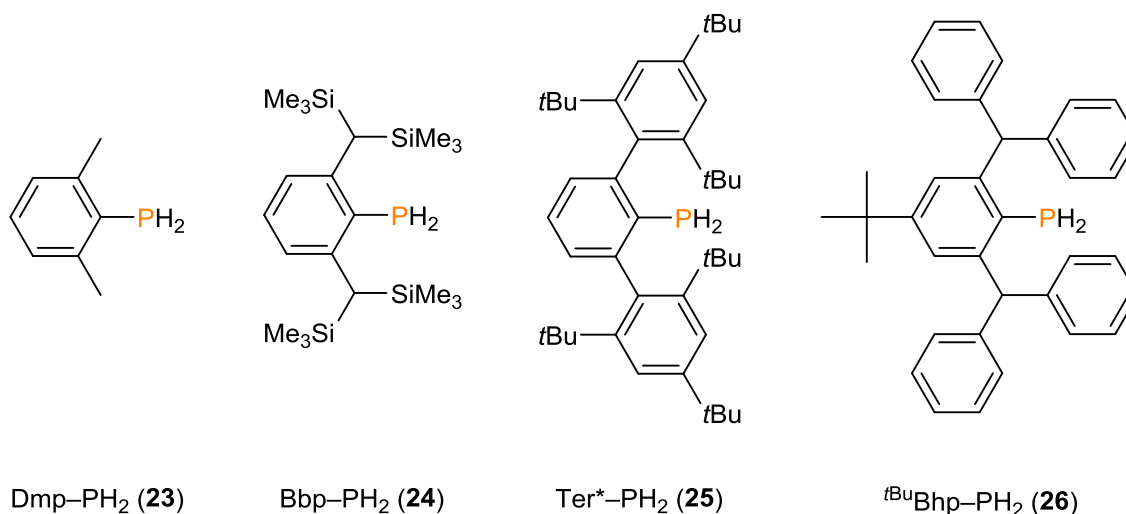


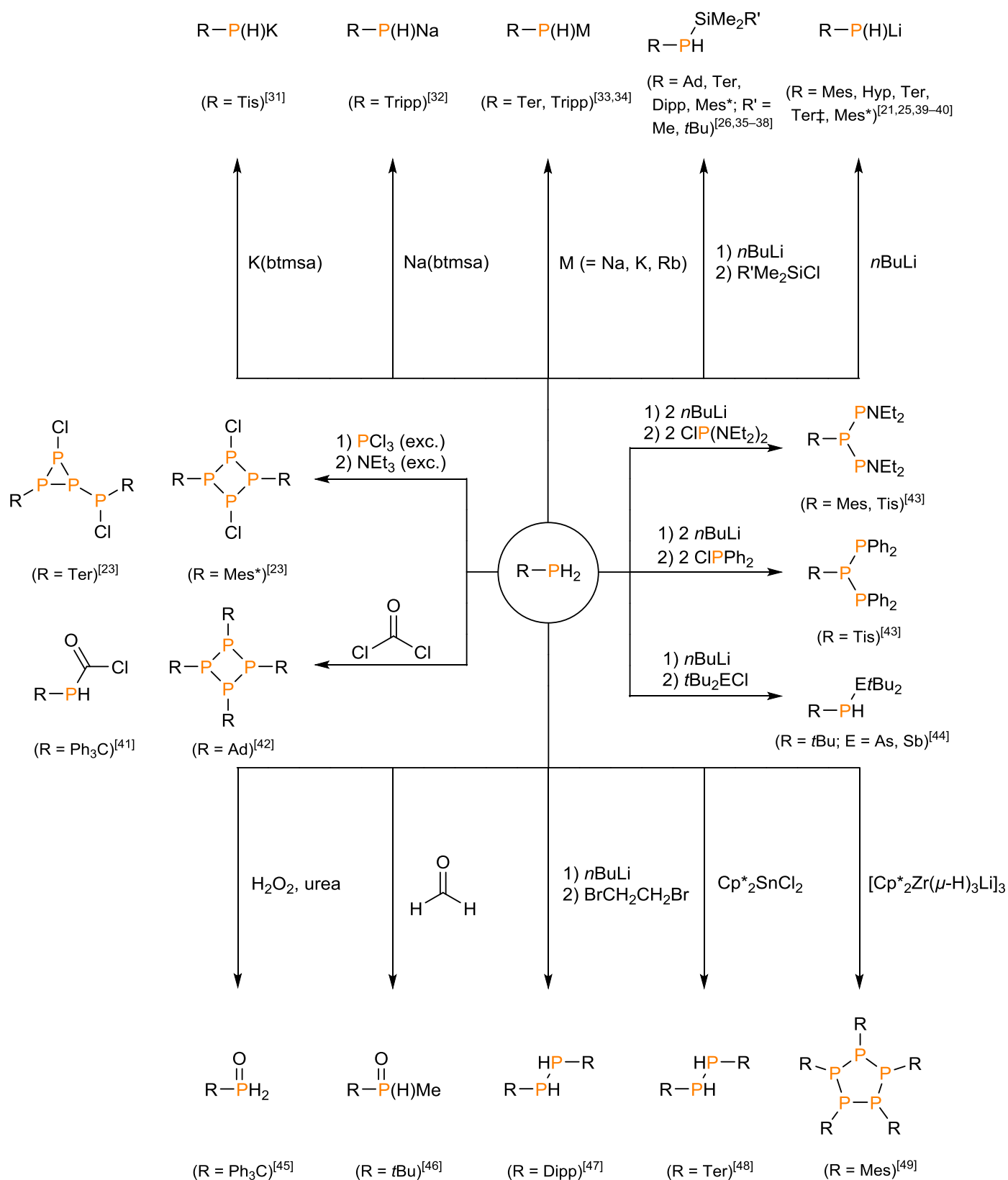
Figure 5. Other, hitherto unknown bulky phosphines.

The 2,6-dimethylphenyl and 2,6-bis(bis(trimethylsilyl)methyl)phenyl moieties found in **23** and **24** are already used as substituents in biradical chemistry in our group and could also serve as starting points for phosphine chemistry. Ter*-I, a formal precursor to phosphine **25**, was just recently synthesized for the first time by SCHROCK *et al.* in good yields.^[30] Since this substituent is probably among the largest 2,6-phenyl derivatives, this could prove to stabilize new pnictogen compounds.

Lastly, a variation of the 2,6-bis(benzhydryl)phenylphosphine **1** should not exhibit differences in steric bulk. However, the *tert*-butyl group in *para*-position at **26** should enhance solubility, when compared to a methyl group. Increasing steric bulk proves to be a problem when it comes to reactions in solution, which is especially noticeable when two substituents are attached to the phosphorus atom.^[1]

2.3 Reactivity of Primary Phosphines

Since primary phosphines are known for a range of sterically demanding substituents, as indicated by Figure 4, the reactivity of these compounds has been investigated intensively over the last few decades. The goal of many experiments was to prepare novel transition metal complexes, which may be applied in homogeneous catalysis. Apart from this, a great amount of research dealt with main group chemistry, especially small ring systems. An overview of these reactions can be found in Scheme 8, where only the initial steps are shown and subsequent reactions are not considered for better comprehension.



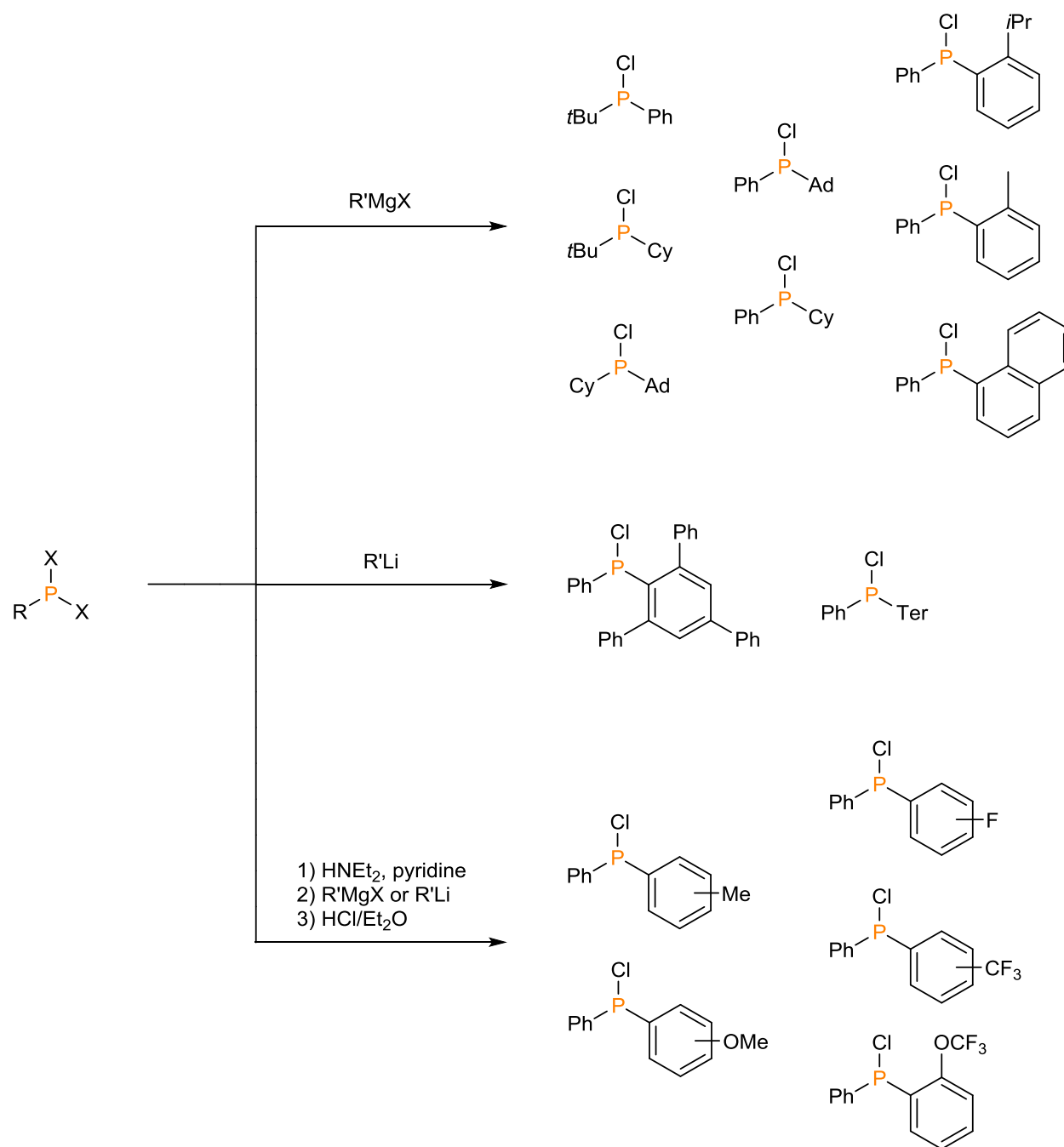
Scheme 8. Reactivity of bulky phosphines displayed in Figure 4.

Several alkali metal salts have been isolated by reacting the respective phosphines with metal organic reagents or even the elemental metals. These can subsequently be further functionalized in metathesis reactions, with the precipitation of insoluble alkali metal halides as a powerful driving force. Several ring systems of different sizes and constitutions could be isolated by reacting the phosphines with phosphorus trichloride and triethylamine, phosgene, as well as a zirconium complex. Another similar transition metal complex led to phosphine dehydrocoupling. Oxidations to phosphorus(V) species were achieved by using hydrogen peroxide or formaldehyde. Most of these reactions were only tested on a specific phosphine. However, in some reactions the difference in steric bulk actually gave rise to varying products, so obviously the outcome for a phosphine $R-PH_2$ depends on the substituent R.

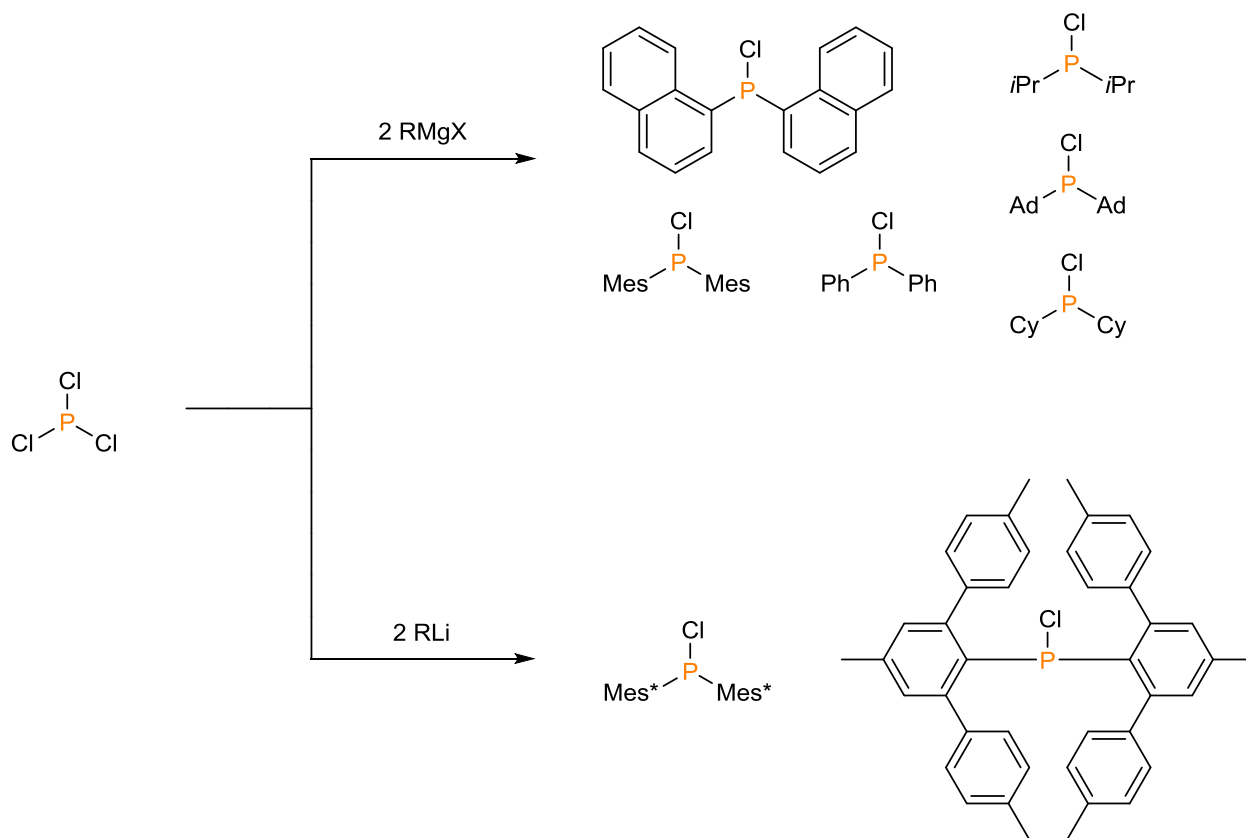
2.4 Synthesis of Secondary Phosphines

Secondary phosphines, as defined for this work, are compounds of the type R_2PX , with X either being a hydrogen or halogen atom. When discussing this class of molecules, one has to distinguish between symmetric and asymmetric secondary phosphines. The former have two equal substituents bonded to the phosphorus atom, while the latter have two different groups. Several of these phosphines with bulky groups have already been prepared according to similar reaction protocols, starting from the respective dihalophosphines (Scheme 9).^[50–58]

In general, either a GRIGNARD or organolithium reagent is used to introduce the second carbocycle or other substituent. In some cases, one halogen atom from the starting compound was exchanged for a diethylamino group prior to reacting it with the organometallic reagent. Conclusive reaction with an excess of hydrogen chloride also leads to the monohalophosphine. However, this additional substitution step does not seem necessary when the organometallic compounds are used in precise stoichiometric amounts.

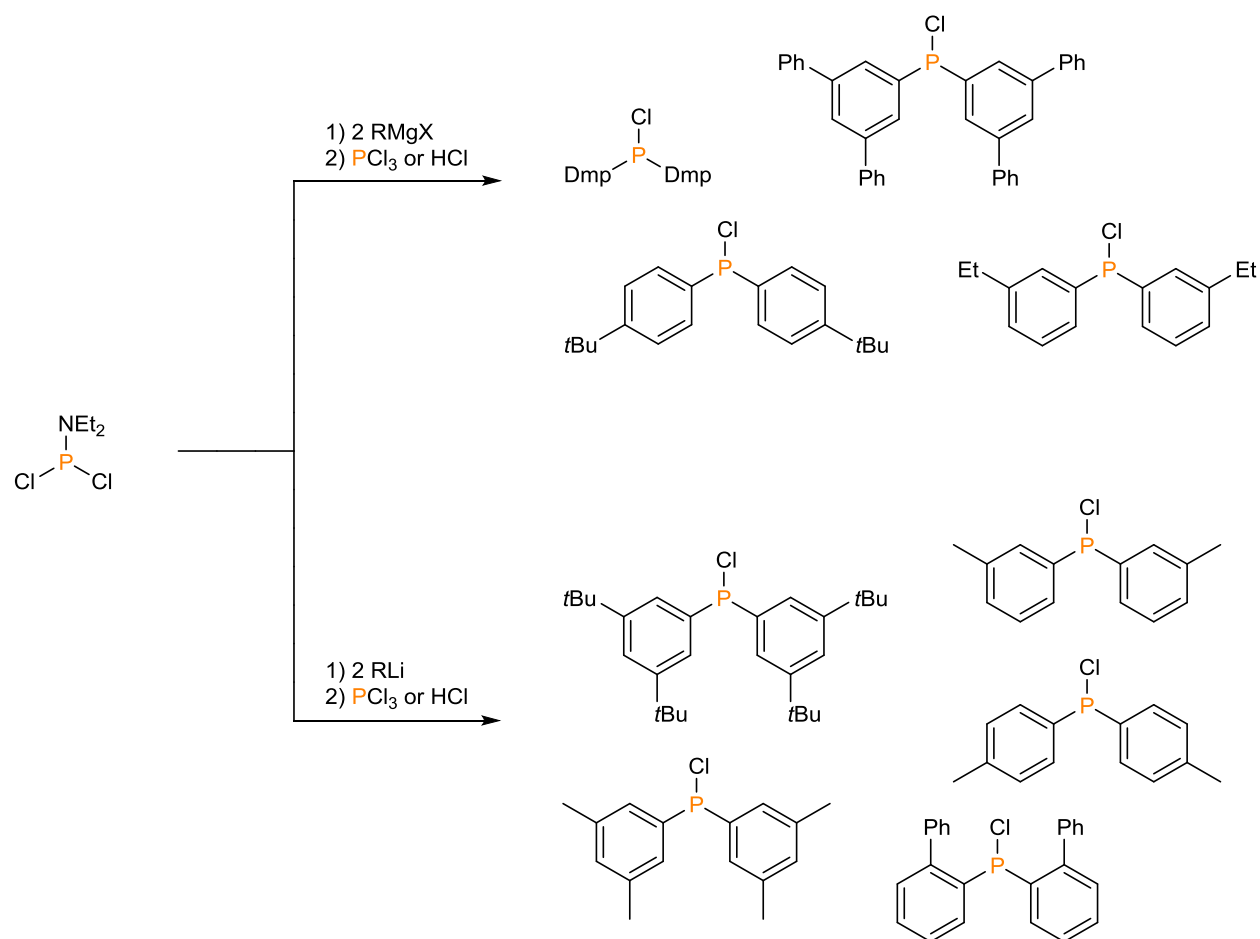
**Scheme 9.** Synthesis of asymmetric secondary phosphines.^[50–58]

While the same approaches can be used to prepare symmetric secondary phosphines, the use of phosphorus trichloride simplifies the whole process by being readily available in high purity (Scheme 10).^[59–63] In order to prepare the sterically demanding phosphines, two equivalents of the respective organometallic compounds are used.



Scheme 10. Synthesis of symmetric secondary phosphines, starting from phosphorus trichloride.^[59–63]

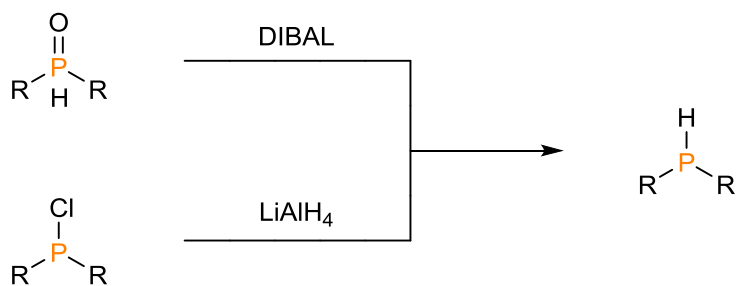
In several cases, dichloro(diethylamino)phosphane is used instead of phosphorus trichloride, in a similar way as in Scheme 9. The diethylamino group is analogously removed by addition of either phosphorus trichloride or hydrogen chloride (Scheme 11).^[64–70]



Scheme 11. Synthesis of symmetric secondary phosphines, starting from dichloro(diethylamino)phosphane.^[64–70]

There are actually some products, which were not only prepared according to Scheme 10, but also according to Scheme 11. Thus, the presence of an amino group in the starting material should not pose a necessity and the significantly cheaper phosphorus trichloride should suffice.

Preparation of compounds of the type R₂PH or RR'PH is not possible directly *via* the displayed paths due to differences in polarity between P–X and P–H bonds. While reduction of suitable double-substituted phosphorus(V) species is an option, the simple reaction of halophosphines with lithium aluminium hydride has been shown to work in numerous instances (Scheme 12).^[57,71–75]



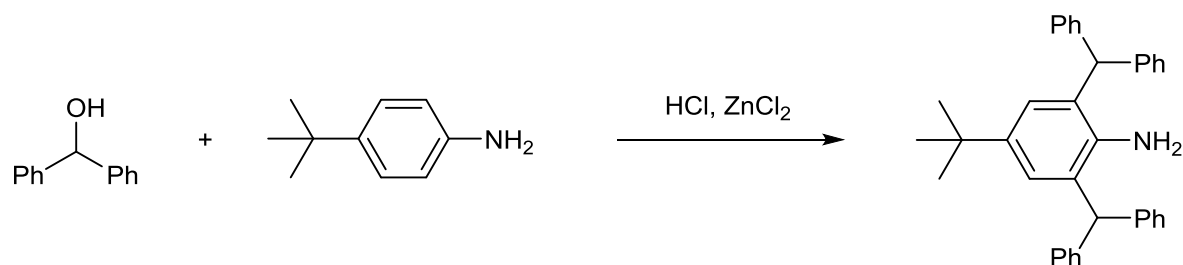
Scheme 12. Synthesis of double-substituted phosphines (only symmetric phosphines are shown, the same procedure applies to asymmetric phosphines).^[57,71–75]

Therefore, the successful isolation of the PH compound obviously depends on obtaining the PX compound in adequate purity, which might be a problem, as highly reactive organometallic reagents can undergo side reactions with labile intermediates.

3. Results and Discussion

3.1 Synthesis of ^tBuBhp-NH₂ (27)

Based on the experimental protocol by FORTIER *et al.*, the synthesis of the primary amine **27** was slightly altered according to the previous synthesis of ^{Me}Bhp-NH₂ by SCHARNHÖLZ.^[1,76] Starting from the *para*-substituted aniline and diphenylmethanol, both solids were heated to 150 °C. Instead of adding the LEWIS acid and hydrochloric acid consecutively, all reactants were merged from the beginning (Scheme 13).

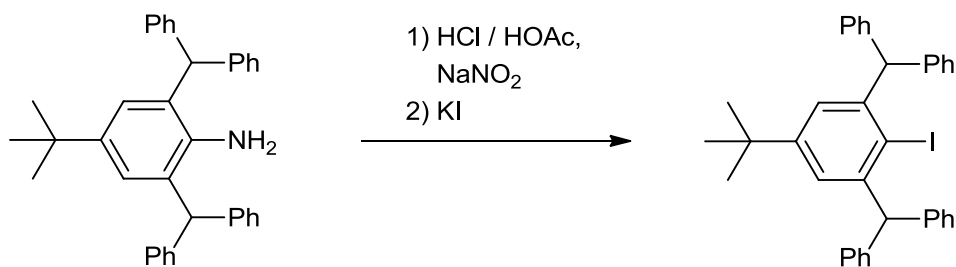


Scheme 13. Synthesis of ^tBuBhp-NH₂ (**27**).^[76]

The reaction proceeded as planned, however rigorous stirring was found to be essential for the highly viscous melt, which can be achieved by using a big stir bar or even a mechanical stirrer. Additionally, the product had to be recrystallized from benzene, since the initial white solid caused extra undesired signals in the ¹H NMR spectrum. Due to these factors and possibly insufficient reaction time, the yield turned out significantly lower than reported. Although it was said to be stable towards air, ^{Me}Bhp-NH₂ still turned from white to light beige over the course of a few weeks, even when stored under an argon atmosphere and shielded from light. Interestingly, this was not observed in the case of **27**, which remained an all white solid.

3.2 Synthesis of ^tBuBhp-I (28)

SCHARNHÖLZ previously reported that the iodo derivate was found to be the most reactive one in subsequent reactions, which is why syntheses of the chloro and bromo derivatives were abandoned from the beginning. The same protocol already used for the synthesis of ^{Me}Bhp-I could be applied again (Scheme 14).



Scheme 14. Synthesis of $^t\text{BuBhp-I}$ (**28**).

Multiple recrystallizations were not found to be necessary, as the first batch was already clean enough, according to the ^1H NMR spectrum. At 2.108(3) Å, the C–I bond is expectedly just as long as in the methyl analog. The two phenyl rings on each side are also only slightly twisted when compared to $^{\text{Me}}\text{Bhp-I}$, since the *tert*-butyl substituent in *para*-position barely has a repulsive effect.

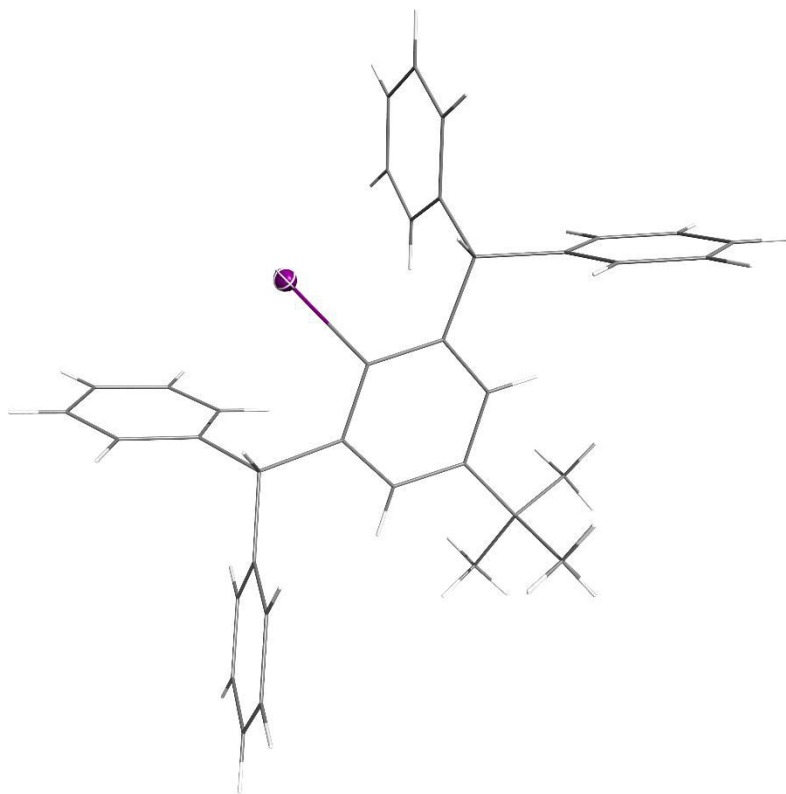


Figure 6. ORTEP depiction of the single-crystal structure of $^t\text{BuBhp-I}$ (**28**). Thermal ellipsoids set at 50 % probability at 123(2) K. The Bhp moiety is displayed as wireframe.

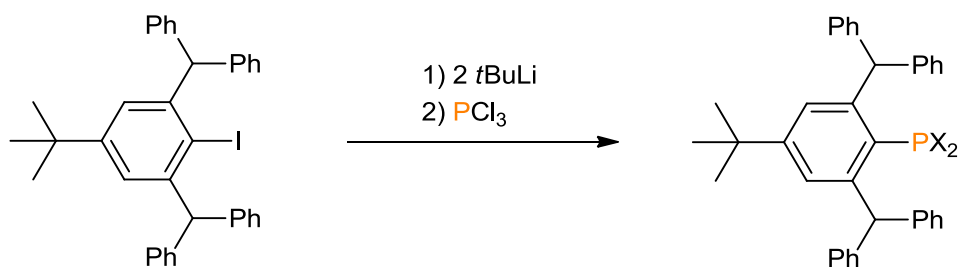
Due to high rotational flexibility, several C–I stretching vibrations, merged with rocking and twisting motions of the aromatic ring systems, are visible in the IR and RAMAN spectra.

Appropriate IR-active vibrations can be found at 556 cm^{-1} , 495 cm^{-1} and 474 cm^{-1} , while related vibrations in the RAMAN spectrum are located at 643 cm^{-1} , 583 cm^{-1} and 225 cm^{-1} .

Similar to the preparation of **27**, intense stirring is necessary in order to ensure sufficient mixing between the aqueous and organic phases. Independent of the scale the reaction is run on, yields never exceed 50-55 %.

3.3 Synthesis of $^{t\text{Bu}}\text{Bhp-PX}_2$ ($\text{X} = \text{Cl, I}$) (**29**)

Consecutive addition of two equivalents *tert*-butyllithium and phosphorus trichloride leads to the dihalophosphine **29**. The reaction was carried out multiple times and always gave a mixture of phosphines, with the dichlorophosphine being the major product and the chloriodophosphine being the other one (Scheme 15).



Scheme 15. Synthesis of $^{t\text{Bu}}\text{Bhp-PX}_2$ (**29**) ($\text{X} = \text{Cl, I}$).

According to the ^{31}P NMR spectrum, the diiodophosphine is only formed in relatively small amounts (Figure 7).

The ^{31}P NMR spectrum of the analogous $^{\text{Me}}\text{Bhp-PX}_2$ also displays a signal around +178 ppm, which may be assigned to phosphorus triiodide ($\delta = +178\text{ ppm}$, Figure 8).^[77]

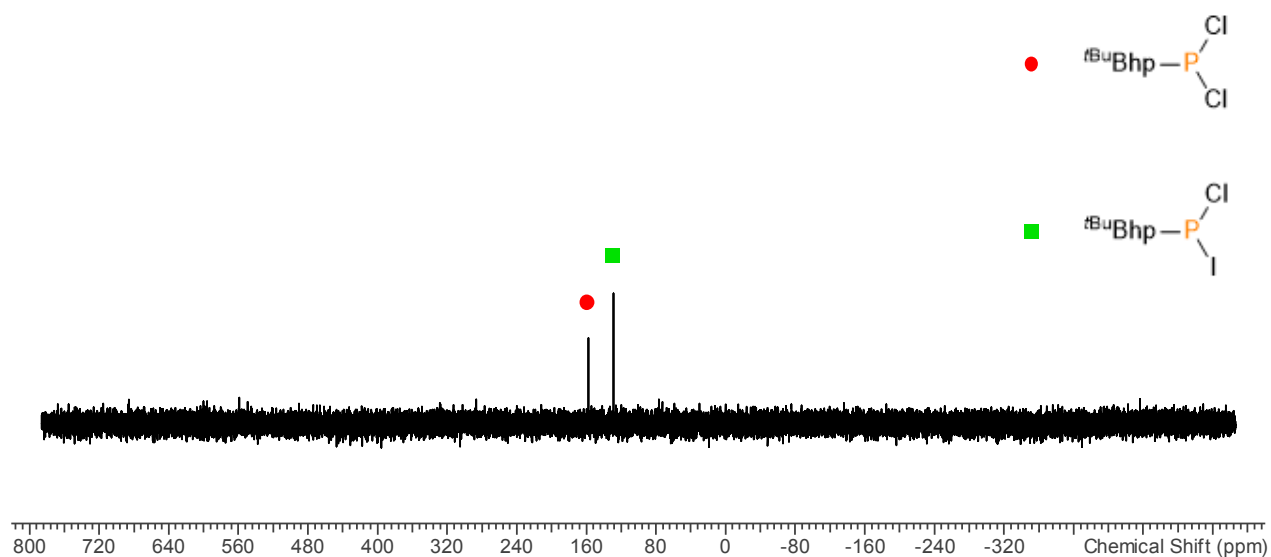


Figure 7. ^{31}P NMR spectrum of **29** in CD_2Cl_2 .

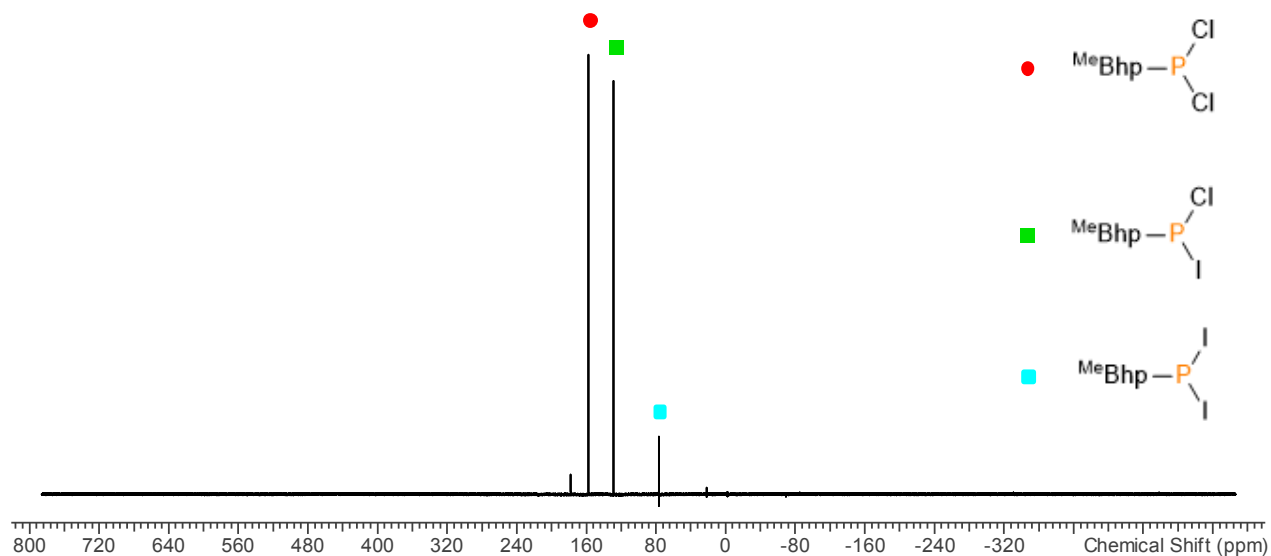


Figure 8. ^{31}P NMR spectrum of $\text{MeBhp}-\text{PX}_2$ in CD_2Cl_2 .

The reaction mixture displays an intense yellow color when kept at $-80\text{ }^\circ\text{C}$. However, as soon as the cooling bath is removed, the mixture instantly turns dark red, no matter how many hours it is stirred beforehand. Crystals were grown from vapor diffusion of *n*-pentane into dichloromethane (Figure 9).

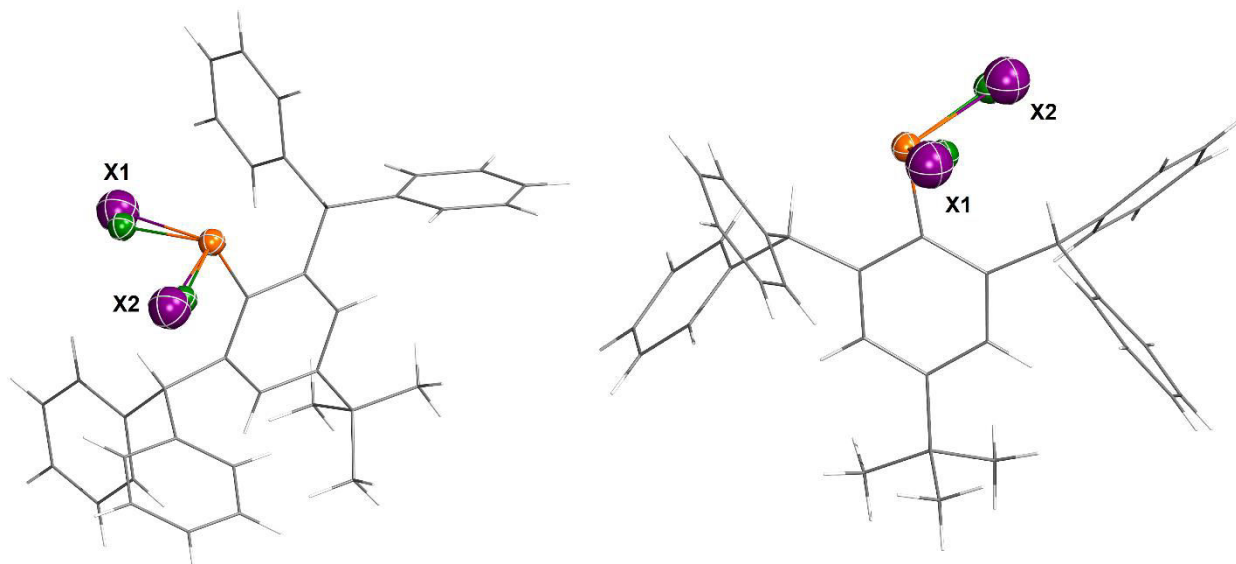


Figure 9. ORTEP depiction of the single-crystal structure of $^t\text{BuBhp-PX}_2$ (**29**) from different perspectives. Thermal ellipsoids set at 50 % probability at 123(2) K. The Bhp moiety is displayed as wireframe.

The single-crystal structure shows severe disordering with X1 statistically being a chlorine atom in 71 % and an iodine atom in 29 % of the cases. The same applies to X2, where a chlorine atom can be found in 93 % and an iodine atom in 7 % of the cases. This shows, that the diiodophosphine is indeed formed, the probability is just rather low.

Intense IR-active P–Cl stretching can be found at 532 cm^{-1} and 472 cm^{-1} , respective RAMAN-active vibrations are present at 531 cm^{-1} , 480 cm^{-1} and 466 cm^{-1} . A shoulder at the latter IR vibration may be caused by the mixed dihalophosphine due to signal overlapping, as the presence of an iodine atom slightly shifts the energy value of it.

While selecting suitable crystals for X-ray diffraction measurements, it was found, that apart from the block-shaped ones of **29**, also several needles were present. At first, this was thought to be another possible modification. Mounting these crystals actually revealed that it is a mixture of the starting compound **28** and the chlorine derivate $^t\text{BuBhp-Cl}$ **30** (Figure 10).

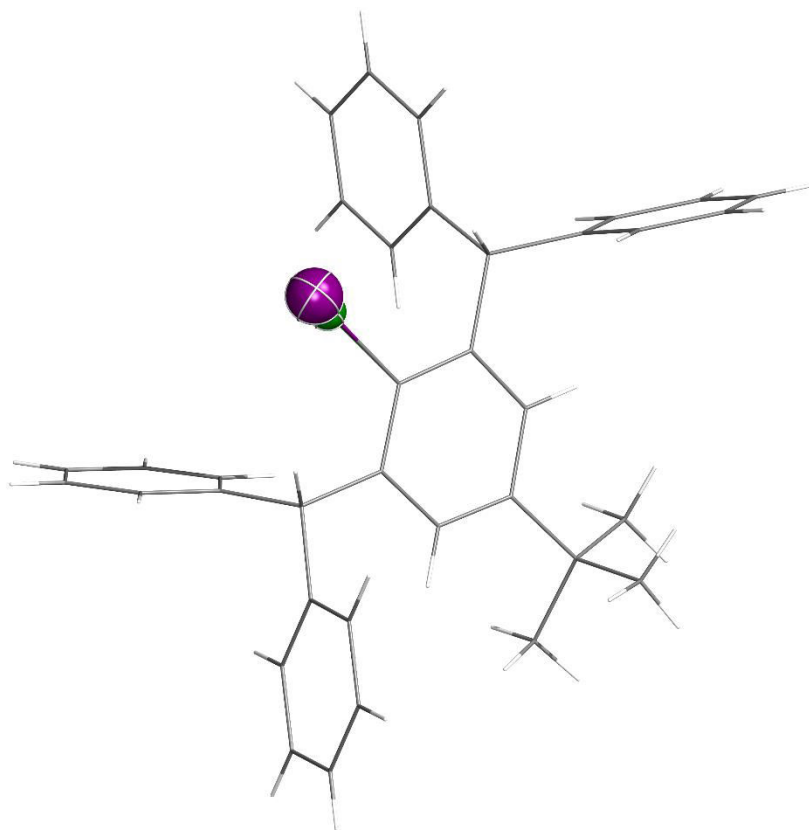


Figure 10. ORTEP depiction of the single-crystal structure of ^tBuBhp-Cl (**30**) and ^tBuBhp-I (**28**). Thermal ellipsoids set at 50 % probability at 123(2) K. The Bhp moiety is displayed as wireframe.

The refinement of the crystal structure shows that it was composed of 3 % of **28** and 97 % of the chlorine derivate **30**. Signals stemming from the methine protons of the benzhydryl moieties for these two compounds can be found around +6 ppm in the ¹H NMR spectrum. However, integration shows that the percentage of **30** relative to the main product **29** does not even exceed 1 % (Figure 11).

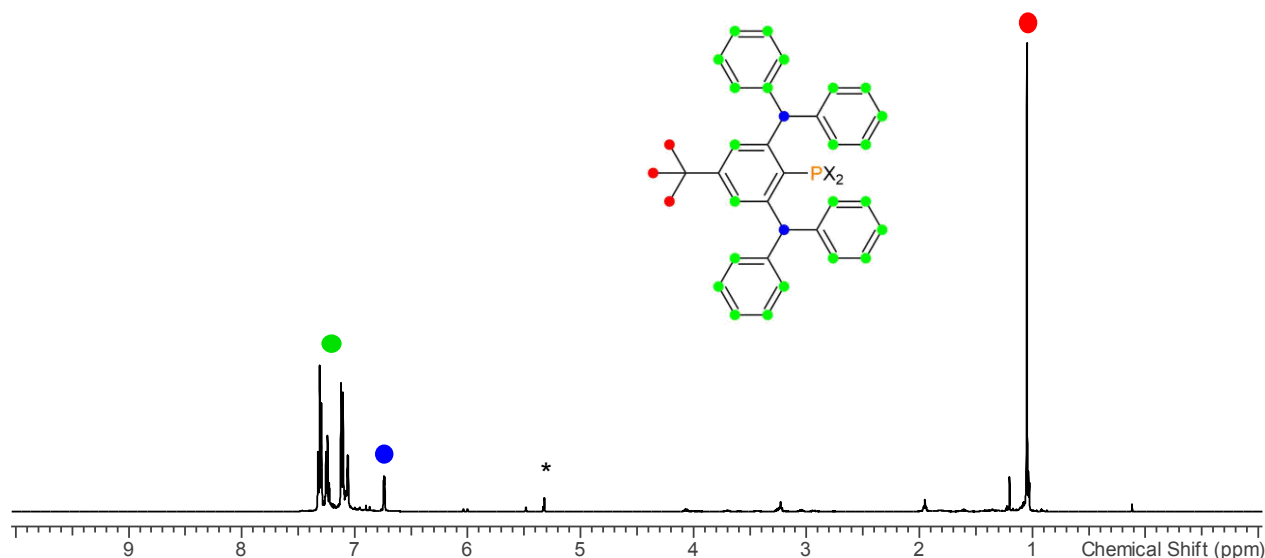
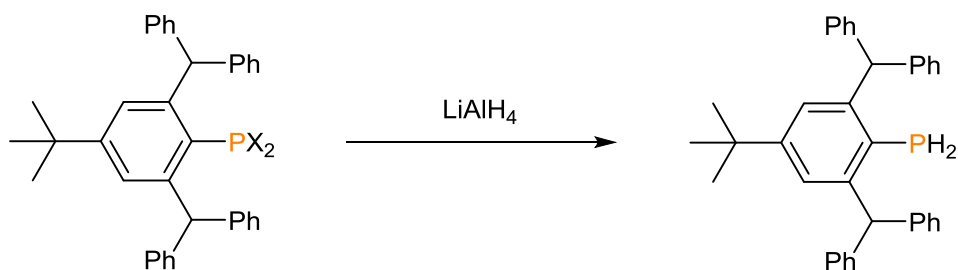


Figure 11. ^1H NMR spectrum of $^t\text{BuBhp-PX}_2$ in CD_2Cl_2 (solvent signal marked by asterisk).

SCHARNHÖLZ already made similar observations with the *p*-methyl derivate, where $^{\text{Me}}\text{Bhp-Cl}$ was formed in small quantities, when the reaction mixture was immediately warmed to ambient temperature after the addition of phosphorus trichloride. Nevertheless, even when stirred for several hours at $-80\text{ }^\circ\text{C}$, this side reaction could not be prevented. Fractional crystallization might be employed, if this purity is not sufficient for follow-up reactions.

3.4 Synthesis of $^t\text{BuBhp-PH}_2$ (**31**)

Analogously to the previously reported synthesis of **1** by SCHARNHÖLZ, reaction of **29** with an excess of lithium aluminium hydride yielded phosphine **31** (Scheme 16).^[1] Even after thorough drying, the product emits a characteristic phosphine stench.



Scheme 16. Synthesis of $^t\text{BuBhp-PH}_2$ (**31**).

The ^{31}P NMR spectrum exhibits a triplet at -155.5 ppm with a J coupling constant of -210 Hz, which is expectedly almost identical to **1**.

Instead of crystallizing the product, the solvent used for extraction might just be removed *in vacuo*, giving a white powder. The final ^1H NMR spectrum of this approach only shows minor additional signals (Figure 12). If higher purity is needed, recrystallization from a mixture of dichloromethane and *n*-pentane or toluene and *n*-pentane should work similar to **1**. The latter approach also yielded single-crystals (Figure 13).

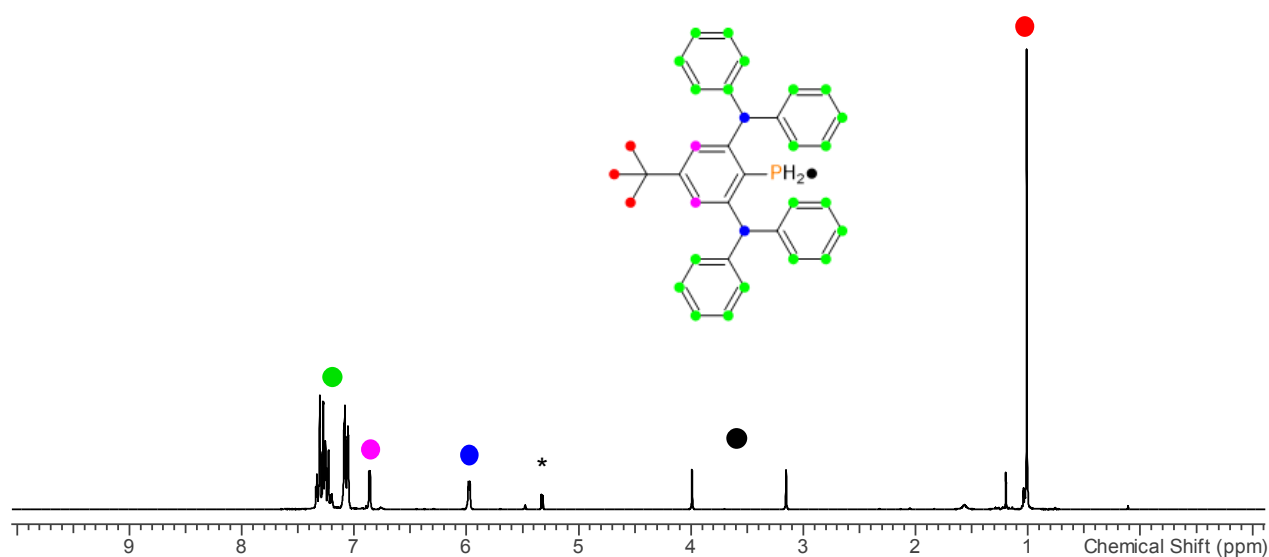


Figure 12. ^1H NMR spectrum of **31** in CD_2Cl_2 (solvent signal marked by asterisk).

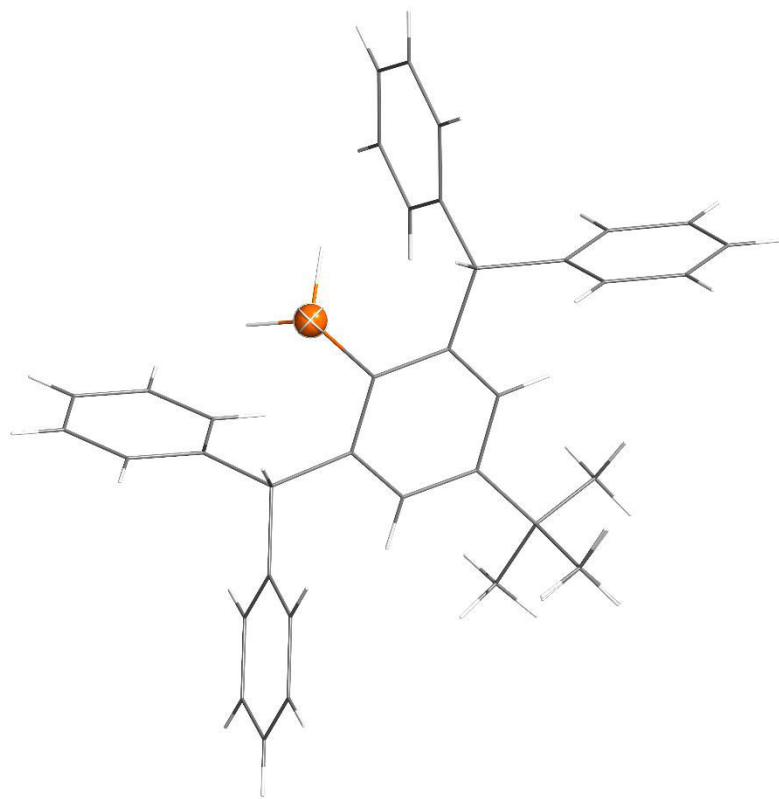


Figure 13. ORTEP depiction of the single-crystal structure of ^tBuBhp-PH₂ (**31**). Thermal ellipsoids set at 50 % probability at 123(2) K. The Bhp moiety is displayed as wireframe.

The structure is almost identical to **1**, however the C–P bond in **31** is slightly shortened (1.838(2) Å *versus* 1.854(1) Å).

3.5 Reactivity of ^{Me}Bhp–PX₂ towards ZnCl₂

In an effort to obtain the dichlorophosphine ^{Me}Bhp–PCl₂ in high purity, the crude product mixture from the analogous reaction displayed in Scheme 15 was stirred over an excess of ZnCl₂. The goal was to substitute any present iodine atoms bonded to the phosphorus with chlorine atoms. Unfortunately, this did not work out as planned, since a completely new singlet can be found at +182.6 ppm in the ³¹P and ³¹P{¹H} NMR spectrum (Figure 14).

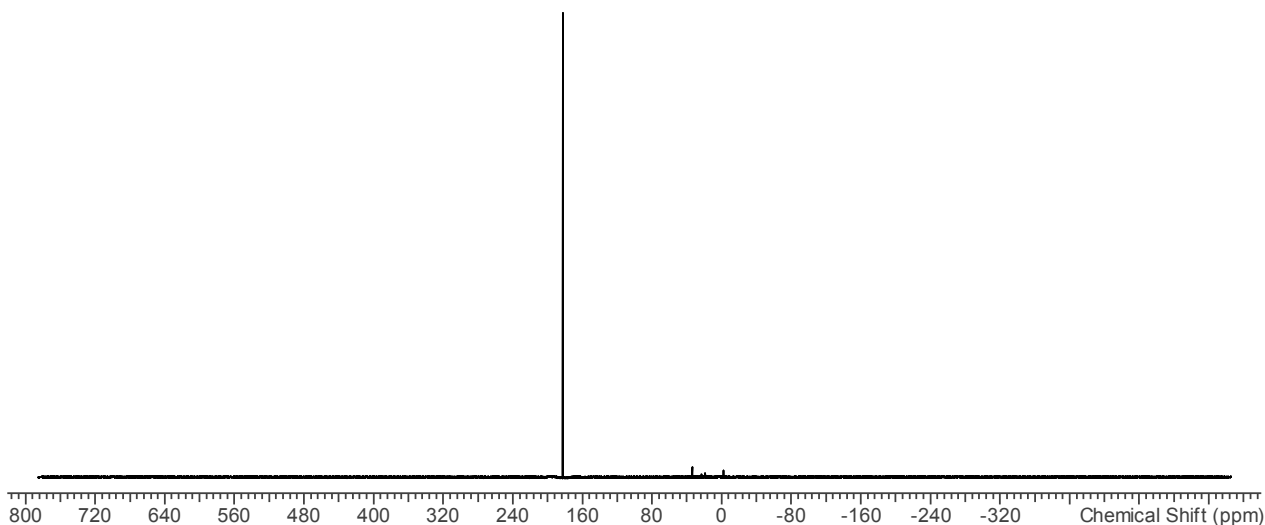
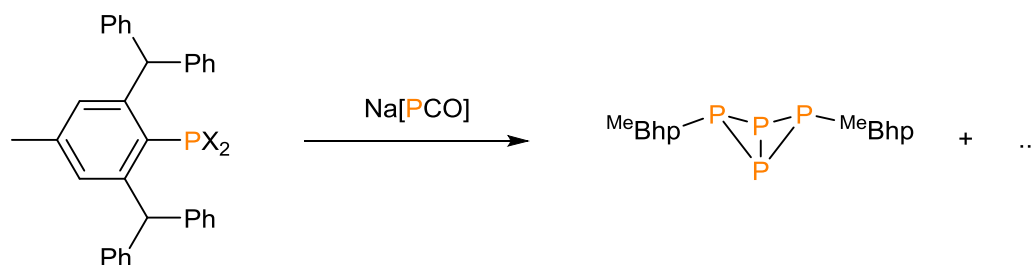


Figure 14. ^{31}P NMR spectrum of the product mixture of $^{\text{Me}}\text{Bhp-PX}_2$ and ZnCl_2 in CD_2Cl_2 .

This chemical shift can neither be assigned to $^{\text{Me}}\text{Bhp-PCl}_2$ (+157.6 ppm), $^{\text{Me}}\text{Bhp-PClI}$ (+128.9 ppm) nor $^{\text{Me}}\text{Bhp-PI}_2$ (+76.7 ppm). However, it is clearly very selective, as there are only minor additional signals. A slight low-field shift indicates deshielding of the phosphorus atom, which might be caused by abstraction of Cl^- and formation of a cation. On the other hand, this should drastically change the chemical shift, instead of just 15 ppm. It also would not explain the formation of just a single phosphorus species from a mixture of three different starting materials. Crystallization attempts only yielded zinc chloride, coordinated by tetrahydrofuran. Even though the mixture was filtered in benzene, small amounts of ZnCl_2 are always present and interfere with crystallization of the desired product.

3.6 Reactivity of $^{\text{Me}}\text{Bhp-PX}_2$ towards $[\text{PCO}]^-$

In order to form P–P bonds, the nucleophile $[\text{PCO}]^-$ can be exchanged for halides, using suitable transfer reagents. After the exchange, either irradiation or elevated temperatures can cause the elimination of carbon monoxide.^[78] SCHARNHÖLZ previously tried a reaction with $\text{Na}[\text{PCO}]$, which gave an *exo-exo*-tetraphosphabicyclobutane as the major product (Scheme 17).^[1]



Scheme 17. Reaction of $^{\text{Me}}\text{Bhp-PX}_2$ with Na[PCO].^[1]

Based on a protocol by BERTRAND *et al.*, another reaction with the novel transfer reagent $[\text{Bu}_3\text{MeN}][\text{PCO}]$ was tried.^[78] Therefore, $^{\text{Me}}\text{Bhp-PX}_2$ was reacted both with one and two equivalents of $[\text{PCO}]^-$. Since the calculation of the molar mass of the dihalophosphine is based on ^{31}P NMR spectra, stoichiometry cannot be satisfied precisely.

For the two reactions, both reactants were added together and dissolved in precooled toluene and subsequently stirred for one day. While the mixture with one equivalent of $[\text{PCO}]^-$ barely changed color from yellow to orange (and additional formation of traces of a brown solid), the mixture with two equivalents visibly changed color to dark red. The ^{31}P NMR spectrum for the former reaction reveals a large singlet at +157.1 ppm, which can be assigned to $^{\text{Me}}\text{Bhp-PCl}_2$, with several smaller signals in the high-field range, which can be assigned to the *endo-exo* and *exo-exo* isomers of the tetrakisphosphabicyclobutane (Figure 15). The high amount of starting material indicates that the reaction barely progressed, at first thought to be caused by either a lack of solubility of $[\text{Bu}_3\text{MeN}][\text{PCO}]$ or insufficient reaction time.

The reaction with two equivalents, which was carried out under the same conditions, interestingly gave a completely different result (Figure 16).

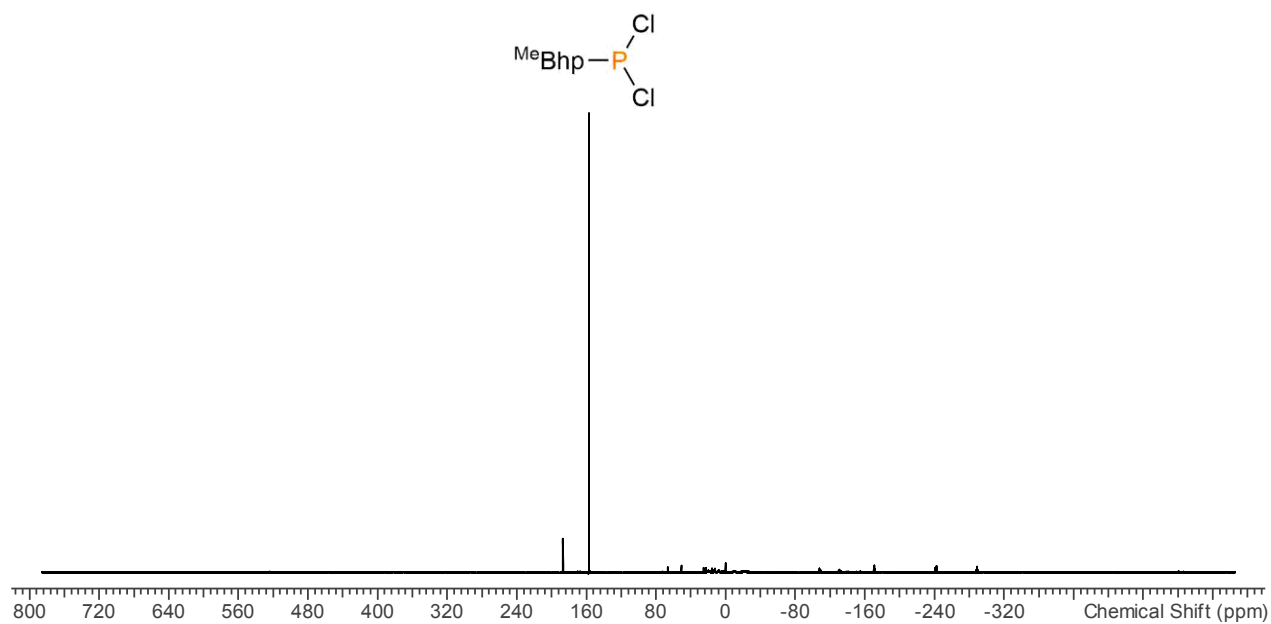


Figure 15. ^{31}P NMR spectrum of the product mixture of $\text{MeBhp}-\text{PX}_2$ and one equivalent of $[\text{Bu}_3\text{MeN}][\text{PCO}]$ in C_6D_6 .

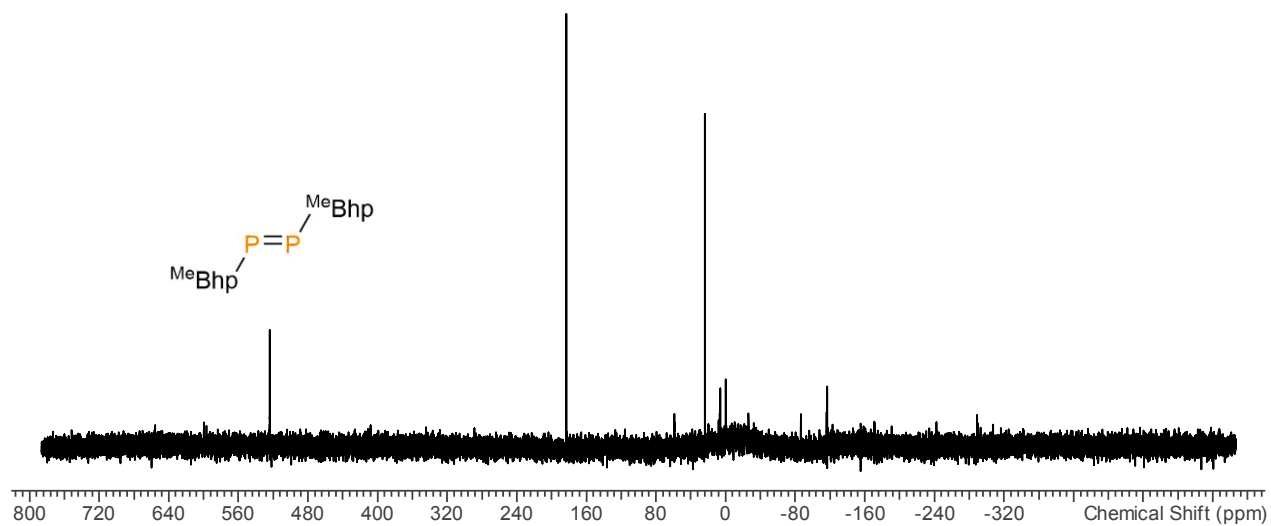


Figure 16. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product mixture of $\text{MeBhp}-\text{PX}_2$ and two equivalents of $[\text{Bu}_3\text{MeN}][\text{PCO}]$ in C_6D_6 .

While there are again some traces of both isomers of the tetraphosphabicyclobutane, three major singlets can be found at +23.6 ppm, +183.1 ppm and +523.8 ppm. The first of these signals splits to a doublet in the coupled ^{31}P NMR spectrum. The second signal exhibits almost the exact shift as found in the reaction with ZnCl_2 (see chapter 3.5). The significant low-field shift of the last signal might actually indicate the presence of a phosphorus-containing cation or rather a diphosphene.

No $[\text{PCO}]^-$ can be found in either of the two reactions (signal around -390 ppm). A ^{31}P NMR experiment, in which solely $[\text{Bu}_3\text{MeN}][\text{PCO}]$ was dissolved in CD_2Cl_2 , revealed two additional singlets at 107 ppm and 277 ppm, indicating decomposition. This might be attributed to the pseudohalogen character of the anion, as well as the polarity of the solvent and should be considered for similar experiments.

Attempts at obtaining single-crystals from a toluene, as well as a tetrahydrofuran solution were unsuccessful thus far.

3.7 Reactivity of $^{\text{Me}}\text{Bhp-PH}_2$ towards ECl_3 ($\text{E} = \text{P, As, Sb, Bi}$)

As already shown in Scheme 8, phosphines react differently with phosphorus trichloride, depending on the bulky substituent. SCHARNHÖLZ previously carried out a reaction on NMR scale, revealing formation of the already mentioned tetraphosphabicyclobutane.^[1] Since this experiment was not done according to the usual protocol, which involves cooling and consecutive addition of reagents, it was retried. The phosphine **1** was reacted with phosphorus trichloride, using triethylamine, as well as DBU as additional base.

DBU is known to react more selectively, as it is a non-nucleophilic base. Indeed, the ^{31}P NMR spectra of both reactions show, that the reaction with DBU gives less products (Figure 17). The main signal at +157.0 ppm can be assigned to $^{\text{Me}}\text{Bhp-PCl}_2$. Other signals, that could be assigned belong to the tetraphosphabicyclobutane and $^{\text{Me}}\text{Bhp-P(H)Cl}$ (+7.9 ppm).

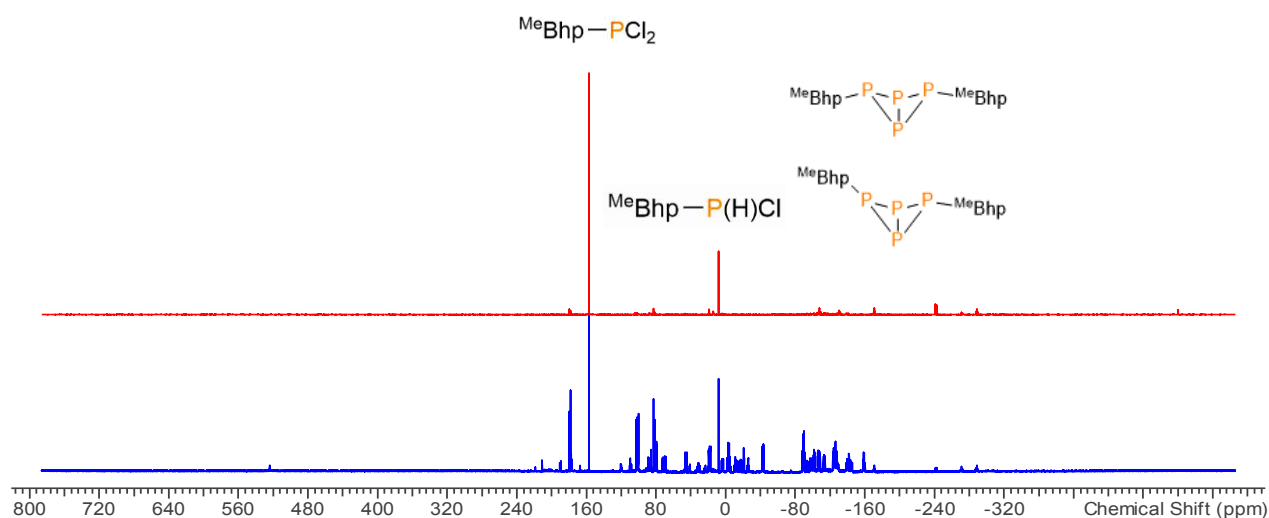


Figure 17. ^{31}P NMR spectra of the product mixtures of $^{\text{Me}}\text{Bhp-PH}_2$ with PCl_3 and NEt_3 (bottom) and with PCl_3 and DBU (top) in C_6D_6 .

As a kind of additional verification, the same reaction was carried out with **31** instead of **1**. Products are similar, but the reaction seems to be slightly more selective (possibly caused by different purities of starting materials, Figure 18).

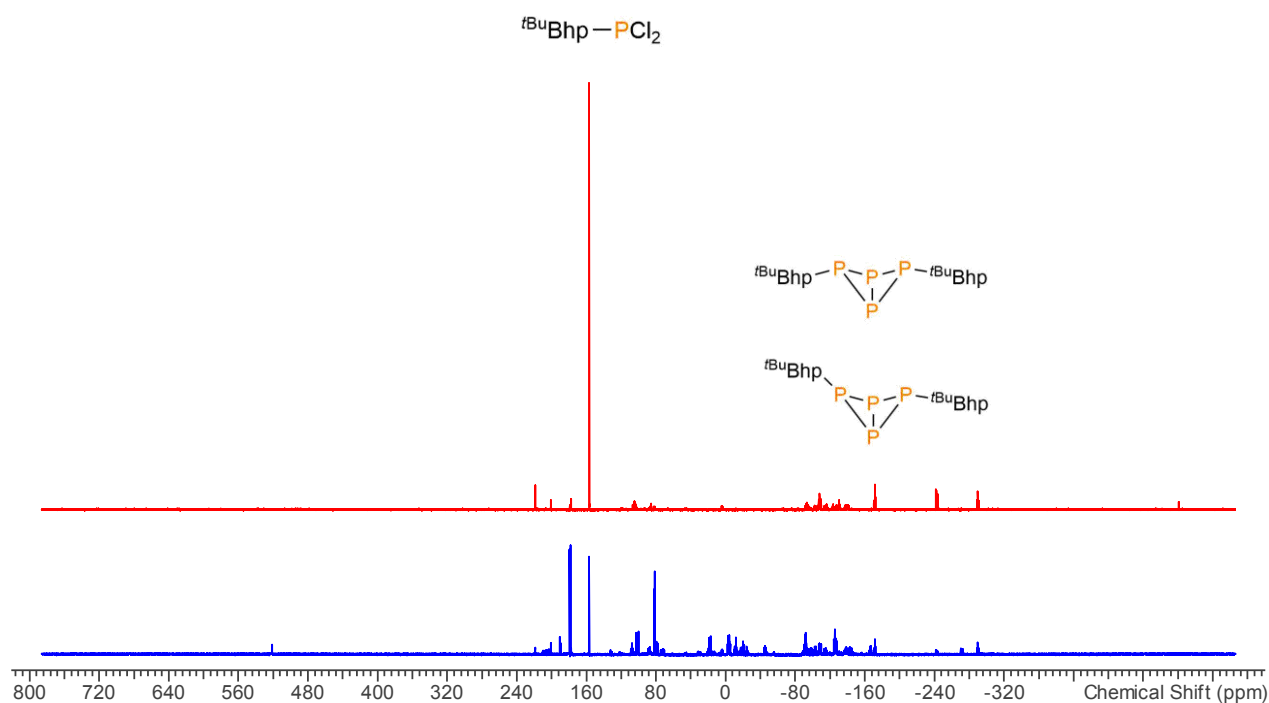
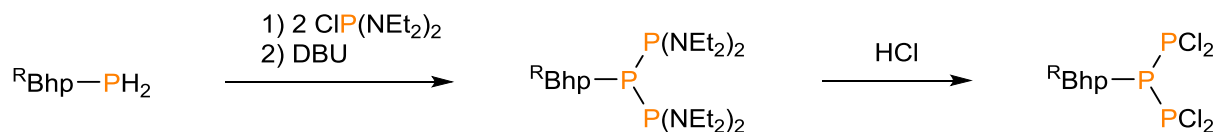


Figure 18. ^{31}P NMR spectra of the product mixtures of $^{\text{tBu}}\text{Bhp-PH}_2$ with PCl_3 and NEt_3 (bottom) and with PCl_3 and DBU (top) in C_6D_6 .

A further attempt was the reaction of both **1** and **31** with $\text{ClP}(\text{NEt}_2)_2$ and DBU. As shown in Scheme 8, similar reactions gave triphosphines, where diethylamino groups might be further exchanged for chlorine atoms by reaction with HCl , enabling possible building blocks for novel ring systems (Scheme 18).



Scheme 18. Possible reaction of $\text{R}^{\text{Bhp}}-\text{PH}_2$ with $\text{ClP}(\text{NEt}_2)_2$ and DBU and subsequent reaction with HCl ($\text{R} = \text{Me}, t\text{Bu}$).

The ^{31}P NMR spectra show a mixture of several phosphorus species (Figure 19).

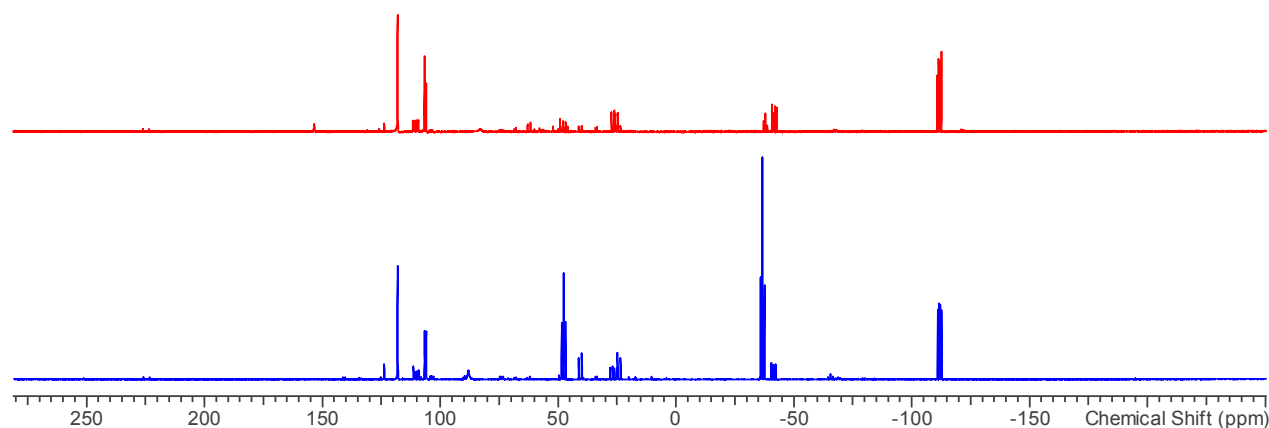


Figure 19. ^{31}P NMR spectra of the product mixtures of $\text{Me}^{\text{Bhp}}-\text{PH}_2$ with $\text{ClP}(\text{NEt}_2)_2$ and DBU (bottom) and $t\text{Bu}^{\text{Bhp}}-\text{PH}_2$ with $\text{ClP}(\text{NEt}_2)_2$ and DBU (top) in C_6D_6 .

Depending on the substituent at the phosphorus atom, chemical shifts and J coupling constants differ, as evidenced by several literature values (Table 1).^[43] Nevertheless, signals caused by these compounds are always a triplet and a doublet with equal coupling.

Table 1. Chemical shifts and J coupling constants for compounds of the type $\text{RP}(\text{P}(\text{NEt}_2)_2)_2$.^[43]

R	δ / ppm	J / Hz
Cy	-51.1 (t), +105.0 (d)	169
<i>t</i> Bu	-21.4 (t), +111.6 (d)	203
Mes	-74.5 (t), +106.8 (d)	169
SiMe ₃	-120.4 (t), +108.7 (d)	177
Si(<i>t</i> Bu)Me ₂	-115.7 (t), +113.3 (d)	227
Tis	-115.3 (t), +112.5 (d)	226
Ad	-25.1 (t), +109.1 (d)	204

While a suitable triplet could actually be identified at -36.7 ppm ($J = 170$ Hz), no corresponding doublet was found. Under the condition that all three phosphorus nuclei are not magnetically equivalent, this would result in three doublets of doublets with an integral ratio of 1:1:1. This is not the case, either. Instead, there are different sets of signals that might be attributed to only a few molecules, as evidenced by equal J coupling.

Since reaction outcomes expectedly did not really differ between **1** and **31**, only the *p*-methyl derivate **1** was further utilized. Also, only DBU was used as a base, due to higher selectivity when compared to triethylamine. Phosphorus trichloride is known to react solely with triethylamine under certain circumstances.^[79]

Reactions with the heavier congeners of phosphorus trichloride were all carried out according to a similar protocol. After adding ECl_3 ($\text{E} = \text{As}, \text{Sb}, \text{Bi}$) at -80 °C, DBU was added at the same temperature and after slowly warming the mixture to ambient temperature, it was left stirring for one day. Products for every reaction were extracted with toluene. The first reaction with AsCl_3 resulted in an orange mixture. A variety of products was formed, however, mostly singlets (Figure 20).

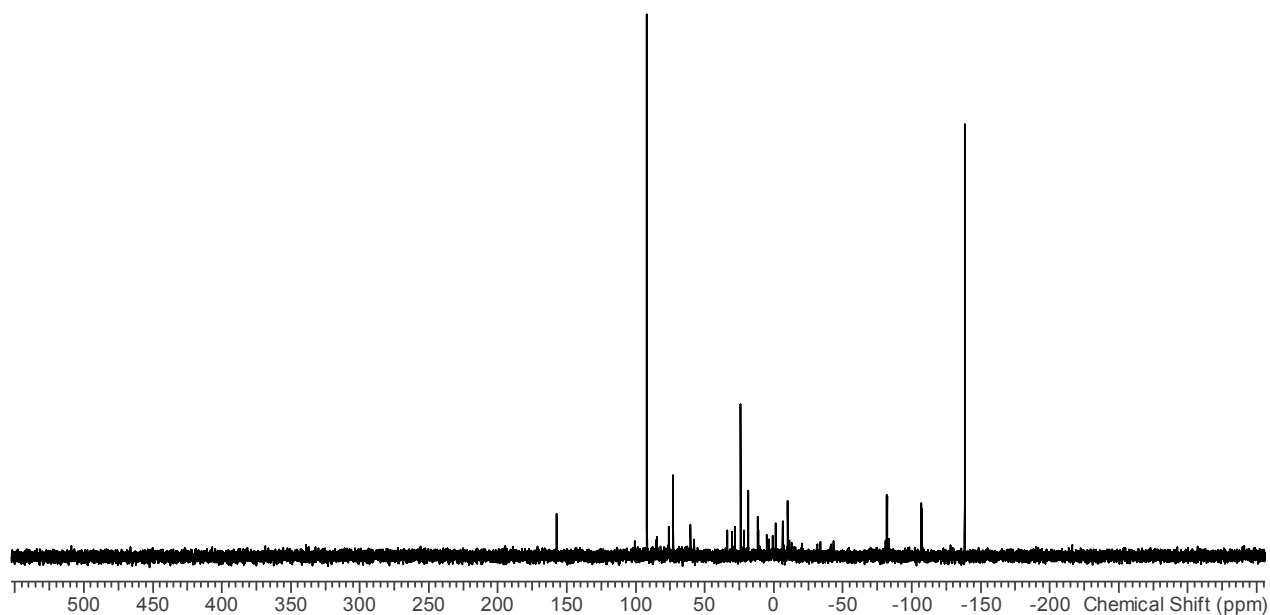


Figure 20. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product mixture of $^{\text{Me}}\text{Bhp-PH}_2$ with AsCl_3 and DBU in C_6D_6 .

The reaction with SbCl_3 , which turned dark orange / red, gave a much cleaner ^{31}P NMR spectrum with seemingly only four different phosphorus species present (Figure 21).

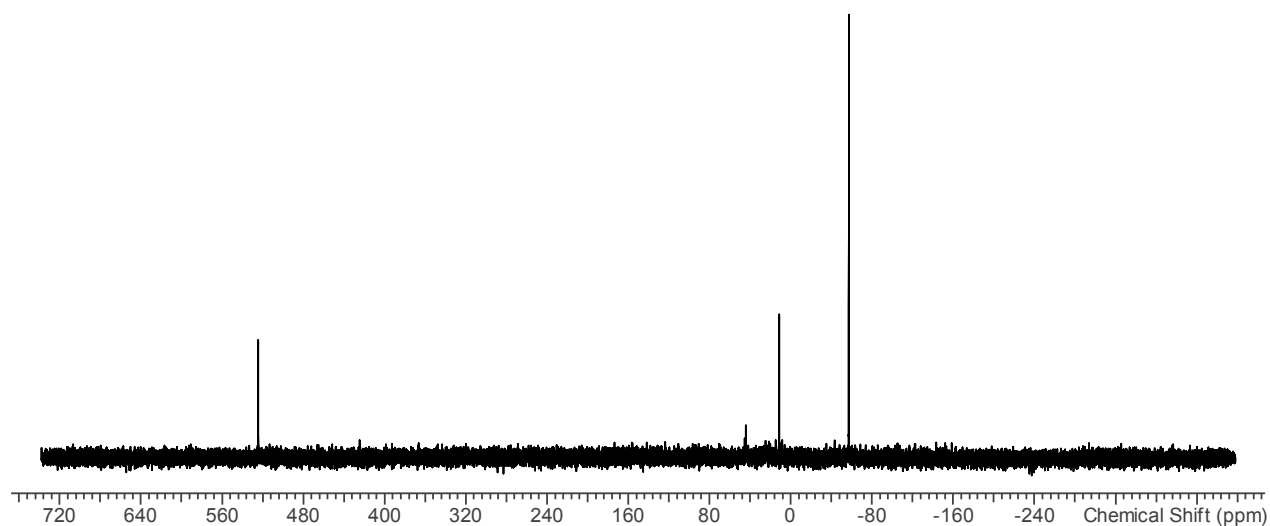


Figure 21. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product mixture of $^{\text{Me}}\text{Bhp-PH}_2$ with SbCl_3 and DBU in C_6D_6 .

The last reaction with BiCl_3 turned black after a short period, a result of the formation of so-called bismuth black, a mixture containing elemental bismuth. This reaction is very common and hardly preventable. Crystallization attempts failed due to recurring formation of bismuth black. Even though the signals have small intensities, the presence of several phosphorus-containing species can be verified (Figure 22).

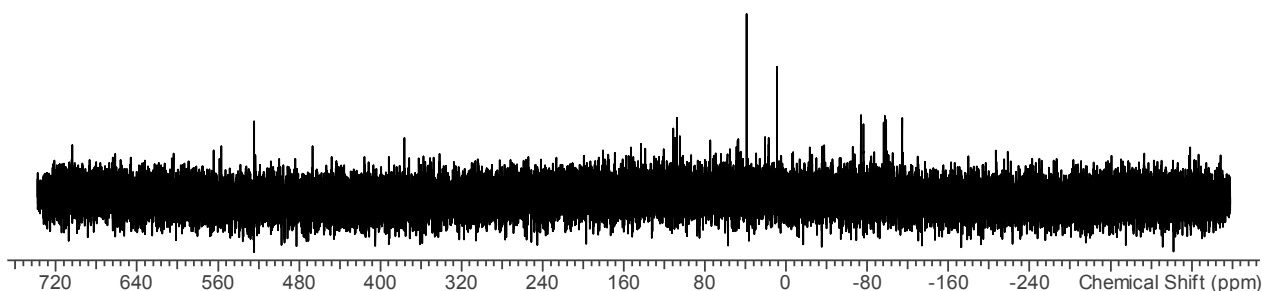
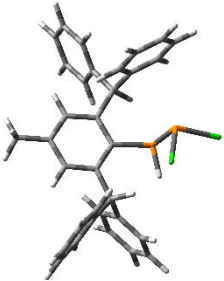
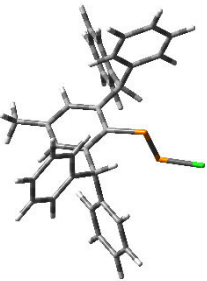
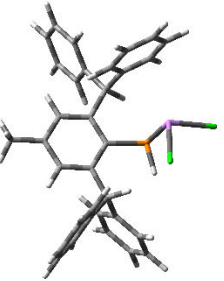
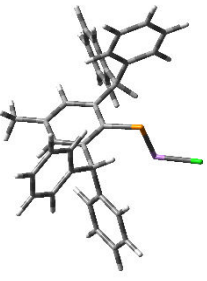
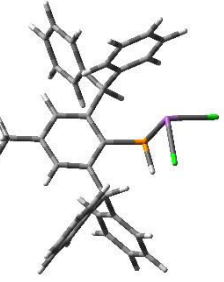
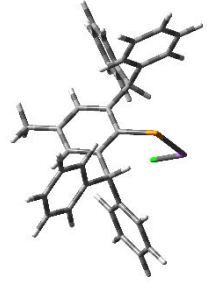
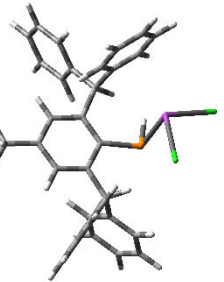
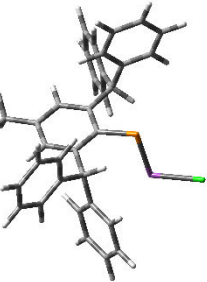


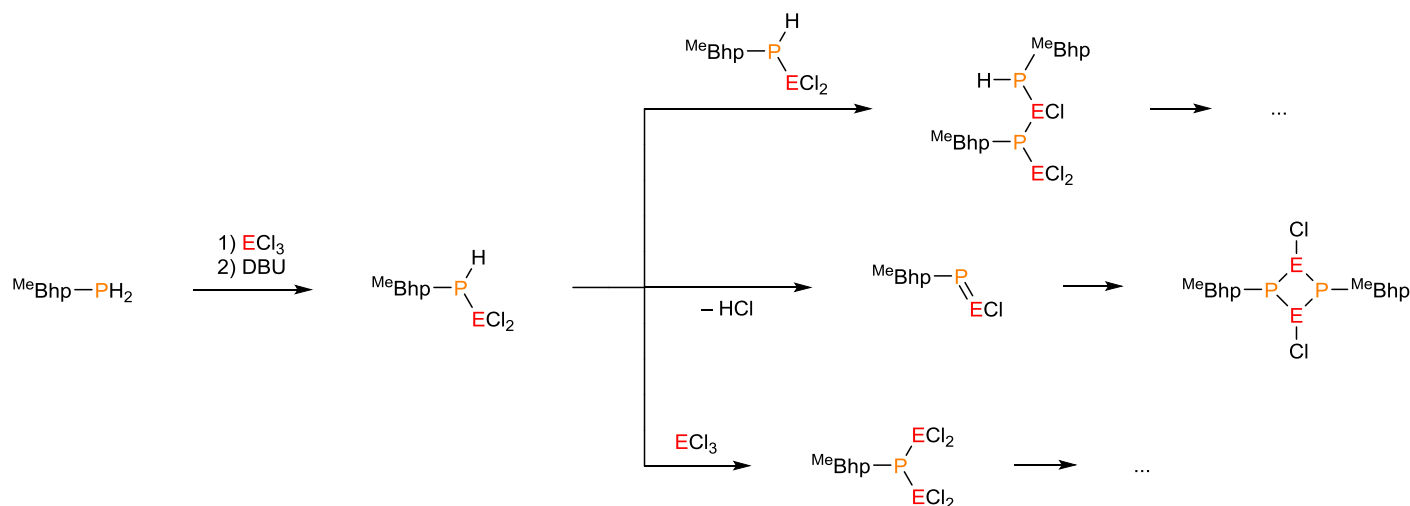
Figure 22. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product mixture of $^{\text{Me}}\text{Bhp-PH}_2$ with BiCl_3 and DBU in C_6D_6 .

To obtain approximate values for chemical shifts and coupling constants, several possible pnictogen species were structurally optimized at the PBE0/cc-pVTZ level for compounds containing phosphorus and arsenic and the PBE0/Def2TZVP level for compounds with antimony and bismuth (Table 2). Compounds with pnictogen double bonds do not seem present at all (excluding the proposed diphosphene $^{\text{Me}}\text{Bhp-P=P-}^{\text{Me}}\text{Bhp}$), compounds with hydrogen in close proximity to phosphorus could not be identified either (no signals that split in the coupled ^{31}P NMR spectrum).

Table 2. Computed NMR data for possible pnictogen compounds.

Compound	³¹ P chemical shift in ppm / <i>J</i> coupling in Hz	Compound	³¹ P chemical shift in ppm / <i>J</i> coupling in Hz
 ^{Me} Bhp-P(H)PCl ₂	-45.5 214.6 / -326	 ^{Me} Bhp-PPCl	+544.6 +582.1 / -527
 ^{Me} Bhp-P(H)AsCl ₂	-42.0	 ^{Me} Bhp-PAsCl	+611.8
 ^{Me} Bhp-P(H)SbCl ₂	-59.1	 ^{Me} Bhp-PSbCl	+696.8
 ^{Me} Bhp-P(H)BiCl ₂	-75.2	 ^{Me} Bhp-PBiCl	+805.4

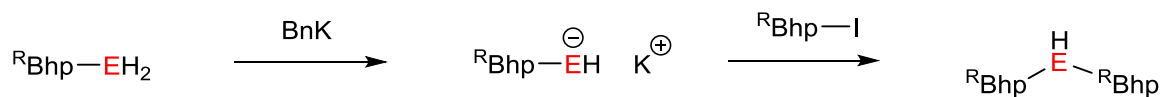
A mixture of reaction products for all three pnictogen halides is not surprising, since several subsequent reactions are imaginable, even if the first substitution takes place in a selective manner (Scheme 19).



Scheme 19. Possible consecutive reactions of MeBhp-PH_2 with ECl_3 and DBU ($\text{E} = \text{P, As, Sb, Bi}$).

3.8 Reactivity of Bhp-PH_2 towards Bhp-I and BnK

In order to prepare secondary amines and phosphines starting from the primary compounds, deprotonation and subsequent reaction with the sterically demanding halide was attempted (Scheme 20).



Scheme 20. Possible preparation of secondary amines and phosphines ($\text{R} = \text{Me, } t\text{Bu}$; $\text{E} = \text{N, P}$).

SCHARNHÖLZ already carried out a few experiments with benzyl potassium.^[1] Since it is an extremely strong base, it was tested if a weaker base would suffice. Therefore, both MeBhp-NH_2 and MeBhp-PH_2 were reacted with sodium *tert*-butoxide. NMR spectra reveal that the starting compounds are still present and deprotonation seemingly did not take place, as integration of the signals indicates. The same experiment was now carried out using benzyl potassium. For the amine, no reaction occurred (as evidenced by integral ratio).

For the phosphine, a new signal appears in the ^1H -coupled ^{31}P NMR spectrum next to the signal of the starting material, which splits to a doublet (Figure 23).

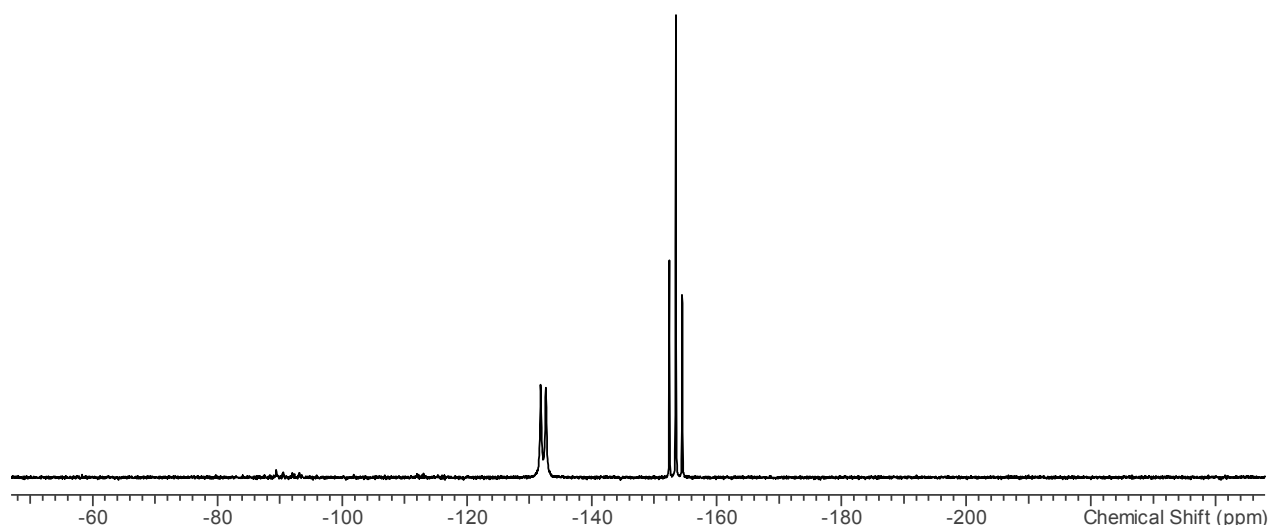


Figure 23. ^{31}P NMR spectrum of the product mixture of $^{\text{Me}}\text{Bhp-PH}_2$ and BnK in C_6D_6 .

Both compounds are present in almost equal percentage. However, after being left standing for three days, the intensity of the doublet drastically decreases and the amount of starting material is now more than seven times the deprotonated species. Obviously, electrically charged compounds display rather low solubility in the employed deuterated benzene, but the reaction mixture was sonicated prior to measuring NMR spectra. It is still possible that minor traces of water advanced into the NMR tube after a few days.

Synthesis of secondary amines was abandoned due to no reaction. For the phosphines three different experiments were run with the intention of preparing both symmetric and asymmetric phosphines. SCHARNHÖLZ was previously successful in the isolation of $(^{\text{Me}}\text{Bhp})_2\text{PH}$ in an experiment on NMR scale.^[1] In a first attempt on a larger scale, benzyl potassium was added first and the halide was added afterwards. This consecutive procedure did give rise to a new signal, that might be attributed to the secondary phosphine, but there was still a high amount of starting material present. Therefore, all reactants were added together as solids, before toluene was added. This way, the ratio of product and starting material was changed. While **1** was still present in the mixture, the major signal could be found at -78.8 ppm, which splits to a doublet ($J = 220$ Hz) in the coupled ^{31}P NMR spectrum (Figure 24).

Interestingly, SCHARNHÖLZ assigned a signal at -95.2 ppm ($J = 239$ Hz) to the intended secondary phosphine. A similar, small signal can be found at -94.4 ppm ($J = 237$ Hz).

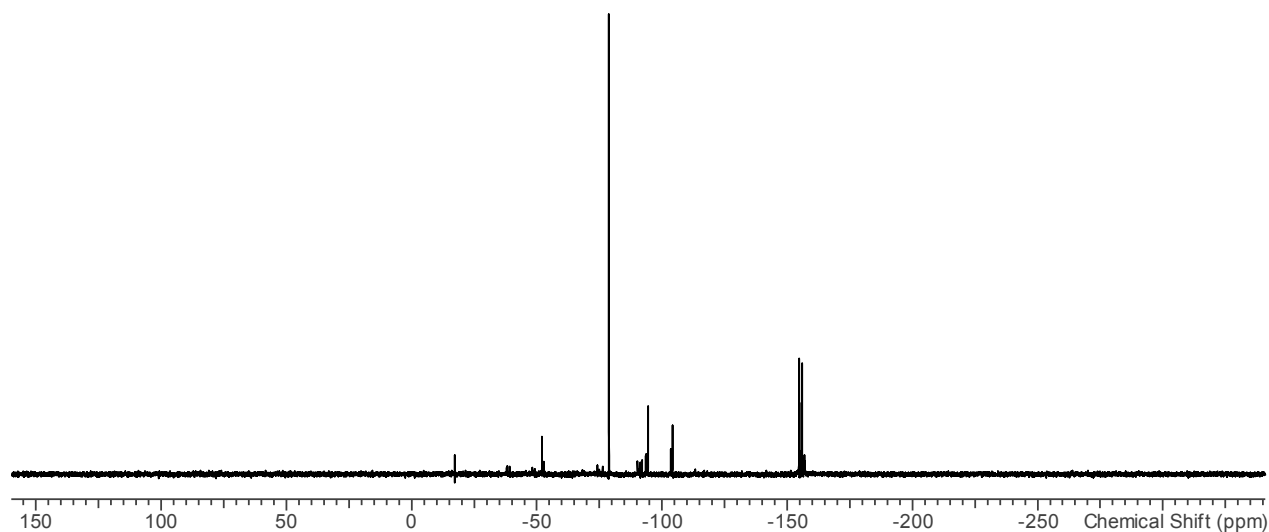


Figure 24. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the product mixture of $^{\text{Me}}\text{Bhp-PH}_2$ with BnK and $^{\text{Me}}\text{Bhp-I}$ in CD_2Cl_2 .

It remains unclear, why the same procedure yields such different outcomes. Reactions with the *p*-*tert*-butyl derivatives gave similar results, with the main signal also being found around -78 ppm (Figure 25). Additionally, in the reaction of $^t\text{BuBhp-PH}_2$ with $^t\text{BuBhp-I}$, two completely new singlets can be found at -116.9 ppm and -112.5 ppm, which split to indefinable multiplets in the coupled ^{31}P NMR spectrum.

All three reaction mixtures turned bright orange / red after a short period, with the reaction of both *p*-*tert*-butyl derivatives being the most clear one, which might be ascribed to higher solubility, as already mentioned in the introductory part. Also, the secondary phosphines should exhibit significantly lower solubility, relative to the primary phosphines. Nonetheless, barely any solids remained on the frit after filtering the mixtures in toluene. All of these clues hint at another reaction outcome than planned. Unfortunately, no single-crystals could be obtained to shed light on the situation. It does not seem reasonable to start from these phosphines, though, because of unselective consecutive reactions of intermediary phosphides.

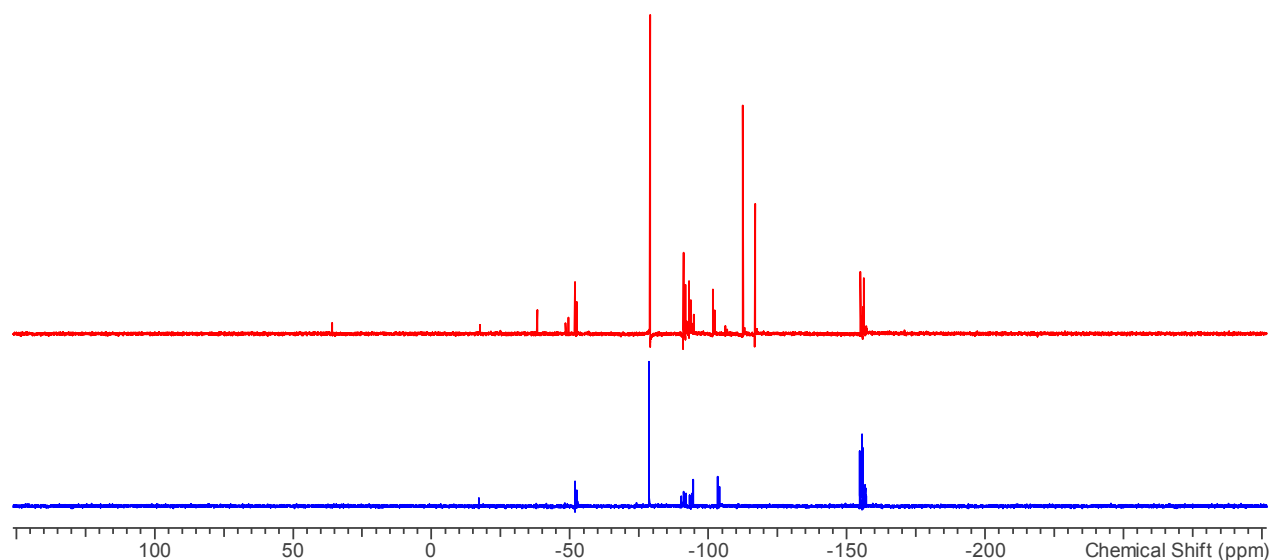


Figure 25. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the product mixtures of $^{\text{Me}}\text{Bhp-PH}_2$ with BnK and $^{\text{tBu}}\text{Bhp-I}$ (bottom) and $^{\text{tBu}}\text{Bhp-PH}_2$ with BnK and $^{\text{tBu}}\text{Bhp-I}$ (top) in CD_2Cl_2 .

3.9 Reactivity of Bhp-PX₂ towards Bhp-Li

As already discussed in Chapter 2.4, common pathways to secondary phosphines actually start from the dihalophosphines, which can be reacted with organometallic reagents. SCHARNHÖLZ also tried the reaction of the organolithium compound with half an equivalent of phosphorus trichloride, but could only isolate a diphosphine.^[1] Analogously to the reactions in Chapter 3.8, three experiments were run. For all of them, the organolithium precursor was prepared by adding two equivalents of *tert*-butyllithium to the iodo species. Afterwards, the dihalophosphines were added at $-80\text{ }^\circ\text{C}$ and left stirring for one day, which resulted in yellow mixtures. The intended product should cause a singlet, both in the coupled and decoupled ^{31}P NMR spectrum, with a low-field shift compared to the hydrogen-substituted analog. Spectra are very similar and two singlets can be found in all of them, one around $+87\text{ ppm}$ and one around $+524\text{ ppm}$ (Figure 26). The latter signal is shifted too much, so the former is more likely to actually belong to the monohalophosphine. This also agrees well with literature values of similar compounds.^[59,63]

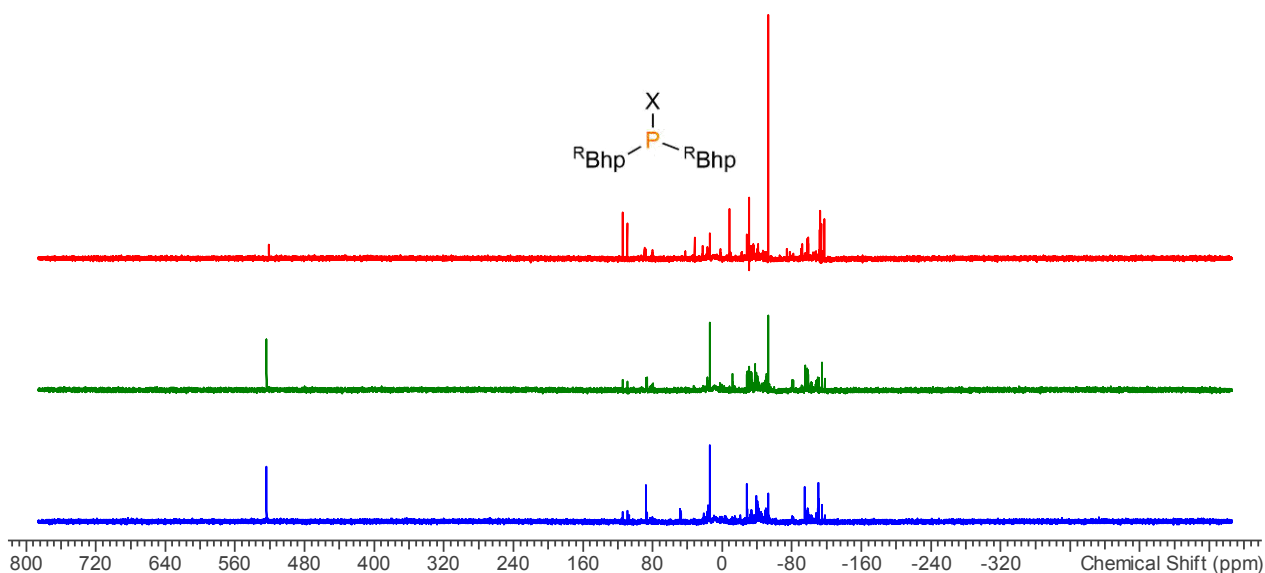


Figure 26. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the product mixtures of $^{\text{Me}}\text{Bhp-PX}_2$ and $^{\text{Me}}\text{Bhp-Li}$ (bottom), $^{\text{Me}}\text{Bhp-PX}_2$ and $^{\text{tBu}}\text{Bhp-Li}$ (middle) and $^{\text{tBu}}\text{Bhp-PX}_2$ and $^{\text{tBu}}\text{Bhp-Li}$ (top) in C_6D_6 .

Unfortunately, the intended product is among the signals with weak intensity and no single-crystals could be isolated thus far. The signal around +524 ppm is also visible in the reaction with two equivalents of $[\text{PCO}]^-$, as well as in the reaction of phosphine **1** with SbCl_3 and BiCl_3 . Therefore, this undesired by-product seems to be readily formed, whenever highly reactive intermediary phosphorus species are present. Even though different solvents were used in the aforementioned reactions (toluene, tetrahydrofuran and diethyl ether) and the mixtures were cooled, formation could not be prevented.

3.10 Reactivity of Bhp–Li towards PCl_3

Another way of obtaining symmetric secondary phosphines is based on the reaction of half an equivalent of phosphorus trichloride with the respective lithium salts.^[63] The downside of this approach is the instability of these organometallic compounds at ambient temperature. SCHARNHÖLZ tried a similar reaction, but could only obtain an open-chain dichlorodiphosphine, which was thought to be the product of an additional intermediary metal-halide-exchange.^[1] The reaction was tried again by quickly adding phosphorus trichloride to the intense red solution of Bhp–Li, which was prepared before, at $-80\text{ }^\circ\text{C}$. Upon addition, the mixture instantly turns yellow and stays at this color. After stirring for 2 hours, volatiles were removed and a ^{31}P NMR spectrum of the solids in deuterated benzene was measured (Figure 27).

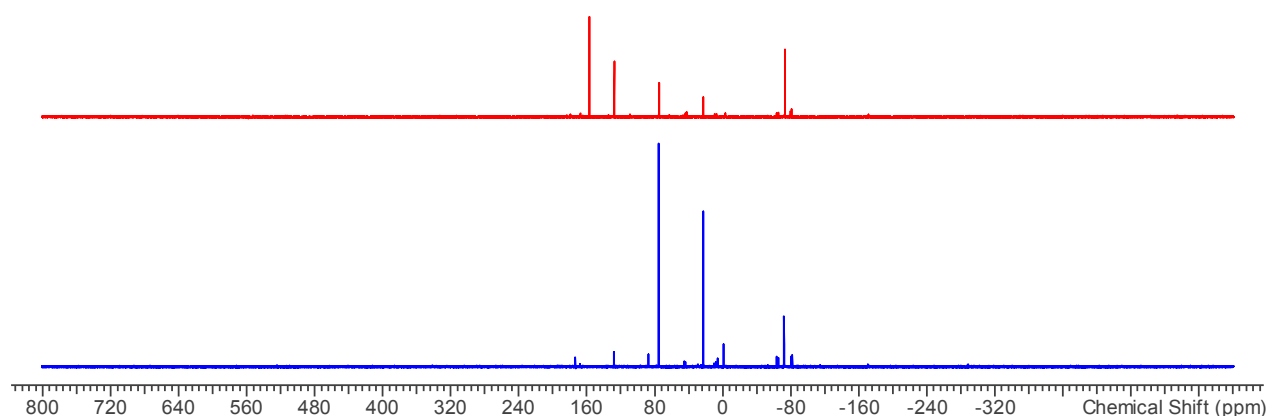


Figure 27. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the product mixtures of $^{\text{Me}}\text{Bhp-Li}$ and PCl_3 (bottom) and $^{\text{tBu}}\text{Bhp-Li}$ and PCl_3 (top) in C_6D_6 .

The outcome for these two reactions differs, with the main signal for the methyl derivate being found at +75 ppm, which is very likely just $^{\text{Me}}\text{Bhp-PI}_2$. For the *tert*-butyl derivate the main signal is located at +157 ppm, which can be attributed to $^{\text{tBu}}\text{Bhp-PCl}_2$. Smaller signals are caused by $^{\text{tBu}}\text{Bhp-PClH}$ (+128 ppm) and $^{\text{tBu}}\text{Bhp-PI}_2$. A signal caused by the intended secondary phosphine is located at +88 ppm, but only with relatively small intensity and only when using $^{\text{Me}}\text{Bhp-Li}$.

It seems that for the *tert*-butyl derivate, more than half an equivalent of PCl_3 might have been added. Due to rather small scales, this cannot be ruled out. Of course, halogen interchange between chlorine and iodine is possible and a molecule like $(\text{Bhp})_2\text{PI}$ would cause a signal that would be shifted to higher field, when compared to the chlorine analog. However, it seems that neither of these reactions worked out as intended. A larger scale with more precise amounts of phosphorus trichloride might prove to be more successful.

3.11 Reactivity of Bhp–Mg–I towards PCl_3

The last approach is also based on organometallic compounds, but in this case a GRIGNARD reagent is used. This involves the advantage of being able to add the organometallic mixture to phosphorus trichloride, because GRIGNARD reagents are more stable towards elevated temperatures, which could lead to less side reactions. Unfortunately, iodo precursors are the most reactive halogen compounds when preparing the organometallic reagent and can already undergo side reactions like C–C coupling reactions. To test the influence of the sterically demanding substituent, as well as the present halogen, a reaction with $\text{Mes}^*\text{--Br}$ was carried out as well. The GRIGNARD reagents were prepared by stirring a mixture of the respective halide and previously activated magnesium turnings (stirred without solvent for several weeks to scrape off oxide layers) in excess for 5 days, with repetitive refluxing. A change to a darker color indicated that reaction took place. The GRIGNARD reagents were then used without further purification and added dropwise to a solution of phosphorus trichloride in tetrahydrofuran at $-80\text{ }^\circ\text{C}$ *via* syringe. After stirring overnight and removing all volatiles, the light yellow residues were used for ^{31}P NMR measurements. The results between using the methyl and *tert*-butyl derivatives differ curiously enough (Figures 28 and 29). While the main signal for the former can be found at +219 ppm (most probably unreacted phosphorus trichloride) and smaller ones at +178 ppm and +113 ppm, none of these can be found in the spectrum of the latter reaction. The *tert*-butyl derivate exhibits signals at +201 ppm and +38 ppm. It is very likely that the reaction for the methyl derivate did not fully take place, even though identical conditions were used for both reactions. Interestingly, neither of these spectra show a signal that could be attributed to the intended secondary phosphine.

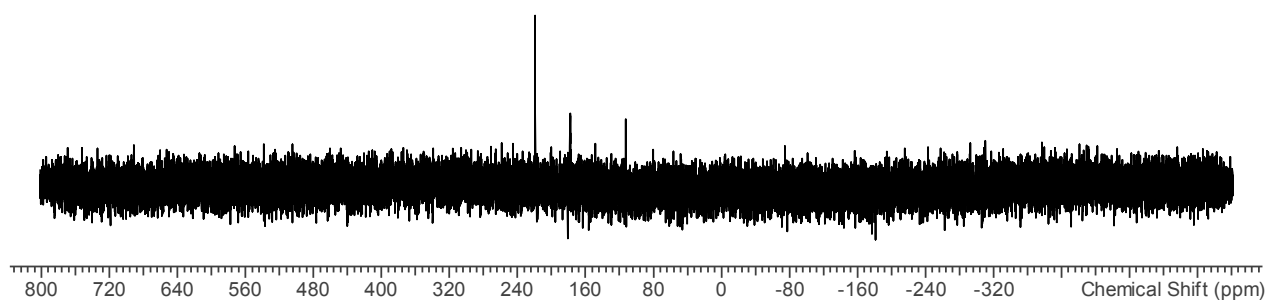


Figure 28. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the product mixture of $^{\text{Me}}\text{Bhp-Mg-I}$ and PCl_3 in C_6D_6 .

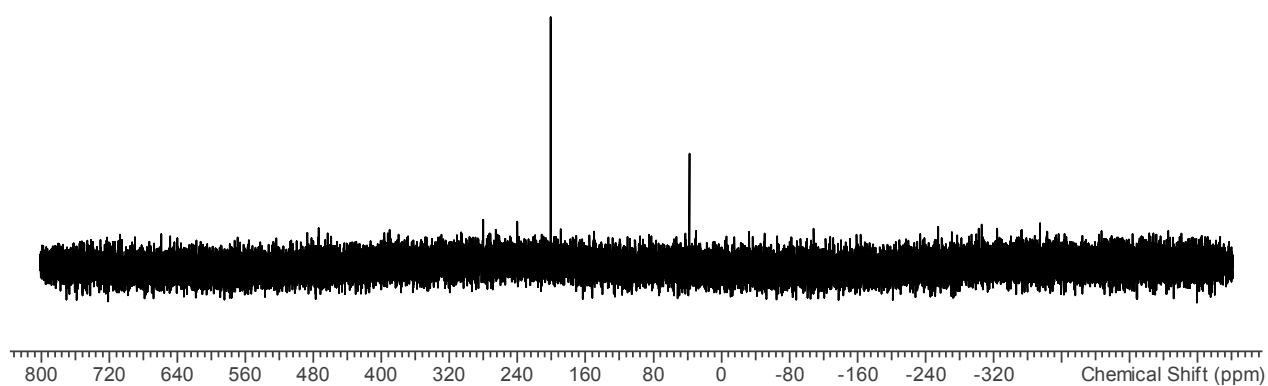


Figure 29. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the product mixture of $^{\text{tBu}}\text{Bhp-Mg-I}$ and PCl_3 in C_6D_6 .

The reaction of the supermesityl GRIGNARD reagent gave yet another result (Figure 30). Two main singlets can be found at +153 ppm and +151 ppm (ratio 2 : 1) and several smaller signals between +38 and +220 ppm (the latter should again be caused by phosphorus trichloride).

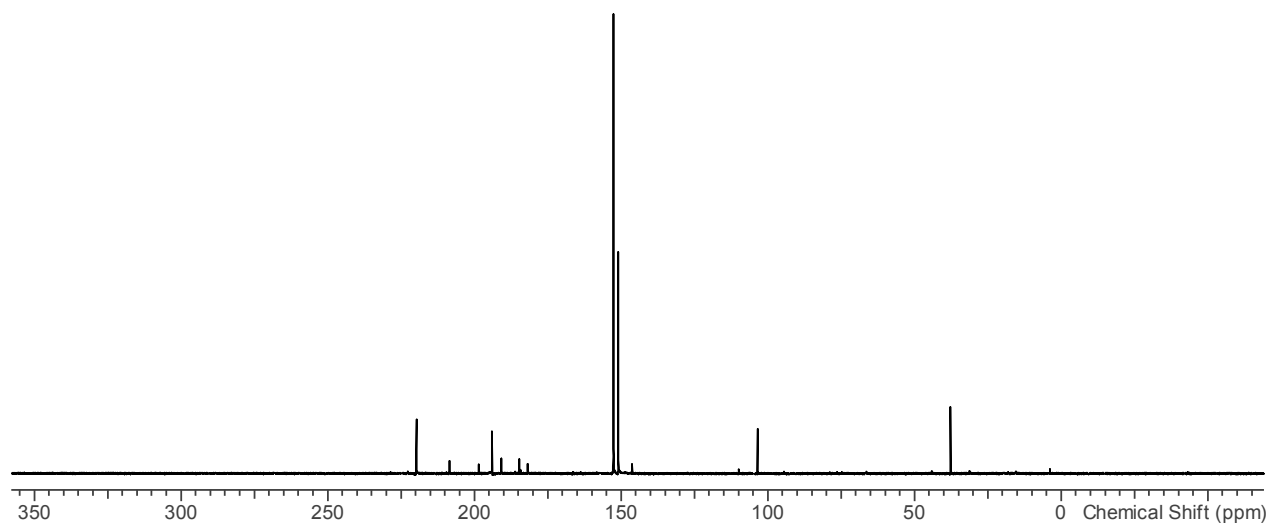


Figure 30. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the product mixture of $\text{Mes}^*\text{-Mg-Br}$ and PCl_3 in C_6D_6 .

While it seems appealing to attribute the two major singlets to compounds of the type $(\text{Mes}^*)_2\text{PCl}$ and $(\text{Mes}^*)_2\text{PBr}$, the distance between those signals would be expected to be larger. Additionally, the signals should be shifted to higher field. Using a bromine-substituted precursor also seems to lead to a more diverse product mixture, as compared to iodo derivatives. Nevertheless, none of these GRIGNARD reactions gave the desired product.

4. Quantitative Evaluation of DFT Computations

Nowadays, barely any scientific results are published without additional theoretical investigations and computational chemistry has become an important and increasingly accessible tool. With a variety of applications to choose from, the fundamentals remain the same. The final goal of any computational approach is to solve the general time-independent SCHRÖDINGER equation with the wave function Ψ (Equation 2) for a specific system (molecule), which can then be used to calculate properties like chemical shifts, partial charges, vibrational frequencies and so on.^[80] Unfortunately, it's not possible to solve this equation exactly for a multi-electron system. However, using several approximations and simplifications, a wave function can be calculated.

$$\hat{H}\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) = E\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M)$$

Equation 2. Time-independent SCHRÖDINGER equation, where $\hat{H}$ represents the Hamiltonian (or HAMILTON operator), E equals the energetic eigenvalue and $\vec{x}$ and $\vec{R}$ represent the coordinates of the electrons and nuclei in the system.^[80]

Due to significant differences in mass between nuclei and the electrons surrounding them, electrons can actually be viewed as moving in a field of non-moving point-like nuclei, which is called the BORN-OPPENHEIMER approximation. When trying to solve the SCHRÖDINGER equation, a specific starting structure is entered, containing information about the number of electrons and the charge and location of the nuclei. Now, appropriate multi-electron wave functions are tried on this system until the calculated energy is minimized. Using all imaginable functions would obviously be impossible and come with an unimaginable computational cost. Therefore, a subset of functions is used, which should ideally give results close to reality, while at the same time not being too time-consuming. So-called basis sets are functions, which serve as the foundation for the construction of a suitable wave function.

The HARTREE-FOCK (HF) method uses a SLATER determinant to describe the ground-state wave function (Equation 3). This determinant consists of N one-electron wave functions (orbitals) and considers that electrons are indistinguishable and that the wave function is antisymmetric with respect to electrons being interchanged.

$$\Psi_0 \approx \Phi_{SD} = \frac{1}{\sqrt{N!}} \begin{bmatrix} X_1(\vec{x}_1) & \cdots & X_N(\vec{x}_1) \\ \vdots & \ddots & \vdots \\ X_1(\vec{x}_N) & \cdots & X_N(\vec{x}_N) \end{bmatrix}$$

Equation 3. SLATER determinant as an approximate solution for the wave function Ψ_0 . N equals the number of electrons, X represents a one-electron wave function.

The wave functions (or spin orbitals) X are varied in order to find the minimal energy. However, the HF approximation is quite an oversimplification, as a SLATER determinant only describes the interaction of an electron with the electrostatic field of all other electrons, without exact electron correlation.

Due to approximations, the calculated ground state energy is always higher than the actual energy of a system. The difference between these two energies is the so-called correlation energy, which mainly stems from errors in consideration of electronic repulsions.

Another way of calculating properties of a system is based on the electron density, which also happens to be an observable, for instance *via* X-ray diffraction experiments. HOHENBERG and KOHN proved in 1964, that the electron density uniquely defines a ground-state wave function and therefore the energy of a system. One year later, KOHN and SHAM put this to use by suggesting that the classical HF approach is a better fit for the calculation of kinetic energies only and the remaining, comparably small contribution by electron interaction can be approximated by a functional (which is unknown in its explicit form). Therefore, the theoretical approach of this so-called Density Functional Theory is exact and does not completely rely on approximations.

Apart from pure DFT methods, including the BP86 and B97D3 functionals, hybrid methods like B3LYP, M062X and PBE1PBE (also known as PBE0) are based on a mixture of HF exchange and DFT exchange-correlation and often give better results, making them more popular within the scientific community.^[82–88]

Even though one can usually assume that a larger basis set goes along with more accurate results, the actual outcome is still somewhat empirical. Using a higher number of functions for each atom often increases computation time by several days, yet the difference in accuracy does not necessarily justify this approach. In order to test this, a variety of different functionals and basis sets was used to optimize the geometries of a test set of 15 different pnictogen compounds (Table 3).^[89–95]

Among these molecules are 2 cations, 2 anions, 2 biradicals and a mixture of open-chain and cyclic systems. Even though several benchmark publications exist, they usually deal with rather small molecules.^[96–101] Molecules with more than 50 atoms are rarely discussed, as the computational effort is quite high and using a number of different functionals and basis sets is very time-consuming. The higher number of atoms also comes with increased significance of non-covalent interactions within the molecule, which is why results based on different levels of theory can differ drastically.

Cartesian coordinates from single-crystal structures were used as starting points for geometric optimizations. For evaluations, all bonds and angles containing a pnictogen atom were considered. Data from single-crystal structures was treated like a normal distribution and the respective value plus / minus three times the standard deviation (99.73 % of all values are included in this range) served as an upper / lower limit. The absolute value of the difference between a calculated and experimental value was then used and a mean error was calculated for each combination of method and basis set (Figure 31).

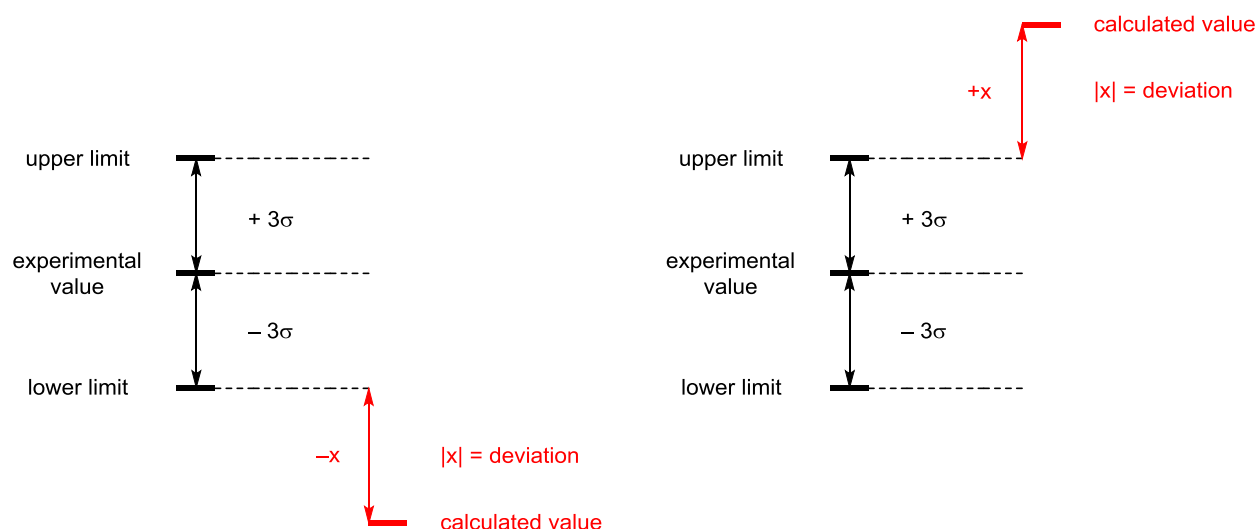


Figure 31. Employed method to obtain deviations for bond lengths and angles.

In addition to the usual **NMR = spinspace** keyword used to compute J coupling constants, the option **NMR = mixed** was employed, which is supposed to give better results for so-called valence-oriented basis sets.^[81]

The calculated absolute shifts $\sigma_{\text{calc},X}$ were referenced to the experimental absolute shift of 85 % H_3PO_4 in the gas phase ($\sigma_{\text{ref},1} = 328.35$ ppm), using PH_3 ($\sigma_{\text{ref},1} = 594.45$ ppm) as a secondary standard (see Appendix for a more elaborate explanation). For each combination of method and basis set, $\sigma_{\text{calc},\text{PH}_3}$ had to be computed (Table 4).

In total, 1500 computation jobs were run and evaluated with respect to accuracy of results and amount of time.

4. Quantitative Evaluation of DFT Computations

Table 3. Computed compounds (top left) with single crystal (right; bond lengths in Å, angles in degrees) and NMR (bottom left) parameters ($R_1 = i\text{Pr}$, $R_2 = \text{Ad}$, $R_3 = \text{Mes}$, $R_4 = t\text{Bu}$, $R_5 = \text{SiMe}_3$, $R_6 = \text{Ph}$, $R_7 = \text{Cy}$).

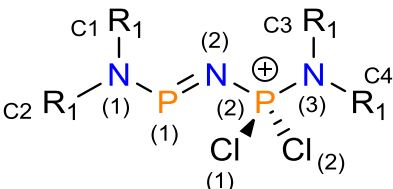
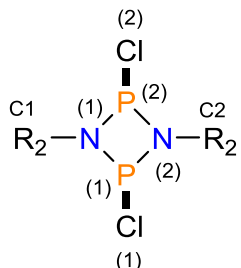
 $[(i\text{Pr})_2\text{NPNP}(\text{Cl}_2)\text{N}(i\text{Pr})_2]^+ \text{ (32)}^{[102]}$ (number of atoms: 47)			C1-N1 C2-N1 N1-P1 P1-N2 N2-P2 P2-Cl1 P2-Cl2 P2-N3 N3-C3 N3-C4 C1-N1-C2 C1-N1-P1 C2-N1-P1 N1-P1-N2 P1-N2-P2 N2-P2-N3 N2-P2-Cl1 N2-P2-Cl2 Cl1-P2-Cl2 Cl1-P2-N3 Cl2-P2-N3 P2-N3-C3 P2-N3-C4 C3-N3-C4	1.490(3) 1.510(2) 1.611(2) 1.597(2) 1.557(2) 1.9986(8) 2.0055(8) 1.596(2) 1.502(3) 1.497(3) 116.8(2) 125.9(1) 117.2(1) 104.95(9) 129.4(1) 112.41(9) 113.01(8) 111.79(8) 100.65(3) 109.13(7) 109.18(7) 125.1(1) 117.7(1) 117.1(2)
δ / ppm	J / Hz			
P_A	P_A			
P_X	112			
 <i>cis</i>-[AdNPCI]₂ (33)^[103] (number of atoms: 56)			C1-N1 N1-P1 N1-P2 P1-Cl1 P2-Cl2 P1-N2 P2-N2 N2-C2 C1-N1-P1 C1-N1-P2 N1-P1-Cl1 N1-P2-Cl2 N1-P2-N2 N1-P1-N2 P1-N1-P2 Cl1-P1-N2 Cl2-P2-N2 P1-N2-P2 P1-N2-C2 P2-N2-C2	1.472(2) 1.696(2) 1.695(1) 2.1266(7) 2.1255(7) 1.698(1) 1.696(1) 1.473(2) 131.1(1) 130.7(1) 104.23(6) 104.77(6) 81.72(7) 81.65(7) 98.15(7) 103.55(6) 102.99(6) 98.00(7) 129.7(1) 127.5(1)
δ / ppm				
P_A	+206.0			

Table 3 (continued). Computed compounds (top left) with single crystal (right; bond lengths in Å, angles in degrees) and NMR (bottom left) parameters ($R_1 = i\text{Pr}$, $R_2 = \text{Ad}$, $R_3 = \text{Mes}$, $R_4 = t\text{Bu}$, $R_5 = \text{SiMe}_3$, $R_6 = \text{Ph}$, $R_7 = \text{Cy}$).

		C1-N1	1.474(2)
P _A	δ / ppm +183.3	N1-P1	1.708(2)
		N1-P2	1.713(2)
		P1-Cl1	2.0440(8)
		P1-Cl2	2.0643(9)
		P2-Cl3	2.0592(8)
		P2-Cl4	2.0411(9)
		C1-N1-P1	111.2(1)
		C1-N1-P2	111.0(1)
		N1-P1-Cl1	105.49(6)
		N1-P1-Cl2	103.92(6)
		Cl1-P1-Cl2	96.97(3)
		P1-N1-P2	137.80(9)
		N1-P2-Cl3	104.91(6)
		N1-P2-Cl4	105.78(6)
		Cl3-P2-Cl4	96.58(4)
TerN(PCl ₂) ₂ (34) ^[102] (number of atoms: 56)		C1-N1	1.443(3)
P _A	δ / ppm +210.5	N1-P1	1.709(2)
		P1-Cl1	2.097(1)
		P1-N2	1.705(2)
		N2-C2	1.436(3)
		N2-P2	1.701(2)
		P2-Cl2	2.0987(8)
		P2-N1	1.704(2)
		C1-N1-P1	131.8(2)
		N1-P1-Cl1	106.63(8)
		N1-P1-N2	81.3(1)
		Cl1-P1-N2	102.68(8)
		P1-N2-P2	98.1(1)
		P1-N2-C2	127.8(2)
		C2-N2-P2	129.8(2)
		N2-P2-N1	81.5(1)
		N2-P2-Cl2	105.81(7)
		Cl2-P2-N1	103.60(7)
		P2-N1-P1	97.8(1)
		P2-N1-C1	127.1(2)
<i>cis</i> -[DippNPCl] ₂ (35) ^[103] (number of atoms: 64)			

4. Quantitative Evaluation of DFT Computations

Table 3 (continued). Computed compounds (top left) with single crystal (right; bond lengths in Å, angles in degrees) and NMR (bottom left) parameters ($R_1 = iPr$, $R_2 = Ad$, $R_3 = Mes$, $R_4 = tBu$, $R_5 = SiMe_3$, $R_6 = Ph$, $R_7 = Cy$).

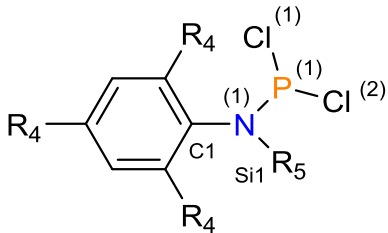
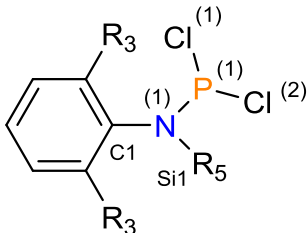
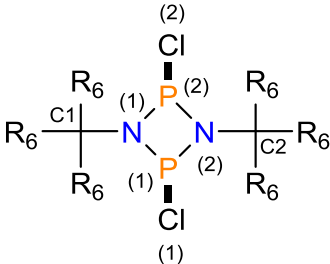
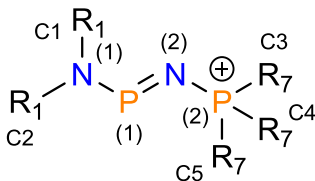
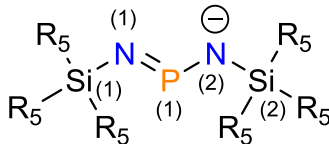
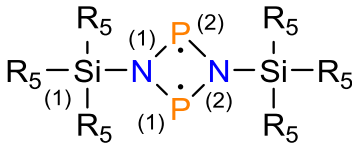
 Mes*N(SiMe₃)PCl₂ (36)^[103] (number of atoms: 64)		C1–N1 1.486(2) N1–Si1 1.812(2) N1–P1 1.658(2) P1–Cl1 2.1189(8) P1–Cl2 2.0944(8) C1–N1–Si1 114.6(1) C1–N1–P1 117.5(1) Si1–N1–P1 127.85(9) N1–P1–Cl1 107.36(6) N1–P1–Cl2 102.63(6) Cl1–P1–Cl2 92.56(3)
P _A	δ / ppm +174.5	
 TerN(SiMe₃)PCl₂ (37)^[103] (number of atoms: 66)		C1–N1 1.466(1) N1–Si1 1.8110(8) N1–P1 1.6760(8) P1–Cl1 2.0932(4) P1–Cl2 2.1021(4) C1–N1–Si1 121.87(6) C1–N1–P1 110.95(6) Si1–N1–P1 127.17(5) N1–P1–Cl1 107.48(3) N1–P1–Cl2 101.79(3) Cl1–P1–Cl2 95.50(2)
P _A	δ / ppm +168.2	
 <i>cis</i>-[Ph₃CNPCl]₂ (38)^[103] (number of atoms: 74)		C1–N1 1.504(3) N1–P1 1.694(2) N1–P2 1.718(2) P1–Cl1 2.1529(8) P2–Cl2 2.1172(8) P1–N2 1.701(2) P2–N2 1.716(2) N2–C2 1.499(2) C1–N1–P1 130.6(1) C1–N1–P2 125.3(1) N1–P1–Cl1 104.36(7) N1–P2–Cl2 105.60(7) N1–P2–N2 81.02(8) N1–P1–N2 82.14(8) Cl1–P1–N2 102.59(7) Cl2–P2–N2 104.65(7) P1–N2–C2 133.8(1) P2–N2–C2 125.3(1) P1–N1–P2 97.82(9) P1–N2–P2 97.66(9)
P _A	δ / ppm +197.6	

Table 3 (continued). Computed compounds (top left) with single crystal (right; bond lengths in Å, angles in degrees) and NMR (bottom left) parameters ($R_1 = iPr$, $R_2 = Ad$, $R_3 = Mes$, $R_4 = tBu$, $R_5 = SiMe_3$, $R_6 = Ph$, $R_7 = Cy$).

 [(<i>i</i>Pr)₂NPNP(Cy)₃]⁺ (39)^[102] (number of atoms: 75)			C1-N1	1.494(7)
δ / ppm J / Hz P_A P_A +49.1 P_X +303.8 24	C2-N1	1.505(6)		
	N1-P1	1.626(4)		
	P1-N2	1.570(6)		
	N2-P2	1.626(3)		
	P2-C3	1.821(4)		
	P2-C4	1.817(4)		
	P2-C5	1.818(4)		
	C1-N1-C2	116.0(4)		
	C1-N1-P1	124.7(4)		
	C2-N1-P1	119.1(4)		
	N1-P1-N2	106.0(3)		
	P1-N2-P2	139.2(3)		
	N2-P2-C3	107.7(2)		
	N2-P2-C4	105.2(2)		
	N2-P2-C5	112.0(2)		
	C3-P2-C4	108.6(2)		
	C3-P2-C5	107.6(2)		
	C4-P2-C5	115.5(2)		
 [HypNPNHyp]⁻ (40)^[105] (number of atoms: 83)			Si1-N1	1.744(2)
δ / ppm P_A +401.5			N1-P1	1.586(2)
			P1-N2	1.585(2)
			N2-Si2	1.741(2)
			Si1-N1-P1	127.0(1)
			N1-P1-N2	106.9(1)
			P1-N2-Si2	126.8(1)
 [HypNP]₂ (41)^[106] (number of atoms: 84)			Si1-N1	1.789(3)
δ / ppm P_A +322.4			N1-P1	1.692(3)
			N1-P2	1.689(3)
			P1-N2	1.698(3)
			P2-N2	1.684(3)
			N2-Si2	1.790(3)
			Si1-N1-P1	133.5(2)
			Si1-N1-P2	130.3(2)
			N1-P1-N2	83.7(1)
			N1-P2-N2	84.2(1)
			P1-N1-P2	96.1(1)
			P1-N2-P2	96.0(1)
			P1-N2-Si2	133.5(2)
			P2-N2-Si2	130.3(2)

4. Quantitative Evaluation of DFT Computations

Table 3 (continued). Computed compounds (top left) with single crystal (right; bond lengths in Å, angles in degrees) and NMR (bottom left) parameters ($R_1 = iPr$, $R_2 = Ad$, $R_3 = Mes$, $R_4 = tBu$, $R_5 = SiMe_3$, $R_6 = Ph$, $R_7 = Cy$).

[Mes*PPNMes*][−] (42)^[107] (number of atoms: 97)				C1–P1 1.867(2) P1–P2 2.0644(6) P2–N1 1.625(1) N1–C2 1.411(2) C1–P1–P2 98.04(5) P1–P2–N1 104.29(5) P2–N1–C2 125.2(1)	
δ / ppm J / Hz P_A P_X				P_A +242.2 P_X +486.4 −546	
Mes*PPN(PCl₂)Mes* (43)^[107] (number of atoms: 100)				C1–P1 1.853(2) P1–P2 2.0353(5) P2–N1 1.751(1) N1–P3 1.687(1) N1–C2 1.466(2) P3–Cl1 2.0638(5) P3–Cl2 2.1062(5) C1–P1–P2 94.0(4) P1–P2–N1 104.29(4) P2–N1–C2 112.04(8) P2–N1–P3 117.35(6) C2–N1–P3 128.95(8) N1–P3–Cl1 106.94(4) N1–P3–Cl2 100.37(4) Cl1–P3–Cl2 98.62(2)	
δ / ppm J / Hz P_A P_M P_A P_M P_X				P_A +160.8 P_M +395.2 +242 P_X +461.6 −10 −562	

Table 3 (continued). Computed compounds (top left) with single crystal (right; bond lengths in Å, angles in degrees) and NMR (bottom left) parameters ($R_1 = i\text{Pr}$, $R_2 = \text{Ad}$, $R_3 = \text{Mes}$, $R_4 = t\text{Bu}$, $R_5 = \text{SiMe}_3$, $R_6 = \text{Ph}$, $R_7 = \text{Cy}$).

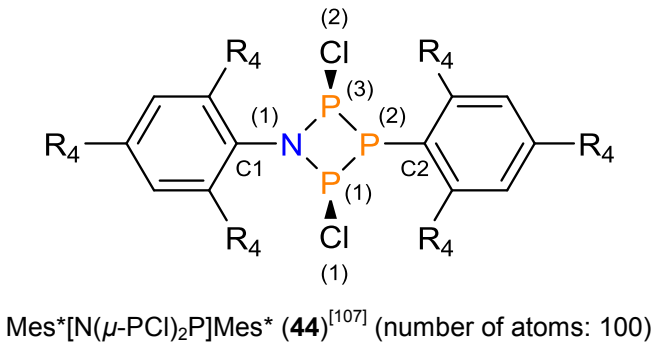
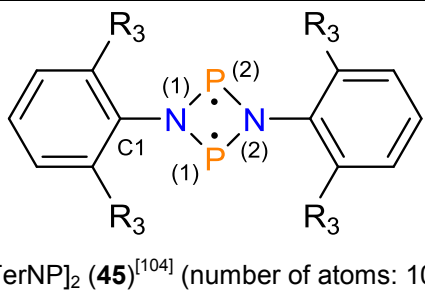
 Mes*[N(μ-PCl)₂P]Mes* (44)^[107] (number of atoms: 100)			C1–N1 1.471(2) N1–P1 1.715(2) P1–Cl1 2.1062(7) P1–P2 2.2522(7) P2–C2 1.875(2) P2–P3 2.2603(7) P3–Cl2 2.1311(6) P3–N1 1.720(2) C1–N1–P1 114.6(1) N1–P1–Cl1 104.17(6) N1–P1–P2 87.87(5) Cl1–P1–P2 99.60(3) P1–P2–P3 75.79(2) P1–P2–C2 99.69(6) C2–P2–P3 102.78(6) P2–P3–N1 87.48(5) P2–P3–Cl2 92.44(3) Cl2–P3–N1 109.08(5) P3–N1–P1 107.60(8) P3–N1–C1 133.8(1)	
δ / ppm J / Hz P_A P_A P_A -26.4 P_X +207.2 -174				
 [TerNP]₂ (45)^[104] (number of atoms: 102)			C1–N1 1.423(2) N1–P1 1.718(1) N1–P2 1.715(1) C1–N1–P1 129.6(1) C1–N1–P2 130.8(1) N1–P1–N2 80.48(8) N1–P2–N2 80.64(8) P1–N1–P2 99.44(6)	
δ / ppm P_A +289.8				

Table 3 (continued). Computed compounds (top left) with single crystal (right; bond lengths in Å, angles in degrees) and NMR (bottom left) parameters ($R_1 = iPr$, $R_2 = Ad$, $R_3 = Mes$, $R_4 = tBu$, $R_5 = SiMe_3$, $R_6 = Ph$, $R_7 = Cy$).

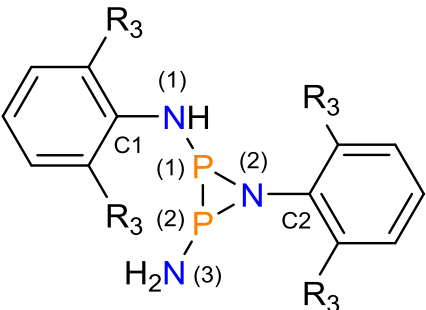
 TerN(H)P(NTer)PNH₂ (46)^[108] (number of atoms: 106)			C1–N1	1.406(3)
			N1–P1	1.725(2)
			P1–N2	1.729(2)
			P1–P2	2.2064(8)
			P2–N2	1.755(2)
			N2–C2	1.413(2)
			P2–N3	1.673(2)
			C1–N1–P1	130.3(2)
			N1–P1–P2	103.07(7)
			N1–P1–N2	96.64(9)
			P1–N2–C2	133.9(1)
			P1–P2–N3	106.88(9)
			P1–P2–N2	50.19(5)
			P1–N2–P2	78.57(7)
			N3–P2–N2	107.5(1)
			P2–N2–C2	127.6(1)
			P2–P1–N2	51.24(6)
			δ / ppm	J / Hz
				P_A
P_A	–59.2			
P_B	–50.7	–114		

Table 4. σ_{calc} (PH₃) in ppm for every used basis set and method.

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	+591.93	+587.27	+588.33	+618.52	+604.92
Def2SVP	+614.67	+608.96	+614.79	+640.70	+629.06
Def2SVPP	+600.26	+593.96	+599.70	+630.27	+615.49
cc-pVDZ	+612.54	+605.56	+611.48	+639.89	+625.78
cc-pVTZ	+573.03	+572.69	+578.11	+599.11	+596.63

Due to convergence problems, the integration grid had to be changed for some computations (**int** = **ultrafine** or **int** = **superfine**). These are marked in the respective detailed overview tables (see Appendix).

In general, the optimization of a starting structure is the most time-consuming part and computations of vibrational frequencies and NMR data are finished in a significantly shorter amount of time. The job CPU times for each optimization are plotted in Figures 32 to 36, with each graph representing all jobs for one specific functional. The real time of an optimization equals the displayed time, divided by the number of CPUs.

Assuming a number of 40 cores is used, no job took longer than three days.

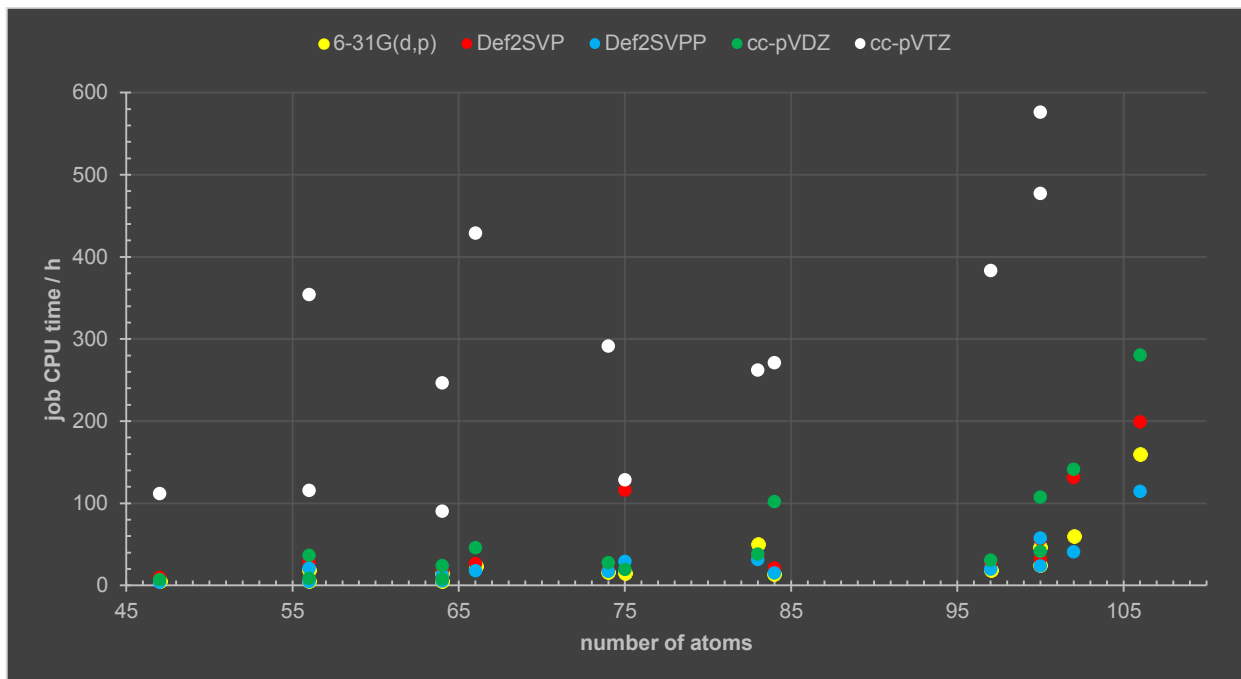


Figure 32. Job CPU times for the optimization of the molecule test set, using the B3LYP functional (note that the two molecules with the highest number of atoms are not displayed for the cc-pVTZ basis set, due to computation times of 1493 h and 1855 h).

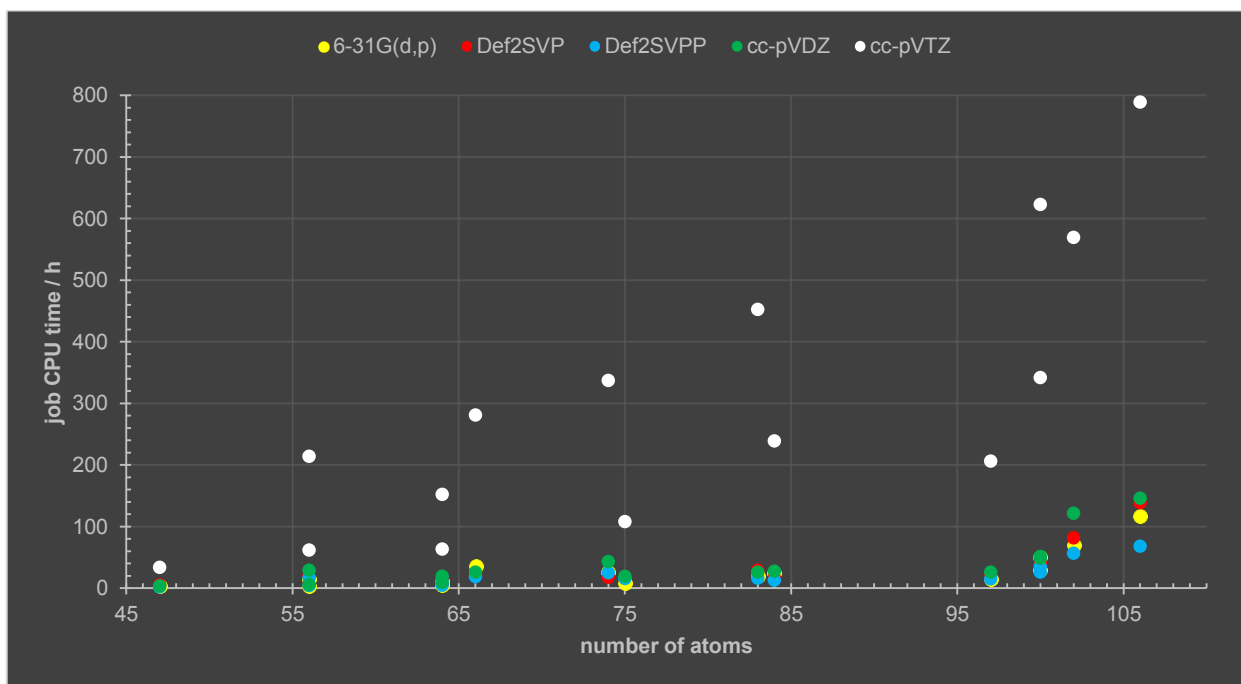


Figure 33. Job CPU times for the optimization of the molecule test set, using the B97D3 functional.

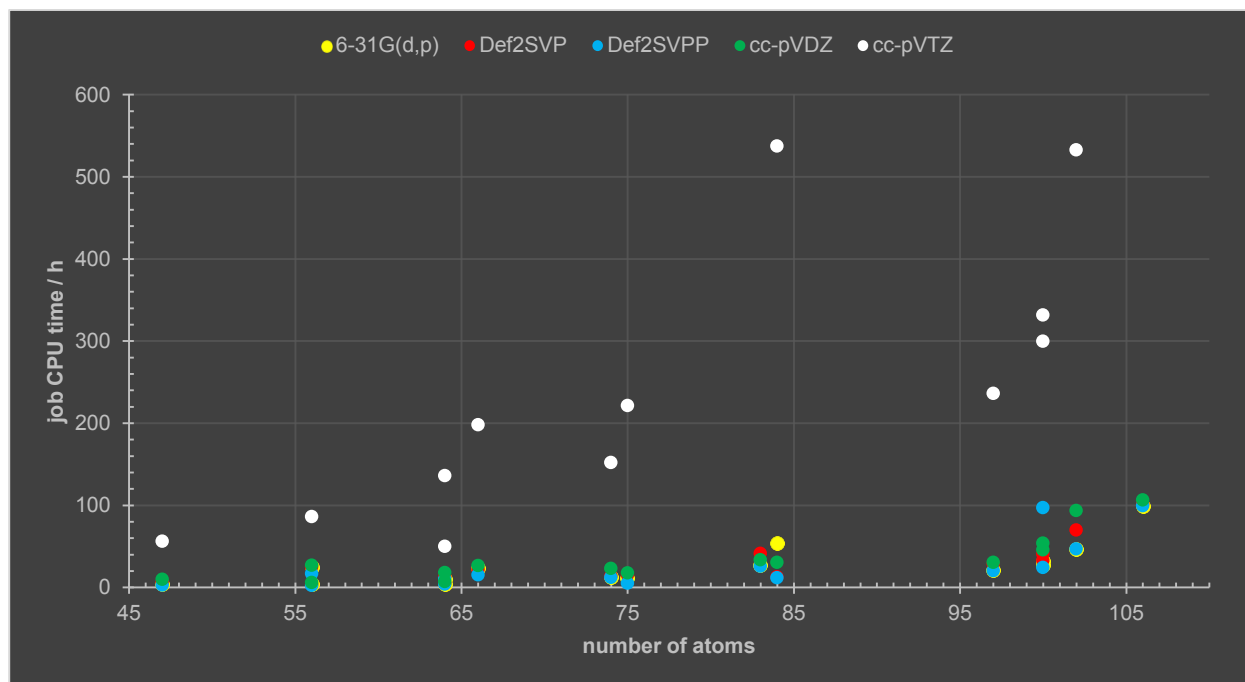


Figure 34. Job CPU times for the optimization of the molecule test set, using the BP86 functional (note that one molecule with 56 and one with 106 atoms are not displayed for the cc-pVTZ basis set, due to computation times of 1009 h and 1477 h).

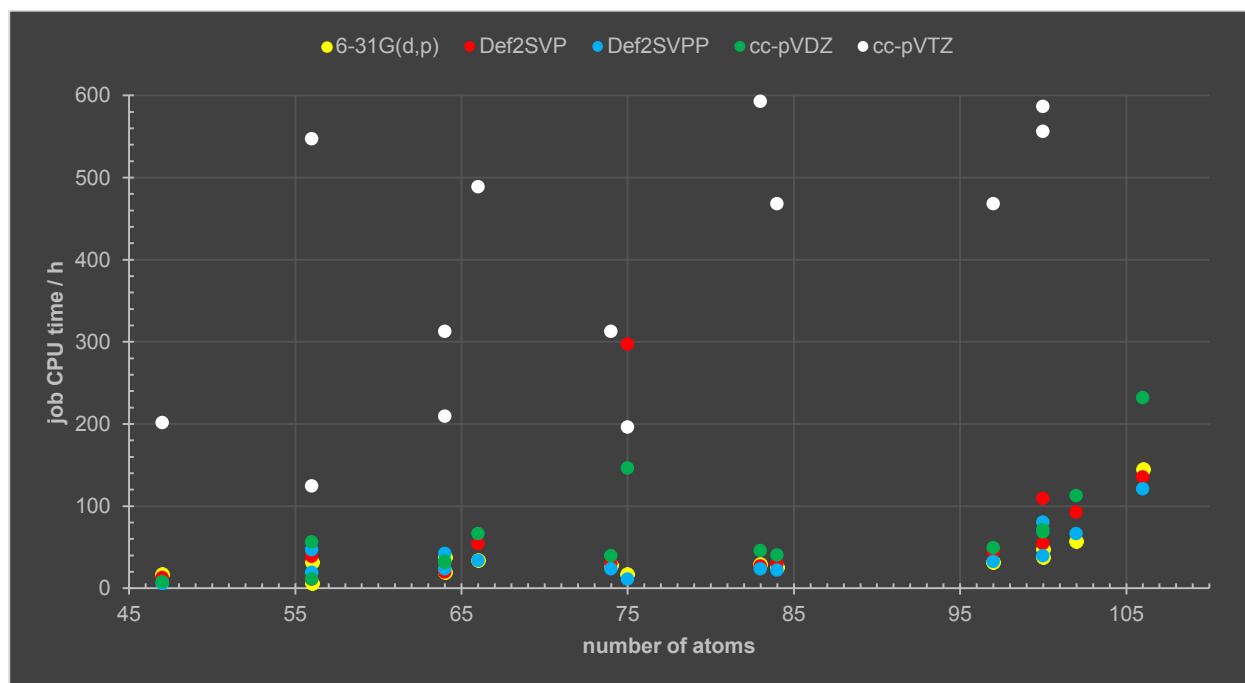


Figure 35. Job CPU times for the optimization of the molecule test set, using the M062X functional (note that the two molecules with the highest number of atoms are not displayed for the cc-pVTZ basis set, due to computation times of 1220 h and 1593 h).

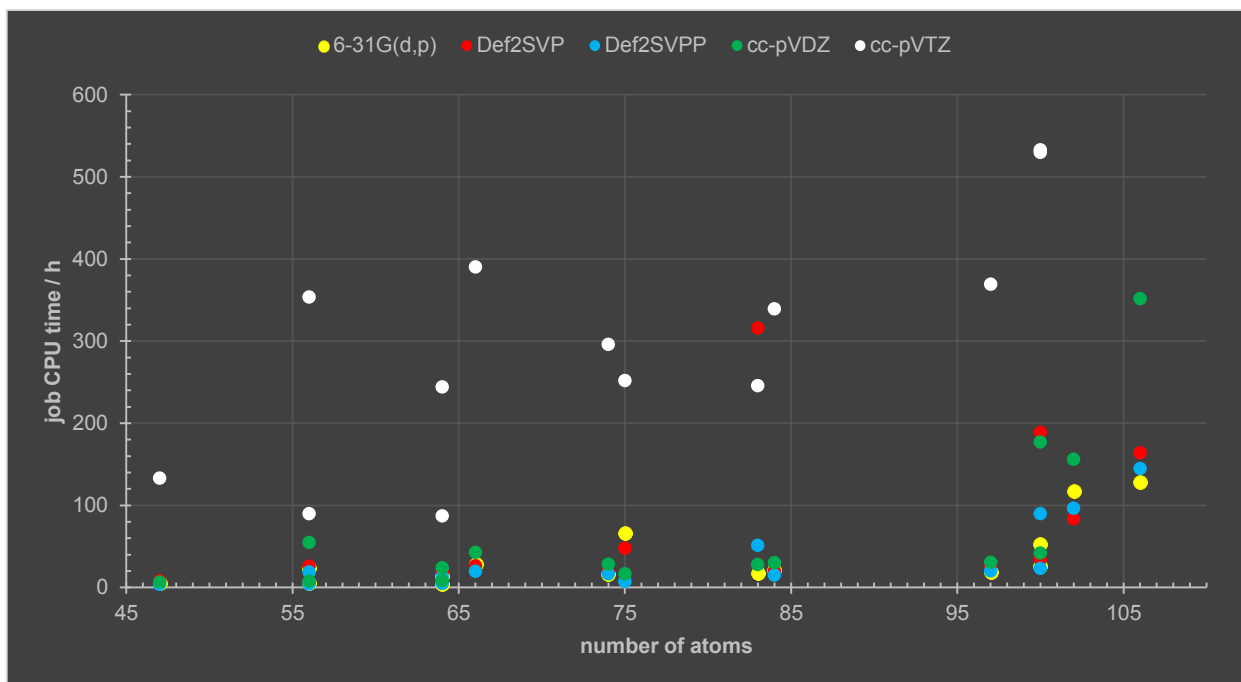


Figure 36. Job CPU times for the optimization of the molecule test set, using the PBE1PBE functional (note that the two molecules with the highest number of atoms are not displayed for the cc-pVTZ basis set, due to computation times of 2087 h and 2329 h).

The results of comparing calculated bond lengths, angles and NMR data with experimental values can be found in Tables 5 to 9. To calculate the mean errors, the absolute values were used for chemical shifts, since it does not matter in which direction a signal is shifted when identifying compounds. Nonetheless, the signed values can be found in the Appendix.

Table 5. Mean error of bond lengths in Å.

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	±0.0254	±0.0294	±0.0356	±0.0150	±0.0136
Def2SVP	±0.0262	±0.0306	±0.0357	±0.0133	±0.0161
Def2SVPP	±0.0263	±0.0307	±0.0355	±0.0135	±0.0162
cc-pVDZ	±0.0357	±0.0404	±0.0463	±0.0206	±0.0237
cc-pVTZ	±0.0191	±0.0224	±0.0281	±0.0069	±0.0086

4. Quantitative Evaluation of DFT Computations

Table 6. Mean error of angles in degrees.

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	±0.968	±1.265	±1.030	±0.994	±0.842
Def2SVP	±0.993	±1.017	±1.077	±1.052	±0.852
Def2SVPP	±0.988	±1.058	±1.073	±1.109	±0.873
cc-pVDZ	±0.885	±1.358	±1.082	±1.038	±0.853
cc-pVTZ	±0.962	±1.072	±0.956	±0.837	±0.777

Table 7. Mean error of chemical shifts in ppm.

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	±29.1	±29.1	±26.3	±31.1	±27.4
Def2SVP	±24.5	±30.6	±22.3	±32.7	±21.4
Def2SVPP	±28.4	±39.8	±26.2	±32.0	±33.8
cc-pVDZ	±22.0	±22.1	±17.2	±33.8	±18.5
cc-pVTZ	±26.0	±17.1	±25.9	±39.8	±16.2

Table 8. Mean error of spin-spin coupling constants in Hz.

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	±24	±49	±24	±45	±35
Def2SVP	±47	±60	±29	±55	±50
Def2SVPP	±47	±60	±33	±56	±52
cc-pVDZ	±40	±53	±28	±69	±48
cc-pVTZ	±17	±31	±23	±49	±23

Table 9. Mean error of spin-spin coupling constants (**NMR = mixed**) in Hz.

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	±34	±27	±36	±44	±23
Def2SVP	±16	±23	±26	±36	±13
Def2SVPP	±15	±24	±24	±36	±13
cc-pVDZ	±26	±30	±35	±45	±25
cc-pVTZ	±47	±26	±48	±53	±38

While optimizations give the best results with both the M062X and PBE1PBE functionals, the latter gives more accurate chemical shifts, which is especially important when dealing with unknown compounds, which are yet to be identified. The cc-pVTZ basis set might be the most time-consuming, but this also comes with the highest accuracy in most instances. However, this basis set was only defined for atoms from hydrogen to argon and calcium to krypton, so whenever dealing with heavier atoms, another basis set has to be applied. Another basis set with triple-zeta valence, and therefore similar properties, for this case would be Def2TZVP.^[91,92]

Adding additional diffuse functions to the cc-pVDZ and cc-pVTZ basis sets by using the prefix AUG- might further increase the accuracy of results.^[94,109] These basis sets were actually tested on a few molecules but often led to convergence issues, even when structures were optimized with a smaller basis set prior to employing the augmented approach, and are therefore not part of this work. Of course, there are always several input details that can be changed to still obtain results, but this should be kept in mind.

The B97D3 functional, which incorporates empirical dispersion, does not stand out in any way, which is owed to the fact that dispersion does not have a significant influence on the evaluated parameters, but more on the spatial orientation of substituents, as well as reaction energies.

In 72 % of the evaluated computations, the keyword variation **NMR = mixed** gave a more accurate coupling constant than the common **NMR = spinspin**. Especially the Def2SVP and Def2SVPP basis sets stand out, with errors being decreased by up to 39 Hz.

5. Summary and Outlook

The novel primary phosphine, bearing the Bhp moiety, could be prepared with a *tert*-butyl group in *para*-position in an analogous procedure to the previously synthesized *para*-methyl derivate. The synthesis of secondary phosphines was only marginally successful and they were merely observed in a small percentage among several other products. A problem with increasingly bigger substituents are scrambling reactions and also C–H activation between reactive pnictogen centers and sterically demanding groups.^[110] The Bhp moiety might actually be at the upper limit in terms of preparing secondary phosphines with sterical bulk. Different isomers of tetraphosphabicyclobutanes, as well as a proposed diphosphene were observed in different concentrations in almost every reaction and therefore represent thermodynamic minima, which are hard to circumvent. In terms of the activation of small molecules, the preparation of secondary phosphines should be approached starting from substituents with less bulk, which can be gradually increased, depending on the reaction outcome.

For future computations, the combination of the PBE0 functional and the cc-pVTZ basis set can be highly recommended, as it gave the most accurate results in the majority of evaluated results. If atoms beyond krypton are present in the input structures, the Def2TZVP basis set might give similar results. However, this was not tested in this work.

6. Appendix

6.1 Working Technique

All syntheses and experiments, excluding the synthesis of the amine and halide starting materials, were carried out under oxygen- and moisture-free conditions, using SCHLENK or drybox techniques. Therefore, glassware was heated three times with a heat gun (650 °C) *in vacuo* and subsequently flushed with argon. Substances sensitive to hydrolysis or oxidation were handled under argon atmosphere inside a drybox. Solvents were dried and distilled under argon atmosphere and handled *via* syringes, which were purged with argon three times prior to use.

Solvents and reactants were obtained from commercial sources or synthesized. Dichloromethane (CH_2Cl_2) was purified according to a literature procedure, dried over P_4O_{10} , stored over CaH_2 and freshly distilled and degassed prior to use.^[111] Diethyl ether (Et_2O), tetrahydrofuran (THF), benzene (C_6H_6) and toluene (C_7H_8) were dried over Na/benzophenone and freshly distilled prior to use. *n*-Pentane was dried over Na/benzophenone/tetraglyme (tetraglyme = $\text{Me}(\text{OCH}_2\text{CH}_2)_4\text{OMe}$) and freshly distilled prior to use. Deuterated dichloromethane (CD_2Cl_2) was dried over P_4O_{10} , stored over CaH_2 and freshly distilled and degassed prior to use. Deuterated benzene (C_6D_6) was dried over Na and freshly distilled prior to use.

The following table gives an overview about other employed chemicals.

6. Appendix

Reactant	Source	Purification
[Bu ₃ MeN][PCO]	synthesized by PHILIP STOER	-
acetic acid (99.5 %)	ChemSolute	-
antimony trichloride	Merck	sublimation
arsenic trichloride	Sigma-Aldrich	drying over P ₄ O ₁₀ , distillation, degassing
benzyl potassium	synthesized by MORITZ SCHARNHÖLZ ^[1]	-
bis(diethylamino)chlorophosphane	old stock	distillation
bismuth trichloride	abcr GmbH	sublimation
1,8-diazabicyclo[5.4.0]undec- 7-ene	old stock	drying over CaH ₂ , distillation
diphenylmethanol	Tokyo Chemical Industry	-
hydrochloric acid (37.0 %)	ChemSolute	-
lithium aluminium hydride	abcr GmbH	sublimation
magnesium	Abcr GmbH	-
magnesium sulfate	Grüssing GmbH	-
4-methylaniline	J & K Scientific	-
phosphorus trichloride	Merck	drying over P ₄ O ₁₀ , distillation, degassing
potassium carbonate	Grüssing GmbH	-
potassium iodide	VK Labor- und Feinchemikalien	-
sodium nitrite	KMF Laborchemie	-
sodium sulfate	Riedel-de Haën	-
sodium sulfite	VWR	-
4- <i>tert</i> -butylaniline	abcr GmbH	distillation
<i>tert</i> -butyllithium	Sigma-Aldrich	-
triethylamine	ChemSolute	drying over Na, distillation
zinc chloride	Riedel-de Haën	sublimation

6.2 Analytical and Computational Methods

6.2.1 X-ray Single-crystal Structure Determination

Appropriate crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 123(2) K during measurements. Data was collected on a Bruker Kappa Apex II CCD diffractometer or a Bruker D8 Quest CMOS diffractometer, using monochromatic graphite Mo K α radiation ($\lambda = 0.71073$ Å). Structures were solved by direct methods (SHELXTL) and refined by full-matrix least squares procedures (SHELXL-2014/7).^[112,113] Semi-empirical absorption corrections were applied (SADABS).^[114] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to phosphorus atoms were refined freely. Other hydrogen atoms were refined at calculated positions, using a riding model. Disordered molecular groups were split in parts, with their occupancy being refined freely.

Detailed crystallographic data can be found in Chapter 6.5 of the appendix.

6.2.2 NMR Spectroscopy

NMR spectra were obtained on a Bruker AVANCE 250, 300 or 500 MHz spectrometer and were referenced internally to the deuterated solvent (^{13}C : CD_2Cl_2 $\delta_{\text{ref}} = 54.0$ ppm, C_6D_6 $\delta_{\text{ref}} = 128.4$ ppm), to protic impurities in the deuterated solvent (^1H : CHDCl_2 $\delta_{\text{ref}} = 5.32$ ppm, C_6HD_5 $\delta_{\text{ref}} = 7.16$ ppm) or externally (^{31}P : 85% H_3PO_4 $\delta_{\text{ref}} = 0$ ppm). All measurements were carried out at ambient temperature.

6.2.3 IR Spectroscopy

IR spectra of crystalline samples were recorded on a Nicolet 380 FT-IR spectrometer with a Smart Orbit ATR unit at ambient temperature.

6.2.4 RAMAN Spectroscopy

RAMAN spectra of crystalline samples were recorded using a LabRAM HR 800 Horiba Jobin YVON Raman spectrometer equipped with an Olympus BX41 microscope with variable lenses. The samples were excited by a red LASER (633 nm, 17 mW). All measurements were carried out at ambient temperature.

6.2.5 Elemental Analysis

Elemental analyses were obtained using an Elementar vario Micro cube CHNS analyzer.

6.2.6 Melting Points

Melting points (uncorrected) were determined using a Stanford Research Systems EZ Melt at a heating rate of 5 °C/min.

6.2.7 DFT Computations

All computations were carried out using the Gaussian09 program package.^[115] The KOHN-SHAM wave function was calculated using the pure DFT functionals B97D3 and BP86, as well as the hybrid DFT functionals B3LYP, M062X and PBE0 and the basis sets 6-31G(d,p), Def2SVP, Def2SVPP, cc-pVDZ and cc-pVTZ.^[82–95]

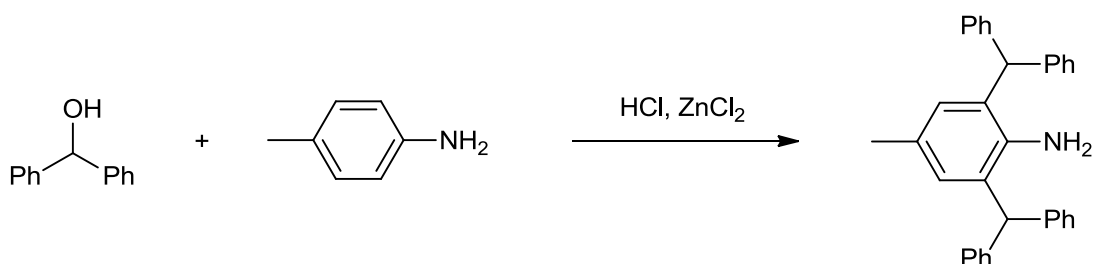
All structures were fully optimized and confirmed as minima by frequency analyses. Chemical shifts and coupling constants were derived by the GIAO method.^[116–120] The calculated absolute shifts ($\sigma_{\text{calc},X}$) were referenced to the experimental absolute shift of 85 % H_3PO_4 in the gas phase ($\sigma_{\text{ref},1} = 328.35$ ppm), using PH_3 ($\sigma_{\text{ref},2} = 594.45$ ppm) as a secondary standard:^[121,122]

$$\begin{aligned}\delta_{\text{calc},X} &= (\sigma_{\text{ref},1} - \sigma_{\text{ref},2}) - (\sigma_{\text{calc},X} - \sigma_{\text{calc},\text{PH}_3}) \\ &= \sigma_{\text{calc},\text{PH}_3} - \sigma_{\text{calc},X} - 266.1 \text{ ppm}\end{aligned}$$

The values for $\sigma_{\text{calc},\text{PH}_3}$ can be found in Table 3 in Chapter 4. It should be emphasized that all computations were carried out for single, isolated gas phase molecules. There may be significant differences between gas phase, solution and solid state data.

6.3 Syntheses of Starting Materials

6.3.1 ^{Me}Bhp-NH₂

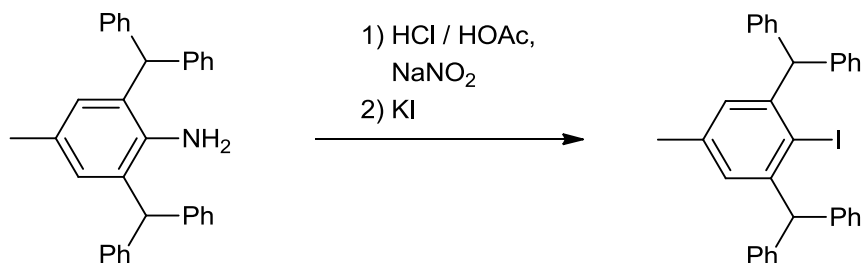


Diphenylmethanol (114.794 g, 623.10 mmol), 4-methylaniline (33.252 g, 310.30 mmol) and zinc chloride (21.657 g, 158.90 mmol) are placed together in a 1 L round-bottom flask with a big stir bar. After adding concentrated hydrochloric acid (35 mL, 1142.35 mmol), the flask is equipped with a condenser and the mixture is subsequently heated to 150 °C for 2 hours in an oil bath. After cooling to ambient temperature, the formed orange solid is dissolved in dichloromethane (600 mL). Residual acid is neutralized via slow addition of an aqueous potassium carbonate solution (55 g in 400 mL). Organic and aqueous layers are separated and the former is washed twice with water. After drying over sodium sulfate, the solution is decanted and volatiles are completely removed at the rotary evaporator. The crude product is crushed into a fine powder and eventually washed with cold ethyl acetate, leaving a white solid, which is dried again *in vacuo*. Yield: 102.977 g (75.5 %).

Mp.: 178-184 °C. CHN calcd. (exptl.) in %: C 90.16 (90.32), H 6.65 (6.81), N 3.19 (2.79). ¹H NMR (CD₂Cl₂, 500.1 MHz): δ = 2.03 (s, 3 H, *p*-CH₃), 3.35 (s, 2 H, NH₂), 5.46 (s, 2 H, CHPh₂), 6.43 (s, 2 H, *m*-H), 7.13 (m, 8 H, Ph), 7.25 (tt, 4 H, ³*J*(¹H, ¹H) = 7.25 Hz, ⁴*J*(¹H, ¹H) = 1.22 Hz, *p*-H (Ph)), 7.31 (m, 8 H, Ph). IR (ATR, 32 scans, cm⁻¹): $\tilde{\nu}$ = 3443 (w), 3377 (w), 3083 (vw), 3052 (w), 3023 (w), 3000 (w), 2941 (vw), 2914 (w), 2864 (w), 1951 (vw), 1939 (vw), 1881 (vw), 1811 (vw), 1791 (vw), 1770 (vw), 1624 (w), 1599 (w), 1583 (w), 1550 (vw), 1492 (m), 1463 (m), 1442 (m), 1319 (w), 1292 (w), 1271 (w), 1253 (w), 1236 (w), 1177 (w), 1156 (w), 1133 (w), 1115 (w), 1076 (w), 1030 (w), 1001 (w), 966 (vw), 942 (vw), 921 (w), 911 (w), 882 (w), 863 (w), 830 (w), 752 (s), 696 (vs), 637 (m), 620 (m), 602 (s), 554 (s), 499 (m), 488 (m), 480 (m), 472 (m). Raman (633 nm, 20 s, 10 scans, cm⁻¹): $\tilde{\nu}$ = 3379 (1), 3067 (2), 3060 (2), 3056 (2), 3050 (2), 3038 (1), 3000 (1), 2919 (1), 2871 (1), 1626 (2), 1599 (3), 1583 (3), 1496 (2), 1453 (2), 1446 (2), 1383 (3), 1292 (2), 1275 (2), 1255 (2), 1187 (2), 1176 (3), 1156 (2), 1077 (2), 1031 (3), 1003 (8), 985 (3),

923 (2), 909 (2), 865 (2), 847 (2), 833 (3), 818 (2), 769 (2), 749 (2), 703 (2), 682 (2), 638 (3), 620 (3), 617 (3), 603 (3), 559 (2), 541 (2), 500 (3), 481 (3), 465 (3), 394 (3), 293 (3), 278 (3), 249 (3), 240 (3), 220 (4), 207 (2), 159 (4),

6.3.2 ^{Me}Bhp-I

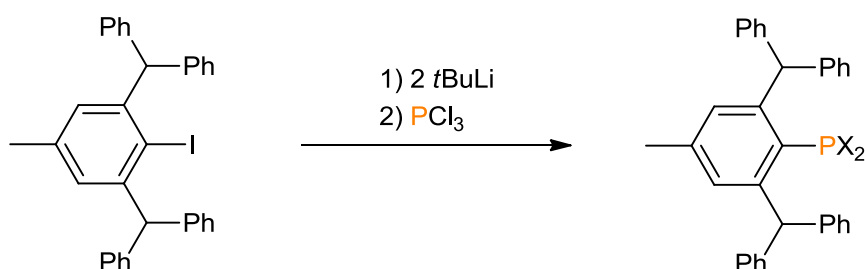


In a 2 L two-necked round-bottom flask, equipped with a condenser without stopper, a dropping funnel and a big stir bar, ^{Me}Bhp-NH₂ (50.866 g, 115.71 mmol) is dissolved in dichloromethane (400 mL). After cooling in an ice bath, concentrated hydrochloric acid (70 mL, 2284.70 mmol) and glacial acetic acid (70 mL, 1223.98 mmol) are added to the solution. An aqueous (40 mL) solution of sodium nitrite (9.675 g, 140.24 mmol) is then added dropwise and the resulting red mixture is left stirring for 20 minutes. Afterwards, an aqueous (300 mL) solution of potassium iodide (207.000 g, 1246.99 mmol) is added dropwise at 0 °C. As gas formation slows down, the residual solution can be poured into the reaction vessel. The mixture is subsequently warmed to ambient temperature and remaining iodine/triiodide is reduced by adding an aqueous (600 mL) solution of sodium sulfite (121.700 g, 965.57 mmol). After rigorous stirring, the orange organic layer is separated from the colorless aqueous layer. The former is washed with water to pH neutrality and the latter is washed twice with dichloromethane. Organic phases are combined, dried over sodium sulfate and decanted, giving an intense red solution. After evaporating the volatiles, the crude product is dissolved in toluene and *n*-pentane (3:2) and left in the refrigerator overnight. Crystals are washed with *n*-pentane, giving a mostly white solid. Yield: 31.275 g (49.1 %).

Mp.: 168-170 °C. CHN calcd. (exptl.) in %: C 72.00 (73.38), H 4.94 (5.18). ¹H NMR (CD₂Cl₂, 500.1 MHz): δ = 2.12 (s, 3 H, *p*-CH₃), 6.07 (s, 2 H, CHPh₂), 6.70 (s, 2 H, *m*-H), 7.11 (d, 8 H, ³*J*(¹H,¹H) = 7.32 Hz, *o*-H (Ph)), 7.26 (m, 4 H, *p*-H (Ph)), 7.32 (m, 8 H, *m*-H (Ph)). IR (ATR, 32 scans, cm⁻¹): $\tilde{\nu}$ = 3103 (vw), 3083 (vw), 3058 (w), 3023 (w), 3002 (w), 2916 (vw), 2893 (vw), 1947 (vw), 1879 (vw), 1811 (vw), 1764 (vw), 1597 (w), 1581 (w), 1556 (vw), 1492 (m),

1447 (m), 1424 (w), 1409 (w), 1321 (w), 1282 (vw), 1243 (w), 1177 (w), 1154 (w), 1078 (w), 1030 (w), 1001 (m), 985 (w), 968 (vw), 909 (w), 882 (w), 857 (w), 826 (w), 783 (w), 764 (m), 750 (m), 736 (m), 696 (vs), 639 (m), 620 (m), 604 (s), 571 (w), 538 (m), 505 (m), 497 (w), 474 (m), 451 (w). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu} = 3066$ (2), 3042 (1), 2896 (1), 1600 (2), 1587 (1), 1240 (1), 1178 (1), 1158 (1), 1031 (2), 1005 (10), 992 (1), 980 (1), 870 (1), 828 (1), 784 (1), 643 (1), 636 (1), 621 (1), 619 (1), 609 (1), 606 (1), 297 (1), 265 (1), 253 (2), 242 (1), 233 (1), 192 (1), 153 (1), 141 (2).

6.3.3 $^{\text{Me}}\text{Bhp-PX}_2$

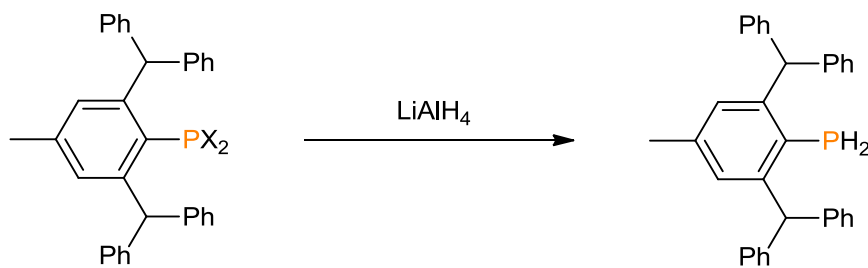


A 250 mL Schlenk flask containing $^{\text{Me}}\text{Bhp-I}$ (5.696 g, 10.35 mmol) and a stir bar is degassed and flushed with argon three consecutive times. After adding tetrahydrofuran (50 mL), the colorless solution is cooled to and kept at $-80\text{ }^{\circ}\text{C}$, whereupon a 1.7 M solution of *tert*-butyllithium in pentane (12.2 mL, 20.74 mmol) is added dropwise. The resulting red mixture is then stirred for 30 min. Afterwards, phosphorus trichloride (2.3 mL, 26.29 mmol) is quickly added *via* syringe, turning the mixture instantly yellow. Stirring at low temperature is continued for two hours and concluded by removing all volatiles *in vacuo*. The red solid is subsequently dissolved in dichloromethane and filtered with a celite-packed frit. Volatiles are removed *in vacuo*, leaving a mixture of differently substituted halophosphines (percentage by ^{31}P NMR: $^{\text{Me}}\text{Bhp-PCl}_2 = 62.1\%$, $^{\text{Me}}\text{Bhp-PClH} = 31.1\%$, $^{\text{Me}}\text{Bhp-PI}_2 = 3.7\%$). Yield: 5.081 g (88.1 %).

Mp.: $175\text{--}180\text{ }^{\circ}\text{C}$. CHN calcd. (exptl.) in %: C 68.94 (65.21), H 4.73 (4.77). ^{31}P NMR (CD_2Cl_2 , 202.5 MHz): $\delta = 76.7$ (s, 1 P, $^{\text{Me}}\text{Bhp-PI}_2$), 128.9 (s, 1 P, $^{\text{Me}}\text{Bhp-PClH}$), 157.6 (s, 1 P, $^{\text{Me}}\text{Bhp-PCl}_2$), 178.1 (s). ^1H NMR (CD_2Cl_2 , 500.1 MHz): $\delta = 2.17$ (s, 3 H, *p*- CH_3), 6.77 (m, 4 H, $\text{CHPh}_2 + m\text{-H}$), 7.22 (m, 20 H, Ph). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu} = 3083$ (vw), 3056 (w), 3025 (w), 1947 (vw), 1877 (vw), 1803 (vw), 1597 (w), 1583 (w), 1552 (w), 1494 (m), 1449 (w), 1409 (w), 1337 (w), 1276 (w), 1241 (w), 1201 (w), 1179 (w), 1156 (w), 1076 (w), 1045 (w), 1030 (w), 1001 (w), 911 (w), 882 (w), 855 (w), 847 (w), 822 (w), 781 (vw), 762 (m),

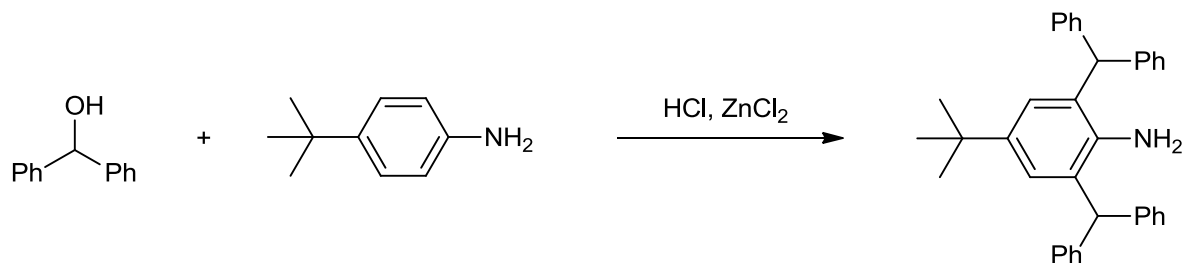
744 (m), 694 (vs), 645 (m), 633 (m), 620 (m), 604 (m), 544 (m), 525 (m), 484 (s), 468 (vs), 449 (s). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu} = 3063$ (6), 3056 (6), 2916 (5), 1599 (8), 1586 (7), 1496 (6), 1376 (5), 1240 (5), 1180 (5), 1162 (5), 1045 (5), 1033 (5), 1005 (10), 990 (4), 884 (3), 865 (3), 857 (3), 833 (3), 785 (2), 747 (2), 648 (2), 636 (2), 620 (3), 607 (2), 548 (1), 526 (2), 485 (2), 480 (2), 450 (2), 396 (1), 365 (1), 347 (1), 338 (1), 308 (2), 273 (1), 244 (2),

6.3.4 $^{\text{Me}}\text{Bhp-PH}_2$



In a 500 mL Schlenk flask, a solution of $^{\text{Me}}\text{Bhp-PX}_2$ (2.340 g, 4.20 mmol) in tetrahydrofuran (20 mL) is added to a suspension of LiAlH_4 (0.350 g, 9.22 mmol) in tetrahydrofuran (20 mL) at 0 °C and left stirring at ambient temperature overnight. Afterwards, the mixture is carefully quenched with water (100 mL) and dried *in vacuo*. The residue is dissolved in dichloromethane and filtered. The filtrate is washed with water twice, dried over MgSO_4 and decanted. Removing all volatiles *in vacuo* leaves a glass-like residue that gives a fine white powder when scraped off the flask. Yield: 1.324 g (69.0 %).

Mp.: 156-58 °C. CHN calcd. (exptl.) in %: C 86.81 (86.55), H 6.40 (6.14). ^{31}P NMR (CD_2Cl_2 , 202.5 MHz): $\delta = -155.2$ (t, $^1J(^{31}\text{P}, ^1\text{H}) = -212$ Hz, 1 P, PH_2). ^1H NMR (CD_2Cl_2 , 500.1 MHz): $\delta = 2.10$ (s, 3 H, $p\text{-CH}_3$), 3.58 (d, $^1J(^1\text{H}, ^{31}\text{P}) = -210$ Hz, 2 H, PH_2), 5.98 (d, $^4J(^1\text{H}, ^{31}\text{P}) = 3.1$ Hz, 2 H, CHPh_2), 6.65 (s, 2 H, $m\text{-H}$), 7.20 (m, 20 H, Ph). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu} = 3083$ (vw), 3058 (vw), 3023 (vw), 2916 (vw), 2320 (vw), 2310 (w), 1597 (w), 1583 (vw), 1552 (vw), 1492 (w), 1449 (w), 1436 (w), 1181 (vw), 1154 (vw), 1094 (w), 1076 (w), 1030 (w), 1004 (w), 968 (w), 911 (w), 882 (vw), 851 (w), 837 (w), 818 (w), 783 (w), 762 (w), 744 (m), 736 (w), 699 (vs), 643 (w), 620 (m), 604 (m), 536 (w), 509 (w), 476 (w), 445 (w). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu} = 3058$ (3), 3001 (1), 2978 (1), 2920 (1), 2302 (1), 1600 (2), 1584 (1), 1556 (1), 1495 (1), 1453 (1), 1379 (1), 1297 (1), 1244 (1), 1180 (2), 1164 (1), 1157 (1), 1077 (1), 1053 (1), 1031 (3), 1004 (10), 985 (2), 918 (1), 866 (1), 833 (1), 786 (1), 748 (1), 637 (1), 620 (1), 608 (1), 598 (1), 539 (1), 495 (1), 372 (1), 293 (1), 269 (1), 242 (1), 163 (2).

6.3.5 *t*BuBhp–NH₂

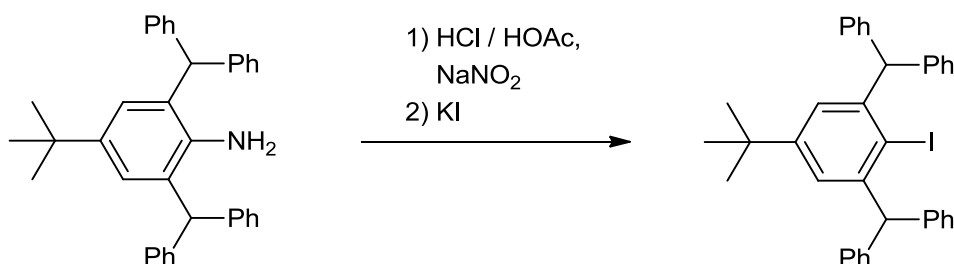
*t*BuBhp*–NH₂ is prepared according to a literature procedure by FORTIER *et al.*, which was slightly altered.^[76]

Diphenylmethanol (48.753 g, 264.63 mmol), 4-*tert*-butylaniline (19.726 g, 132.19 mmol) and zinc chloride (9.826 g, 72.10 mmol) are placed together in a 1 L round-bottom flask with a big stir bar. After adding concentrated hydrochloric acid (15 mL, 489.58 mmol), the flask is equipped with a condenser and the mixture is subsequently heated to 150 °C for 2 hours in an oil bath. After cooling to ambient temperature, the formed orange solid is dissolved in dichloromethane (300 mL). Residual acid is neutralized via slow addition of an aqueous potassium carbonate solution (25 g in 200 mL). Organic and aqueous layers are separated and the former is washed twice with water. After drying over sodium sulfate, the solution is decanted and volatiles are completely removed at the rotary evaporator. The crude product is crushed into a fine powder and washed with cold methanol. The resulting white solid is dissolved in boiling benzene and left to crystallize at ambient temperature. The product was isolated in three consecutive fractions. Yield: 37.390 g (58.7 %).

Mp.: 211–214 °C. CHN calcd. (exptl.) in %: C 89.77 (90.13), H 7.32 (7.45), N 2.91 (2.50). ¹H NMR (CD₂Cl₂, 500.1 MHz): δ = 0.99 (s, 9 H, *p*-*t*Bu), 3.33 (s, 2 H, NH₂), 5.47 (s, 2 H, CHPh₂), 6.63 (s, 2 H, *m*-H), 7.14 (dd, 8 H, ³*J*(¹H¹H) = 7.37 Hz, ⁴*J*(¹H¹H) = 1.51 Hz, *o*-H (Ph)), 7.24 (tt, 4 H, ³*J*(¹H,¹H) = 7.32 Hz, ⁴*J*(¹H,¹H) = 1.32 Hz, *p*-H (Ph)), 7.31 (m, 8 H, *m*-H (Ph)). IR (ATR, 32 scans, cm^{−1}): $\tilde{\nu}$ = 3423 (w), 3357 (vw), 3081 (vw), 3058 (w), 3027 (w), 2959 (w), 2899 (vw), 2864 (vw), 1951 (vw), 1892 (vw), 1817 (vw), 1799 (vw), 1628 (w), 1599 (w), 1492 (m), 1471 (m), 1447 (m), 1424 (w), 1391 (vw), 1362 (w), 1339 (vw), 1319 (vw), 1294 (w), 1271 (w), 1243 (w), 1189 (vw), 1156 (vw), 1137 (vw), 1117 (vw), 1078 (w), 1030 (w), 1004 (vw), 948 (vw), 925 (vw), 911 (w), 892 (w), 865 (w), 835 (w), 814 (vw), 760 (s), 736 (s), 696 (vs), 659 (m), 643 (m), 624 (s), 608 (s), 585 (m), 521 (w), 509 (w), 486 (w), 472 (w), 439 (w).

Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu} = 3360$ (1), 3056 (3), 3039 (1), 3003 (1), 2965 (1), 2862 (1), 1628 (1), 1601 (2), 1586 (1), 1466 (1), 1298 (1), 1274 (1), 1257 (1), 1246 (1), 1196 (1), 1171 (2), 1158 (1), 1120 (1), 1076 (1), 1031 (3), 1003 (9), 992 (1), 984 (1), 950 (1), 910 (1), 867 (1), 836 (2), 751 (1), 738 (1), 645 (1), 634 (1), 620 (1), 613 (1), 607 (1), 589 (1), 523 (1), 252 (1), 242 (3), 220 (3), 156 (3).

6.3.6 ^tBuBhp-I

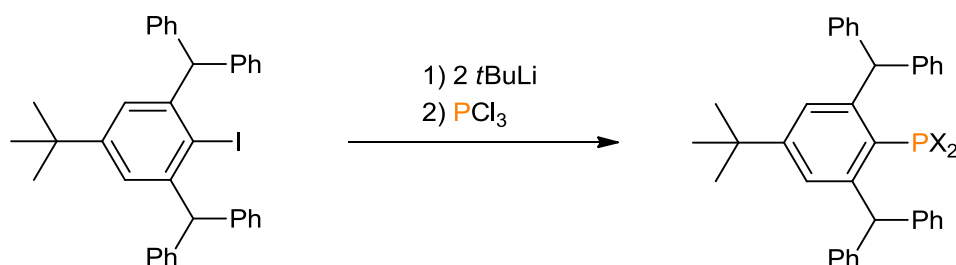


In a 1 L two-necked round-bottom flask, equipped with a condenser without stopper, a dropping funnel and a big stir bar, ^tBuBhp-NH₂ (15.522 g, 32.23 mmol) is dissolved in dichloromethane (150 mL). After cooling in an ice bath, concentrated hydrochloric acid (25 mL, 815.96 mmol) and glacial acetic acid (25 mL, 437.14 mmol) are added to the solution. An aqueous (40 mL) solution of sodium nitrite (2.829 g, 41.01 mmol) is then added dropwise and the resulting yellow mixture is left stirring for 30 minutes. Afterwards, an aqueous (100 mL) solution of potassium iodide (53.664 g, 323.28 mmol) is added dropwise at 0 °C, leading to an instant color change to dark red. As gas formation slows down, the residual solution can be poured into the reaction vessel. The mixture is subsequently warmed to ambient temperature and remaining iodine/triiodide is reduced by adding an aqueous (150 mL) solution of sodium sulfite (31.685 g, 251.39 mmol). After rigorous stirring, the yellow organic layer is separated from the colorless aqueous layer. The former is washed with water to pH neutrality and the latter is washed twice with dichloromethane. Organic phases are combined, dried over magnesium sulfate and decanted. After evaporating the volatiles, the crude product is dissolved in toluene with addition of small amounts of *n*-pentane and left in the refrigerator overnight. Crystals are washed with *n*-pentane, giving a white solid. Yield: 10.670 g (55.9 %).

Mp.: 187-190 °C. CHN calcd. (exptl.) in %: C 72.97 (73.99), H 5.61 (5.69). ¹H NMR (CD₂Cl₂, 300.1 MHz): $\delta = 1.05$ (s, 9 H, *p*-*t*Bu), 6.06 (s, 2 H, CHPh₂), 6.89 (s, 2 H, *m*-H), 7.11 (m, 8 H, *o*-H (Ph)), 7.30 (m, 12 H, *p*-H (Ph), *m*-H (Ph)).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75.5 MHz): δ = 31.2 (s, $\text{C}(\text{CH}_3)_3$), 34.8 (s, $\text{C}(\text{CH}_3)_3$), 62.8 (s, CHPh_2), 108.2 (s, C_I), 126.9 (s, $p\text{-C}(\text{Ph})$), 127.5 (s, $o\text{-C}(\text{Ph})$), 128.8 (s, $m\text{-C}(\text{Ph})$), 130.4 (s, $m\text{-C}$), 144.0 (s, C_tBu), 147.3 (s, $\text{ipso-C}(\text{Ph})$), 150.7 (s, $o\text{-C}$). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3081 (vw), 3058 (vw), 3025 (w), 3000 (vw), 2959 (w), 2864 (w), 1953 (vw), 1883 (vw), 1599 (w), 1581 (w), 1556 (vw), 1492 (m), 1475 (w), 1449 (m), 1416 (w), 1399 (w), 1362 (w), 1335 (w), 1251 (w), 1205 (w), 1175 (w), 1144 (w), 1076 (w), 1030 (w), 1004 (m), 913 (w), 892 (w), 859 (w), 832 (vw), 810 (vw), 767 (m), 746 (m), 699 (vs), 639 (m), 620 (m), 604 (m), 581 (m), 556 (w), 507 (w), 495 (w), 474 (m). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3055 (5), 3030 (1), 3003 (1), 2974 (1), 2962 (1), 2923 (1), 2905 (1), 2886 (1), 1603 (2), 1584 (1), 1455 (1), 1451 (1), 1322 (1), 1298 (1), 1274 (1), 1244 (1), 1176 (3), 1157 (1), 1078 (1), 1032 (2), 1004 (9), 994 (1), 986 (1), 946 (1), 836 (2), 769 (1), 751 (1), 643 (2), 634 (1), 620 (2), 513 (1), 259 (1), 248 (1), 239 (2), 225 (1), 188 (1), 156 (3), 136 (4). MS (EI, 70 eV, m/z): 592 (M^+ , 95 %), 577 ($\text{M} - \text{Me}$) $^+$, 17 %), 535 ($[\text{M} - \text{tBu}]^+$, 4 %), 465 ($[\text{M} - \text{I}]^+$, 70 %), 167 ($[\text{CHPh}_2]^+$, 100 %).

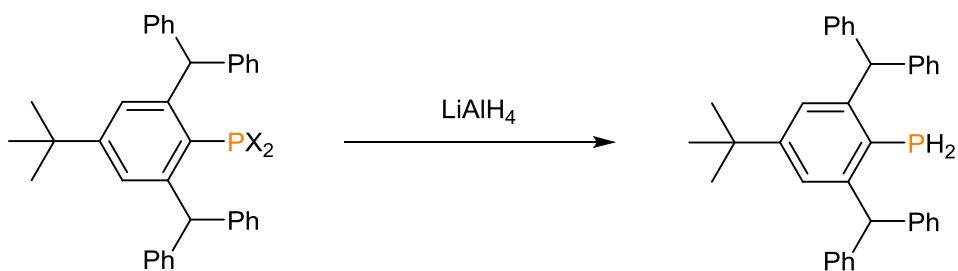
6.3.7 $^t\text{BuBhp-PX}_2$



A 100 mL Schlenk flask containing $^t\text{BuBhp-I}$ (5.375 g, 9.07 mmol) and a big stir bar is degassed and flushed with argon three consecutive times. After adding tetrahydrofuran (50 mL), the colorless solution is cooled to and kept at $-80\text{ }^\circ\text{C}$, whereupon a 1.7 M solution of *tert*-butyllithium in pentane (10.7 mL, 18.19 mmol) is added dropwise. The resulting red mixture is then stirred for 30 min. Afterwards, phosphorus trichloride (2.3 mL, 26.29 mmol) is quickly added via syringe, turning the mixture instantly yellow. Stirring at low temperature is continued for two hours and concluded by removing all volatiles *in vacuo*. The red solid is subsequently dissolved in anhydrous dichloromethane and filtered with a celite-packed frit. Volatiles are removed *in vacuo*, leaving a mixture of differently substituted halophosphines (percentage by ^{31}P NMR: $^t\text{BuBhp-PCl}_2$ = 55.4 %, $^t\text{BuBhp-PClH}$ = 44.6 %, $^t\text{BuBhp-PI}_2$ not observed). Yield: 4.930 g (89.3 %).

CHN calcd. (exptl.) in %: C 71.08 (67.75), H 5.47 (5.73). ^{31}P NMR (CD_2Cl_2 , 202.5 MHz): $\delta = 128.8$ (s, 1 P, $^t\text{BuBhp-PCl}_2$), 157.4 (s, 1 P, $^t\text{BuBhp-PCl}_2$). ^1H NMR (CD_2Cl_2 , 300.1 MHz): $\delta = 1.01$ – 1.04 (m, 9 H, p - $t\text{Bu}$), 6.69–6.78 (d, $^4J(^1\text{H}, ^{31}\text{P}) = 3.6$ Hz, 2 H, CHPh_2), 7.21 (m, 22 H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75.5 MHz): $\delta = 30.8$ – 31.6 (s, $\text{C}(\text{CH}_3)_3$), 34.6–35.4 (s, $\text{C}(\text{CH}_3)_3$), 57.6 (s, CHPh_2), 126.7–127.2 (s, p -C (Ph)), 128.5–128.9 (s, o -C (Ph)), 129.8–130.1 (s, m -C (Ph)), 130.4–130.7 (s, m -C), 144.8 (s, $\text{C}t\text{Bu}$), 149.1–149.4 (s, $ipso$ -C (Ph)), 155.5–155.8 (s, o -C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu} = 3083$ (vw), 3056 (w), 3025 (w), 2965 (w), 2866 (w), 1945 (vw), 1875 (vw), 1801 (vw), 1597 (m), 1583 (w), 1541 (w), 1492 (m), 1449 (m), 1409 (w), 1362 (w), 1249 (w), 1195 (w), 1183 (w), 1078 (w), 1030 (m), 946 (w), 911 (w), 894 (w), 826 (w), 764 (m), 742 (m), 696 (vs), 643 (m), 628 (w), 620 (m), 604 (m), 585 (m), 532 (m), 509 (w), 472 (vs), 443 (m). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu} = 3055$ (2), 2968 (1), 2952 (1), 2907 (1), 2891 (1), 1599 (5), 1583 (1), 1429 (1), 1203 (1), 1194 (1), 1187 (1), 1170 (2), 1154 (1), 1041 (3), 1030 (2), 1001 (5), 832 (1), 620 (1), 531 (1), 480 (3), 466 (1), 415 (1), 379 (1), 329 (1), 317 (1), 248 (1), 230 (1), 219 (1), 212 (2), 186 (1), 157 (1), 146 (2), 123 (3). MS (EI, 70 eV, m/z): 566 (M^+ , 74 %), 531 ($[\text{M} - \text{Cl}]^+$, 98 %), 496 ($[\text{M} - \text{Cl}_2]^+$, 40 %), 466 ($[\text{M} - \text{PCl}_2]^+$, 42 %), 167 ($[\text{CHPh}_2]^+$, 100 %).

6.3.8 $^t\text{BuBhp-PH}_2$



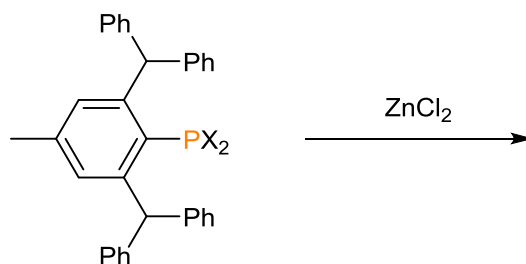
In a 250 mL Schlenk flask, a solution of $^t\text{BuBhp-PX}_2$ (4.283 g, 7.04 mmol) in tetrahydrofuran (40 mL) is added to a suspension of LiAlH_4 (0.795 g, 20.95 mmol) in tetrahydrofuran (40 mL) at 0 °C and left stirring at ambient temperature for overnight. Afterwards, the mixture is carefully quenched with water (150 mL) and dried *in vacuo*. The residue is dissolved in dichloromethane and filtered. The filtrate is washed with water twice, dried over MgSO_4 and decanted. Removing all volatiles *in vacuo* leaves a glass-like residue that gives a fine white powder when scraped off the flask. Yield: 2.351 g (67.0 %).

Mp.: 228–234 °C. CHN calcd. (exptl.) in %: C 86.71 (85.75), H 7.08 (6.89). ^{31}P NMR (CD_2Cl_2 , 101.3 MHz): $\delta = -155.5$ (t, $^1J(^{31}\text{P}, ^1\text{H}) = -210$ Hz, 1 P, PH_2).

^1H NMR (CD_2Cl_2 , 250.1 MHz): δ = 1.01 (s, 9 H, *p*-tBu), 3.57 (d, $^1J(^1\text{H}, ^{31}\text{P}) = -210$ Hz, 2 H, $\text{P}(\text{H}_2)$), 5.98 (d, $^4J(^1\text{H}, ^{31}\text{P}) = 3.0$ Hz, 2 H, CHPh_2), 6.86 (d, $^4J(^1\text{H}, ^1\text{H}) = 2.1$ Hz, 2 H, *m*-H), 7.07 (m, 8 H, Ph), 7.28 (m, 12 H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 125.8 MHz): δ = 31.2 (s, $\text{C}(\text{CH}_3)_3$), 34.9 (s, $\text{C}(\text{CH}_3)_3$), 57.2 (d, $^3J(^{13}\text{C}, ^{31}\text{P}) = 10$ Hz, CHPh_2), 126.3 (s, *p*-C (Ph)), 126.9 (s, *o*-C (Ph)), 128.9 (s, *m*-C (Ph)), 130.3 (s, *m*-C), 144.3 (s, *tert*-Bu), 147.8 (d, $^4J(^{13}\text{C}, ^{31}\text{P}) = 9$ Hz, *ipso*-C (Ph)), 150.5 (s, *o*-C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3081 (vw), 3058 (vw), 3025 (w), 3000 (vw), 2961 (w), 2901 (vw), 2862 (vw), 2326 (vw), 1807 (vw), 1595 (w), 1541 (vw), 1490 (w), 1475 (w), 1449 (w), 1405 (w), 1362 (w), 1337 (vw), 1247 (w), 1203 (vw), 1156 (w), 1096 (vw), 1076 (w), 1030 (w), 1004 (w), 944 (vw), 915 (w), 892 (w), 828 (vw), 808 (vw), 764 (m), 746 (m), 732 (w), 699 (vs), 639 (w), 620 (m), 604 (m), 583 (w), 507 (w), 474 (w), 414 (w). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3054 (4), 3002 (1), 2972 (1), 2923 (1), 2908 (1), 2864 (1), 2329 (2), 1598 (3), 1583 (2), 1450 (1), 1322 (1), 1297 (1), 1247 (2), 1188 (2), 1181 (2), 1174 (3), 1156 (2), 1075 (1), 1050 (2), 1031 (3), 1003 (10), 944 (1), 869 (1), 837 (1), 772 (1), 748 (1), 647 (1), 640 (1), 632 (1), 618 (2), 246 (2), 238 (2). MS (EI, 70 eV, m/z): 498 (M^+ , 92 %), 497 ($[\text{M} - \text{H}]^+$, 100 %), 167 ($[\text{CHPh}_2]^+$, 10 %).

6.4 Reactions of Starting Materials

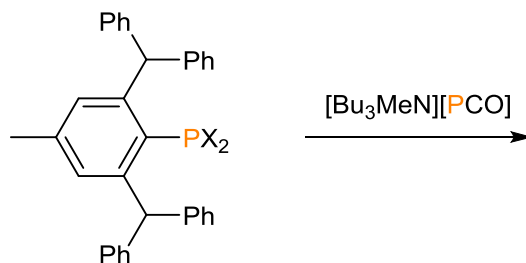
6.4.1 ^{Me}Bhp-PX₂ + ZnCl₂



In a 20 mL vial equipped with a stir bar, ^{Me}Bhp-PX₂ (0.150 g, 0.27 mmol) and ZnCl₂ (0.227 g, 1.67 mmol) are placed together as solids. Afterwards, tetrahydrofuran (8 mL) is added and the mixture is left stirring for 1 day. The next day, volatiles are removed *in vacuo*, the residue is dissolved in toluene, filtered and concentrated. The product mixture was used for NMR measurements.

³¹P{¹H} NMR (CD₂Cl₂, 202.5 MHz): $\delta = -2.3$ (s), 18.8 (s), 22.9 (s), 33.7 (s), 182.6 (s).

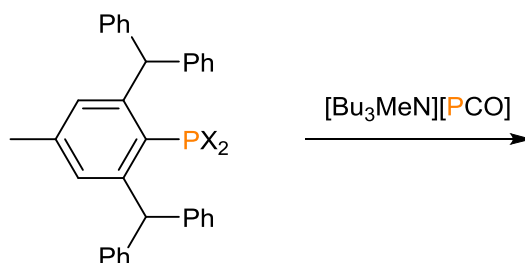
6.4.2 ^{Me}Bhp-PX₂ + [Bu₃MeN][PCO]



In a 25 mL Schlenk flask equipped with a stir bar, ^{Me}Bhp-PX₂ (0.150 g, 0.27 mmol) and [Bu₃MeN][PCO] (0.070 g, 0.27 mmol) are placed together as solids. Afterwards, precooled toluene (10 mL) is added at -80 °C and the mixture is subsequently left stirring at ambient temperature for 1 day, turning it orange. The next day, the mixture is filtered and concentrated. The product mixture was used for NMR measurements.

³¹P NMR (C₆D₆, 202.5 MHz): $\delta = -289.0$ (t, $J(^{31}\text{P}, ^{31}\text{P}) = 178$ Hz), -242.2 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 225$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 208$ Hz), -171.0 (t, $J(^{31}\text{P}, ^{31}\text{P}) = 178$ Hz), -130.9 (m), -108.0 (m), 0.1 (s), 14.0 (m), 23.6 (m), 50.9 (s), 66.4 (s), 157.1 (s, 1 P, ^{Me}Bhp-PCl₂), 186.9 (s).

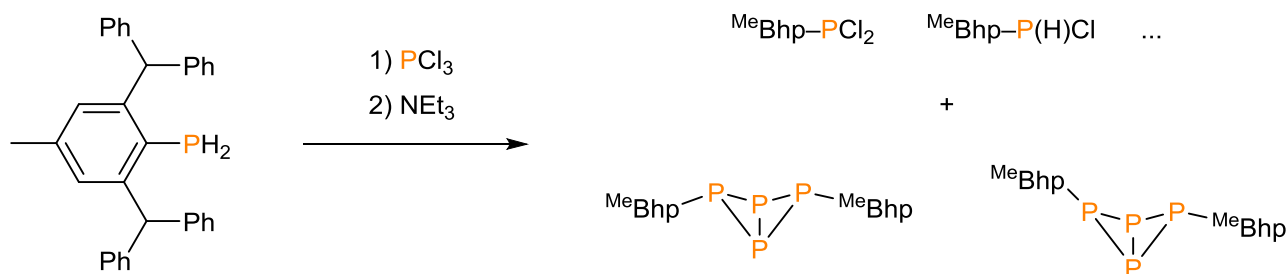
6.4.3 $^{\text{Me}}\text{Bhp-PX}_2 + 2 [\text{Bu}_3\text{MeN}][\text{PCO}]$



In a 25 mL Schlenk flask equipped with a stir bar, $^{\text{Me}}\text{Bhp-PX}_2$ (0.150 g, 0.27 mmol) and $[\text{Bu}_3\text{MeN}][\text{PCO}]$ (0.140 g, 0.54 mmol) are placed together as solids. Afterwards, precooled toluene (10 mL) is added at $-80\text{ }^{\circ}\text{C}$ and the mixture is subsequently left stirring at ambient temperature for 1 day, turning it dark red. The next day, the mixture is filtered and concentrated. The product mixture was used for NMR measurements.

^{31}P NMR (C_6D_6 , 202.5 MHz): $\delta = -289.1$ (m), -242.2 (dd, $J = 229\text{ Hz}$, $J = 212\text{ Hz}$), -171.1 (m), -155.5 (s), -116.2 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 195\text{ Hz}$), -86.9 (s), 0.1 (s), 6.3 (s), 23.7 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 576\text{ Hz}$), 58.8 (s), 183.1 (s), 523.8 (s).

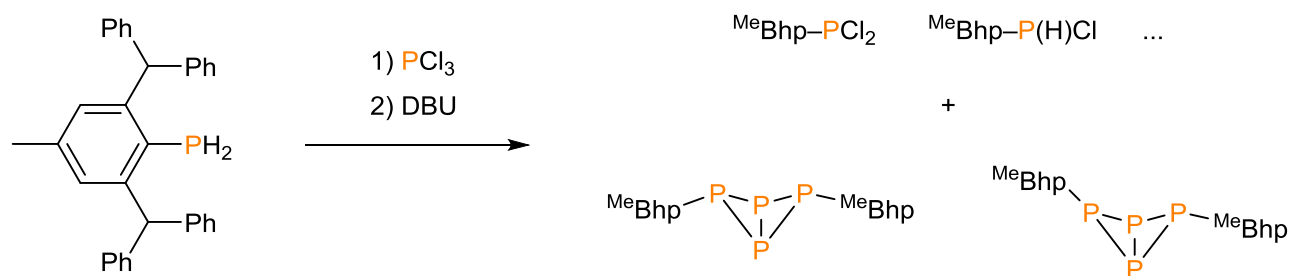
6.4.4 $^{\text{Me}}\text{Bhp-PH}_2 + \text{PCl}_3 + \text{NEt}_3$



In a 100 mL Schlenk flask, phosphorus trichloride (0.3 mL, 3.43 mmol) is added to a stirred solution of $^{\text{Me}}\text{Bhp-PH}_2$ (0.722 g, 1.58 mmol) in diethyl ether (40 mL) at $-80\text{ }^{\circ}\text{C}$. After stirring for 5 minutes, triethylamine (1.1 mL, 7.94 mmol) is added at the same temperature *via* syringe. The yellow mixture is slowly warmed to ambient temperature and left stirring overnight. Afterwards, all volatiles are removed *in vacuo*. The solid residue is dried thoroughly and the product is extracted with toluene. The filtrate is concentrated and stored in the refrigerator. The product mixture was used for NMR measurements.

^{31}P NMR (C_6D_6 , 202.5 MHz): $\delta = -288.7$ (t, $^1J(^{31}\text{P}, ^{31}\text{P}) = 178$ Hz, 2 P, *bridgehead-P* (*exo-exo*- $^{\text{Me}}\text{Bhp-P}_4\text{-}^{\text{Me}}\text{Bhp}$)), -271.3 (t, $J = 229$ Hz), -242.0 (dd, $^1J(^{31}\text{P}, ^{31}\text{P}) = 229$ Hz, $^1J(^{31}\text{P}, ^{31}\text{P}) = 203$ Hz, 2 P, *bridgehead-P* (*endo-exo*- $^{\text{Me}}\text{Bhp-P}_4\text{-}^{\text{Me}}\text{Bhp}$)), -170.9 (t, $^1J(^{31}\text{P}, ^{31}\text{P}) = 178$ Hz, 2 P, $^{\text{Me}}\text{Bhp-P}$ (*exo-exo*- $^{\text{Me}}\text{Bhp-P}_4\text{-}^{\text{Me}}\text{Bhp}$)), -159.1 (td, $J(^{31}\text{P}, ^{31}\text{P}) = 180$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 140$ Hz), -142.0 (m), -125.9 (m), -113.4 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 220$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 187$ Hz), -107.5 (m), -100.4 (m), -94.2 (m), -89.7 (td, $J(^{31}\text{P}, ^{31}\text{P}) = 203$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 170$ Hz), -43.0 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 242$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 131$ Hz), -25.9 (t, $J(^{31}\text{P}, ^{31}\text{P}) = 157$ Hz), -20.6 (t, $J = 229$ Hz), -17.0 (m), -12.2 (m), -3.4 (dt, $J(^{31}\text{P}, ^{31}\text{P}) = 244$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 200$ Hz), 3.7 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 220$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 170$ Hz), 7.9 (d, $^1J(^{31}\text{P}, ^1\text{H}) = 203$ Hz, 1 P, $^{\text{Me}}\text{Bhp-P(H)Cl}$), 18.4 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 237$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 187$ Hz), 31.1 (m), 44.8 (m), 70.6 (m), 81.1 (m), 87.2 (m), 101.5 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 288$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 237$ Hz), 109.4 (t, $J(^{31}\text{P}, ^{31}\text{P}) = 203$ Hz), 120.2 (m), 157.0 (s, 1 P, $^{\text{Me}}\text{Bhp-PCl}_2$), 178.8 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 246$ Hz), 190.0 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 280$ Hz), 210.8 (s), 524.1 (s).

6.4.5 $^{\text{Me}}\text{Bhp-PH}_2 + \text{PCl}_3 + \text{DBU}$

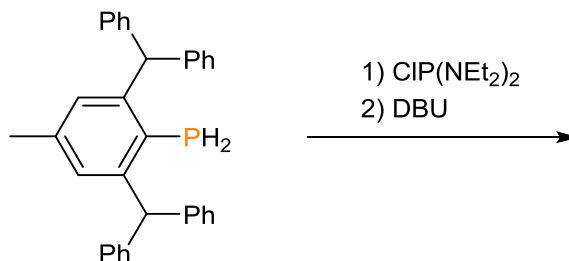


In a 100 mL Schlenk flask, phosphorus trichloride (0.1 mL, 1.14 mmol) is added to a stirred solution of $^{\text{Me}}\text{Bhp-PH}_2$ (0.240 g, 0.53 mmol) in diethyl ether (10 mL) at -80 °C. After stirring for 5 minutes, 1,8-diazabicyclo[5.4.0]undec-7-ene (0.1 mL, 0.67 mmol) is added at the same temperature *via* syringe. The beige mixture is slowly warmed to ambient temperature and left stirring overnight. Afterwards, all volatiles are removed *in vacuo*. The solid residue is dried thoroughly and the product is extracted with toluene. The filtrate is concentrated and stored in the refrigerator. The product mixture was used for NMR measurements.

^{31}P NMR (C_6D_6 , 202.5 MHz): $\delta = -520.3$ (s), -288.9 (t, $^1J(^{31}\text{P}, ^{31}\text{P}) = 178$ Hz, 2 P, *bridgehead-P* (*exo-exo*- $^{\text{Me}}\text{Bhp-P}_4\text{-}^{\text{Me}}\text{Bhp}$)), -271.4 (t, $J(^{31}\text{P}, ^{31}\text{P}) = 237$ Hz), -242.1 (dd, $^1J(^{31}\text{P}, ^{31}\text{P}) = 229$ Hz, $^1J(^{31}\text{P}, ^{31}\text{P}) = 203$ Hz, 2 P, *bridgehead-P* (*endo-exo*- $^{\text{Me}}\text{Bhp-P}_4\text{-}^{\text{Me}}\text{Bhp}$)),

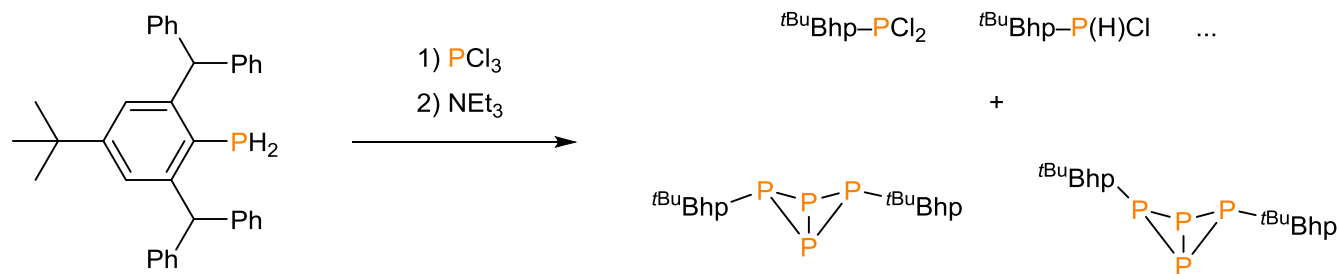
–170.9 (t, $^1J(^{31}\text{P}, ^{31}\text{P}) = 178$ Hz, 2 P, $^{\text{Me}}\text{Bhp-P}$ (*exo-exo*- $^{\text{Me}}\text{Bhp-P}_4$ - $^{\text{Me}}\text{Bhp}$)), –130.9 (m), –107.9 (m), 7.9 (d, $J(^{31}\text{P}, ^1\text{H}) = 203$ Hz, 1 P, $^{\text{Me}}\text{Bhp-P(H)Cl}$), 14.0 (s), 18.8 (s), 82.5 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 237$ Hz), 157.0 (s, 1 P, $^{\text{Me}}\text{Bhp-PCl}_2$), 178.8 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 237$ Hz).

6.4.6 $^{\text{Me}}\text{Bhp-PH}_2 + \text{CIP(NEt}_2)_2 + \text{DBU}$



In a 100 mL Schlenk flask, bis(diethylamino)chlorophosphine (0.2 mL, 0.95 mmol) is added to a stirred solution of $^{\text{Me}}\text{Bhp-PH}_2$ (0.232 g, 0.51 mmol) in diethyl ether (10 mL) at -80 °C. After stirring for 5 minutes, 1,8-diazabicyclo[5.4.0]undec-7-ene (0.1 mL, 0.67 mmol) is added at the same temperature *via* syringe. The yellow mixture is slowly warmed to ambient temperature and left stirring overnight. Afterwards, all volatiles are removed *in vacuo*. The solid residue is dried thoroughly and the product is extracted with toluene. The filtrate is concentrated and stored in the refrigerator. The product mixture was used for NMR measurements.

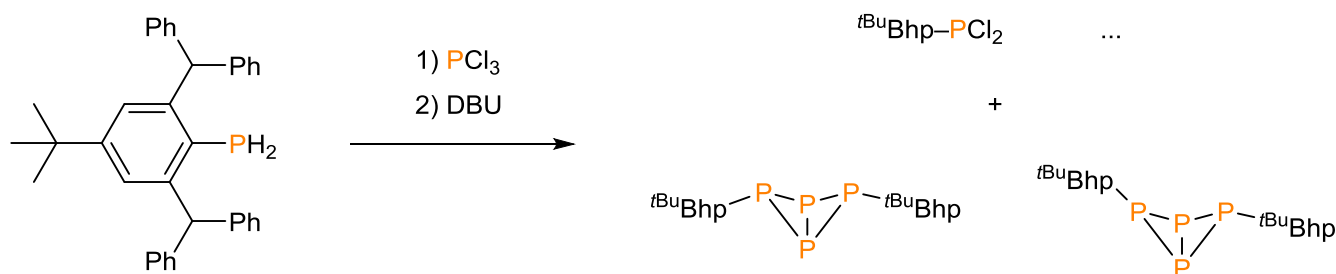
^{31}P NMR (C_6D_6 , 202.5 MHz): $\delta = -111.7$ (dd, $J = 220$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 136$ Hz), -65.3 (t, $J(^{31}\text{P}, ^{31}\text{P}) = 203$ Hz), -41.4 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 229$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 153$ Hz), -36.6 (t, $J(^{31}\text{P}, ^{31}\text{P}) = 170$ Hz), 24.2 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 254$ Hz), 26.6 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 322$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 229$ Hz), 33.8 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 119$ Hz), 40.6 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 263$ Hz), 47.6 (t, $J(^{31}\text{P}, ^{31}\text{P}) = 165$ Hz), 62.5 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 246$ Hz), 68.1 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 127$ Hz), 74.0 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 191$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 81$ Hz), 88.1 (s), 103.6 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 208$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 89$ Hz), 106.3 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 127$ Hz), 110.3 (m), 118.1 (s), 123.7 (s), 140.8 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 161$ Hz).

6.4.7 $t^{\text{Bu}}\text{Bhp-Ph}_2 + \text{PCl}_3 + \text{NEt}_3$ 

In a 25 mL Schlenk flask, phosphorus trichloride (0.06 mL, 0.69 mmol) is added to a stirred solution of $t^{\text{Bu}}\text{Bhp-Ph}_2$ (0.152 g, 0.31 mmol) in diethyl ether (8 mL) at -80°C . After stirring for 5 minutes, triethylamine (0.2 mL, 0.73 mmol) is added at the same temperature *via* syringe. The yellow mixture is slowly warmed to ambient temperature and left stirring overnight. Afterwards, all volatiles are removed *in vacuo*. The solid residue is dried thoroughly and the product is extracted with toluene. The filtrate is concentrated and stored in the refrigerator. The product mixture was used for NMR measurements.

^{31}P NMR (C_6D_6 , 202.5 MHz): $\delta = -289.9$ (t, $^1J(^{31}\text{P}, ^{31}\text{P}) = 178$ Hz, 2 P, *bridgehead-P (exo-exo- $t^{\text{Bu}}\text{Bhp-P}_4-t^{\text{Bu}}\text{Bhp}$)*), -271.3 (t, $J(^{31}\text{P}, ^{31}\text{P}) = 229$ Hz), -242.5 (dd, $^1J(^{31}\text{P}, ^{31}\text{P}) = 229$ Hz, $^1J(^{31}\text{P}, ^{31}\text{P}) = 203$ Hz, 2 P, *bridgehead-P (endo-exo- $t^{\text{Bu}}\text{Bhp-P}_4-t^{\text{Bu}}\text{Bhp}$)*), -171.6 (t, $^1J(^{31}\text{P}, ^{31}\text{P}) = 178$ Hz, 2 P, $^{\text{Me}}\text{Bhp-P (exo-exo- $t^{\text{Bu}}\text{Bhp-P}_4-t^{\text{Bu}}\text{Bhp}$)}$), -166.3 (td, $J(^{31}\text{P}, ^{31}\text{P}) = 182$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 136$ Hz), -140.6 (m), -126.3 (m), -114.7 (m), -108.4 (m), -103.3 (m), -97.4 (m), -91.9 (td, $J(^{31}\text{P}, ^{31}\text{P}) = 203$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 170$ Hz), -45.3 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 233$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 131$ Hz), -24.5 (t, $J(^{31}\text{P}, ^{31}\text{P}) = 157$ Hz), -20.2 (t, $J(^{31}\text{P}, ^{31}\text{P}) = 229$ Hz), -16.9 (m), -11.5 (m), -3.8 (dt, $J(^{31}\text{P}, ^{31}\text{P}) = 246$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 203$ Hz), 4.0 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 220$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 170$ Hz), 7.5 (s, 1 P, $t^{\text{Bu}}\text{Bhp-P(H)Cl}$), 18.4 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 237$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 187$ Hz), 30.6 (m), 44.9 (s), 72.5 (m), 79.9 (m), 81.6 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 246$ Hz), 87.5 (m), 101.4 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 288$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 229$ Hz), 108.1 (t, $J(^{31}\text{P}, ^{31}\text{P}) = 203$ Hz), 121.0 (m), 131.7 (m), 156.7 (s, 1 P, $t^{\text{Bu}}\text{Bhp-PCl}_2$), 178.6 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 246$ Hz), 190.1 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 271$ Hz), 200.9 (s), 219.0 (s), 521.0 (s).

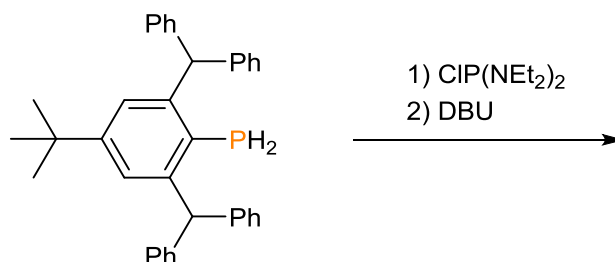
6.4.8 $^{t\text{Bu}}\text{Bhp-Ph}_2 + \text{PCl}_3 + \text{DBU}$



In a 25 mL Schlenk flask, phosphorus trichloride (0.06 mL, 0.69 mmol) is added to a stirred solution of $^{t\text{Bu}}\text{Bhp-Ph}_2$ (0.149 g, 0.30 mmol) in diethyl ether (8 mL) at $-80\text{ }^\circ\text{C}$. After stirring for 5 minutes, 1,8-diazabicyclo[5.4.0]undec-7-ene (0.06 mL, 0.40 mmol) is added at the same temperature *via* syringe. The yellow mixture is slowly warmed to ambient temperature and left stirring overnight. Afterwards, all volatiles are removed *in vacuo*. The solid residue is dried thoroughly and the product is extracted with toluene. The filtrate is concentrated and stored in the refrigerator. The product mixture was used for NMR measurements.

^{31}P NMR (C_6D_6 , 202.5 MHz): $\delta = -520.9$ (s), -289.9 (t, $^1J(^{31}\text{P}, ^{31}\text{P}) = 178$ Hz, 2 P, *bridgehead-P* (*exo-exo*- $^{t\text{Bu}}\text{Bhp-P}_4\text{-}^{t\text{Bu}}\text{Bhp}$)), -242.5 (dd, $^1J(^{31}\text{P}, ^{31}\text{P}) = 229$ Hz, $^1J(^{31}\text{P}, ^{31}\text{P}) = 203$ Hz, 2 P, *bridgehead-P* (*endo-exo*- $^{t\text{Bu}}\text{Bhp-P}_4\text{-}^{t\text{Bu}}\text{Bhp}$)), -171.6 (t, $^1J(^{31}\text{P}, ^{31}\text{P}) = 178$ Hz, 2 P, $^{\text{Me}}\text{Bhp-P}$ (*exo-exo*- $^{t\text{Bu}}\text{Bhp-P}_4\text{-}^{t\text{Bu}}\text{Bhp}$)), -139.7 (m), -128.8 (m), -122.8 (m), -115.7 (m), -107.7 (m), -102.6 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 187$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 170$ Hz), -97.3 (m), -93.4 (t, $J(^{31}\text{P}, ^{31}\text{P}) = 229$ Hz), 81.8 (m), 85.6 (s), 104.9 (m), 156.7 (s, 1 P, $^{t\text{Bu}}\text{Bhp-PCl}_2$), 177.5 (s), 200.8 (s), 218.0 (s).

6.4.9 $^{t\text{Bu}}\text{Bhp-Ph}_2 + \text{ClP}(\text{NEt}_2)_2 + \text{DBU}$

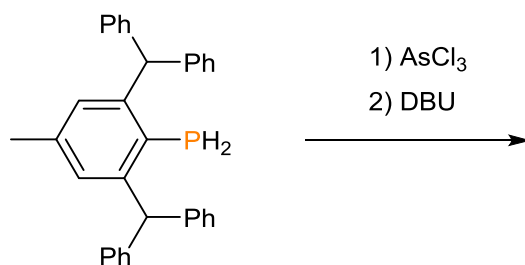


In a 25 mL Schlenk flask, bis(diethylamino)chlorophosphine (0.13 mL, 0.62 mmol) is added to a stirred solution of $^{t\text{Bu}}\text{Bhp-Ph}_2$ (0.153 g, 0.31 mmol) in diethyl ether (8 mL) at $-80\text{ }^\circ\text{C}$.

After stirring for 5 minutes, 1,8-diazabicyclo[5.4.0]undec-7-ene (0.12 mL, 0.80 mmol) is added at the same temperature via syringe. The yellow mixture is slowly warmed to ambient temperature and left stirring overnight. Afterwards, all volatiles are removed *in vacuo*. The solid residue is dried thoroughly and the product is extracted with toluene. The filtrate is concentrated and stored in the refrigerator. The product mixture was used for NMR measurements.

$^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz): $\delta = -111.8$ (dd, $J = 220$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 136$ Hz), -41.7 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 229$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 153$ Hz), -37.8 (t, $J(^{31}\text{P}, ^{31}\text{P}) = 170$ Hz), 25.7 (m), 33.9 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 127$ Hz), 40.8 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 263$ Hz), 48.2 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 237$ Hz), 52.2 (s), 57.9 (s), 62.4 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 237$ Hz), 68.2 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 127$ Hz), 106.4 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 136$ Hz), 110.2 (m), 118.1 (s), 153.4 (s).

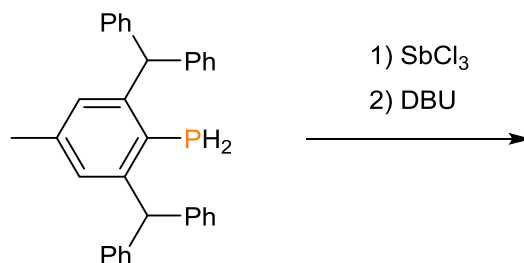
6.4.10 $^{\text{Me}}\text{Bhp-PH}_2 + \text{AsCl}_3 + \text{DBU}$



In a 50 mL Schlenk flask, arsenic trichloride (0.05 mL, 0.60 mmol) is added to a stirred solution of $^{\text{Me}}\text{Bhp-PH}_2$ (0.150 g, 0.33 mmol) in diethyl ether (10 mL) at -80 °C. After stirring for 5 minutes, 1,8-diazabicyclo[5.4.0]undec-7-ene (0.12 mL, 0.80 mmol) is added at the same temperature via syringe. The yellow mixture is slowly warmed to ambient temperature and left stirring overnight. Afterwards, all volatiles are removed *in vacuo*. The solid residue is dried thoroughly and the product is extracted with toluene. The filtrate is concentrated and stored in the refrigerator. The product mixture was used for NMR measurements.

^{31}P NMR (C_6D_6 , 101.3 MHz): $\delta = -138.3$ (s), -107.1 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 18$ Hz), -81.9 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 18$ Hz), -32.6 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 233$ Hz), -8.6 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 389$ Hz), -0.6 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 236$ Hz), 4.1 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 171$ Hz), 11.4 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 36$ Hz), 18.4 (s), 21.5 (s), 24.0 (s), 29.1 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 236$ Hz), 33.8 (s), 60.4 (s), 72.9 (s), 76.1 (s), 84.8 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 33$ Hz), 92.0 (s), 157.2 (s).

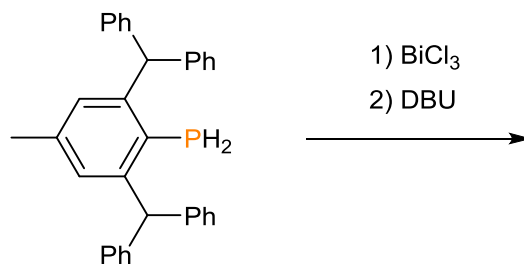
6.4.11 ^{Me}Bhp-PH₂ + SbCl₃ + DBU



A solution of antimony trichloride (0.090 g, 0.40 mmol) in diethyl ether (5 mL) is added to a stirred solution of ^{Me}Bhp-PH₂ (0.150 g, 0.33 mmol) in diethyl ether (5 mL) at -80 °C. After stirring for 5 minutes, 1,8-diazabicyclo[5.4.0]undec-7-ene (0.12 mL, 0.80 mmol) is added at the same temperature via syringe. The red mixture is slowly warmed to ambient temperature and left stirring overnight. Afterwards, all volatiles are removed *in vacuo*. The solid residue is dried thoroughly and the product is extracted with toluene. The filtrate is concentrated and stored in the refrigerator. The product mixture was used for NMR measurements.

³¹P NMR (C₆D₆, 101.3 MHz): δ = -57.3 (s), 11.2 (s), 44.7 (d, $J(^{31}\text{P}, ^{31}\text{P})$ = 91 Hz), 524.4 (s).

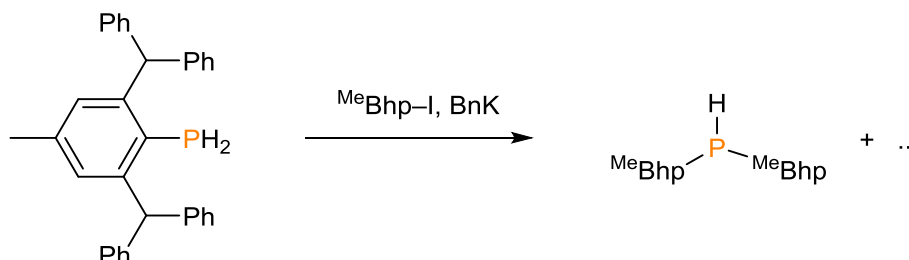
6.4.12 ^{Me}Bhp-PH₂ + BiCl₃ + DBU



A solution of bismuth trichloride (0.109 g, 0.35 mmol) in diethyl ether (5 mL) is added to a stirred solution of ^{Me}Bhp-PH₂ (0.150 g, 0.33 mmol) in diethyl ether (5 mL) at -80 °C. After stirring for 5 minutes, 1,8-diazabicyclo[5.4.0]undec-7-ene (0.12 mL, 0.80 mmol) is added at the same temperature via syringe, slowly changing the color from yellow to black. The mixture is slowly warmed to ambient temperature and left stirring overnight. Afterwards, all volatiles are removed *in vacuo*. The solid residue is dried thoroughly and the product is extracted with toluene. The filtrate is concentrated and stored in the refrigerator. The product mixture was used for NMR measurements.

^{31}P NMR (C_6D_6 , 101.3 MHz): $\delta = -114.3$ (s), -97.6 (m), -75.1 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 269$ Hz), 8.9 (s), 39.0 (s), 108.3 (m), 524.4 (s).

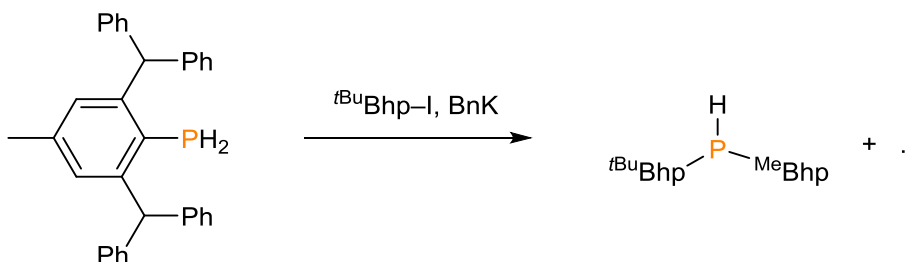
6.4.13 $^{\text{Me}}\text{Bhp-PH}_2 + ^{\text{Me}}\text{Bhp-I} + \text{BnK}$



In a 20 mL vial equipped with a stir bar, $^{\text{Me}}\text{Bhp-PH}_2$ (0.150 g, 0.33 mmol), $^{\text{Me}}\text{Bhp-I}$ (0.181 g, 0.33 mmol) and BnK (0.043 g, 0.33 mmol) are placed together as solids. Afterwards, toluene (8 mL) is added and the mixture is left stirring for 1 day. The next day, the orange mixture is filtered, *n*-pentane is added and the filtrate is left to crystallize. The residue on the frit is washed with dichloromethane and after adding a small amount of *n*-pentane, this filtrate is also left to crystallize. The product mixture was used for NMR measurements.

^{31}P NMR (CD_2Cl_2 , 202.5 MHz): $\delta = -155.6$ (m), -103.9 (dd, $J = 212$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 136$ Hz), -94.4 (d, $J = 237$ Hz), -78.8 (d, $J = 220$ Hz), -52.4 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 136$ Hz), -48.7 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 136$ Hz), -17.2 (s).

6.4.14 $^{\text{Me}}\text{Bhp-PH}_2 + ^{t\text{Bu}}\text{Bhp-I} + \text{BnK}$

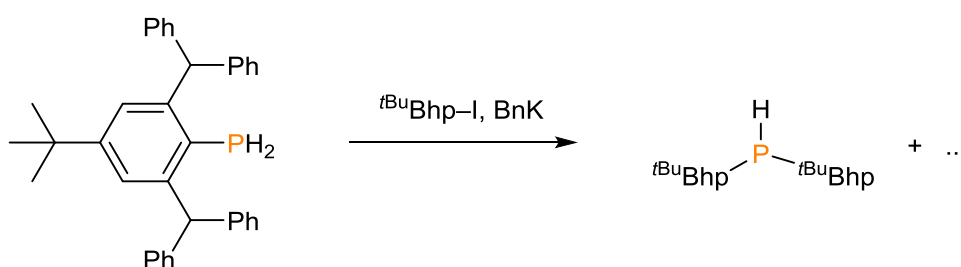


In a 20 mL vial equipped with a stir bar, $^{\text{Me}}\text{Bhp-PH}_2$ (0.150 g, 0.33 mmol), $^{t\text{Bu}}\text{Bhp-I}$ (0.195 g, 0.33 mmol) and BnK (0.043 g, 0.33 mmol) are placed together as solids. Afterwards, toluene (8 mL) is added and the mixture is left stirring for 1 day. The next day, the red mixture is filtered, *n*-pentane is added and the filtrate is left to crystallize.

The residue on the frit is washed with dichloromethane and after adding a small amount of *n*-pentane, this filtrate is also left to crystallize. The product mixture was used for NMR measurements.

^{31}P NMR (CD_2Cl_2 , 202.5 MHz): $\delta = -155.7$ (m), -103.7 (dd, $J = 212$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 136$ Hz), -93.9 (d, $J = 237$ Hz), -78.6 (d, $J = 220$ Hz), -52.2 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 136$ Hz), -48.6 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 195$ Hz), -17.2 (s).

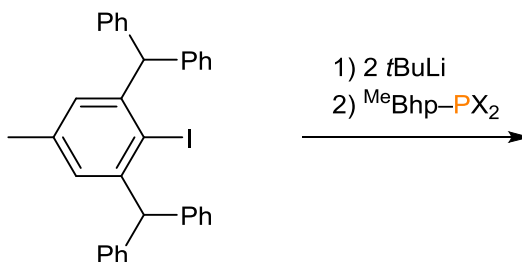
6.4.15 $^t\text{BuBhp-PH}_2 + ^t\text{BuBhp-I} + \text{BnK}$



In a 20-mL-vial equipped with a stir bar, $^t\text{BuBhp-PH}_2$ (0.150 g, 0.33 mmol), $^t\text{BuBhp-I}$ (0.195 g, 0.33 mmol) and BnK (0.043 g, 0.33 mmol) are placed together as solids. Afterwards, toluene (8 mL) is added and the mixture is left stirring for 1 day. The next day, the red mixture is filtered, *n*-pentane is added and the filtrate is left to crystallize. The residue on the frit is washed with dichloromethane and after adding a small amount of *n*-pentane, this filtrate is also left to crystallize. The product mixture was used for NMR measurements.

^{31}P NMR (CD_2Cl_2 , 202.5 MHz): $\delta = -155.7$ (m), -116.9 (m), -112.5 (m), -101.9 (dd, $J = 216$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 140$ Hz), -92.7 (m), -78.9 (d, $J = 220$ Hz), -52.1 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 144$ Hz), -49.0 (d, $J(^{31}\text{P}, ^{31}\text{P}) = 187$ Hz), -38.2 (s), -17.6 (s), 35.9 (s).

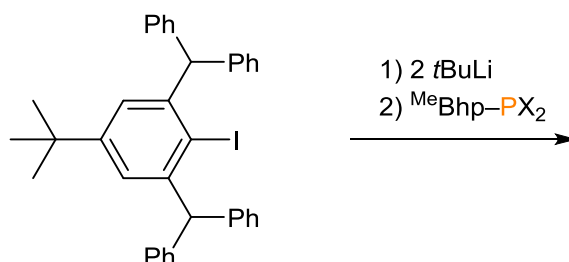
6.4.16 $^{\text{Me}}\text{Bhp-Li} + ^{\text{Me}}\text{Bhp-PX}_2$



In a 25 mL Schlenk flask, a 1.7 M solution of *tert*-butyllithium in pentane (0.32 mL, 0.54 mmol) is added dropwise to a stirred solution of ^{Me}Bhp-I (0.150 g, 0.27 mmol) in tetrahydrofuran (5 mL) at -80 °C, turning the colorless solution orange red. After stirring for 10 minutes, a solution of ^{Me}Bhp-PX₂ (0.152 g, 0.27 mmol) in tetrahydrofuran (5 mL) is added at the same temperature *via* syringe. The yellow mixture is slowly warmed to ambient temperature, resulting in a dark red color, and left stirring overnight. Afterwards, all volatiles are removed *in vacuo*. The solid residue is dried thoroughly and the product is extracted with toluene. The filtrate is concentrated and stored in the refrigerator. The product mixture was used for NMR measurements.

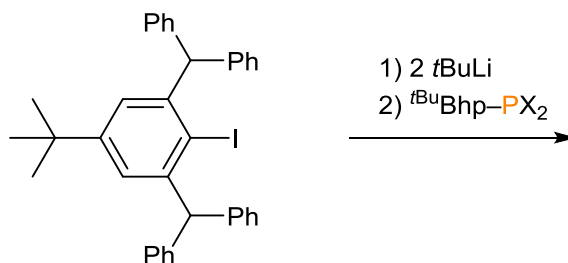
³¹P NMR (C₆D₆, 202.5 MHz): δ = -111.1 (dd, J = 212 Hz, $J(^{31}\text{P}, ^{31}\text{P})$ = 144 Hz), -98.3 (m), -95.0 (d, J = 246 Hz), -39.6 (d, J = 280 Hz), -33.1 (m), -28.5 (d, $J(^{31}\text{P}, ^{31}\text{P})$ = 153 Hz), 14.5 (d, $J(^{31}\text{P}, ^{31}\text{P})$ = 500 Hz), 47.9 (m), 87.5 (s), 523.8 (s).

6.4.17 ^tBuBhp-Li + ^{Me}Bhp-PX₂



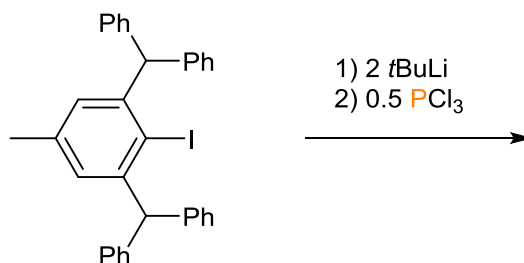
In a 25 mL Schlenk flask, a 1.7 M solution of *tert*-butyllithium in pentane (0.3 mL, 0.51 mmol) is added dropwise to a stirred solution of ^tBuBhp-I (0.150 g, 0.25 mmol) in tetrahydrofuran (5 mL) at -80 °C, turning the colorless solution orange red. After stirring for 10 minutes, a solution of ^{Me}Bhp-PX₂ (0.141 g, 0.25 mmol) in tetrahydrofuran (5 mL) is added at the same temperature *via* syringe. The yellow mixture is slowly warmed to ambient temperature, resulting in a dark red color, and left stirring overnight. Afterwards, all volatiles are removed *in vacuo*. The solid residue is dried thoroughly and the product is extracted with toluene. The filtrate is concentrated and stored in the refrigerator. The product mixture was used for NMR measurements.

³¹P NMR (C₆D₆, 202.5 MHz): δ = -114.5 (dd, J = 212 Hz, $J(^{31}\text{P}, ^{31}\text{P})$ = 144 Hz), -98.2 (m), -80.9 (dd, $J(^{31}\text{P}, ^{31}\text{P})$ = 326 Hz, J = 216 Hz), -53.1 (d, J = 220 Hz), -39.6 (m), -32.8 (m), 14.4 (d, $J(^{31}\text{P}, ^{31}\text{P})$ = 509 Hz), 86.7 (dd, $J(^{31}\text{P}, ^{31}\text{P})$ = 187 Hz, $J(^{31}\text{P}, ^{31}\text{P})$ = 93 Hz), 523.8 (s).

6.4.18 ${}^t\text{BuBhp-Li} + {}^t\text{BuBhp-PX}_2$ 

In a 25 mL Schlenk flask, a 1.7 M solution of *tert*-butyllithium in pentane (0.3 mL, 0.51 mmol) is added dropwise to a stirred solution of ${}^t\text{BuBhp-I}$ (0.150 g, 0.25 mmol) in tetrahydrofuran (5 mL) at $-80\text{ }^{\circ}\text{C}$, turning the colorless solution orange red. After stirring for 10 minutes, a solution of ${}^t\text{BuBhp-PX}_2$ (0.154 g, 0.25 mmol) in tetrahydrofuran (5 mL) is added at the same temperature *via* syringe. The yellow mixture is slowly warmed to ambient temperature, resulting in a dark red color, and left stirring overnight. Afterwards, all volatiles are removed *in vacuo*. The solid residue is dried thoroughly and the product is extracted with toluene. The filtrate is concentrated and stored in the refrigerator. The product mixture was used for NMR measurements.

${}^{31}\text{P}$ NMR (C_6D_6 , 202.5 MHz): $\delta = -112.9$ (m), -98.6 (m), -53.0 (d, $J = 229$ Hz), -33.3 (m), -28.9 (m), -8.6 (s), 14.4 (d, $J({}^{31}\text{P}, {}^{31}\text{P}) = 500$ Hz), 17.0 (s), 31.7 (s), 88.6 (dd, $J({}^{31}\text{P}, {}^{31}\text{P}) = 187$ Hz, $J({}^{31}\text{P}, {}^{31}\text{P}) = 76$ Hz), 109.1 (s), 114.3 (s), 521.0 (s).

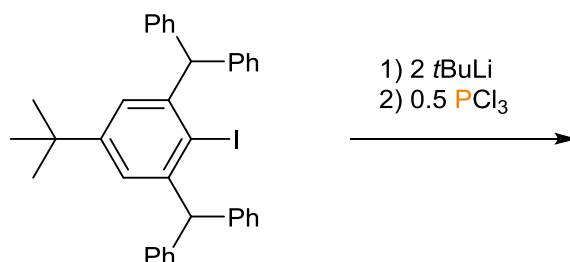
6.4.19 ${}^{\text{Me}}\text{Bhp-Li} + \frac{1}{2} \text{PCl}_3$ 

In a 25 mL Schlenk flask, a 1.7 M solution of *tert*-butyllithium in pentane (0.54 mL, 0.92 mmol) is added dropwise to a stirred solution of ${}^{\text{Me}}\text{Bhp-I}$ (0.252 g, 0.46 mmol) in tetrahydrofuran (8 mL) at $-80\text{ }^{\circ}\text{C}$, turning the colorless solution red. After stirring for 10 minutes, phosphorus trichloride (0.02 mL, 0.23 mmol) is added at the same temperature *via* syringe.

The yellow mixture is slowly warmed to ambient temperature and left stirring for 2 hours. Afterwards, all volatiles are removed *in vacuo*. The product mixture was used for NMR measurements.

^{31}P NMR (C_6D_6 , 121.5 MHz): $\delta = -289.9$ (t, $^1J(^{31}\text{P}, ^{31}\text{P}) = 177$ Hz, 2 P, *bridgehead-P* (*exo-exo*- $^{\text{Me}}\text{Bhp-P}_4\text{-}^{\text{Me}}\text{Bhp}$)), -170.9 (t, $^1J(^{31}\text{P}, ^{31}\text{P}) = 179$ Hz, 2 P, $^{\text{Me}}\text{Bhp-P}$ (*exo-exo*- $^{\text{Me}}\text{Bhp-P}_4\text{-}^{\text{Me}}\text{Bhp}$)), -81.2 (dd, $J = 208$ Hz, $J(^{31}\text{P}, ^{31}\text{P}) = 182$ Hz), -72.2 (d, $J = 192$ Hz), -64.6 (dd, $J(^{31}\text{P}, ^{31}\text{P}) = 239$ Hz, $J = 229$ Hz), -0.8 (s), 5.7 (s), 8.0 (d, $J = 31$ Hz), 9.9 (d, $J = 26$ Hz), 23.0 (s), 44.4 (d, $J = 187$ Hz), 75.4 (s, 1 P, $^{\text{Me}}\text{Bhp-PI}_2$), 87.6 (s), 128.1 (s, 1 P, $^{\text{Me}}\text{Bhp-PClI}$), 167.8 (s), 173.3 (s), 523.9 (s).

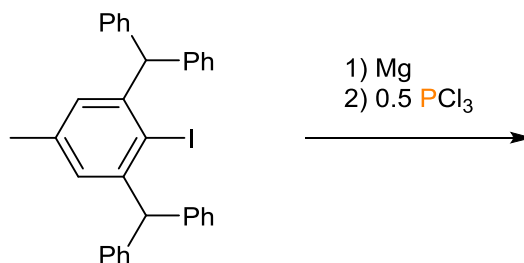
6.4.20 $^t\text{BuBhp-Li} + \frac{1}{2} \text{PCl}_3$



In a 25 mL Schlenk flask, a 1.7 M solution of *tert*-butyllithium in pentane (0.54 mL, 0.92 mmol) is added dropwise to a stirred solution of $^{\text{Me}}\text{Bhp-I}$ (0.252 g, 0.46 mmol) in tetrahydrofuran (8 mL) at -80 °C, turning the colorless solution red. After stirring for 10 minutes, phosphorus trichloride (0.02 mL, 0.23 mmol) is added at the same temperature *via* syringe. The yellow mixture is slowly warmed to ambient temperature and left stirring for 2 hours. Afterwards, all volatiles are removed *in vacuo*. The product mixture was used for NMR measurements.

^{31}P NMR (C_6D_6 , 121.5 MHz): $\delta = -73.2$ (d, $J = 192$ Hz), 22.5 (s), 74.8 (s, 1P, $^t\text{BuBhp-PI}_2$), 127.6 (s, 1 P, $^t\text{BuBhp-PClI}$), 156.8 (s, 1 P, $^t\text{BuBhp-PCl}_2$).

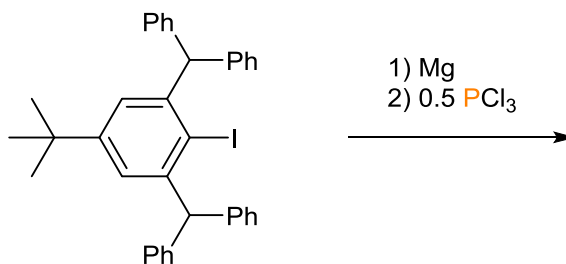
6.4.21 ^{Me}Bhp-I + Mg + ½ PCl₃



In a 25 mL Schlenk flask, magnesium turnings (0.110 g, 4.53 mmol) and ^{Me}Bhp-I (0.252 g, 0.46 mmol) are stirred in tetrahydrofuran (8 mL) for 5 days with repeated heating periods (60 °C) until the colorless solution changes color to light yellow. Afterwards, the GRIGNARD solution is added to a stirred solution of phosphorus trichloride (0.02 mL, 0.23 mmol) in tetrahydrofuran (3 mL) in a 25 mL Schlenk flask at -80 °C. The mixture is subsequently warmed to ambient temperature and left stirring overnight. The next day, volatiles are removed *in vacuo*. The product mixture was used for NMR measurements.

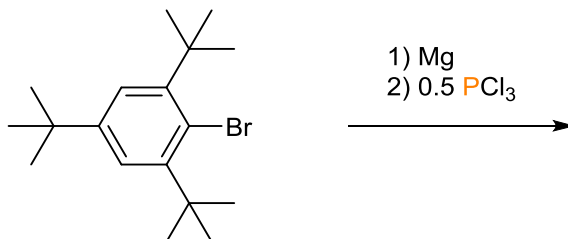
³¹P{¹H} NMR (C₆D₆, 121.5 MHz): δ = 112.8 (s), 178.1 (s), 219.1 (s, 1 P, PCl₃).

6.4.22 ^{tBu}Bhp-I + Mg + ½ PCl₃



In a 25 mL Schlenk flask, magnesium turnings (0.111 g, 4.57 mmol) and ^{tBu}Bhp-I (0.271 g, 0.46 mmol) are stirred in tetrahydrofuran (8 mL) for 5 days with repeated heating periods (60 °C) until the colorless solution changes color to light yellow. Afterwards, the GRIGNARD solution is added to a stirred solution of phosphorus trichloride (0.02 mL, 0.23 mmol) in tetrahydrofuran (3 mL) in a 25 mL Schlenk flask at -80 °C. The mixture is subsequently warmed to ambient temperature and left stirring overnight. The next day, volatiles are removed *in vacuo*. The product mixture was used for NMR measurements.

³¹P{¹H} NMR (C₆D₆, 121.5 MHz): δ = 37.9 (s), 200.9 (s).

6.4.23 Mes*–Br + Mg + $\frac{1}{2}$ PCl₃

In a 25 mL Schlenk flask, magnesium turnings (0.223 g, 9.17 mmol) and Mes*–Br (0.298 g, 0.92 mmol) are stirred in tetrahydrofuran (8 mL) for 5 days with repeated heating periods (60 °C) until the colorless solution changes color to light yellow. Afterwards, the GRIGNARD solution is added to a stirred solution of phosphorus trichloride (0.04 mL, 0.46 mmol) in tetrahydrofuran (3 mL) in a 25 mL Schlenk flask at –80 °C. The mixture is subsequently warmed to ambient temperature and left stirring overnight. The next day, volatiles are removed *in vacuo*. The product mixture was used for NMR measurements.

³¹P{¹H} NMR (C₆D₆, 121.5 MHz): δ = 37.7 (s), 103.5 (s), 146.2 (s), 151.0 (s), 152.6 (s), 181.8 (s), 184.7 (s), 190.8 (s), 194.0 (s), 198.5 (s), 208.5 (s), 219.7 (s, 1 P, PCl₃).

6.5 Structural Data

Table 10. Crystallographic details of **28**, **29** and **30**.

Compound	28	29	30
Chem. Formula	C ₃₆ H ₃₃ I	C ₃₆ H ₃₃ Cl _{1.63} I _{0.37} P	C ₃₆ H ₃₃ Cl _{0.97} I _{0.03}
Formula weight [g/mol]	592.52	600.87	503.59
Color	colorless	colorless	colorless
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	<i>Pnma</i>	<i>P2_{1/n}</i>	<i>Pnma</i>
<i>a</i> [Å]	19.007(2)	11.2059(5)	18.860(1)
<i>b</i> [Å]	24.840(2)	19.1823(9)	24.720(1)
<i>c</i> [Å]	5.9476(6)	14.8511(6)	5.8735(2)
α [°]	90	90	90
β [°]	90	105.670(2)	90
γ [°]	90	90	90
<i>V</i> [Å ³]	2808.1(5)	3073.7(2)	2738.4(2)
<i>Z</i>	4	4	4
$\rho_{\text{calcd.}}$ [g/cm ³]	1.402	1.298	1.221
μ [mm ⁻¹]	1.163	0.621	0.191
<i>T</i> [K]	123(2)	123(2)	123(2)
Measured reflections	62311	67030	27513
Independent reflections	5162	8147	3365
Reflections with $I > 2\sigma(I)$	4899	6650	2613
<i>R</i> _{int}	0.0380	0.0712	0.0865
<i>F</i> (000)	1208	1245	1068
<i>R</i> ₁ (<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)])	0.0470	0.0712	0.0695
<i>wR</i> ₂ (<i>F</i> ²)	0.0982	0.1540	0.1434
GooF	1.303	1.266	1.163
No. of Parameters	176	504	181

Table 11. Crystallographic details of **31**.

Compound	31
Chem. Formula	C ₃₆ H ₃₅ P
Formula weight [g/mol]	498.61
Color	colorless
Crystal system	orthorhombic
Space group	<i>Pnma</i>
<i>a</i> [Å]	18.868(4)
<i>b</i> [Å]	24.821(5)
<i>c</i> [Å]	5.947(1)
α [°]	90
β [°]	90
γ [°]	90
<i>V</i> [Å ³]	2785(1)
<i>Z</i>	4
$\rho_{\text{calcd.}}$ [g/cm ³]	1.189
μ [mm ⁻¹]	0.121
<i>T</i> [K]	123(2)
Measured reflections	38890
Independent reflections	3777
Reflections with $I > 2\sigma(I)$	3273
<i>R</i> _{int}	0.0545
<i>F</i> (000)	1064
<i>R</i> ₁ (<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)])	0.0532
<i>wR</i> ₂ (<i>F</i> ²)	0.1424
GooF	1.134
No. of Parameters	185

6.6 Additional Data for DFT Computations

Table 12. Average unsigned deviations for bond lengths / angles in Å / degrees for $[(iPr)_2NPNP(Cl_2)N(iPr)_2]^+$ (**32**) (**int = ultrafine**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0212 / 0.401	0.0247 / 0.517	0.0320 / 0.607	0.0089 / 0.626	0.0125 / 0.432
Def2SVP	0.0206 / 0.581	0.0246 / 0.457	0.0305 / 0.575	0.0103 / 0.617	0.0140 / 0.481
Def2SVPP	0.0207 / 0.562	0.0248 / 0.481	0.0307 / 0.612	0.0103 / 0.626	0.0141 / 0.468
cc-pVDZ	0.0306 / 0.587	0.0348 / 0.795	0.0416 / 0.969	0.0186 / 0.782	0.0222 / 0.750
cc-pVTZ	0.0156 / 0.405	0.0192 / 0.378	0.0255 / 0.617	0.0060 / 0.416	0.0091 / 0.533

Table 13. Deviations for chemical shifts / **spin-spin coupling** in ppm / Hz for $[(iPr)_2NPNP(Cl_2)N(iPr)_2]^+$ (**32**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	-10.9	-21.9	-10.3	+13.5	-11.4
	-20.4 / -2	-43.1 / +2	-24.1 / +13	+25.1 / -9	-14.6 / -4
Def2SVP	+1.9	-12.5	+7.9	+20.7	+2.0
	-5.5 / -33	-33.1 / -14	-5.4 / -8	+41.5 / -18	+1.8 / -23
Def2SVPP	-12.1	-26.8	-6.9	+10.5	-11.4
	-20.1 / -31	-47.8 / -13	-21.0 / -7	+30.7 / -18	-12.1 / -21
cc-pVDZ	+4.0	-8.4	+9.8	+26.4	+2.1
	+8.5 / -6	-17.5 / +3	+7.5 / +16	+56.6 / +5	+14.9 / +1
cc-pVTZ	+16.5	+7.1	+25.3	+34.0	+17.5
	+34.2 / -3	+10.3 / +21	+34.9 / +24	+81.2 / +9	+35.5 / +10

Table 14. Deviations for spin-spin coupling (**NMR = mixed**) in Hz for $[(iPr)_2NPNP(Cl_2)N(iPr)_2]^+$ (**32**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	+39	+46	+58	+23	+36
Def2SVP	-4	+24	+25	+9	+7
Def2SVPP	-1	+25	+26	+9	+10
cc-pVDZ	+32	+50	+57	+36	+39
cc-pVTZ	+22	+54	+53	+32	+38

Table 15. Average unsigned deviations for bond lengths / angles in Å / degrees for *cis*-[AdNPCl]₂ (**33**)

(int = ultrafine).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0260 / 0.519	0.0312 / 0.546	0.0370 / 0.809	0.0099 / 0.204	0.0124 / 0.388
Def2SVP	0.0270 / 0.507	0.0322 / 0.446	0.0366 / 0.688	0.0134 / 0.389	0.0158 / 0.385
Def2SVPP	0.0269 / 0.520	0.0321 / 0.457	0.0365 / 0.699	0.0149 / 0.852	0.0157 / 0.398
cc-pVDZ	0.0377 / 0.437	0.0426 / 0.617	0.0483 / 0.771	0.0208 / 0.402	0.0239 / 0.351
cc-pVTZ	0.0199 / 0.452	0.0238 / 0.311	0.0295 / 0.547	0.0047 / 0.218	0.0070 / 0.373

Table 16. Deviations for chemical shifts in ppm for *cis*-[AdNPCl]₂ (**33**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	-21.9	-24.0	-14.6	-20.8	-40.0
Def2SVP	-15.8	-21.9	-5.8	-13.0	-32.4
Def2SVPP	-29.7	-36.4	-20.5	-11.7	-45.5
cc-pVDZ	-5.7	-11.7	+2.5	-6.6	-25.3
cc-pVTZ	+11.8	+5.5	+21.5	+6.4	-12.5

Table 17. Average unsigned deviations for bond lengths / angles in Å / degrees for TerN(PCl₂)₂ (**34**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0390 / 1.256	0.0466 / 1.040	0.0512 / 1.276	0.0184 / 0.872	0.0206 / 1.000
Def2SVP	0.0378 / 0.934	0.0450 / 0.840	0.0508 / 0.280	0.0192 / 0.682	0.0217 / 0.477
Def2SVPP	0.0378 / 0.945	0.0451 / 0.874	0.0480 / 0.692	0.0192 / 0.699	0.0218 / 0.507
cc-pVDZ	0.0501 / 1.208	0.0569 / 0.873	0.0611 / 1.223	0.0299 / 0.790	0.0323 / 0.784
cc-pVTZ	0.0310 / 1.045	0.0367 / 0.701	0.0413 / 1.011	0.0124 / 0.805	0.0139 / 0.767

Table 18. Deviations for chemical shifts in ppm for TerN(PCl₂)₂ (**34**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	+14.4	+20.9	+31.9	+11.2	-4.8
Def2SVP	+18.6	+19.3	+35.9	+9.8	-2.1
Def2SVPP	+4.6	+4.8	+21.2	-0.6	-15.2
cc-pVDZ	+22.1	+25.4	+40.1	+17.2	+1.7
cc-pVTZ	+29.8	+31.9	+46.5	+26.6	+5.7

Table 19. Average unsigned deviations for bond lengths / angles in Å / degrees for *cis*-[DippNPCI]₂ (**35**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0274 / 0.818	0.0323 / 0.804	0.0381 / 0.852	0.0104 / 1.199	0.0140 / 0.798
Def2SVP	0.0287 / 0.809	0.0336 / 0.828	0.0382 / 0.798	0.0137 / 1.372	0.0171 / 0.803
Def2SVPP	0.0286 / 0.806	0.0336 / 0.824	0.0383 / 0.797	0.0136 / 1.375	0.0170 / 0.802
cc-pVDZ	0.0389 / 0.799	0.0435 / 0.850	0.0492 / 0.853	0.0214 / 1.223	0.0253 / 0.797
cc-pVTZ	0.0205 / 0.832	0.0247 / 0.804	0.0302 / 0.865	0.0052 / 1.044	0.0081 / 0.847

Table 20. Deviations for chemical shifts in ppm for *cis*-[DippNPCI]₂ (**35**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	-16.7	-18.6	-10.1	+3.9	-31.3
Def2SVP	-4.6	-11.3	+5.1	+11.2	-19.5
Def2SVPP	-18.8	-26.0	-10.0	+1.5	-32.8
cc-pVDZ	-3.1	-9.5	+4.7	+17.5	-20.0
cc-pVTZ	+7.5	+1.3	+15.2	+23.4	-13.5

Table 21. Average unsigned deviations for bond lengths / angles in Å / degrees for Mes*N(SiMe₃)PCl₂ (**36**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0322 / 0.591	0.0376 / 0.438	0.0424 / 0.519	0.0118 / 0.084	0.0157 / 0.258
Def2SVP	0.0330 / 0.450	0.0382 / 0.311	0.0420 / 0.451	0.0155 / 0.237	0.0193 / 0.165
Def2SVPP	0.0326 / 0.395	0.0379 / 0.371	0.0418 / 0.431	0.0149 / 0.402	0.0189 / 0.155
cc-pVDZ	0.0432 / 0.506	0.0474 / 0.219	0.0521 / 0.438	0.0235 / 0.116	0.0275 / 0.134
cc-pVTZ	0.0237 / 0.498	0.0275 / 0.409	0.0319 / 0.405	0.0056 / 0.277	0.0082 / 0.241

Table 22. Deviations for chemical shifts in ppm for Mes*N(SiMe₃)PCl₂ (**36**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	+21.7	+25.6	+33.8	+13.0	-2.8
Def2SVP	+15.1	+14.4	+26.8	+5.7	-10.0
Def2SVPP	+0.9	-0.5	+11.8	-4.7	-23.7
cc-pVDZ	+24.3	+23.5	+35.3	+15.3	-2.8
cc-pVTZ	+34.1	+32.0	+44.6	+24.1	+4.2

Table 23. Average unsigned deviations for bond lengths / angles in Å / degrees for TerN(SiMe₃)PCl₂ (**37**) (int = ultrafine).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0277 / 0.302	0.0342 / 0.711	0.0404 / 0.316	0.0112 / 1.070	0.0139 / 0.135
Def2SVP	0.0308 / 0.522	0.0378 / 0.865	0.0416 / 0.609	0.0147 / 1.323	0.0191 / 0.509
Def2SVPP	0.0304 / 0.515	0.0374 / 0.871	0.0412 / 0.584	0.0145 / 1.375	0.0185 / 0.503
cc-pVDZ	0.0401 / 0.393	0.0447 / 0.843	0.0489 / 0.342	0.0230 / 1.168	0.0271 / 0.333
cc-pVTZ	0.0193 / 0.298	0.0248 / 0.479	0.0288 / 0.392	0.0048 / 0.995	0.0068 / 0.181

Table 24. Deviations for chemical shifts in ppm for TerN(SiMe₃)PCl₂ (**37**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	+22.4	+22.8	+33.4	+11.9	-1.9
Def2SVP	+22.0	+20.4	+33.2	+10.3	-2.6
Def2SVPP	+8.2	+5.5	+18.9	-0.2	-15.6
cc-pVDZ	+29.7	+20.7	+36.8	+17.8	+2.9
cc-pVTZ	+7.0	+29.4	+41.4	+19.5	-0.7

Table 25. Average unsigned deviations for bond lengths / angles in Å / degrees for *cis*-[Ph₃CNPCI]₂ (**38**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0267 / 0.770	0.0292 / 2.903	0.0369 / 0.841	0.0123 / 0.595	0.0146 / 0.696
Def2SVP	0.0273 / 0.770	0.0331 / 0.598	0.0366 / 0.829	0.0155 / 0.754	0.0177 / 0.731
Def2SVPP	0.0272 / 0.773	0.0328 / 0.669	0.0365 / 0.834	0.0154 / 0.755	0.0176 / 0.734
cc-pVDZ	0.0374 / 0.742	0.0403 / 3.026	0.0469 / 0.774	0.0229 / 0.777	0.0251 / 0.732
cc-pVTZ	0.0193 / 0.775	0.0209 / 2.615	0.0283 / 0.738	0.0062 / 0.620	0.0085 / 0.718

Table 26. Deviations for chemical shifts in ppm for *cis*-[Ph₃CNPCI]₂ (**38**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	-22.8	-8.8	-20.3	-19.7	-42.8
Def2SVP	-14.3	-26.4	-8.8	-14.9	-33.9
Def2SVPP	-28.5	-40.7	-23.9	-25.3	-47.3
cc-pVDZ	-7.9	-0.5	-3.9	-7.3	-30.0
cc-pVTZ	+8.5	+17.7	+13.0	+6.0	-17.2

Table 27. Average unsigned deviations for bond lengths / angles in Å / degrees for $[(i\text{Pr})_2\text{NPNP}(\text{Cy})_3]^+$ (**39**) (**int = ultrafine**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0143 / 0.522	0.0138 / 0.893	0.0239 / 1.067	0.0013 / 0.731	0.0051 / 0.742
Def2SVP	0.0143 / 0.386	0.0135 / 0.663	0.0235 / 0.876	0.0015 / 0.622	0.0051 / 0.593
Def2SVPP	0.0151 / 0.342	0.0145 / 0.664	0.0242 / 0.798	0.0023 / 0.567	0.0059 / 0.499
cc-pVDZ	0.0239 / 0.973	0.0238 / 1.387	0.0339 / 1.497	0.0096 / 1.202	0.0144 / 1.236
cc-pVTZ	0.0095 / 0.464	0.0080 / 0.819	0.0187 / 0.981	0.0004 / 0.875	0.0012 / 0.912

Table 28. Deviations for chemical shifts / **spin-spin coupling** in ppm / Hz for $[(i\text{Pr})_2\text{NPNP}(\text{Cy})_3]^+$ (**39**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	-41.4	-43.2	-35.9	-22.2	-43.8
	-25.2 / -5	-46.3 / -3	-26.9 / +0	+29.9 / +6	-17.6 / +3
Def2SVP	-39.1	-48.3	-28.3	-27.3	-40.6
	-11.4 / -8	-39.8 / -9	-11.7 / -3	+39.9 / +4	-3.6 / -1
Def2SVPP	-53.6	-62.6	-43.2	-37.8	-54.2
	-28.7 / -11	-56.4 / -12	-31.1 / -8	+28.1 / +3	-20.1 / -3
cc-pVDZ	-39.1	-46.9	-28.1	-24.1	-42.4
	+6.7 / +4	-18.9 / -2	+5.5 / +6	+63.0 / +8	+15.3 / +11
cc-pVTZ	-15.6	-26.4	-6.0	-2.7	-16.7
	+29.3 / +7	+5.9 / +11	+32.3 / +12	-27.9 / +19	+35.3 / +20

Table 29. Deviations for spin-spin coupling (**NMR = mixed**) in Hz for $[(i\text{Pr})_2\text{NPNP}(\text{Cy})_3]^+$ (**39**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	+6	+11	+12	+17	+16
Def2SVP	-3	-1	+2	+11	+7
Def2SVPP	-6	-6	-4	+8	+3
cc-pVDZ	+15	+14	+18	+22	+24
cc-pVTZ	+9	+18	+16	+24	+25

Table 30. Average unsigned deviations for bond lengths / angles in Å / degrees for [HypNPNHyp][−] (40)

(int = ultrafine, int = superfine, scf = xqc).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0159 / 3.849	0.0149 / 5.866	0.0173 / 0.848	0.0090 / 6.515	0.0118 / 2.233
Def2SVP	0.0155 / 4.777	0.0155 / 2.603	0.0171 / 1.771	0.0106 / 3.537	0.0118 / 1.366
Def2SVPP	0.0155 / 4.500	0.0153 / 3.178	0.0171 / 1.462	0.0111 / 3.544	0.0114 / 2.129
cc-pVDZ	0.0158 / 1.442	0.0277 / 5.710	0.0306 / 1.667	0.0108 / 5.442	0.0133 / 2.258
cc-pVTZ	0.0151 / 5.531	0.0139 / 3.324	0.0163 / 2.682	0.0112 / 3.760	0.0121 / 1.898

Table 31. Deviations for chemical shifts in ppm for [HypNPNHyp][−] (40).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	−109.1	−95.3	−104.3	−8.1	−85.2
Def2SVP	−99.2	−94.9	−93.2	−16.1	−79.6
Def2SVPP	−112.1	−105.8	−106.2	−26.1	−88.7
cc-pVDZ	−65.5	−64.2	−59.5	+27.3	−49.6
cc-pVTZ	−56.3	−55.4	−50.6	+35.3	−40.7

Table 32. Average unsigned deviations for bond lengths / angles in Å / degrees for [HypNP]₂ (41)

(int = ultrafine, int = superfine).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0247 / 0.951	0.0277 / 1.374	0.0367 / 0.979	0.0083 / 1.339	0.0135 / 1.054
Def2SVP	0.0267 / 0.998	0.0296 / 1.420	0.0380 / 1.207	0.0106 / 1.366	0.0161 / 1.283
Def2SVPP	0.0265 / 0.978	0.0299 / 1.447	0.0380 / 1.221	0.0103 / 1.396	0.0159 / 1.281
cc-pVDZ	0.0396 / 1.077	0.0429 / 1.518	0.0515 / 1.290	0.0225 / 1.450	0.0287 / 1.317
cc-pVTZ	0.0151 / 0.835	0.0175 / 1.205	0.0269 / 0.813	0.0031 / 1.094	0.0049 / 1.046

Table 33. Deviations for chemical shifts in ppm for [HypNP]₂ (41).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	−29.8	−36.6	−18.4	−13.0	−43.3
Def2SVP	−35.0	−48.8	−22.4	−24.7	−47.0
Def2SVPP	−48.9	−62.4	−36.2	−34.1	−60.0
cc-pVDZ	−4.8	−17.2	+7.7	+9.8	−18.5
cc-pVTZ	+6.8	−5.6	+22.0	+20.7	−14.7

Table 34. Average unsigned deviations for bond lengths / angles in Å / degrees for [Mes*PPNMe₃]⁺ (42).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0325 / 4.463	0.0309 / 5.620	0.0326 / 4.416	0.0271 / 5.825	0.0261 / 4.839
Def2SVP	0.0355 / 6.433	0.0360 / 8.382	0.0358 / 6.933	0.0344 / 10.373	0.0303 / 7.097
Def2SVPP	0.0364 / 6.902	0.0369 / 8.934	0.0365 / 7.376	0.0346 / 10.404	0.0310 / 7.511
cc-pVDZ	0.0321 / 3.083	0.0349 / 4.704	0.0398 / 3.419	0.0240 / 4.364	0.0234 / 3.385
cc-pVTZ	0.0333 / 4.969	0.0333 / 6.600	0.0327 / 5.241	0.0264 / 6.202	0.0268 / 5.323

Table 35. Deviations for chemical shifts / **spin-spin coupling** in ppm / Hz for [Mes*PPNMe₃]⁺ (42).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	+7.0	-26.2	-5.1	+49.9	-27.9
	+2.7 / +24	-69.8 / +89	-49.9 / +41	+113.9 / +62	-7.2 / +56
Def2SVP	+20.6	-15.2	+12.3	+68.9	-11.3
	-7.8 / +65	-92.9 / +100	-61.1 / +63	+78.4 / +83	-20.0 / +87
Def2SVPP	+7.2	-28.9	-2.0	+67.6	-24.4
	-26.2 / +64	-112.5 / +99	-79.8 / +61	+65.8 / +84	-37.4 / +86
cc-pVDZ	+17.4	-19.9	+7.3	+57.7	-17.1
	+24.6 / +66	-54.3 / +89	-25.8 / +64	+129.6 / +141	+11.9 / +87
cc-pVTZ	+41.6	+3.1	+32.6	+89.2	+4.3
	+42.3 / -35	-41.2 / +10	-11.2 / -30	+154.8 / +78	+25.8 / +10

Table 36. Deviations for spin-spin coupling (**NMR = mixed**) in Hz for [Mes*PPNMe₃]⁺ (42).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	-81	-26	-58	-45	-42
Def2SVP	-48	+7	-27	-23	-12
Def2SVPP	-46	+6	-29	-22	-13
cc-pVDZ	-54	+1	-30	-7	-17
cc-pVTZ	-111	-43	-85	-53	-52

Table 37. Average unsigned deviations for bond lengths / angles in Å / degrees for Mes*PPN(PCI₂)Mes* (43) (**int = ultrafine**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0286 / 0.953	0.0351 / 0.941	0.0393 / 0.830	0.0170 / 0.813	0.0181 / 0.532
Def2SVP	0.0281 / 0.814	0.0341 / 1.612	0.0385 / 2.136	0.0172 / 0.726	0.0205 / 1.404
Def2SVPP	0.0281 / 0.810	0.0341 / 1.696	0.0379 / 1.657	0.0172 / 0.729	0.0208 / 1.490
cc-pVDZ	0.0382 / 0.859	0.0442 / 1.615	0.0486 / 1.805	0.0236 / 0.873	0.0253 / 0.748
cc-pVTZ	0.0230 / 0.777	0.0263 / 1.516	0.0310 / 0.838	0.0152 / 0.827	0.0154 / 0.518

Table 38. Deviations for chemical shifts / **spin-spin coupling** in ppm / Hz for Mes*PPN(PCI₂)Mes* (43).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	+17.6	+19.8	+18.1	+12.1	-12.4
	+67.0 / -52	+1.6 / -80	+28.4 / -41	+128.2 / +24	+30.0 / -43
	+48.7 / -17 / +30	-26.1 / +17 / +113	+6.3 / -12 / +13	+89.5 / -6 / +43	+11.4 / -15 / +95
Def2SVP	+18.8	+26.5	+38.1	+3.6	-6.4
	+54.3 / -62	-28.9 / -85	-22.2 / -2	+135.9 / -74	+4.9 / -37
	+47.9 / -2 / +98	-35.6 / +20 / +162	-2.7 / -3 / +57	+119.0 / -6 / +50	+3.7 / -2 / +150
Def2SVPP	+5.2	+13.1	+16.5	-6.8	-17.3
	+39.1 / -62	-42.2 / -87	-11.9 / -35	+125.0 / -75	-9.4 / -47
	+32.8 / -3 / +99	-51.0 / +19 / +161	-17.3 / -1 / +59	+109.0 / -6 / +50	-10.4 / -3 / +153
cc-pVDZ	+24.8	+33.6	+34.8	+16.7	-7.7
	+60.3 / -38	-21.4 / -81	+5.5 / -19	+123.6 / +24	+25.6 / -40
	+52.2 / -10 / +116	-28.9 / +15 / +164	+6.3 / -5 / +56	+87.2 / -13 / +113	+14.9 / -8 / +169
cc-pVTZ	+32.6	+36.0	+30.1	+23.9	+0.0
	+79.3 / +8	+7.6 / -48	+37.4 / +15	+152.5 / +56	+36.7 / +33
	+47.3 / -11 / -22	-6.0 / +22 / +68	+9.3 / -3 / -45	+113.1 / -3 / +68	-5.9 / -10 / +60

Table 39. Deviations for spin-spin coupling (**NMR = mixed**) in Hz for Mes*PPN(PCl₂)Mes* (**43**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	+10	-24	+18	+22	+19
	-25 / -68	+13 / +12	-19 / -78	-31 / -109	-24 / +3
Def2SVP	-5	-30	+59	+2	+16
	-19 / -28	+11 / +52	-16 / -40	-42 / -54	-18 / +36
Def2SVPP	-6	-33	+42	+0	+16
	-20 / -27	+11 / +51	-17 / -36	-42 / -54	-20 / +38
cc-pVDZ	+9	-43	+47	+19	+17
	-27 / -41	+11 / +42	-21 / -56	-43 / -79	-25 / +29
cc-pVTZ	+18	+3	+52	+94	+81
	-21 / -115	+17 / +5	-17 / -104	-23 / -116	-22 / -21

Table 40. Average unsigned deviations for bond lengths / angles in Å / degrees for [Mes*N(μ-PCl)₂PMes*] (**44**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0273 / 1.592	0.0288 / 1.444	0.0376 / 1.608	0.0058 / 0.929	0.0080 / 1.166
Def2SVP	0.0290 / 1.171	0.0295 / 1.058	0.0382 / 1.209	0.0092 / 0.673	0.0118 / 0.720
Def2SVPP	0.0290 / 1.075	0.0294 / 1.003	0.0382 / 1.086	0.0091 / 0.669	0.0117 / 0.619
cc-pVDZ	0.0399 / 1.139	0.0404 / 1.040	0.0488 / 1.113	0.0175 / 0.650	0.0198 / 0.679
cc-pVTZ	0.0211 / 1.323	0.0213 / 0.852	0.0294 / 1.225	0.0011 / 0.491	0.0032 / 0.755

Table 41. Deviations for chemical shifts / **spin-spin coupling** in ppm / Hz for [Mes*N(μ-PCl)₂PMes*] (**44**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	+26.2	+11.3	+21.6	+16.0	-6.3
	+8.3 / +25	+8.5 / +10	+13.7 / +21	+4.7 / +71	-22.7 / +34
Def2SVP	+18.1	+1.3	+14.2	+7.1	-11.6
	+1.6 / +48	-3.2 / +20	+9.3 / +32	-5.9 / +99	-27.5 / +56
Def2SVPP	+3.7	-13.9	-0.3	-3.8	-25.5
	-11.5 / +48	-16.8 / +21	-3.7 / +33	-16.7 / +101	-40.0 / +56
cc-pVDZ	+20.4	+1.4	+16.0	+7.3	-13.5
	+17.3 / +27	+10.7 / -19	+23.4 / +8	+10.7 / +98	-15.1 / +33
cc-pVTZ	+18.7	+0.7	+15.9	+4.5	-13.7
	+24.0 / -27	+18.2 / -53	+30.3 / -43	+19.5 / +64	-9.2 / -9

Table 42. Deviations for spin-spin coupling (**NMR = mixed**) in Hz for [Mes*N(μ -PCl)₂PMes*] (**44**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	-36	-62	-33	+23	-23
Def2SVP	-9	-29	-5	+64	+5
Def2SVPP	-7	-29	-5	+64	+6
cc-pVDZ	-29	-60	-29	+43	-19
cc-pVTZ	-49	-66	-51	+20	-30

Table 43. Average unsigned deviations for bond lengths / angles in Å / degrees for [TerNP]₂ (**45**)

(int = ultrafine).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0174 / 0.363	0.0285 / 0.970	0.0300 / 0.849	0.0110 / 0.466	0.0178 / 0.518
Def2SVP	0.0201 / 0.356	0.0342 / 0.833	0.0320 / 0.812	0.0126 / 0.525	0.0176 / 0.609
Def2SVPP	0.0199 / 0.354	0.0343 / 0.826	0.0319 / 0.804	0.0127 / 0.543	0.0176 / 0.616
cc-pVDZ	0.0267 / 0.490	0.0417 / 1.035	0.0391 / 0.967	0.0194 / 0.566	0.0239 / 0.752
cc-pVTZ	0.0063 / 0.195	0.0247 / 0.586	0.0228 / 0.554	0.0035 / 0.300	0.0078 / 0.355

Table 44. Deviations for chemical shifts in ppm for [TerNP]₂ (**45**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	-31.4	-47.5	-25.9	-22.5	-56.4
Def2SVP	-33.7	-54.0	-25.7	-20.7	-50.3
Def2SVPP	-47.6	-69.3	-40.5	-31.5	-64.6
cc-pVDZ	-10.3	-32.5	-4.7	-2.0	-29.7
cc-pVTZ	+4.7	-18.8	-33.0	+3.4	-20.8

Table 45. Average unsigned deviations for bond lengths / angles in Å / degrees for TerN(H)P(NTer)PNH₂ (**46**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	0.0195 / 1.240	0.0271 / 0.626	0.0317 / 1.443	0.0107 / 0.690	0.0102 / 1.169
Def2SVP	0.0208 / 1.443	0.0279 / 0.840	0.0323 / 1.538	0.0122 / 0.754	0.0136 / 0.838
Def2SVPP	0.0214 / 1.543	0.0280 / 0.824	0.0330 / 1.638	0.0129 / 0.800	0.0140 / 0.898
cc-pVDZ	0.0330 / 1.183	0.0401 / 0.943	0.0460 / 0.907	0.0225 / 0.956	0.0235 / 0.988
cc-pVTZ	0.0133 / 1.514	0.0198 / 0.503	0.0249 / 1.168	0.0066 / 0.407	0.0057 / 0.663

Table 46. Deviations for chemical shifts / **spin-spin coupling** in ppm / **Hz** for TerN(H)P(NTer)PNH₂ (**46**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	-46.6	-4.7	-32.4	-25.8	-53.4
	-28.3 / +3	-16.6 / +77	-13.0 / +51	-29.1 / +141	-35.4 / +29
Def2SVP	-30.6	-3.9	-12.5	-17.5	-28.5
	-22.6 / +5	-19.6 / +68	-8.3 / +63	-27.2 / +105	-30.9 / +47
Def2SVPP	-47.5	-19.6	-29.1	-30.6	-44.2
	-37.9 / +5	-33.4 / +66	-24.9 / +63	-36.5 / +110	-44.3 / +46
cc-pVDZ	-26.7	+15.5	+1.5	-4.9	-29.9
	-9.4 / +50	-2.5 / +53	+10.7 / +53	-15.6 / +146	-17.1 / +31
cc-pVTZ	-22.0	+12.4	+3.5	-1.7	-16.6
	-2.2 / -19	+4.3 / -18	+13.1 / -13	-6.0 / +95	-8.4 / -30

Table 47. Deviations for spin-spin coupling (**NMR = mixed**) in Hz for TerN(H)P(NTer)PNH₂ (**46**).

	B3LYP	B97D3	BP86	M062X	PBE1PBE
6-31G(d,p)	-10	+20	+14	+78	-23
Def2SVP	+8	+31	+34	+82	+2
Def2SVPP	+10	+30	+35	+88	+1
cc-pVDZ	-3	+22	+21	+109	-30
cc-pVTZ	-28	+2	+2	+65	-33

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