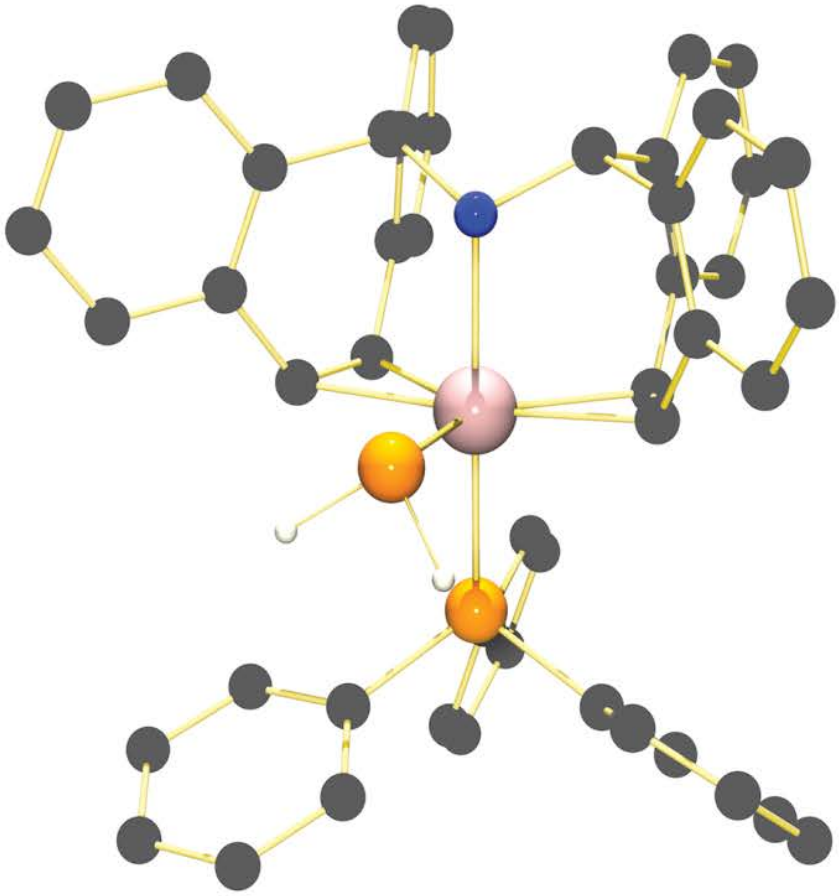
Alkoxide Packaged Sodium Dihydrogenphosphide: Synthesis and Reactivity



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"Lucifer revealed the shining day and night fled."

Ovid, Metamorphoses 8. 1 ff (trans. Melville) (Roman epic C1st B.C. to C1st A.D.)

Abstract

This work aims to describe the activation of white phosphorus to form highly functionalized compounds. White phosphorus is used as starting material as it is a highly reactive and selective reagent. From white phosphorus new synthesis routes towards sodium dihydrogenphosphide were developed. Previous routes towards sodium dihydrogenphosphide were dangerous and laborious. In this work new procedures are described to synthesize sodium dihydrogenphosphide conveniently at room temperature and apply them on a large scale not requiring high pressures or special equipment. By determining intermediates in the formation of sodium dihydrogenphosphide reaction mechanisms were elucidated.

Functionalization of prepared sodium dihydrogenphosphide was of primary interest. In a procedure described by Stein et al. bis(mesitoyl)phosphide was synthesized with sodium dihydrogenphosphide. Although Stein's route is extremely useful for the synthesis of a wide variety of bis acyl phosphine oxide (BAPO) compounds, low yields in the acylation step resulted in the loss of valuable mesitoyl chloride. Here, a new procedure is described to prepare bis(mesitoyl)phosphide in high yield (80%). Instead of using alkoxide packaged sodium dihydrogenphosphide, a mixture of sodium phosphides was used with *tert*-butanol (one equivalent compared to phosphorus). This mixture with a reduced amount of sodium *tert*-butanolate however, keeps the reactivity towards mesitoyl chloride high and selective. Furthermore, other mesitoyl containing compounds were tested for their reactivity towards sodium dihydrogenphosphide of trisodium phosphide. A variety of products is formed and a new sodium bistrityl phosphide compound was synthesized.

Interested in the reactivity of alkoxide packaged sodium dihydrogenphosphide as possible precursor for the preparation of sodium pentaphosphacyclopentadienide its reactivity towards white phosphorus was investigated. Sodium pentaphosphacyclopentadienide is an interesting precursor for metal complexes as analogue of the cyclopentadienyl ligand. The synthesis of this phosphorus containing analogue is difficult with low reaction yields (10-20%). Sodium pentaphosphacyclopentadienide in moderate yield (40%) was prepared by the reaction of sodium dihydrogenphosphide with white phosphorus in the presence of benzophenol. In this reaction, benzophenol is reduced by sodium dihydrogenphosphide to diphenylmethanol. Sodium pentaphosphacyclopentadienide is also formed in the reaction of sodium dihydrogenphosphide and benzophenone, although in low yields (<10%). However, trisodium heptaphosphide is formed in 76% yield as an alkoxide packaged cluster. The progress of this

reaction was monitored and several intermediates and products have been determined. Other benzophenone, quinone and oxidizing agents have been tested. The reaction of sodium dihydrogenphosphide with benzopinacolone formed Mono Acetyl Phosphine (MAP). This could be confirmed by X-ray analysis. MAP is unstable and decomposes at room temperature when isolated.

The applicability of sodium dihydrogenphosphide for the synthesis of metal phosphido complexes was studied in depth to fill gaps in literature. The parent complexes of the phosphido group metal complexes are interesting precursors for the introduction of phosphine groups in organic synthesis. Several nickel carbonyl phosphido complexes were synthesized which however appeared reactive and thus highly unstable. 1) The phosphido nickel complexes react with tetraphenyl phosphonium chloride to form triphenylphosphine, pentaphenylphosphine and other compounds. In contrast, 2) the reaction of iron pentacarbonyl with alkoxide packaged sodium dihydrogenphosphide resulted in the formation of sodium phosphaethynolate (NaOCP). This reaction is very fast and only proceeds when sodium *tert*-butanolate is present. When 3) sodium dihydrogenphosphide is used, only small amounts of NaOCP are formed, and a large part of iron pentacarbonyl is transformed to Collmans reagent. 4) Addition of extra sodium *tert*-butanolate resulted in the formation of NaOCP in high yield.

Several rhodium phosphido complexes were synthesized, revealing the different binding modes of phosphide as a ligand. These compounds were stable at room temperature under an argon atmosphere. Also a unique rhodium amide compound was synthesized which is the first of its kind for rhodium. This compound is very reactive and insoluble, only X-ray diffraction could establish its formation.

Diffusion measurements on [($trop_3P$)Rh]X complexes revealed the different ion pairing modes of the $BArF_{24}$, OTf and PF_6 anions. Whereas PF_6 and OTf are forming a tight ion pair, $BArF_{24}$ forms a free ion pair. The OTf anion coordinates to the free axial site of the ($trop_3P$)Rh cation, but is easily displaced by better ligands. ($trop_3P$)RhOH is not formed by the addition of water, as reported by Fischbach, however, could be obtained by a direct preparation.

Zusammenfassung

In dieser Arbeit wird die Aktivierung von weißem Phosphor beschrieben, um hochfunktionalisierte Verbindungen zu bilden. Aufgrund seiner hohen Aktivität und Selektivität wird weißer Phosphor als Startmaterial verwendet. Ausgehend vom weißen Phosphor wurden neue Synthesewege zum Natriumdihydrogenphosphid entwickelt. Frühere Synthesewege zum Natriumdihydrogenphosphid waren abhängig von gefährlichen und laborintensiven Prozeduren. In dieser Arbeit werden neue Wege beschrieben, um Natriumdihydrogenphosphid bequem und bei Raumtemperatur zu synthetisieren. Dieses Verfahren kann auch für große Ansätze und ohne die Verwendung von hohem Druck oder speziellen Apparaturen verwendet werden. Darüber hinaus war es möglich die Reaktion zu verfolgen und Zwischenprodukte bei der Bildung von Natriumdihydrogenphosphid zu bestimmen, was zu einem besseren Verständnis der Reaktion führte.

Die Funktionalisierung von synthetisiertem Natriumdihydrogenphosphid wurde untersucht. In einer Vorschrift, beschrieben von Stein et al. wurde „bismesitoyl phosphid“ ausgehend vom Natriumdihydrogenphosphid synthetisiert. Obwohl der von Stein entwickelte Syntheseweg sehr brauchbar in der Synthese einer großen Anzahl von BAPO Verbindungen ist, führen die geringen Ausbeuten im Acetylierungsschritt zum Verlust von wertvollem Mesitoylchlorid. In dieser Arbeit wird eine neue Methode beschrieben, um “bismesitoyl phosphide” in hohen Ausbeuten (80%) zu synthetisieren. Anstelle von Alkoxide packaged Natriumdihydrogenphosphide zu verwenden, wird ein Gemisch aus Natriumphosphide und *tert*-Butanol (ein Äquivalent im Vergleich zum Phosphor) genommen. Dieses Gemisch, mit einem geringeren Anteil an Natrium-*tert*-butanolat, hält eine hohe und selektive Reaktivität in Richtung „mesitoyl chloride“. Des Weiteren wurden andere Mesitoyl enthaltende Verbindungen auf ihre Reaktivität in Bezug auf Natriumdihydrogenphosphid oder Natriumphosphid getestet. Eine neue Natriumbistritylphosphidverbindung wurde synthetisiert und eine Anzahl an Produkten konnte gebildet werden.

Interessiert an der Reaktivität von Alkoxid packaged Natriumdihydrogenphosphid als möglichen Precursor für die Präparation von Natriumpentaphosphacyclopentadienid, haben wir seine Reaktivität gegen weißen Phosphor untersucht. Natriumpentaphosphacylcopentadienid ist ein interessanter Precursor für Metallkomplexe, als Analogon zu den Cyclopentadienylliganden. Die Synthese dieses phosphorenthaltenden Analogon ist schwierig und die Ausbeuten der Reaktion sind niedrig. Wir konnten Natriumpentaphosphacyclopentadienid in moderaten Ausbeuten (40%), durch die Reaktion

von Natriumdihydrogenphosphid mit weissem Phosphor in Anwesenheit von Benzophenol, darstellen. In dieser Reaktion wird Benzophenon durch Natriumdihydrogenphosphid zu Diphenylmethanol reduziert. Selbst die Reaktion von Benzophenon mit Natriumdihydrogenphosphid resultiert in der Bildung von Natriumpentaphosphacyclopentadienid, wenngleich in geringen Ausbeuten. Dennoch wird Trinatriumheptaphosphid in 76% Ausbeute als ein Alkoxid packaged Cluster gebildet. Der Reaktionsfortschritt dieser Reaktion wurde verfolgt und mehrere Zwischenprodukte wurden bestimmt. Andere Benzophenone, Quinone und oxidierende Reagenzien wurden getestet. Die Reaktion von Natriumdihydrogenphosphid mit Benzopinakolon führte zu monoacylphosphin (MAP) und wurde durch Röntgenstrukturanalyse bestimmt. MAP ist instabil und zersetzt sich bei Raumtemperatur, wenn es isoliert wird. Dies wurde zuvor von Liotta beschrieben, jedoch konnten sie die Verbindung nicht isolieren und analysieren.

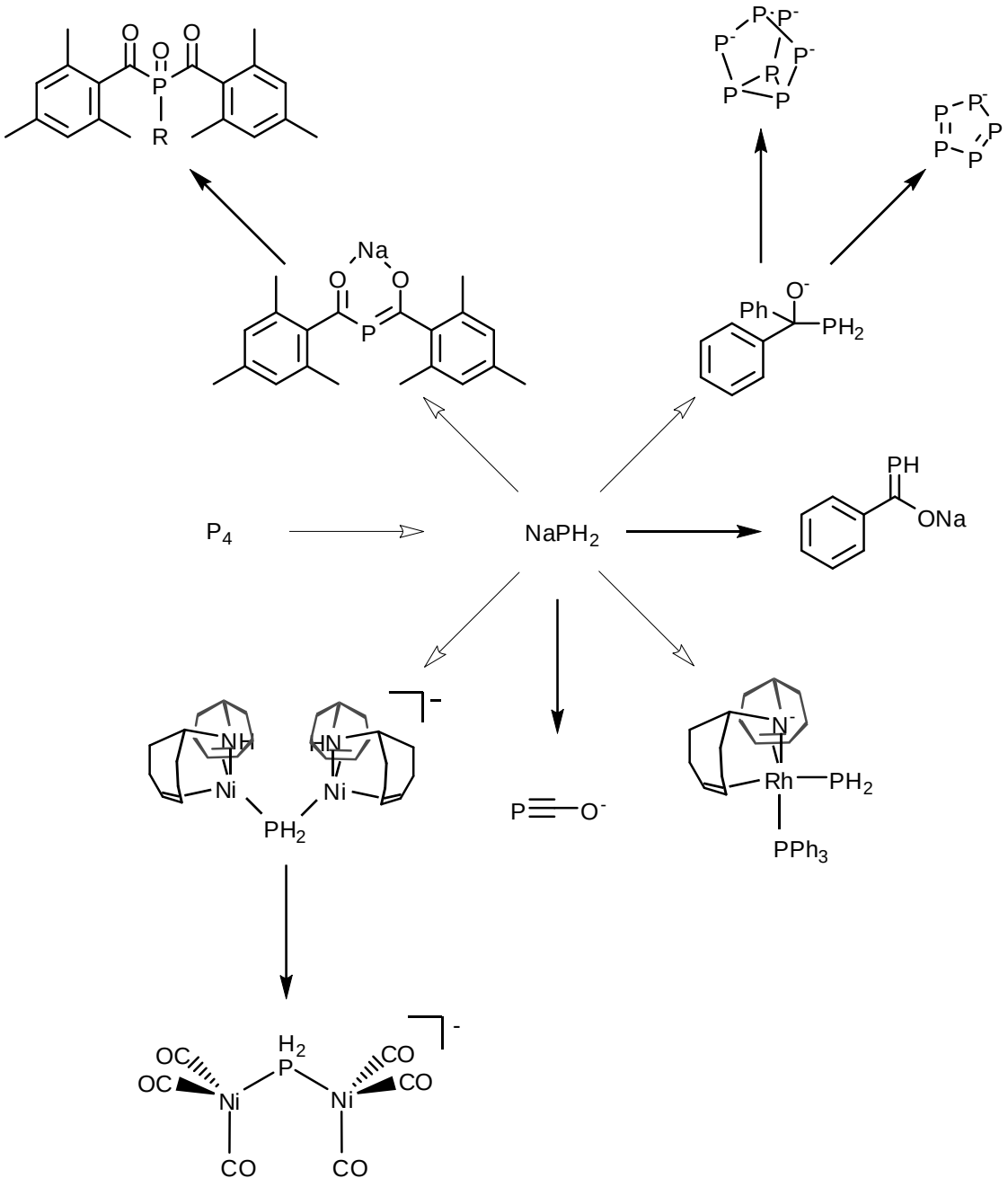
Weitere Untersuchungen von Natriumdihydrogenphosphid als zentraler precursor wurden für die Synthese von Metalphosphidkomplexen durchgeführt. Diese Anfangskomplexe der Phosphido-Metall-Komplexe wurden bisher ungenügend untersucht und könnten interessante Ausgangstoffe für die Einführung von Phosphinen in die organische Synthese sein. Verschiedene Nickelcarbonylphosphidkomplexe wurde synthetisiert; diese Komplexe sind jedoch höchst instabil und reaktiv. Das Phosphid reagiert mit Tetraphenylphosphoniumchlorid zum Triphenylphosphin, Phenylphosphin und andere Verbindungen. Im Gegensatz dazu resultierte die Reaktion von Eisenpentacarbonyl mit Alkoxid packaged Natriumdhydrogenphosphid in der Bildung von NaOCP. Diese Reaktion ist sehr schnell und läuft nur in Anwesenheit von Natrium-*tert*-Butanolat ab. Wenn Natriumdihydrogenphosphid verwendet wird, werden nur geringe Mengen an NaOCP gebildet und ein großer Teil des Eisenopentacarbonyls wird in Collmans Reagenz umgewandelt. Die Zugabe von zusätzlichem Natrium-*tert*-butanolat führt zu der Bildung von NaOCP in hohen Ausbeuten.

Verschiedene Rhodium-Phosphido-Komplexe wurden synthetisiert und konnten die verschiedenen Bindungsmodi der Phosphide als Liganden zeigen. Diese Verbindungen waren unter Raumtemperatur und Argonatmosphäre stabil. Es wurde ebenfalls eine Rhodiumamidverbindung synthetisiert, welche für Rhodium die erste ihrer Art ist. Die Verbindung ist sehr reaktiv und unlöslich, weshalb nur eine Röntgenstrukturanalyse ihre Bildung aufklären konnte.

Diffusionsexperimente an ($trop_3P$)RhX-Komplexen zeigten die unterschiedlichen Ionenpaarungsmodi von $BArF_{24}$-, OTf- und PF_6-Anionen. Während PF_6 und OTf ein dichtes Ionenpaar bilden, bildet $BArF_{24}$ ein freies Ionenpaar. Das an der freien axialen Seite des

($trop_3P$)Rh-Kations koordinierte OTf-Anion kann allerdings leicht durch bessere Liganden ersetzt werden. ($trop_3P$)RhOH wird nicht, wie durch Fischbach beschrieben, durch die Zugabe von Wasser gebildet, jedoch kann es durch die direkte Präparation erhalten werden.

Graphical abstract



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Chapter 1

Chapter 1. Introduction

Phosphorus is a widespread element in nature; it is an essential building block in biology whereas it has also multiple applications in industry. In living cells phosphorus is a part of adenosine tri- or diphosphate (ATP or ADP, respectively)[1] being universal energy carriers also present in the blueprint of life, deoxyribonucleic acid and ribonucleic acid (DNA and RNA).[1] In addition, phosphorus serves as the strengthener of bones and teeth in combination with calcium. In industry, phosphorus released from the natural apatite, is used in food technology (as food additives), in agrochemistry (fertilizers, pesticides) and in medicine (as compartment of buffers and drugs).[1]

To release phosphorus from phosphate rock (apatite) the industry commonly uses two procedures: usually the phosphorus ore is converted to phosphoric acid via the "wet" process (Scheme 1a).[1] Subsequently the apatite phosphate rock is grinded: the powder is reacted with sulfuric acid, after which the insoluble calcium sulphate is removed by filtration. Apatite can also be converted to white phosphorus (P_4) via the electric furnace oven method (Scheme 1b).[2] This involves the heating of a mixture of apatite, silica and coke in an electric furnace to a temperature of about 1450 ^{o}C. Although the production of phosphoric acid via the white phosphorus route results in a higher purity product versus the "wet" process, the lower costs of the latter method are decisive for the mass production of primarily fertilizers. The product of the electric furnace oven method is preferred as the starting material for the synthesis of organophosphorus and related compounds.

a) $Ca_5(PO_4)_3F + 5\ H_2SO_4 + 10\ H_2O \longrightarrow 3\ H_3PO_4 + HF + 5\ CaSO_4{\cdot}2H_2O$

b) $4\ Ca_5(PO_4)_3F + 18\ SiO_2 + 30\ C \longrightarrow 3\ P_4 + 18\ CaSiO_3 + 30\ CO + 2\ CaF_2$

Scheme 1: a) Synthesis of H_3PO_4 from fluoroapatite via the "wet" process. b) Synthesis of white phosphorus from fluoroapatite via the electric furnace oven method.

Elemental phosphorus

White phosphorus (= elemental phosphorus) was discovered by accident by Hennig Brand in 1669.[1] In his search for gold, Brand distilled urine and collected the gasses in water. Instead of the anticipated gold he obtained a white waxy solid which spontaneously ignited in air and glowed in the dark. The name phosphorus is derived from this feature, meaning "bearer of light" in ancient Greek. During the first century after its discovery, white phosphorus was produced from urine.[2] By the end of the 18th century bone-ash became the main feedstock for the production of white phosphorus.[2] The development of the previously described electric furnace oven procedure in 1888 was a big step forward. With this method it became possible to produce white phosphorus from apatite on a large industrial scale.[2] Since then the chemistry of phosphorus has been developed continuously.

Several allotropes of elemental phosphorus exist. The main allotropic forms are white, red and black but only the first two forms are of industrial relevance. The simplest and well defined allotrope is white phosphorus, that has a tetrahedral structure with bond lengths of about 2.21 Å and interbond angles of 60^{o} (Figure 1).[3]

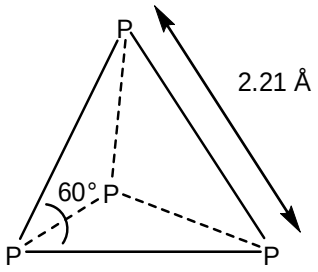
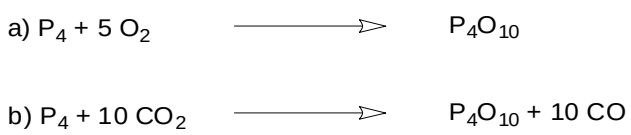


Figure 1: Schematic drawing of the tetrahedral structure of white phosphorus.



Scheme 2: Reaction of white phosphorus with a) oxygen and b) carbon dioxide.

White phosphorus spontaneously oxidizes in air and burns in oxygen and carbon dioxide to form phosphorus pentoxide (Scheme 2).[1] The pyrophoric properties of white phosphorus have been utilized in early times for the production of matches and for various military purposes (bombs and smoke screens).[2,4] Under reduced oxygen pressure white phosphorus emits a cold greenish phosphorescent glow (chemo luminescence) due to the slow oxidation of the emitted

vapor.[5] The origin of the glow is still not fully understood. Recently Nitschke *et al.* reported the inclusion of white phosphorus into a self-assembled tetrahedral capsule; the confined space inside the capsule stabilized white phosphorus under air and prevented a reaction with oxygen to form phosphorus pentoxide.[6]

White phosphorus can be selectively converted into the amorphous red allotrope by heating P_4 at 250-280 ^{o}C for 48 hours under the exclusion of air.[1] White phosphorus also slowly converts into the red allotrope under the influence of light or X-ray radiation. Red phosphorus exists in a variety of different forms; some of these forms are crystalline. In contrast to white phosphorus, red phosphorus is non-pyrophoric, relatively stable in air and moisture and has a reduced toxicity. Consequently, red phosphorus is often the preferred reagent for laboratory reactions. However, on an industrial scale white phosphorus is favored mainly because of the high costs of converting white phosphorus into the red allotrope. Furthermore, reactions of white phosphorus are often more selective and faster than comparable reactions with the red allotrope.

Another allotrope of elemental phosphorus is black phosphorus.[1] The black allotrope of phosphorus can be produced by heating white phosphorus under high pressure. Black phosphorus is thermodynamically the most stable form of the element.[1] Three crystalline forms of black phosphorus as well as an amorphous form are known.

Besides these three allotropes of phosphorus several other forms of phosphorus allotropes have been reported, most notably violet phosphorus or Hittorf's phosphorus.[1]

Elemental phosphorus is essentially used in the synthesis of phosphorus chlorides; the main starting material for the production of organophosphorus compounds. For example, triphenylphosphine, a commonly used ligand in metallophosphorus chemistry and a reagent in organic synthesis, is prepared industrially by a reaction between chlorobenzene, molten sodium and phosphorus trichloride (PCl_3).[1] Industrially, phosphorus chlorides are prepared from the direct action of dry chlorine gas on red phosphorus suspended in PCl_3.[1] However, substitution of the chlorine atom in PCl_3 with organic ligands has some serious drawbacks. One of these drawbacks is the formation of large amounts of hazardous and corrosive wastes (hydrogen chloride, alkyl halides, *etc*.), damaging the process equipment and being harmful for the environment if the release is uncontrolled. Modern requirements for environmental safety of industrial plants dictate the need to develop organophosphorus compounds production processes free from the chlorination stage.[7] This has drawn special attention to the chemistry of elemental phosphorus.

Functionalization of white phosphorus via transition metal complexes

One of the topics currently under investigation in phosphorus chemistry is the coordination and functionalization of white phosphorus via metal complexes.[8] Ideally, metal complexes mediate a catalytic process that directly combines white phosphorus and organic molecules. However, until now, a suitable methodology is lacking. Several coordination topologies of white phosphorus have been found (Figure 2) prompting many investigations into the coordination and reactivity of white phosphorus to metal complexes.

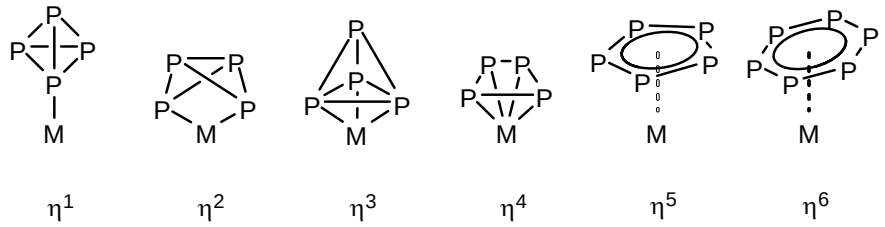
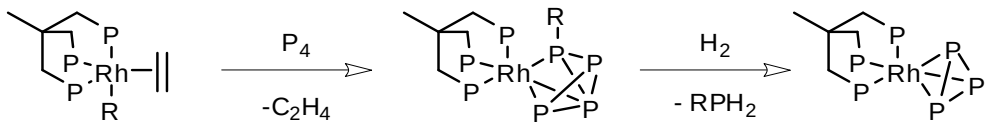


Figure 2: Different coordination modes for phosphorus.

Some examples of complexes bearing η^1- to η^2-P_4 ligands are known while of η^4-tetraphosphorus ligands two pairs have been described. The first reported transition metal complex with white phosphorus as a ligand was $[(PPh_3)_2Rh(\eta^2\text{-}P_4)Cl]$.[9] This complex was obtained by the reaction of the Wilkinson complex $[(PPh_3)_3RhCl]$, with white phosphorus at low temperature. Monohapto tetraphosphorus ligands are considered rare, the first example of such a complex, $[\{N(CH_2CH_2PPh_3)_3\}Ni(\eta^1\text{-}P_4)]$, was described by Sacconi *et al.* in 1979.[10] Scherer *et al.* have synthesized several metal complexes containing a planar *cyclo*-P_4 ligand via photolysis of niobium[11] and tantalum[12] precursors with white phosphorus. A η^3-coordinated P_4 species has not been reported yet.[13] Other coordination modes of activated white phosphorus are the η^5-P_5 coordination and the η^6-P_6 ligand.[14] These ligands are formed by the cothermolysis of white phosphorus with a suitable metal complex. Phosphorus ligand η^5-P_5 will be discussed more detailed later in this chapter.

Reports on the functionalization of white phosphorus with transition metal complexes are very limited. Peruzzini *et al.* reported the first metal mediated P_4 functionalization. Metal complex $[(triphos)RhR(\eta^2\text{-}C_2H_4)]$ [R = Me, Et, Ph] reacts with white phosphorus to afford rhodium complex $[(triphos)Rh(\eta^{2:1}\text{-}P_4R)]$. Subsequent reaction of this complex with hydrogen gives the alkyl or arylphosphines PH_2R in moderate yields (Scheme 3).[15,16]



Scheme 3: Activation of white phosphorus and formation of organophosphorus compounds.

Although the direct synthesis of organophosphorus compounds via metal activation and catalysis is attractive, no working examples have been published up to date.
Alkali metal dihydrogenphosphides (MPH_2) are promising starting reagents which on its turn are synthesized from the element phosphorus and alkali metals.

Synthesis of MPH_2 from elemental phosphorus

As mentioned before, metal dihydrogenphosphides are promising reagents for the synthesis of a variety of functionalized organophosphorus compounds. However, most methods for the preparation of metal dihydrogenphosphides are laborious and dangerous. A typical method for the preparation of MPH_2 is the deprotonation of phosphine with strong bases such as triphenylmethyl sodium, phenyl lithium or butyl lithium (Scheme 5).[17] Another method for the preparation of MPH_2 (M = Li – Cs) is the reduction of phosphine in ammonia solutions of alkaline metals (Scheme 5). The formed MPH_2 compounds in both synthesis methods are insoluble in most organic solvents. Furthermore, lithium dihydrogenphosphide is unstable at room temperature. However, the low solubility can be overcome to a certain extent by the addition of crown-ethers.
A major drawback of the previously described synthesis of MPH_2 is the use of phosphine (PH_3); a volatile and highly toxic gas (more toxic than HCN) of limited thermal stability and poorly soluble in organic solvents. Phosphine can be produced in several ways (Scheme 4a-e), by the hydrolysis of, for instance calcium phosphide, by the reaction of aqueous alkaline hydroxide with white phosphorus or phosphonium iodide, heating of phosphoric acid or hydrogenation of PCl_3 (Scheme 4).[18-25]

a) $Ca_3P_2 + 6\ H_2O \longrightarrow 2\ PH_3 + 3\ Ca(OH)_2$

b) $PH_4I + KOH \longrightarrow PH_3 + KI + H_2O$

c) $4\ P + 3\ KOH + 3\ H_2O \longrightarrow PH_3 + 3\ KHPO_2$

d) $4\ H_3PO_4 \longrightarrow PH_3 + 3\ H_3PO_4$

e) $PCl_3 + LiAlH_4 \longrightarrow PH_3$

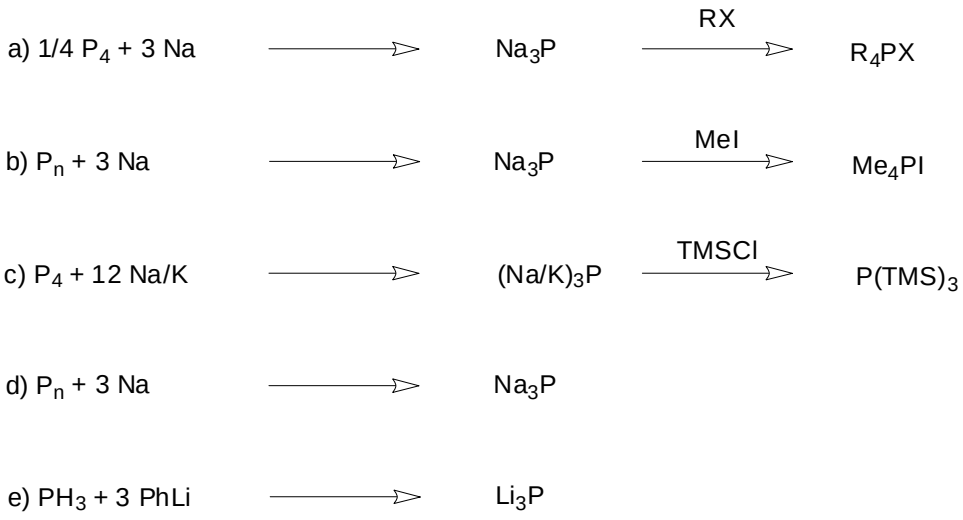
Scheme 4: Synthesis of phosphine from a) calcium phosphide b) phosphonium iodide c) white phosphorus aqueous alkaline d) phosphoric acid e) hydrogenation of phosphorus trichloride.

Another way to prepare MPH_2 is the controlled hydrolysis of tris(alkali)metalphosphides ("MP_3"). However, the synthesis routes towards "M_3P" are rather complicated and laborious. Furthermore, it is not known if the structure of the formed metal phosphide is in fact M_3P because only amorphous powders have been obtained. An X-ray structure of M_3P has been obtained by accident in an approach very different from the methods described here under high temperature and pressure.[26]

The reduction of white phosphorus with sodium in an organic solvent for the synthesis of alkali metal phosphides was first reported by Cahours in 1862 [27] and by Letts and Collie in 1881 (Scheme 5a).[28] The produced alkali metal phosphide was further reacted with benzyl chloride, methyl iodide or ethyl iodide to the tetraorganylphosphonium halogenide. The yields of these reactions were irreproducible and always lower than 40 %. Peterson *et al.* found that the yields in the reaction were correlated with the particle size of the alkali metal used.[29] The yields of these reactions could be increased to 60 % by using sodium dispersions. Polar and aprotic solvents and the use of electron carriers like diphenyl or naphthalene increases the yields of the previously described reaction. In 1968 Peterson, in corporation with Proctor & Gamble, patented a naphthalene based route for the reduction of white and red phosphorus to "MP_3" (Scheme 5a,b).[30] Around the same time a similar procedure was patented by Minklei in corporation with Hooker Chemical Corporation which only describes the use of white phosphorus.[31]

Becker *et al.* reported the formation of "$(Na/K)_3P$" from sodium-potassium alloy and white phosphorus in diglyme (Scheme 5c).[32] Subsequent conversion of the formed phosphide with tris(methylsilyl)chloride (TMSCl) resulted in the formation of tris(trimethylsilyl)phosphane

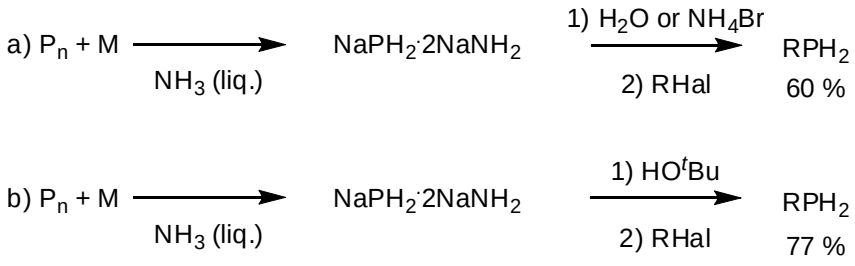
($P(TMS)_3$) in 60 – 75 % yield. On the other hand, "Li_3P" was prepared by Issleib and Tzschach by the complete metallation of PH_3 with phenyllithium in diethylether (Scheme 5e).[33]



Scheme 5: Various synthesis routes towards "Na_3P" starting from phosphorus and alkali metals in organic solvents and subsequent transitions.

Evers *et al.* reported in the 1950s, the reduction of white phosphorus, P_4, with sodium or lithium in liquid ammonia to the diphosphanediide $Na_2(P_2H_2) \times 2\ NaNH_2$.[34,35] In these reports the formation of $Na_4P_2{\cdot}2NH_3$ was mentioned as the intermediate species. However, careful analysis of the structure resulted in the identification of diphosphanediide as the formed species following the reduction of white phosphorus with sodium in liquid ammonia.[36] In this reaction liquid ammonia is the electron carrier, like naphthalene and diphenyl in the previously described preparations of "Na_3P". Careful addition of ammonium bromide or water produces $NaPH_2$ as a thermally unstable, pyrophoric substance being insoluble in organic solvents (Scheme 6).

Indications about the composition of $NaPH_2$ were only obtained by reaction with alkyliodides which yielded 60% of the corresponding primary phosphanes.[35] The synthesis of $NaPH_2$ was refined by the addition of *tert*-butanol in diethylether during the reduction, as described by Brandsma *et al*. instead of ammonium bromide or water. Subsequent addition of alkylhalides gave the corresponding alkylphosphanes in yields up to 77 % (Scheme 6).[34,37-39]



Scheme 6: Synthesis of primary alkylphosphanes from elemental phosphorus a) route developed by Evers b) route developed by Brandsma.

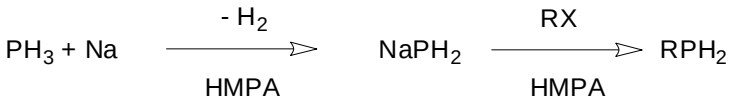
Using this refined method developed by Brandsma *et al.* our group demonstrated and investigated the versatility of the alkoxide packaged $NaPH_2$[40] and succeeded in growing $NaPH_2$ crystals from a dme solution with a crystal structure similar to $LiPH_2$(dme).[41] Both structures are coordination polymers with an almost linearly coordinated M-P-M angle. An interesting feature of the $NaPH_2$ structure in contrast to the $LiPH_2$ structure is the unusual coordination mode of the dme ligands. Instead of acting like a bidentate κ^2-ligand to a Na^+ cation, they interconnect neighboring helices in a κ^1,κ^1 coordination mode. Alkoxide packaged $NaPH_2$ crystals were obtained by the reaction of $NaPH_2$(dme) with sodium *tert*-butanolate at 80 °C in toluene. The formed crystals have the formula $[Na_{13}(PH_2)(O^tBu)_{12}]$ and the twelve *tert*-butoxide groups form an icosahedron and fully encapsulate the central PH_2^- anion. The advantage of the alkoxide packaged $NaPH_2$ is its solubility in organic ethereal solvents and thermal stability in solution. With the previously described method it becomes possible to synthesize $NaPH_2 \cdot xNaO^tBu$ in a controllable way.

Among the alkali metal dihydrogenphosphides, MPH_2 (M = Li - Cs), sodium dihydrogenphosphide, $NaPH_2$, is the most interesting because of the low cost and low toxicity of sodium.

Reactions of earth alkali metal phosphides

There is limited research regarding the study of the reactivity of metal phosphides with organic halides. Despite this, phosphorylation of organyl halides is practical and allows producing a wide variety of substrates. In most cases, the metal phosphides used in the phosphorylation reactions are generated *in situ* and are thus not isolated; this is true for the synthesis of alkylphosphanes already described by Evers and Brandsma. In the following part the preparation of several alkylphosphines and allylphosphines from alkali metal phosphides

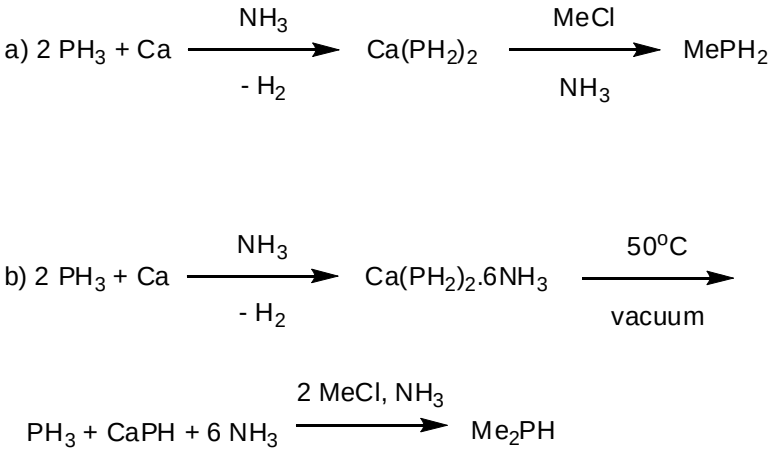
will be discussed. For instance, alkylphosphines and allylphosphines have been obtained in moderate to good yields (55-78%) by a one pot procedure described by Tang *et al*. (Scheme 7).[42]



R = Me, Et, CH_2=$CHCH_2$; X = Cl, Br.

Scheme 7: Synthesis of alkylphosphines and allylphosphines from phosphine and sodium in HMPA.

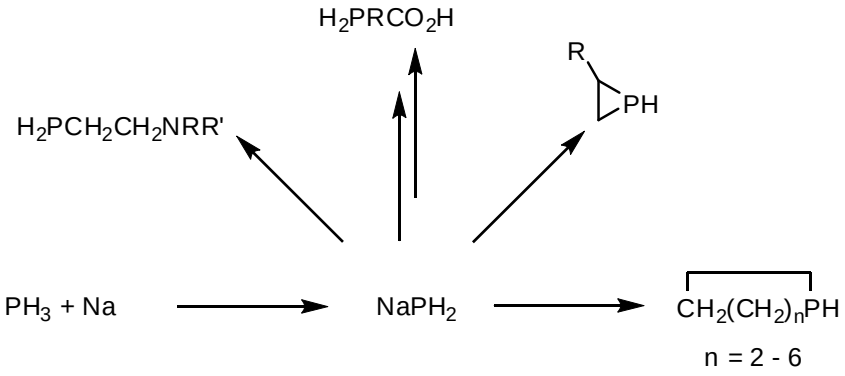
$NaPH_2$ can be obtained by dispersed sodium in hexamethylphosphotriamide (HMPA) in the presence of phosphine. Higher efficiency was achieved when calcium metal was used in liquid ammonia with phosphine. The reaction between chloromethane and $Ca(PH_2)_2$ gives methylphosphine in 87% yield (Scheme 8).[43] Formation of dimethylphosphine from CaPH and chloromethane in liquid ammonia has been reported, although in a relatively low yield (33%).[43] The formation of secondary phosphines is cumbersome due to the difficulty of formation of disubstituted derivatives upon metallation of phosphine.



Scheme 8: Synthesis of a) $MePH_2$ and b) Me_2PH from PH_3 and Ca.

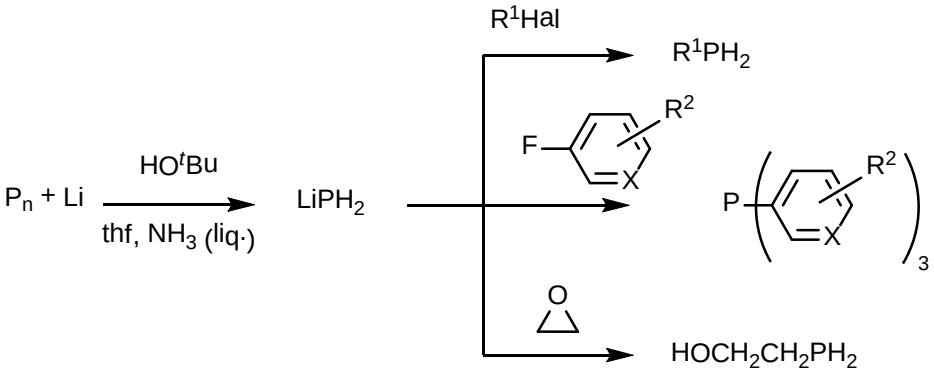
Regarding aromatic phosphines, phenylphosphine can be prepared from phosphine and potassium in liquid ammonia which slowly reacts with bromo- and iodobenzene.[24] A mixture of (5-isopropyl-2-methylphenyl)phosphine is formed when 2-bromo-4-isopropyl-1-methylbenzene reacts with sodium phosphide or lithium phosphide in boiling ether.[44] The

synthesis of several substituted and cyclic alkylphosphines in a yield of (25-85%) has been described via the *in situ* generation of sodium dihydrogenphosphide in the "phosphine-alkali metal-liquid ammonia" system (Scheme 9).[45-47]



Scheme 9: Possible transformations of $NaPH_2$ formed from phosphine and sodium in liquid ammonia.

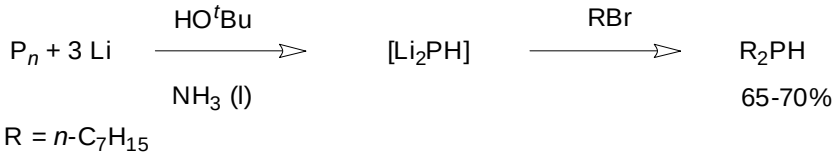
Several primary alkyl phosphines and symmetric triarylphosphines (yields 36-60%) are formed in high yields from the "elemental phosphorus-alkali metal-liquid ammonia" system (Scheme 10).[38,48,49]



R = n-C_9H_{19}, $PhCH_2$, cyclo-C_5H_9; X = CH, N.

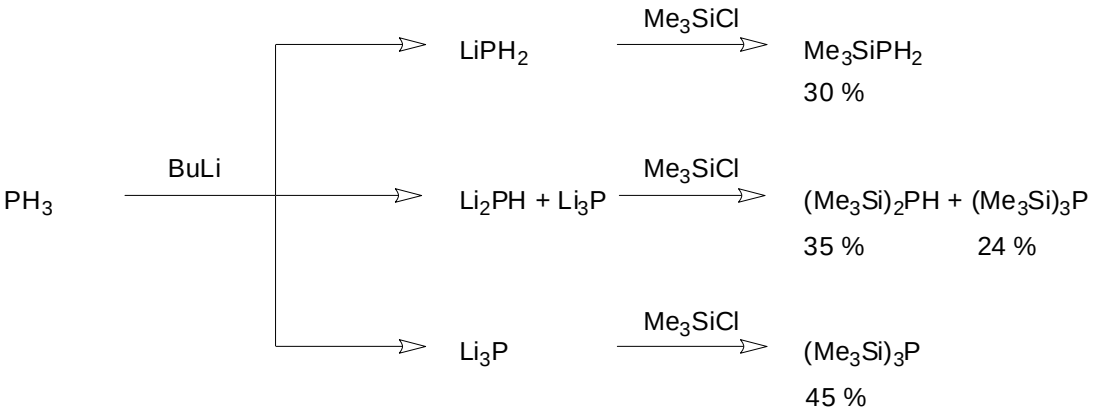
Scheme 10: Synthesis of alkyl and aryl phosphine compounds starting from P_n and lithium in liquid ammonia.

By using one equivalent of *tert*-butanol, with a P_n/Li ratio of 1:3, doubly charged phosphide anions are expected to be formed. From these doubly charged phosphide anions, dialkylphosphines are selectively obtained by subsequent alkylation in good yield (Scheme 11).[39]



Scheme 11: Synthesis of dialkylphosphines from lithium and phosphorus in liquid ammonia.

Another method for the production of mono, double or triple charged phosphide anions is the deprotonation of phosphine with butyl lithium. Depending on the ratio, the reaction gives rise to lithium phosphide, trilithium phosphide or a mixture of trilithium phosphide and dilithium phosphide. Reaction of the phosphides with trimethylsilylchloride resulted, depending on the phosphide anion, in the formation of a mixture of bis- and tris(trimethylsilyl)phosphine or tris(trimethylsilyl)phosphine in low to moderate yields (Scheme 12).[50]



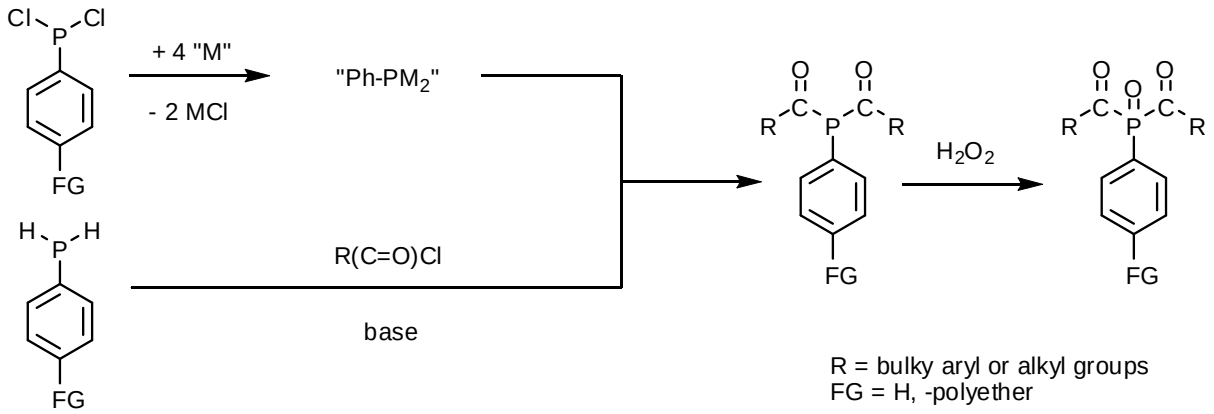
Scheme 12: Synthesis of $(Me_3Si)_{3-n}PH_n$ from phosphine and butyl lithium.

Although there are several reports about the preparation of primary phosphines from alkali metal phosphides, research is hampered because of the dangerous and laborious preparation of MPH_2 compounds previously described. Our group has developed a new synthesis route towards bis(acyl)phosphineoxides using soluble “organic” sodium dihydrogenphosphide.

Synthesis of BAPOs from MPH_2

Bis(acyl)phosphine oxides (BAPOs) are very efficient photoinitiators and have several advantages over acetophenone and benzophenone based photoinitiators, based on the easy excitation in yellow to red light (λ = 350-440 nm).[51-54] Furthermore a BAPO photoinitiator

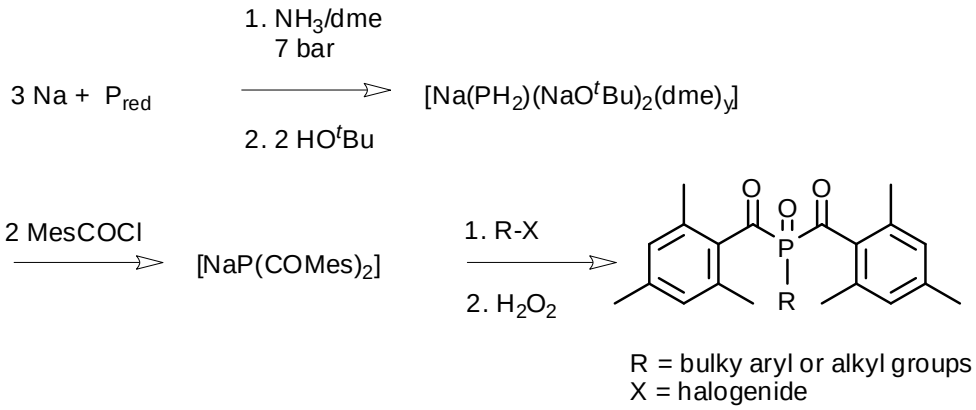
can generate up to four radicals in contrast to acetophenone and benzophenone based photoinitiators. Although BAPOs are more efficient than other photoinitiators, they are expensive and difficult to synthesize. Nevertheless, their outstanding activity justifies complicated chemical reactions and expensive starting materials. The few reported procedures of BAPOs start from dichlorophenylphosphane or phenylphosphane (Scheme 13).[55,56]



Scheme 13: The "classical" synthesis of Phenyl BAPOs.

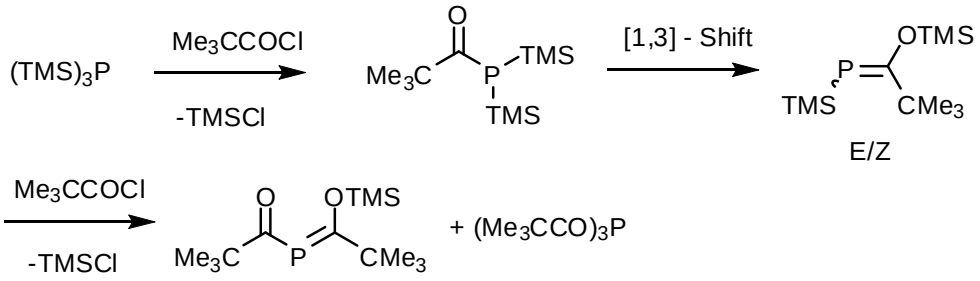
Although it is relatively easy to vary the acyl group, functionalization of the phosphorus moiety is much more difficult. Functionalized dichlorophenylphosphanes and phenylphosphanes as starting materials are difficult to prepare and to handle on large scale.[57,58] However, the main problem of this method is the incompatibility of the dichlorophosphanyl group and metallation reagents towards functional groups. In order to circumvent these problems, our group has recently developed a new method for the synthesis of BAPOs starting from basic chemicals such as sodium and red phosphorus.[59] Instead of starting from functionalized dichlorophenylphosphanes and phenylphosphanes, the functional group is only introduced after the acylation of *in situ* prepared sodium dihydrogenphosphide. This methodology reduces the possibility of unwanted side reactions of the pendant functional groups.

In a typical procedure red phosphorus is reduced by sodium in liquid ammonia with the subsequent addition of *tert*-butanol. The *in situ* generated $NaPH_2$ is acylated by mesitoyl chloride to form sodium bis(mesitoyl)phosphide (Scheme 14).[59]



Scheme 14: The "Stein" route towards BAPOs starting from red phosphorus and sodium.

Bis(acyl)phosphides are already known since 1977 when Becker *et al.* synthesized [*tert*-Butyl(trimethylsiloxy)methylene](pivaloyl)phosphane from tris(trimethylsilyl)phosphane (TMSP) and pivaloylchloride (Scheme 15).[60,61] By protonolysis with methanol, bis(pivaloyl)phosphane is formed under cleavage of methyltrimethylsilylether. Furthermore, Becker *et al.* were able to synthesize lithium-bis(benzoyl)phosphide as thf and dme-adducts from $LiPH_2$ and benzoylchloride.[62,63] Several other bis(acyl)phosphides have been reported and structurally characterized. However, none of these has been utilized for the preparation of BAPOs.



Scheme 15: Synthesis of [*tert*-Butyl(trimethylsiloxy)methylene](pivaloyl)phosphane from tris(trimethylsilyl)phosphane and pivaloylchloride.

The advantage of bis(mesitoyl)phosphides is due to their participation in nucleophilic substitution reactions with alkylhalogenides or cross coupling with aryl iodides catalyzed by palladium to form the corresponding bis(acyl)phosphides (BAP).[64] Subsequently, the obtained phosphanes are easily oxidized with hydrogen peroxide to the corresponding BAPOs. To prove the applicability of this new modular approach several functionalized BAPOs have recently been synthesized in our group (Figure 3).

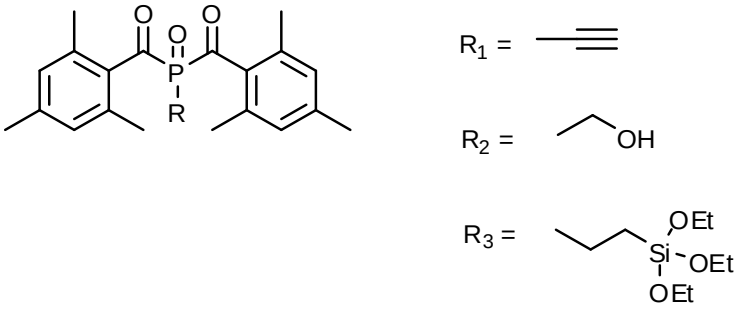


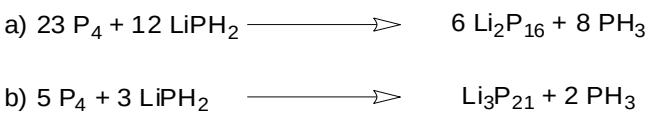
Figure 3: Some examples of different types of synthesized BAPOs.

Polyphosphides formed by nucleophilic cleavage of white phosphorus with MPH_2

Although there are only a limited number of reports about the reactivity of MPH_2 compounds, several describe the reaction of metal dihydrogenphosphides towards white phosphorus. The research groups of Baudler and von Schnering have synthesized various polyphosphides by nucleophilic cleavage of white phosphorus.[65-68] For instance, trilithium heptaphosphide can be synthesized by nucleophilic cleavage of white phosphorus with an excess of lithium dihydrogenphosphide in boiling dme (Scheme 16).[65] An interesting feature of the heptaphosphide ion is its valence tautomerization.[69] Like in Bullvalene, the valence tautomerization observed in trilithium heptaphosphide is a degenerated Cope rearrangement.

Scheme 16: Synthesis of Li_3P_7 from white phosphorus and lithium dihydrogenphosphide.

Similarly to the synthesis of heptaphosphide, the cleavage of white phosphorus by lithium dihydrogenphosphide under different stoichiometric conditions gives rise to dilithium hexadecaphosphide (Li_2P_{16})[66], trilithium henicosaphosphide (Li_3P_{21})[70] or tetralithium hexacosaphosphide (Li_4P_{26})[71] (Scheme 17).



Scheme 17: Synthesis of a) lithium hexadecaphosphide and b) trilithium henicosaphosphide starting from sodium dihydrogenphosphide and white phosphorus.

However, some of these polyphosphides could only be obtained as a mixture of products. Of the previously mentioned lithium polyphosphides, only Li_2P_{16} and Li_4P_{26} have been isolated in the pure state and the structure was confirmed by detailed ^{31}P NMR and single crystal X-ray diffraction analysis.[66] The sodium polyphosphides (Na_2P_{16}, Na_3P_{19} and Na_3P_{21}) can be made by the cleavage of white phosphorus with sodium in the presence of 18-crown-6 under different stoichiometric conditions, were Na_3P_{21} could be isolated in a pure crystalline state.[70] The ions of P_{16}^{2-} and P_{21}^{3-} exhibit a striking resemblance to the structural units of Hittorfs phosphorus (Figure 4).

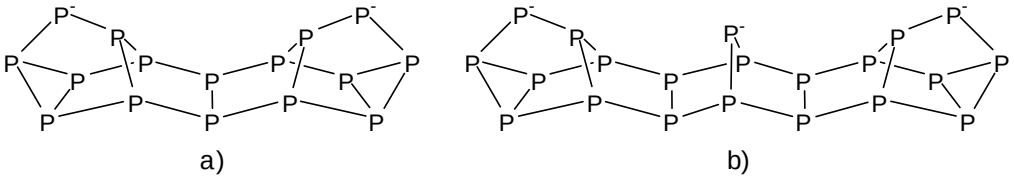
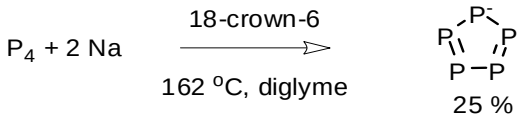


Figure 4: Structures of a) P_{16}^{2-} and b) P_{21}^{3-}.

In addition to the above mentioned polyphosphides the particularly interesting pentaphosphacyclopentadienide ion (P_5^-) is formed by the cleavage of white phosphorus with sodium (P/Na = 3:1) in boiling diethyleneglycol dimethyl ether.[72,73] A more convenient approach to the synthesis of pentaphosphacyclopentadienide ion is the degradation of red phosphorus with KPH_2 (P/KPH_2 = 1.9:1) in boiling dimethylformamide (dmf) which, under appropriate conditions, provides almost exclusively the polyphosphides KP_5 and K_2HP_7.[74] After separation of byproducts, pure solutions of MP_5 can be obtained in thf (M = Li), in thf/18-crown-6 (M = Na), or in dmf (M = K) respectively. The synthesis of sodium pentaphosphacyclopentadienide was further elaborated by Milyukov *et al.*[75] Heating a mixture of white phosphorus and sodium in diethylene glycol dimethyl ether in the presence of dibenzo-18-crown-6 gives a pure solution of sodium pentaphosphacyclopentadienide in 25 % yield (Scheme 18).



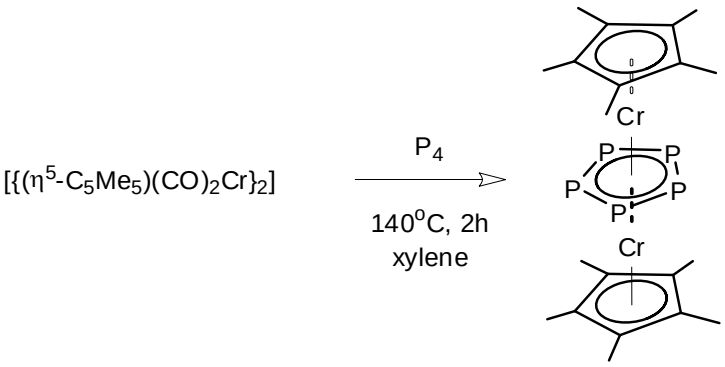
Scheme 18: Synthesis of NaP_5 from white phosphorus and sodium with a catalytic amount of 18-crown-6.

The pentaphosphacyclopentadienide ion is of special interest because it is isolobal to the cyclopentadienide ion. This means that both structures have frontier orbitals that are equal in

number, have the same symmetries, the same occupation by electrons, and are similar in size. The P_5^- anion has been the subject of several theoretical surveys.[76,77] All calculations point out that the aromaticity of P_5^- is comparable with the cyclopentadienyl ion and benzene. Although the aromaticity is comparable, it is not a donor ligand like cyclopentadienyl. For example, in $[Ti(P_5)_2]^-$ the η^5-P_5 ligand acts as acceptor of electron density.[78] Since the *cyclo*-P_5^- anion is isolobal to the cyclopentadienyl ion, there has been some effort to make η^5-P_5^- metal complexes and compare those to the well known Cp^- metal complexes.

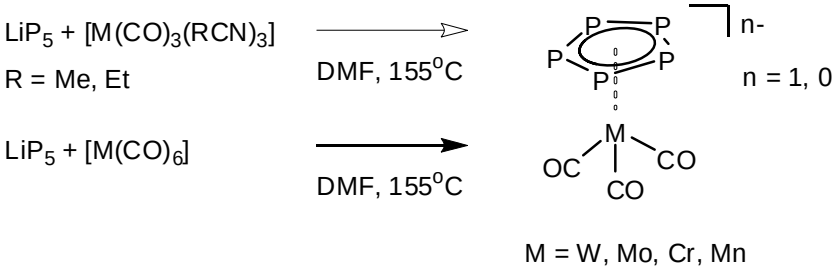
Pentaphosphacyclopentadienide as a ligand for metal complexes

At about the same time of the discovery of the pentaphosphacyclopentadienide ion in solution, the first metal complex with a μ,η^5-P_5 ligand had been isolated and characterized. In 1986, Scherer *et al.* reported a μ,η^5-P_5 tripledecker complex synthesized from $Cr(CO)_6$, pentamethylcyclopentadiene (Cp*) and white phosphorus in about 8% yield (Scheme 19).[79]



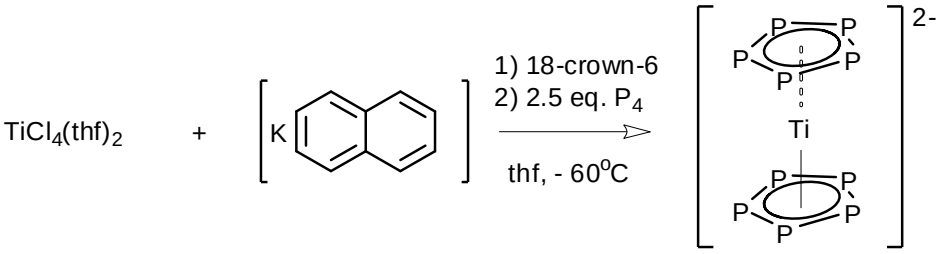
Scheme 19: Synthesis of the first pentaphosphametallocene complex.

Shortly after the discovery of the first tripledecker metallocene also the first classical sandwich complex [Cp*Fe(η^5-P_5)] was reported by Scherer *et al.*[80] Since the discovery of the first η^5-P_5 metal complexes several sandwich and tripledecker and complexes could be prepared by the cothermolysis of white phosphorus with suitable starting complexes in low yield.[81,82] Baudler *et al.* reported the first directed synthesis from the LiP_5 anion, LiC_5Me_5, and $FeCl_2$.[83,84] All these η^5-P_5 metal complexes have in common that an additional (η^5-$C_5R_4^1R^2$) ligand (R^1 = R^2 = Me, H; R^1 = Me(H), R^2 = Et(Me)) is coordinated to the metal center. Baudler *et al.* was able to synthesize the mixed carbonyl(pentaphosphacyclopentadienyl)-metal (M = W, Mo, Cr, Mn) complexes through thermal ligand exchange reactions using LiP_5 as a synthetic reagent (Scheme 20).[85]



Scheme 20: Synthesis of carbonyl(pentaphosphacyclopentadienyl)-metal complexes.

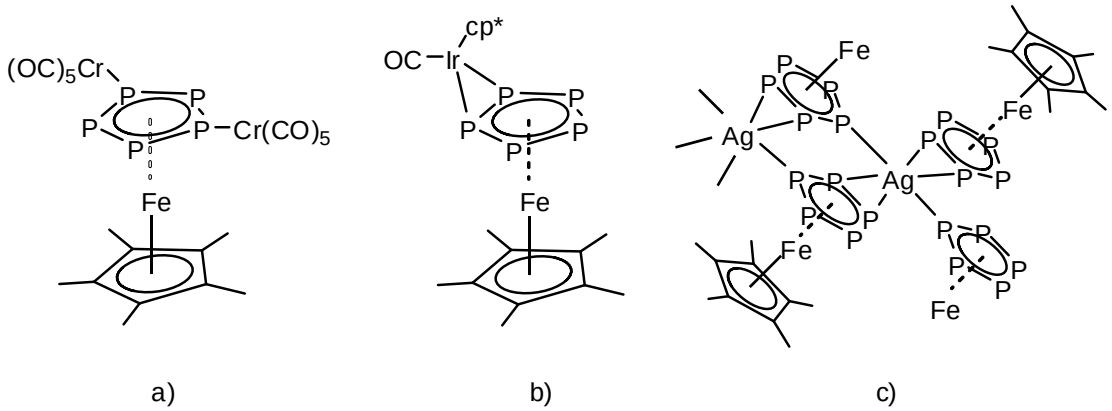
Although it had been possible to synthesize a range of η^5-P_5 containing metal complexes, the full characterization of metallocene analogues with two η^5-P_5 ligands remained elusive until the synthesis of $[(P_5)_2Ti]^{2-}$ in 2002 by Urnezius *et al*. (Scheme 21).[78] Before the synthesis of $[(P_5)_2Ti]^{2-}$ attempts to prepare $[(P_5)_2Fe]$, the analogue of ferrocene resulted in the formation of a high density, insoluble phosphorus containing iron complex.[85]



Scheme 21: Synthesis of $[(P_5)_2Ti]^{2-}$ from $TiCl_4$ and P_4.

The remarkably inert nature of $[(P_5)_2Ti]^{2-}$, in contrast to analogous $[(Cp)_2Ti]^{2-}$ complexes which are non-existent, is likely due to both steric and electronic effects. The strong acceptor ability of coordinated η^5-P_5 rings facilitates removal of electron density from the Ti center and renders the latter much less electron rich. It is worth mentioning the limited reactivity of this species towards good acceptor ligands such as CO, aryl isocyanides, and organophosphites.

The lone pairs of the η^5-P_5 moiety of $[Cp^*Fe(\eta^5\text{-}P_5)]$ are capable to coordinate up to four $[Cr(CO)_5(thf)]$ or $[CpMn(CO)_2(thf)]$ complexes in a η^1-coordination mode.[81,82] A more unusual binding mode was observed when $[Cp^*Fe(\eta^5\text{-}P_5)]$ was reacted with $[Cp^*Ir(CO)_2]$ in toluene.[86] Structural analysis reveals the formed product to be a sandwich complex with μ-η^5:η^2 coordination of the *cyclo*-P_5 ligand (Figure 5).



a) b) c)

Figure 5: a) η^1-Coordinated $Cr(CO)_5$ b) side on coordination of Ir(CO)cp*and c) side-on/end-on coordination of P_5.

Previously demonstrated by Scheer *et al.* the *cyclo*-P_5 ligand is also capable of coordinating in a 1,2,3-coordination mode in the solid state forming a linear polycationic chain consisting of $[Ag\text{-}\{Cp^*Fe(\eta^5\text{:}\eta^2\text{:}\eta^1\text{-}P_5)\}_2]_n[Al\{OC(CF_3)_3\}_4]_n$.[87] In the linear polymeric chain each Ag^+ cation is tetrahedrally coordinated to six phosphorus atoms of four *cyclo*-P_5 moieties through a side-on and an end-on coordination mode (Figure 5).

$[Cp^*Fe(\eta^5\text{-}P_5)]$ formed the basis of the synthesis of inorganic fullerene-like molecules.[88] The reaction of $[Cp^*Fe(\eta^5\text{-}P_5)]$ with CuCl leads to the formation of entirely inorganic fullerene-like molecules possessing 90 inorganic core atoms. The structural design is similar to C_{60} with the *cyclo*-P_5 rings of $[Cp^*Fe(\eta^5\text{-}P_5)]$ molecules surrounded by six-membered P_4Cu_2 rings that results from the coordination of each of the phosphorus lone pairs to CuCl metal centers.

MPH_2 metal complexes

Phosphido and Phosphido bridged metal complexes with alkyl and aryl groups as substituents on the phosphido bridge, are known since the late 1950s and have been studied extensively since then.[33,89-91] Phosphido complexes, formed by P-H activation, are known as key intermediates in hydrophosphination reactions.[92-96] Phosphido bridges often stabilize di- and poly-nuclear complexes with respect to fragmentation. In contrast, the reactivity of complexes containing PH_2 ligands has been the subject of relatively few investigations in the literature. The PH_2 complexes could be of special interest because of the analogy between MPH_2 and MNH_2. Furthermore, PH_2 based complexes are the simplest phosphido ligands possible and could provide a simple way to make primary phosphine compounds.

The first account of a MPH_2 complex was made by Schmitz-DuMont *et al.* in 1958.[97] Although the formation of highly unstable and probably polymeric complexes $Co(PH_2)_2$, $KCo_2(PH_2)_7$ and $Ni(PH_2)_2$ was described, the structures of these complexes could not be determined. In 1968 Schmitz-DuMont *et al.* could determine the ratios of Ni, P and H of the highly unstable $K[Ni(PH_2)_3]$ complex made by the reaction of $[Ni(NH_3)_6]Cl_2$ in liquid ammonia with KPH_2.[98]

Since the first discovery of MPH_2 complexes, several routes towards μ-PH_2 metal complexes have been developed. One of the first described routes was the hydrolysis of μ-$P(SiMe_3)_2$ metal complexes with ROH (Scheme 22).[99-101] Via this route Schäfer *et al.* was able to produce a large amount of mixed μ-PH_2 metal complexes. A second route towards phosphido bridged complexes is the deprotonation of phosphine metal complexes with bases (Scheme 22).[102-104] An unusual reaction for the formation of a PH_2 complex, although often applied in hydrophosphination reactions, is the oxidative addition of phosphine to an iridium metal complex described by Ebsworth.[105-107] The formation of μ-PH_2 metal complexes by the direct method of addition of MPH_2 (M = Li-K) to a metal complex is only described in some reports (Scheme 22).[108]

Hydrolysis of μ-$P(SiMe_3)_2$

$cp(CO)_2Fe[\mu\text{-}P(SiMe_3)_2]Fe(CO)_4 \xrightarrow{2\ MeOH} cp(CO)_2Fe(\mu\text{-}PH_2)Fe(CO)_4 + 2\ Me_3SiOMe$

Deprotonation of PH_3

$[(CO)_5W(thf)] + [(CO)_5WPH_3] \xrightarrow{KH} [(CO)_5W(\mu\text{-}PH_2)W(CO)_5]^-$

Oxidative addition of PH_3

trans-$[Ir(CO)X(PEt_3)_2] \xrightarrow{PH_3} [Ir(CO)XH(PEt_3)_2(PH_2)]$

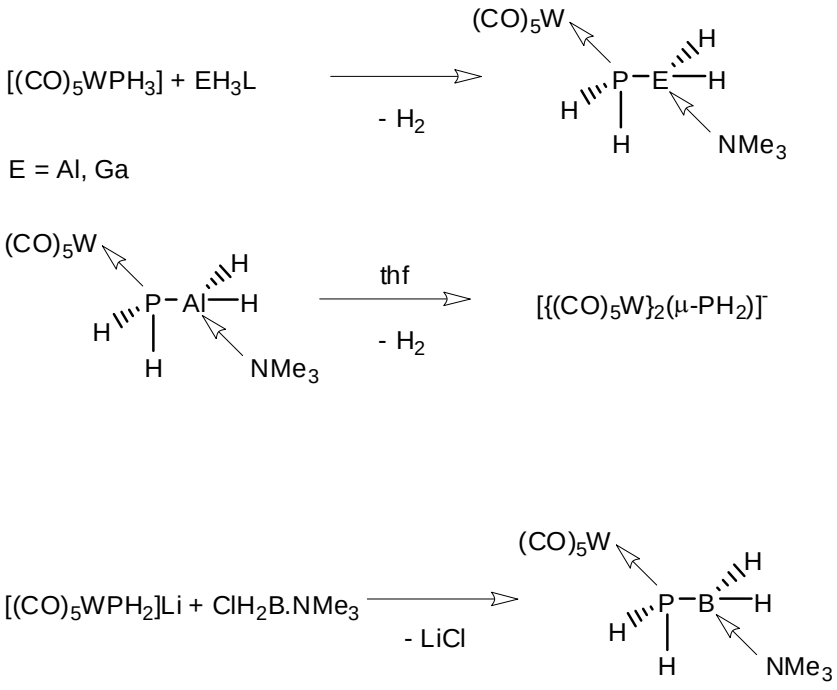
X = Cl, Br.

Scheme 22: Several routes towards PH_2 complexes.

With the PH_2 complexes prepared by Schäfer *et al.* and others it is possible to observe a general trend in the ^{31}P NMR spectroscopic data.[100] Although, the coordination of MPH_2 to a metal center generally results in a shift to higher frequency from the starting compound, more information can be found in the $^1J_{PH}$ coupling constants.[100,109] Coordination of a non bridging

PH_2 ligand to a metal complex generally does not affect the $^1J_{PH}$ coupling constants significantly (between 140-180 Hz). However, a bridging PH_2 ligand between two metal centers has a remarkably higher coupling constant (between 220-300 Hz). This is due to the larger *s* character in the PH bonds upon binding with two metal centers. This correlates with the smaller M-P-M angle which is observed for bridging metal complexes compared to the MPH_2 alkali metal compounds, which have M-P-M angles close to 180°.[108,109] In contrast, the M-PH_2-M angles of transition metal complexes are in the range of 120°.[108,109] Even larger $^1J_{PH}$ coupling constants are observed for bridging PH_2 complexes with metal-metal bonds. Coupling constants for such complexes are in the range from about 300 to 400 Hz.[109] This is in agreement with the smaller angle of the M-P-M bond (~ 105°) and the increased *s* character of the PH bonds. With this method it is possible to distinguish between different coordination modes of the PH_2 ligand.

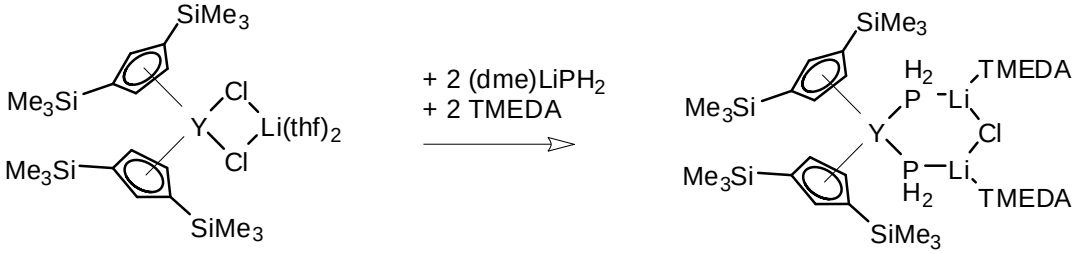
$[H_2EPH_2]$ (E = Al, Ga) is an interesting compound because it has been suggested to play an important role in the formation of aluminum phosphide and gallium phosphide semiconductors by the chemical vapor deposition process. Scheer *et al.* have been able to synthesize Lewis acid/base stabilized phosphanylalane and –gallane complexes (Scheme 23).[104,110]



Scheme 23: Synthesis for the phosphanylborane, - alane and – gallane Lewis acid/base stabilized complexes and the decomposition of phosphanylalane complex in thf.

Reaction of the phosphanylalane complex with thf resulted in the formation of $[\{(CO)_5W\}_2PH_2]^-$ complex under release of H_2. The phosphanylborane compound was synthesized in a slightly different procedure. Starting from $Li[(CO)_5WPH_2]$ and ClH_2BNMe_3, $[(CO)_5W(H_2PBH_2)\cdot NMe_3]$ was produced.[111] UV radiation of this complex leads to the dinuclear phosphanido-bridged complex $[(CO)_8W_2(\mu\text{-}PHBH_2)\cdot NMe_3]$ by H_2 and CO elimination (Scheme 23).[111]

Although several $\mu\text{-}PH_2$ complexes are described in the literature, there is only limited information about PH_2 as a non bridging ligand. Several authors have reported the formation of these non-bridging compounds and could analyze them by spectroscopy; however, they are very unstable. Westerhausen *et al.* have been able to isolate a very reactive bisphosphanyl Yttriate.[112] This compound is one of the very few isolated examples of a non bridging PH_2 complex (Scheme 24).



Scheme 24: Synthesis of the bisphosphanyl Yttriate complex.

Aim of this thesis

In this thesis new synthesis routes towards alkoxide packaged sodium dihydrogenphosphide will be explored. Until now, all the known routes towards sodium dihydrogenphosphide are hazardous procedures, hampering the synthetic access to new organophosphorus products. We were interested in a new and less hazardous way for the production of sodium dihydrogenphosphide in order to create an easily accessible starting material for further research by our group and others. Our aim is to start from white phosphorus, although very poisonous and hazardous to work with, is a common, well defined and cheap starting material. Furthermore the use of liquid ammonia must be avoided in order to circumvent the use of special glassware and apparatus.

After exploring the newly developed procedure for the synthesis of sodium dihydrogenphosphide in detail, the reactivity of $NaPH_2$ was investigated. It appears that sodium dihydrogenphosphide is a very suitable reagent for the synthesis of organophosphorus compounds.

The development of a low cost procedure for the synthesis of BAPOs will be investigated. In previous synthetic routes towards BAPOs the acylation step is always the determinant step that reduces the overall yield considerably (less than 60 %). Optimization of the acylation step in the BAPO synthesis will significantly reduce the production cost for this procedure, mainly because of the expensive nature of mesitoyl chloride as reagent. This aim provides the possibility to synthesize and test several new reagents in the acylation step. Comprised is an evaluation of new methods for the synthesis of a suitable reagent for mesitoyl chloride to prevent the formation of mesitoyl-*tert*-butyl ester.

The synthesis of NaP_5 will be developed because we think that the increased solubility of the alkoxide packaged sodium dihydrogenphosphide increases the reactivity towards white phosphorus, thereby creating a new and convenient pathway to the interesting NaP_5 ligand.

Another topic of interest is the synthesis and reactivity of metal phosphido complexes, with the phosphido group (PH_2), the key compound for all known phosphido complexes. Although there are literature reports about phosphido compounds with large R-groups, knowledge about the PH_2 complexes is scarce. Therefore the synthesis of these compounds is interesting and could give valuable insight into the chemistry of phosphido complexes.

Chapter 2

Chapter 2. New synthesis routes towards alkoxide packaged sodium dihydrogenphosphide

Alkoxide packaged sodium dihydrogenphosphide synthesized from red phosphorus and sodium in liquid ammonia, as described by Brandsma, offers new synthesis routes towards highly functional phosphorus compounds. As seen before, it can be used for the synthesis of primary phosphines and as precursor for the modular synthesis of BAPOs. Although the Brandsma method offers novel synthetic routes, it also has a number of drawbacks: 1) the obligated high pressure of the ammonia/dme solution to proceed to reaction at room temperature (7 bar at 18 °C); 2) the ill defined molecular structure and reactivity and 3) high cost of red phosphorus (both latter extremely relevant in industrial productions). A more convenient method for the synthesis of alkoxide packaged sodium dihydrogenphosphide is therefore required. The new process for the synthesis of sodium dihydrogenphosphide preferably should be one that runs at room temperature, not requiring high pressures and that uses the structurally well defined white phosphorus.

For many years unsaturated organic compounds have been reduced by the Benkeser method as an alternative to the Birch reduction.[113] Comparative studies of the reduction of organic compounds concluded that the Benkeser reduction method usually is more powerful, but is less selective. The Benkeser method uses lithium in low molecular weight amine (methyl-, ethyl-, *n*-propylamines or ethylenediamine) solutions for the reduction of organic compounds. Consequently, it is a potential candidate method for the synthesis of sodium dihydrogenphosphide. The reduction of white phosphorus in the presence of sodium and a low molecular weight amine for the synthesis of alkoxide packaged sodium dihydrogenphosphide is examined in this chapter.

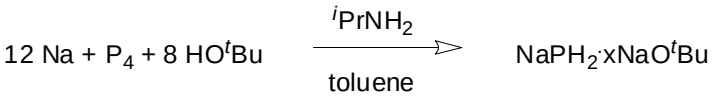
Synthesis of alkoxide packaged sodium dihydrogenphosphide from white phosphorus and sodium in the presence of isopropylamine

Since several low molecular weight amines can be used in the previously described Benkeser reduction, a suitable amine had to be chosen. Isopropylamine was the first amine selected by us for the synthesis of sodium dihydrogenphosphide on the base of the following reasoning: Isopropylamine has a relatively high boiling point (33-34 °C), compared to low molecular weight amines like methyl- and ethylamine (-6 °C and 19 °C respectively) which facilitates handling and avoids high pressures during the reaction.

Preliminary tests indicated that the reduction of white phosphorus in the presence of isopropylamine and sodium in toluene was not feasible. Unlike the Birch type reduction of red phosphorus with sodium in liquid ammonia, white phosphorus is only partially reduced by sodium in a toluene/isopropyl solution (1:1; v/v). The main product is trisodium heptaphosphide (Na_3P_7, $^{31}P\{^1H\}$ NMR: broad singlet, δ = -120 ppm) without further evidence for the formation of highly reduced metal phosphides like $(NaP)_n$ and/or "Na_3P". Subsequent protonation of this mixture with *tert*-butanol resulted only in the partial disappearance of metallic sodium. Spectroscopic analysis of the reaction mixture revealed the formation of trisodium heptaphosphide (28 %) and alkoxide packaged sodium dihydrogenphosphide ($^{31}P\{^1H\}$ NMR: δ = -288.7 ppm, 72 %) as soluble species. Although the main product according to ^{31}P NMR spectrum is sodium dihydrogenphosphide, removal of side products by precipitation certainly will affect the yield. It thus turns out that the sodium/isopropylamine/toluene system is not able to fully reduce white phosphorus to produce highly reduced metal phosphides at room temperature. Protonation of the reaction mixture produces sodium dihydrogenphosphide. However, a large part of the reduced white phosphorus either eludes from the mixture as phosphine (PH_3) or remains as trisodium heptaphosphide in solution.

Benkeser reductions are reportedly often performed in the presence of an alcohol.[113] This decreases the potency of the reduction but increases selectivity. Experimentally the contrary was confirmed on the reduction of white phosphorus in toluene/isopropylamine in the presence of alcohol. Therefore the reaction set-up was changed and white phosphorus was reduced by sodium in a toluene/isopropylamine (1:1; v/v) solution containing two equivalents of *tert*-butanol (related to phosphorus). Upon addition of small sodium parts, the clear colorless solution becomes a dark red/brown suspension. Within ten minutes, the brown suspension has changed into a yellow solution with metallic colored sodium parts. Gas

evolution occurs and the temperature of the reaction mixture rises slightly. The resulting mixture was stirred for several hours until all sodium particles had disappeared. Analysis of the reaction mixture by $^{31}P\{^1H\}$ NMR confirmed the formation of alkoxide packaged sodium dihydrogenphosphide as the main product (Scheme 25, Figure 6). In contrast to the reduction of white phosphorus without *tert*-butanol, the reduction is almost complete and only small amounts of trisodium heptaphosphide (~ 3 %) are present. Sodium dihydrogenphosphide could be isolated as a pale yellow solid in 55 % yield. Although these results demonstrate that the synthesis of alkoxide packaged sodium dihydrogenphosphide under mild conditions is feasible, compared to classical published synthesis routes, the yield is only moderate and large amounts of phosphine are formed. Due to the elution of phosphine during the reaction, the ratio $NaPH_2$:NaO^tBu is 1:4; which is rather high compared to the Birch type reduction of red phosphorus. Therefore, different reaction conditions were scrutinized to increase the yield of the reaction.



Scheme 25: Synthesis of $NaPH_2 \cdot xNaO^tBu$ via the Benkeser method from white phosphorus in isopropylamine and toluene.

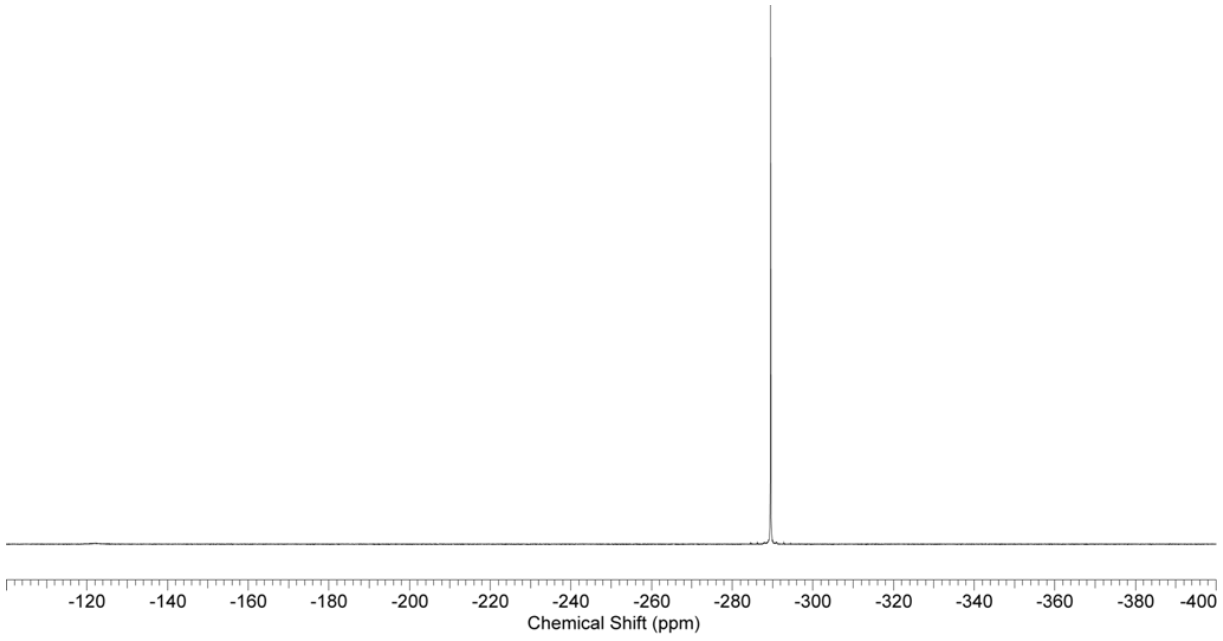


Figure 6: $^{31}P\{^1H\}$ NMR spectrum of sodium dihydrogenphosphide in toluene/isopropylamine after completion of the reaction.

White phosphorus is slightly soluble in arenes like benzene or toluene requiring relatively large amounts of solvent to completely dissolve white phosphorus, for instance 3.7 g P_4 dissolves in 100 g (~115 mL) of benzene,[1] in our case 2.4 g P_4 dissolves in approximately 100 g (~115 mL) toluene. Therefore, in order to decrease the cost of the reaction and the amount of waste, the reaction was scrutinized for the amount of solvent necessary for a successful reaction. Reduction of white phosphorus as a function of its solubility in toluene was tested, keeping reaction conditions constant. A mixture of white phosphorus in toluene/isopropylamine (0.5:1; v/v) with two equivalents of *tert*-butanol was reduced with small freshly cut sodium parts. Although formation of alkoxide packaged sodium dihydrogenphosphide is observed, the reaction is not going to completion even not after prolonging reaction times as the sodium is not completely consumed. Consequently for complete reduction of white phosphorus it requires to be completely dissolved. In order to ascertain complete dissolution of white phosphorus the amount of isopropylamine was decreased to that of toluene, a well known white phosphorus solvent. The reaction proceeds to completion at a toluene/isopropylamine ratio of 2:1 instead of 1:1, but requiring much longer reaction times while a thick yellow suspension formed, hampering the reaction progress. Reducing the amount of isopropylamine to two equivalents (molar equivalent) compared to white phosphorus, the reaction mixture clogged and a mixture of trisodium heptaphosphide, phosphine and sodium dihydrogenphosphide was formed. A reduction reaction of white phosphorus solely performed in isopropylamine with two equivalents of *tert*-butanol did not go to completion at all as well, even not after a prolonged period of stirring. A dark red brown suspension formed which contains trisodium heptaphosphide (50 %) and sodium dihydrogenphosphide (50 %) as soluble products. Without isopropylamine present, the reaction between sodium, white phosphorus and *tert*-butanol in toluene yields sodium dihydrogenphosphide in small and irreproducible amounts while producing large amounts of phosphine. Therefore, the synthesis of sodium dihydrogenphosphide is best to be performed in the presence of an amine.

Although alkoxide packaged sodium dihydrogenphosphide is formed at room temperature from white phosphorus in the presence of isopropylamine, the yield (55%) of the synthesis is moderate. The sodium *tert*-butanolate content is relatively high, approximately 1:4 (sodium dihydrogenphosphide: sodium *tert*-butanolate). Observation of gas evolution during the reduction reaction suggested the formation of phosphine. In the hope of improving the experimental procedures the reaction progress was followed by ^{31}P NMR spectroscopy.

Analysis of the formation of sodium dihydrogenphosphide in isopropylamine/toluene/*tert*-butanol

To get insight into the formation of sodium dihydrogenphosphide from white phosphorus in isopropylamine, samples sequentially taken from the reaction mixture were monitored by ^{31}P NMR. After adding freshly cut sodium parts to white phosphorus in a solution of toluene, isopropylamine and two equivalents of *tert*-butanol, the solution turns immediately into a dark red/brown suspension, indicative for the formation of polyphosphides which was confirmed. (Figure 7).

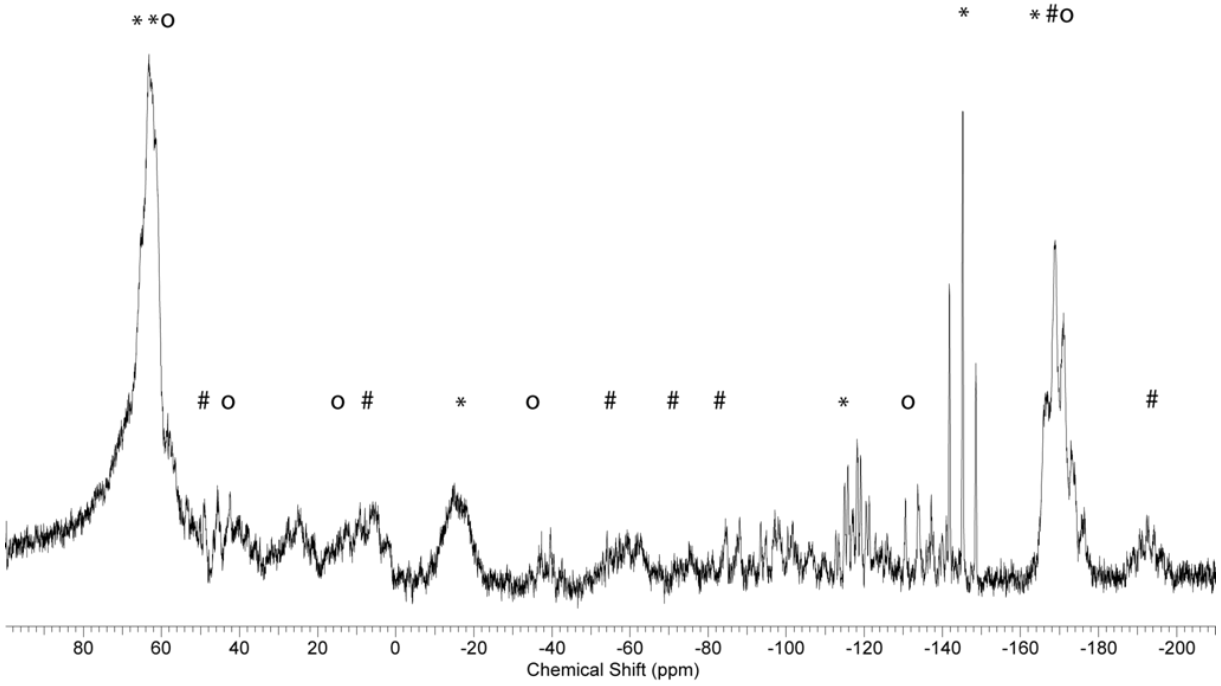


Figure 7: $^{31}P\{^{1}H\}$ NMR spectrum of reaction mixture immediately following addition of sodium. Polyphosphides Na_3P_{21} (*), Na_3P_{19} (#) and Na_2P_{16} (O) are some of the formed polyphosphides.

This is not unexpected since Baudler *et al.* already reported the synthesis of polyphosphides from the reduction of white or red phosphorus in the presence of alkali metals and a catalytic amount of 18-crown-6-ether.[70,114,115] In the early stages of the reaction, sodium heptaphosphide, phosphine and sodium dihydrogenphosphide are absent in the reaction mixture. After 3 minutes the dark red suspension has vanished into an orange solution with large sodium parts still visible. The polyphosphides observed directly after the addition of sodium are further reduced to trisodium heptaphosphide (^{31}P NMR δ = -120 ppm) and an unknown phosphide (^{31}P NMR δ = -231.1, -95.4, 13.5, 172.9 ppm), formation of the unknown

phosphide has been reported by Baudler *et al.* in their study of the synthesis of pentaphosphacyclopentadienide (MP_5) (Figure 8).[74] Also the formation of a small amount of phosphine was observed (^{31}P NMR δ = -245 ppm, $^{1}J_{PH}$ = 145 Hz). At this point in the reaction, the formation of sodium dihydrogenphosphide cannot be observed by ^{31}P NMR.

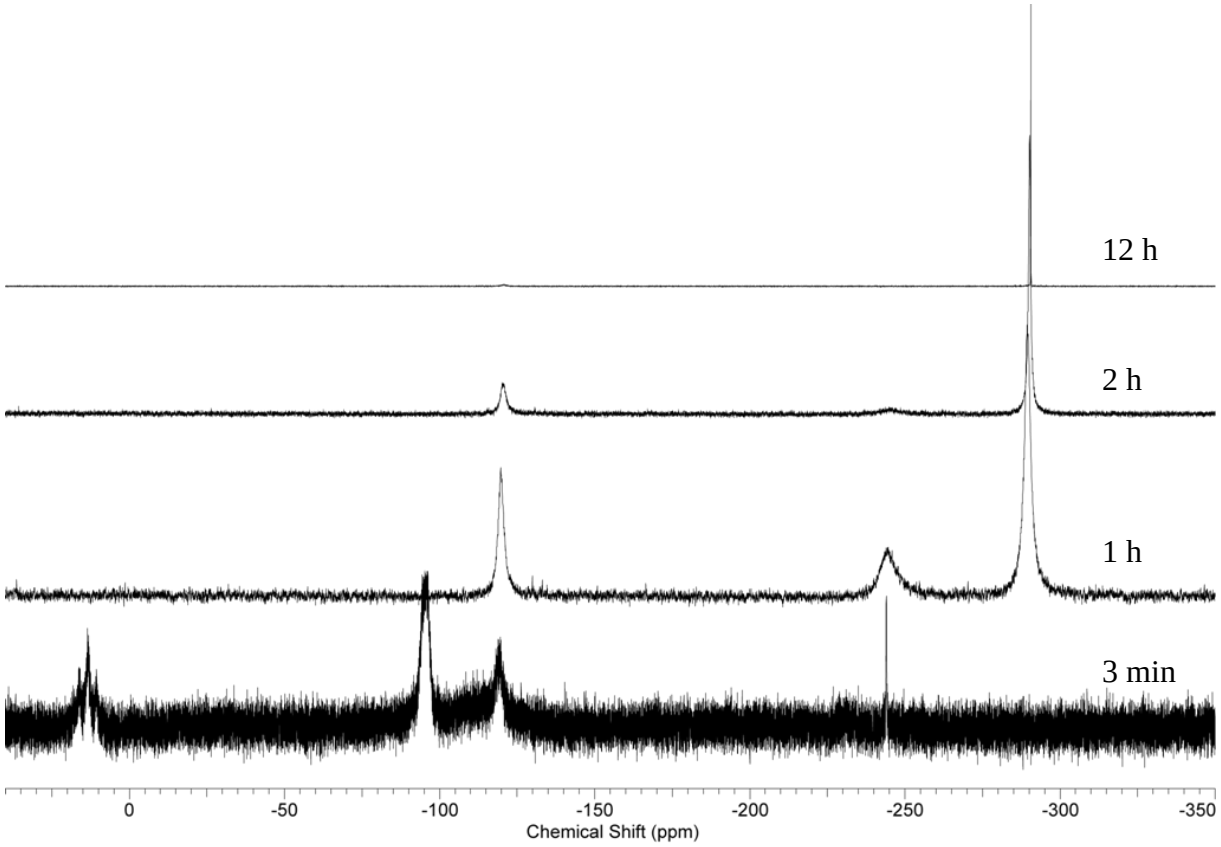


Figure 8: Stacked $^{31}P\{^{1}H\}$ NMR spectra of the reaction of white phosphorus with sodium in isopropylamine, *tert*-butanol and toluene after 3 minutes, one hour, two hours and twelve hours. Alkoxide packaged sodium dihydrogenphosphide (δ = -289 ppm), phosphine (δ = -245 ppm), trisodium heptaphosphide (δ = -120 ppm) and unknown phosphide (δ = 231.1, -95.4, 13.5, 172.9 ppm).

After a reaction time of one hour, trisodium heptaphosphide and phosphine are still present and sodium dihydrogenphosphide (^{31}P NMR δ = -289 ppm, $^{1}J_{PH}$ = 145 Hz) has formed in solution. The broad signals for phosphine and sodium dihydrogenphosphide could be an indication of equilibrium between these two compounds. After a reaction time of 12 hours trisodium heptaphosphide reduced to ~10 % with sodium dihydrogenphosphide as the main product. During the formation of sodium dihydrogenphosphide large amounts of phosphine are formed eluting from the mixture, explaining the moderate yields observed.

The equilibrium reaction between phosphine and sodium dihydrogenphosphide under reaction conditions was confirmed by separate $^{31}P\{^{1}H\}$ NMR magnetization transfer experiments. Sodium dihydrogenphosphide was protonated by 0.5 equivalent of *tert*-butanol in thf in the presence of trisodium heptaphosphide. ^{31}P NMR established the formation of phosphine and line broadening for both the sodium dihydrogenphosphide and phosphine signals occurred. Saturation of the phosphine or sodium dihydrogenphosphide resonance signal resulted in the disappearance of both signals, indicative of an equilibrium between the two species (Figure 9). This is not unexpected because of the similar pKa values of phosphine and sodium *tert*-butanolate.[116,117]

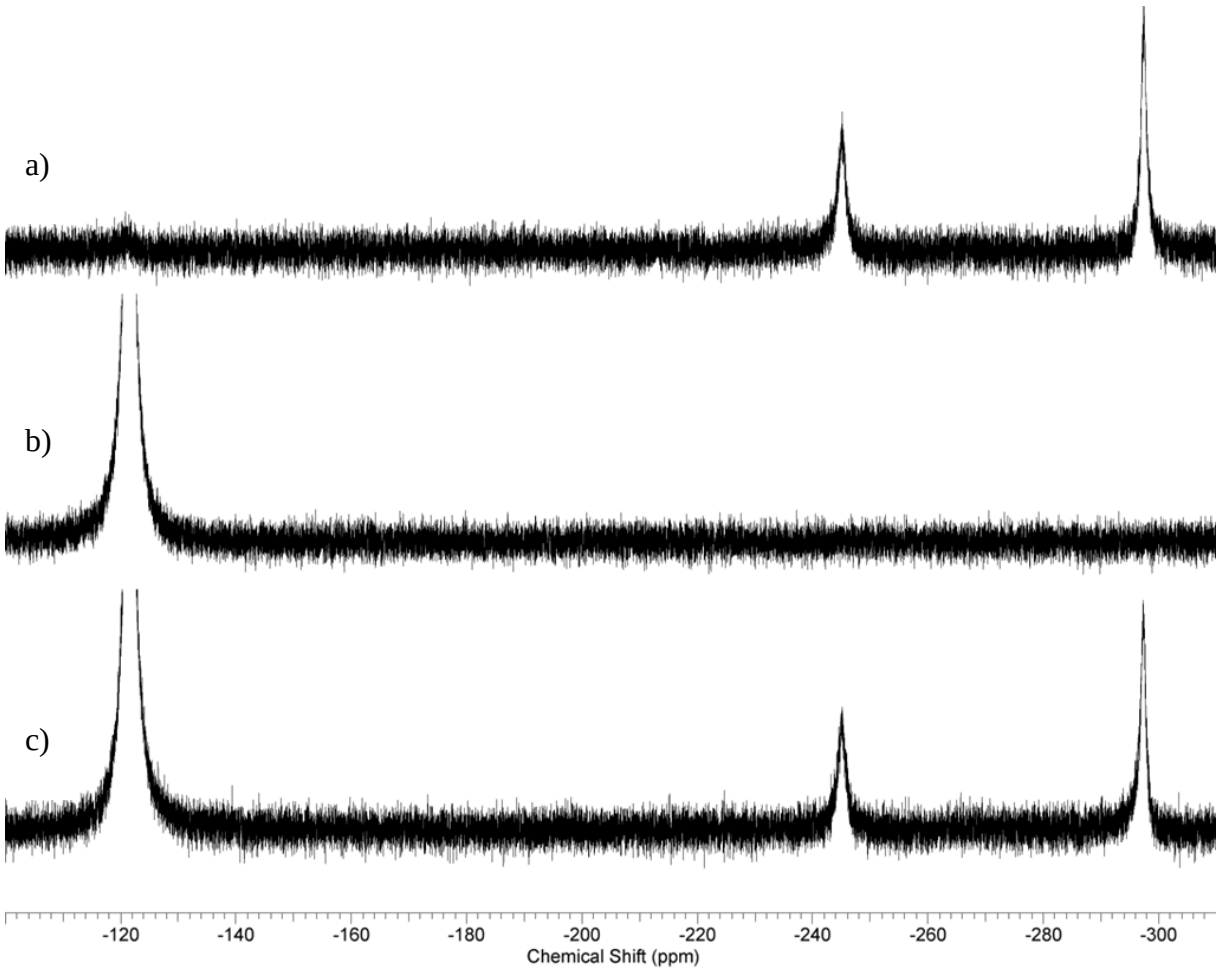


Figure 9: $^{31}P\{^{1}H\}$ NMR magnetization transfer spectra of sodium dihydrogenphosphide, *tert*-butanol and trisodium heptaphosphide. a) Saturation of trisodium heptaphosphide signal. b) Saturation of dihydrogenphosphide. c) $^{31}P\{^{1}H\}$ NMR spectrum without saturation of signals.

As expected, there is no exchange between trisodium heptaphosphide and phosphine or sodium dihydrogenphosphide. However, upon addition of an excess of alcohol to a solution of

trisodium heptaphosphide in thf the slow precipitation of a yellow powder and the partial disappearance and broadening of the trisodium heptaphosphide signal in ^{31}P NMR was observed. The yellow substrate is H_3P_7, a highly insoluble compound.[118] The precipitation of H_3P_7 in thf and the line broadening in ^{31}P NMR disappeared after the addition of an excess of isopropylamine, in accordance with the observation that during the synthesis primary amines increase the reaction rate without formation of a yellow precipitate. To prevent formation of H_3P_7 and prolonged reaction times, a suitable base is thus required.

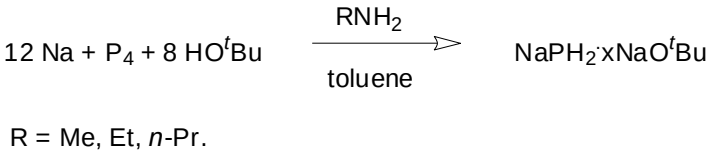
To elaborate further on the reaction mechanism, the conversion of trisodium heptaphosphide to sodium dihydrogenphosphide was followed in the presence of base and sodium. Alkoxide packaged trisodium heptaphosphide dissolved in thf, isopropylamine and *tert*-butanol was reduced by sodium and the mixture was analyzed by ^{31}P NMR. The formation of the reduction product was observed making it likely that the heptaphosphide is reduced to phosphine, as observed for the formation of sodium dihydrogenphosphide previously described. However, formation of sodium dihydrogenphosphide itself was not detected likely due to differential reaction conditions. In contrast the formation of sodium dihydrogenphosphide from sodium heptaphosphide in the presence of ethylenediamine was observed, which is described in detail later in this chapter.

These observations indicate that during the formation of sodium dihydrogenphosphide the volatile phosphine is formed. To prevent the formation of large amounts of phosphine a sufficiently strong base must be present to directly deprotonate phosphine. Alternatively, the reaction must be run in a tightly closed vessel to keep the formed phosphine inside and allowing to be reduced by the remaining sodium. In an attempt to increase the yield of the reaction, a reaction was run in a tightly closed Schlenk tube almost completely filled with solvent, thereby preventing the phosphine to escape. Upon release of the pressure after the reaction has ceased, gas evolution was observed, indicating that even then phosphine is incompletely reduced by sodium. It is clear that to increase the yield of the reaction other methods have to be developed.

Synthesis of sodium dihydrogenphosphide in the presence of methyl-, ethyl or *n*-propylamine

In an attempt to increase the yield of sodium dihydrogenphosphide the qualitative influence of the amine on the reaction was studied; several primary amines were screened. Methylamine

was chosen because it has properties similar to ammonia. As Benkeser and others reported, reaction rates decrease markedly upon lengthening of the alkyl chain, methylamine is therefore likely to increases the yield of sodium dihydrogenphosphide. The low boiling point (-6 °C) of methylamine is a drawback, requiring low temperatures to condense the amine into the reaction vessel. During a reaction at room temperature this necessitates higher pressures. To adjust for the lower boiling amine, the method for the synthesis of sodium dihydrogenphosphide was slightly modified (see experimental section chapter 7). Methylamine was condensed into a suspension of white phosphorus in a toluene/*tert*-butanol mixture at -78 °C, heated to -30 °C and subsequently small sodium parts were added. The reaction vessel was tightly closed and slowly heated to room temperature. The reaction mixture was stirred for 12 hours under pressure and the resulting clear yellow solution was evaporated, yielding a pale yellow solid. The yield of the reaction, about 90 %, was much higher than the previously described synthesis with isopropylamine as base. Furthermore, the amount of trisodium heptaphosphide is negligible. However, due to the toxicity and high costs of methylamine and the use of low temperatures and higher pressures, this method has no genuine advantages over the Birch type reduction (Scheme 26).



Scheme 26: Synthesis of $NaPH_2 \cdot xNaO^tBu$ in the presence of several amines in toluene.

Nevertheless, the high yield and the absence of trisodium heptaphosphide were encouraging to test other primary amines. Exchange of methylamine by ethylamine allows lower pressures because of the higher boiling point (19 °C) of ethylamine. With the solvent exchange as only modification, ethylamine was condensed into a Schlenk tube with a Teflon stopper charged with a suspension of white phosphorus in toluene/*tert*-butanol at -78 °C. This suspension was heated to room temperature and subsequently reduced upon addition of small sodium parts. In contrast to the previously described methylamine and isopropylamine assisted synthesis, the reaction with ethylamine proceeds only very slowly with the formation of a sluggish yellow suspension. After six hours, a considerable amount of sodium is still present. Even after 12 hours the amount of sodium was not decreased. As the synthesis of sodium

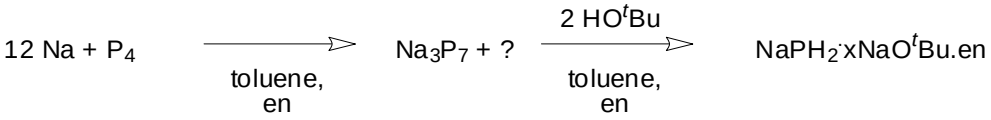
dihydrogenphosphide in the presence of ethylamine is not going to completion, this way was discontinued.

n-Propylamine was tested and similar results compared to isopropylamine were obtained.

Changing the amine as base in the Benkeser type synthesis of sodium dihydrogenphosphide significantly influences the outcome of the reaction. While ethyl- and *n*-propylamine do not increase the yield or even hamper the reaction, impressive yield and selectivity are observed with methylamine. The properties of methylamine resemble those of ammonia[119] prompting it more suitable for the synthesis of sodium dihydrogenphosphide; in agreement with literature in which primary amines with short alkyl chains increase the reaction rate. The low carbon to nitrogen ratio in methylamine turns out to be favorable for the outcome of the reaction. Given the higher pressures involved during the reduction of white phosphorus with methylamine and moderate yields with isopropylamine and *n*-propylamine the added value of ethylenediamine in the synthesis of sodium dihydrogenphosphide was questioned.

Synthesis of sodium dihydrogenphosphide in the presence of ethylenediamine

Ethylenediamine (en), a low molecular weight amine with a low carbon to nitrogen ratio similar to methylamine, is potentially a suitable amine for probing the synthesis of alkoxide packaged sodium dihydrogenphosphide. Because of the low carbon to nitrogen ratio there were high expectations with regard to yield at least as high as with that in the Birch type reduction of red phosphorus in ammonia developed by Brandsma. Ethylenediamine used in Benkeser reductions reportedly is a powerful reagent and its use frequently results in the over-reduction of the substrate.[113,120,121] Therefore, white phosphorus was reduced by sodium in a toluene/ethylenediamine (1:1; v/v) solution. This mixture was stirred for four hours until the remaining sodium parts became black, signaling the end of the reduction. Analysis showed the complete reduction of white phosphorus to trisodium heptaphosphide (^{31}P NMR: δ = -122 ppm (s)) and an unknown phosphide (very broad signals in ^{31}P NMR: δ = -90, 5, 121, 175 ppm) (Scheme 27).

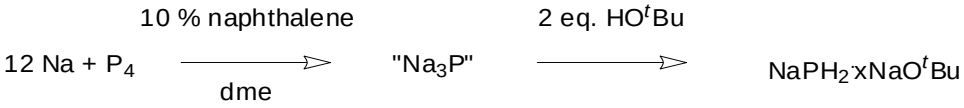


Scheme 27: Synthesis of $NaPH_2 \cdot xNaO^tBu$ from white phosphorus and sodium in the presence of ethylenediamine.

The formed mixture was protonated with two equivalents of *tert*-butanol. In contrast to the Benkeser reduction, no phosphine evolution was observed. The reaction mixture was stirred for an additional 12 hours forming a two phase system. Evaporation of the solvent yielded a pale yellow powder turning out to be sodium dihydrogenphosphide in 85 % yield. The product contains one equivalent of ethylenediamine. Even prolonged drying under vacuum did not remove the ethylenediamine, rendering the produced sodium dihydrogenphosphide unsuitable for the synthesis of bis(acyl)phosphides because of the reactivity of amines towards acid chlorides. On the other hand the contamination of sodium dihydrogenphosphide with ethylenediamine still allows the synthesis of NaOCP from diethyl carbonate without apparently influencing the yield of this reaction.
In sum: reduction of white phosphorus via the Benkeser method in low molecular weight amines offers a benign route towards alkoxide packaged sodium dihydrogenphosphide with a yield of up to 90% with the use of methylamine.

Synthesis of sodium dihydrogenphosphide from white phosphorus, sodium, *tert*-butanol and naphthalene

Because of the reported large amount of amine needed for the synthesis of sodium dihydrogenphosphide, a way to find better alternative routes was proceeded. From literature it is known that red phosphorus is reduced by sodium in the presence of naphthalene which acts as an electron carrier at elevated temperatures.[122] The feasibility of a similar procedure with white phosphorus was tested. Because white phosphorus is much more reactive and better soluble in organic solvents than red phosphorus, less drastic reaction conditions can be used.



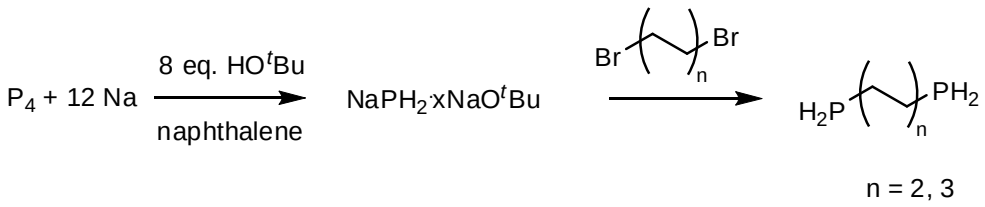
Scheme 28: Synthesis of $NaPH_2 \cdot xNaO^tBu$ from sodium, white phosphorus with naphthalene in dme.

The reduction of white phosphorus by sodium in dme in the presence of 10 mol % naphthalene resulted in the formation of a black amorphous suspension presumably trisodium phosphide ("Na_3P") although not definitely confirmed. The formed amorphous "Na_3P" was slowly protonated by two equivalents of *tert*-butanol, which rose the temperature rapidly

under gas formation. Stirring the clear yellow solution for an additional two hours, followed by filtration over celite and evaporation of the solvent, yielding sodium dihydrogenphosphide at 70 % as a pale yellow powder in the presence of 3 % naphthalene as registered by ^{1}H NMR (Scheme 28). Thus, the synthesis of alkoxide packaged sodium dihydrogenphosphide from white phosphorus and sodium in the presence of naphthalene offers an easy access to the previously difficult accessible sodium dihydrogenphosphide.

Synthesis of alkylphosphines from sodium dihydrogenphosphide

With the new developed ways for the synthesis of alkoxide packaged sodium dihydrogenphosphide in hand, the reactivity towards alkyl bromides in line with the work of Brandsma and others was tested, but with application of updated methods (Scheme 29).



Scheme 29: Synthesis of bis phosphine alkyl chains from white phosphorus and sodium under mild reaction conditions in the presence of naphthalene.

Starting from white phosphorus and sodium with 10 mol % naphthalene in dme or thf, it was possible to synthesize primary bisalkylphosphines. In a procedure similar to the production of sodium dihydrogenphosphide, white phosphorus was reduced by sodium to the corresponding dihydrogenphosphide. Without further work up of the reaction mixture, dibromobutane or dibromohexane were reacted with sodium dihydrogenphosphide. The products were analyzed by ^{31}P NMR, with the signals of the corresponding diphosphines at -139.3 ppm (t, $^1J_{PH}$ = 189.6 Hz) for 1,4-diphosphinobutane and -139.2 ppm (t, $^1J_{PH}$ = 188.4 Hz) for 1,6-diphosphinohexane. Small amounts of phospholane (^{31}P NMR: δ = -71.3 ppm, $^1J_{PH}$ = 179.2 Hz)[123] are observed as side product in the synthesis of 1,4-diphosphinobutane. It is clear from these experiments that from simple and cheap starting materials, functionalized phosphines can be synthesized with relative ease. These phosphines can be transformed to more functionalized organophosphorus compounds by well established routes.

Conclusions

New synthesis routes for alkoxide packaged sodium dihydrogenphosphide have been found with moderate to good yield. In contrast to the Brandsma method, the synthesis of sodium dihydrogenphosphide can be performed without the use of ammonia omitting high pressures. This opens easily accessible new synthesis routes towards highly functionalized phosphorus compounds even in bulk quantities.

Starting from white phosphorus and sodium in toluene or thf, sodium dihydrogenphosphide can be synthesized by a Benkeser type reduction. The reduction needs to be performed in the presence of *tert*-butanol and a primary amine. Several amines were tested: isopropylamine and *n*-propylamine gave yields of 55 %; methylamine even of 90 %. This increase in yield is attributed to the properties of methylamine, being similar to ammonia.

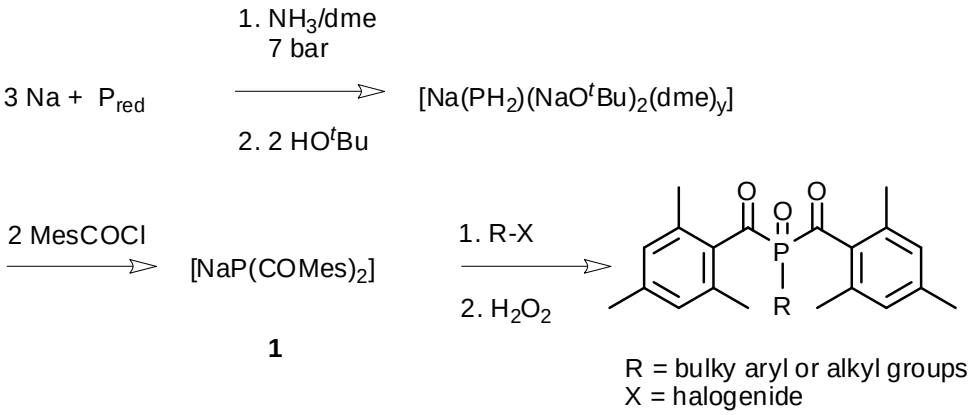
Concerning the reaction mechanism; in the presence of *tert*-butanol and primary amine, white phosphorus is directly reduced by sodium to polyphosphides (Na_3P_{21} *etc.*). These polyphosphides are further reduced to presumably Na_3P_7 and an unknown phosphide. Due to the presence of *tert*-butanol, Na_3P_7 is further reduced to PH_3 and sodium dihydrogenphosphide ($NaPH_2$). The lower yield in the isopropylamine performed synthesis is attributed to the elution of phosphine from the reaction mixture. Higher yields were obtained when ethylenediamine was used as base. In the presence of sodium, white phosphorus is reduced to trisodium heptaphosphide in ethylenediamine and toluene. Subsequent addition of *tert*-butanol further reduces trisodium heptaphosphide into sodium dihydrogenphosphide in good yield. This method has a drawback as ethylenediamine is still present in the product. This was circumvented by the synthesis of sodium dihydrogenphosphide with naphthalene as electron carrier.

With this room temperature procedure, sodium dihydrogenphosphide can be synthesized in good yield without the use of high pressures. The reactivity of the sodium dihydrogenphosphide synthesized is similar to the procedures reported by Brandsma for the synthesis of primary phosphines.

Chapter 3

Chapter 3. Synthesis of bis(acyl)phosphides

Bis(acyl)phosphine oxides (BAPOs), as mentioned in the introduction, are very efficient photoinitiators and have several advantages over acetophenone and benzophenone based photoinitiators. However, BAPO photoinitiators also have several disadvantages. For example, they are difficult to synthesize and therefore expensive. Our research group has recently found a new method for the synthesis of BAPOs starting from simple materials like red phosphorus and sodium (Scheme 30).[59] Via a Birch type reduction and subsequent protonation, alkoxide packaged sodium dihydrogenphosphide is generated *in situ*. The sodium bis(mesitoyl)phosphide (**1**) building block is formed by the subsequent acylation of sodium dihydrogenphosphide with mesitoyl chloride. From this product several types of BAPOs can be synthesized with relative ease.[59,64]



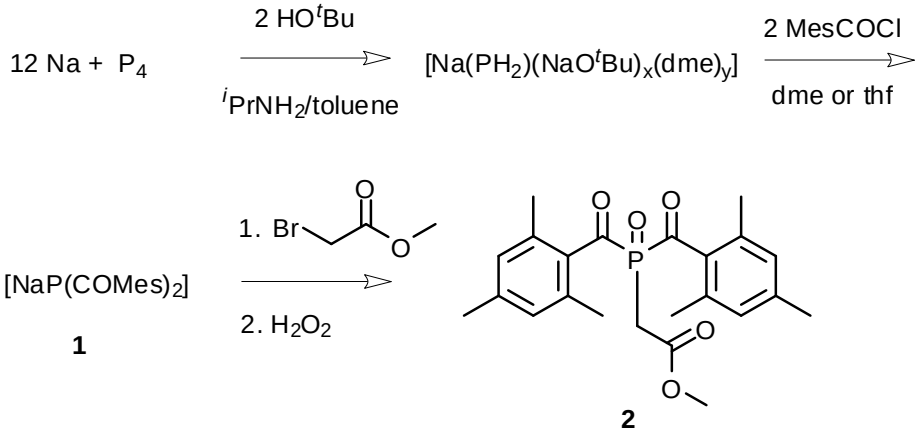
Scheme 30: Synthesis of BAPOs starting from sodium and red phosphorus.

The advantage of this procedure is that highly functionalized phosphorus compounds can be synthesized from relatively inexpensive chemicals. Although this method has several advantages over more classical methods for the synthesis of BAPOs, there are still some drawbacks. The first drawback, the synthesis of alkoxide packaged sodium dihydrogenphosphide has been resolved in chapter one. One of the remaining challenges is to increase the yield of the acylation step. In all the previously described synthesis routes towards BAPOs the yield of the acylation step is generally lower than 60 %.[64] To increase yield and given the costs of mesitoyl chloride, a new and improved synthesis route for the sodium bis(mesitoyl)phosphide starting material would be cost saving and reduce waste.

Several possibilities for improvement of the yield in the acylation step are evaluated. First of all, the reaction conditions during the acylation reaction were studied. Next, replacing mesitoyl chloride with another mesitoyl containing reagent with a good leaving group could diminish nucleophilic attack from sodium *tert*-butanolate. Decreasing the amount of sodium *tert*-butanolate formed upon protonolysis to produce the sodium dihydrogenphosphide is a third option. These options were sequentially examined.

One pot synthesis of methyl-BAPO acetate (2) from $NaPH_2 \cdot xNaO^tBu$

One of the advantages of the modular approach is the possibility to synthesize BAPOs in a one pot procedure. To test the applicability of the synthesis routes for sodium dihydrogenphosphide, described in the first chapter, the one pot synthesis of methyl-BAPO acetate **2** was investigated (Scheme 31).



Scheme 31: Synthesis of methyl BAPO acetate from white phosphorus and sodium via the Benkeser method.

Starting from white phosphorus and sodium in a toluene/isopropylamine/*tert*-butanol solution sodium dihydrogenphosphide was synthesized. After the completion of the reaction the solvent was removed to prevent the primary amine from reacting with mesitoyl chloride in the acylation step, thereby decreasing the yield of the reaction and wasting expensive acid chloride. Sodium dihydrogenphosphide was suspended in toluene and the subsequent reaction with mesitoyl chloride resulted in the formation of a dark red suspension with the formation of several unidentified products, which were observed by ^{31}P NMR. Therefore a solvent change is necessary for the acylation of sodium dihydrogenphosphide. The subsequent reaction steps were performed in thf or dme.

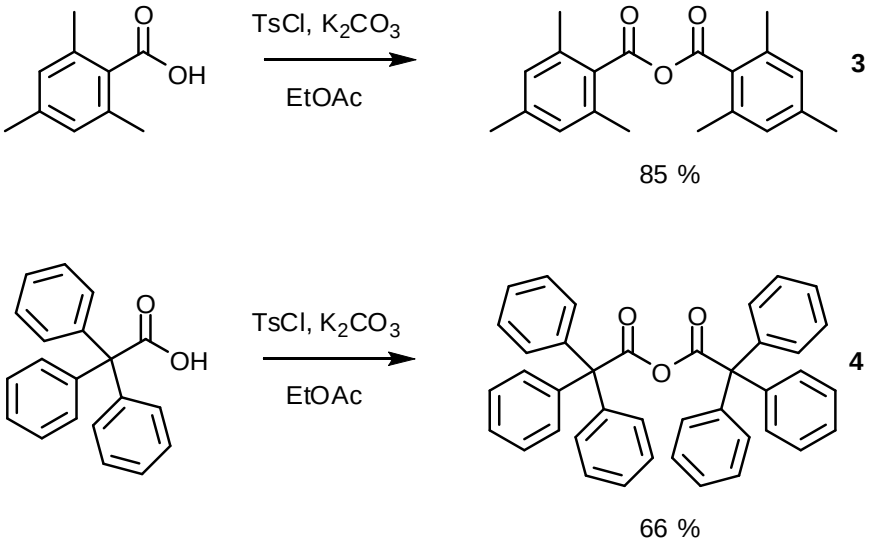
The acylation of sodium dihydrogenphosphide with two equivalents of mesitoyl chloride in thf or dme results in the formation of sodium bis(mesitoyl)phosphide **1**. However, ^{31}P NMR revealed that the acylation was incomplete. Two broad signals in the ^{31}P NMR, at 6.0 ppm ($^{1}J_{PH}$ = 129.7 Hz) and 12.1 ppm ($^{1}J_{PH}$ = 157.4 Hz), indicate the presence of E/Z mesitoylphosphide. Integration of the signals revealed an approximate 1:1 ratio of mesitoylphosphide and bis(mesitoyl)phosphide. Complete conversion to the bis(mesitoyl)phosphide was achieved by the addition of two additional equivalents of mesitoyl chloride. Complete conversion of bis(mesitoyl)phosphide to methyl-BAP acetate was achieved by the addition of one equivalent of methyl bromoacetate (^{31}P NMR: δ = 46.2 ppm). The oxidation of BAP to form BAPO was performed after filtration of the formed salts. Oxidation of BAP in the presence of salts hampered the selective formation of methyl-BAPO acetate and gave rise to several byproducts. BAPO **2** can be crystallized easily from hexane in 55 % yield. The remaining oil contained large amounts of the mesitoyl *tert*-butyl ester, a side product in the reaction formed from the substitution reaction of mesitoyl chloride with sodium *tert*-butanolate.

Several reaction conditions were tested to prevent the formation of mesitoyl *tert*-butyl ester. For example, decreasing the temperature or a very slow addition of mesitoyl chloride to a solution of alkoxide packaged sodium dihydrogenphosphide were tested. However, every procedure approximately needed four equivalents of mesitoyl chloride for full conversion to **1**. After these results other ways to prevent the formation of mesitoyl *tert*-butyl ester were investigated.

Prevention of the formation of the ester can be done in two possible ways. First, change the mesitoyl chloride for another, less reactive substrate towards sodium *tert*-butanolate, or second, decrease the amount of sodium *tert*-butanolate in the reaction mixture. First, the reactivity of sodium dihydrogenphosphide was tested towards several mesitoyl anhydrides, esters and carboxylates.

Anhydride synthesis

Several new organic anhydrides and carboxylates were synthesized to assess their reactivity towards sodium dihydrogenphosphide. The already known 2,4,6-trimethylbenzoic anhydride (**3**) was synthesized via an adjusted literature procedure.[125] A suspension of mesitoic acid and potassium carbonate in ethylacetate was reacted with tosyl chloride (TsCl). After a reaction time of twelve hours the solvent was removed and after workup **3** was obtained in good yield (85 %) and high purity (Scheme 32).

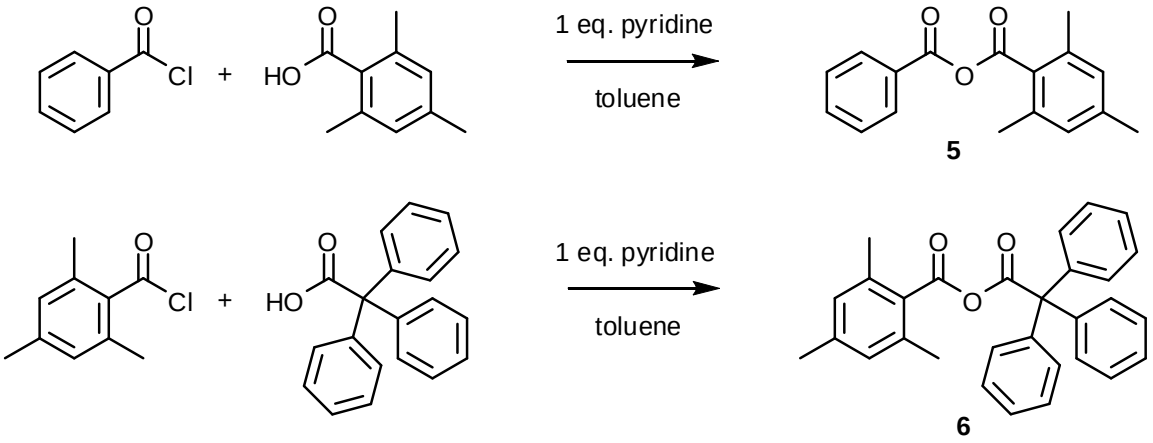


Scheme 32: Synthesis of bismesitoylanhydride (**3**) and bis(2,2,2-triphenyl)acetic anhydride (**4**).

A similar procedure was then used for the synthesis of 2,2,2-triphenylacetic anhydride (**4**). A suspension of 2,2,2-triphenylacetic acid and potassiumcarbonate in ethylacetate was reacted with tosyl chloride. The solvent was evaporated after twelve hours and after work-up (**4**) was obtained in 66 % yield.

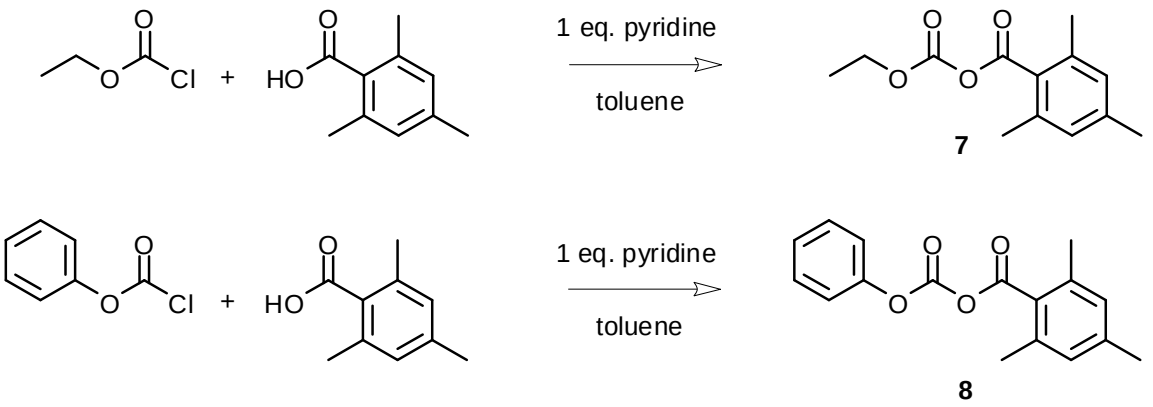
Two new asymmetric mesitoyl anhydrides were synthesized via a procedure similar to one described by Penn *et al.*[126] A solution of benzoyl chloride and one equivalent of pyridine in toluene were stirred until a white precipitation was formed. The formed benzoyl pyridine salt was reacted with mesitoic acid for twelve hours. After subsequent work-up benzoic 2,4,6-trimethylbenzoic anhydride (**5**) could be isolated in 49 % yield. The synthesis of the asymmetric 2,4,6-trimethylbenzoic 2,2,2-triphenylacetic anhydride (**6**) was performed in a similar fashion as the previously described compound. A solution of mesitoyl chloride and one equivalent of pyridine in toluene were stirred until a white precipitation was formed. The

formed mesitoyl pyridine salt was reacted with 2,2,2-triphenylacetic acid for twelve hours. After subsequent work-up, **6** could be isolated as a solid in 24 % yield (Scheme 33).



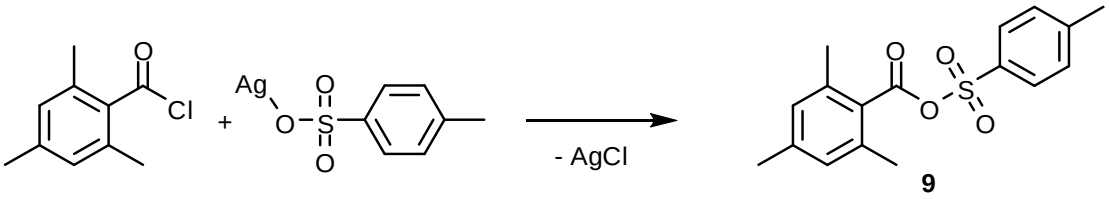
Scheme 33: Synthesis of asymmetric anhydrides (**5**) and (**6**).

Two asymmetric mesitoic carbonic anhydrides were synthesized via a procedure similar to the synthesis of the asymmetric anhydrides. Ethylcarbonic 2,4,6-trimethylbenzoic anhydride (**7**) was synthesized from ethyl carbonochloridate and mesitoic acid in toluene with one equivalent of pyridine. After workup of the reaction mixture **7** was obtained as a colorless oil in moderate yield (54 %). 2,4,6-Trimethylbenzoic (phenylcarbonic) anhydride (**8**) was synthesized from phenyl carbonochloridate and mesitoic acid in toluene with one equivalent of pyridine. After workup of the reaction mixture, **8** was obtained as a white solid in moderate yield (47 %) (Scheme 34).



Scheme 34: Synthesis of mixed carbonic anhydrides (**7**) and (**8**).

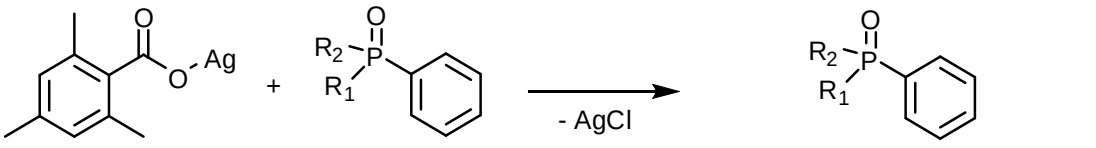
The interest focused on mesitoyl compounds which are stable, easy to handle and less reactive to base. A commonly used good leaving group is the tosyl group. Therefore a convenient way to produce mesitoyl-*p*-toluenesulfonate (**9**) was investigated. Attempts to start from mesitoic acid and tosyl chloride or from sodium tosylate and mesitoyl chloride did not result in the formation of the desired product. However, it was possible to synthesize **9** via an adapted synthesis, reported by Sarlo *et al.*[127] Starting from silver *p*-toluenesulfonate[128] and mesitoyl chloride it was possible to synthesize **9** in decent yield (75 %) (Scheme 35).



Scheme 35: Synthesis of mesitoyl *p*-toluenesulfonate (**9**).

Mesitoyl-*p*-toluenesulfonate could not be synthesized from the silver mesitoate[129] and 4-toluenesulfonyl chloride. As the synthesis of the sodium salts shows, silver mesitoate is not a strong enough nucleophile, thereby hampering the reaction.

Another attempt was made to synthesize some 2,4,6-trimethylbenzoic acid anhydride phospha-oxides and test their reactivity towards sodium dihydrogenphosphide. Phenylphosphonic acid was first analyzed as a feedstock for the synthesis of 2,4,6-trimethylbenzoic acid dianhydride phenylphosphonic acid (**11a**). Attempts to synthesize **11a** from phenylphosphonic acid, mesitoyl chloride and pyridine failed and the desired product was not formed. Therefore the starting materials were changed; instead of phenylphosphonic acid, phenylphosphonic dichloride was used as starting material. **11a** was synthesized from phenylphosphonic dichloride and silver mesitoate in 34 % yield (Scheme 36).



10a: R_1,R_2 = Cl
10b: R_1 = Cl, R_2 = Ph

11a: R_1,R_2 = OCOMes
11b: R_1 = OCOMes, R_2 = Ph

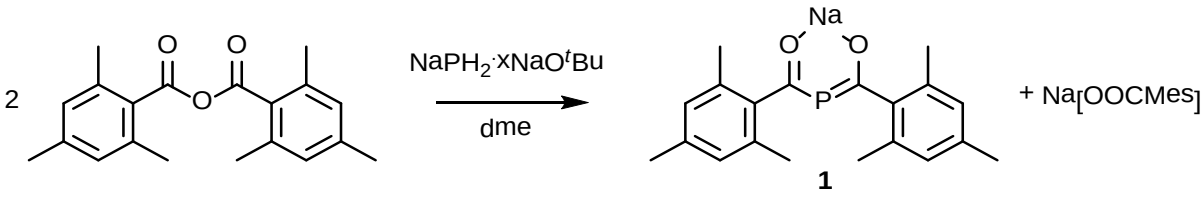
Scheme 36: Synthesis of **11a** and **11b** form silver mesitoate and phenylphosphonic chloride.

2,4,6-Trimethylbenzoic acid anhydride diphenylphosphinic acid (**11b**) could be synthesized in a similar manner starting from diphenylphosphinic chloride and silver mesitoate in 48 % yield. Both phospha-oxides are unstable and decompose slowly at room temperature, as was also observed for similar compounds prepared by Lindner *et al.*[130,131]

With these inorg/-anhydrides and carbonic anhydrides available, investigation was started on the reactivity of these compounds towards sodium dihydrogenphosphide.

Bis(acyl)phosphide synthesis from anhydrides and carbonic anhydrides

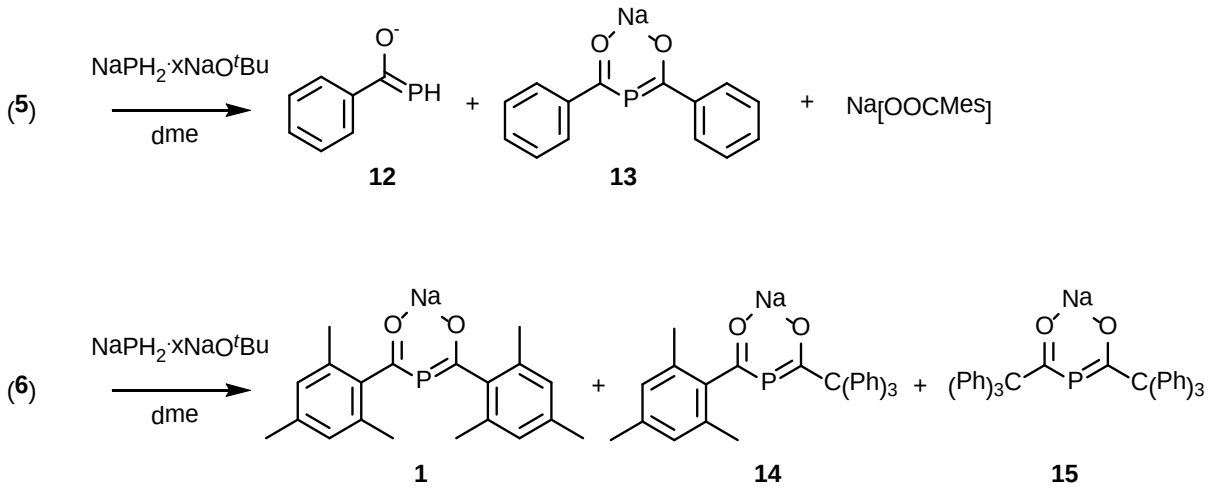
Anhydride **3** is readily converted to bis(mesitoyl)phosphide by sodium dihydrogenphosphide in thf or dme. For complete conversion to bis(mesitoyl)phosphide, two equivalents of **3** are necessary (Scheme 37). In contrast to, for example, the formation of bis(mesitoyl)phosphide from mesitoyl chloride and sodium dihydrogenphosphide, the purification of the desired product is difficult. The formed sodium salt of mesitoic acid has almost the same solubility as bis(mesitoyl)phosphide and separation of both compounds is difficult.



Scheme 37: Synthesis of bis(mesitoyl)phosphide from sodium dihydrogenphosphide and mesitoylanhydride.

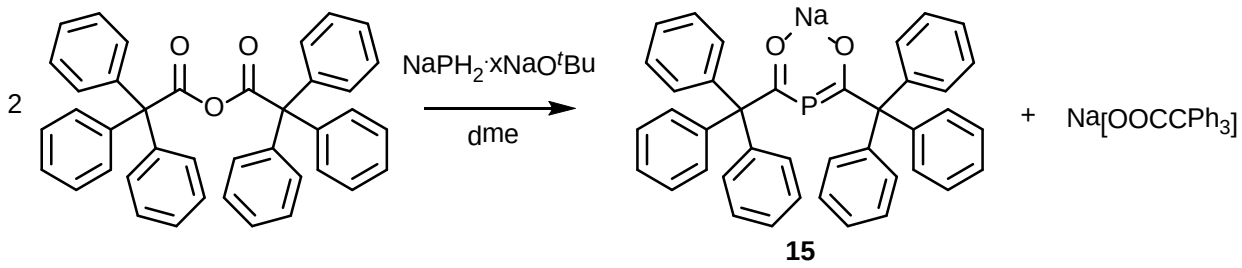
Furthermore, only a maximum of 50 % of mesitoic acid is converted to bis(mesitoyl)phosphide theoretically, rendering this method unsuitable for industrial purposes. To avoid the use of four equivalents of mesitoic acid for the preparation of bis(mesitoyl)phosphide compounds, **5** and **6** were tested. Reaction of sodium dihydrogenphosphide with anhydride **5** resulted in the formation of several products. In ^{31}P NMR analysis of the reaction, $(PhCO)_2PNa$ (**13**) (δ = 63.7 ppm)[62] and PhCOPHNa (δ = 5.3 ppm, d, $^1J_{PH}$ = 144.8 Hz) were observed (Scheme 38). However, no evidence was found for the formation of **1**. The formation of products exclusively made from the benzoic part of the anhydride suggests that the more sterically hindered mesitoyl moiety is less susceptible to nucleophilic attack. To prevent this, the 2,2,2-triphenyl group was introduced into the

anhydride. Analysis of the reaction of **6** with sodium dihydrogenphosphide by ^{31}P NMR revealed the formation of three main species, $(MesCO)_2PNa$ (**1**) (δ = 81.7 ppm); (MesCO)P(OC(CPh$_3$))Na (**14**) (δ = 88.7 ppm) and [((Ph$_3$C)CO)$_2$P]Na (**15**) (δ = 97.9 ppm) in an approximate 1:2:1 ratio (Scheme 38).



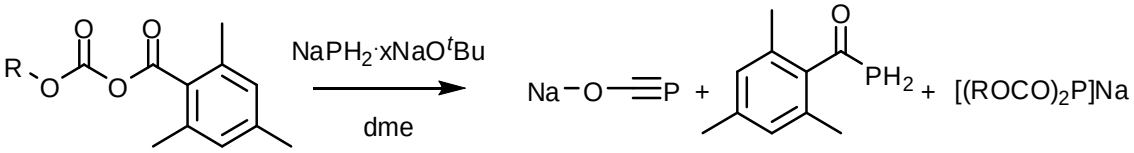
Scheme 38: Reactions of asymmetric anhydrides with $NaPH_2{\cdot}xNaO^tBu$.

Increasing the steric bulk on one side of the anhydride increases the yield of the desired bis(acyl)phosphide, however, byproducts are observed in large quantities. Full confirmation of the formation of the previously unknown acyl phosphide [((Ph$_3$C)CO)$_2$P]Na (**15**) was obtained when sodium dihydrogenphosphide was reacted with **4**. Analysis of the reaction by ^{31}P NMR showed a signal at 97.9 ppm. In a separate experiment **15** could be isolated in 69 % yield as a yellow solid (Scheme 39).



Scheme 39: Synthesis of [((Ph$_3$C)CO)$_2$P]Na.

Mixed carbonic anhydrides **7** and **8** react with sodium dihydrogenphosphide to form NaOCP (^{31}P NMR: δ = -387.0 ppm), PH_3, $MesCOPH_2$ (^{31}P NMR: δ = -105 ppm)[132], and $(ROCO)_2PNa$ (^{31}P NMR: for R = Et; δ = -31.1 ppm (**16**) and for R = Ph; δ = -28.0 ppm (**17**))[133] (Scheme 40). Similar products were observed by Becker *et al.* in a study to the intermediates formed in the reaction of $LiPH_2$ with dimethyl carbonate.[133,134]

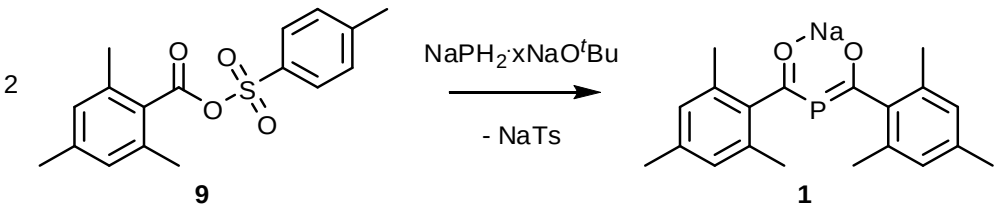


7: R = Et
8: R = Ph

16: R = Et
17: R = Ph

Scheme 40: Reaction of carbonic anhydrides with sodium dihydrogenphosphide.

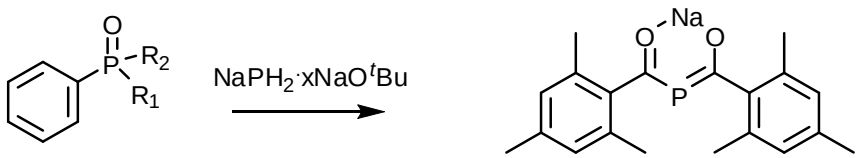
Addition of two equivalents of mesitoyl-*p*-toluenesulfonate **9** to a solution of sodium dihydrogenphosphide resulted in the formation of bis(mesitoyl)phosphide **1** and mesitoylphosphide (Scheme 41). Sodium *p*-toluenesulfonate precipitates from the solution offering a more simple way to purify the formed bis(mesitoyl)phosphide in contrast to the reaction with the symmetrical mesitoyl anhydride. However, sulfonate **9** is very susceptible to nucleophilic attack from sodium *tert*-butanolate thus decreasing the overall yield of **1**.



9 **1**

Scheme 41: Synthesis of bis(mesitoyl)phosphide from mesitoyl *p*-toluenesulfonate.

Mixed inorganic anhydrides **11b** and **11a** react with sodium dihydrogenphosphide to form only small amounts of bis(mesitoyl)phosphide (< 10 %) (Scheme 42).



11a: R_1,R_2 = OCOMes
11b: R_1 = OCOMes, R_2 = Ph

1
< 10 %

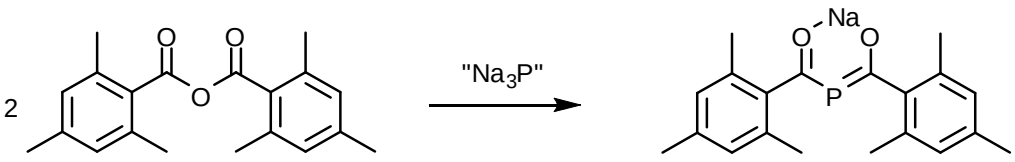
Scheme 42: Synthesis of sodium bis(mesitoyl)phosphide from inorganic anhydrides.

Therefore these organic and inorganic anhydrides are not a suitable alternative for the synthesis of bis(mesitoyl)phosphide. From these observations it was clear that other methods to form sodium bis(mesitoyl)phosphide in high yields had to be investigated.

Synthesis of bis(acyl)phosphides from "Na_3P"

Another method to reduce the formation of mesitoyl *tert*-butyl ester would be to decrease the amount of sodium *tert*-butanolate. The formation of bis(mesitoyl)phosphide from "Na_3P" and mesitoyl chloride is reported by Daniel Stein, although, the yields are moderate, ~50 %. Reaction of "$(Na/K)_3P$" with mesitoyl chloride resulted in the subsequent formation of bis(mesitoyl)phosphide. The yields obtained with this procedure were variable and not reproducible.

The reaction of "Na_3P" with **3** was tested in an attempt to obtain **1** in a more selective and reproducible manner. Trisodium phosphide suspended in dme was reacted with **3** for 30 minutes. During the reaction the black suspension turned into a bright yellow solution. Spectroscopic analysis of the solution with an internal standard revealed the formation of **1** in ~30 % yield (Scheme 43).



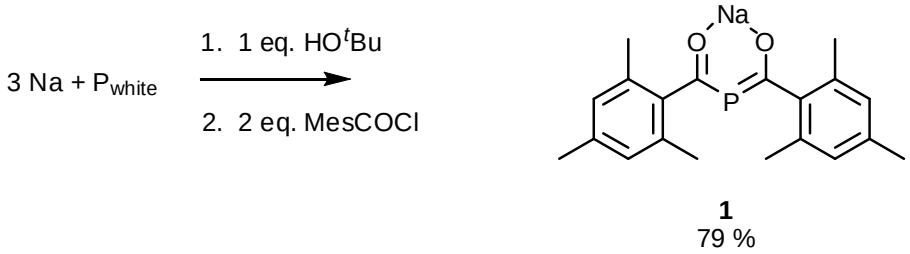
3

1
30 %

Scheme 43: Synthesis of sodium bis(mesitoyl)phosphide from mesitoyl anhydride and trisodium phosphide.

Synthesis of bis(acyl)phosphides from "Na_2PH"

Formation of the mesitoyl *tert*-butyl ester could be prevented if the amount of sodium *tert*-butanolate, present in the reaction mixture is reduced. However, from previous reports and experiments it is also clear that the reaction of "Na_3P" with mesitoyl chloride resulted in the formation of **1** in variable yields. To circumvent this problem and obtain a more reproducible way for the preparation of **1**, investigation of the synthesis of "Na_2PH" and its reactivity towards mesitoyl chloride was started (Scheme 44). Reduction of white phosphorus with sodium in the presence of naphthalene resulted in the formation of "Na_3P". Protonolysis of "Na_3P" with one equivalent of *tert*-butanol gives a mixture of sodium phosphides. The black suspension contains large amounts of sodium dihydrogen phosphide (δ = -309 ppm and -292 ppm) according to ^{31}P NMR and "Na_3P". However, small amounts of "Na_2PH" were also observed in the ^{31}P NMR spectrum at -405 ppm ($^1J_{PH}$ = 96 Hz), -412 ppm ($^1J_{PH}$ = 94 Hz) and -417 ppm ($^1J_{PH}$ = 93 Hz) (Figure 10).



1
79 %

Scheme 44: Synthesis of sodium bis(mesitoyl)phosphide from sodium, white phosphorus, MesCOCl and one equivalent of HO^{t}Bu.

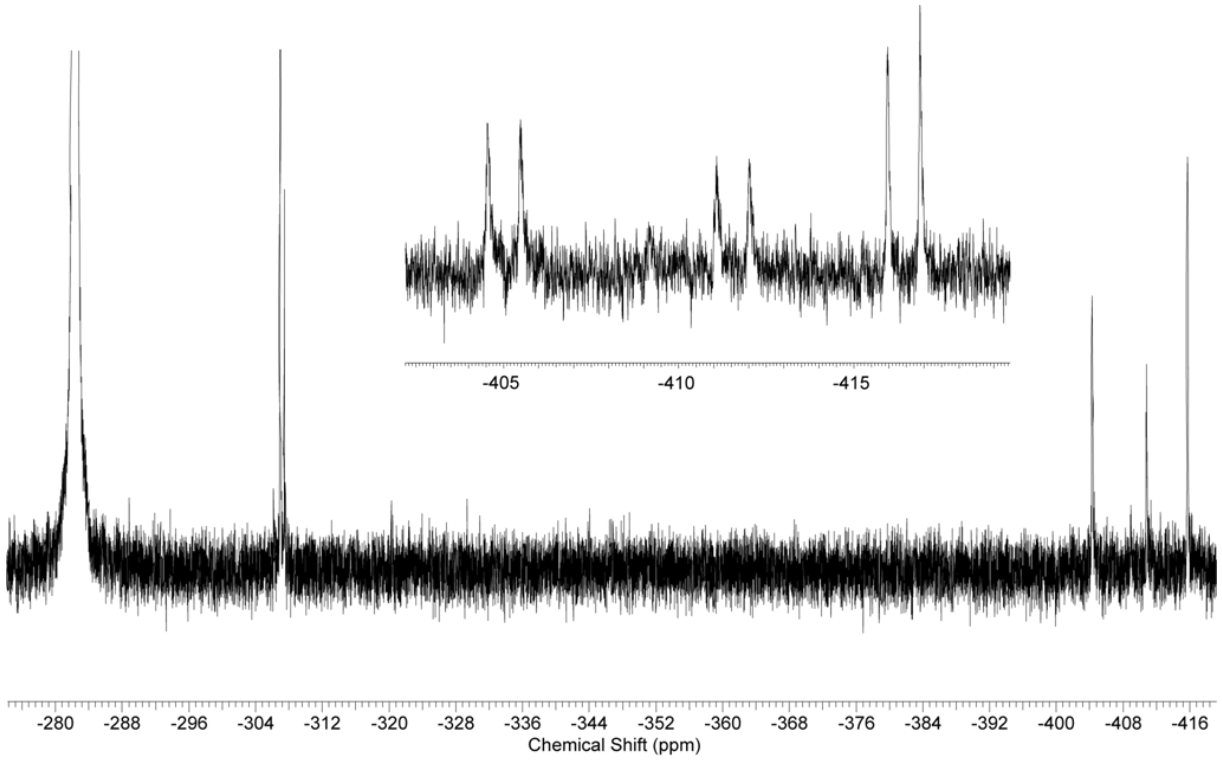


Figure 10: $^{31}P\{^{1}H\}$ NMR spectrum of "Na_3P" in tetraglyme after the addition of one equivalent of *tert*-butanol. The inset shows the ^{31}P spectrum of "Na_2PH" in tetraglyme.

These species are most probably alkoxide packaged sodium clusters of "Na_2PH", analogues to the alkoxide packaged $NaPH_2 \cdot xNaO^tBu$ clusters observed and analyzed by Stein. Although this mixture contains just 5 % "Na_2PH" in solution (determined from the integrals in the ^{31}P NMR spectrum), and mainly consists of "Na_3P" as precipitate and sodium dihydrogenphosphide, it was nevertheless reacted with mesitoyl chloride. Addition of mesitoyl chloride to the black suspension resulted in a rapid increase in the temperature while during the addition of acid chloride the suspension became orange with a white/yellow precipitation. A yellow solid formed after filtration over celite and evaporation of the solvent. This solid was resuspended in toluene. The formed bright yellow solid was **1** containing about one equivalent of dme. The residual yellow orange solution was further worked up resulting in a second fraction of **1**. The overall yield of this reaction was 79 %. Encouraged by these results the reduction of white phosphorus with sodium was further investigated. In an attempt to circumvent the use of naphthalene as electron carrier for the reduction of white phosphorus, another synthesis route for "Na_3P" was sought. The direct reaction of white phosphorus with liquid sodium at elevated temperatures was studied. However, upon contact of white phosphorus with the sodium suspension at high temperature a very exothermic uncontrollable

reaction took place. This method for the production of "Na_3P" from white phosphorus and sodium proved unsuitable for laboratory use.

Conclusions

Several routes have been tested for the synthesis of sodium bis(mesitoyl)phosphide **1**. The best results were obtained when mesitoyl chloride was reacted with a suspension of "Na_3P" with one equivalent of *tert*-butanol. **1** prepared via this method could be obtained in 79 %, a 20 % increase in yield compared to previously reported methods.

To investigate new synthesis routes towards **1**, several previously unknown asymmetric mesitoyl anhydrides and carbanhydrides were synthesized. The reactivity of the asymmetric anhydrides towards sodium dihydrogenphosphide resulted in the formation of several phosphide products. Increase of the steric bulk of the R-group, from Ph to CPh_3, resulted in an increase in the formation of **1**. However, several mixed bis(acyl)phosphides were formed. The new compound **15** was synthesized from anhydride **4** and sodium dihydrogenphosphide in moderate yield.

The reactivity of sodium dihydrogenphosphide towards asymmetric carbonic anhydrides resulted in the formation of NaOCP and several byproducts without formation of **1**.

Reactions of sodium dihydrogenphosphide with mesitoyl-*p*-toluenesulfonate **9** yield bis(mesitoyl)phosphide. However, **9** reacts rapidly with sodium *tert*-butanolate to form the mesitoyl *tert*-butyl ester and therefore yields are low and large excesses of **9** are necessary.

Bis(mesitoyl)phenylphosphane oxide and bisphenyl(mesitoyl)phosphane oxide were synthesized according to literature procedures, however, they are unstable and react unselectively with sodium dihydrogenphosphide.

Formation of **1** was observed in the reaction of "Na_3P" with **3**, however in low yield.

In conclusion: the best method for the production of bis(acyl)phosphide **1** as building block is the reduction of white phosphorus by sodium in the presence of naphthalene and one equivalent of *tert*-butanol. Acylation is preferably done with mesitoyl chloride, while other tested compounds react unselectively or produce large amounts of waste material.

Chapter 4

Chapter 4. Synthesis of NaP_5

The pentaphosphacyclopentadienide ion (NaP_5) was first observed and described in the late 1980's by Baudler *et al.*[85] According to quantum mechanical calculations and backed up by experimental evidence, the anion exists as a planar 5-membered ring with six π-electrons, satisfying the aromaticity principle. Furthermore, the pentaphosphacyclopentadienide ion is an isolobal analogue of the cyclopentadienide anion (cp^-) and therefore could be an interesting ligand in metal organic chemistry (Figure 11).

a) **18** b)

Figure 11: Structures of the a) P_5^- (**18**) and b) cp^- anions.

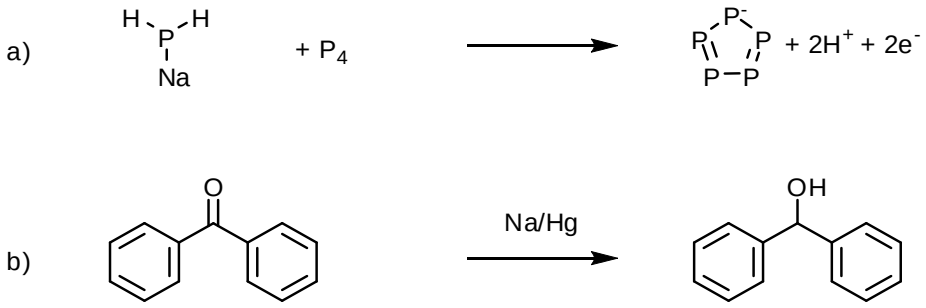
Initially, the pentaphosphacyclopentadienide ion was prepared from white phosphorus and sodium in bis(2-methoxyethyl) ether (diglyme) forming a mixture of polyphosphides. From this mixture a relatively pure solution of the anion (**18**) could be isolated in about 5 % yield by a laborious low temperature recrystallization.[85] Another, more straightforward method for the synthesis of NaP_5 is to boil a mixture of alkaline metal dihydrogenphosphide MPH_2 (M = Li, Na, K) and white phosphorus in ethereal solvents. Although pure solutions of pentaphosphacyclopentadienide ion can be obtained via this method, the formation of large amounts of toxic phosphine requires special apparatus. The yield increased to 12 % when 18-crown-6-ether was used as an additive in solution and purification of the anion solution became more straightforward.[74] Over the years the procedures for the synthesis of NaP_5 gradually improved. In 2006 Milyukov *et al.* reported an improved method for the preparation of NaP_5 starting from white phosphorus and sodium with a catalytic amount of phase transfer catalyst (dibenzo-18-crown-6-ether) with an overall yield of 25 %.[75]

With our previously described alkoxide packaged sodium dihydrogenphosphide, the synthesis of sodium pentaphosphacyclopentadienide (NaP_5) from white phosphorus was investigated as a possible precursor for P_5^- metal complexes.

The reactivity of sodium dihydrogenphosphide towards benzophenone

Sodium pentaphosphacyclopentadienide can be synthesized from white phosphorus and alkali metal dihydrogenphosphides, as previously mentioned. However, to increase the yield of the reaction, the formation of polyphosphides and phosphine must be prevented. Therefore, a method has to be developed which decreases the formation of phosphine and trisodium heptaphosphide. The formation of the pentaphosphacyclopentadienide ion from sodium dihydrogenphosphide and white phosphorus is formally a two electron oxidation reaction whereby two protons are released (Scheme 45a).

To prevent the formation of phosphine a suitable substrate has to be found which readily undergoes reduction and at the same time accepts two protons. Considering this, the reactivity of sodium dihydrogenphosphide towards benzophenones and benzoquinones was investigated. Benzophenone, for instance, can be reduced by sodium to diphenylmethanol in strongly alkaline solutions or with sodium amalgam (Scheme 45b).[135-137]



Scheme 45: a) Oxidation reaction of $NaPH_2$ with white phosphorus. b) Reduction of benzophenone to diphenylmethanol.

To test the applicability of benzophenone as a potential oxidant, the reactivity of sodium dihydrogenphosphide towards benzophenone was tested. The reaction of alkoxide packaged sodium dihydrogenphosphide with benzophenone in thf or dme resulted in a dark blue solution. This dark blue solution is an indication that ketyl radicals are formed. Analysis of the reaction mixture by ^{31}P NMR revealed the formation of two species with relatively sharp signals at -67.2 ppm (t, $^1J_{PH}$ = 179 Hz) and -67.6 ppm (t, $^1J_{PH}$ = 176 Hz) (Figure 12).

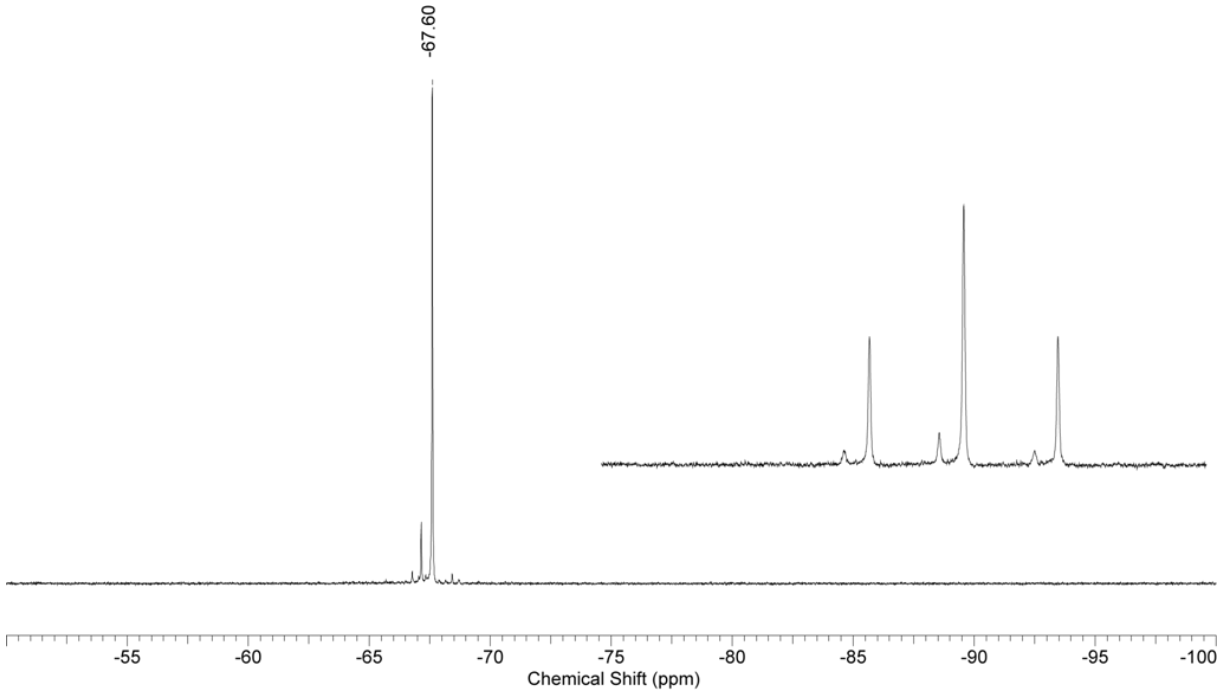


Figure 12: $^{31}P\{^{1}H\}$ NMR spectrum of species formed in reaction of $NaPH_2 \cdot xNaO^tBu$ with benzophenone. The inset shows the proton coupled spectrum of the formed species.

The chemical shifts of the unknown species in ^{31}P NMR are shifted 231 ppm towards higher frequency and the $^{1}J_{PH}$ coupling constant increases by 31 Hz to 180 Hz compared to sodium dihydrogenphosphide. From the proton coupled ^{31}P NMR spectrum it can be concluded that two protons are connected to the phosphorus atom via a single bond. The ratio, with which both species are formed, however, changed in each experiment and depends on the concentration.

Upon brief contact with air the dark solution decolorized. However, the solution regained its intense blue color after the NMR tube had been sealed again. The formed intermediates from the reaction of alkoxide packaged sodium dihydrogenphosphide and benzophenone are stable for several days in thf. In contrast to this, the intermediate formed from sodium dihydrogenphosphide decomposes at room temperature within several hours.

To gain insight into the formed species and the decomposition products it was decided to analyze the reaction further by NMR and EPR spectroscopy.

NMR spectroscopic study of diphenyl (phosphino) methanolate (19)

Although the formation of ketyl radicals was observed in solution, ^{31}P NMR signals of the intermediate were sharp and the intermediate product was stable when produced from

alkoxide packaged sodium dihydrogenphosphide in thf. Therefore, the formed intermediate can be studied by NMR spectroscopy.

In a typical NMR experiment, alkoxide packaged sodium dihydrogenphosphide and benzophenone were reacted in a Young NMR tube. As expected in the ^{31}P NMR the previously observed species at -68.2 ppm and -68.7 ppm were found with coupling constants of $^{1}J_{PH}$ = 177.0 Hz and $^{1}J_{PH}$ = 178.5 Hz respectively. The ^{1}H NMR spectrum reveals the clean formation of two very similar benzophenone containing products. The ^{1}H, ^{31}P correlation spectrum of the intermediate species clearly shows a cross coupling between both signals centered around -68 ppm and two doublets in the ^{1}H NMR spectrum at 3.48 ppm and 3.55 ppm with $^{1}J_{PH}$ coupling constant of 176.4 Hz and 178.3 Hz respectively (Figure 13).

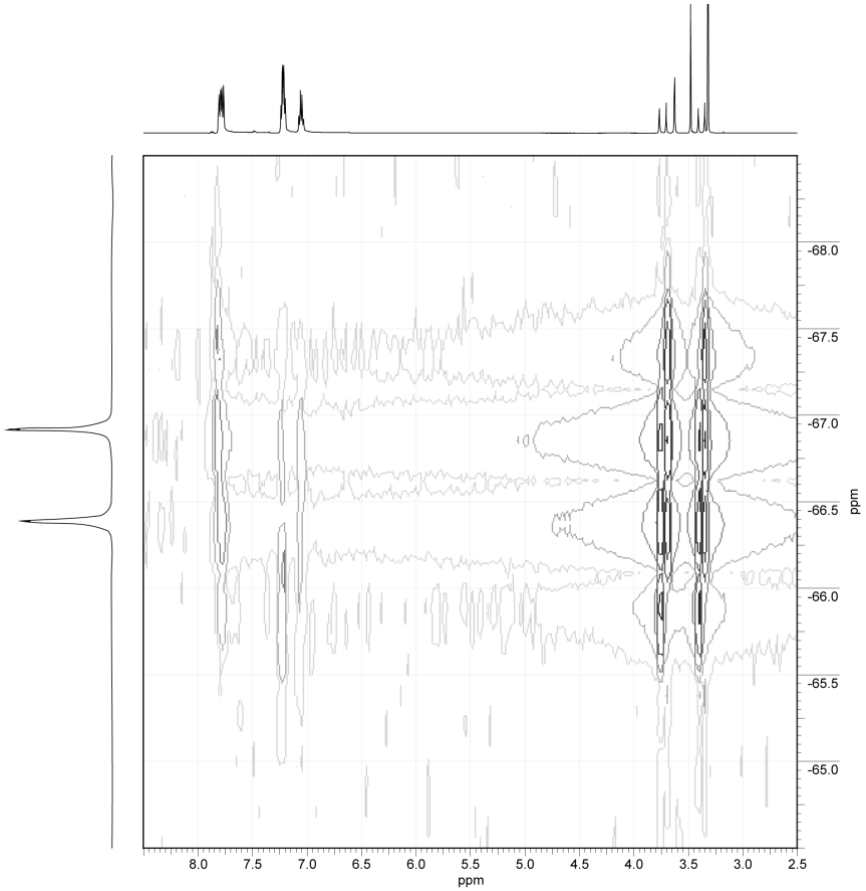


Figure 13: ^{31}P, ^{1}H correlation spectrum of reaction between "organic" sodium dihydrogenphosphide and benzophenone in thf-d_8.

A very weak $^{5}J_{PH}$ coupling signal is also observed between the *o*-proton signals of benzophenone and the phosphine moiety hydrogen atoms (Figure 13). This is an indication that the dihydrogenphosphide moiety is coordinated to the carbonyl function of

benzophenone. No cross-peaks could be observed between the *o*-protons of benzophenone and the protons of dihydrogenphosphide in a ^{1}H, ^{1}H COSY experiment. However, HMBC (Long range) ^{1}H, ^{13}C correlation spectra revealed a strong cross coupling between the *ipso* carbon of benzophenone and the proton signals of the PH_2 moiety (Figure 14).

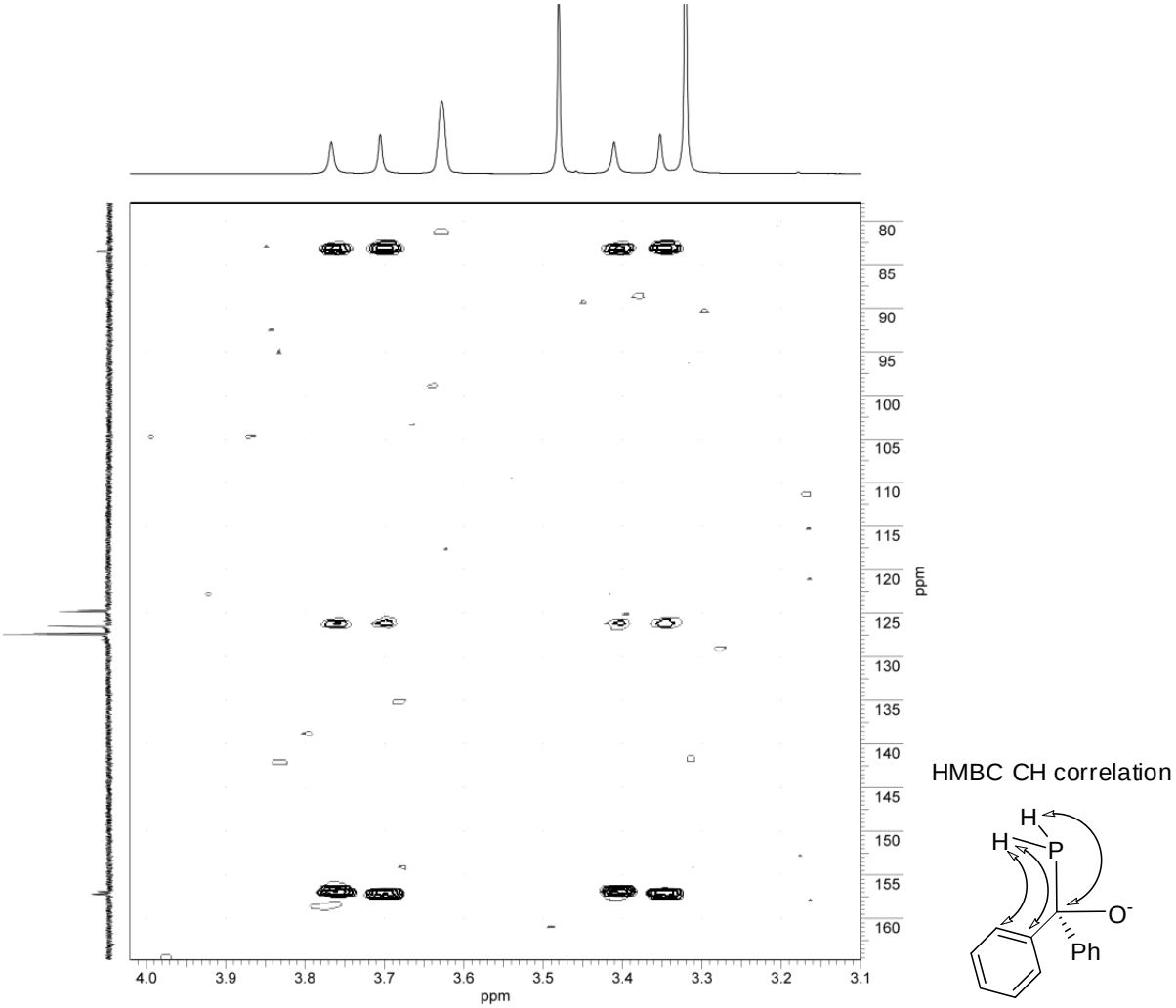


Figure 14: Part of the HMBC (Long range) correlation spectrum of alkoxide packaged sodium dihydrogenphosphide with benzophenone. Inset displays the long range couplings of the phosphine moiety protons with the different carbon atoms of benzophenone.

Furthermore, a similar $^{2}J_{HC}$ coupling is observed for C_{benz} and H_p in the spectrum. A weak ^{1}H, ^{13}C coupling is observed for the PH_2 moiety and the carbon atom in the ortho-position. All these measurements suggest the formation of diphenyl (phosphino) methanolate species (**19**) from the nucleophilic addition of sodium dihydrogenphosphide with the carbonyl function of benzophenone. Very recently a comparable product was observed by Barozzino *et. al.* by the reaction of lithium phosphido-borane ($Ph_2P(BH_3)Li$) with benzaldehyde and cyclohexanone.

If, however, sodium dihydrogenphosphide is used instead of alkoxide packaged sodium dihydrogenphosphide, diphenyl (phosphino) methanolate is not stable at room temperature and decomposes within hours to form diphenylmethanol. The stability of diphenyl (phosphino) methanolate is also influenced by the presence of 18-crown-6-ether. In the presence of 18-crown-6-ether, diphenyl (phosphino) methanolate decomposes immediately and instead only diphenylmethanol is present in the solution (thf-d_8, C*H*OH δ = 6.25 ppm). Furthermore, the formation of Na_3P_7 (δ = -122 ppm) and small amounts of NaP_5 (δ = 467 ppm) were detected by ^{31}P NMR spectrum (Figure 15) (Scheme 46). Barozzino also reported the reduction of benzaldehyde and cyclohexanone after reacting with lithium phosphido-borane.

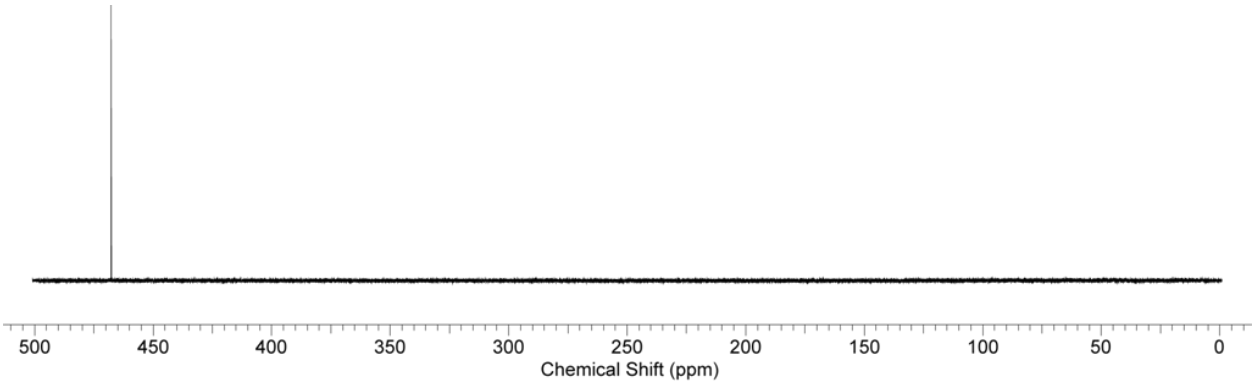
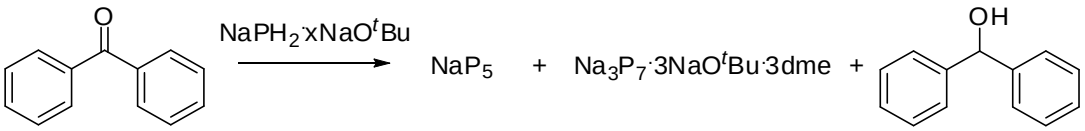


Figure 15: $^{31}P\{^1H\}$ NMR of NaP_5 in thf-d_8 after the reaction of benzophenone and sodium dihydrogenphosphide in the presence of 18-crown-6-ether.



Scheme 46: Reaction of benzophenone with alkoxide packaged sodium dihydrogenphosphide in dme.

In a separate experiment diphenylmethanol could be isolated in 66% yield after the reaction of sodium dihydrogenphosphide with benzophenone.

Crystalstructure of trisodium heptaphosphide (20)

Bright yellow crystals of trisodium heptaphosphide sodium *tert*-butanolate cluster ($Na_3P_7.3NaO^tBu.3dme$) grew directly from a dme solution. The crystals could be isolated in about 70 % yield and were suitable for X-ray diffraction. These highly pyrophoric crystals are very sensitive towards air and moisture (Figure 16).

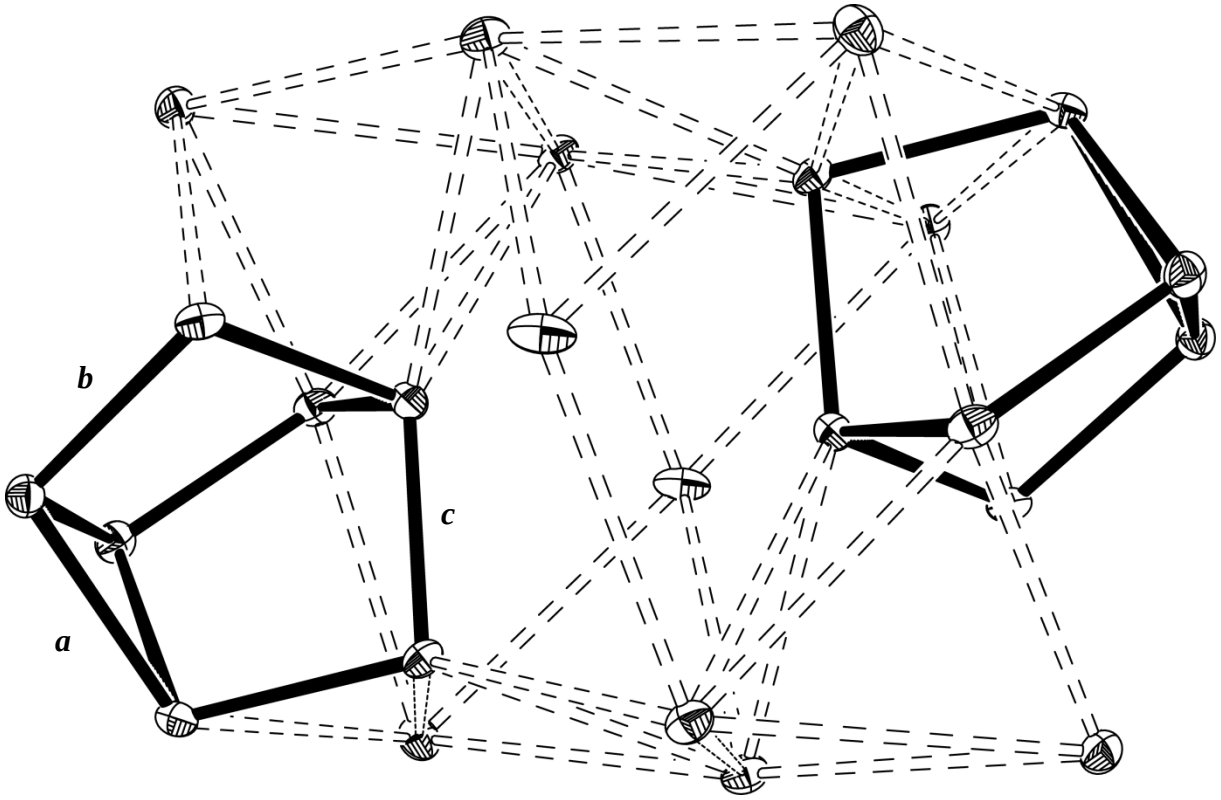


Figure 16: Crystal structure of $[Na_3P_7{\cdot}3NaO^tBu{\cdot}3dme]_2$. Isolated from the reaction mixture of $NaPH_2{\cdot}xNaO^tBu$ with benzophenone in dme. Dme and *tert*-butanoate molecules were omitted for clarity. Thermal ellipsoids at 50 % probability level. Mean distance [Å] *a* 2.262, mean distance *b* 2.150, mean distance *c* 2.181.

The P_7^{3-} anion is coordinated to seven sodium ions. Sodium ions Na2 and Na3 coordinate in a η^3-like manner to the formally negatively charged phosphorus P1,2 and P2,6 and the phosphorus atom P3 of the triangular base of the cage. This is in contrast with sodium ion Na4, which only coordinates to the formally negatively charged phosphorus P1 and P2 in an η^2-like manner. Bridging alkali metal atoms to the phosphorus cage have also been reported by Hönle and Korber.[68,138]

Several different crystal structures of the P_7^{3-} ion are known as solvate isolated ion or as highly coordinated solvent free structure. The P_7^{3-} cage in the described cluster is similar to the other reported P_7^{3-} structures.[68,139]

The formation of trisodium heptaphosphide during the reaction indicates that benzophenone is able to oxidize sodium dihydrogenphosphide and it could therefore be possible to synthesize NaP_5 from sodium dihydrogenphosphide and benzophenone alone. It was indeed found, as previously mentioned, that the sole reaction of sodium dihydrogenphosphide with benzophenone results in the formation of NaP_5. The yield was however less than 10 %.

The reaction described herein and the intermediate species bear resemblance to the nucleophilic addition reactions of alkyllithium and Grignard reagents to carbonyl functions.[140-144] Nucleophilic addition of methyllithium and allyllithium to benzaldehyde or benzophenone goes through an electron transfer (ET)- radical coupling (RC) mechanism. Because radical formation was observed, the interest focused on the produced radical species.

EPR Spectroscopic study of the formed radical species

Paramagnetic species were detected by monitoring the reaction of benzophenone with alkoxide packaged sodium dihydrogenphosphide in thf with EPR (Figure 17). The complex appearance of the spectrum is the result of ion pairing. It is well known that mono negative anions produced by the reduction of alkali earth metals form ion pairs in solvents like thf or 2-methyltetrahydrofuran (HTMF).[145,146] To exclude the formation of radical anions from side reactions, sodium *tert*-butanolate was reacted with benzophenone. This solution was EPR silent, confirming that radical species are only formed by the reaction of sodium dihydrogenphosphide with benzophenone.

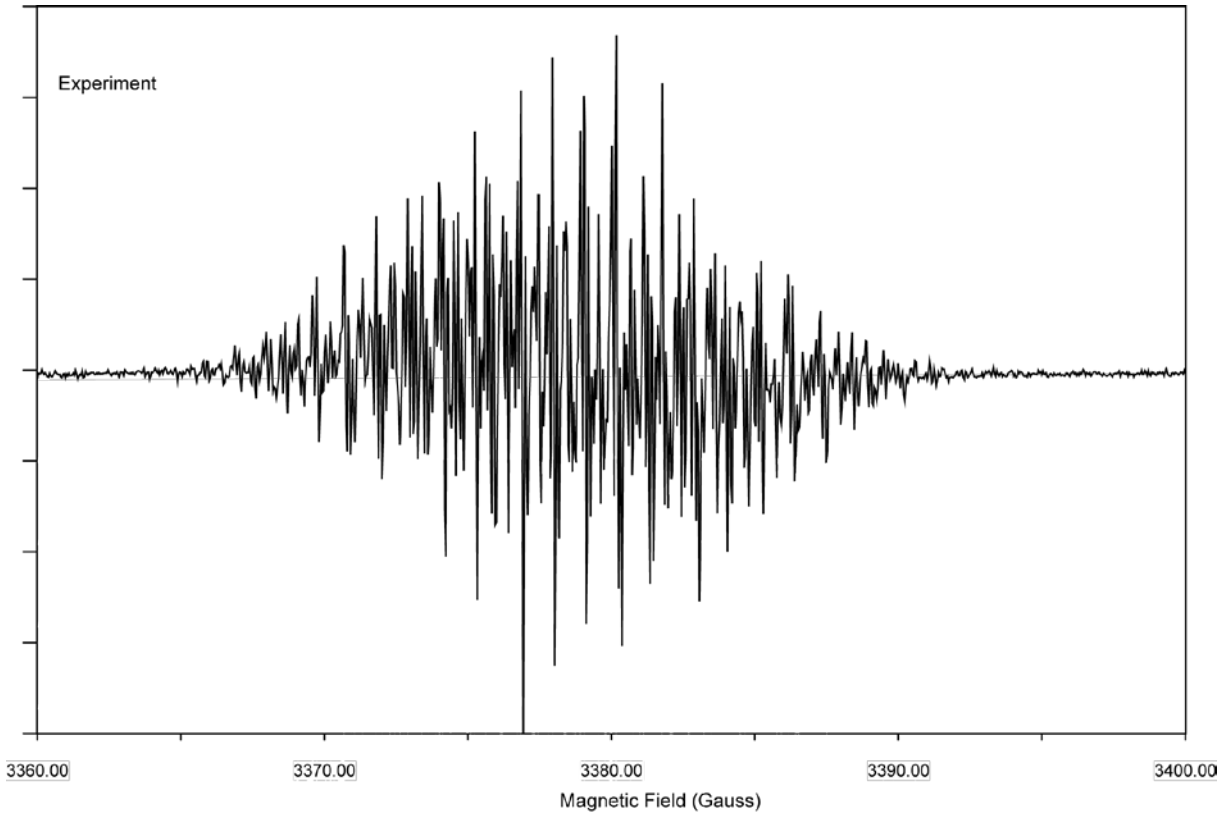


Figure 17: EPR spectrum of a 0.5 mM solution of sodium dihydrogenphosphide and benzophenone in thf.

Characterization of the formed radical species

In order to get more information about the radical species which were formed during the reaction, several additional EPR measurements were made. Sodium dihydrogenphosphide was reacted with benzophenones **21a-21d** in thf (Figure 19). These benzophenones were selected because there is abundant EPR data in the literature for the ketyl radicals formed from these benzophenones. However, all reactions of benzophenones **21b-d** with sodium dihydrogenphosphide in thf gave rise to complex EPR spectra (See Appendix 8).

The EPR spectra of **21a-21d** measured in thf were difficult to analyze because of the large number of hydrogen atoms of benzophenone with which the delocalized electron interacts and anion pair formation of the radical with sodium (*vide infra*). To reduce the number of hyperfine couplings in the EPR spectra of these benzophenones, the number of nuclei with spin I>0 with which the delocalized electron can interact must be decreased as well. Therefore the reaction of benzophenone **21e** with sodium dihydrogenphosphide was analyzed by EPR spectroscopy. Although the number of hyperfine couplings decreased significantly in the EPR spectrum three different paramagnetic species were observed, probably as a result of ion pair

formation (Appendix 8). Therefore, to reduce ion pair formation, an EPR spectrum of benzophenone **21e** with sodium dihydrogenphosphide was measured in bis(2-(2-methoxyethoxy)ethyl) ether (tetraglyme). The cation solvating power of tetraglyme is higher than in thf or dme and therefore the association of the radical with the counter ion is decreased (Figure 18).

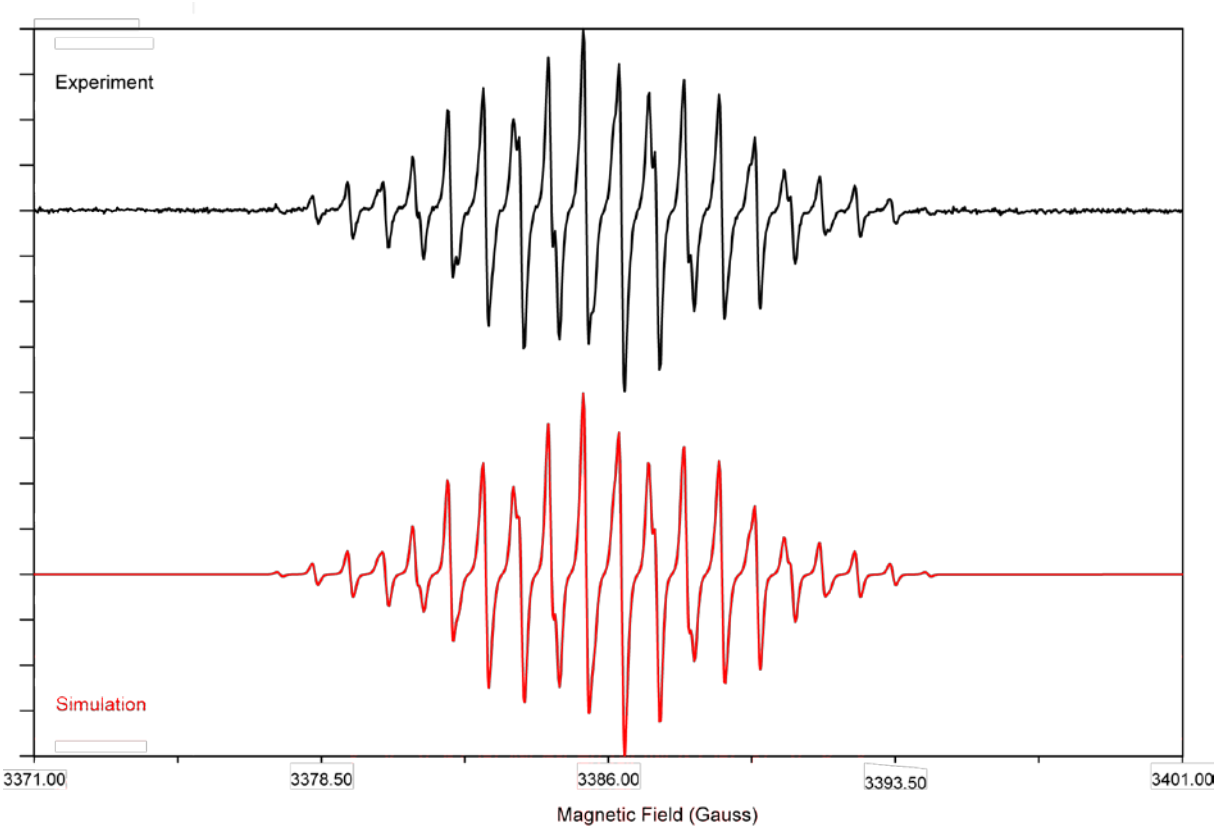


Figure 18: EPR spectrum of **21e** and sodium dihydrogenphosphide in tetraglyme. Top: Experimental spectrum, bottom: Simulated spectrum. Frequency: 9.497 GHz; 2.0040 g-value (vs. DPPH): hyperfine coupling constants [mT]: $a_{H,ortho}$: 0.262; $a_{H,meta}$: 0.091; a_{Na}: 0.093.

Indeed, the use of tetraglyme for the determination of the radical anion formed by the reaction of sodium dihydrogenphosphide with benzophenone derivative **21e** significantly reduces the complexity of the EPR spectrum. The spectrum could be simulated with values taken from benzophenone type radicals since literature data on *p*-chlorobenzophenone ketyl radicals is scarce. From this simulation, it is obvious that the formed radical is the ketyl anion radical of benzophenone **21e**. Because tetraglyme significantly reduced the ion pair formation, a similar experiment was performed with benzophenone and sodium dihydrogenphosphide in tetraglyme. The EPR spectrum of this reaction is highly resolved and could be simulated and

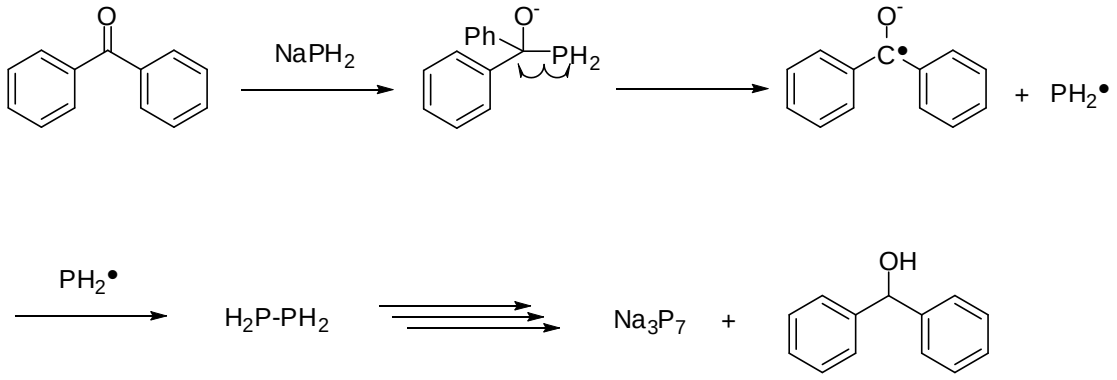
compared with literature values (Table 1). The measured spectrum matches the literature values very nicely.[147-149]

Further evidence for the formation of the ketyl anion radical was provided by the reaction of sodium dihydrogenphosphide with benzophenone in dme or thf in the presence of 18-crown-6-ether (Appendix 8). 18-Crown-6-ether has a similar effect on the association and formation of ion pairs as tetraglyme. The obtained spectra could be simulated and compared with literature data of ketyl radical anions. The obtained spectra matched the reported data nicely (Table 1).

Table 1: Simulated hyperfine coupling constants for benzophenone radical anion formed when sodium dihydrogenphosphide is reacted with benzophenone.

	$a_{H,ortho}$	$a_{H,meta}$	$a_{H,para}$	a_{Na}
Benzophenone/18-crown-6	0.260	0.087	0.345	0.128
Benzophenone/tetraglyme	0.260	0.087	0.350	0.109
Benzophenone/Na[147-149]	0.260	0.088	0.345	0.116

A possible reaction pathway for the formation of sodium heptaphosphide, NaP_5 and the benzophenone ketyl radical could be the homolytic splitting or cleavage of the phosphorus carbon bond forming the benzophenone ketyl radical and a $PH_2^{\bullet}$ radical. The produced $PH_2^{\bullet}$ radical could form P_2H_4 in a radical coupling reaction. And from P_2H_4 in a decomposition pathway Na_3P_7 is formed. (Scheme 47). From literature it is known that Na_3P_7 can be formed from P_2H_4 in highly alkaline solutions[150]and the formation of P_2H_4 from $PH_2^{\bullet}$ has been reported.[151]



Scheme 47: Proposed mechanism for the formation of trisodium heptaphosphide and diphenylmethanol from benzophenone and sodium dihydrogenphosphide.

Reactions of sodium dihydrogenphosphide with benzophenones and benzoquinones

Our previous measurements indicated the formation of NaP_5 from the reaction of benzophenone with sodium dihydrogenphosphide. Although the formed amount of NaP_5 is rather low (less than 10 %) these results encouraged us to investigate the influence of substituents on benzophenone on the formation of NaP_5. Furthermore, other easily reducible organic compounds were tested (Figure 19).

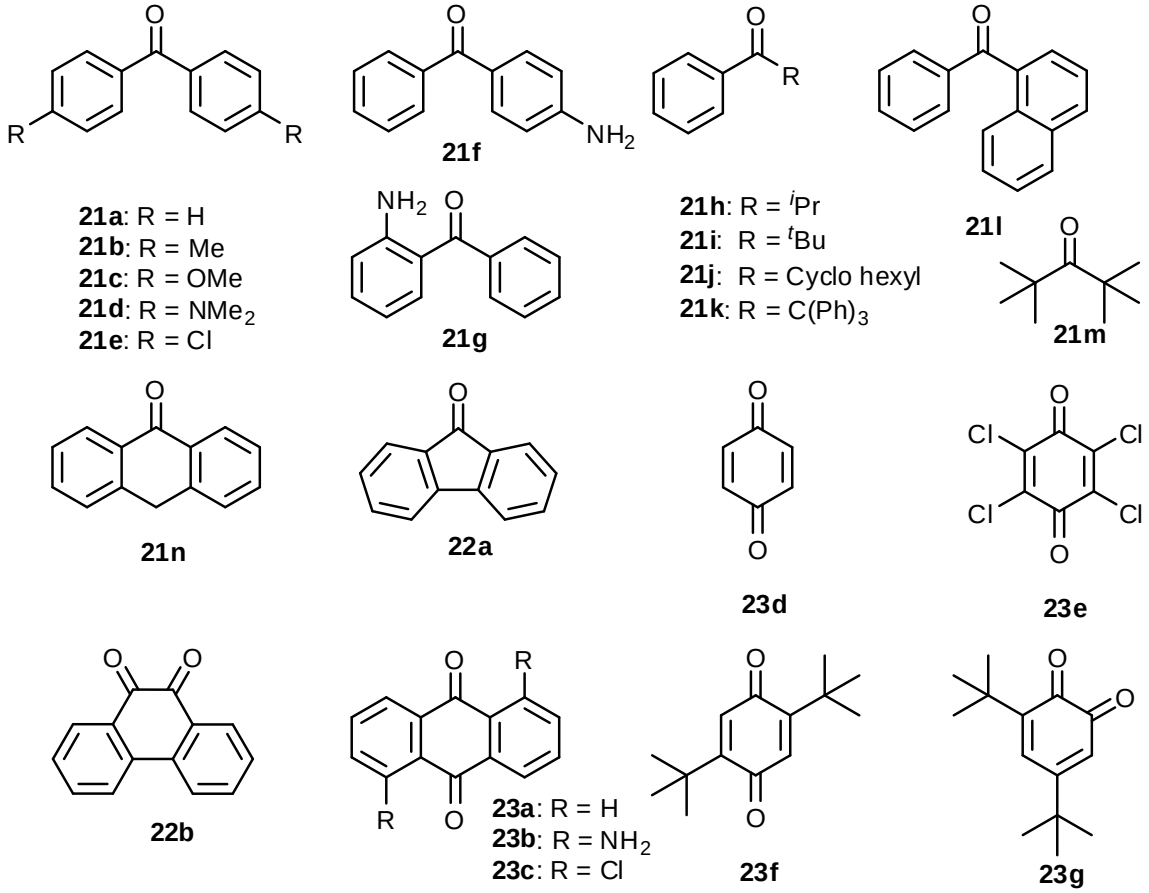


Figure 19: The substituted benzophenones and -quinones tested in the reaction with sodium dihydrogenphosphide.

Table 2: Table of substituted benzophenones and quinones used to test the reactivity of sodium dihydrogenphosphide. (Reactions denoted with X show the formation of NaP_5 in low yields, less than 10%, during the reaction).

benzophenone/ benzoquinone	NaP_5	^{31}P NMR of intermediates
21a	X	- 68 ppm (t, $^1J_{PH}$ = 175 Hz)$_{thf}$
21b	X	-67 ppm (t, $^1J_{PH}$ = 178 Hz)$_{thf}$
21c	X	- 69 ppm (d, $^1J_{PH}$ = 176 Hz)$_{thf}$
21d	X	- 68 (d, $^1J_{PH}$ = 176 Hz)$_{thf}$
21e	X dme	
21f	-	- 67 (d, $^1J_{PH}$ = 175 Hz)$_{thf}$
21g	-	
21h	-	67.2, 36.2 and 25.4 ppm
21i	X	-102.8 ppm (dd, $^1J_{PH}$ = 168 Hz, $^1J_{PH}$ = 193 Hz)
21j	-	-89 ppm (t, $^1J_{PH}$ = 177 Hz)
21k	-	0.2 ppm (d,$^1J_{PH}$ = 150 Hz); - 18 ppm (d,$^1J_{PH}$ = 146 Hz)
21l	X	- 69.8 ppm (t, $^1J_{PH}$ = 179 Hz); -70.2 ppm (t, $^1J_{PH}$ = 177 Hz)$_{thf}$
21m	-	No reaction
21n	-	
22a	X	
22b	X	
23a	X	
23b	-	
23c	-	
23d	-	
23e	-	
23f	-	
23g	X	

All benzophenones (**21a**-**21e**), except the amine substituted ones (**21f** and **21g**), form NaP_5 in small quantities during the reaction (< 10 %) (Table 2). Similar to the reduction of benzophenone with sodium dihydrogenphosphide, the reduced or partly reduced substituted benzophenones and trisodium heptaphosphide could be isolated. Furthermore, the formation of diphenyl(phosphino)methanolate species was observed with a chemical shift of around -69

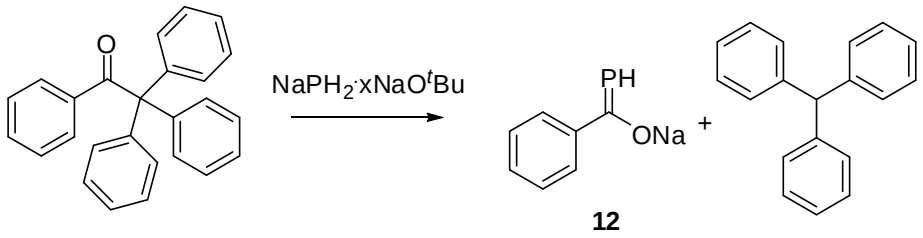
ppm and a $^1J_{PH}$ coupling constant of around 177 Hz, as was observed with the reaction of benzophenone. This indicates that the reactivity of sodium dihydrogenphosphide towards these compounds is the same and similar intermediates are formed. The asymmetric ketones (**21h**-**21l**) also react with sodium dihydrogenphosphide to form phosphino methanolate species. Reaction of asymmetric ketones **21h** and **21j** with sodium dihydrogenphosphide gave rise to the formation of large quantities of phosphine; this is probably caused by the relatively acidic proton in 2- position to form the enolate. The formation of the phosphine was absent in, for example, the reaction of sodium dihydrogenphosphide with **21i** and **21m** where formation of the enolate is impossible.

Isolation of reaction products

Interested in the structure of the intermediate species formed by the reaction of sodium dihydrogenphosphide with substituted benzophenones and quinones, several attempts were made to isolate the intermediate species observed during the reaction. None of the tested methods worked and often a dark blue oil was obtained. However, the reaction of sodium dihydrogenphosphide with 9,10-phenanthrenequinone (**22b**) in dme resulted in the formation of bright red crystals. These crystals are extremely air sensitive and immediately change their color from dark red to green and eventually into a colorless solid when in contact with air. It was possible to isolate these dark red crystals from the reaction mixture and analyze them by NMR and X-ray diffraction.

Although the X-ray structure could not be resolved well, it could be shown that a single unit cell of the crystals consisted of three doubly reduced phenanthrenequinone molecules. Since only one equivalent of sodium dihydrogenphosphide was used, the further reduction of phenanthrenequinone could only be caused by sodium *tert*-butanolate. In a separate experiment, it was indeed found that sodium *tert*-butanolate was able to form reduced phenanthrenequinone species.

The reaction between **21k** and sodium dihydrogenphosphide resulted in the formation of sodium benzoylphosphide (**12**). Analysis of the reaction mixture by ^{31}P NMR spectroscopy revealed two signals at 0.1 ppm (d, $^1J_{PH}$ = 159.1 Hz) for the minor isomer and 11.4 ppm (d, $^1J_{PH}$ = 139.6 Hz) for the major isomer (Scheme 48).



12

Scheme 48: Synthesis of sodium mesitoylphosphanide from alkoxide packaged sodium dihydrogenphosphide and benzopinacolone.

In ^{1}H NMR the P*H* signals are at δ = 4.00 ($^1J_{PH}$ = 140.0 Hz) for the major isomer and 4.69 ppm ($^1J_{PH}$ = 158.6 Hz) for the minor isomer.

This highly unstable product could be isolated by precipitation with hexanes at -30 °C from a dme solution and were analyzed by spectroscopic methods. This species was first reported by Liotta *et al.*[152] while Stein[64] was able to get an X-ray structure of the related sodium mesitoyl phosphanide. Crystals suitable for X-ray diffraction of the synthesized sodium benzoyl phosphanide were grown by cooling down the reaction mixture to -30 °C. Bright yellow crystals grew overnight (Figure 20). The structure of the sodium benzoylphosphanide is similar to the structure of sodium mesitoyl phosphanide reported by Stein. The bond lengths of the phosphorus-carbon (P1-C1) and carbon-oxygen (C1-O5) bond are 1.75 Å and 1.27 Å respectively and lie in the range of bond lengths observed by Stein. The elongated carbon-oxygen bond (compared to 1.23 Å for a CO double bond) is an indication of a phosphaenolate structure. This is also confirmed by NMR resonance spectra (E/Z diastereo isomers). There is a distinct difference between the sodium-oxygen bond observed by Stein and in the benzoyl phosphanide structure **12** (Na1-O5), 2.21 Å and 2.33 Å respectively. The sodium-oxygen bond of structure **12** is within the expected range found in other Na-alkoxide compounds.

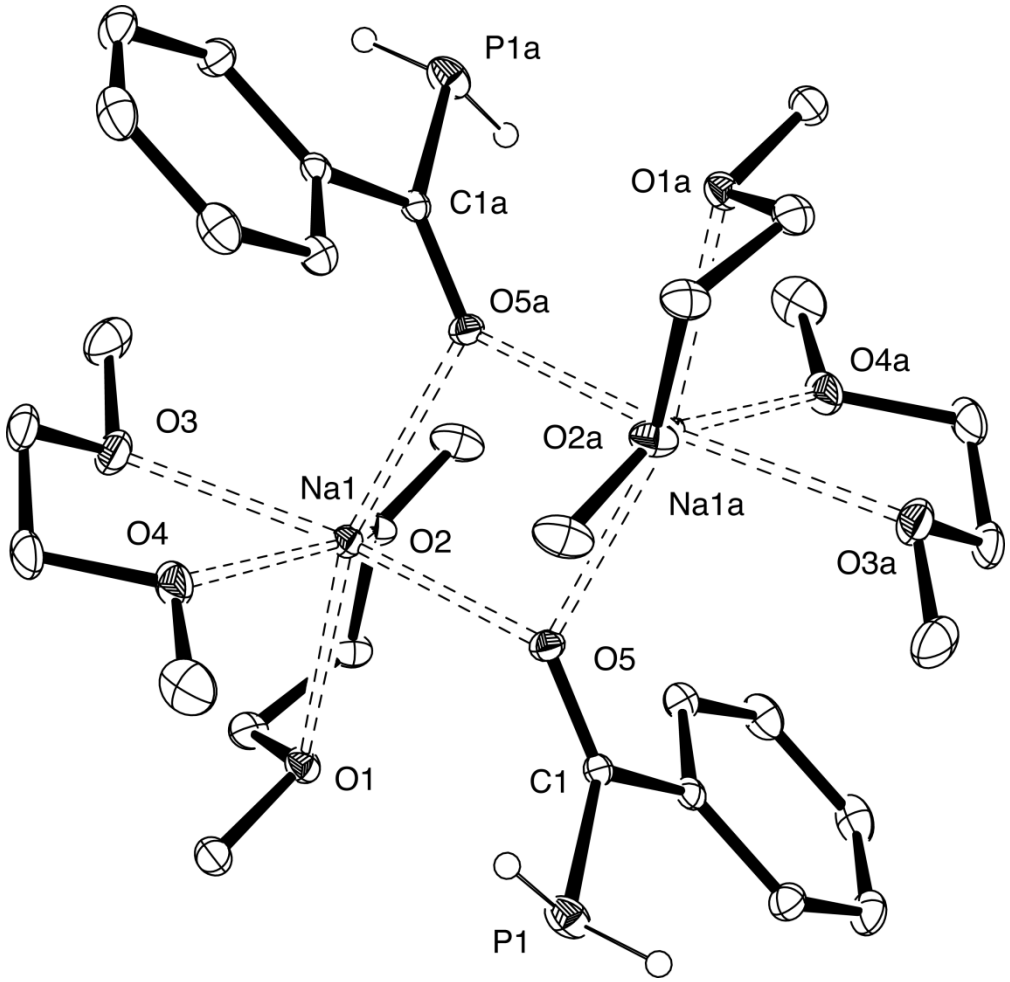


Figure 20: Crystal structure of NaOPCPh (**12**). Selected bond lengths [Å] and angles [°]: P1-C1 1.751(1), P1a-C1a 1.751(1), C1-O5 1.273(1), C1a-O5a 1.273(1), Na1-O5 2.327(1), Na1-O5a 2.330(1), Na1a-O5 2.330(1), Na1a-O5a 2.327(1), Na1-Na1a 3.401, P1-C1-O5 125.47, P1a-C1a-O5a 125.47.

Synthesis of NaP_5 from sodium dihydrogenphosphide and white phosphorus

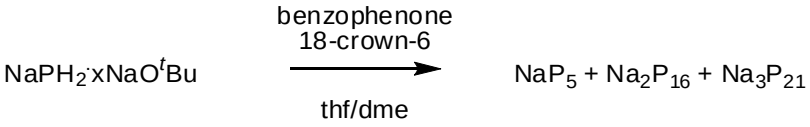
The previous experiments indicated that NaP_5 is formed directly from the reaction of alkoxide packaged sodium dihydrogenphosphide and benzophenone. Although NaP_5 is formed in low yield (< 10 %), it was thought that the presence of benzophenone could increase the yield in the preparation of NaP_5 from alkoxide packaged sodium dihydrogenphosphide and white phosphorus.

At room temperature or elevated temperatures, alkoxide packaged sodium dihydrogenphosphide reacts with white phosphorus to form primarily alkoxide packaged trisodium heptaphosphide in good yield. Furthermore, small amounts of NaP_5 are present in solution. Alkoxide packaged trisodium heptaphosphide is insoluble in dme and crystallizes

from the reaction mixture as bright yellow crystals or as a pale yellow solid, depending on the concentration of the solution. Therefore, dme would be the solvent of choice for further investigation of the reaction of alkoxide packaged sodium dihydrogenphosphide with white phosphorus. Employing dme as solvent considerably facilitates the separation of NaP_5 and trisodium heptaphosphide. However, white phosphorus is almost insoluble in dme and therefore a combination of solvents was used.

White phosphorus was completely dissolved in thf and to this solution a sodium dihydrogenphosphide solution was added drop wise which resulted in the formation of NaP_5. However, due to the presence of thf, separation of trisodium heptaphosphide is more difficult since it is soluble in thf. If 18-crown-6-ether is used as an additive in the reaction, NaP_5 is formed in 9 % yield under benign reaction conditions.

The yield of NaP_5 significantly increased in the presence of benzophenone reactant. The reaction of white phosphorus with alkoxide packaged sodium dihydrogenphosphide in the presence of benzophenone and 18-crown-6-ether yields NaP_5 in about 28 % yield (according to ^{31}P NMR with PPh_3 as internal standard) (Scheme 49).



Scheme 49: Reaction of alkoxide packaged sodium dihydrogenphosphide with white phosphorus in the presence of benzophenone and 18-crown-6-ether.

As side products in this reaction Na_2P_{16} and Na_3P_{21} could be isolated as a mixture of products. The yield of the reaction was increased further when white phosphorus was reacted with sodium dihydrogenphosphide, benzophenone and 18-crown-6-ether at elevated temperatures (55 °C). To a solution of benzophenone and 18-crown-6-ether in thf was added alkoxide packaged sodium dihydrogenphosphide in dme. The dark blue solution was rapidly heated to 55 °C and white phosphorus dissolved in thf was added drop wise to the solution. Stirring the mixture overnight gave a yellow solution with a red precipitation. According to ^{31}P NMR measurements with PPh_3 as internal standard, NaP_5 is formed in 44 % yield. This method is convenient for the production of NaP_5 in high yield starting from sodium dihydrogenphosphide and white phosphorus in the presence of benzophenone and 18-crown-6-ether.

Conclusions

It was shown that NaP_5 solutions can be made by the reaction of alkoxide packaged sodium dihydrogenphosphide with white phosphorus in the presence of benzophenone and 18-crown-6-ether in moderate yield. The reaction of sodium dihydrogenphosphide with benzophenone results in the formation of an intermediate species which slowly decomposes in dme and is relatively stable in thf solutions. This intermediate, diphenyl (phosphino) methanolate, was characterized by NMR spectroscopic methods since it is not possible to isolate the intermediate. Decomposition of this species to polyphosphides, like trisodium heptaphosphide and NaP_5, and diphenylmethanol was observed. Crystals of alkoxide packaged trisodium heptaphosphide grew directly from the reaction mixture of alkoxide packaged sodium dihydrogenphosphide with benzophenone in good yield. Several benzophenone and anthraquinone substrates were tested in the reaction with alkoxide packaged sodium dihydrogenphosphide. Generally, substituted benzophenones, except the benzophenones with amino groups, behaved similar and formation of NaP_5 and trisodium heptaphosphide was observed. However, if good leaving groups are present, as for example in the reaction with benzopinacolone, formation of benzoylphosphide is observed. It was possible to isolate and grow crystals of sodium benzoylphosphide, a species first observed by Liotta *et al.* Nevertheless, they were never able to fully characterize it.

Chapter 5

Chapter 5. Synthesis of Rhodium and Nickel phosphido complexes

Phosphido metal complexes have been known since the late 1950s.[33,89-91] Since then the chemistry of these complexes has gradually more expanded. For example, hydrophosphination is a well known catalytic reaction involving phosphido complexes in the catalytic cycle.[92-96] Although phosphido transition metal complexes ([$(L_nM)PR_2$]) with large alkyl and phenyl R groups are fairly common and well studied, the chemistry of the parent complex (R = H) is less known.

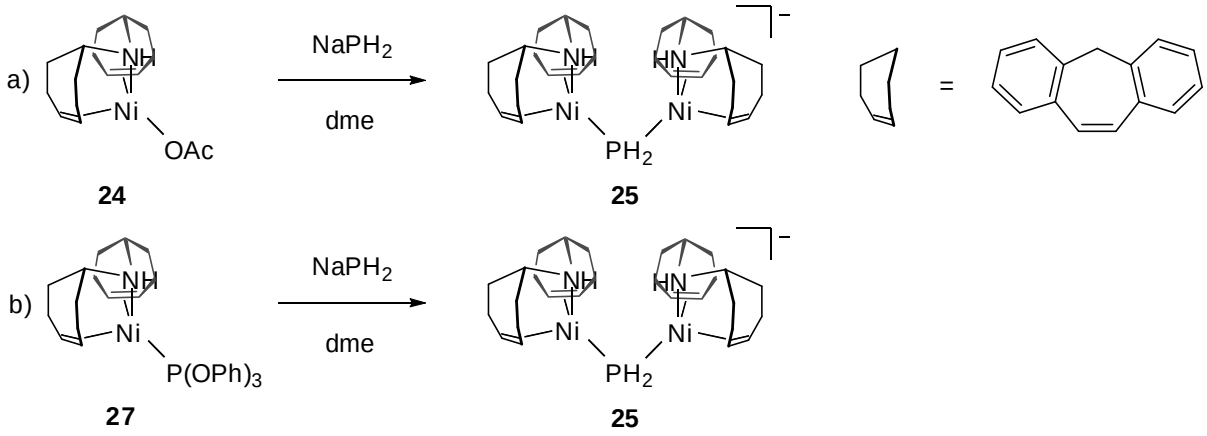
A lot of effort in the synthesis and characterization of μ-PH_2 complexes was performed by Schäfer e*t al.*[99-101,109] Most of the produced complexes are simple transition metal complexes containing carbonyl or cyclopentadienyl ligands.

The reactivity of low valent transition metal complexes towards sodium dihydrogenphosphide was surveyed.

Synthesis of [{($trop_2NH$)Ni}$_2$(μ-PH_2)]Na (25)

A first attempt to synthesize phosphido nickel complexes was by the reaction of ($trop_2NH$)$NiOAcF_3$ (**24**) with sodium dihydrogenphosphide. Starting from **24** and alkoxide packaged sodium dihydrogenphosphide in thf, several metal complexes were formed. Interestingly, instead of the expected neutral ($trop_2NH$)$NiPH_2$ complex, one of the formed products was the anionic diamagnetic metal complex [{($trop_2NH$)Ni}$_2$(μ-PH_2)]Na (**25**), deduced from the available NMR data and crystal structure, vide infra. Apparently, ($trop_2NH$)$NiOAcF_3$ is readily reduced by alkoxide packaged $NaPH_2$ to form formally a zero valent Ni^0 species. The tendency for being reduced by phosphido compounds is common for nickel (I) and (II) complexes.[101,153,154] Another complex formed was a non-bridging phosphido metal complex observed in ^{31}P NMR spectra with a chemical shift of δ = -261.2 (t, $^1J_{PH}$ = 164.7 Hz). Encouraged by these results, a different route towards μ-PH_2 nickel complex **25** was developed. Instead of starting from a Ni^{1+} precursor the zero valent nickel complex ($trop_2NH$)$NiPPh_3$ (**26**) was used as the starting material, to prevent the reduction of the metal complex by sodium dihydrogenphosphide. The reaction of complex **26** with sodium dihydrogenphosphide in dme is fast and forms the phosphido bridged complex **25** as very

dark red crystals in dme in good yield (74 %) (Scheme 50). Better results were obtained when [(trop$_2$NH)Ni(P(OPh)$_3$)] (**27**) was reacted with sodium dihydrogenphosphide. Triphenylphosphite is a more labile ligand for nickel complexes than triphenylphosphine. Therefore it is easier to displace it for dihydrogenphosphide to form complex **25**.



Scheme 50: Synthesis of [{(trop$_2$NH)Ni}$_2$(μ-PH$_2$)]Na from a) Ni^{1+} and b) Ni^0 precursors.

Crystal structure of [{(trop$_2$NH)Ni}$_2$(μ-PH$_2$)]Na (25)

Crystals of complex **25**, suitable for X-ray diffraction, grow directly from the reaction mixture as very dark brown needles in dme (Figure 21). Complex **25** is one of the first compounds of the class [(L$_n$M)$_2$PH$_2$]$^-$. Compared to complex (trop$_2$NH)NiPPh$_3$, the Ni-N and Ni-P bonds of complex **25** are slightly elongated. Complex (trop$_2$NH)NiPPh$_3$ has bond lengths of 2.194(2) Å and 2.164(5) Å for the Ni-N and Ni-P bonds respectively compared to 2.239(6) Å and 2.249(1) Å for complex **25**.[155] This elongation is probably due to the larger σ-donating ability of PH$_2^-$ compared to PPh$_3$. The Ni-P-Ni angle (123.2°) of the bridging PH$_2$ ligand is comparable to other X-ray structures of bridging phosphido ligands without metal-metal bonds.

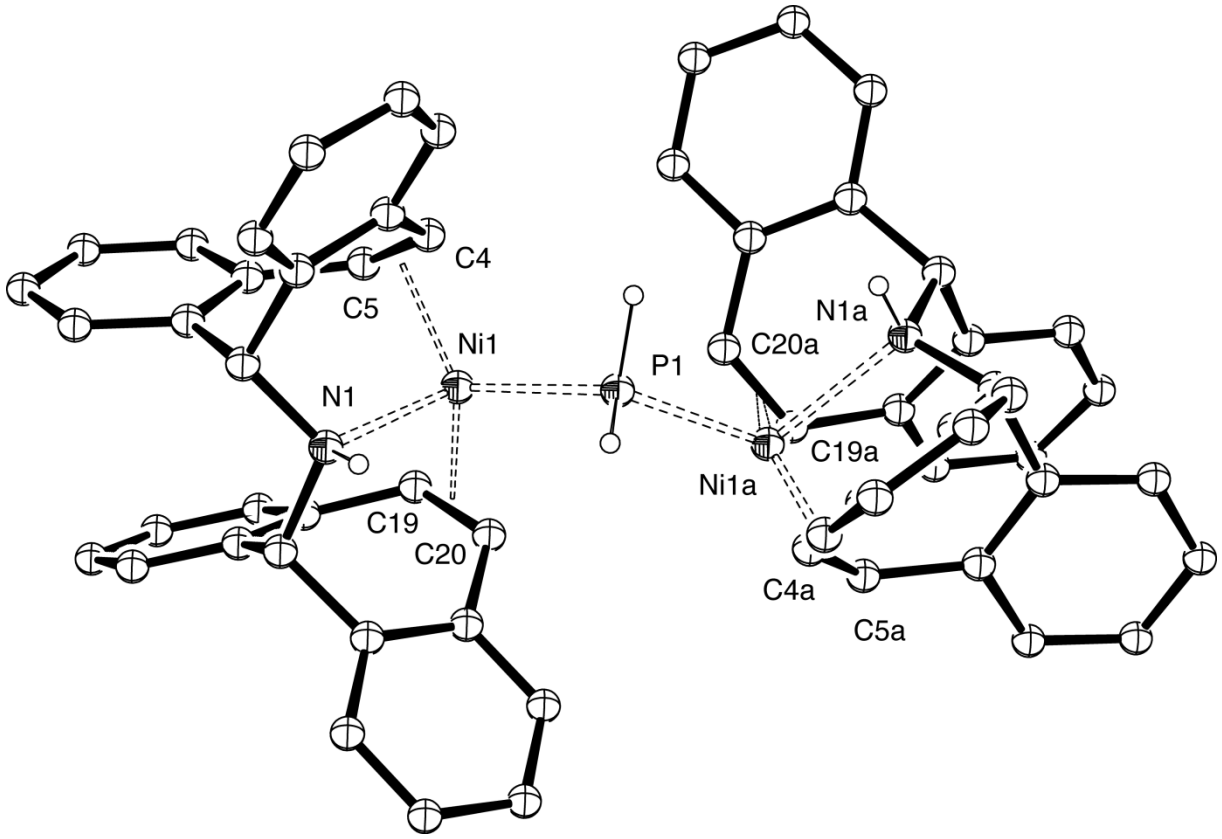


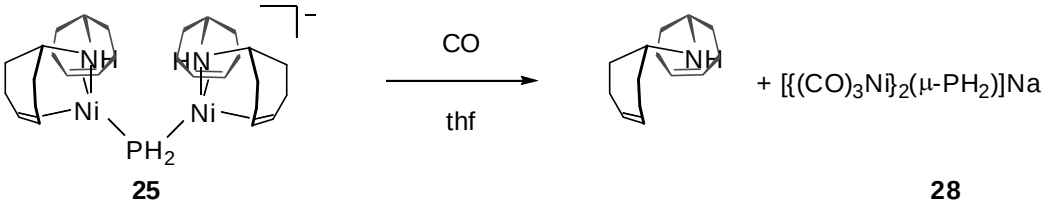
Figure 21: ORTEP diagram of $[(trop_2NH)_2Ni_2(\mu\text{-}PH_2)]^-$. Counter ion $[Na(dme)_3]^+$ omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1-P1 2.249(1), Ni1-N1 2.239(6), Ni-Ct(19-20) 1.982, Ni-Ct(4-5) 1.902, Ni1a-P1 2.249(1), Ni1a-N1a 2.239(6), Ni1-Ct(19-20) 1.982, Ni-Ct(4-5) 1.902, Ni1-Ct(19-20) 1.982, Ni-Ct(4-5) 1.902, Ni1-P1-Ni1a 123.20, P1-Ni1-N1 109.64, P1-Ni1a-N1a 109.64.

Comparison of the NMR data confirms the higher back donation of PH_2^- compared to PPh_3. The olefinic ^1H NMR signals of complex **25** are at lower frequency compared to those of the starting material (δ = 4.15 ppm and δ = 4.48 ppm for complex **25**; δ = 4.39 ppm and δ = 5.12 ppm for $[(trop_2NH)NiPPh_3]$). A similar trend is observed for in the ^{13}C NMR spectra for the olefinic carbon atoms (δ = 59.8 ppm and δ = 65.5 ppm for complex **25**; δ = 67.9 ppm and δ = 69.5 ppm for $[(trop_2NH)NiPPh_3]$).

Reactivity of complex 25 towards CO

With this complex in hand, the reactivity was tested towards CO. It was thought that the bridging PH_2 ligand could react with CO to form NaOCP. A sample of complex **25** in thf was placed under a CO atmosphere and the sample was analyzed by ^{31}P NMR spectroscopy. Instead of a reaction between CO and PH_2^- the tridentate $trop_2NH$ ligand was substituted by

CO. A new species was observed in the ^{31}P NMR spectrum with a chemical shift of δ = -218.3 (t, $^{1}J_{PH}$ = 239.5 Hz) (Scheme 51).



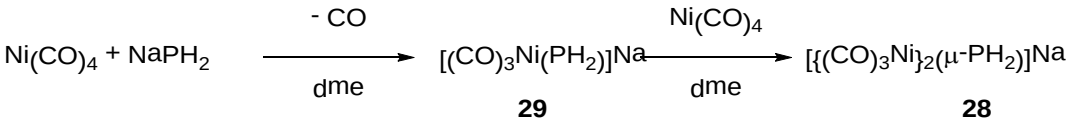
25 **28**

Scheme 51: Formation of $[\{(CO)_3Ni\}_2(\mu\text{-}PH_2)]Na$ from **25** in thf under a CO atmosphere.

Interestingly, according to ^{31}P NMR measurements, PH_2^- is a very good ligand for zero valent nickel carbonyl complexes and is not displaced by CO at low pressures (1 bar). The ^{31}P NMR data suggested the formation of a $\mu\text{-}PH_2^-$ nickel complex. Interested in the formed complex $[\{(CO)_3Ni\}_2(\mu\text{-}PH_2)]Na$ (**28**), vide infra, complex **28** was synthesized on a larger scale starting from $Ni(CO)_4$ and $NaPH_2$.

Synthesis of phosphido nickel carbonyl complexes

Starting from sodium dihydrogenphosphide in dme or thf with one equivalent of $Ni(CO)_4$ in a thf solution, $[(CO)_3NiPH_2]^-$ (**29**) is formed selectively releasing one equivalent of CO. Another equivalent of $Ni(CO)_4$ yields $[\{(CO)_3Ni\}_2(\mu\text{-}PH_2)]Na$ (**28**) selectively (Scheme 52).

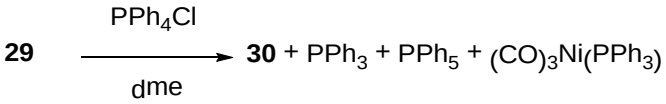


29 **28**

Scheme 52: Synthesis of **28** complex starting from $Ni(CO)_4$ and $NaPH_2$.

The anionic phosphido complexes **29** and **28** are highly reactive and unstable species. Complex **29** can be isolated as a yellow liquid by precipitation from the reaction solution with hexanes. The isolated complex is very unstable and decomposes very quickly, even at -30 °C. Anionic nickel complex **28** is more stable and can be isolated as a yellow liquid, although after a short time period this complex decomposes as well. Complex **28** is comparable to $[\{(CO)_3Ni\}_2P(R)_2]^-$ (with R = Ph, Cy) reported by Schieferstein.[156]

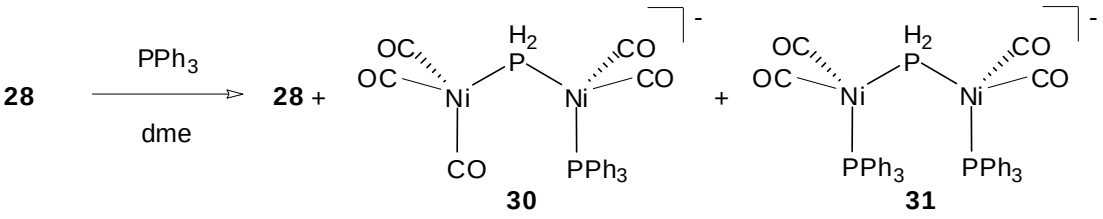
Attempts to convert the highly unstable nickel phosphido complexes into more stable complexes by counterion exchange were not successful. The sodium cation was exchanged for the tetraphenylphosphonium (PPh_4^+) cation. For μ-PH_2 complex **28** salt exchange with PPh_4^+ was rather straightforward, however, the isolated product was still unstable and could only be obtained as an orange liquid. Phosphido complex **29** reacts with PPh_4^+ to form several products including PPh_3, PPh_5 and **30**, vide infra (Scheme 53). It is known that secondary amides (MNR_2) react with tetraphenylphosphonium salts to form PPh_3, PPh_5 and other products, depending on the size of the R-group.[157,158] Syeferth reported on the reaction of lithiumalkyls with tetraphenylphosphonium salts.[159,160]



Scheme 53: Reaction of complex **29** with tetraphenylphosphonium chloride in dme.

The observation that triphenylphosphine (PPh_3) is able to displace a carbonyl ligand from the **28** complex led us believe that this complex could be stabilized by phosphine or phosphite ligands.

Two equivalents of triphenylphosphine only partially displace a carbonyl ligand from **28** and a mixture of **28** and mono (**30**) and bis (**31**) triphenylphosphine nickel complexes is formed. Even a 20 fold excess of PPh_3 at room temperature is not able to fully convert phosphido complex **28** to the desired mono or bis PPh_3 nickel phosphido complex and a mixture of these two complexes is obtained (Scheme 54).

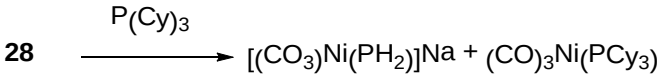


Scheme 54: Reaction of **28** with PPh_3 in dme to form complexes **30** and **31**.

As the reaction of PPh_3 did not fully convert complex **28** to bis phosphine complex (**31**) a chelating ligand might induce full conversion. Therefore, complex **28** was reacted with one equivalent of diphenylphosphinepropane (DPPP). Although the mono **32** and bridging **33**

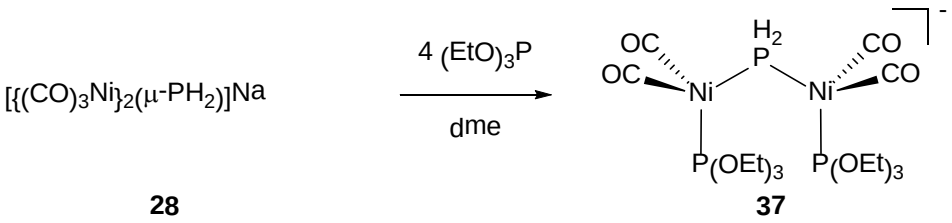
diphosphine coordinated species are formed, there is no full conversion, even with a twofold excess of DPPP.

The strongly electron donating and sterically hindered tricyclohexylphosphine (Cy_3P) is able to destabilize one of the Ni-PH_2 bonds when it is reacted with **28**; forming a mixture of $(CO)_3NiP(Cy)_3$, **29** and free ligand (Scheme 55).



Scheme 55: Reaction of **28** with $P(Cy)_3$ in dme to form **29** and $(CO)_3Ni(PCy_3)$.

To decrease the electron density on nickel and form more stable μ-PH_2 nickel complexes π-accepting phosphite ligands were tested. The reaction of triphenyl phosphite ($(PhO)_3P$) with **28** resulted in the formation of the mono **35** and bis **36** phosphite nickel phosphido complexes, similar to the reaction of PPh_3 with **28**. If however, a fourfold excess of triethyl phosphite ($(EtO)_3P$) is used, **28** is completely converted to the bis triethylphosphite nickel carbonyl complex (**37**) (Scheme 56). This complex can be isolated as a bright yellow liquid which is unstable. Complex **37** can be converted to the phosphonium salt by ion exchange with PPh_4Cl. This air sensitive and reactive complex can be isolated as an orange liquid.



28 **37**

Scheme 56: Preparation of $(CO)_3NiPH_2Ni(CO)_3$ (**37**) in dme from **28** and $(EtO)_3P$.

NMR spectroscopy of phosphido nickel carbonyl compounds

Nickel phosphido complexes **28**, **29** and **37** are completely characterized by NMR spectroscopy. In Table 3 the chemical shifts and coupling constants are given.

Table 3: NMR data for complexes **28**, **29** and **37**. [a] All spectra were recorded in thf-d_8 at room temperature.

Compound	^{1}H NMR[a]	^{31}P NMR[a]		^{13}C NMR[a]	
	[ppm]	[ppm]	$^{1}J_{PH}$ [Hz]	[ppm]	$^{2}J_{PC}$ [Hz]
$NaPH_2$	-1.34	-298.9	151.6	-	-
29	-0.12	-260.8	170.9	203.72	6.7
28	1.22	-218.3	239.5	201.67	0.7
37	1.25	-215.9	227.0	204.93	4.3; 11.1

Upon reaction of sodium dihydrogenphosphide with $Ni(CO)_4$ to form **29** the chemical shift of the hydrogen and phosphorus atoms shift to higher frequency by 1.22 ppm in ^{1}H NMR and 38.1 ppm in ^{31}P NMR respectively compared to dihydrogenphosphide. The $^{1}J_{PH}$ coupling constant increases by 29.3 Hz indicating a slight increase in the *s* character of the P-H bond.[161] Formation of the μ-PH_2 nickel carbonyl complex **28** results in a shift to higher frequency of the hydrogen and phosphorus chemical shift by 1.10 ppm in ^{1}H NMR and 42.5 ppm ^{31}P NMR respectively compared to **29**. The $^{1}J_{PH}$ coupling constant of this complex is 239.5 Hz and is comparable to other phosphido bridged metal complexes.[100,104,108,109,162-164] Coordination of triethyl phosphite to complex **28** has a negligible effect on both hydrogen and phosphorus chemical shifts.

Bodner *et al.* studied the effect of phosphorus ligands on the ^{13}C NMR shift of transition metal carbonyl complexes.[165] In case of $LNi(CO)_3$ complexes a high correlation between the metal carbonyl chemical shifts and ν-CO frequencies was found. Because of this correlation, with the help of ^{13}C NMR chemical shift of the carbonyl ligands a parameter of the ratio of σ basicity to the π acidity of L can be determined. This parameter can be obtained by subtracting the chemical shift value of $Ni(CO)_4$ from the value for $LNi(CO)_3$. Increase of the magnitude of this parameter implies an increase in the ratio of the σ basicity to the π acidity or a net increase in the donor ability of L.[165] As expected, although dihydrogenphosphide is not a tertiary phosphorus ligand, the ^{13}C chemical shift of the carbonyl ligands is shifted by 12.1 ppm to higher frequency compared to $Ni(CO)_4$ ($\delta_{Ni(CO)4}$ = 191.6 ppm) for **29**. This implies a higher degree of σ basicity of sodium dihydrogenphosphide as ligand. The ^{13}C chemical shift of μ-PH_2 metal complex **28** is slightly less shifted from $Ni(CO)_4$, this is due to the fact that some of the electron density of sodium dihydrogenphosphide is spread over two nickel metal centers. This is in agreement with the ν(CO) data of complexes **28** and **29**, vide infra. Compared to the bridging phosphido nickel complex **28**, coordination of two triethyl

phosphite ligands only slightly shifts the ^{13}C signal of the carbonyl ligands to higher frequency. Triethyl phosphite is a relatively weak π accepting phosphite compared to other phosphite ligands.[166] However, compared to carbonyl ligands the π-accepting property of triethyl phosphite and phosphites is smaller,[167] accounting for the higher frequency shift of the carbonyl signal.

IR spectra of phosphido nickel carbonyl complexes

Nickel carbonyl complexes **28** and **29** are characterized by their IR spectra. In Table 4 the ν(CO) data are given.

Table 4: table of ν(CO) A_1 IR frequencies.

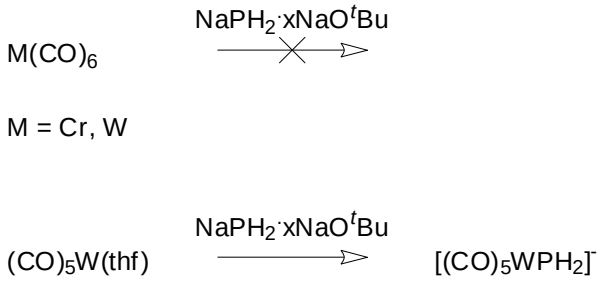
Compound	ν (cm^{-1})
$Ni(CO)_4$	2045
$Ni(CO)_3PPh_3$ (dcm)[168]	2063, 1987
$Ni(CO)_2(PPh_3)_2$ (dcm)[169]	1994, 1933
$(CO)_6Ni_2PR_2$ R= C_6H_{11} (thf)[156]	2030 (s), 2006 (st), 1945 (br, sst)
$(CO)_6Ni_2PR_2$ R= C_6H_5 (thf)[156]	2039 (s), 2019 (st), 1960 (br, sst)
$[Ni_2(CO)_4(\mu\text{-}PPh_2)_2]^{2-}$ [170]	1904, 1846
$[\{(CO)_3Ni\}_2(\mu\text{-}PH_2)]^-$ (**28**)	2022
$[(CO)_3Ni(PH_2)]^-$ (**29**)	2016, 1935 (br)
$[(CO)_4((EtO)_3P)_2Ni_2(\mu\text{-}PH_2)]^-$ (**37**)	1984, 1960, 1910

Compared to $Ni(CO)_4$ the ν(CO) A_1 frequencies of all phosphido nickel complexes are shifted to lower frequency. This is not unexpected since negative oxidation states decrease the ν(CO) frequency of carbonyl complexes.[167] Especially metal complex **37** has a low ν(CO) A_1 frequency due to the presence of two non π-accepting ligands. The observation that Cy_3P did not form the phosphido bridged analogue of **37** might be due to the fact that it is a strong electron donating ligand,[166,167] so strong that upon coordination the remaining carbonyl ligands are not able to compensate the increased electron density as π-acceptors and form the non bridging phosphido complex instead.

Reactivity of metal carbonyl complexes towards sodium dihydrogenphosphide

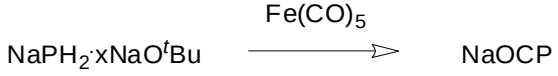
Interested in the reactivity of other metal carbonyl complexes with sodium dihydrogenphosphide, the reactivity of $M(CO)_6$ (M = Cr, W) and $Fe(CO)_5$ with sodium dihydrogenphosphide was investigated.

In contrast to the reaction of $Ni(CO)_4$ with sodium dihydrogenphosphide, the reaction of sodium dihydrogenphosphide with $M(CO)_6$ (M = Cr, W) is unselective. In the case of $Cr(CO)_6$ a black metallic powder is obtained, an insoluble orange powder is obtained in case of $W(CO)_6$ as starting material. According to literature, $[W(CO)_5PH_2]^-$ can be made starting from $(CO)_5W(thf)$ (Scheme 57).[108]



Scheme 57: Reaction of $M(CO)_6$ with sodium dihydrogenphosphide.

The reactivity of alkoxide packaged sodium dihydrogenphosphide with iron pentacarbonyl ($Fe(CO)_5$) is remarkably different from the previously described reactions. Instead of displacing a carbonyl ligand, as in $Ni(CO)_4$, to form phosphido complexes, alkoxide packaged sodium dihydrogenphosphide reacts with the carbonyl ligand to form phosphaalkyne NaO-C≡P (**38**) (^{31}P NMR δ = - 388 ppm) (Scheme 58).

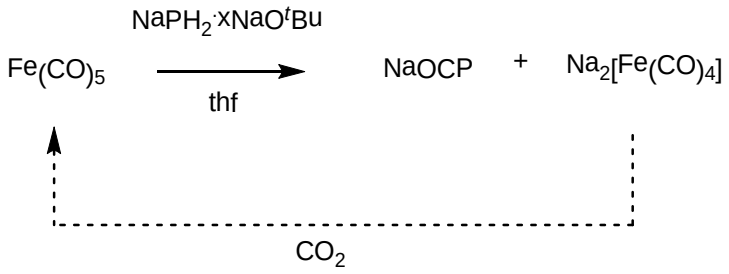


Scheme 58: Synthesis of NaOCP from $Fe(CO)_5$ and alkoxide packaged sodium dihydrogenphosphide.

The reaction is very fast, upon addition of iron pentacarbonyl to a solution of alkoxide packaged sodium dihydrogenphosphide, **38** is formed immediately. In the ^{31}P NMR no other phosphorus containing products could be observed. Because of the very fast reaction and

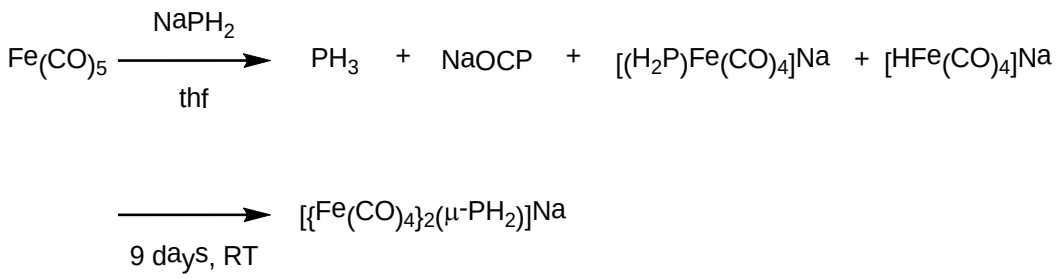
formation of **38**, the reaction was investigated in more detail in order to find a possible catalytic pathway for the synthesis of **38**.

Upon addition of $Fe(CO)_5$ to a solution of alkoxide packaged sodium dihydrogenphosphide in thf-d_8, **38** is formed immediately. $Fe(CO)_5$ is converted to $Na_2[Fe(CO)_4]$ [171] as indicated by ^{13}C NMR (^{13}C NMR δ = 231.5 ppm). From literature it is known that $Na_2[Fe(CO)_4]$ can be converted again to $Fe(CO)_5$ by the addition of CO_2.[172] Therefore, to obtain a catalytic cycle alkoxide packaged sodium dihydrogenphosphide was reacted with $Fe(CO)_5$ under a CO_2 atmosphere. Unfortunately, alkoxide packaged sodium dihydrogenphosphide reacts with CO_2 to form a gel of unknown composition (Scheme 59).



Scheme 59: Proposed catalytic cycle for the synthesis of NaOCP.

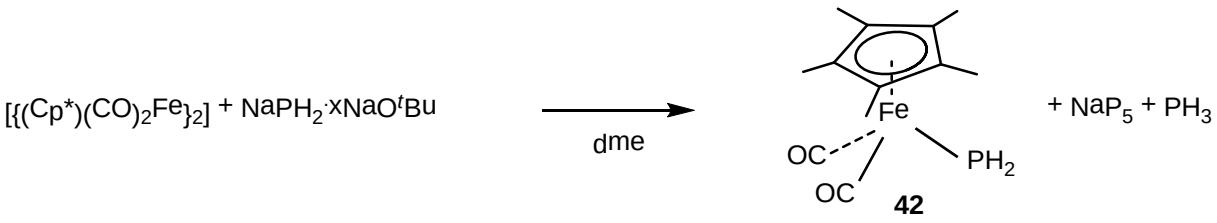
$Fe(CO)_5$ reacts differently with sodium dihydrogenphosphide and only a small amount of PH_2^- is converted to **38** according to ^{31}P NMR. The main phosphorus product observed is phosphine (PH_3) and small amounts of $Na[(H_2P)Fe(CO)_4]$ (^{31}P NMR δ = -196.2 ppm, $^1J_{PH}$= 147.9 Hz). Several iron carbonyl compounds are formed, for instance $Na[HFe(CO)_4]$ (Collmans reagent)[173], $Na_2[Fe_2(CO)_8]$ and residual $Fe(CO)_5$ [174] is present. Leaving this reaction mixture for over one week under an argon atmosphere, $[\{Fe(CO)_4\}_2(\mu\text{-}PH_2)]Na$[175] and an unknown compound (^{31}P NMR δ = 46.36 ppm (J_{PP}= 153.5 Hz), δ = 164.48 ppm (J_{PP}= 153.5 Hz)) are formed (Scheme 60).



Scheme 60: Reaction of $Fe(CO)_5$ with sodium dihydrogenphosphide.

These results suggest that the presence of sodium *tert*-butanolate is very important for the formation of **38**. This is confirmed by the addition of sodium *tert*-butanolate to a reaction mixture of sodium dihydrogenphosphide and $Fe(CO)_5$. Upon addition of sodium *tert*-butanolate and subsequent analysis of the reaction mixture **38** is the only phosphorus containing species present in solution according to ^{31}P NMR.

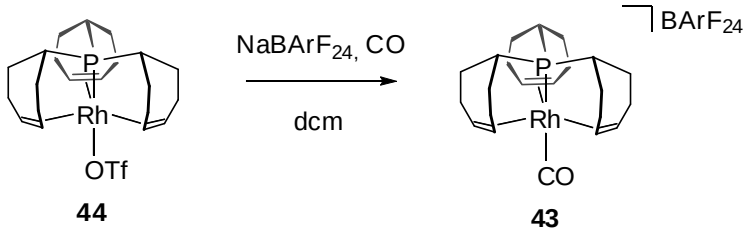
Another iron carbonyl complex was tested for its reactivity towards alkoxide packaged sodium dihydrogenphosphide. It was hoped that in other carbonyl complexes the carbonyl ligand could be activated to form **38**. Cyclopentadienyliron dicarbonyl dimer (**41**) was reacted with alkoxide packaged sodium dihydrogenphosphide at room temperature (Scheme 61).



Scheme 61: Reaction of Cyclopentadienyliron dicarbonyl dimer with alkoxide packaged sodium dihydrogenphosphide.

From ^{31}P NMR the formation of NaP_5 (^{31}P NMR δ = 467 ppm) and complex (**42**) (^{31}P NMR δ = -173.2 ppm (t, $^1J_{PH}$ = 149.8 Hz))[176] were observed. However, also phosphine and a broad signal for the Na_3P_7 cluster could be determined in the reaction mixture; this reaction is thus not very selective. Interesting is the formation of NaP_5 and Na_3P_7 as reaction products, the iron carbonyl compound is able to oxidize sodium dihydrogenphosphide to polyphosphides. The use of iron, or other metal complexes, could therefore also be a way to develop a new and high yield synthesis route towards NaP_5.

A selective reaction and possibly catalytic reaction for the formation of **38** with metal complexes would be an interesting idea. Therefore, an attempt was made to synthesize $(trop_3P)FeCO$. However, the route chosen for the synthesis of this complex was not working. Therefore the similar complex $[(trop_3P)RhCO]BArF_{24}$ (**43**) was synthesized.



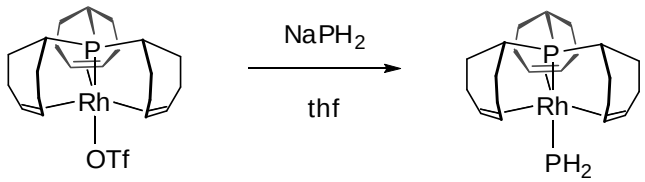
44 **43**

Scheme 62: Synthesis of [(trop$_3$P)RhCO]BarF$_{24}$ from [(trop$_3$P)RhOTf] and CO.

[(trop$_3$P)RhCO]BArF$_{24}$ (**43**) was synthesized from (trop$_3$P)RhOTf (**44**) and CO in dcm in high yield (Scheme 62). **43** was reacted with NaPH$_2$, however, several products were formed, without the formation of **38**. One of the formed products was (trop$_3$P)RhPH$_2$ (**45**) although only in very small amounts. The formation of this rhodium complex with PH_2^- in the axial position was interesting because no phosphido rhodium complexes are known so far.

Synthesis of (trop$_3$P)RhPH$_2$ (45)

Complex **45** can be selectively prepared from **44** and sodium dihydrogenphosphide. It cannot be isolated as a pure solid and in solution after standing for several days a black precipitation was formed (Scheme 63).



44 **45**

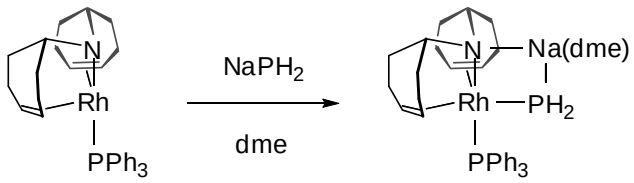
Scheme 63: Synthesis of (trop$_3$P)RhPH$_2$ from NaPH$_2$ and (trop$_3$P)RhOTf.

Phosphido complex **45** is comparable to the diphenylphosphido complex (trop$_3$P)RhPPh$_2$ and the phenylphosphide complex (trop$_3$P)RhPHPh synthesized by Fischbach.[177] Compared to free alkoxide packaged sodium dihydrogenphosphide, the ^{31}P NMR chemical shift of the phosphido ligand is shifted to higher frequency by 167 ppm to δ = -131.6 ppm. The ^{31}P NMR signal of the trop$_3$P ligand is shifted to lower frequency by 13.7 ppm to δ = 177.7 ppm. The signal for the trop$_3$P ligand is in a similar chemical shift range as the diphenylphosphido

rhodium complex reported by Fischbach (^{31}P NMR δ = 176.7 ppm). In ^{1}H NMR the phosphido chemical shift is centered at δ = 0.09 ppm, a shift to higher frequency of 1.43 ppm compared to alkoxide packaged sodium dihydrogenphosphide, with a $^{1}J_{PH}$ coupling constant of 156.3 Hz. As expected, the small $^{1}J_{PH}$ coupling constant of the phosphido group is an indication that the formed complex is a non bridging phosphido group. Interested in the structure and properties of these complexes, other phosphido rhodium complexes were synthesized.

Synthesis of [(trop$_2$N)Rh(PPh$_3$)PH$_2$]Na(dme) (46)

Phosphido complex **46** can easily be prepared from (trop$_2$N)RhPPh$_3$ and sodium dihydrogenphosphide in dme in 75% yield (Scheme 64).



46

Scheme 64: Synthesis of [(trop$_2$N)Rh(PPh$_3$)PH$_2$]Na(dme) from (trop$_2$N)RhPPh$_3$ and NaPH$_2$.

The bright red crystalline complex is very stable and is the first example of an isolated PH_2^- rhodium complex. An unusual feature of this complex is that the phosphido ligand is a non bridging ligand. There are only a few examples of terminal phosphido complexes and these are all very unstable. Complex **46** can be stored under argon at room temperature for a few months.

^{31}P NMR gives a clear indication for the formed product. Two separate signals, a broadened doublet at δ = -168.5 ppm and a doublet of doublets at δ = 44.4 ppm for PH_2^- and PPh$_3$ respectively with a $^{2}J_{PP}$ coupling constant of 9.1 Hz. In ^{1}H NMR spectrum the PH$_2$ signal is a double doublet at δ = 0.45 ppm with a $^{1}J_{PH}$ coupling constant of 180.5 Hz. The olefinic hydrogen signals are at δ = 3.64 ppm and δ = 3.94 ppm, a shift of 1.05 ppm and 1.68 ppm to lower frequency compared to starting material [Rh(trop$_2$N)(PPh$_3$)]. A similarly shift 0.86 ppm to lower frequency is observed for the benzylic hydrogen atoms of both compounds. A shift to lower frequency is also observed in the ^{13}C NMR spectra for the olefinic carbon groups (δ =

56.8 ppm and δ = 62.0 ppm for **46**; δ = 76.2 ppm and δ = 84.5 ppm for [Rh(trop$_2$N)(PPh$_3$)]), indicating strong back donation from the phosphido ligand.

Crystal structure of [(trop$_2$N)Rh(PPh$_3$)PH$_2$]Na(dme)

Complex **46** crystallizes as bright red crystals from the reaction mixture (Figure 22).

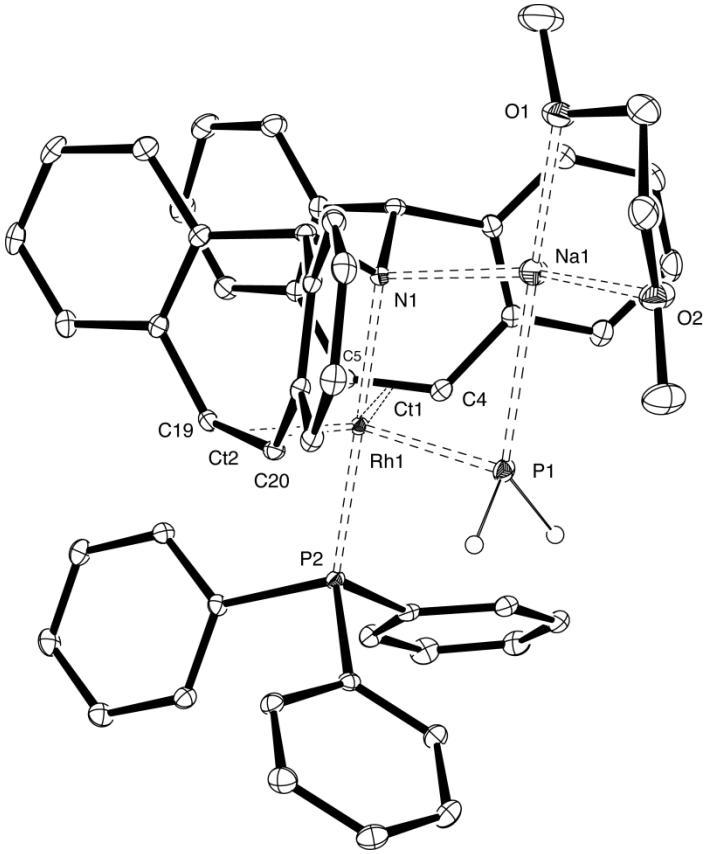


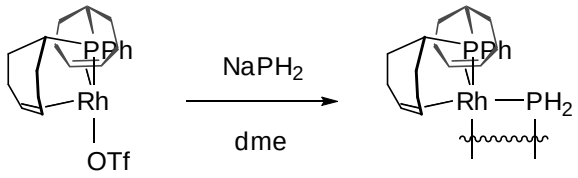
Figure 22: Crystal structure of [(trop$_2$N)Rh(PH$_2$)(PPh$_3$)]Na(dme). Measured bond lengths [Å] and angles [°] (Ct1 = centroid C4=C5, Ct2 = centroid C19=20): Rh-P1 2.4223(5), Rh-P2 2.3015(7), Rh-N1 2.167(2), Na1-P1 2.766(1), N1-Na1 2.466(2), Rh-Ct1 2.064, Rh-Ct2 2.049, Rh-C4 2.202(2), Rh-C5 2.166(3), Rh-C19 2.157(3), Rh-C20 2.186(2), C4=C5 1.430(3), C19=C20 1.436(3), N-Rh-P1 91.03, N-Rh-P2 178.91, Ct1-Rh-Ct2 141.87.

Compared to the structure of [Rh(trop$_2$N)(PPh$_2$tol)] the Rh1-P2 bond (2.4223 vs. 2.316 Å), and the Rh-N bond are significantly elongated in complex **46** (2.167 vs. 2.007 Å) and the N-Rh-PPh$_3$ is almost linear (178.91°) compared to complex [Rh(trop$_2$N)(PPh$_2$tol)] (166.18°). The increase in Rh-N bond length in complex **46** is caused by the increase of electron density on rhodium caused by PH_2^- as fifth ligand. This is confirmed by comparing the NMR data for complex **46** and that of the related compound [Rh(trop$_2$N)(PPh$_3$)] (see previous page). The increase in bond length is virtually non-existent for the C4-C5, C19-C20, Rh-Ct1 and Rh-Ct2

bonds (1.430, 1.436, 2.064 and 2.049 Å for complex **46** and 1.423, 1.407, 2.058 and 2.070 Å for [Rh($trop_2$N)(PPh_2tol)]).

Synthesis of [($trop_2$PPh)Rh(μ-PH_2)]$_2$ (47)

Phosphido bridging rhodium complex **47** can be prepared from ($trop_2$PPh)RhOTf in dme in moderate yield (Scheme 65).



47

Scheme 65: Synthesis of rhodium phosphido complex **47** from ($trop_2$PPh)RhOTf and sodium dihydrogenphosphide in dme.

The bright yellow complex is stable at room temperature under an argon atmosphere. It is almost insoluble in thf or dme and only ^{1}H and ^{31}P NMR data could be obtained.

Crystal structure of [($trop_2$PPh)Rh(μ-PH_2)]$_2$

Complex **47** crystallizes as bright yellow crystals from the reaction mixture (Figure 23).
The Rh1-P2-Rh1a bond angle is small (104.89°) compared to reported values in literature for phosphido complexes which contain no metal-metal bond (~120°). The Rh-PH_2 bonds in complex **47** (2.3899 and 2.3770 Å) are shorter than the Rh-PH_2 bond of complex **46** (2.4223 Å).

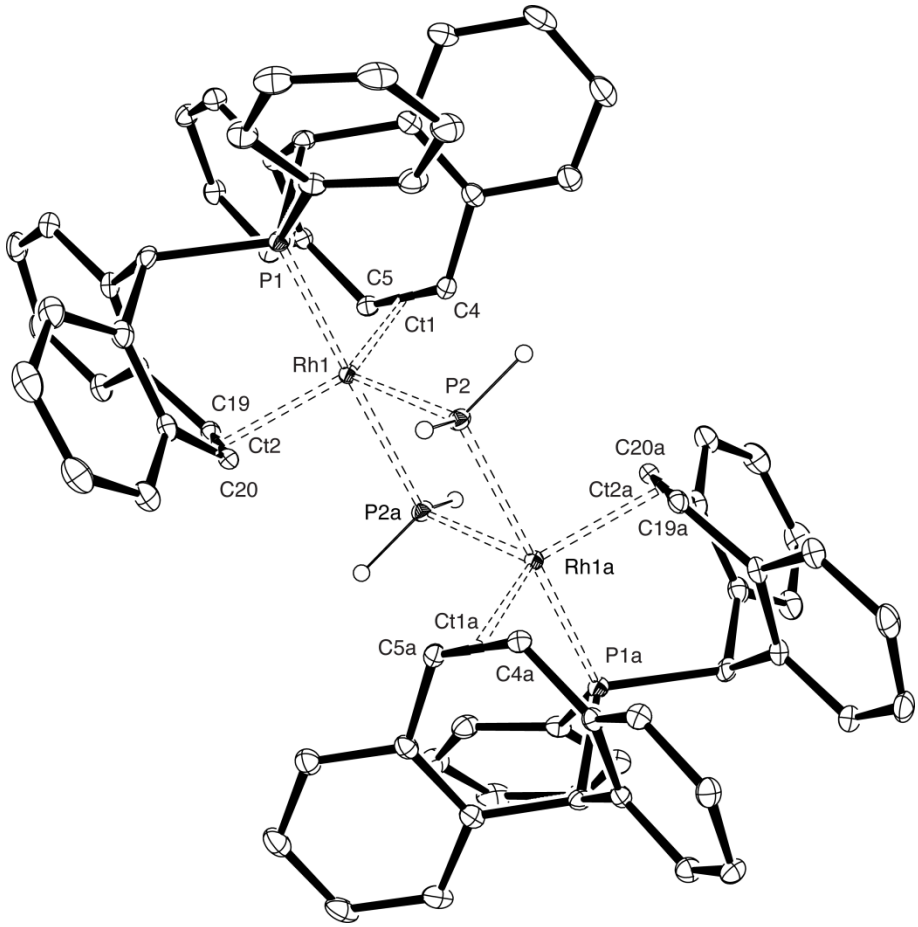
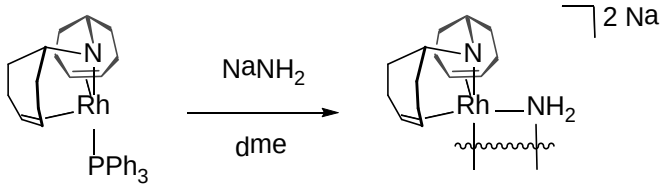


Figure 23: structure of $[(trop_2PPh)Rh(PH_2)]_2$, one dme solvent molecule omitted for clarity. Measured bond lengths [Å] and angles [°] (Ct1 = centroid C4=C5, Ct2 = centroid C19=20): Rh1-P1 2.2531(6), Rh1-P2 2.3899(6), Rh1a-P2a 2.3770(6), Rh1-Ct1 2.082, Rh1-Ct2 2.066, Rh1-C4 2.205(2), Rh1-C5 2.192(2), Rh1-C19 2.178(2), Rh1-C20 2.193(2), C4=C5 1.417(3), C19=C20 1.425(3), Rh1-P2-Rh1a 104.89, P1-Rh1-P2a 176.9, P1-Rh1-P2 101.85.

Synthesis of $[(trop_2N)Rh(\mu\text{-}NH_2)]_2$ (48)

In an attempt to compare phosphido complexes with amido rhodium complexes, the synthesis of the amido analogue of complex **46** was attempted. Rhodium amido complex **48** was synthesized from $(trop_2N)RhPPh_3$ and sodium amide in dme. The complex crystallizes slowly as bright orange crystals directly from the reaction mixture in about a week (Scheme 66).



48

Scheme 66: Synthesis of rhodium amide complex starting from $(trop_2N)RhPPh_3$ and $NaNH_2$ in dme.

The bright orange complex is very reactive and should be stored under an argon atmosphere. Interestingly, the formed complex has a different configuration compared to complex **46**, vide infra. Instead of the expected mono coordination of the amide, as in complex **46**, each rhodium complex is binding with two amide ligands. And these amido ligands are bridging ligands, instead of the terminal phosphido ligand of complex **46**. Interestingly, complex **48** is the only amido complex, derived from ammonia, known for rhodium. There are rhodium amido complexes known however,[178-182] these complexes are made from primary or secondary amines. NMR data of this complex could not be obtained because of its low solubility. However a crystal structure could be obtained.

Crystal structure of $[(trop_2N)Rh(\mu\text{-}NH_2)]_2Na_2(dme)_6$

Crystals of **48** suitable for X-ray analysis grew directly from the reaction mixture in dme (Figure 24).

Very recently, the first example of a rhodium amido complex was published online by Oro *et al.*[1] The three complexes were made through N-H activation of ammonia. Of the complexes formed, two were Rh_3N_3 six-membered metallacycles and a dinuclear complex. The reported Rh-N bonds of these complexes are between 2.058 and 2.089 Å, slightly shorter than the Rh-N bonds of complex **48** (between 2.092 and 2.195 Å).

[1] http://onlinelibrary.wiley.com/doi/10.1002/anie.201104745/pdf

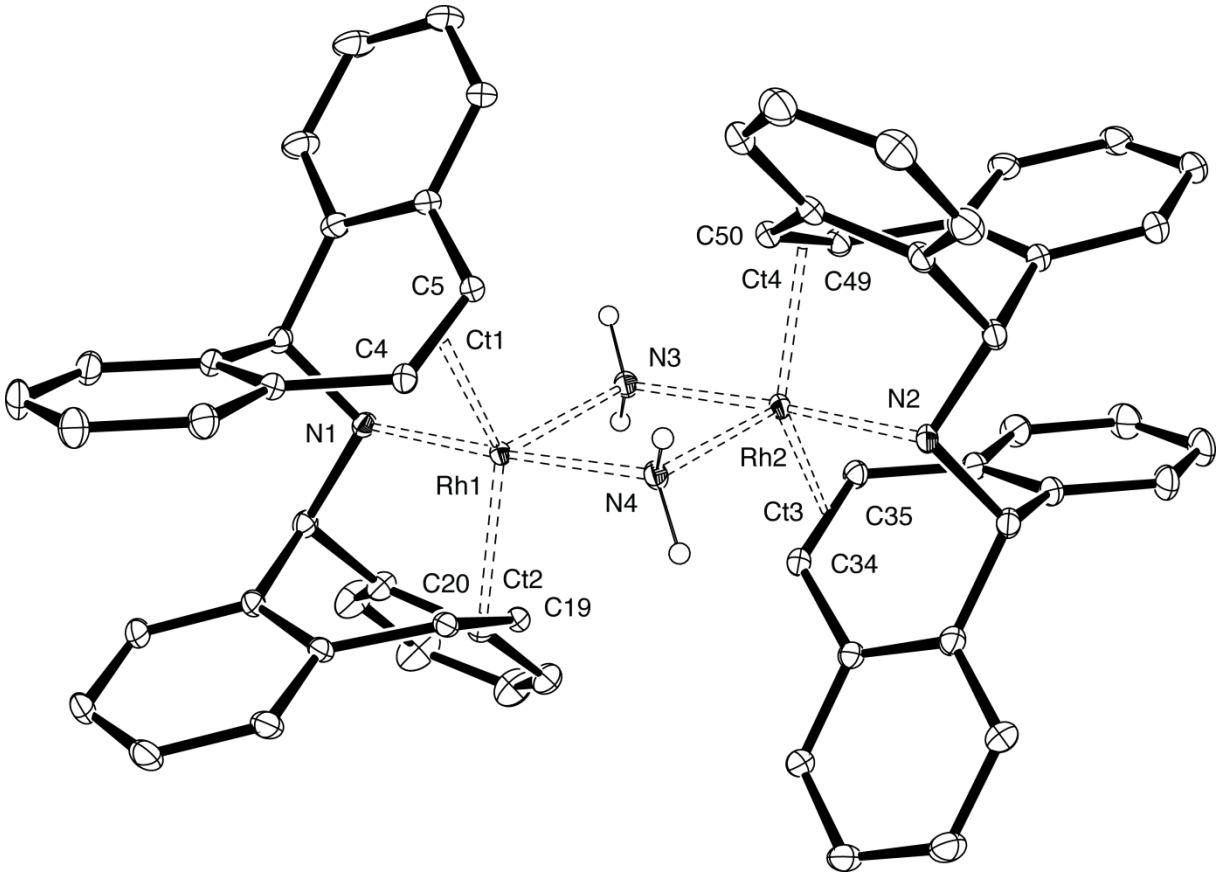


Figure 24: structure of $[(trop_2N)Rh(NH_2)]_2[Na_2(dme)_6]_2$, both $[Na(dme)_3]^+$ counterions are omitted for clarity. Measured bond lengths [Å] and angles [°](Ct1 = centroid C4=C5, Ct2 = centroid C19=20, Ct3 = centroid C34=C35, Ct4 = centroid C49=C50): Rh1-N1 2.084(2), Rh1-N3 2.179(2), Rh1-N4 2.104(2), Rh2-N2 2.082(2), Rh2-N3 2.092(2), Rh2-N4 2.195(2), Rh1-Ct1 1.994, Rh-Ct2 1.991, Rh1-C4 2.129(2), Rh1-C5 2.112(2), Rh1-C19 2.109(2), Rh1-C20 2.126(2), Rh2-Ct3 1.993, Rh2-Ct4 2.001, Rh2-C34 2.109(2), Rh2-C35 2.129(2), Rh2-C49 2.125(2), Rh2-C50 2.128(2), C4=C5 1.441(2), C19=C20 1.468(3), C34=C35 1.439(2), C49=C50 1.442(2), Rh1-N3-Rh2 102.86, Rh1-N4-Rh2 101.93, N1-Rh1-N3 94.37, N1-Rh1-N4 172.03, N2-Rh2-N3 173.71, N2-Rh2-N4 96.17.

Diffusion measurements of $[(trop_3P)Rh]X$ cation complexes

Fischbach reported an equilibrium between $[(trop_3P)Rh(H_2O)]PF_6$, $[(trop_3P)Rh]PF_6$, and $(trop_3P)RhOH$ after the addition of water to complex $[(trop_3P)Rh]PF_6$. The interest was focused on the formation of the $(trop_3P)RhOH$ complex because it could be a potential precursor for rhodium oxo complexes (Rh=O) and a possible source for $OH^{\bullet}$ and $Rh^{\bullet}$ radicals. $[(trop_3P)Rh]PF_6$ formed clusters in dichloromethane as determined from PGSE diffusion measurements and ^1H, ^{19}F HOESY measurements.[177] However, instead of coordination to the expected free axial position of rhodium, PF_6^- is interacting with the benzylic protons of the $trop_3P$ ligand.[183] Interested in the unexpected ion pair coordination of $[(trop_3P)Rh]PF_6$

complex, the coordination behavior of OTf^- and $BArF_{24}^-$ with the $[(trop_3P)Rh]^+$ cation was investigated. An overview of the chemical shift data of the $(trop_3P)RhX$ (X = OTf^-, $BArF_{24}^-$, PF_6^-) complexes is given in **Table 5**.

Table 5: NMR data of $[(trop_3P)Rh]X$ (X = OTf^-, $BArF_{24}^-$, PF_6^-) complexes in CD_2Cl_2.

Compound	^{31}P NMR		^1H NMR [ppm]		^{13}C NMR [ppm]	
	[ppm]	[Hz]	H_{olef}	H_{benz}	C_{olef}	C_{benz}
$[Rh(trop_3P)]OTf$	190.5	164	5.95	3.84	79.4^{thf}	48.4^{thf}
$[Rh(trop_3P)]BArF$	187.2	162	5.74	3.86	80.2	48.8
$[Rh(trop_3P)]PF_6$	194.9	157	6.13	4.30	79.7	48.0

Fischbach reported the synthesis of $[(trop_3P)Rh(H_2O)]OTf$ (**51**) from $(trop_3P)RhCl$ and AgOTf. However, the formation of the aqua complex (**51**) instead of $[(trop_3P)Rh]OTf$ (**44**) was quite puzzling because dry solvents and reactants were used and the primary reason for the formation of the aqua complex was based on the crystal structure of the complex.[177] As for $[(trop_3P)Rh]PF_6$, the coordinated water molecule should be slightly acidic and an equilibrium was expected between $[(trop_3P)Rh(H_2O)]OTf$, $[(trop_3P)Rh]OTf$ and $(trop_3P)RhOH$, however, no equilibrium was found for this complex. Therefore PGSE diffusion measurements and ^1H, ^{19}F HOESY on a freshly prepared batch of $(trop_3P)RhOTf$ were used to make a distinction between the formation of aqua complex (**51**) or $[(trop_3P)Rh]OTf$ complex (**44**) (Figure 25).

As can be seen in Figure 25 there is a strong correlation in the ^1H, ^{19}F HOESY spectrum between the olefinic protons of the $trop_3P$ ligand and the fluorine atoms of the OTf^- anion. This is a strong indication that the OTf^- anion coordinates to the free axial site of the rhodium metal complex forming complex $(trop_3P)RhOTf$ (**44**) (Scheme **67**: Synthesis of (trop3P)RhOTf from AgOTf and (trop3P)RhCl.Scheme 67). Furthermore, the PGSE diffusion constants for both triflate anion and metal complex are similar, therefore, these compounds must be interacting with each other forming the $(trop_3P)RhOTf$ (**44**) complex.

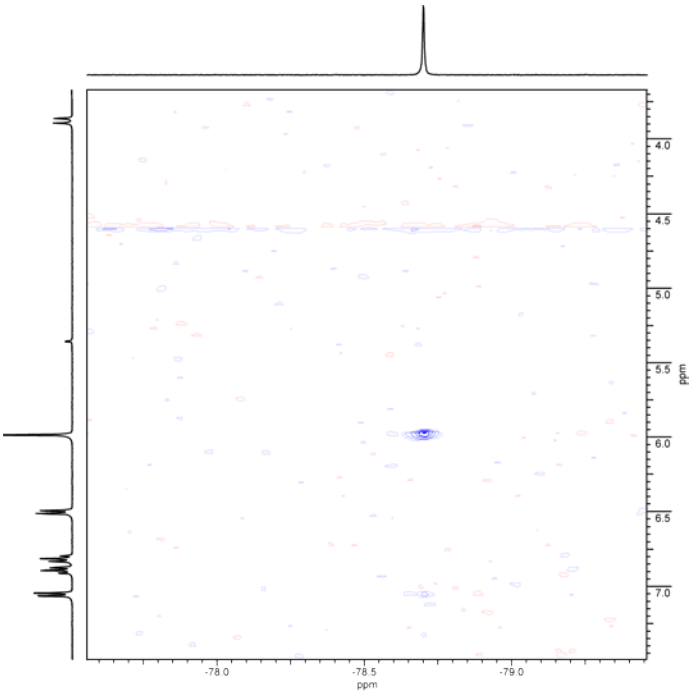
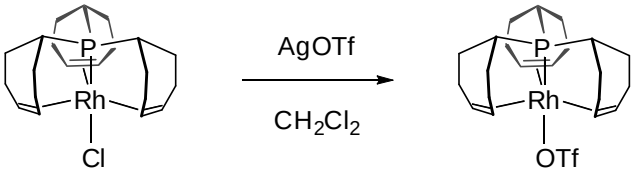


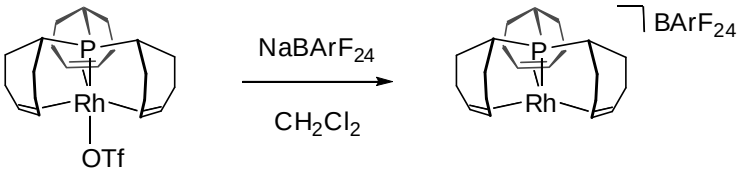
Figure 25: ^{1}H, ^{19}F HOESY NMR of ($trop_3P$)RhOTf (**44**) in CD_2Cl_2.



44

Scheme 67: Synthesis of ($trop_3P$)RhOTf from AgOTf and ($trop_3P$)RhCl.

The water complex **51** observed by Fischbach as crystal structure is probably formed during the crystallization and is not present when the complex is made under strict exclusion of air and water. A crystal structure of **44** was obtained by Fischbach when [($trop_3P$)Rh(PPh_2)] was oxidized by FcOTf. This structure shows the triflate anion coordinated to the rhodium on the free axial site of the metal complex as a tightly bound ion pair.[177] Addition of one equivalent of water to complex **44**, to generate aqua complex [($trop_3P$)Rh(H_2O)]OTf resulted in the direct precipitation of a yellow powder which is insoluble in all common organic solvents. In an attempt to generate the hydroxide species, either in equilibrium or as single species, complex ($trop_3P$)RhBArF_{24} (**49**) was synthesized (Scheme 68).



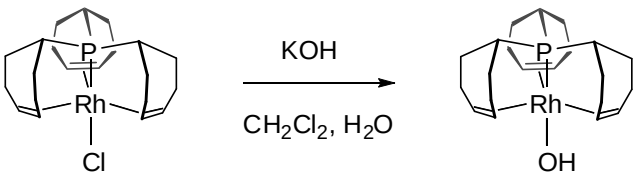
44 **49**

Scheme 68: Synthesis of [(trop$_3$)Rh]BArF$_{24}$ from (trop$_3$P)RhOTf in dcm.

It was thought that the counter anion would form a free ion pair with [(trop$_3$P)Rh]$^+$, thereby increasing the solubility of the complex and probably also the solubility of [(trop$_3$P)Rh(H$_2$O)]BArF$_{24}$. PGSE diffusion measurements of complex **49** indicated the formation of a free ion pair complex, while no ^{1}H, ^{19}F HOESY correlation between complex and anion was observed. Therefore, complex **49** exists as a free ion pair in solution. Upon addition of H$_2$O to complex **49** a yellow solid appears and in ^{1}H and ^{31}P NMR, no evidence is found for an equilibrium between [(trop$_3$P)Rh]BArF$_{24}$, [(trop$_3$P)Rh(H$_2$O)]BArF$_{24}$, and [(trop$_3$P)Rh(OH)]. Therefore, other routes had to be developed to synthesize [(trop$_3$P)Rh(OH)]. In the next part, the synthesis and reactivity of [(trop$_3$P)Rh(OH)] and related compounds is described.

Synthesis of (trop$_3$P)RhOH and (trop$_3$P)RhXPh (X = O, S, Se)

Although [(trop$_3$P)Rh(OH)] was not observed in an equilibrium reaction of complex **44** or **49** with H$_2$O, a direct method for the synthesis of the desired rhodium hydroxide complex was found. The proposed hydroxide rhodium complex could be formed starting from (trop$_3$P)RhCl and KOH in a water/dichloromethane biphasic mixture (Scheme 69).

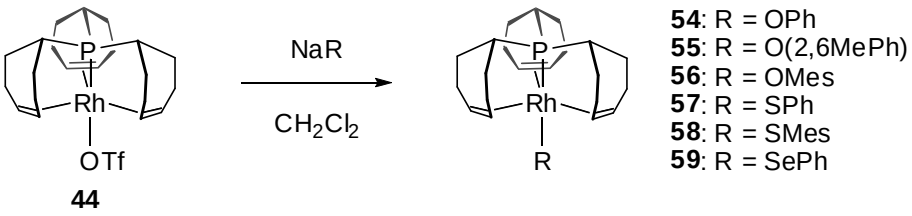


52 **53**

Scheme 69: Synthesis of (trop$_3$P)RhOH starting from KOH and (trop$_3$P)RhCl in a water/dichloromethane mixture.

This mixture was vigorously stirred for two days at room temperature. ^{31}P NMR analysis of the reaction mixture revealed the slow formation of a complex (^{31}P NMR: δ 178 ppm ($^{1}J_{RhP}$ = 135 Hz)). Another method to prepare **53** is to react **44** with a NaOH solution in dcm or thf. Again, the formed species has the same spectral parameters as the compound described earlier; therefore, in two different synthesis routes the same species can be made. It was impossible to obtain a crystal structure of (trop$_3$P)RhOH. The formation of (trop$_3$P)RhCl from (trop$_3$P)RhOH is always observed and is the only species which crystallized. A reason for this observation is that (trop$_3$P)RhOH forms radicals in solution under the influence of light and therefore is unstable in solution. Therefore the focus was turned to other group 16 containing ligands for [(trop$_3$P)Rh]$^+$ complexes. It was thought that these ligands would be more stable and therefore offer a better platform to investigate the formation of radical species [(trop$_3$P)Rh] or phenoxyl (PhO$^\bullet$) radicals under UV irradiation or via oxidation reactions. Phenoxyl radicals are interesting because, for instance, copper catalyzed radical polymerization of 2,6-dimethylphenol leads to poly(2,6-dimethyl-1,4-phenylene oxide), which, used in combination with polystyrene is an engineering plastic with sales approaching one billion dollar per year.[184-186]

In addition to the formed hydroxide complex also the phenoxide and derivatives were made (Scheme 70).



44

Scheme 70: Synthesis of (trop$_3$P)RhXPh (X = O, S, Se) complexes from (trop$_3$P)RhOTf and the corresponding sodium salts.

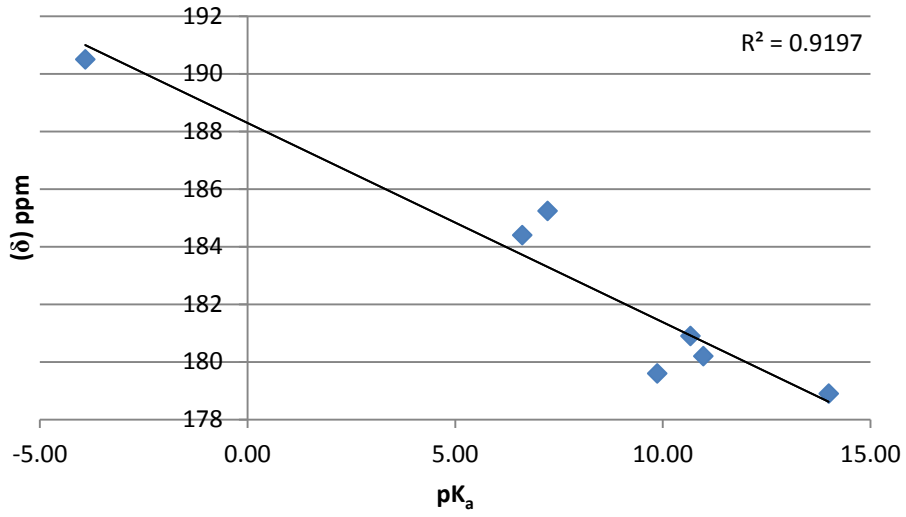
The ^{31}P NMR signals are in a similar chemical shift range, this is also an indication that complex (trop$_3$P)RhOH was formed (Table 6).

Table 6: NMR data of ($trop_3P$)RhOH compared to ($trop_3P$)RhCl and other group 16 complexes. [a] All spectra were measured in CD_2Cl_2.

Compound	^{1}H NMR[a]		^{31}P NMR[a]	
	H_{benz}	H_{olef}	[ppm]	$^1J_{PH}$ [Hz]
($trop_3P$)RhCl	3.97	5.93	191.7	148
($trop_3P$)RhOH (**53**)	3.84	5.52	178.9	135
($trop_3P$)RhOPh (**54**)	3.86	5.67	179.6	146
($trop_3P$)RhO(2,6MePh) (**55**)	3.80	5.90	180.9	147
($trop_3P$)RhOMes (**56**)	3.80	5.88	180.2	147
($trop_3P$)RhSPh (**57**)	3.98	5.54	184.4	134
($trop_3P$)RhSMes (**58**)	3.93	5.62	185.6	134
($trop_3P$)RhSePh (**59**)	-	-	-	-

A range of ($trop_3P$)RhXPh (X = O, S and Se) complexes was prepared. When the ^{31}P NMR chemical shift data of these complexes was correlated with the pKa of the corresponding alcohols and thiol ligands, a linear correlation (R^2 = 0.9197) seems to exist between the pKa of the ligand and the chemical shift of the phosphorus atom of the $trop_3P$ ligand (Chart 1). However, this correlation is only obtained from the 7 complexes prepared, and only tested for group 16 complexes. More complexes need to be prepared to obtain further reliable correlation data. These data suggests that the increased basicity of the axial ligand results in a decrease of the ^{31}P NMR frequency, thus increasing the electron density on phosphorus.

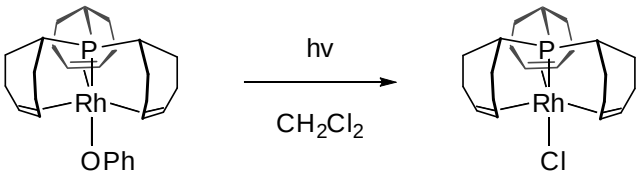
Chart 1: Correlation chart between the pK_a of the axial group 16 ligands and the ^{31}P NMR chemical shift of phosphorus of ($trop_3P$). All NMR-data was collected in CD_2Cl_2. The pK_a data was taken from R.Williams[187] and Bordwell.[188]



UV experiments with ($trop_3P$)RhXPh complexes (X = O, S)

In order to form phenoxyl radicals or rhodium centered radicals, the prepared phenoxide rhodium complexes were irradiated with UV-light. Complex **54** in dcm was completely converted to the complex ($trop_3P$)RhCl within two hours (Scheme 71). This could be caused by the formation of rhodium radical species with the abstraction of a chloride molecule from dichloromethane. The same sample did not decompose to ($trop_3P$)RhCl in dcm when placed at room temperature under the exclusion of light. Heating a sample of RhOPh in dcm for several hours did not result in the decomposition of the complex, thereby excluding heat as a possible trigger for this reaction. Reactions with radical traps under UV irradiation, like for instance nitrosobenzene which is a common radical trap for phenoxyl radicals,[189-191] in dichloromethane or thf did not result in the spin trapping of radical species or EPR signals, in thf, no reaction was observed at all. The stability of phenoxazine-10-oxyl radicals formed in the reaction of phenoxyl with nitrosobenzene is low in dichloromethane.[191]

UV irradiation of **55** in dcm showed in the formation of the expected ($trop_3P$)RhCl complex, but also the formation of 3,3',5,5'-tetramethyldiphenoquinone (DPQ). DPQ is the C-C coupled radical adduct of 2,6-dimethylphenol.

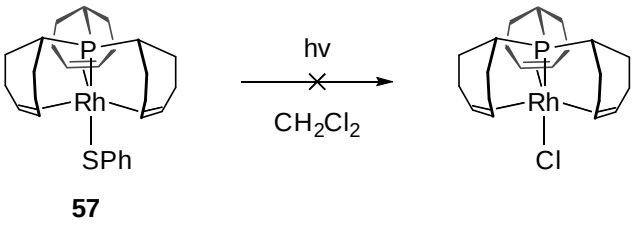


54

Scheme 71: hν irradiation of ($trop_3P$)RhOPh in dcm.

The thought was that it could be possible to spin trap the formed radicals when more stable radical species could be formed from the metal complex. Therefore, complex ($trop_3P$)RhSPh (**57**) was tested in the UV irradiation experiments. The yellow product was only slightly soluble in dichloromethane, however, not in thf or other common solvents. To complement this row of metal complexes, also ($trop_3P$)RhSePh (**59**) was tested, this complex is insoluble in thf, dichloromethane, chloroform, DMSO, therefore hampering the UV irradiation

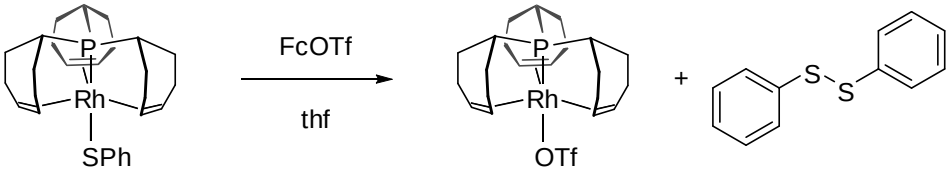
experiments. UV irradiation of complex **57** for two hours did only marginally decompose this complex to ($trop_3P$)RhCl, indicating that this complex is much more stable under UV irradiation in dcm than complex **54**, or the low solubility hampers the formation of thiyl radicals (Scheme 72).



57

Scheme 72: hν irradiation of ($trop_3P$)RhSPh in dcm.

Radical species formed by complex **57** could not be observed in EPR experiments and also spin trapping with nitrosobenzene did not produce measurable stable radicals. Although the formation of diphenyldisulfide was observed when complex **57** was oxidized by FcOTf, suggesting that the phenylsulfide ligand is reduced in a radical reaction and a $[(trop_3P)Rh]^+$ complex is formed (Scheme 73). Several mild oxidation reactions of sulfur compounds are known and all produce diphenyl disulfide as main product.[192-194]



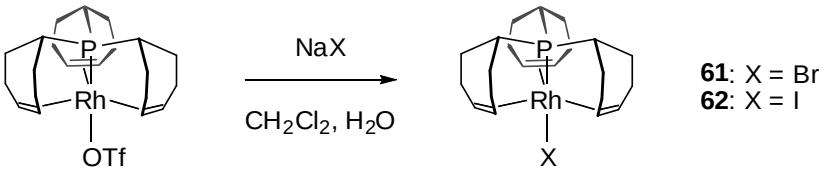
57 **44**

Scheme 73: Oxidation of ($trop_3P$)RhSPh with FcOTf in thf to form ($trop_3P$)RhOTf and diphenyl disulphide.

Another test to determine if thiyl radicals were formed is the thiyl radical mediated cleavage of allylic C-N bonds.[195,196] For this reason N-allyl dicyclohexylamine[195] was synthesized and oxidized together with ($trop_3P$)RhSPh by FcOTf in thf. No indication of C-N bond cleavage was found in the reaction, therefore, no conclusive radical reaction pathway for the formation of diphenyl disulfide was found.

Synthesis of ($trop_3P$)RhX (X = Cl, Br and I) complexes

Several ($trop_3P$)RhX (X = Cl, Br (**60**) and I (**61**)) complexes were made to investigate the influence of halogen exchange on the frequency shift of the phosphorus atom of the $trop_3P$ ligand trans to the halogen (Scheme 74). As observed for group 16 ligands, group 17 elements could have a similar effect.



Scheme 74: Synthesis of ($trop_3P$)RhX (X = Br and I) starting from ($trop_3P$)RhOTf in dcm.

Starting from rhodium complex **44**, complex **60** and **61** could be synthesized in high yield by the addition of an excess of NaX (X = Br or I) dissolved in a small amount of water. The addition of NaF to complex **44** did not form ($trop_3P$)RhF and only starting material was recovered.

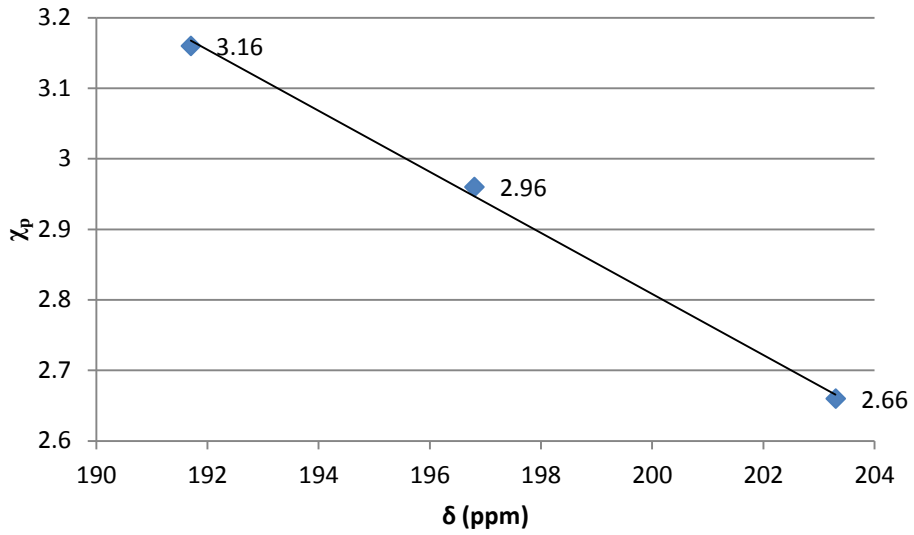
Table 7: NMR data of complexes ($trop_3P$)RhCl, 60 and 61 in CD_2Cl_2.

Compound	^{31}P NMR		^{1}H NMR [ppm]		^{13}C NMR [ppm]	
	[ppm]	Hz	H_{olef}	H_{benz}	C_{olef}	C_{benz}
[($trop_3P$)RhCl]	191.7	147.5	5.93	3.97	79.4	48.4
[($trop_3P$)RhBr]	196.8	148.2	6.03	3.93	78.7	48.7
[($trop_3P$)RhI]	203.3	146.8	6.28	3.92	76.8	48.9

Changing the halogenides in the axial position of the metal complex does not significantly affect the NMR properties of the metal complex. In general, the ^{31}P chemical shift of the $trop_3P$ ligand is shifted to higher frequency, going from 191.7 ppm for the chloride to 203.3 ppm for iodine. This is also observed in the previously described complexes when going from O to S the frequency of the phosphorus atom in ($trop_3P$) increased. Plotting the ^{31}P NMR chemical shift against the revised Pauling electronegativity (χ_p)[197] of the halogenides, a linear correlation is observed (R^2 = 0.9979) (Chart 2). It is already known that a convincing correlation between electronegativities and chemical shifts exists.[198] In this case an increase in

the electronegativity of the axial halogen ligand increases the electron density on the phosphorus atom.

Chart 2, Correlation between revised Pauling electronegativity (χ_p) of the halogenides and ^{31}P NMR chemical shift of the trop$_3$P ligand of complexes (trop$_3$P)RhCl, (trop$_3$P)RhBr and (trop$_3$P)RhI in CD_2Cl_2.



A similar, however small, increase in frequency is observed for the olefinic proton chemical shifts in the ^{1}H NMR. All the other frequency shifts in ^{1}H and ^{13}C NMR spectra are negligible. All attempts to crystallize these complexes for X-ray diffraction analysis were not successful, although a very rough picture of (trop$_3$P)RhI could be obtained which is similar to the already described (trop$_3$P)RhCl complex.

Conclusions

Several phosphido metal complexes can be synthesized, from the anionic nickel complex **25** to the formally neutral rhodium complexes **46** and **47**. Most of the trop containing metal complexes are stable at room temperature and the phosphido groups are relatively stable and unreactive. This is in contrast to the phosphido nickel carbonyl complexes **28**, **29** and **37**. These complexes are unstable and very reactive. Complex **29** reacts with tetraphenylphosphonium chloride to form triphenylphosphine and phenylphosphine. The phosphido nickel carbonyl complexes could be isolated however, these complexes are liquid,

and hence no crystal structures could be obtained. In contrast to nickel carbonyl, iron carbonyl reacts with alkoxide packaged sodium dihydrogenphosphide to form NaOCP. In this reaction iron carbonyl is converted to $Na_2[Fe(CO)_4]$. However, further conversion of $Na_2[Fe(CO)_4]$ to $Fe(CO)_5$ by CO_2 is inhibited by sodium dihydrogenphosphide which reacts with CO_2 to form a gel of unknown composition. The reaction of sodium dihydrogenphosphide is remarkably different from the alkoxide packaged one and sodium *tert*-butanolate is essential for the formation of NaOCP from $Fe(CO)_5$ and sodium dihydrogenphosphide. When only dihydrogenphosphide is used, the main phosphorus containing product observed in ^{31}P NMR is phosphine. However, phosphine can be converted into NaOCP in the presence of sodium *tert*-butanolate, $Na[HFe(CO)_4]$ and $Fe(CO)_5$.

Several group 16 $(trop_3P)Rh$ metal complexes were made. These complexes, especially the oxygen containing complexes are unstable under UV light irradiation and formation of $(trop_3P)RhCl$ is determined in dichloromethane. Reaction of complex **57** with FcOTf resulted in the formation of diphenyl disulphide, although slowly, and $(trop_3P)RhOTf$. This is an indication that radical species are formed during the oxidation of the sulphide. Some evidence for the generation of metallo radicals is provided by the slow decomposition of complex **49** in light in dichloromethane to form $(trop_3P)RhCl$.

Chapter 6

Chapter 6. General Conclusions and Outlook

Two new convenient synthesis routes towards sodium dihydrogenphosphide were found. The use of white phosphorus assures a higher reactivity and more selectivity in reactions at room temperature compared to reactions with red phosphorus requiring high pressures and the use of ammonia. The first route uses primary amines in a solvent mixture with white phosphorus, sodium and *tert*-butanol, an adaptation of the Benkeser reduction. Yields of up to 90% have been achieved with $MeNH_2$ as primary amine, however, this amine has a low boiling point and offers no real advantages over the older methods requiring liquid ammonia. However alkoxide packaged sodium dihydrogenphosphide can be prepared under mild reaction conditions with ethylenediamine as primary amine in high yields. In this reaction procedure, white phosphorus is reduced to trisodium heptaphosphide and subsequent addition of *tert*-butanol results in the formation of alkoxide packaged sodium dihydrogenphosphide at room temperature. The use of other primary amines like isopropylamine or ethylamine resulted in the formation of sodium dihydrogenphosphide, although in considerably lower yields. The reaction progress in these reactions was examined and resulted in a better understanding of the reaction sequences which in turn can be the base for improved reaction conditions.

A second method for the synthesis of alkoxide packaged sodium dihydrogenphosphide circumvents the use of primary amines. In this procedure, naphthalene is used as an electron carrier for the reduction of white phosphorus. The reaction is performed at room temperature and gives alkoxide packaged sodium dihydrogenphosphide in high yield (70%). The advantage of this route is the possibility to form BAPO compounds in a one pot procedure, without the need to change solvents or removing ammonia or primary amines.

With the use of alkoxide packaged sodium dihydrogenphosphide new routes towards sodium bis(mesitoyl)phosphide were investigated. From these investigations, it became clear that sodium *tert*-butanolate is the main reason for the low yields in the acylation step when mesitoyl chloride was used. Nucleophilic attack of sodium *tert*-butanolate at mesitoyl chloride resulted in the formation of *tert*-butyl mesitoyl ether. Exchanging mesitoyl chloride by several newly synthesized mesitoyl containing anhydrides and carbonic anhydrides only moderately acylated sodium dihydrogenphosphide, several side products were formed. When asymmetric anhydrides were used, mixed bis(acyl)phosphides were obtained. Analysis of the reaction products revealed that the sterically hindered side of the anhydride reacted not at all or

significantly slower. Therefore, anhydrides and carbonic anhydrides are not suitable reactants for the synthesis of bis(acyl)phosphides. To avoid using anhydrides and reduce the influence of sodium *tert*-butanolate on the yield of the reaction, the amount of sodium *tert*-butanolate was reduced. To a mixture of phosphorus and sodium with naphthalene only one equivalent of *tert*-butanol (compared to phosphorus) was used. When this amount of *tert*-butanol was used, a mixture of sodium dihydrogenphosphide, disodium hydrogenphosphide and trisodium phosphide was formed. This mixture reacts with mesitoyl chloride to form bis(mesitoyl)phosphide in good yield (79%).

Alkoxide packaged sodium dihydrogenphosphide can be used for the synthesis of pentaphosphacyclopentadienide. Pentaphosphacyclopentadienide was obtained in moderate yield (~40%) from the reaction of sodium dihydrogenphosphide with white phosphorus in the presence of benzophenone and crown ether. Benzophenone is reduced by sodium dihydrogenphosphide to the benzophenone ketyl radical. This radical could be detected by EPR and the reduced product diphenylmethanol was obtained from the reaction mixture. Even the reaction of sodium dihydrogenphosphide with benzophenone results in the formation of small amounts of sodium pentaphosphacyclopentadienide (~7%) and trisodium heptaphosphide clusters in 76% yield as bright crystalline solid. Other benzophenones and -quinones show similar behavior towards sodium dihydrogenphosphide. However, benzopinacolone reacts with sodium dihydrogenphosphide to form MAP. MAP is highly instable and decomposes quickly when it is isolated from solution. However, an X-ray structure could be obtained to confirm the product.

Several nickel carbonyl phosphido complexes have been made. These highly unstable complexes are very reactive and $[(CO)_3NiPH_2]^-$ reacts with tetraphenylphosphonium chloride to form triphenylphosphine and pentaphenylphosphine. The isolated metal complexes are liquid at room temperature and decompose when isolated even at low temperature. In contrast, iron pentacarbonyl has a markedly different reactivity versus nickel carbonyl with alkoxide packaged sodium dihydrogenphosphide. Iron carbonyl reacts with alkoxide packaged sodium dihydrogenphosphide to form NaOCP. This reaction is very fast converting iron carbonyl to $Na_2[(CO)_4Fe]$. Sodium dihydrogenphosphide reacts with iron pentacarbonyl to form only small amounts of NaOCP, however, large amounts of PH_3 were produced. This can be converted to NaOCP by the addition of sodium *tert*-butanolate. Therefore, the reaction to form NaOCP from iron carbonyl needs an excess of strong base to complete the reaction.

New phosphido rhodium metal complexes and one amide complex were synthesized. The phosphido complexes were relatively stable and some crystal structures could be obtained. However, the complexes were not reactive and no reaction could be developed for these complexes.

Outlook

The easy accessibility of alkoxide packaged sodium dihydrogenphosphide should offer new synthesis routes towards a variety of highly functionalized phosphorus compounds. As already tested in this thesis, primary phosphines are easily accessible and further transformations of the primary phosphines offer highly functionalized phosphines in simple reaction steps without the use of special equipment. Furthermore, phosphido metal complexes are easily accessible with the use of sodium dihydrogenphosphide. Selecting the right metal complex could favor new synthesis routes for highly functional phosphine compounds with phosphido metal complexes as intermediates.

The synthesis of NaP_5 in higher yields, compared to classical methods, could offer new and easy synthesis routes towards pentaphosphacyclopentadienide metal complexes. Starting from metal precursors with labile ligands, NaP_5 would be an interesting ligand, as it is isolobal to cyclopentadienide and therefore could have similar coordination behavior.

Chapter 7

Chapter 7. Experimental

7.1 Methods and Materials

General techniques: all manipulations were carried out under the strict exclusion of air and moisture on a standard vacuum line in oven-dried flasks under an atmosphere of argon. Solvents were distilled under argon from sodium/benzophenone (toluene, thf, diethyl ether, dme, and tetraglyme), sodium/benzophenone/tetraglyme (hexane), and calcium hydride (CS_2). Air sensitive compounds were stored and weighed in gloveboxes (M Braun: lab master 130). Reactions in small quantities were performed within the glovebox.

White phosphorus: non purified white phosphorus was stored under water in the absence of air and light. White phosphorus was purified by washing with acetone, ethanol and subsequently diethyl ether and dried under vacuum. Care should be taken during vacuum drying because of sublimation of white phosphorus, use large flasks and do not apply vacuum above room temperature. White phosphorus was further purified by dissolving it in CS_2, filtration and evaporation of the solvent yielding a white waxy solid. All the solvent fractions should be carefully handled and rinsed with a 5 % $CuSO_4$ solution to dispose of dissolved white phosphorus.
White phosphorus is highly pyrophoric, it burns in oxygen and carbon monoxide, and is very toxic, as little as 50 mg can be fatal to humans.

(Alkoxide packaged) sodium dihydrogenphosphide is a very pyrophoric compound which burns when it comes into contact with air. Sodium dihydrogenphosphide was stored at -30 °C to prevent decomposition. It reacts violently with water under the formation of phosphine and with primary and secondary alcohols. Large amounts of sodium dihydrogenphosphide were destroyed by the slow addition of 2-propanol into a solution of sodium dihydrogenphosphide in thf under an argon atmosphere. Afterwards all glassware was rinsed with a sodium hypochlorite solution to oxidize all remaining phosphides.

(Alkoxide packaged) trisodium heptaphosphide is a very pyrophoric compound which burns when it comes into contact with air. Trisodium heptaphosphide was stored at -30 °C to prevent decomposition. It reacts violently with water and alcohols. Large amounts of trisodium heptaphosphide were destroyed by the slow addition of 2-propanol to a solution of

trisodium heptaphosphide in thf. Afterwards all glassware was rinsed with a sodium hypochlorite solution to oxidize all remaining phosphides.

"Na_3P" is a very pyrophoric compound which burns violently when it comes into contact with air. "Na_3P" was stored at -30 °C to prevent decomposition. It reacts violently with water and alcohols. Large amounts of "Na_3P" were destroyed by the slow addition of 2-propanol to a suspension of "Na_3P" in thf under an argon atmosphere. Afterwards all glassware was rinsed with a sodium hypochlorite solution to oxidize all remaining phosphides.

Nickel Carbonyl: is a volatile and extremely toxic liquid. Reactions with nickel carbonyl should be performed in a well ventilated fume hood. Nickel carbonyl solution in dme was stored at -30 °C. For preparative use, the nickel carbonyl solution was kept constantly at -20 °C in an ice bath. An excess of nickel carbonyl can be quenched by the addition of an ethereal solution of triphenylphosphine. Upon addition of an excess triphenylphosphine CO is released and the less volatile and toxic $Ni(CO)_3PPh_3$ is formed.

Chemicals: basic chemicals were ordered at ABCR, Acros, Aldrich, Fluka or TCI. White phosphorus was obtained from Thermphos. Benzophenone was sublimed prior to use. Ethylene diamine was dried over MolSieves 4Å, distilled and stored over MolSieves 4Å. Anthraquinone; 4,4'-dichlorobenzophenone; 4,4'-dimethylbenzophenone; 4,4'-dimethoxybenzophenone; 9,10-phenanthrenequinone and benzopinacolone were recrystallized from ethanol and dried under high vacuum at 45°C for 2 days. 18-Crown-6-ether was recrystallized three times from acetonitrile and dried under high vacuum. Mesitoyl acid chloride was distilled prior to use. Mesitoyl methyl ester and mesitoyl ethyl ester were distilled over Na_2SO_4 under vacuum and stored over MolSieves 4Å. Isopropylamine and *n*-propylamine were distilled under argon from CaH_2 and stored over MolSieves 4Å.
The following organic and metal organic compounds were prepared according to literature methods: $NaPH_2$, MesCOOAg, TosAg, $[cp^*FeBr(\mu\text{-}CO)CO]_2$, $(CO)_4FePPh_3$, $(phen)_3CuCl_2$, $(trop_2PPh)RhOTf$, $(trop_2N)RhPPh_3$, $(trop_2NH)NiPPh_3$, $(trop_2NH)NiOAc$, $(trop_3P)RhOTf$, $(trop_3P)RhCl$.

EPR spectroscopic investigations were performed in collaboration with the group of Prof. Koppenol at the laboratory of inorganic chemistry at the ETH Zürich (Dr. Reinhard Kissner).

Electron paramagnetic resonance spectra were obtained with a Bruker EMX 080 equipped with a microwave-bridge ER 041 XG and the dielectric mixing resonator ER 4117 D-MVT. The instrument settings used in a typical experiment were: gain = 2×10^4; resolution = 1024 points; measurement field = 3382 G; microwave power = 0.6362 mW; modulation amplitude = 0.1 G; frequency = 9.497 GHz. Data acquisition and analysis were carried out with AQUISIT software (Bruker). Spectra were simulated with WinSim 2002. The samples were brought into the cavity by means of a regular EPR tube.

IR spectra were recorded on a Perkin-Elmer-Spectrum 2000 FT-IR-Raman spectrometer with KBr beam splitter (range 500-4000 cm^{-1}). Solution spectra of air stable substrates were measured in a 0.5 mm KBr cell, for solid compounds the ATR technique was applied. Solution spectra of highly air sensitive compounds were measured on a Mettler Toledo ReactIR^{tm}4000 FT-IR spectrometer in collaboration with the group of Prof. Togni at the laboratory of inorganic chemistry at the ETH Zürich (Dr. Jan Welch). The absorption bands are described as follows: strong (s), very strong (vs), middle (m), weak (w), or broad (br).

Mass spectra of organic compounds were recorded on a Finnigan MAT SSQ 7000 mass spectrometer using electron ionization. GC-MS measurements were performed on a Finnigan MAT GCQ combined with a MAT SSQ 7000 mass spectrometer using electron ionization.

Melting points were determined with a Büchi melting point apparatus and are not corrected. Samples were prepared in open glass capillaries when not air sensitive. Air sensitive compounds were prepared in sealed glass capillaries.

Solution NMR spectra were recorded on Bruker Avance 700, 500, 400, 300, 250 and 200 MHz spectrometers at room temperature. The chemical shifts (δ) are measured according to IUPAC and expressed in ppm relative to TMS, H_3PO_4 for ^1H, ^{13}C and ^{31}P respectively. The assignments were accomplished by multidimensional methods. Coupling constants *J* are given in Herz (Hz) as absolute values. Where a first order analysis is appropriate, the multiplicity of the signals is indicated as s, d, t, q, or m for singlets, doublets, triplets, quartets, or multiplets respectively. Quaternary carbons are indicated as C_{quat}, aromatic carbon atoms as C_{aryl}, and olefinic carbon atoms as C_{olef} when not noted otherwise.

X-ray crystallographic measurements were performed on Bruker SMART 1K and SMART APEX platforms with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The reflex intensities were measured by CCD area detectors. The collected frames were processed with the proprietary software SAINT[199] and an absorption correction was applied (SADABS[200]). Solution and refinement of the structures were performed with SHELXS-97[201] and SHELXL-97[202] respectively. In general, all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in their idealized positions and allowed to ride on the respective carbon atoms. Associated crystallographic data and other experimental details are summarized in the crystallographic tables in Chapter 8.

7.2 Experimental Part

Experimental Part for Chapter 2

Synthesis of $NaPH_2 \cdot xNaO^tBu$ with $^iPrNH_2$ in toluene.

1.55 g (12.5 mmol) P_4 was completely dissolved in 75 mL toluene. To this solution 75 mL $^iPrNH_2$, ca. 10.8 mL (110 mmol, 2.2 eq.) HO^tBu and 3.45 g (150 mmol, 3eq.) freshly cut sodium parts (30-50 mg) were added successively. Immediately after addition of the sodium parts the reaction mixture became a dark red suspension. Within an hour the solution became yellow with sodium parts still present. Stirred for an additional 5 hours at RT, clear pale yellow solution, analysis of the reaction mixture showed the formation of $NaPH_2$ and Na_3P_7 in a ~30:1 ratio. The reaction mixture was filtered over celite and the filtrate was concentrated to dryness. The pale yellow solid was dried under vacuum and stored at -30 ^oC in the glove box. Yield: 12.5 g (28.3 mmol, 56.6 % calculated from P_4, $NaPH_2 \cdot 4NaO^tBu$)

^1H NMR (250.1 MHz, thf-d_8, 25^oC): δ (ppm) = - 1.34 (d, $^1J_{PH}$ = 153.9 Hz, 2H), 1.05 (s, 36H, $OC(CH_3)_3$).
$^{13}C\{^1H\}$ NMR (62.9 MHz, thf-d_8, 25^oC): δ (ppm) = 37.47 (s, $3CH_3$), 66.45 (s, C_{quat}).
^{31}P NMR (101.3 MHz, thf-d_8, 25^oC): δ (ppm) = -298.9 (t, $^1J_{PH}$= 153 Hz).

Analysis of the reaction of P_4, *tert*-Butanol and sodium in $^iPrNH_2$/toluene

300 mg (2.42 mmol) P_4 was completely dissolved in 15 mL toluene. To this solution 15 mL $^iPrNH_2$, ca. 1.85 mL (19.37 mmol, 2 eq.) HO^tBu and 668 mg (29.06 mmol, 2 eq.) freshly cut sodium parts (30-50 mg) were added successively. Immediately after addition of sodium a 0.5 mL aliquot of the reaction mixture was transferred to an NMR tube under an argon atmosphere. After 5, 10 and 60 minutes respectively another sample was taken and analyzed by ^{31}P NMR. Upon completion of the reaction, a final ^{31}P NMR measurement was performed. Because phosphine was formed during the reaction the samples were taken and transferred under an argon atmosphere with a syringe through a Teflon septum.

Equilibrium reaction between $NaPH_2 \cdot xNaO^tBu$, Na_3P_7 and HO^tBu

A Young NMR tube was charged with 22 mg (0.05 mmol) $NaPH_2 \cdot xNaO^tBu$ and 2 mg (0.025 mmol) HO^tBu in 0.5 mL thf. To this solution 17 mg (0.01 mmol) Na_3P_7 cluster was added and the resulting solution was analyzed by ^{31}P NMR.

Synthesis of $NaPH_2 \cdot xNaO^tBu$ in $MeNH_2$/toluene

A Schlenk tube equipped with a Teflon valve was charged with a solution of 300 mg (2.42 mmol) P_4 in 15 mL toluene and 1.95 mL (20.3 mmol, 2.1 eq.) HO^tBu. The solution was cooled to -78 °C and approximately 15 mL $MeNH_2$ was condensed into the Schlenk tube. The suspension was heated to -30 °C and subsequently 668 mg (29.1 mmol, 2 eq.) freshly cut sodium parts (30-50 mg) were added to this solution. The Schlenk tube was tightly closed and slowly heated to room temperature. This mixture was stirred for 12 hours. The resulting clear pale yellow solution was concentrated to dryness. The pale yellow powder was dried under vacuum and stored at -30 °C in the glove box.
Yield: 2.12 g (8.54 mmol, 88 %)

^{31}P NMR (101.3 MHz, thf, 25°C): δ (ppm) = -298.8 (t, $^1J_{PH}$= 152 Hz).

Synthesis of $NaPH_2 \cdot xNaO^tBu$ in ethylenediamine/toluene

To 300 mg (2.42 mmol) P_4 dissolved in 15 mL toluene and 15 mL ethylenediamine, 668 mg (29.06 mmol, 2 eq.) freshly cut sodium parts (30-50 mg) were added. The resulting mixture was stirred for four hours. To this orange/yellow reaction mixture with some black sodium parts 1.85 mL (19.37 mmol, 2 eq.) HO^tBu was added. The reaction mixture was stirred for an additional 12 hours. During the reaction the mixture turned into a yellow two phase system. The solution was concentrated to dryness. The resulting pale yellow powder was dried under vacuum and stored at -30 °C in the glove box.
Yield: 2.87 g (8.24 mmol, 85%).

^1H NMR (300.1 MHz, thf-d_8, 25°C): δ (ppm) = -1.35 (d, 2H, $^1J_{PH}$ = 151.6 Hz, PH_2), 1.05 (s, OC(CH_3)$_3$), 1.22 (s, br, 4H, NH_2), 2.61 (m, br, 4H, NC$H_{2(en)}$).

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, thf-d_8, 25°C): δ (ppm) = 37.5 ppm (s, *C*H_3), 45.9 (s, H_2NCH_2), 66.5 (s, O*C*$(CH_3)_3$).
^{31}P NMR (121.5 MHz, thf-d_8, 25°C): δ (ppm) = -298.9 (t, $^{1}J_{PH}$ = 152 Hz).

IR (ATR): 3370 (w), 3323 (w), 3256 (w), 2947 (s), 2855 (s), 1612 (w), 1591 (m), 1468 (m), 1372 (w), 1343 (m), 1310 (w), 1203 (vs), 1077 (w), 1053 (w), 1011 (w), 958 (vs), 943 (s), 877 (s), 744 (m).

Synthesis of $NaPH_2 \cdot xNaO^tBu$ with naphthalene

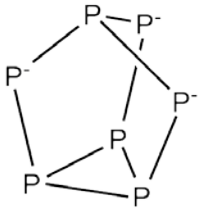
600 mg (4.84 mmol) P_4 and 248 mg (1.94 mmol, 10 mol%) naphthalene were suspended in 30 mL dme. To this suspension 1.34 g (58.11 mmol, 3 eq.) freshly cut Na parts (30-50 mg) were added. The reaction mixture was stirred for 12 hours during which it becomes a black suspension. To this black suspension 3.9 mL (40.7 mmol, 2.1 eq.) HO^tBu in dme was added dropwise. Upon addition of the alcohol the temperature of the suspension rises quickly and gas evolution was observed. The yellow/brown reaction mixture was stirred for an additional two hours. The solution was filtered over celite and the filtrate was evaporated to dryness. The pale yellow powder was dried under vacuum and stored at -30 °C in the glove box.
Yield: 5.80 g (77%)

^{1}H NMR (300.1 MHz, thf-d_8, 25°C): δ (ppm) = -1.35 (d, 2H, $^{1}J_{PH}$ = 153.1 Hz, P*H*$_2$), 1.05 (s, C*H*$_3$), 3.27 (s, 6H, OC*H*$_{3(dme)}$), 3.43 (s, 4H, OC*H*$_{2(dme)}$).
^{31}P NMR (121.5 MHz, thf-d_8, 25°C): δ (ppm) = -299.0 (t, $^{1}J_{PH}$ = 153 Hz).

IR (ATR): 2941 (s), 2852 (m), 1920 (w), 1459 (m), 1368 (m), 1341 (s), 1244 (w), 1205 (vs), 1126 (m), 1086 (vs), 1032 (w), 1016 (w), 960 (vs), 935 (s), 860 (s), 840 (m), 785 (m), 745 (m).

Synthesis of the $(Na_3P_7)_2.6NaO^tBu.6dme$ cluster (20)

MF: $C_{48}H_{114}Na_{12}O_{18}P_{14}$
M_r: 1688.92



To a suspension of 30 mg (0.25 mmol) P_4 in 10 mL dme, 265 mg (0.5 mmol) $NaPH_2 \cdot xNaO^tBu$ in 5 mL dme was added dropwise. This mixture was heated for 12 hours at 80 °C after which the yellow reaction mixture with a pale yellow precipitation was slowly cooled to room temperature. Upon cooling of the reaction mixture pale yellow crystals were formed. The crystalline solid was filtered off and dried under high vacuum for 2 hours. The pale yellow solid was stored at -30 ^oC in the glove box.
Yield: 115 mg (0.07 mmol, 82 %, calculated from $NaPH_2$)

Mp: > 220 °C.
^1H NMR (250.1 MHz, thf-d_8): δ (ppm) = 1.09 (s, CH_3), 3.31 (s, OC$H_{3(dme)}$), 3.47 (s, OC$H_{2(dme)}$).
^{31}P NMR (101.3 MHz, thf-d_8): δ (ppm) = -121.6 ppm (s, br).

IR (ATR): 3550 (br m), 2933 (br s), 2852 (m), 2821 (m), 1468 (s), 1447 (s), 1366 (m), 1344 (s), 1277 (w), 1241 (m), 1203 (s), 1124 (s), 1087 (vs), 1022 (s), 960 (vs), 861 (s), 840 (m), 747 (m).

"Na_3P"

To a mixture of 300 mg (2.4 mmol) P_4 and 248 mg (0.9 mmol) naphthalene in 20 mL dme, 668 mg (29 mmol) freshly cut sodium parts (30-50 mg) were added. This mixture became a dark suspension upon addition of sodium. The suspension was stirred vigorously for 12 hours. The suspension was left to stand to precipitate the black solid, decantation of the solution and

short drying under high vacuum yielded a black powder which was stored at -30 ^{o}C in the glove box.

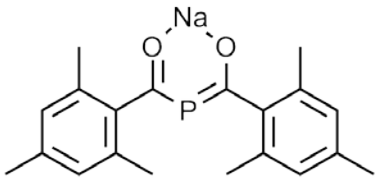
Yield: 1.19 g (the exact yield was not determined)

Experimental Part for Chapter 3

Synthesis of sodium bis(2,4,6-trimethylbenzoyl)phosphanide (1)

MF: $C_{20}H_{22}NaO_2P$

M_r: 348.35



1.50 g (12.11 mmol) P_4 and 620 mg (4.84 mmol, 10 mol %) naphthalene were suspended in 50 mL dme. To this suspension 3.34 g (145.3 mmol, 3 eq.) freshly cut sodium parts (30-50 mg) were added. The resulting mixture was stirred for 12 hours whereby a black suspension was formed. To this black suspension a diluted solution of 4.63 mL (48.43 mmol, 1 eq.) HO^{t}Bu in 15 mL dme was added dropwise. During addition of the alcohol the temperature of the suspension increased. The black suspension was stirred for an additional two hours. To this suspension 17.69 g (96.86 mmol) mesitoyl chloride was added dropwise. During addition of mesitoyl chloride the temperature increased rapidly. After addition of mesitoyl chloride the orange/yellow suspension was slowly cooled to room temperature. The suspension was filtered over celite and the filtrate was evaporated. The remaining yellow solid was suspended in ~80 mL toluene and the bright yellow precipitate was filtered off, yielding the first fraction of sodium bis(mesitoyl)phosphide. The remaining toluene solution of the filtrate was reduced to approximately 30 mL. A second fraction of sodium bis(mesitoyl)phosphide precipitated from the filtrate and was collected by filtration. The remaining yellow solution of the filtrate was evaporated and the remaining orange oil was washed with hexanes. Upon washing with hexanes a 3rd batch of sodium bis(mesitoyl)phosphide precipitated and the precipitate was combined with the second fraction. Both fractions were washed with hexanes (3x 20 mL) and dried under high vacuum yielding a pale yellow powder.

Fraction one: 12.15 g (27.7 mmol, 58 %), combined fractions (two and three): 3.67 g (10.5 mmol, 22 %) combined yield of bis(mesitoyl)phosphide 79 %.

Mp: 208 °C decomposition.

^{1}H NMR (300.1 MHz, C_6D_6, 25°C): δ (ppm) = 2.09 (s, C*H*$_3$, 6H), 2.49 (s, OC*H*$_2$), 2.56 (s, OC*H*$_3$), 2.59 (s, CH_3, 12H), 6.67 (s, H_{aryl}, 4H).
^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 25°C): δ (ppm) = 19.93 (br s, *C*H$_3$, 4C), 20.99 (s, *C*H$_3$, 2C), 58.01 (s, dme, *C*H$_3$), 70.11 (s, dme, *C*H$_2$), 128.31 (s, C_{aryl}, 4C), 133.78 (d, C_{quat}, $^{3}J_{CP}$ = 2.3 Hz, 4C), 136.46 (br s, C_{quat}, 2C), 145.36 (d, C_{quat}, $^{2}J_{CP}$ = 37.9 Hz, 2C), 236.2 (d, C_{quat}, $^{1}J_{CP}$ = 94.0 Hz, 2C).
^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6, 25°C): δ (ppm) = 83.1 (br s).

IR (ATR): 2915 (m), 1609 (m), 1557 (s), 1520 (s), 1470 (s), 1454 (s), 1417 (s), 1376 (m), 1296 (m), 1248 (m), 1204 (s), 1139 (s), 1113 (s), 1068 (m), 1030 (m), 983 (w), 957 (m), 883 (vs), 843 (vs), 720 (s), 677 (m), 630 (m).

Synthesis of sodium bis(2,4,6-trimethylbenzoyl)phosphanide (1)

To a suspension of 10 mg (~0.1 mmol) "Na_3P" in 5 mL dme, 62 mg (0.2 mmol) 2,4,6-trimethylbenzoic anhydride was added. The solution was stirred for 30 minutes at room temperature. Upon stirring the black suspension slowly turned into a clear yellow solution. ^{31}P NMR analysis showed the formation of sodium bis(mesitoyl)phosphide, no other side products were observed in ^{31}P NMR. The product was not isolated. From ^{31}P NMR data with an internal standard (triphenylphosphine) the yield of the reaction is approximately 30 %.

^{31}P{^{1}H} NMR (101.3 MHz, dme, 25°C): δ (ppm) = 82 (s).

Synthesis of sodium bis(2,4,6-trimethylbenzoyl)phosphanide (1)

To a solution of 344 mg (1 mmol) $NaPH_2 \cdot x NaO^tBu$ in 30 mL dme, 620 mg (2 mmol) 2,4,6-trimethylbenzoic anhydride was added. This mixture was stirred for one hour. The clear orange/yellow solution was evaporated yielding a yellow/orange solid. To this solid was added toluene and the mixture was left to stand for one week upon which a yellow product precipitated. The clear yellow solution was decanted and the remaining yellow precipitation was washed with hexane and dried under vacuum.
Yield: 251 mg (0.72 mmol, 72 %).

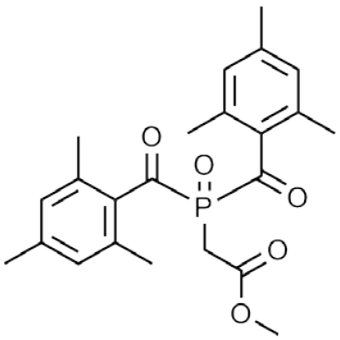
Synthesis of sodium bis(2,4,6-trimethylbenzoyl)phosphanide (1) from *p*-tolylsulfonic 2,4,6-trimethylbenzoic anhydride

To a solution of 172 mg (0.5 mmol) $NaPH_2 \cdot xNaO^tBu$ in 10 mL dme, 318 mg (1.0 mmol) 2,4,6-trimethylbenzoic tosylate was added. This mixture was stirred for 30 minutes and analyzed by ^{31}P NMR. According to the spectrum only partial conversion to bis(mesitoyl)phosphide was observed. Additional 105 mg (0.3 mmol) 2,4,6-trimethylbenzoic tosylate was added to the reaction mixture. According to ^{31}P NMR, mesitoyl phosphide was still present. This mixture was filtered over celite and the resulting bright yellow solution was evaporated yielding a yellow waxy solid.

Methyl 2-(bis(2,4,6-trimethylbenzoyl)phosphoryl)acetate (2)

MF: $C_{23}H_{27}O_5P$

M_r: 414.43



To 1.1 g (3.6 mmol) $NaPH_2 \cdot xNaO^tBu$ dissolved in 10 mL thf, 1.2 mL (7.19 mmol, 1.31 g) mesitoyl chloride in 10 mL thf was added dropwise. The resulting mixture was stirred for one hour at 0°C and two hours at room temperature. To the formed yellow suspension 0.34 mL (3.6 mmol, 0.55 g) methyl bromoacetate was added dropwise and the suspension was stirred for a further 12 hours. The suspension was filtered over celite and the solvent was evaporated to dryness. The residual yellow oil was dissolved in 15 mL ethanol and cooled to 0°C. To this solution 0.35 mL (3.6 mmol, 35 % solution in water) aqueous H_2O_2 solution was added dropwise. The reaction mixture was stirred for an additional 30 minutes at 0 ^oC and two hours at room temperature. The solution was evaporated and the yellow oil was crystallized from hexane yielding bright yellow crystals.

Yield: 0.78g (1.88 mmol, 52% yield calculated from mesitoyl chloride)

Performing reactions without diluted mesitoyl chloride affords 0.63 g (1.54 mmol, 43 %) Methyl 2-(bis(2,4,6-trimethylbenzoyl)phosphoryl)acetate.

Mp: 101-102 °C.

^{1}H NMR (300.1 MHz, C_6D_6, 25°C): δ (ppm) = 2.03 (s, C*H*$_3$, 6H), 2.44 (s, C*H*$_3$, 12H), 3.26 (s, OC*H*$_3$, 3H), 3.44 (d, C*H*$_2$, $^{2}J_{PH}$= 12.2 Hz, 2H), 6.61 (s, H_{aryl}, 4H).

^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 25°C): δ (ppm) = 20.04 (s, *C*H$_3$, 4C), 21.02 (s, *C*H$_3$, 2C), 34.74 (d, *C*H$_2$, $^{1}J_{CP}$= 48.89 Hz), 52.07 (s, OCH$_3$), 136.20 (d, C_{quat}, J_{CP}= 43.6 Hz, 2C), 136.71 (s, C_{quat}, 4C), 141.45 (s, C_{quat}, 2C), 165.7 (s, *C*OOMe), 214.13 (d, *C*=O, $^{1}J_{CP}$= 54.7 Hz, 2C).

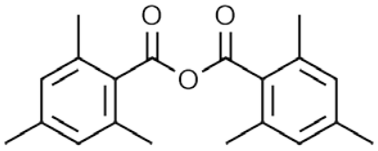
^{31}P NMR (121.5 MHz, C_6D_6, 25°C): δ (ppm) = 18.22 (t, $^{2}J_{PH}$= 12.33 Hz).

IR (ATR): 3010 (w), 2987 (w), 2953 (w), 2925 (w), 1742 (vs), 1669 (s), 1645 (s), 1606 (s), 1559 (w), 1455 (m), 1444 (m), 1424 (s), 1381 (m), 1296 (m), 1260 (vs), 1221 (s), 1203 (vs), 1152 (m), 1100 (s), 1134 (m), 1004 (s), 942 (w), 888 (m), 875 (vs), 865 (s), 849 (s), 821 (m), 764 (m), 739 (m), 712 (m), 648 (m), 621 (m).

Synthesis of 2,4,6-Trimethylbenzoic Anhydride (3)

MF: $C_{20}H_{22}O_3$

M_r: 310.39



To a suspension of 1.64 g (10 mmol) 2,4,6-trimethylbenzoic acid and 6 g K_2CO_3 in 100 mL ethyl acetate, 0.97 g (5 mmol) tosyl chloride in 5 mL ethyl acetate was added slowly. The suspension was stirred for 12 hours. Ethyl acetate was evaporated and the white residue was suspended in 100 mL toluene, and stirred vigorously for 10 minutes. The suspension was filtered over celite, the organic solution was dried over Na_2SO_4, filtered and evaporated. The highly pure white substrate was dried under high vacuum for several hours.

Yield: 1.32 g (4.25 mmol, 85 %).

Mp: 100 °C.

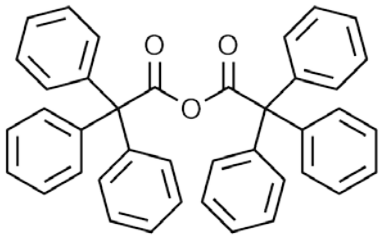
^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): δ (ppm) = 2.30 (s, C*H*$_3$, 3H), 2.41 (s, C*H*$_3$, 6H), 6.88 (s, H_{aryl}, 4H).

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 25°C): δ (ppm) = 20.02 (s, *C*H_3, 4C), 21.17 (s, *C*H_3, 2C), 128.85 (s, C_{aryl}, 4C and C_{quat}, 2C), 136.30 (s, C_{aryl}, 4C), 140.72 (s, C_{quat}, 2C), 165.37 (s, *C*=O, 2C).

IR (ATR): 2923 (w), 2159 (br), 1977 (br), 1788 (s), 1734 (s), 1609 (s), 1575 (m), 1453 (m), 1378 (w), 1216 (s), 1146 (s), 1035 (m), 971 (vs), 937 (vs), 848 (vs), 778 (vs), 729 (m), 710 (s), 600 (s), 548 (s).

Synthesis of 2,2,2-triphenylacetic anhydride (4)

MF: $C_{40}H_{30}O_3$
M_r: 558.66



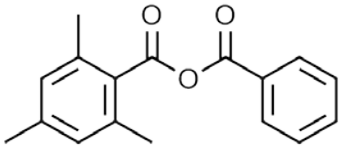
To a suspension of 2.88 g (10 mmol) triphenylacetic acid and 6 g K_2CO_3 in 250 mL ethyl acetate, 0.97 g (5 mmol) tosyl chloride was added slowly. The suspension was stirred for 12 hours. Ethyl acetate was evaporated and the white solid was suspended in 100 mL toluene, and stirred vigorously for 10 minutes. The solution was filtered over celite, the organic solution was dried over Na_2SO_4, filtered and evaporated. The highly pure white solid was dried under high vacuum for several hours. Triphenylacetic anhydride can be crystallized from hexane.
Yield: 1.85 g (3.3 mmol, 66 %).

Mp: 179 °C
^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ (ppm) = 7.03 (m, H_{aryl}, 6H), 7.23 (m, H_{aryl}, 9H)
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$, 25°C): δ (ppm) = 68.00 (s, C_{quat}, 2C), 127.02 (s, C_{aryl}, 6C), 127.92 (s, C_{aryl}, 12C), 129.98 (s, C_{aryl}, 12C), 141.36 (s, C_{quat}, 2C), 168.02 (s, *C*=O, 2C).

IR (ATR): 3055 (w), 2159 (br), 2029 (br), 1812 (s), 1749 (m), 1595 (m), 1492 (s), 1446 (s), 1189 (m), 1160 (m), 1092 (s), 1058 (vs), 1001 (s), 950 (vs), 913 (m), 899 (s), 835 (m), 761 (m), 743 (s), 718 (s), 693 (vs), 654 (m), 627 (s), 616 (s), 595 (s).

Synthesis of benzoic 2,4,6-trimethylbenzoic anhydride (5)

MF: $C_{17}H_{16}O_3$
M_r: 268.31



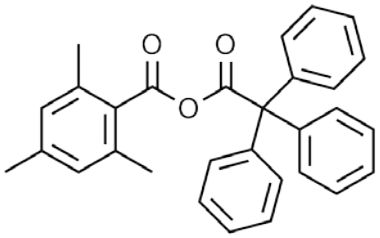
To 0.313 mL (3.45 mmol) benzoyl chloride in 20 mL toluene, 0.28 mL (3.5 mmol, 1.01 eq.) pyridine was added. This mixture was stirred for several hours and subsequently 0.566 mg (3.45 mmol) 2,4,6-trimethylbenzoic acid was added to the reaction mixture. The solution was stirred for a further 12 hours at room temperature. The suspension was filtered over celite and the solvent evaporated yielding a white solid.
Yield: 454 mg (49 %, 1.69 mmol).

Mp: 43-45 °C
^{1}H NMR (300.1 MHz, $CDCl_3$): δ (ppm) = 2.31 (s, C*H*$_3$, 3H), 2.45 (s, C*H*$_3$, 6H), 6.91 (s, H_{aryl}, 2H), 7.48 (m, H_{aryl}, 2H, $^1J_{HH}$= 7.9 Hz), 7.64 (m, H_{aryl}, 1H, J_{HH}= 1.3, 7.2 Hz), 8.08 (d, H_{aryl}, 2H, J_{HH}= 1.3, 7.9 Hz).
^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ (ppm) = 20.24 (s, *C*H$_3$, 2C), 21.21 (s, *C*H$_3$, C), 128.78 (s, C_{aryl}, 2C),128.87 (s, C_{quat}, C), 128.97 (s, C_{aryl}, 2C), 130.52 (s, C_{aryl}, 2C), 134.40 (s, C_{aryl}, C), 136.58 (s, C_{quat}, 2C), 140.92 (s, C_{quat}), 162.37 (s, *C*O), 165.26 (s, *C*O).

IR (ATR): 2925 (w), 1782 (s), 1721 (s), 1687 (br, m), 1610 (m), 1600 (m), 1584 (m), 1453 (m), 1425 (br, m), 1378 (m), 1326 (w), 1314 (w), 1294 (br, m), 1267 (m), 1253 (w), 1212 (vs), 1179 (m), 1153 (s), 1073 (w), 1032 (m), 1010 (s), 979 (vs), 947 (s), 849 (s), 799 (s), 747 (s), 697 (vs).

Synthesis of 2,4,6-trimethylbenzoic 2,2,2-triphenylacetic anhydride (6)

MF: $C_{30}H_{26}O_3$
M_r: 434.53



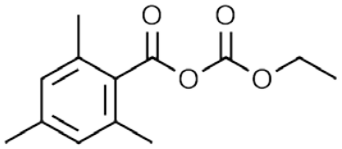
To 365 mg (2 mmol) mesitoyl chloride in 10 mL toluene, 0.16 mL (2 mmol, 1 eq.) pyridine was added. This mixture was stirred for three hours and subsequently 0.576 mg (2 mmol) 2,2,2-triphenylacetic acid was added to the reaction mixture. The solution was stirred for a further 12 hours at room temperature, filtered over celite and the organic solvent was evaporated yielding white solid. The product was purified by crystallization from hexanes yielding colorless crystals.
Yield: 209 mg (24 %, 0.48 mmol).

Mp: 128 °C.
^{1}H NMR (250.1 MHz, $CDCl_3$, 25°C): δ (ppm) = 2.05 (s, C*H*$_3$, 6H), 2.24 (s, C*H*$_3$, 3H), 6.76 (s, H_{aryl}, 2H), 7.29 (br, H_{aryl}, 15H).
^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$, 25°C): δ (ppm) = 19.67 (s, *C*H$_3$, 2C), 21.14 (s, *C*H$_3$, C), 68.17 (s, C_{quat}, C), 127.20 (s, C_{aryl}, 3C), 128.02 (s, C_{aryl}, 6C), 128.69 (s, C_{aryl}, 2C), 130.12 (s, C_{aryl}, 6C), 136.61 (s, C_{quat}, 2C), 140.68 (s, C_{quat}, C), 141.54 (s, C_{quat}, 3C), 165.00 (s, *C*O), 168.92 (s, *C*O).

IR (ATR): 2361 (w), 2159 (br), 1976 (br), 1802 (s), 1742 (s), 1611 (m), 1489 (m), 1446 (s), 1380 (w), 1236 (s), 1157 (m), 1103 (vs), 1077 (s), 1033 (m), 1015 (w), 975 (vs), 945 (vs), 897 (s), 846 (s), 770 (m), 758 (vs), 733 (s), 701 (vs), 665 (s), 621 (m), 602 (s), 592 (s), 553 (s).

Synthesis of (ethyl carbonic) 2,4,6-trimethylbenzoic anhydride (7)

MF: $C_{13}H_{16}O_4$
M_r: 236.36



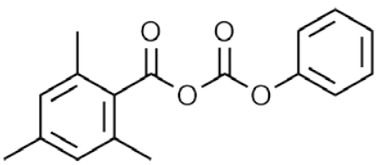
To 0.269 mL (3.45 mmol) ethyl chloroformate in 20 mL toluene, 0.28 mL (3.5 mmol, 1.01 eq.) pyridine was added. This mixture was stirred for several hours and subsequently 566 mg (3.45 mmol) 2,4,6-trimethylbenzoic acid was added to the reaction mixture. The solution was stirred for a further 12 hours at room temperature, filtered over celite and the solvent was evaporated yielding a colorless oil.
Yield: 438 mg (54 %, 1.85 mmol).

^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): δ (ppm) = 1.38 (t, C*H*$_3$, $^3J_{HH}$= 7.1 Hz, 3H), 2.29 (s, C*H*$_3$, $^3J_{HH}$= 7.1 Hz, 3H), 2.38 (s, C*H*$_3$, 6H), 4.37 (q, OC*H*$_2$, 2H), 6.87 (s, H_{aryl}, 2H).
^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25°C): δ (ppm) = 13.96 (s, *C*H$_3$), 20.08 (s, *C*H$_3$, 2C), 21.20 (s, *C*H$_3$), 65.77 (s, *C*H$_2$), 128.87 (s, C_{aryl}, 2C and C_{quat}), 136.67 (s, C_{quat}, 2C), 141.00 (s, C_{quat}), 149.33 (s, *C*O), 164.06 (s, *C*O).

IR (ATR): 2984 (w), 2919 (w), 1800 (s), 1748 (s), 1610 (m), 1457 (m), 1381 (m), 1369 (m), 1296 (m), 1265 (m), 1196 (vs), 1147 (vs), 1050 (s), 990 (vs), 933 (s), 897 (m), 852 (s), 772 (m), 711 (w), 691 (w).

Synthesis of benzoic 2,4,6-trimethylbenzoic anhydride (8)

MF: $C_{17}H_{16}O_4$
M_r: 284.31



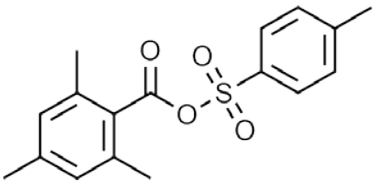
To 0.434 mL (3.45 mmol) phenyl chloroformate in 20 mL toluene, 0.28 mL (3.5 mmol, 1.01 eq.) pyridine was added. This mixture was stirred for several hours and subsequently 566 mg (6.9 mmol) 2,4,6-trimethylbenzoic acid was added to the reaction mixture. The solution was stirred for a further 12 hours at room temperature, filtered over celite and the solvent was evaporated yielding a colorless oil.
Yield: 464 mg (47 %, 1.63 mmol).

^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): δ (ppm) = 2.34 (s, C*H*$_3$, 3H), 2.48 (s, C*H*$_3$, 6H), 6.95 (s, H_{aryl}, 2H), 7.32 (m, H_{aryl}, 3H), 7.45 (m, H_{aryl}, 2H).
^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25°C): δ (ppm) = 20.22 (s, *C*H$_3$), 21.24 (s, *C*H$_3$), 120.76 (s, C_{aryl}, 2C), 126.74 (s, C_{aryl}), 129.03 (s, C_{aryl}, 2C), 129.56 (s, C_{quat}), 129.68 (s, C_{aryl}, 2C), 136.98 (s, C_{quat}, 2C), 141.40 (s, C_{aryl}), 147.87 (*C*O), 150.72 (s,C_{quat}), 163.49 (s, *C*O).

IR (ATR): 2976 (w), 2959 (w), 2925 (w), 1806 (s), 1749 (s), 1609 (m), 1591 (w), 1575 (w), 1493 (m), 1481 (m), 1455 (m), 1384 (w), 1267 (m), 1252 (m), 1186 (vs), 1141 (vs), 1071 (m), 1036 (m), 1011 (s), 995 (vs), 944 (vs), 858 (vs), 834 (m), 826 (m), 774 (m), 754 (vs), 709 (s), 691 (vs).

Synthesis of mesitoyl-*p*-toluenesulfonate (9)

MF: $C_{17}H_{18}O_4S$
M_r: 318.39



To 588 mg (2 mmol) silver *p*-toluene sulfonate suspended in 10 mL Et_2O, 365 mg (2 mmol) mesitoyl chloride was added dropwise. The suspension was stirred for 3 hours under the exclusion of light. The suspension was filtered over celite and evaporation of the organic solvent yielded a white solid. The solid was washed with hexanes and crystallized from Et_2O/hexanes at -30 °C.
Yield: 477 mg (75 %, 1.5 mmol).

Mp: 79 °C

^{1}H NMR (300.1 MHz, CD_2Cl_2, 25°C): δ (ppm) = 2.23 (s, CH_3, 6H), 2.27 (s, CH_3, 3H), 2.47 (s, CH_3, 3H), 6.86 (s, H_{aryl}, 2H), 7.41 (d, H_{aryl}, 2H, $^{3}J_{HH}$= 8.2 Hz), 7.97 (d, H_{aryl}, 2H, $^{3}J_{HH}$= 8.2 Hz).

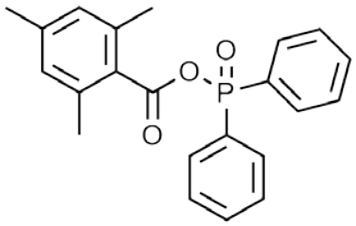
^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 25°C): δ (ppm) = 19.80 (s, 2C, CH_3), 21.04 (s, CH_3), 21.61 (s, CH_3), 128.97 (s, C_{aryl}), 129.93 (s, C_{aryl}), 136.56 (s, C_{quat}, 2C), 141.73 (s, C_{aryl}).

IR (ATR): 2923 (w), 2959 (w), 2856 (w), 2651 (w), 1773 (m), 1680 (s), 1610 (s), 1592 (m), 1436 (s), 1376 (s), 1293 (s), 1227 (m), 1192 (s), 1178 (vs) 1153 (s), 1091 (s), 1037 (m), 967 (s), 933 (vs), 860 (s), 808 (s), 779 (s), 768 (s), 742 (vs), 696 (vs), 655 (vs).

(2,4,6-trimethylbenzoyloxy)diphenylphosphanoxide (11b)

MF: $C_{22}H_{21}O_3P$

M_r: 364.37



To 271 mg (1 mmol) silver mesitylate suspended in 5 mL Et_2O, 237 mg (1 mmol) diphenylphosphinic chloride was added dropwise. The suspension was stirred at room temperature for 12 hours. The resulting suspension was filtered over celite and the remaining solution was left for crystallization at -30 °C overnight. The organic solvent was decanted from the white solid. The product was washed with hexanes and dried under vacuum.
Yield: 176 mg (48 %, 0.48 mmol).

Mp: 112 °C

^{1}H NMR (300.1 MHz, CD_2Cl_2, 25°C): δ (ppm) = 1.95 (s, CH_3, 3H), 2.27 (s, CH_3, 6H), 6.52 (s, H_{aryl}, 2H), 6.97-7.07 (m, H_{aryl}, 6H), 7.94-8.01 (m, H_{aryl}, 4H).

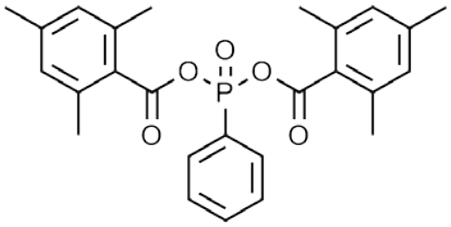
^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, 25°C): δ (ppm) = 20.21 (s, 2C, CH_3), 20.94 (s, CH_3), 128.64 (d, C_{aryl}, J_{PC} = 13.7 Hz), 129.07 (s, C_{aryl}), 131.99 (d, C_{aryl}, J_{PC} = 10.5 Hz), 132.16 (d, J_{PC} = 2.9 Hz), 136.40 (s, C_{aryl}), 140.32 (s, C_{aryl}).

^{31}P NMR (121.5 MHz, C_6D_6, 25°C): δ (ppm) = 24.77 (br m).

bis(2,4,6-trimethylbenzoyloxy)phenylphosphanoxide (11a)

MF: $C_{26}H_{27}O_5P$

M_r: 450.46



To 271 mg (1 mmol) silver mesitylate suspended in 10 mL Et_2O, 102.6 mg (0.5 mmol, 74 µL, 1.39 g mL^{-1}) freshly distilled phenylphosphonic dichloride was added dropwise. The suspension was stirred at room temperature for 12 hours, filtered over celite and the remaining solution was left for crystallization at -30 °C overnight yielding a white precipitation. The solvent was decanted and the white solid dried under vacuum.
Yield: 245 mg (34 %, 0.169 mmol).

^{1}H NMR (300.1 MHz, CD_2Cl_2, 25°C): δ (ppm) = 2.28 (s, C*H*$_3$, 6H), 2.33 (s, C*H*$_3$, 12H), 6.89 (s, H_{aryl}, 4H), 7.55-7.61 (m, H_{aryl}, 2H), 7.66-7.72 (m, H_{aryl}, 1H), 7.96-8.05 (m, H_{aryl}, 2H).
^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 25°C): δ (ppm) = 20.24 (s, 4C, *C*H$_3$), 21.02 (s, 2*C*H$_3$), 128.88 (d, J_{PC}= 16.5 Hz, C_{aryl}, 2C), 129.09 (s, C_{aryl}, 4C), 132.07 (d, J_{PC}= 11.7 Hz, C_{aryl}, 2C), 133.90 (d, J_{PC}= 3.8 Hz, C_{aryl}, C), 136.90 (s, C_{aryl}, 4C), 141.54 (s, C_{quat}, 2C), 163.51 (d, J_{PC}= 8.7 Hz, 2C).
^{31}P NMR (121.5 MHz, CD_2Cl_2, 25°C): δ (ppm) = 8.50 (m, $^5J_{PH}$ = 1.1 Hz, $^4J_{PH}$ = 4.6 Hz, $^3J_{PH}$ = 14.6 Hz).

IR (ATR): 2959 (w), 2923 (w), 2856 (w), 1744 (s), 1609 (m), 1570 (w), 1444 (m), 1420 (m), 1379 (m), 1295 (s), 1254 (m), 1232 (s), 1161 (s), 1128 (s), 1047 (s), 1028 (s), 995 (vs), 955 (s), 846 (vs), 828 (vs), 799 (vs), 770 (vs), 756 (vs), 715 (m), 694 (vs), 607 (m).

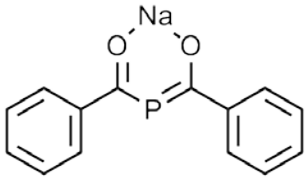
Reaction of the organic and inorganic anhydrides with $NaPH_2$·xNaO^tBu

To 34 mg (0.1 mmol) $NaPH_2$·xNaO^tBu in 0.5 mL thf 0.2 mmol anhydride was added. This mixture was shaken very well and analyzed by ^{31}P NMR.

Sodium bis(benzoyl)phosphanide (13)

MF: $C_{14}H_{10}NaO_2P$

M_r: 264.19

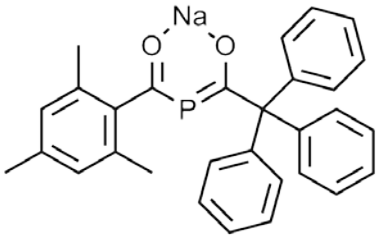


$^{31}P\{^1H\}$ NMR (101.3 MHz, dme, 25°C): δ (ppm) = 63.7 (s).

Sodium (2,4,6-trimethylbenzoyl)(2,2,2-triphenylacetyl)phosphanide (14)

MF: $C_{30}H_{26}NaO_2P$

M_r: 472.49

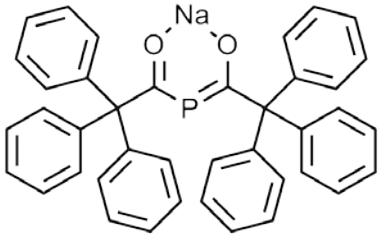


$^{31}P\{^1H\}$ NMR (101.3 MHz, dme, 25°C): δ (ppm) = 88.7 (s).

Synthesis of sodium bis(2,2,2-triphenylacetyl)phosphanide (15)

MF: $C_{40}H_{30}NaO_2P$

M_r: 596.63



To a solution of 172 mg (0.5 mmol) $NaPH_2 \cdot xNaO^tBu$, 558 mg (1.0 mmol, 2 eq) 4 was added. Upon addition of the anhydride the solution turns yellow/orange and the solvent was stirred for a further 30 minutes. The solvent was removed yielding a bright yellow solid, toluene was added and the resulting solution was left for one week upon which colorless crystals were formed. The yellow solution was decanted and evaporated yielding a yellow powder. The

sample was further crystallized from a dme/hexanes mixture yielding a yellow crystalline solid.

Yield: 213 mg (0.36 mmol, 72 %).

Mp: > 150°C slow decomposition.

^{1}H NMR (300.1 MHz, CD_2Cl_2, 25°C): δ (ppm) = 7.14 (m, H_{aryl}, 12H), 7.25 (m, H_{aryl}, 18H).

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_2Cl_2, 25°C): δ (ppm) = 76.90 (d, $^{2}J_{PC}$ = 32.2 Hz, C_{quat}, 2C), 126.04 (s, C_{aryl}, 6C), 127.11 (s, C_{aryl}, 12C), 131.42 (d, $^{4}J_{PC}$ = 3.3 Hz, C_{aryl}, 12C), 145.45 (d, $^{3}J_{PC}$ = 2.6 Hz, C_{aryl}, 6C_{quat}), 234.96 (d, $^{1}J_{PC}$ = 107.4 Hz, *C*=O, 2C).

$^{31}P\{^{1}H\}$ NMR (101.3 MHz, dme, 25°C): δ (ppm) = 97.9 (s).

IR (ATR): 3055 (m), 3019 (w), 2927 (m), 2822 (m), 1621 (m), 1586 (s), 1575 (s), 1487 (s), 1470 (m), 1443 (m), 1367 (s), 1329 (w), 1260 (m), 1244 (m), 1186 (m), 1152 (w), 1083 (s), 1034 (s), 982 (s), 904 (m), 861 (m), 793 (m), 737 (vs), 697 (vs), 671 (m), 605 (m).

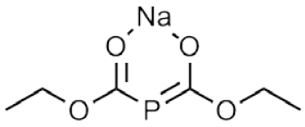
Reaction of the carbonic anhydrides with $NaPH_2$·xNaO^tBu

To 34 mg (0.1 mmol) $NaPH_2$·xNaO^tBu in 0.5 mL thf, 0.2 mmol carbonic anhydride was added. This mixture was shaken very well and analyzed by ^{31}P NMR.

Sodium bis(ethyl carbonic)phosphanide (16)

MF: $C_6H_{10}NaO_4P$

M_r: 200.10

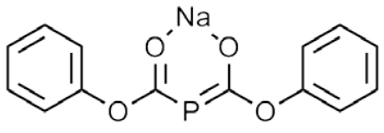


$^{31}P\{^{1}H\}$ NMR (101.3 MHz, dme, 25°C): δ (ppm) = -31.1 (s).

Sodium bis(benzoic)phosphanide (17)

MF: $C_{14}H_{10}NaO_4P$

M_r: 296.19



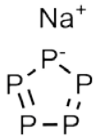
$^{31}P\{^{1}H\}$ NMR (101.3 MHz, dme, 25^{o}C): δ (ppm) = -28.0 (s).

Experimental Part for Chapter 4

Synthesis of NaP_5 (18)

MF: NaP_5

M_r: 177.86



20 mg (0.11 mmol) benzophenone and 29 mg (0.1 mmol) 18-crown-6-ether were dissolved in 5 mL thf. To this solution, 53 mg (0.1 mmol) $NaPH_2 \cdot xNaO^tBu$ in 5 mL dme was added dropwise. This solution was heated to 55 °C and subsequently 14 mg (0.1 mmol) P_4 dissolved in 1 mL thf was added. The suspension was stirred for 12 hours resulting in a red solution with red precipitation. The solution contains NaP_5 and the precipitate consists of polyphosphides like Na_2P_{16} and Na_3P_{21}. The supernatant was extracted by syringe and analyzed by ^{31}P NMR.

Yield: ~40% (0.045 mmol). The yield was calculated from an internal standard (PPh_3) and the signals were integrated respectively.

$^{31}P\{^1H\}$ NMR (101.3 MHz, dme, 25°C): δ (ppm) = 468 (s).

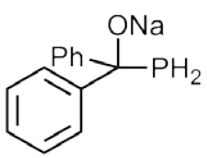
Synthesis of NaP_5 (18) from sodium dihydrogenphosphide and benzophenone/quinine

An NMR tube was charged with 34 mg (0.1 mmol) $NaPH_2 \cdot xNaO^tBu$ in dme. To this solution one equivalent of benzophenone/benzoquinone and 26 mg (0.1 mmol) triphenylphosphine as internal standard was added. The resulting reaction mixture was analyzed by ^{31}P NMR.

Diphenyl(phosphino)methanolate (19)

MF: $C_{13}H_{12}NaOP$

M_r: 238.20



An NMR tube was charged with 17 mg (0.1 mmol) $NaPH_2 \cdot xNaO^tBu.dme$, dissolved in 0.4 mL thf-d_8. To this solution 18 mg (0.1 mmol) benzophenone was added and the suspension was shaken vigorously. The NMR measurements were performed at room temperature.

^{1}H NMR (500.2 MHz, thf-d_8, 25°C): δ (ppm) = 3.48 (d, $^1J_{PH}$ = 176.4 Hz, 2H), 3.55 (d, $^1J_{PH}$ = 178.3 Hz, 2H), 7.00 (t, $^3J_{HH}$ = 7.0 Hz, H_{aryl}, 2H), 7.02 (t, $^3J_{HH}$ = 7.2 Hz, H_{aryl}, 2H), 7.17 (t, $^3J_{HH}$ = 7.3 Hz, H_{aryl}, 4H), 7.18 (t, $^3J_{HH}$ = 7.3 Hz, H_{aryl}, 4H), 7.70 (d, $^3J_{HH}$ = 7.0 Hz, H_{aryl}, 4H), 7.76 (d, $^3J_{HH}$ = 7.0 Hz, H_{aryl}, 4H).
^{13}C{^{1}H} NMR (125.8 MHz, thf-d_8, 25°C): 83.70 (s, C_{quat}), 83.77 (s, C_{quat}), 124.98 (s, C_{aryl}, 2C), 125.11 (s, C_{aryl}, 2C), 126.68 (d, C_{aryl}, 4C), 126.72 (d, C_{aryl}, 4C), 127.54 (s, C_{aryl}, 4C), 127.71 (s, C_{aryl}, 4C), 157.20 (d, $^2J_{CP}$ = 13.2 Hz, C_{aryl}, 2C), 157.48 (d, $^2J_{CP}$ = 12.7 Hz, C_{aryl}, 2C)
^{31}P NMR (202.5 MHz, thf-d_8, 25°C): δ (ppm) = -68.7 ppm (t, $^1J_{PH}$ = 177.0 Hz), -68.2 ppm (t, $^1J_{PH}$ = 178.5 Hz).

Na_3P_7 cluster (20) from $NaPH_2 \cdot xNaO^tBu$ and benzophenone

To a solution of 182 mg (1 mmol) benzophenone in 5 mL dme, 344 mg (1 mmol) $NaPH_2 \cdot xNaO^tBu$ was added and this mixture was shaken until all alkoxide packaged sodium dihydrogenphosphide had been dissolved. The deep blue solution was left standing for 12 hours. Bright yellow crystals grew from this solution. The solution was decanted and the crystals were washed with hexanes.
Yield: 85 mg (71%, 0.05 mmol).

Mp: > 220 °C.
^{1}H NMR (250.1 MHz, thf-d_8, 25°C): δ (ppm) = 1.04 (s, CH_3), 3.26 (s, OC$H_{3(dme)}$), 3.59 (s, OC$H_{2(dme)}$).
^{31}P{^{1}H} NMR (101.3 MHz, thf-d_8, 25°C): δ (ppm) = -121.6 ppm (s, br).

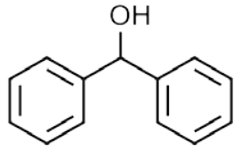
IR (ATR): 3550 (br m), 2933 (br s), 2852 (m), 2821 (m), 1468 (s), 1447 (s), 1366 (m), 1344 (s), 1277 (w), 1241 (m), 1203 (s), 1124 (s), 1087 (vs), 1022 (s), 960 (vs), 861 (s), 840 (m), 747 (m).

General procedure for the reaction of $NaPH_2 \cdot xNaO^tBu$ with substituted benzophenones

To 2 mmol benzophenone/quinone in 10 mL thf, 2 mmol $NaPH_2 \cdot xNaO^tBu$ in 2 mL dme was added. After stirring for one day Et_2O was added to the reaction mixture and subsequently a saturated aqueous NH_4Cl solution. The organic layer was separated from the water layer. The organic layer was washed with water and dried over sodium sulphate and filtered.

Diphenylmethanol

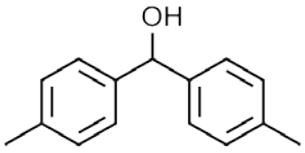
MF: $C_{13}H_{12}O$
M_r: 184.23



Mp: 65°C
^{1}H NMR (250.1 MHz, $CDCl_3$, 25°C): δ (ppm) = 5.86 (s, C*H*OH, 1H), 7.24-7.44 (m, H_{aryl}, 10H).
$^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 25°C): δ (ppm) = 76.17 (s, *C*HCO, 1C), 126.50 (s, C_{aryl}, 4C), 127.50 (s, C_{aryl}, 2C), 128.43 (s, C_{aryl}, 4C), 143.77 (s, C_{aryl}, 2C).

Di-*p*-tolylmethanol

MF: $C_{15}H_{16}O$
M_r: 212.29



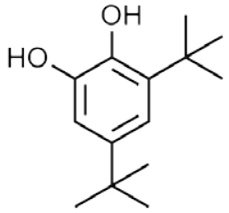
^{1}H NMR (250.1 MHz, $CDCl_3$, 25°C): δ (ppm) = 2.33 (s, C*H*$_3$, 6H), 5.76 (s, C*H*OH, 1H), 7.13 (d, $^{3}J_{HH}$ = 7.9 Hz, 4H), 7.26 (d, $^{3}J_{HH}$ = 8.1 Hz, 4H).

^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$, 25°C): δ (ppm) = 31.91 (s, *C*H$_3$, 6C), 75.82 (s, *C*HCO, 1C), 126.39 (s, C_{aryl}, 4C), 129.05 (s, C_{aryl}, 4C), 137.02 (s, C_{aryl}, 2C), 141.10 (s, C_{aryl}, 2C).

3,5-di-tert-butylcatechol

MF: $C_{14}H_{22}O_2$

M_r: 222.32



Mp: 95 °C (lit. 97 °C).

^{1}H NMR (500.2 MHz, $CDCl_3$, 25°C): δ (ppm) = 1.26 (s, CH_3, 9H), 1.40 (s, CH_3, 9H), 6.75 (d, $^{4}J_{HH}$ = 0.9 Hz, 1H), 6.87 (d, $^{4}J_{HH}$ = 0.9 Hz, 1H).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, 25°C): δ (ppm) = 29.67 (s, *C*H$_3$, 3C), 31.57 (s, *C*H$_3$, 3C), 34.33 (s, C_{quat}, C), 34.83 (s, C_{quat}, C), 110.42 (s, C_{aryl}, C), 115.97 (s, C_{aryl}, C), 135.70 (s, C_{quat}, C), 140.78 (s, C_{quat}, C), 142.15 (s, C_{quat}, C), 142.40 (s, C_{quat}, C).

IR (ATR): 3451 (br, s), 3239 (br, m), 1589 (s), 1483 (s), 1420 (s), 1361 (s), 1301 (vs), 1232 (s), 1200 (s), 1158 (s), 1106 (s), 911 (m), 858 (vs), 801 (s), 733 (s), 655 (s), 643 (s), 607 (s).

Sodium salt of 9,10-phenanthrenequinone

To 41 mg (0,2 mmol) 9,10-phenanthrenequinone in 2.5 mL dme, 68 mg (0,2 mmol) $NaPH_2 \cdot xNaO^tBu$ in 2 mL dme was added. This mixture was left to stand for one day during which red crystals grew. These highly air sensitive crystals could be isolated and analyzed by NMR and IR.

Yield: 67 mg (0,045 mmol, 68 %).

^{1}H NMR (500.2 MHz, thf-d_8, 25°C): δ (ppm) = 1.27 (br s, CH_3), 6.60 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H)*, 6.82 (t, $^{3}J_{HH}$ = 7.9 Hz, 2H)*, 7.01 (m, $^{3}J_{HH}$ = 6.6 Hz, 2H), 7.12 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H)$^{\#}$, 7.20 (t, $^{3}J_{HH}$ = 7.9 Hz, 2H)$^{\#}$, 7.31 (m, $^{3}J_{HH}$ = 7.2 Hz, 2H), 7.98 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H)*, 8.00 (d, $^{3}J_{HH}$ =

8.1 Hz, 2H)$^{\#}$, 8.03 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H)*, 8.34 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 8.41 (m, $^{3}J_{HH}$ = 8.3 Hz, 2H), 8.55 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H)$^{\#}$.

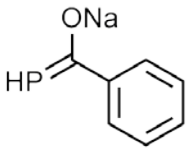
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, thf-d_8, 25°C): δ (ppm) = 114.01 (s, C_{quat}), 116.68 (s, C_{aryl}), 118.62 (s, C_{aryl}), 118.78 (s, C_{aryl}), 119.42 (s, C_{aryl}), 121.11 (s, C_{aryl}), 121.50 (s, C_{aryl}), 121.71 (s, C_{aryl}), 122.08 (s, C_{aryl}), 122.70 (s, C_{aryl}), 122.77 (s, C_{aryl}), 122.82 (s, C_{aryl}), 124.20 (s, C_{aryl}), 124.27 (s, C_{quat}), 124.43 (s, C_{aryl}), 125.72 (s, C_{aryl}), 126.04 (s, C_{quat}), 128.91 (s, C_{quat}), 129.67 (s, C_{quat}), 133.32 (s, C_{quat}), 133.44 (s, C_{quat}), 133.51 (s, C_{quat}), 133.73 (s, C_{quat}), 148.21 (s, C_{quat}), 148.61 (s, C_{quat}), 148.89 (s, C_{quat}), 149.75 (s, C_{quat}).

IR (ATR): 3050 (w), 2942 (m), 2879 (m), 2849 (m), 1590 (m), 1552 (s), 1506 (m), 1470 (s), 1437 (s), 1377 (vs), 1338 (vs), 1241 (m), 1198 (s), 1113 (s), 1090 (m), 1069 (s), 1055 (s), 1025 (s), 993 (w), 975 (s), 923 (s), 853 (s), 789 (m), 753 (vs), 722 (vs), 681 (m).

Synthesis of sodium phenyl(phosphinylidene)methanolate (12)

MF: C_7H_6NaOP

M_r: 160.09



To 104 mg (0.3 mmol) benzopinacolone suspended in 4 mL dme, 17 mg (0.3 mmol) $NaPH_2$ was added directly. Upon addition of sodium dihydrogenphosphide the white suspension turned into a bright yellow solution. NaPHOPh was isolated by the addition of 4 mL hexane and left for crystallization at -30 °C. Crystals suitable for X-ray diffraction were grown from the mother liquor at -30 °C overnight. NaPHOPh is unstable as a solid and decomposes within one hour at room temperature.

^{1}H NMR (300.1 MHz, thf-d_8/C_6D_6, 25°C): δ (ppm) = 4.00 (d, $^{1}J_{PH}$ = 140.0 Hz, 1H), 4.69 (d, $^{1}J_{PH}$ = 158.6 Hz, 1H)*, 7.19 (m, H_{aryl}), 8.04 (d, $^{3}J_{HH}$ = 6.8 Hz, 2H)*, 8.27 (d, $^{3}J_{HH}$ = 5.8 Hz, 2H).

^{31}P NMR (101.3 MHz, thf-d_8/C_6D_6, 25°C): δ (ppm) = 0.1 (d, $^{1}J_{PH}$ = 159.1 Hz)*, 11.4 (d, $^{1}J_{PH}$ = 139.6 Hz).

(* the minor isomer)

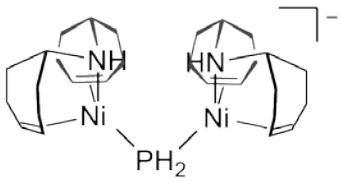
Detection of the ketyl radicals by EPR

To a 5 mM benzophenone/quinine solution in dme or thf one equivalent of “inorganic” or “organic” sodium dihydrogenphosphide was added. Approximately 0.4 mL were immediately taken from the reaction mixture and instantly put in an EPR tube. The sample was cooled to -196 °C until the measurement. The measurement was performed at room temperature.

Experimental Part for Chapter 5

$[(trop_2NH)_2Ni_2(PH_2)]Na(dme)_3$ (25)

MF: $C_{72}H_{78}N_2NaNi_2O_6P$
M_r: 1238.75



To 45 mg (0.06 mmol) $(trop_2NH)NiPPh_3$ dissolved in 3 mL dme, 3.5 mg (0.06 mmol) $NaPH_2$ in 2 mL dme was added. The solution turned dark red and dark red crystals suitable for X-ray diffraction grew slowly from the solution. The red crystals were washed with hexane and dried in vacuum.

Yield: 27 mg (0.02 mmol, 70 %).

^{1}H NMR (300.1 MHz, thf-d_8, 25°C): δ (ppm) = 1,07 (s, N*H*, 2H), 1.88 (d, $^1J_{PH}$ = 225.8 Hz, 2H), 4.15 (t, $^4J_{PH}$ = 9.9 Hz, 4H, H_{olef}), 4.24 (s, H_{benz}, 4H), 4.48 (d, $^3J_{HH}$ = 9.6 Hz, 4H), 6.43-6.55 (m, H_{aryl}, 4H), 6.66-6.70 (m, H_{aryl}, 4H), 6.72-6.75 (m, H_{aryl}, 4H), 6.79-6.84 (m, H_{aryl}, 8H), 7.08 (d, $^3J_{HH}$ = 7.6 Hz, 4H).
$^{13}C\{^1H\}$ NMR (125.8 MHz, thf-d_8, 25°C): δ (ppm) = 59.77 (br, C_{olef}, 4C), 65.53 (s, C_{olef}, 4C), 72.25 (s, C_{benz}, 4C), 120.63 (s, C_{aryl}, 4C), 122.44 (s, C_{aryl}, 4C), 126.85 (s, C_{aryl}, 4C), 127.53 (s, C_{aryl}, 8C), 128.57 (s, C_{aryl}, 4C), 128.75 (s, C_{aryl}, 4C), 130.06 (s, C_{aryl}, 4C), 134.43 (s, C_{quat}, 4C), 139.83 (s, C_{quat}, 4C), 142.06 (s, C_{quat}, 4C), 145.39 (s, C_{quat}, 4C).
^{31}P NMR (121.5 MHz, thf-d_8, 25°C): δ (ppm) = -70.9 (t, $^1J_{PH}$ = 228.9 Hz).

IR (ATR): 3309 (w), 2983 (m), 2923 (m), 2824 (m), 2195 (m), 1592 (m), 1483 (s), 1459 (vs), 1395 (m), 1367 (m), 1314 (w), 1296 (w), 1245 (m), 1206 (w), 1191 (m), 1158 (m), 1123 (m), 1104 (m), 1077 (vs), 1023 (s), 945 (w), 907 (w), 882 (w), 855 (s), 837 (s), 742 (vs), 732 (s), 699 (s), 650 (m), 628 (s).

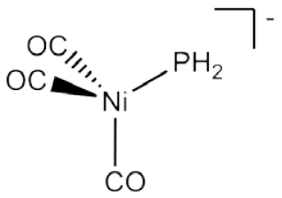
$[(CO)_6Ni_2PH_2]^-$ (28)

A solution of 10 mg of **25** in thf-d_8 was put under 1 bar CO pressure in a Young NMR tube.

^{31}P NMR (202.5 MHz, thf-d_8, 25°C): δ (ppm) = -221.9 (t, $^1J_{PH}$ 239.1 = Hz).

$[(CO)_3NiPH_2]^-$ (29)

MF: $C_3H_2NaNiO_3P$
M_r: 198.70

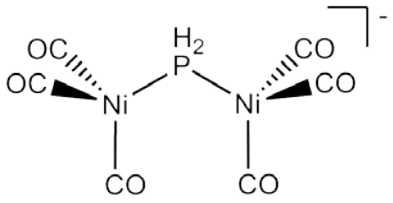


A solution of 34 mg (0.1 mmol) $NaPH_2$ in 0.5 mL dme in a young NMR tube was cooled to -35 °C. $Ni(CO)_4$ was condensed into the NMR tube resulting in a clear yellow solution.

^{1}H NMR (500.2 MHz, thf-d_8, 25°C): δ (ppm) = -0.12 (d, $^1J_{PH}$ = 171.1 Hz).
^{13}C{^{1}H} NMR (125.8 MHz, thf-d_8, 25°C): δ (ppm) = 203.72 (d, $^2J_{PC}$ = 6.7 Hz).
^{31}P NMR (202.5 MHz, thf-d_8, 25°C): δ (ppm) = -260.8 (t, $^1J_{PH}$ = 170.9 Hz).
IR (ATR, [cm^{-1}]): 2016 (CO), 1935 (CO)

$[(CO)_6Ni_2PH_2]^-$ (28)

MF: $C_6H_2NaNi_2O_6P$
M_r: 341.43



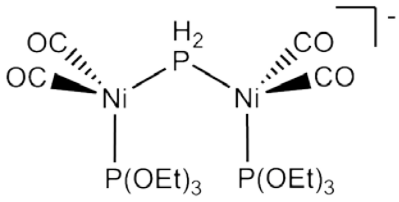
A solution of 34 mg (0.1 mmol) $NaPH_2$ in 0.5 mL dme in a young NMR tube was cooled to

-35 °C. $Ni(CO)_4$ was condensed into the NMR tube resulting in a clear yellow solution with some orange/yellow precipitation.

^{1}H NMR (500.2 MHz, thf-d_8, 25°C): δ (ppm) = 1.22 (d, $^1J_{PH}$ = 239.5 Hz).
^{13}C{^{1}H} NMR (125.8 MHz, thf-d_8, 25°C): δ (ppm) = 201.67 (d, $^2J_{PC}$ = 0.7 Hz).
^{31}P NMR (202.5 MHz, thf-d_8, 25°C): δ (ppm) = -218.3 (t, $^1J_{PH}$ = 239.5 Hz).
IR (ATR, [cm^{-1}]): 2022 (CO)

$[(CO)_4Ni_2(\mu\text{-}PH_2)((EtO)_3P)_2]PPh_4$ (37)

MF: $C_{40}H_{52}Ni_2O_{10}P_4$
M_r: 934.12



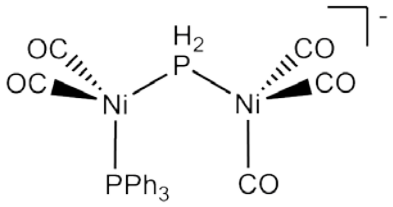
To 56 mg (1 mmol) $NaPH_2$ in 10 mL dme, a 1.1 mL (1.85 M, 341 mg, 2 mmol, 2 eq.) $Ni(CO)_4$ solution in dme was added dropwise. Upon addition of $Ni(CO)_4$ carbon monoxide was released and the solution became bright yellow. After gas evolution has ceased 0.68 mL (4 mmol, 665 mg, 4 eq.) $(EtO)_3P$ was added dropwise to the solution. Again gas evolution was observed and the bright yellow solution was stirred for an additional 2 hours. To the solution was added 750 mg (2 mmol) very fine PPh_4Cl powder. Upon addition of PPh_4Cl the solution turned orange and a white precipitation was formed. The precipitation was filtered over celite and the complex was separated from the solvent by the addition of hexane to yield a yellow solution.

^{1}H NMR (300.1 MHz, thf-d_8, 25°C): δ (ppm) = 1.13 (t, $^1J_{HH}$ = 7.0 Hz, CH_3), 1.25 (dt, $^1J_{PH}$ = 227.3 Hz, $^3J_{PH}$ = 13.7 Hz, μ-PH_2), 3.27 (s, dme, OCH_3), 3.43 (s, dme, OCH_2), 3.90 (m, CH_2), 7.73-7.84 (m, H_{aryl}), 7.93-7.98 (m, H_{aryl}).
^{13}C{^{1}H} NMR (75.5 MHz, thf-d_8, 25°C): δ (ppm) = 17.27 (d, J_{CP} = 6.4 Hz, 6C), 59.40 (m, 6C), 119.14 (d, J_{CP} = 89.6 Hz, 8C), 131.41 (d, J_{CP} = 13.0 Hz, 8C), 135.67 (d, J_{CP} = 10.4 Hz, 8C), 136.45 (d, J_{CP} = 2.9 Hz, 4C), 204.93 (dd, J_{CP} = 4.3 and 11.1 Hz, 4*C*O).

^{31}P NMR (121.5 MHz, thf-d_8, 25°C): δ (ppm) = -215.9 (t, $^2J_{PP}$ = 17.7 Hz, $^1J_{PH}$ = 227.0 Hz), 23.1 (s, PPh_4), 174.5 (d, $^2J_{PP}$ = 17.7 Hz).
IR (ATR, [cm^{-1}]): 1984 (CO), 1960 (CO), 1910 (CO).

$[(CO)_5Ni_2(\mu\text{-}PH_2)(PPh_3)]Na$ (30)

MF: $C_{23}H_{21}NaNi_2O_5P_2$
M_r: 579.73

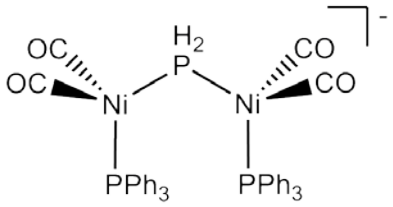


To a 1 mL (0.1 M, 100 µmol) solution of **28** in dme, 26 mg (100 µmol, 1 eq.) PPh_3 was added. CO evolution was observed immediately and a mixture of **30** and **31** was formed.

^{31}P NMR (101.3 MHz, dme, 25°C): δ (ppm) = -206.9 (dt, $^2J_{PP}$ = 15.0 Hz, $^1J_{PH}$ = 231.6 Hz), 37.3 (d, $^2J_{PP}$ = 14.6 Hz).

$[(CO)_4Ni_2(\mu\text{-}PH_2)(PPh_3)_2]Na$ (31)

MF: $C_{40}H_{36}NaNi_2O_4P_3$
M_r: 814.01

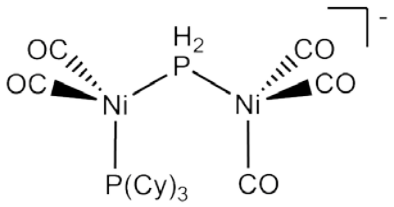


^{31}P NMR (121.5 MHz, dme, 25°C): δ (ppm) = -198.4 (tt, $^2J_{PP}$ = 17.7 Hz, $^1J_{PH}$ = 225.6 Hz), 35.9 (br, $^2J_{PP}$ = 16.3 Hz).

$[(CO)_5Ni_2(\mu\text{-}PH_2)(PCy_3)]Na$ (34)

MF: $C_{23}H_{39}NaNi_2O_5P_2$

M_r: 597.88



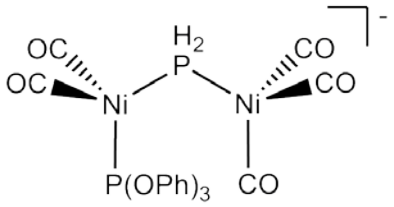
To a 1 mL (0.08 M, 83 µmol) solution of **28** in dme, 23 mg (83 µmol, 1 eq.) PCy_3 was added. CO evolution was observed immediately and a mixture of **34** and **29** was formed.

^{31}P NMR (101.3, dme, 25°C): δ (ppm) = -207.3 (dt, $^2J_{PP}$ = 14.3 Hz, $^1J_{PH}$ = 225.0 Hz), 46.55 (d, $^2J_{PP}$ = 13.9 Hz).

$[(CO)_5Ni_2(\mu\text{-}PH_2)(POPh_3)]Na$ (35)

MF: $C_{23}H_{21}NaNi_2O_8P_2$

M_r: 627.73



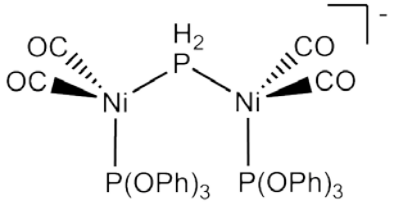
To a 1 mL (0.08 M, 83 µmol) solution of **28** in dme, 26 mg (83 µmol, 1 eq.) $P(OPh)_3$ was added. CO evolution was observed immediately and a mixture of **35** and **36** was formed.

^{31}P NMR (101.3 MHz, dme, 25°C): δ (ppm) = -213.4 (dt, $^2J_{PP}$ = 17.0 Hz, $^1J_{PH}$ = 238.1 Hz), 154.7 (d, $^2J_{PP}$ = 17.0 Hz).

$[(CO)_4Ni_2(\mu\text{-}PH_2)(POPh_3)_2]Na$ (36)

MF: $C_{40}H_{36}NaNi_2O_{10}P_3$

M_r: 910.01

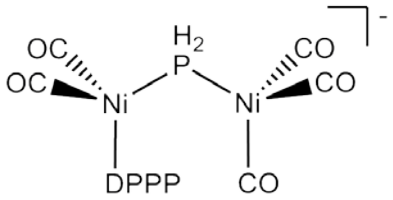


^{31}P NMR (101.3 MHz, dme, 25°C): δ (ppm) = -210.0 (tt, $^{2}J_{PP}$ = 20.0 Hz, $^{1}J_{PH}$ = 237.0 Hz), 154.5 (d, $^{2}J_{PP}$ = 21.2 Hz).

[(CO)$_5$Ni$_2$(μ-PH$_2$)(DPPP)]Na (32)

MF: $C_{32}H_{28}NaNi_2O_5P_3$

M_r: 725.86



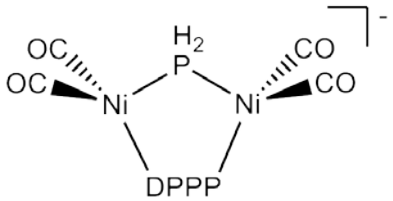
To a 1 mL (0.08 M, 83 μmol) solution of **28** in dme, 34 mg (83 μmol, 1 eq.) DPPP was added. CO evolution was observed immediately and a mixture of **32** and **33** was formed.

^{31}P NMR (101.3 MHz, dme, 25°C): δ (ppm) = -209.9 (dt, $^{2}J_{PP}$ = 10.8 Hz, $^{1}J_{PH}$ = 230.0 Hz), 27.5 (d, $^{2}J_{PP}$ = 10.8 Hz).

[(CO)$_4$Ni$_2$(μ-PH$_2$)(μ-DPPP)]Na (33)

MF: $C_{31}H_{28}NaNi_2O_4P_3$

M_r: 697.85



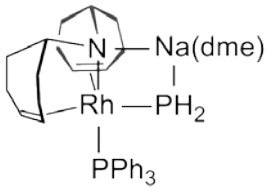
^{31}P NMR (101.3 MHz, dme, 25°C): δ (ppm) = -205.6 (dt, $^{2}J_{PP}$ = 10.0 Hz, $^{1}J_{PH}$ = 224.6 Hz), 28.7 (d, $^{2}J_{PP}$ = 10.0 Hz).

IR measurements of 29 and 28

To a 2 mL 0.1 M dme suspension of $NaPH_2$, a 1.85 M $Ni(CO)_4$ solution in dme was added in intervals. After every interval an IR spectrum was measured. Upon addition of $Ni(CO)_4$, gas evolution was observed and the solution became bright yellow.

[($trop_2N$)Rh(PPh_3)(PH_2)Na(dme)] (46)

MF: $C_{52}H_{49}NNaO_2P_2Rh$
M_r: 907.79



To 38 mg (0.05 mmol) ($trop_2N$)RhPPh_3 in 5 mL dme, 3 mg (0.05 mmol) $NaPH_2$ in 2 mL dme was added. After addition of $NaPH_2$ the solution turned dark red immediately and red crystals were formed overnight. The solvent was decanted and the crystals washed with dme until the washings became colorless. After the red crystals were washed with hexane complex **46** was obtained.
Yield: 34 mg (0.037 mmol, 75 %).

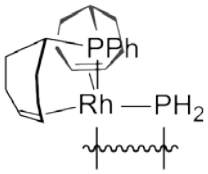
Mp: gradual decomposition above 90 °C.
^{1}H NMR (400 MHz, thf-d_8, 25°C): δ (ppm) = 0.45 (dd, $^3J_{PH}$ = 4.8 Hz , $^1J_{PH}$ = 180.5 Hz, 2H), 3.64 (m, 2H, H_{olef}), 3.94 (m, $^3J_{HH}$ = 9.4 Hz, 2H, H_{olef}), 4.06 (dd, $^4J_{PH}$ = 16.4 Hz, J_{PH} = 1.2 Hz, 2H, H_{benz}), 6.53-6.59 (m, 6H, H_{aryl}), 6.64 (d, $^3J_{HH}$ = 7.3 Hz, 2H, H_{aryl}), 6.74 (m, 4H, H_{aryl}), 6.84 (dt, $^3J_{HH}$ = 7.5 Hz, $^5J_{HH}$ = 1.4 Hz, 2H, H_{aryl}), 6.91 (d, $^3J_{HH}$ = 7.2 Hz, 2H, H_{aryl}), 7.43 (br, 9H, H_{aryl}), 7.74 (br, 6H, H_{aryl}).
^{13}C{^{1}H} NMR (100.6 MHz, thf-d_8, 25°C): δ (ppm) = 56.81 (m, $^2J_{CP}$ = 7.8 Hz, 2C, C_{olef}), 62.02 (d, $^2J_{CP}$ = 8.7 Hz, 2C, C_{olef}), 80.33 (m, J_{CP} = 1.6 Hz, 2C, C_{benz}), 121.60 (s, 2C, C_{arom}), 124.00 (s, 2C, C_{arom}), 125.01 (s, 2C, C_{arom}), 125.97 (s, 2C, C_{arom}), 126.61 (br, 2C, C_{arom}), 126.66 (s, 2C, C_{arom}), 128.5 (br, 6C, C_{arom}), 128.36 (s, 2C, C_{arom}), 128.70 (s, 2C, C_{arom}), 129.32 (d, $^1J_{PC}$ = 14.9 Hz) , 130.00 (br, 3C, C_{arom}), 134.32-135.06 (br, 6C, C_{arom}), 137.16 (s, 2C, C_{arom}), 141.27 (d, $^2J_{PC}$ = 4.6 Hz, 2C, C_{arom}), 142.62 (s, 2C, C_{arom}), 142.69 (s, 2C, C_{arom}).

^{31}P NMR (202.5 MHz, thf-d_8, 25^{o}C): δ (ppm) = -168.53 (d, br, $^{1}J_{PRh}$= 68.7 Hz), 44.35 (dd, $^{1}J_{PRh}$=109.8 Hz, $^{2}J_{PP}$= 9.1 Hz).

IR (ATR): 3774 (w), 3664 (w), 3055 (m), 3044 (m), 3018 (m), 2996 (m), 2906 (m), 2820 (m), 1592 (s), 1480 (s), 1467 (s), 1430 (s), 1398 (m), 1316 (m), 1299 (m), 1253 (m), 1219 (w), 1187 (m), 1156 (w), 1121 (m), 1083 (vs), 1042 (w), 1022 (m), 999 (w), 975 (m), 935 (w), 915 (w), 886 (w), 860 (m), 744 (vs), 696 (vs).

[(trop$_2$PPh)$_2$Rh$_2$(PH$_2$)$_2$] (47)

MF: $C_{72}H_{58}P_4Rh_2$
M_r: 1252.94



To 36 mg (0.05 mmol) (trop$_2$PPh)RhOTf in 2.5 mL dme, 3 mg (0.05 mmol) $NaPH_2$ in 2 mL dme was added. After addition of $NaPH_2$ the solution turned yellow/orange and slowly yellow crystals grew out of the solution. The solvent was decanted and the bright yellow crystals were washed with hexane and dried.
Yield: 15 mg (0.012 mmol, 49 %).

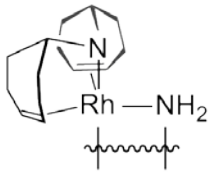
Due to the low solubility of complex **47** only ^{1}H and ^{31}P NMR spectra were given.
^{1}H NMR (500.2 MHz, thf-d$_8$, 25^{o}C): δ (ppm) = 4.47 ppm (d, 4H, $^3J_{HH}$ = 8.8 Hz), 4.53 ppm (d, 4H, $^3J_{HH}$ = 11.7 Hz), 5.50 (s, 4H), 6.59 (d, 4H, $^3J_{HH}$ = 7.2 Hz), 6.69 (m, 12H), 6.79 (m, 8H), 7.00 (t, 4H, $^3J_{HH}$= 7.5, 8.1 Hz), 7.06 (t, 4H, $^3J_{HH}$ = 7.3 Hz), 7.11 (t, 2H, $^3J_{HH}$ = 7.5 Hz), 7.20 (t, 2H, $^3J_{HH}$ = 7.2), 7.79 (d, 2H, = 7.3 Hz).
^{31}P NMR (202.5 MHz, thf-d$_8$, 25^{o}C): δ (ppm) = -183.3 (m, br), 131.9 (dd, $^1J_{PRh}$ = 125.1 Hz, $^2J_{PP}$ = 326.6 Hz).

IR (ATR): 3059 (w), 3002 (w), 2919 (w), 2878 (w), 2811 (w), 1595 (w), 1569 (w), 1482 (s), 1467 (s), 1434 (s), 1404 (m), 1280 (m), 1188 (w), 1120 (s), 1095 (s), 1056 (s), 1020 (m), 981 (s), 842 (s), 735 (vs), 687 (vs).

$[(trop_2N)_2Rh_2(NH_2)_2]Na_2$ (48)

MF: $C_{60}H_{48}N_4Na_2Rh_2$

M_r: 1076.84



To 37 mg (0.049 mmol) $(trop_2N)RhPPh_3$ in 3 mL dme, 3 mg (0,073 mmol) $NaNH_2$ was added. The suspension was left standing for 3 days and slowly orange crystals were formed. These crystals were washed with dme and hexane. The formed crystals were suitable for X-ray diffraction.

Yield: 18 mg (0,017 mmol, 69 %).

Mp: 128 °C decomposition.

Due to the low solubility of the complex, only IR data were taken.

IR (ATR): 3256 (w), 3208 (w), 3055 (m), 3008 (m), 2927 (m), 2885 (m), 2818 (m), 1591 (s), 1482 (s), 1458 (s), 1386 (m), 1367 (m), 1294 (m), 1208 (w), 1190 (m), 1154 (w), 1120 (s), 1076 (vs), 1042 (w), 988 (s), 930 (m), 890 (m), 856 (m), 843 (m), 823 (m), 742 (vs).

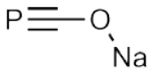
Synthesis of NaOCP (38) with $NaPH_2 \cdot xNaO^tBu$ and $Fe(CO)_5$

To 39 mg (0.197 mmol) $Fe(CO)_5$ in dme, 68 mg (0.197 mmol) $NaPH_2 \cdot xNaO^tBu$ in 2 mL dme was added. Upon addition the solution became dark red immediately.

NaOCP (38)

MF: CNaOP

M_r: 81.97



^{31}P NMR (101.3 MHz, thf-d_8, 25°C): δ (ppm) = -392.6 (s).

$^{13}C\{^1H\}$ NMR (75.5 MHz, thf-d_8, 25°C): δ (ppm) = 167.55 (d, $^1J_{PC}$ = 14.2 Hz).

Reaction of $Fe(CO)_5$ with $NaPH_2 \cdot xNaO^tBu$

To 39 mg (0.197 mmol) $Fe(CO)_5$ in dme, 68 mg (0.197 mmol) $NaPH_2 \cdot xNaO^tBu$ in thf or dme was added.

$[(CO)_4Fe]^{2-}$

$^{13}C\{^1H\}$ NMR (75.5 MHz, thf-d_8, 25°C): δ (ppm) = 231.70 (br).

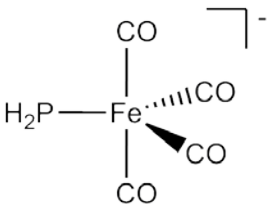
Reaction of $Fe(CO)_5$ with $NaPH_2$

To 140 mg (0.71 mmol) $Fe(CO)_5$ in thf, a suspension of 40 mg (0.71 mmol) $NaPH_2$ in thf was added.

$[(CO)_4Fe\ PH_2]Na$ (39)

MF: $C_4H_2FeNaO_4P$

M_r: 223.86



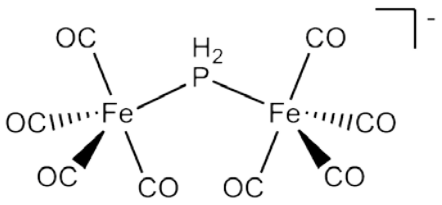
^{1}H NMR (300.1 MHz, thf-d_8, 25^{o}C): δ (ppm) = 0.88 (d, 2H, $^{1}J_{PH}$ = 148.0 Hz).

^{31}P NMR (101.3 MHz, thf-d_8, 25^{o}C): δ (ppm) = -196.2 (t, $^{1}J_{PH}$ = 147.9 Hz).

$[(CO)_4Fe]_2PH_2$ (40)

MF: $C_8H_2Fe_2NaO_8P$

M_r: 391.75



^{1}H NMR (300.1 MHz, thf-d_8, 25^{o}C): δ (ppm) = 3.61 (d, 2H, $^{1}J_{PH}$ = 293.4 Hz).

^{13}C{^{1}H} NMR (75.5 MHz, thf-d_8, 25^{o}C): δ (ppm) = 216.9 (d, $^{2}J_{CP}$ = 14.2 Hz), 217.4 (d, $^{2}J_{CP}$ = 17.3 Hz).

^{31}P NMR (101.3 MHz, thf-d_8, 25^{o}C): δ (ppm) = -88.75 (t, $^{1}J_{PH}$ = 293.6 Hz).

PH_3

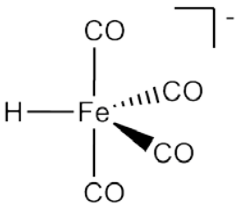
^{1}H NMR (300.1 MHz, thf-d_8, 25^{o}C): δ (ppm) = 1.75 (d, 3H, $^{1}J_{PH}$ = 186.8 Hz).

^{31}P NMR (101.3 MHz, thf-d_8, 25^{o}C): δ (ppm) = -245.6 (t, $^{1}J_{PH}$ = 187.0 Hz).

$[(CO)_4FeH]^-$

MF: $C_4HFeNaO_4$

M_r: 191.88



^{1}H NMR (300.1 MHz, thf-d_8, 25^{o}C): δ (ppm) = -8.80 (s).

^{13}C{^{1}H} NMR (75.5 MHz, thf-d_8, 25^{o}C): δ (ppm) = 222.6 (s).

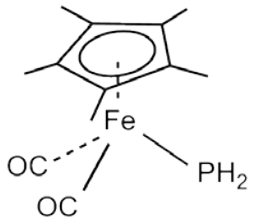
IR measurement of reaction of $Fe(CO)_5$ with "organic" and "inorganic" $NaPH_2$

To a 2 mL 0.2 M solution of $NaPH_2$ (0.4 mmol) in dme, 78 mg (0.4 mmol) $Fe(CO)_5$ was added. The resulting dark red/brown solution was transferred into the IR measuring cell charged with 2 mL dme and the spectrum was recorded.

[cp*$(CO)_2Fe(PH_2)$] (42)

MF: $C_{12}H_{17}FeO_2P$

M_r: 280.08

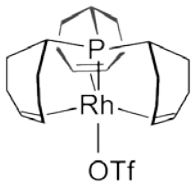


^{31}P NMR (101.3 MHz, thf-d_8): δ (ppm) = -173.2 (t, $^1J_{PH}$ = 149.8 Hz).

(trop$_3$P)RhOTf (44)

MF: $C_{46}H_{33}F_3O_3PRhS$

M_r: 856.69



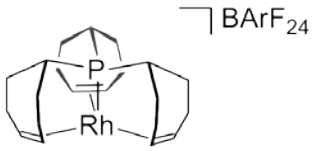
260 mg (0.35 mmol) (trop$_3$P)RhCl and 140 mg (0.54 mmol) silver(I) trifluoromethanesulfonate were combined in 40 mL dcm and stirred at room temperature for 2 hours. The suspended salts were removed by filtration through celite and the resulting solution was concentrated to dryness. The resulting yellow powder was dried in high vacuum.
Yield: 273 mg (0.319 mmol, 91 %)

^{1}H NMR (400 MHz, CD_2Cl_2, 25°C): δ (ppm) = 3.84 (d, $^2J_{PH}$=12.5 Hz, 3H), 5.95 (s, 6H), 6.46 (d, $^3J_{HH}$ = 7.5 Hz, 6H), 6.77 (t, $^3J_{HH}$ = 7.4 Hz, 6H), 6.82 (t, $^3J_{HH}$ = 7.5 Hz, 6H), 6.96 (d, $^3J_{HH}$ = 7.5 Hz, 6H).
^{19}F NMR (376.5 MHz, CD_2Cl_2, 25°C): δ (ppm) = -78.75 (s, OTf).

[(trop$_3$P)Rh]BArF$_{24}$ (49)

MF: $C_{77}H_{45}BF_{24}PRh$

M_r: 1570.83



To a suspension of 177 mg (0.2 mmol) NaBArF$_{24}$ in dcm, 74 mg (0.1 mmol) (trop$_3$P)RhCl was added. This solution was stirred for 5 minutes and filtered over celite and the solvent was evaporated immediately. Due to the reactivity of [(trop$_3$P)Rh]BArF$_{24}$ towards dcm the time in which the metal complex is dissolved in dcm should be as short as possible. This reaction does not work in thf.

Yield: 149 mg (0.095 mmol, 95 %).

Mp: >220 °C

^{1}H NMR (400 MHz, CD_2Cl_2, 25°C): δ (ppm) = 3.86 (d, $^2J_{PH}$=12.0 Hz, 3H), 5.74 (s, 6H), 6.51 (d, $^3J_{HH}$ = 7.5 Hz, 6H), 6.83 (t, $^3J_{HH}$ = 7.5 Hz, 6H), 6.92-6.98 (m, $^3J_{HH}$ = 7.5 Hz, 6H), 7.57 (br, 4H, BArF), 7.73 (m, 8H, BArF).

^{13}C{^{1}H} NMR (62.9 MHz, CD_2Cl_2, 25°C): δ (ppm) = 48.76 (d, $^1J_{PC}$ = 24.8 Hz, 3C), 81.18 (d, $^2J_{PC}$ = 6.4 Hz, 6C), 117.5 (m, pC_{BArF}, C), 124.70 (q, $^1J_{CF}$ = 272.3 Hz, CF_3), 127.41 (d, J_{PC} = 7.9 Hz, 6C), 128.22 (s, 12C), 128.95 (m, mC_{BArF}, C), 130.42 (d, J_{PC} = 1.3 Hz, 6C), 131.94 (d, J_{PC} = 2.6 Hz, 6C), 134.92 (br, oC_{BArF}, C), 161.84 (dd, J_{FC} = 50.1, 99.8 Hz, ipsoC_{BArF}, C).

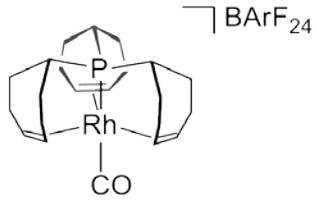
^{31}P{^{1}H} NMR (101.3 MHz, CD_2Cl_2, 25°C): δ (ppm) = 186.2 (d, $^1J_{RhP}$ = 162.2 Hz).

^{19}F NMR (376.5 MHz, CD_2Cl_2, 25°C): δ (ppm) = -62.84 (s, BArF$_{24}$).

[(trop$_3$P)Rh(CO)]BArF$_{24}$ (43)

MF: $C_{78}H_{45}BF_{24}OPRh$

M_r: 1598.84



A suspension of 83 mg (0.11 mmol) NaBArF$_{24}$ in 10 mL dcm was charged under a CO atmosphere. 83 mg (0.11 mmol) (trop$_3$P)RhCl in 10 mL dcm was added via a septum to this suspension. The mixture was stirred for 10 minutes, filtered over celite and the solvent was evaporated yielding a pale yellow solid.

Yield: 152 mg (0.106 mmol, 95 %).

Mp: >220 °C

^{1}H NMR (300.1 MHz, CD_2Cl_2, 25^{o}C): δ (ppm) = 4.25 (d, $^2J_{PH}$=13.9 Hz, 3H), 6.23 (s, 6H), 6.57 (d, $^3J_{HH}$ = 7.6 Hz, 6H), 6.84 (t, $^3J_{HH}$ = 7.6 Hz, 6H), 6.91 (d, $^3J_{HH}$ = 6.6 Hz, 6H), 7.00 (t, $^3J_{HH}$ = 7.6 Hz, 6H), 7.58 (br, 4H, BArF), 7.75 (m, 8H, BArF).

^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 25^{o}C): δ (ppm) = 48.82 (d, $^1J_{PC}$ = 19.6 Hz, 3C), 76.70 (d,$^2J_{PC}$ = 5.8 Hz, 6C), 117.63 (m, pC_{BArF}, C), 124.78 (q, $^1J_{CF}$ = 272.3 Hz, CF_3), 127.92 (d, J_{PC} = 7.0 Hz, 6C), 128.52 (d, J_{PC} = 0.9 Hz, 12C), 128.80 (m, mC_{BArF}, C), 129.26 (s, 12C), 130.54 (d, J_{PC} = 5.3 Hz, 6C), 131.18 (d, J_{PC} = 1.2 Hz, 6C), 134.97 (br, oC_{BArF}, C), 135.56 (s, 6C), 161.90 (dd, J_{FC} = 49.8, 99.7 Hz, *ipso*C_{BArF}, C), 183.71 (dd, $^1J_{RhC}$ = 47.9 Hz, $^2J_{PC}$ = 115.7 Hz, *C*O).

^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25^{o}C): δ (ppm) = 200.6 (d, $^1J_{RhP}$ = 118.2 Hz).

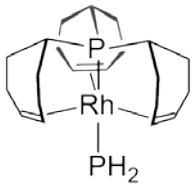
^{19}F NMR (376.5 MHz, CD_2Cl_2, 25^{o}C): δ (ppm) = -62.84 (s, BArF$_{24}$).

IR (ATR): 3067 (w), 3022 (w), 2885 (w), 2074 (s), 1610 (m), 1489 (m), 1456 (w), 1424 (m), 1353 (vs), 1272 (vs), 1113 (br vs), 1000 (w), 944 (w), 885 (s), 838 (s), 791 (w), 764 (w), 746 (s), 681 (s), 668 (s).

(trop$_3$P)RhPH$_2$ (45)

MF: $C_{45}H_{35}P_2Rh$

M_r: 740.61



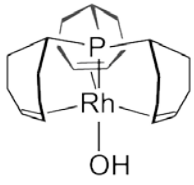
In a NMR tube 18 mg (21 µmol) (trop$_3$P)RhOTf was suspended in 0.4 mL thf-d$_8$. To this suspension 1.2 mg (21 µmol) NaPH$_2$ was added. Upon addition of NaPH$_2$ the suspension became a yellow/brown solution. NMR measurements were performed directly after the reaction. The product could not be isolated and slowly a black precipitation was formed in the solution.

^{1}H NMR (300.1 MHz, thf-d$_8$, 25^{o}C): δ (ppm) = 0.09 (dd, $^3J_{PH}$ = 7.3 Hz, $^1J_{PH}$ = 156.3 Hz, 2H), 4.27 (dd, $^5J_{PH}$ = 3.6 Hz, $^2J_{PH}$ = 13.9 Hz, 3H), 5.56 (s, 6H), 6.45 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 6.60 (t, $^3J_{HH}$ = 7.3 Hz, 6H), 6.71 (t, $^3J_{HH}$ = 7.2 Hz, 6H), 6.82 (d, $^3J_{HH}$ = 7.6 Hz, 6H).
^{13}C{^{1}H} NMR (75.5 MHz, thf-d$_8$, 25^{o}C): δ (ppm) = 48.18 (d, $^1J_{PC}$ = 13.1 Hz, 3C), 75.06 (t,$^2J_{PC}$ = 6.4 Hz, 6C), 126.84 (s, 6C), 127.69 (s, 6C), 128.69 (d, $^1J_{PC}$ = 6.3 Hz, 6C), 131.47 (d, J_{PC} = 1.2 Hz, 6C), 135.79 (d, J_{PC} = 6.5 Hz, 6C), 137.81 (d, J_{PC} = 2.1 Hz, 6C).
^{31}P NMR (121.5 MHz, thf-d$_8$, 25^{o}C): δ (ppm) = -131.6 (dd, $^1J_{RhP}$ = 46.5 Hz, $^2J_{PP}$ = 158.2 Hz), 177.7 (dd, $^1J_{RhP}$ = 114.0 Hz, $^2J_{PP}$ = 158.2 Hz).

(trop$_3$P)RhOH (53)

MF: $C_{45}H_{34}OPRh$

M_r: 724.63

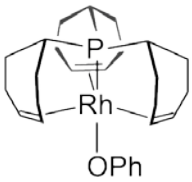


105 mg (0.14 mmol) ($trop_3P$)RhCl was dissolved in 6 mL dcm. To this solution, 20 mL KOH solution (5 M) was added and the reaction mixture was stirred vigorously for one day. After stirring for a day, the KOH solution was decanted and a freshly prepared batch of 20 mL KOH solution (5 M) was added. This solution was stirred overnight. The organic layer was removed by syringe and evaporated yielding a yellow powder.

^{1}H NMR (300.1 MHz, CD_2Cl_2, 25°C): δ (ppm) = 3.84 (d, $^{2}J_{PH}$=13.6 Hz, 3H), 5.52 (s, 6H), 6.43 (d, $^{3}J_{HH}$ = 7.5 Hz, 6H), 6.70 (t, $^{3}J_{HH}$ = 7.5 Hz, 6H), 6.78 (m, $^{3}J_{HH}$ = 7.2, 7.3 Hz, 6H), 6.94 (d, $^{3}J_{HH}$ = 7.2 Hz, 6H).
^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 25°C): δ (ppm) = 48.02 (d, J_{PC} = 20.9 Hz, 3C), 79.97 (d, J_{PC} = 6.6 Hz, 6C), 126.56 (s, 6C), 127.35 (d, J_{PC} = 7.0 Hz, 6C), 127.44 (d, J_{PC} = 1.1 Hz, 6C), 130.52 (d, J_{PC} = 1.2 Hz, 6C), 130.47 (s, 6C), 134.28 (d, J_{PC} = 4.6 Hz, 6C), 136.15 (s, 6C).
^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25°C): δ (ppm) = 178.9 (d, $^{1}J_{RhP}$ = 135.4 Hz).

($trop_3P$)RhOPh (54)

MF: $C_{51}H_{38}OPRh$
M_r: 800.73



To a suspension of 53.9 mg (0.073 mmol) ($trop_3P$)RhCl in 15 mL dcm was added 26.9 mg (0.102 mmol) AgOTf and this solution was stirred for two hours. The brown suspension was filtered over celite and 52.3 mg (0.44 mmol) sodium phenolate was added. This mixture was stirred for a further 10 minutes, filtered over celite and 30 mL hexane was added. A crystalline precipitate was formed. The pale yellow crystals was filtered off and washed with hexane.
Yield: 76 % (44 mg, 0.055 mmol)

Mp: >220 °C

^{1}H NMR (250.1 MHz, CD_2Cl_2, 25°C): δ (ppm) = 3.83 (d, $^{2}J_{PH}$=13.2 Hz, 3H), 5.81 (s, 6H), 6.45 (d, $^{3}J_{HH}$ = 7.4 Hz, 6H), 6.65-6.80 (m, 14H), 6.93 (dd, $^{3}J_{HH}$ = 7.3, 7.5 Hz, 6H), 7.20 (m, 2H).

^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 25°C): δ (ppm) = 48.20 (d, J_{PC} = 22.1 Hz, 3C), 80.64 (d, J_{PC} = 6.9 Hz, 6C), 122.05 (s, 2C), 126.65 (s, 6C), 127.24 (d, J_{PC} = 7.2 Hz, 6C), 127.47 (d, J_{PC} = 0.9 Hz, 6C), 129.19 (s, 2C), 130.49 (d, J_{PC} = 1.4 Hz, 6C), 133.98 (d, J_{PC} = 4.3 Hz, 6C), 135.99 (s, 6C), 163.94 (d, $^{3}J_{PC}$ = 5.2 Hz).

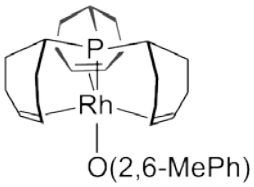
^{31}P{^{1}H} NMR (101.3 MHz, CD_2Cl_2, 25°C): δ (ppm) = 179.16 (d, $^{1}J_{RhP}$= 145.1 Hz).

IR (ATR): 3038 (w), 3009 (w), 1583 (s), 1554 (m), 1471 (vs), 1451 (m), 1416 (m), 1282 (vs), 1218 (m), 1155 (m), 1132 (w), 1108 (m), 1097 (m), 1042 (m), 988 (m), 941 (m), 899 (m), 821 (m), 743 (vs), 731 (vs), 715 (m), 698 (vs), 641 (m).

(trop$_3$P)RhO(2,6-MePh) (55)

MF: $C_{53}H_{42}OPRh$

M_r: 828.78



To a suspension of 14.5 mg (0.02 mmol) (trop$_3$P)RhCl in 5 mL dcm, 7.4 mg (0.03 mmol) AgOTf was added and this suspension was stirred for two hours. The brown suspension was filtered over celite and 14.1 mg (0.05 mmol) sodium 2,6-dimethylphenolate was added. This mixture was stirred for a further 20 minutes, filtered over celite and the solvent was evaporated yielding a pale yellow powder.

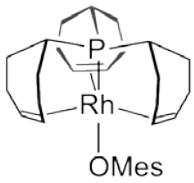
^{1}H NMR (250.1 MHz, CD_2Cl_2, 25°C): δ (ppm) = 2.50 (s, 6H), 3.80 (d, $^{2}J_{PH}$=13.2 Hz, 3H), 5.90 (s, 6H), 6.43 (d, $^{3}J_{HH}$ = 7.5 Hz, 6H), 6.69 (m, 12H), 7.01 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H).

^{31}P{^{1}H} NMR (101.3 MHz, CD_2Cl_2, 25°C): δ (ppm) = 180.92 (d, $^{1}J_{RhP}$= 147.4 Hz).

(trop$_3$P)RhOMes (56)

MF: $C_{54}H_{44}OPRh$

M_r: 842.81



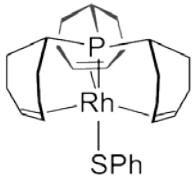
To a suspension of 14.5 mg (0.02 mmol) (trop$_3$P)RhCl in 5 mL dcm, 7.4 mg (0.03 mmol) AgOTf was added and this solution was stirred for two hours. The brown suspension was filtered over celite and 15.4 mg (0.05 mmol) sodium mesitolate was added. This mixture was stirred for a further 20 minutes, filtered over celite and the complex was precipitated by addition of hexanes to the solution.

^{1}H NMR (300.1 MHz, CD_2Cl_2, 25^{o}C): δ (ppm) = 2.20 (s, 3H), 2.47 (s, 6H), 3.80 (d, $^2J_{PH}$=13.1 Hz, 3H), 5.88 (s, 6H), 6.43 (d, $^3J_{HH}$ = 7.3 Hz, 6H), 6.72 (t, $^3J_{HH}$ = 7.3 Hz, 6H), 6.80 (m, $^3J_{HH}$ = 7.3, 7.8 Hz, 6H), 6.91 (dd, $^3J_{HH}$ = 7.5, 7.6 Hz, 6H).
^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 25^{o}C): δ (ppm) = 20.29 (s, C), 20.65 (s, 2C), 48.62 (d, $^2J_{PC}$ = 22.2 Hz, 3C), 80.74 (d, $^3J_{PC}$ = 6.7 Hz, 6C), 126.70 (s, 6C), 127.12 (d, J_{PC} = 7.0 Hz, 6C), 127.41 (s, 6C), 129.65 (s, 6C), 130.14 (s, 6C), 134.15 (d, J_{PC} = 5.0 Hz, 6C), 135.95 (s, 6C).
^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25^{o}C): δ (ppm) = 180.20 (d, $^1J_{RhP}$= 146.5 Hz).

(trop$_3$P)RhSPh (57)

MF: $C_{51}H_{38}PRhS$

M_r: 816.79



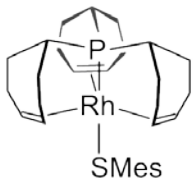
To a suspension of 74.3 mg (0.1 mmol) ($trop_3P$)RhCl in 15 mL dcm, 25.7 mg (0.1 mmol) AgOTf was added and this solution was stirred for two hours. The brown suspension was filtered over celite and 66.1 mg (0.5 mmol) sodium thiophenolate was added. Upon addition of sodium thiophenolate a yellow solid precipitated.

^{1}H NMR (300.1 MHz, $CDCl_3$, 25°C): δ (ppm) = 3.90 (d, $^2J_{PH}$=13.5 Hz, 3H), 5.54 (s, 6H), 6.46 (d, $^3J_{HH}$ = 7.5 Hz, 6H), 6.61-6.84 (m, $^3J_{HH}$ = 7.6 Hz, 18H), 7.27 (m, 2H), 7.69 (d, $^3J_{HH}$ = 7.1 Hz, 6H).
^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25°C): δ (ppm) = 184.4 (d, $^1J_{RhP}$ = 134 Hz).

IR(ATR): 3042 (w), 3011 (w), 1940 (w), 1573 (m), 1556 (s), 1483 (vs), 1473 (vs), 1452 (vs), 1417 (m), 1286 (vs), 1218 (s), 1170 (m), 1158 (m), 1146 (s), 1130 (m), 1017 (s), 937 (s), 898 (s), 849 (s), 743 (vs), 733 (vs) 692 (vs).

($trop_3P$)RhSMes (58)

MF: $C_{54}H_{44}PRhS$
M_r: 858.87

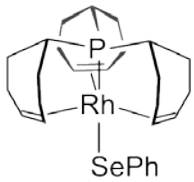


To a suspension of 14.5 mg (0.02 mmol) ($trop_3P$)RhCl in 5 mL dcm, 7.4 mg (0.3 mmol) AgOTf was added and this solution was stirred for two hours. The brown suspension was filtered over celite and 66.1 mg (0.5 mmol) sodium thiomesitolate was added. This mixture was stirred for a further 20 minutes, filtered over celite and the solvent was evaporated yielding a pale yellow powder.

^{1}H NMR (300.1 MHz, CD_2Cl_2, 25°C): δ (ppm) = 2.23 (s, 3H), 2.79 (s, 6H), 3.93 (d, $^2J_{PH}$ = 13.7 Hz, 3H), 5.62 (s, 6H), 6.42 (d, $^3J_{HH}$ = 7.6 Hz, 6H), 6.66-6.84 (m, $^3J_{HH}$ = 7.6 Hz, 18H), 7.02 (s, 2H).
^{31}P{^{1}H} NMR (101.3 MHz, CD_2Cl_2, 25°C): δ (ppm) = 185.6 (d, $^1J_{RhP}$ = 134 Hz).

($trop_3P$)RhSePh (59)

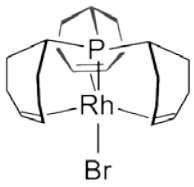
MF: $C_{51}H_{38}PRhSe$
M_r: 863.69



To a suspension of 15.4 mg (0.021 mmol) ($trop_3P$)RhCl in dcm, 10.6 mg (0.041 mmol) AgOTf was added and this solution was stirred for two hours. The brown suspension was filtered over celite and 7.4 mg (0.041 mmol) sodium benzeneselenolate was added. A bright yellow suspension was formed immediately and the solvent was evaporated.
The formed yellow complex was insoluble in dcm, chloroform, thf, DMSO, hexane and no NMR data was recorded.

($trop_3P$)RhBr (60)

MF: $C_{45}H_{35}BrPRh$
M_r: 787.53



To 26 mg (0.03 mmol) ($trop_3P$)RhOTf in 3 mL CH_2Cl_2, 25 mg (1.0 mmol) NaBr in 100 µm H_2O was added and this mixture was shaken well. To this mixture Na_2SO_4 was added, and the suspension was filtered over celite. The solvent was evaporated, dissolved in CH_2Cl_2 and filtered over celite and the solvent evaporated yielding a pale yellow solid.
Yield: 20 mg (0.025 mmol, 84 %).

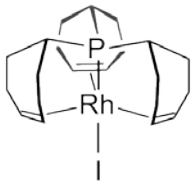
Mp: >220 °C

^{1}H NMR (300.1 MHz, CD_2Cl_2, 25°C): δ (ppm) = 3.93 (d, $^{2}J_{PH}$=13.2 Hz, 3H), 6.03 (s, 6H), 6.45 (d, $^{3}J_{HH}$ = 7.5 Hz, 6H), 6.72 (t, $^{3}J_{HH}$ = 7.5 Hz, 6H), 6.82 (m, $^{3}J_{HH}$ = 7.3 Hz, 7.5 Hz, 6H), 6.97 (dd, $^{3}J_{HH}$ = 7.6 Hz, 7.6 Hz, 6H).
^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 25°C): δ (ppm) = 48.70 (d, J_{PC} = 21.5 Hz, 3C), 78.67 (d, J_{PC} = 6.2 Hz, 6C), 126.78 (s, 6C), 127.40 (d, J_{PC} = 7.0 Hz, 6C), 127.65 (d, J_{PC} = 1.0 Hz, 6C), 130.65 (d, J_{PC} = 1.3 Hz, 6C), 133.75 (d, J_{PC} = 6.0 Hz, 6C), 135.59 (s, 6C).
^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25°C): δ (ppm) = 196.81 (d, $^{1}J_{RhP}$= 148.2 Hz).

IR (ATR): 3055 (w), 3016 (w), 2890 (w), 1599 (w), 1569 (w), 1483 (s), 1451 (m), 1417 (m), 1321 (w), 1287 (s), 1255 (w), 1217 (m), 1172 (s), 1158 (m), 1132 (m), 1109 (m), 1096 (m), 1041 (m), 939 (m), 899 (m), 879 (m), 850 (m), 819 (m), 791 (s), 743 (vs), 731 (vs), 642 (m).

(trop$_3$P)RhI (61)

MF: $C_{45}H_{35}IPRh$
M_r: 834.53



To 26 mg (0.033 mmol) (trop$_3$P)RhOTf in 3 mL CH_2Cl_2, 25 mg (0.15 mmol) KI in 100 µm H_2O was added and this mixture was shaken well. To this mixture Na_2SO_4 was added and the suspension was filtered over celite. The solvent was evaporated, dissolved in CH_2Cl_2 and filtered over celite and solvent evaporated yielding a pale yellow solid.
Yield: 20 mg (0.024 mmol, 79 %).

Mp: >220 °C
^{1}H NMR (300.1 MHz, CD_2Cl_2, 25°C): δ (ppm) = 3.92 (d, $^{2}J_{PH}$=13.2 Hz, 3H), 6.28 (s, 6H), 6.45 (d, $^{3}J_{HH}$ = 7.5 Hz, 6H), 6.72 (t, $^{3}J_{HH}$ = 7.6 Hz, 6H), 6.82 (m, $^{3}J_{HH}$ = 7.3, 7.5 Hz, 6H), 6.96 (dd, $^{3}J_{HH}$ = 7.5, 7.6 Hz, 6H).

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, CD_2Cl_2, 25°C): δ (ppm) = 48.85 (d, J_{PC} = 20.7 Hz, 3C), 76.84 (d, J_{PC} = 6.3 Hz, 6C), 126.94 (s, 6C), 127.51 (d, J_{PC} = 7.0 Hz, 6C), 127.68 (d, J_{PC} = 0.9 Hz, 6C), 130.71 (d, J_{PC} = 1.2 Hz, 6C), 133.56 (d, J_{PC} = 5.3 Hz, 6C), 135.37 (s, 6C).
$^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2, 25°C): δ (ppm) = 203.29 (d, $^{1}J_{RhP}$= 146.8 Hz).

IR (ATR): 3016 (w), 2891 (w), 1599 (w), 1567 (w), 1483 (s), 1451 (m), 1417 (m), 1319 (w), 1286 (s), 1259 (w), 1171 (s), 1132 (m), 1109 (m), 1095 (m), 1040 (m), 971 (w), 939 (m), 898 (m), 818 (m), 791 (s), 743 (vs), 731 (vs). 641 (m).

Chapter 8

Chapter 8. Appendix

Abbreviations

ADP	Adenosine diphosphate
Ar	Aryl
ATP	Adenosine triphosphate
BAP	Bis(acyl)phosphides
BAPO	Bis(acyl)phosphineoxide
$BArF_{24}$	Tetrakis[(3,5-trifluoromethyl)phenyl]borate
Benz	Benzylic
^{t}Bu	*tert*-Butyl
Cp, Cp*	C_5H_5, C_5Me_5
cod	1,5-Cyclooctadiene
Ct	Centroid (Spatial center of two or more atoms in crystal structures)
dme	1,2-Dimethoxyethane
DMSO	Dimethyl sulfoxide
DNA	Deoxyribonucleic Acid
DPPH	2,2-Diphenyl-1-picrylhydrazyl
DPPP	1,3-Bis(diphenylphosphino)propane
Et	Ethyl
HMPA	Hexamethylphosphotriamide
HTMF	2-Methyltetrahydrofuran
MAPO	Mono Acetyl Phopshine oxide
Me	Methyl
MeCN	Acetonitrile
Mes	Mesitylene or 1,3,5-trimethylbenzene
NaOCP	Sodium phosphaethynolate
$OAcF_3$	Trifluoroacetate
OTf	Trifluoromethanesulfonate
Ph	Phenyl
^{i}Pr	*iso*-Propyl

py	Pyridine
RNA	Ribonucleic Acid
thf	Tetrahydrofuran
TMS	Trimethylsilyl
TMSP	Tris(trimethylsilyl)phosphane
trop	5H-dibenzo[a,d]cyclohepten-5-yl
Ts	Tosyl

CSD	Cambridge Structural Database
Eq.	Equivalents
EPR	Electron Paramagnetic Resonance
HV	High Vacuum
MF	Molecular Formula
M.p.	Melting Point
M_r	Molecular Weight
NMR	Nuclear Magnetic Resonance
RT	Room Temperature
UV	Ultraviolet

Crystallographic Data

Crystal data and structure refinement for $Na_3P_7(NaO^tBu)_3(DME)_3$

Identification code	publication_text	
Empirical formula	$C_{26}H_{62}Na_6O_{10}P_7$	
Formula weight	889.52	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 26.375(3) Å	α = 90 °.
	b = 15.0404(15) Å	β = 113.224(2) °.
	c = 26.492(3) Å	γ = 90 °.
Volume	9657.3(17) $Å^3$	
Z	8	
F(000)	3752	
Crystal size	0.25 x 0.19 x 0.15 mm	
Data collection	Oxford XCalibur	
	with Ofxord Saphire CCD detector	
	Mo K_α, graphite monochromator	
Theta range for data collection	1.59 to 26.45 °.	
Limiting indices	-32 =< h =< 32, -18 =< k =< 18, -33 =< l =< 33	
Reflections collected / unique	42596 / 9916 [R(int) = 0.0926]	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9916 / 0 / 458	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0574, wR2 = 0.1255	
R indices (all data)	R1 = 0.0893, wR2 = 0.1404	
Largest diff. peak and hole	0.851 and -0.606 e.$Å^{-3}$	
Operator	Matthias Vogt	

Crystal data and structure refinement for [NaOCP(Ph)](DME)$_2$

Identification code	pbca
Empirical formula	$C_{15}H_{26}Na_1O_5P_1$
Formula weight	340.327
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	Pbca
Unit cell dimensions	a = 15.3459(10) Å α = 90 °.
	b = 15.3747(10) Å β = 90 °.
	c = 15.5411(10) Å γ = 90 °.
Volume	3666.7(4) Å^3
Z	1
F(000)	1456
Crystal size	0.20 x 0.15 x 0.10 mm
Data collection	Oxford XCalibur
	with Ofxord Saphire CCD detector
	Mo K_α, graphite monochromator
Theta range for data collection	2.29 to 30.83 °.
Limiting indices	-21 =< h =< 21, -21 =< k =< 21, -21 =< l =< 21
Reflections collected / unique	39490 / 5534 [R(int) = 0.0591]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5534 / 2 / 308
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0461, wR2 = 0.0994
R indices (all data)	R1 = 0.0719, wR2 = 0.1107
Largest diff. peak and hole	0.531 and -0.392 e.Å^{-3}
Operator	Matthias Vogt

Crystal data and structure refinement for $[Ni(trop_2N)]_2(\mu\text{-}PH_2)Na(DME)_3$

Identification code	sadc2c
Empirical formula	$C_{72}H_{78}N_2NaNiO_6P$
Formula weight	1380.69
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2/c
Unit cell dimensions	a = 26.267(2) Å α = 90 °.
	b = 18.3372(17) Å β = 131.921(2) °.
	c = 17.7512(16) Å γ = 90 °.
Volume	6361.9(10) $Å^3$
Z	2
F(000)	1524
Crystal size	0.19 x 0.12 x 0.08 mm
Data collection	Oxford XCalibur
	with Ofxord Saphire CCD detector
	Mo K_α, graphite monochromator
Theta range for data collection	1.60 to 28.34 °.
Limiting indices	-35 =< h =< 34, -24 =< k =< 24, -23 =< l =< 23
Reflections collected / unique	32560 / 7939 [R(int) = 0.0465]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7939 / 0 / 408
Goodness-of-fit on F^2	1.101
Final R indices [I>2sigma(I)]	R1 = 0.0939, wR2 = 0.2350
R indices (all data)	R1 = 0.1146, wR2 = 0.2504
Largest diff. peak and hole	2.363 and -1.557 e.$Å^{-3}$
Operator	Matthias Vogt

Crystal data and structure refinement for [Rh(trop$_2$N)(PH$_2$)(PPh$_3$)]Na(DME)

Identification code	mv090503coen
Empirical formula	$C_{52}H_{49}NNaO_2P_2Rh$
Formula weight	907.76
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P21
Unit cell dimensions	a = 18.497(2) Å α = 90 °.
	b = 14.0697(15) Å β = 117.000(2) °.
	c = 18.724(2) Å γ = 90 °.
Volume	4341.9(8) Å^3
Z	4
F(000)	1880
Crystal size	0.22 x 0.06 x 0.03 mm
Data collection	Oxford XCalibur
	with Ofxord Saphire CCD detector
	Mo K_α, graphite monochromator
Theta range for data collection	1.89 to 28.35 °.
Limiting indices	-24 =< h =< 24, -18 =< k =< 18, -24 =< l =< 24
Reflections collected / unique	44225 / 10792 [R(int) = 0.0523]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10792 / 0 / 728
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0363, wR2 = 0.0819
R indices (all data)	R1 = 0.0496, wR2 = 0.0875
Largest diff. peak and hole	0.741 and -0.341 e.Å^{-3}
Operator	Matthias Vogt

Crystal data and structure refinement for $[Rh(trop_2PPh)(PH_2)]_2(DME)$

Identification code	mv090504coen
Empirical formula	$C_{40}H_{39}O_2P_2Rh$
Formula weight	716.58
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P21/c
Unit cell dimensions	a = 11.3559(6) Å α = 90 °.
	b = 14.0487(7) Å β = 100.9550(10) °.
	c = 20.3833(10) Å γ = 90 °.
Volume	3192.6(3) $Å^3$
Z	4
F(000)	1480
Crystal size	0.18 x 0.11 x 0.07 mm
Data collection	Oxford XCalibur
	with Ofxord Saphire CCD detector
	Mo K_α, graphite monochromator
Theta range for data collection	1.77 to 28.34 °.
Limiting indices	-15 =< h =< 14, -18 =< k =< 18, -27 =< l =< 27
Reflections collected / unique	32734 / 7937 [R(int) = 0.0468]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7937 / 0 / 562
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0340, wR2 = 0.0801
R indices (all data)	R1 = 0.0450, wR2 = 0.0852
Largest diff. peak and hole	0.824 and -0.326 e.$Å^{-3}$
Operator	Matthias Vogt

Crystal data and structure refinement for $[Rh(trop_2N)_2(NH_2)_2]Na_2(DME)_6$

Identification code	publication_text
Empirical formula	$C_{84}H_{108}N_4Na_4O_{12}Rh_2$
Formula weight	1663.567
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 15.7578(6) Å α = 69.0890(10) °.
	b = 16.1911(6) Å β = 84.9600(10) °.
	c = 17.0868(6) Å γ = 82.1700(10) °.
Volume	4030.7(3) $Å^3$
Z	2
F(000)	1696
Crystal size	0.29 x 0.22 x 0.15 mm
Data collection	Oxford XCalibur
	with Ofxord Saphire CCD detector
	Mo K_α, graphite monochromator
Theta range for data collection	1.31 to 36.40 °.
Limiting indices	-26 =< h =< 26, -27 =< k =< 27, -28 =< l =< 28
Reflections collected / unique	108678 / 37790 [R(int) = 0.0465]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	37790 / 0 / 1255
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0517, wR2 = 0.1068
R indices (all data)	R1 = 0.0872, wR2 = 0.1230
Largest diff. peak and hole	2.494 and -1.029 e.$Å^{-3}$
Operator	Matthias Vogt

EPR spectra

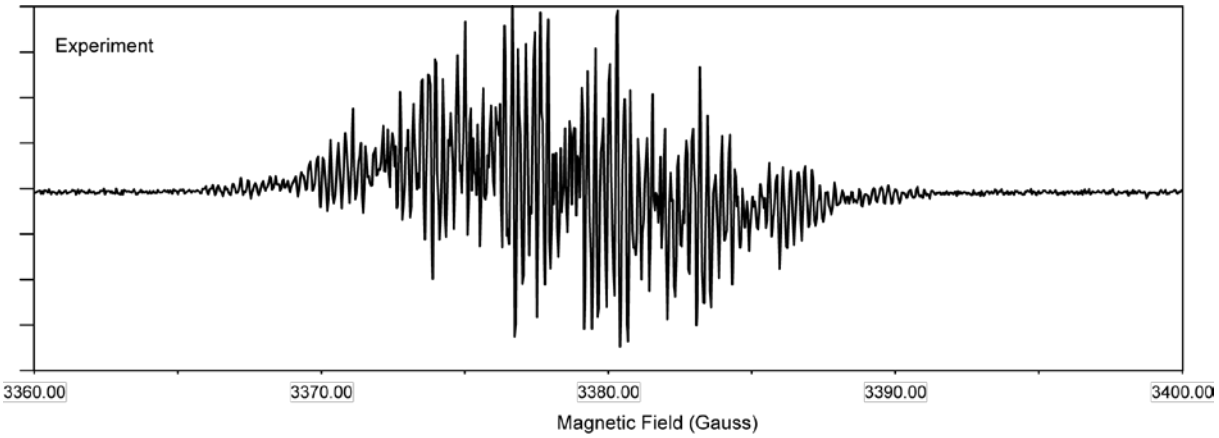


Figure 26: EPR spectrum of $NaPH_2 \cdot xNaO^tBu$ and 4,4'-dimethoxy diphenylketone (**21c**) in thf.

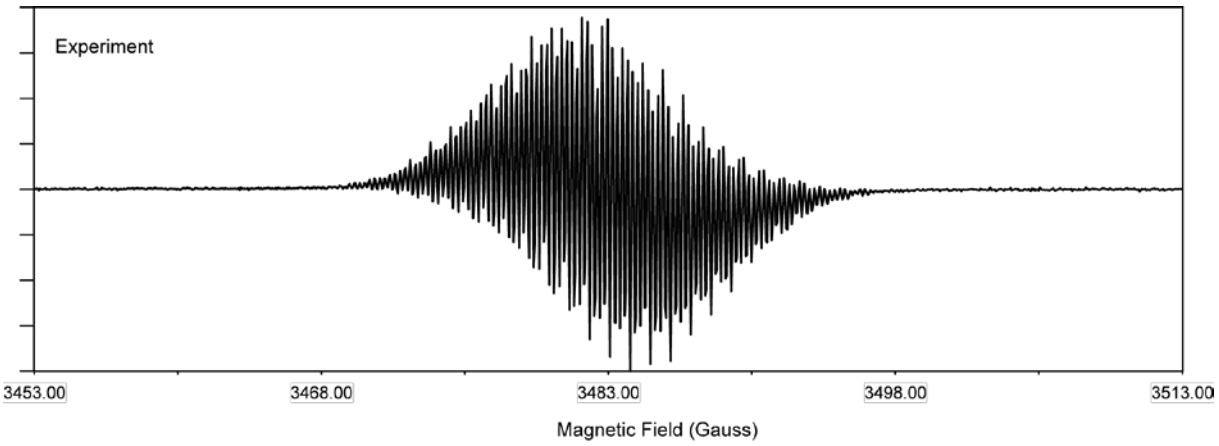


Figure 27: EPR spectrum of $NaPH_2 \cdot xNaO^tBu$ and Michlers ketone (**21d**) in thf.

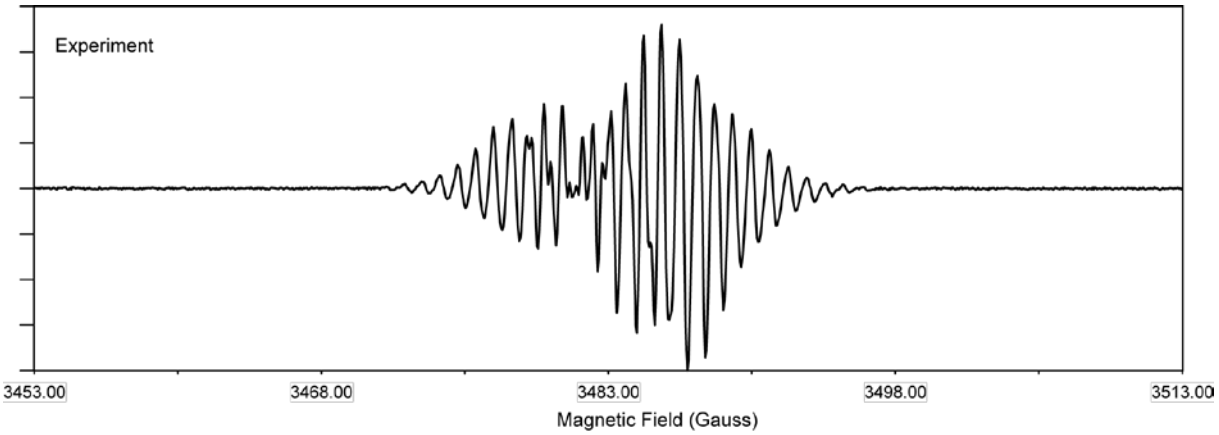


Figure 28: EPR spectrum of $NaPH_2 \cdot xNaO^tBu$ and 4,4'-dichloro diphenylketone (**21e**) in thf.

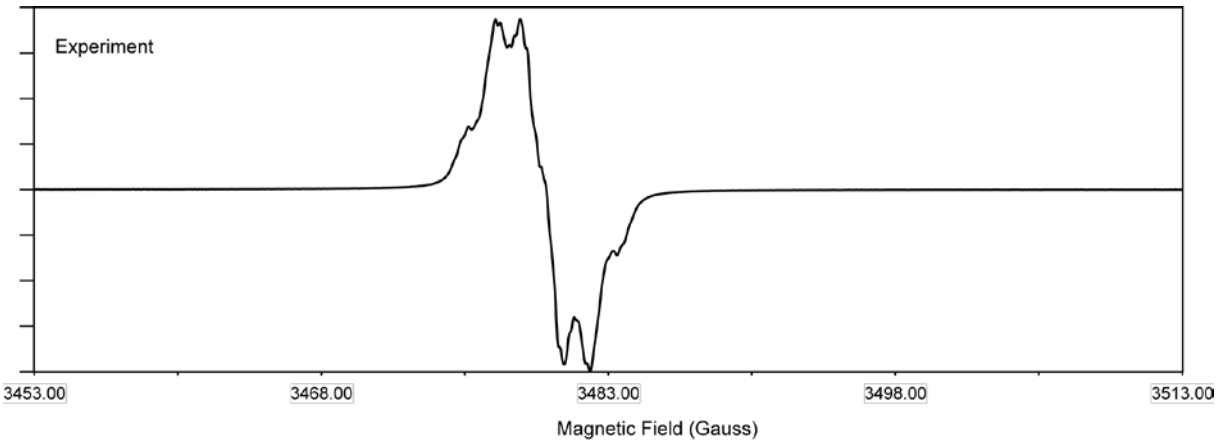


Figure 29: EPR spectrum of $NaPH_2 \cdot xNaO^tBu$ and 9,10-phenanthrenequinone (**22b**) in thf.

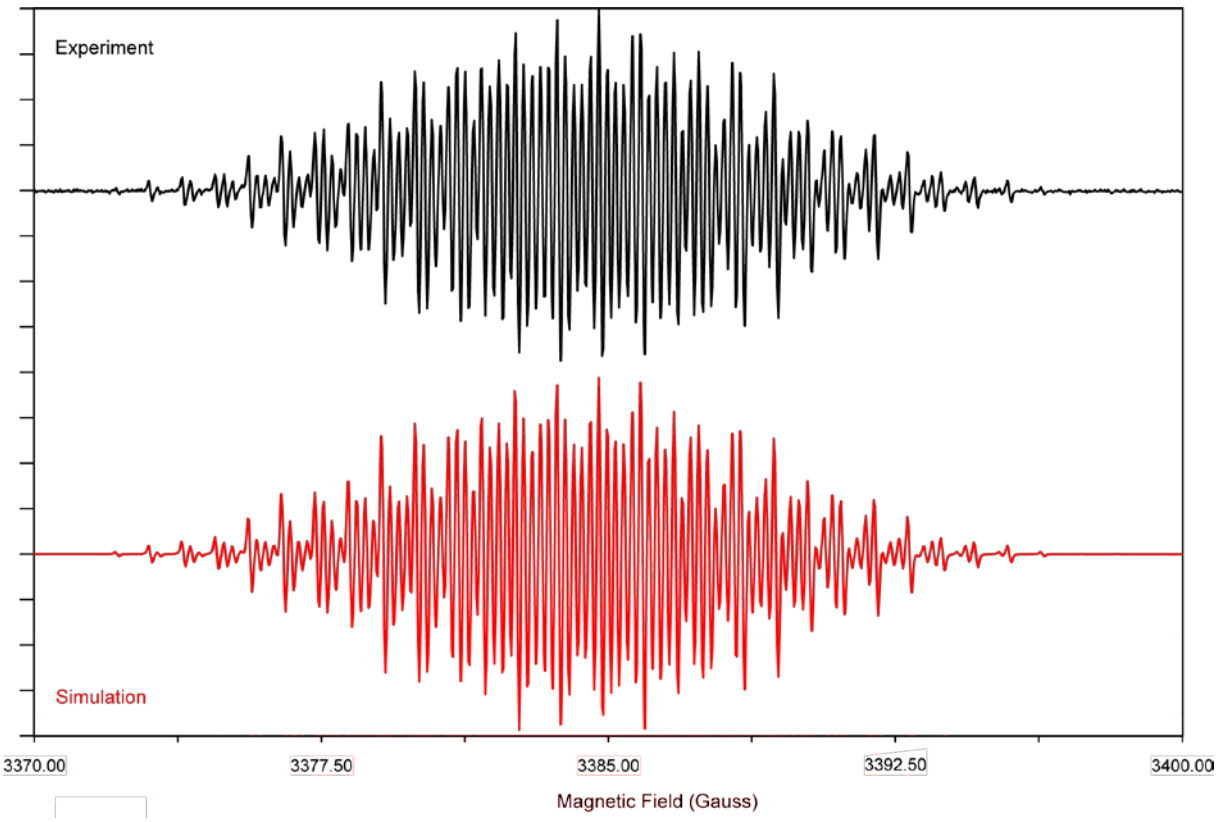


Figure 30: EPR spectrum of **21a** and sodium dihydrogenphosphide in tetraglyme. Top: Experimental spectrum, bottom: simulated spectrum. Frequency: 9.492 GHz; 2.0035 g-value (vs. DPPH): hyperfine coupling constants [mT]: $a_{H,ortho}$: 0.260; $a_{H,meta}$: 0.087; $a_{H,para}$: 0.350; a_{Na}: 0.109.

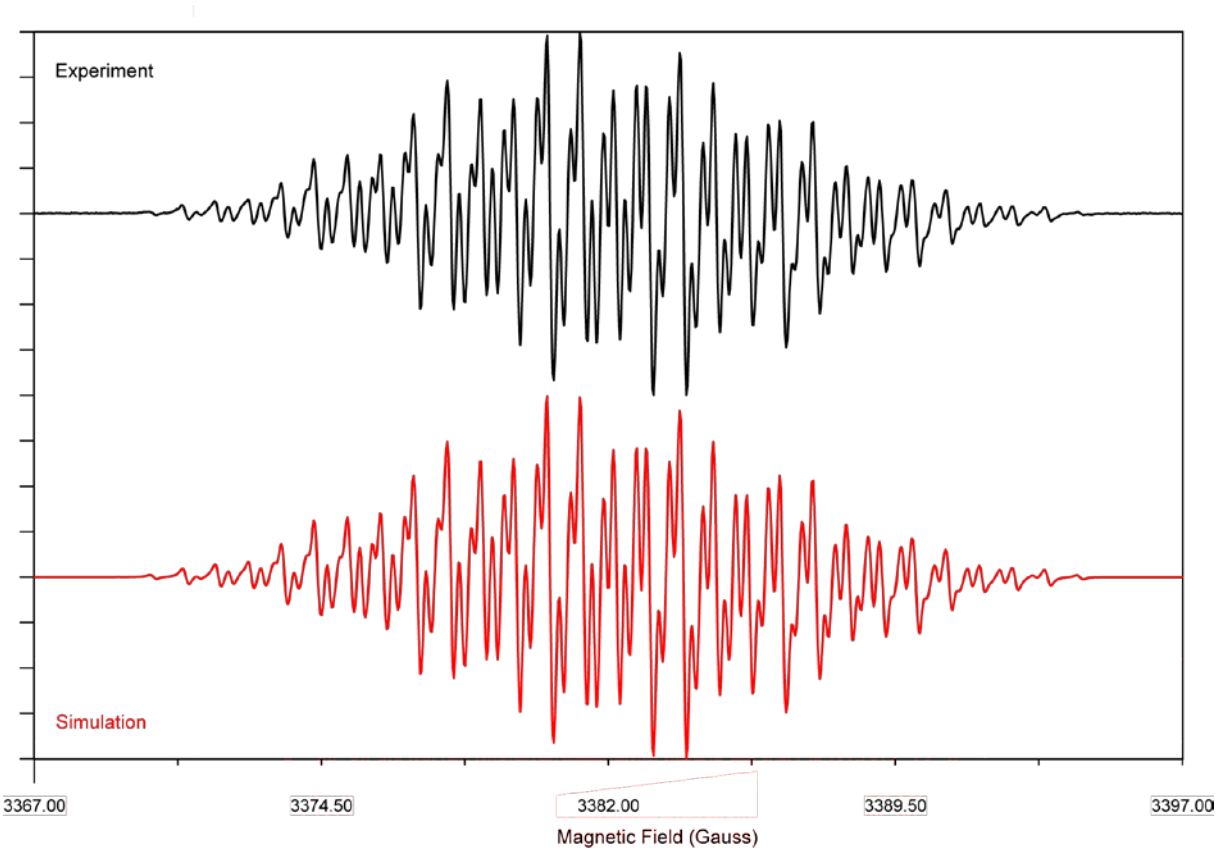


Figure 31: EPR spectrum of **21a**, sodium dihydrogenphosphide and 18-crown-6-ether in thf. Top: Experimental spectrum, bottom: simulated spectrum. Frequency: 9.487 GHz; 2.0042 g-value (vs. DPPH): hyperfine coupling constants [mT]: $a_{H,ortho}$: 0.257; $a_{H,meta}$: 0.085; $a_{H,para}$: 0.350; a_{Na}: 0.118.

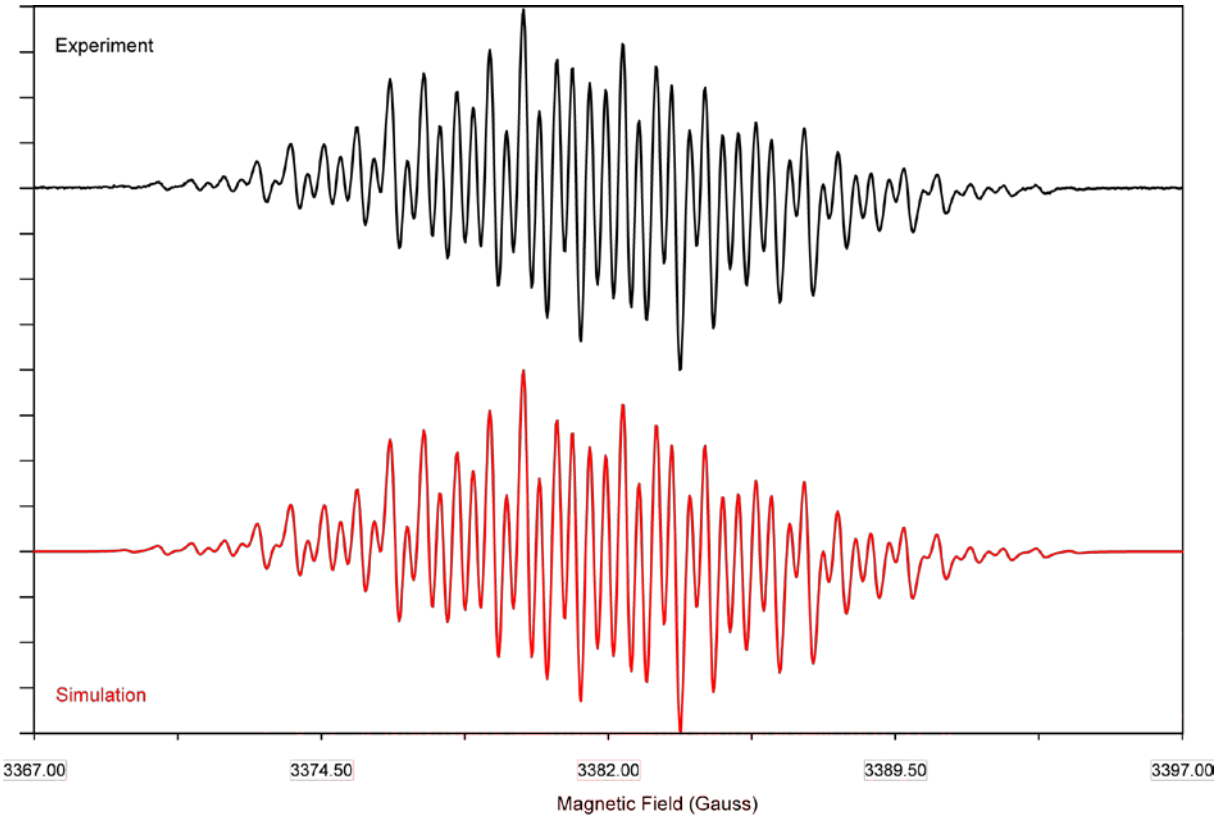


Figure 32: EPR spectrum of **21a**, sodium dihydrogenphosphide and 18-crown-6-ether in dme. Top: Experimental spectrum, bottom: simulated spectrum. Frequency: 9.482 GHz; 2.0032 g-value (vs. DPPH): hyperfine coupling constants [mT]: $a_{H,ortho}$: 0.260; $a_{H,meta}$: 0.087; $a_{H,para}$: 0.348; a_{Na}: 0.128.

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